Number of LVs   **Continuum Parameter**

Chemometrics Tutorial

for PLS_Toolbox and Solo

Barry M. Wise

Neal B. Gallagher

Rasmus Bro

Jeremy M. Shaver

Willem Windig

R. Scott Koch

EIGENVECTOR
RESEARCH INCORPORATED

Chemometrics Tutorial
for PLS_Toolbox and Solo

Barry M. Wise
Neal B. Gallagher
Rasmus Bro
Jeremy M. Shaver
Willem Windig
R. Scott Koch

Eigenvector Research, Inc.
3905 West Eaglerock Drive
Wenatchee, WA 98801

helpdesk@eigenvector.com
www.eigenvector.com
FAX: (509)662-9214

Eigenvector Research, Inc., Software License Agreement

READ THE TERMS AND CONDITIONS OF THIS LICENSE AGREEMENT CAREFULLY BEFORE USING THIS SOFTWARE. THIS LICENSE AGREEMENT REPRESENTS THE ENTIRE AGREEMENT BETWEEN YOU (THE "LICENSEE" - EITHER AN INDIVIDUAL OR AN ENTITY) AND EIGENVECTOR RESEARCH, INC., ("EVRI") CONCERNING THE PLS_TOOLBOX COMPUTER SOFTWARE CONTAINED HEREIN ("PROGRAM"), AND THE ACCOMPANYING USER DOCUMENTATION.

BY USING THE SOFTWARE, YOU ACCEPT THE TERMS OF THIS AGREEMENT. IF YOU ARE NOT WILLING TO DO SO, RETURN THE UNOPENED SOFTWARE IMMEDIATELY FOR A FULL REFUND.

LICENSE GRANT: This license permits licensee to install and use one copy of the Program on a single computer. If licensee has multiple licenses for the Program, then Licensee may at any time have as many copies of the Program and its Electronic Documentation in use as it has licenses. "Use" means that a copy is loaded into temporary memory or installed into the permanent memory of a computer, except that a copy installed on a network server for the sole purpose of distribution to other computers is not in "use". Licensee is responsible for limiting the number of possible concurrent users to the number licensed. Each copy of the Program may be used on a backup computer (when the original is disabled) or a replacement computer. Replacements may be either permanent or temporary, at the same or different site as the original computer. The Hardcopy documentation provided with the Program may not be copied.

Licensee shall use the Program only for its internal operations. "Internal operations" shall include use of the Program in the performance of consulting or research for third parties who engage Licensee as an employee or independent contractor. Licensee may allow use of the Program by employees, consultants, students and/or (in the case of individual licensees) colleagues, but Licensee may not make the Program available for use by third parties generally on a "time sharing" basis.

Licensee may make copies of the Program only for backup or archival purposes. All copies of Program, Electronic Documentation and Hardcopy Documentation shall contain all copyright and proprietary notices in the originals. Licensee shall not re-compile, translate or convert "M-files" contained in the Program for use with any software other than MATLAB®, which is a product of The MathWorks, Inc. 3 Apple Hill Drive, Natick, MA 01760-2098, without express written consent of EVRI. Licensee shall not re-distribute "M-files" contained in the Program, or any derivative thereof, without express written consent of EVRI.

Licensee shall take appropriate action by instruction, agreement, or otherwise with any persons permitted access to the Program, so as to enable Licensee to satisfy the obligations under this agreement.

TERM OF AGREEMENT. This Agreement shall continue until terminated by EVRI or Licensee as provided below.

TERMINATION. EVRI may terminate this license by written notice to Licensee if Licensee (a) breaches any material term of this Agreement, (b) fails to pay the amount charged for this license within Thirty (30) days after the date due, or (c) ceases conducting business in the normal course, becomes insolvent or bankrupt, or avails itself of or becomes subject to any proceedings pertaining to insolvency or protection of creditors. Licensee may terminate this Agreement at any time by written notice to EVRI. Licensee shall not be entitled to any refund if this Agreement is terminated, except of license fees paid for any Licensed Product for which the testing period has not expired at the time of termination. Upon termination, Licensee shall promptly return all copies of the Programs and Documentation in Licensee's possession or control, or promptly provide written certification of their destruction.

LIMITED WARRANTY; LIMITATION OF REMEDIES. For a period of ninety (90) days from delivery, EVRI warrants that (a) the media shall be free of defects, or replaced at no cost to Licensee, and (b) the Program will conform in all material respects to the description of such Program's operation in the Documentation. In the event that the Program does not materially operate as warranted, licensees exclusive remedy and EVRI's sole liability under this warranty shall be (a) the correction or workaround by EVRI of major defects within a reasonable time or (b) should such correction or workaround prove neither satisfactory nor practical, termination of the License and refund of the license fee paid to EVRI for the Program. THE FOREGOING WARRANTY IS IN LIEU OF ALL OTHER WARRANTIES, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO THE WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE. EVRI SHALL NOT BE LIABLE FOR ANY SPECIAL, INCIDENTAL OR CONSEQUENTIAL DAMAGES, INCLUDING WITHOUT LIMITATION LOST PROFITS. Licensee accepts responsibility for its use of the Program and the results obtained therefrom.

LIMITATION OF REMEDIES AND LIABILITY. The remedies described in this License Agreement are your exclusive remedies and EVRI's entire liability. IN NO EVENT WILL EVRI BE LIABLE TO YOU FOR ANY DAMAGES, INCLUDING LOST PROFITS, LOST BENEFITS, OR OTHER INCIDENTAL OR CONSEQUENTIAL DAMAGES, RESULTING FROM THE USE OF OR INABILITY TO USE THE PROGRAM OR ANY BREACH OF WARRANTY. EVRI's LIABILITY TO YOU FOR ACTUAL DAMAGES FOR ANY CAUSE WHATSOEVER, AND REGARDLESS OF THE FORM OF ACTION, WILL BE LIMITED TO THE MONEY PAID FOR THE PROGRAM OBTAINED FROM EVRI THAT CAUSED THE DAMAGES OR THAT IS THE SUBJECT MATTER OF, OR IS DIRECTLY RELATED TO, THE CAUSE OF ACTION. Some states do not allow the exclusion or limitation of incidental or consequential damages, so the above limitation may not apply to you.

GENERAL PROVISIONS. Licensee may not assign this License without written consent of EVRI, except to an affiliate, subsidiary or parent company of Licensee. Should any act of Licensee purport to create a claim. lien, or encumbrance on any Program, such claim, lien, or encumbrance shall be void. All provisions regarding indemnification, warranty, liability and limits thereon, and protection of proprietary rights and trade secrets, shall survive termination of this Agreement, as shall all provisions regarding payment of amounts due at the time of termination. Should Licensee install the Programs outside the United States, Licensee shall comply fully with all applicable laws and regulations relating to export of technical data. This Agreement contains the entire understanding of the parties and may be modified only by written instrument signed by both parties.

PAYMENT: Payment is due in United States currency within thirty days of receipt of the Program. Absent appropriate exemption certificates(s), Licensee shall pay all taxes.

GOVERNMENT LICENSEES. RESTRICTED RIGHTS LEGEND. Use, duplication, or disclosure by the U.S. Government is subject to restrictions as set forth in subparagraph (c)(1)(ii) of the Rights in Technical Data and Computer Software clause at DFARS 52.227-7013.

Licensor is Eigenvector Research, Inc., 3905 West Eaglerock Drive, Wenatchee, WA 98801.

Table of Contents

1. Introduction

NOTE: most of the content for this chapter has been moved into our documentation wiki. This content is available in Solo and PLS_Toolbox from the Help menu of the Analysis GUI or Workspace Browser and in MATLAB with PLS_Toolbox using the help browser, or by typing the command: helppls

The documentation is also available on-line on the Eigenvector Research website at:

    http://wiki.eigenvector.com

The remainder of this manual is dedicated to a tutorial explaining multivariate analysis and demonstrating the analysis of data using PLS_Toolbox and Solo.

About PLS_Toolbox, Solo, and MATLAB

PLS_Toolbox is a collection of essential and advanced chemometric routines built within the MATLAB® computational environment. It contains the tools required by engineers and scientists to explore their data and build predictive models. PLS_Toolbox gets its name from the Partial Least Squares (PLS) regression method, which has become the standard calibration method in many chemical applications. Although PLS_Toolbox has grown far beyond just PLS, the name remains.

Solo is PLS_Toolbox without MATLAB. We us the MATLAB® Compiler™ to compile all of the PLS_Toolbox GUI interfaces into a standalone application. The only difference between the two products is access to the MATLAB command line.

Users of earlier versions have provided much of the impetus for inclusion of additional routines and improvements to existing routines. We encourage you to make suggestions for routines you would find valuable for inclusion in future versions, and appreciate your comments on how we can improve PLS_Toolbox. We are especially indebted to those of you who have shared your routines and improvements to our routines with us.

PLS_Toolbox is frequently updated with new routines as research in the field of chemometrics continues. It is the intention Eigenvector Research Inc. to keep PLS_Toolbox as close to the state-of-the-art as practical. As our own research in chemometrics continues we will add routines that we find useful. Every attempt will be made to turn significant research results, whether our own or those of others, into working methods in the shortest time possible. New routines will initially be distributed to our users through our web site at www.eigenvector.com, and then incorporated into future versions of the toolbox. It is our goal to make PLS_Toolbox a repository of current state of the art techniques, and include these techniques long before stand-alone packages appear on the market.

Table 1-1. Suggested Study Guide

If you:	Then do the following:
Are new to MATLAB	Read Chapter 2, Getting Started
Are new to, or rusty with, Linear Algebra	Read Chapter 3, Introduction to Linear Algebra
Are new to the field of Chemometrics	Read Chapter 4-12
Are a knowledgeable chemometrician, but new to PLS_Toolbox	Read Chapters 2, follow examples in Chapters 4-12 as needed, and skim chapter 16.
A returning PLS_Toolbox user	Read Chapter 15, skim other chapters for specific information
Want to learn more about the Distribution Fitting Tool Set	Read Chapter 14, see the PLS_Toolbox Reference Manual sections for DFT
Want to learn more about Robust methods and the LIBRA Toolbox	Read Chapter 13
Need more information about Preprocessing	Read Chapter 7

2. Getting Started with MATLAB, PLS_Toolbox, and Solo

PLS_Toolbox can be used in many different ways. One can work either from PLS_Toolbox graphical user interfaces (GUIs) or from the MATLAB development environment, or both. Solo is comprised of only the GUIs from PLS_Toolbox.

We'll begin this chapter by showing a simple demonstration of loading an Excel file into MATLAB and exploring it from the command line. The next section will cover, in detail, the PLS_Toolbox GUI environment. The final section of this chapter is a "quick start" guide on using PLS_Toolbox GUIs; we'll show how to quickly build a principal components analysis (PCA) model and a partial least squares (PLS) model.

Working with MATLAB

About MATLAB

MATLAB, an acronym for MATrix LABoratory, is a product of The MathWorks, Inc., (Natick, MA). MATLAB is built around the LAPACK and BLAS linear algebra engines. It is a computational environment especially suited to problems in matrix algebra, allowing the user to do matrix computations in a command language that looks very much like standard linear algebra notation. MATLAB, which is required to run the toolbox routines, is not an inexpensive package (as you probably already know). However, because of its large collection of built-in functions, powerful graphics, easy-to-learn language, extensibility, and flexible environment, it is a great value. Another positive aspect of MATLAB is that it is available for many platforms, including Mac OS X, Microsoft Windows, Unix, and Linux. Thus, PLS_Toolbox can be run on all these platforms.

MATLAB can be used in the "command line" mode, where single line commands are entered at the command prompt (>>), executed immediately, and the results displayed. MATLAB contains hundreds of commands; a complete description of MATLAB commands is contained in the manuals provided with the software and through onscreen help.

We have continued to expand our use of GUIs (Graphical User Interfaces) with PLS_Toolbox. Version 4.0 has integrated GUIs into eleven of our most popular chemometric routines. The updated GUIs include a more sophisticated layout allowing quick access to tools and information, including contextual menus, short cuts, and integrated help.

Before entering the GUI environment the user must first enter and navigate the command mode. Thus, some minimal understanding of the command mode is required even of the beginner. Although a good number of powerful methods are available through our GUIs,

there are still several routines only accessible from the command line. It is the intention of this section to get the new MATLAB user sufficiently comfortable with the command line mode to load data, do simple manipulations of data, execute PLS_Toolbox GUI routines, and finally save data and models to permanent media.

Startup

After starting MATLAB from the Desktop, the default three-part window will appear as shown in Figure 2-1. Clicking the **Start** button in the lower left-hand corner will display a list of MATLAB tools, shortcuts, and documentation. Mousing over the top item, **MATLAB**, will display a submenu that should have **PLS_Toolbox** listed at or near the bottom. Should it not be found, please install PLS_Toolbox as described in Chapter 1, Installing PLS_Toolbox.
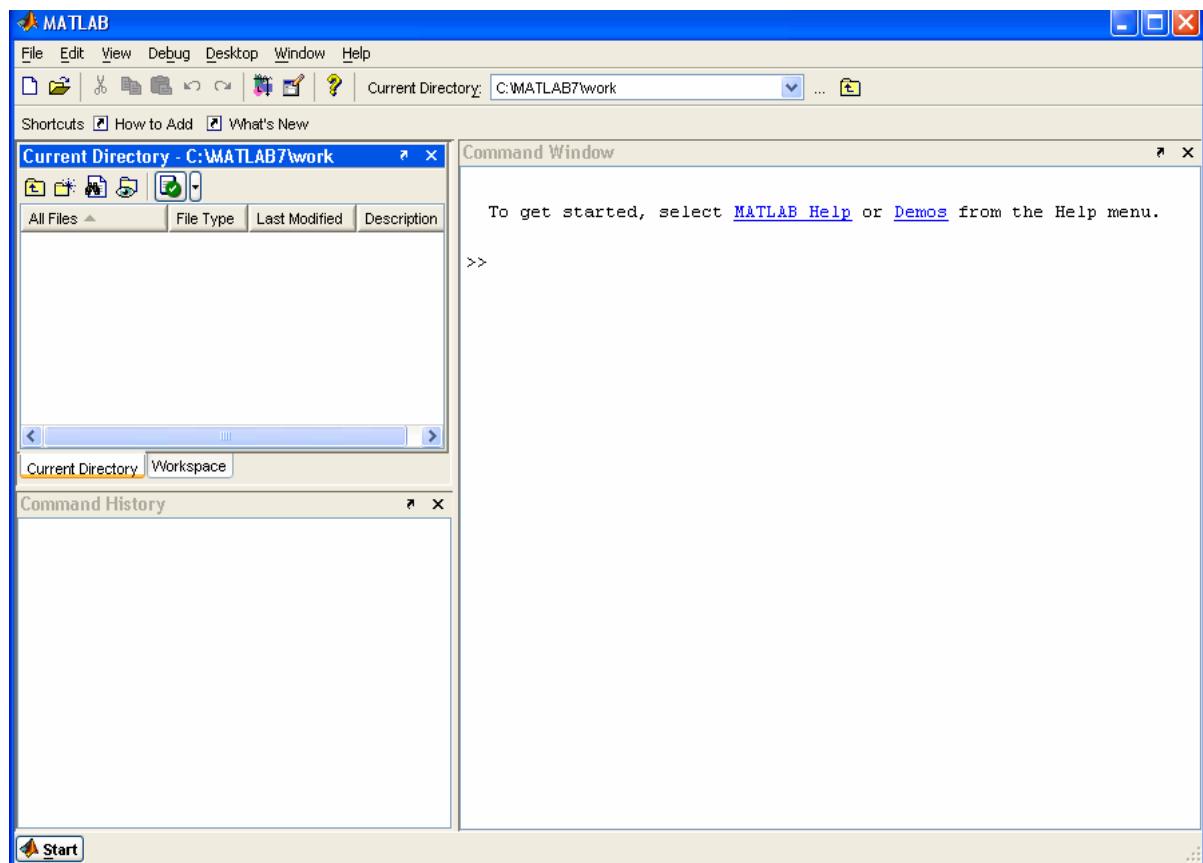
Figure 2.1. Default MATLAB desktop at startup.

Command Window

The heart of MATLAB is the **Command Window**. It is where commands can be directly entered by typing them followed by a **return**. The >> prompt shows that the **Command Window** is ready for entering a command.

Together, MATLAB and PLS_Toolbox contain hundreds of commands in the form of **scripts** and **functions**. A script is simply a series of commands that are executed when the command is called. A function is similar to a script except that arguments are passed to it when it is called and it returns other arguments calculated by the function. A script runs in the base Workspace and does not return value. Once a script or function has been defined, it can be called from the command window or by other functions or scripts.

One of the most useful commands for a beginner is `demo`. (Note that MATLAB is case sensitive and the commands `Demo`, `DEMO` and `demO` would be interpreted by MATLAB as different (and most likely undefined) commands.) If the user types `demo` in the **Command Window** (followed by a **return**), the MATLAB help browser will appear at the Getting Started with Demos page. It is well worth the time for a new user to explore both MATLAB and PLS_Toolbox demonstrations.

Another useful command is the `help` command. It is executed by typing `help` followed by the name of the command. For example, type `help demo` to see instructions on using the `demo` command. The `demo` command requires that you remember the exact name of the command. If you cannot remember the command name, then use the `lookfor` command followed by a key word. For example, `lookfor demonstration` will cause MATLAB to search for all commands that use the word *demonstration* in the first line of their help file.
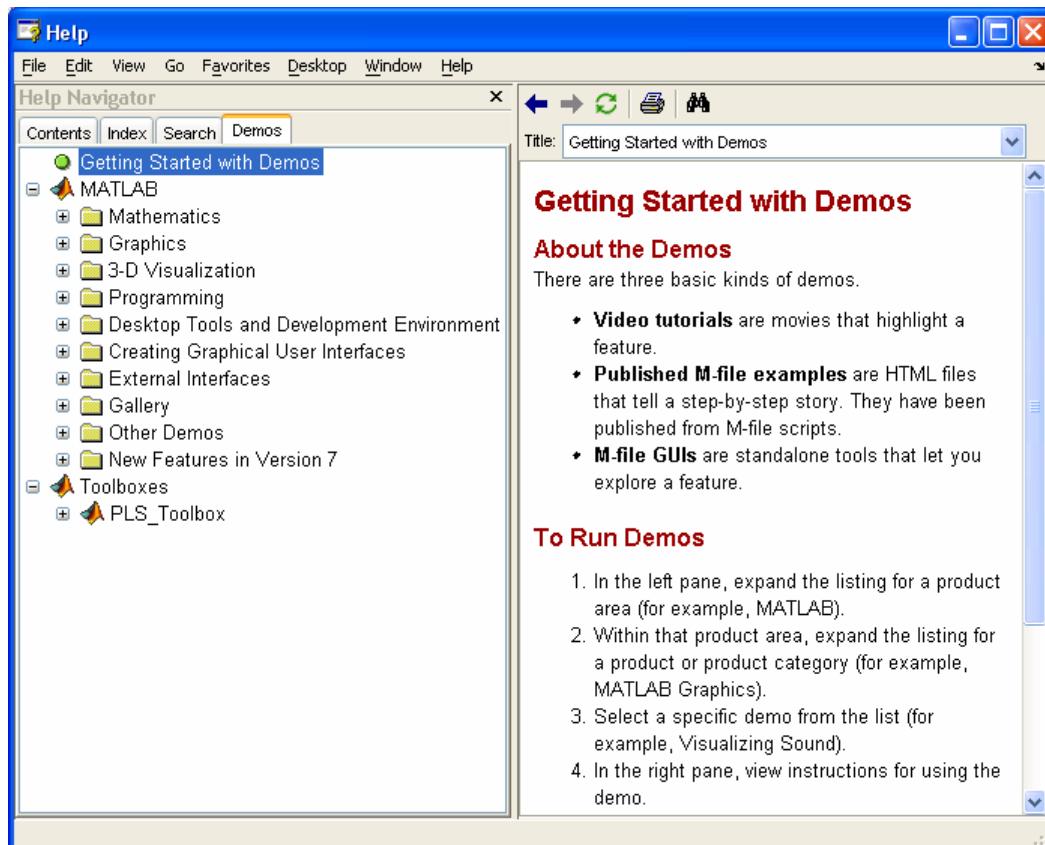
Figure 2-2. MATLAB demos window.

Finally, provided the **Documentation** files have been loaded into the computer when MATLAB was installed, detailed help may be obtained using the **Help** menu choice in the top MATLAB command bar.

A record of executed commands can be viewed by scrolling up the **Command Window** or by examining the **Command History** window.

Entering Data

Before MATLAB can do calculations, it needs data to work on. Typing the following command:

```
» A=[2 5 3 6
7 3 2 1
5 2 0 3]
```

defines the variable A equal to the matrix enclosed within the square brackets. The spaces between the numbers delineate the columns and each **return** starts a new row. The same results are obtained if we use the command:

```
» A=[2 5 3 6; 7 3 2 1; 5 2 0 3]
```

where the **returns** have been replaced by **semicolons**. Either way MATLAB will respond by typing the resulting matrix:

```
A =

   2   5   3   6
   7   3   2   1
   5   2   0   3
```

If you do not wish to see MATLAB echo (print out) the result, end the command with a semicolon. For example, if you type:

```
» A=[2 5 3 6; 7 3 2 1; 5 2 0 3];
```

the variable A will be defined as before, but MATLAB will not echo the result. When working with very large matrices, the use of the semicolon can prevent thousands of elements from being printed on the screen.

Table 2-1. Properties of a number of beers.

	Specific Gravity	App Extr	Alcohol (%w/w)	Real Ext	O.G.	RDF	Calories	pH	Color	IBU	VDK (ppm)
Shea's Irish	1.01016	2.60	3.64	4.29	11.37	63.70	150.10	4.01	19.0	16.1	0.02
Iron Range	1.01041	2.66	3.81	4.42	11.82	64.00	156.30	4.33	11.6	21.1	0.04
Bob's 1st Ale	1.01768	4.50	3.17	5.89	12.04	52.70	162.70	3.93	30.7	21.1	0.11
Manns Original	1.00997	2.55	2.11	3.58	7.77	54.90	102.20	4.05	58.9	18.2	0.05
Killarney's Red	1.01915	4.87	3.83	6.64	14.0	54.30	190.20	4.36	12.3	17.9	0.02
Killian's Irish	1.01071	2.74	3.88	4.48	12.0	64.10	158.80	4.28	53.0	14.2	0.03

Typing in data by hand can become very tedious for large data sets. MATLAB can read a variety of files from other major programs that store data. For example, we may wish to load an Excel file (included as demonstration data with PLS_Toolbox and shown in Table 2-1) containing data for six brands of beer and eleven properties for each beer (Analytical data courtesy The Gambrinus Company, San Antonio, TX).

These data can be found in the file Redbeerdata.xls in the PLS_Toolbox/dems directory. Note: PLS_Toolbox includes several functions for reading .xls and other data files directly into the DataSet Object format typically used with its functions (see, for example, xlsreadr). However, here we will use only the built-in MATLAB-based functions in order to more fully explore MATLAB commands. Redbeerdata.xls may be loaded into MATLAB by first selecting the **File/Import Data...** menu from the **Command Window**. Once the appropriate file has been found and chosen in the **Import** window, the data **Import Wizard** will present the window shown in Figure 2-3.
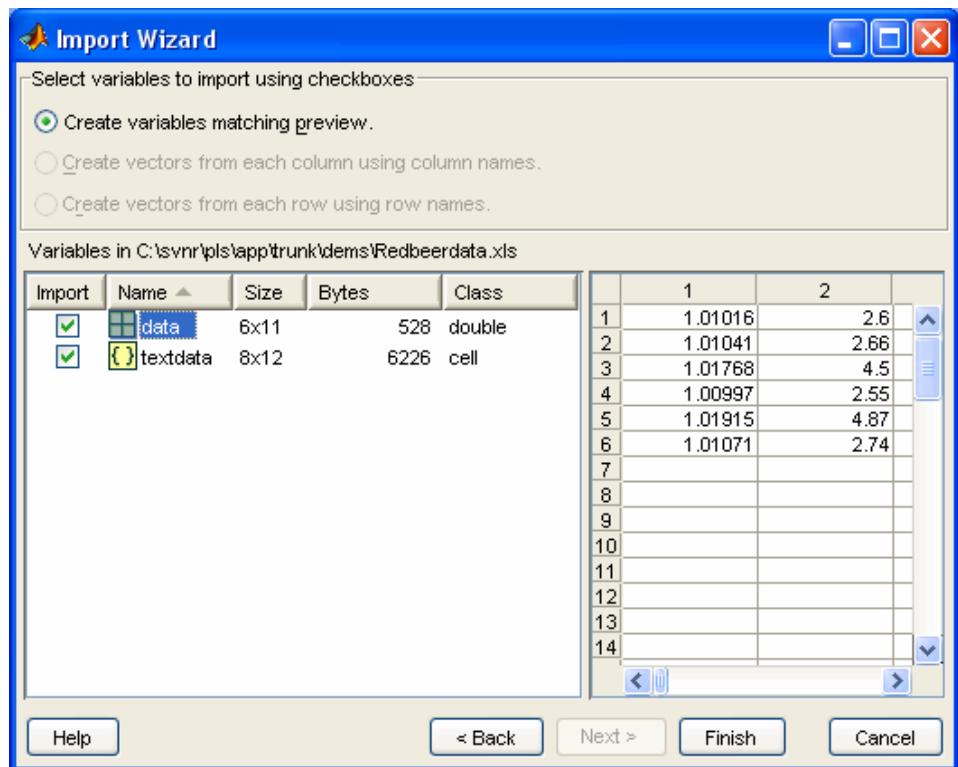
Figure 2-3. MATLAB Import Wizard window with `data` highlighted.
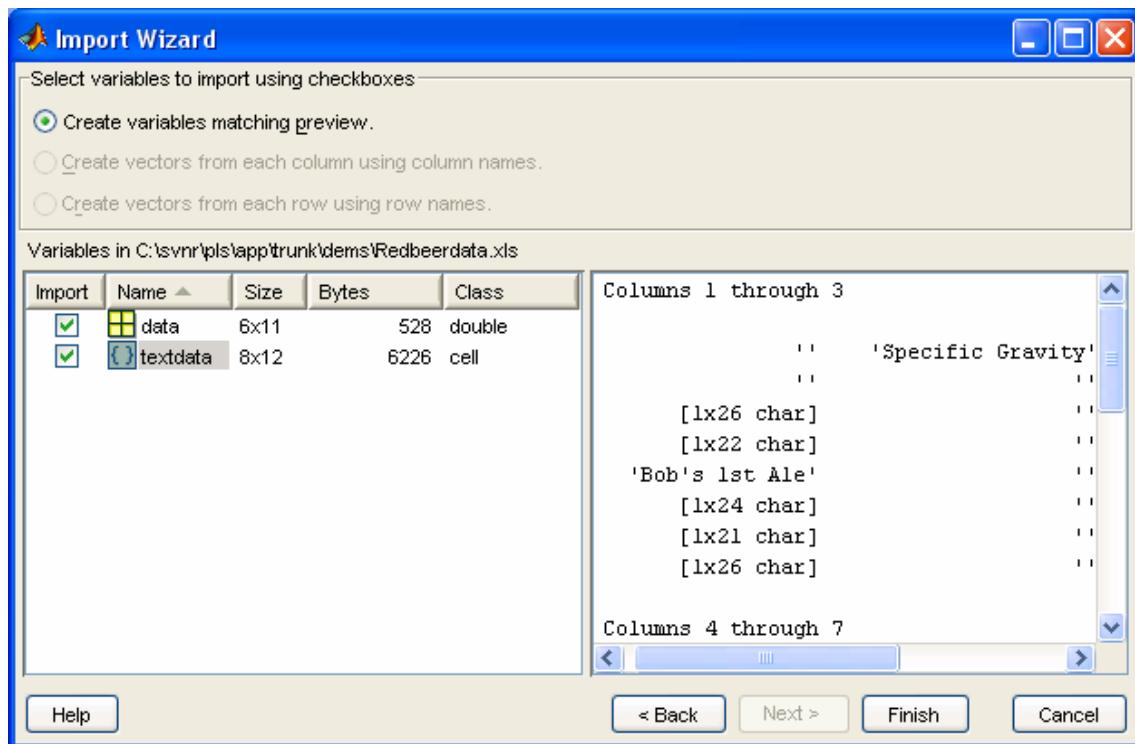
Figure 2-4. MATLAB Import Wizard window with `textdata` highlighted.

14

The Import Wizard has divided the data into a numerical data matrix (`data`) and a text data matrix (`textdata`). Notice that the matrix `data` is a 6 x 11 matrix of numbers in this case. (Matrix notation always refers to rows first followed by the columns.) The variable `textdata` is an 8 x 12 matrix of text cells. Highlight the variable `data` and one can examine the first 10 x 10 part of the matrix to make sure that MATLAB has properly delineated the numerical data. Highlighting the variable `textdata`, as shown in the figure above, allows the user to see that it is made of text cells from the column and row labels, and that the numerical data have been removed, leaving blank cells.

Clicking on the **Finish** button will complete the loading of the data into MATLAB.

Examining the MATLAB Workspace

We can examine MATLAB's data memory or **Workspace** by typing `whos` at the prompt.

```
» whos

 Name          Size      Bytes  Class

 data          6x11        528  double array
 textdata      8x12       6226  cell array

Grand total is 395 elements using 6226 bytes
```

If you prefer, the Workspace can be examined by choosing **Workspace** in the **View** menu. A **Workspace** window will appear.

When we examine the Workspace after loading the data we see that the matrix, `data`, is a 6 x 11 matrix of double precision numbers or **double array**. Typing the name of one of the matrices will cause MATLAB to list the matrix to the screen. For instance, typing `data` at the command prompt produces:

```
» data

data =

 Columns 1 through 7

  1.0102  2.6000  3.6400  4.2900  11.3700  63.7000 150.1000
  1.0104  2.6600  3.8100  4.4200  11.8200  64.0000 156.3000
  1.0177  4.5000  3.1700  5.8900  12.0400  52.7000 162.7000
  1.0100  2.5500  2.1100  3.5800   7.7700  54.9000 102.2000
  1.0192  4.8700  3.8300  6.6400  13.9800  54.3000 190.2000
  1.0107  2.7400  3.8800  4.4800  11.9900  64.1000 158.8000

 Columns 8 through 11

  4.0100  19.0000  16.1000   0.0200
```

```
4.3300  11.6000  21.1000  0.0400
3.9300  30.7000  21.1000  0.1100
4.0500  58.9000  18.2000  0.0500
4.3600  12.3000  17.9000  0.0200
4.2800  53.0000  14.2000  0.0300
```

We can examine just one element of the matrix by indicating the row number, followed by the column number; for example, if we wish to examine the number in the third row and second column we would type:

```
» data(3,2)

ans =

   4.5000
```

Notice that the answer to our request has been assigned to a temporary variable called ans.

We can similarly examine the complete second row by typing:

```
» data(2,:)

ans =

 Columns 1 through 7

  1.0104  2.6600  3.8100  4.4200  11.8200  64.0000 156.3000

 Columns 8 through 11

  4.3300  11.6000  21.1000  0.0400
```

where the colon represents all the columns.

As we saw in the import wizard, the text data are made up of an 8 x 12 matrix of cells containing our sample and variable labels and several empty cells where the numbers had been. This can be seen by typing the matrix name, textdata. Cell arrays are a handy way to store different length matrices as is often the case when dealing with text. Notice that the sample labels are located in rows 3 though 8 of the first column. We can define a new vector, also a cell array, containing our sample names by typing:

```
» SampleLabels=textdata(3:8,1)

SampleLabels =

  'Michael Shea's Irish Amber'
  'Iron Range Amber Lager'
```

```
'Bob's 1st Ale'
'Manns Original Brown Ale'
'Killarney's Red Lager'
'George Killian's Irish Red'
```

where (3:8,1) is read as rows 3 through 8 inclusive and only column 1. Since the SampleLabels matrix is only 8 rows long, we could have also typed

» SampleLabels=textdata(3:end,1);

where end indicates the last row (and the semicolon was used to suppress the screen echo).

We can similarly define a matrix of variable labels by isolating row 1, columns 2 through 12 by typing:

» VariableLabels=textdata(1,2:end)

VariableLabels =

 Columns 1 through 3

   'Specific Gravity' 'Apparent Extract' 'Alcohol (%w/w)'

 Columns 4 through 9

   'Real Extract (%w/w)' 'O.G.' 'RDF' 'Calories' 'pH' 'Color'

 Columns 10 through 11

   'IBU**' ' VDK*** (ppm)'

Type whos to see how we have done. Fortunately, these labels are in a form (cell array of stirngs) where the PLS_Toolbox GUIs can read them directly.

Saving your work

We have done a great deal of work, so it would be a good idea to save our data to disk. Before we save the data, there may be some variables that we would like to remove, for example the variable ans. Perhaps the most dangerous command in MATLAB is the 'clear' command. The command clear ans will remove only the variable ans. However, when clear is not followed by the names of any variables to be removed, it will remove all the variables in MATLAB memory! To save the remaining variables choose **File/Save Workspace as...** from the **Command Window** and give your data a name such as **Beerdata**. The resulting file will be a MATLAB data file with the **.mat** file extension. At some later date, when you wish to reload these data, you may use the **Import Data...** choice in the **File** menu as before.

Note: For those who prefer not to let their finger leave the keyboard, you may use the commands 'load' and 'save' to load and save data respectively. Just type `help load` or `help save` for specific instructions in using these commands. The 'save' command has several advantages in that it allows all or just the specified matrices to be saved and can save the data in several formats such as ASCII. The main disadvantage is that it will save the data in the current directory. You may determine the current directory and its content by using the command 'what'. Use 'cd' to change the current directory (or use the full path name of where the files should be saved).

The Solo and PLS_Toolbox GUI Environment

Most of the higher-level data analysis tools can be accessed through Graphical User Interfaces (GUIs) in PLS_Toolbox. In many cases a GUI can make data analysis faster and easier to perform and interpret than using the command line analogs.

PLS_Toolbox is organized around 4 main GUI tools (Figure 2-5). Each tool is dedicated to a specific step in the data analysis process.

1) The **Browse** GUI is the PLS_Toolbox "desktop" environment. Here one has access to all loaded data, available analysis methods, the DataSet Editor, and other top level tools. With its "drag and drop" functionality, a user can quickly begin a number of data analysis tasks.

2) The **DataSet Editor** is the primary data-handling GUI in PLS_Toolbox. It provides a variety of functions and tools for loading, editing, and saving data. As its name suggests, the object used in PLS_Toolbox for managing data is the DataSet Object (see chapter 16 for more information).

3) The **Analysis** GUI is the core interface with PLS_Toolbox data modeling and exploration functions. This is where you will create and explore your models.

4) The **PlotGUI** interface is the principal data visualization tool for PLS_Toolbox. It provides a vast number of tools for labeling, manipulating, and publishing plots generated using PLS_Toolbox.
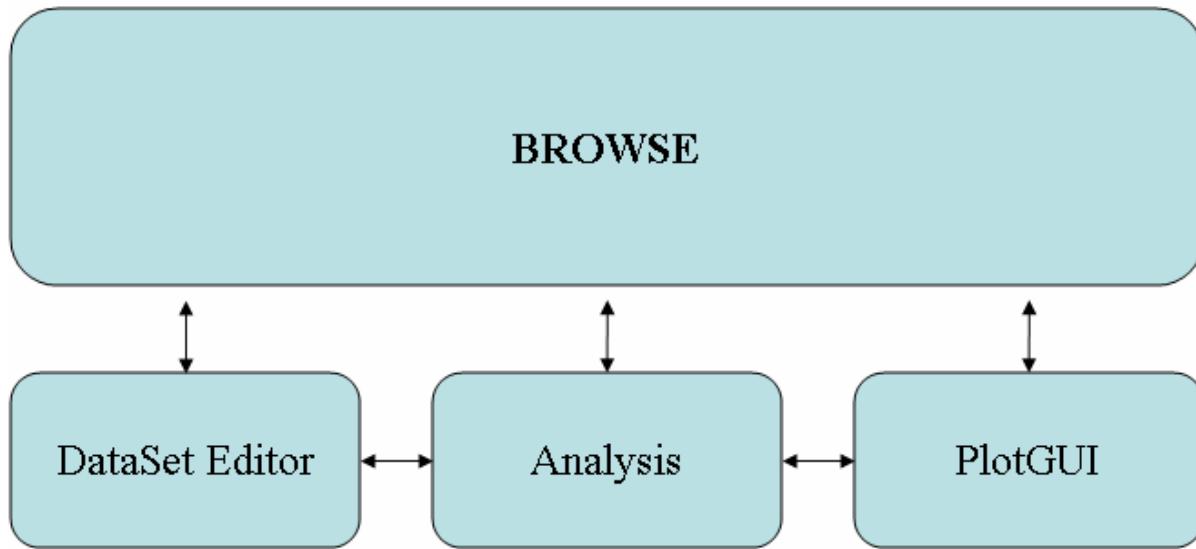
Figure 2-5. GUI diagram.

Browse
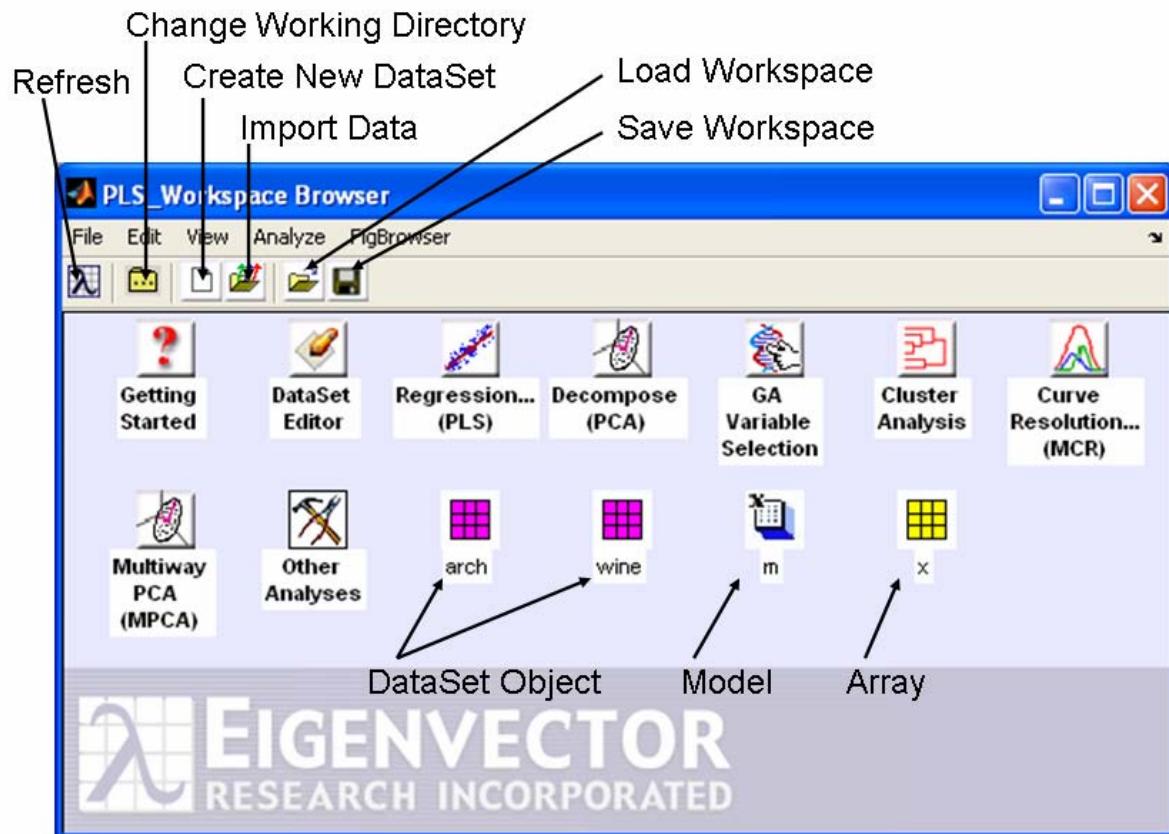
Figure 2-6. PLS_Toolbox Browser.

The **Browser** window (Figure 2-6) shows icons for tools and objects in the PLS_Toolbox workspace. Each analysis icon opens its respective interface in the named mode (*e.g.*, **Decompose** will open the **Analysis** window with PCA already selected). The browse environment is "drag and drop" enabled so you can click on a DataSet icon, drag it over an analysis icon, and release the click to start the analysis. This will open the **Analysis** window with the method pre-selected and load the data. Likewise, you can drag an existing data or model icon from the browse window over to an Analysis window and "drop" the data /model into an ongoing analysis.

Although the **FigBrowser** utility can help you manage figures (see below), you can also set the **Browser** to display figures using setplspref (see setplspref and getplspref in the manual for more information) from the command line using the following command:

```
>> setplspref('browse', 'viewfigures', 'true')
```

Once you've set the preferences, you'll have to restart the Browser for the new preferences to take affect.

FigBrowser

As you work through an analysis you often can generate lots of figures. To help manage and view those figures, there is a utility called **FigBrowser** (Figure 2-7). It creates a thumbnail image of each open figure/window and displays it (Figure 2-8).
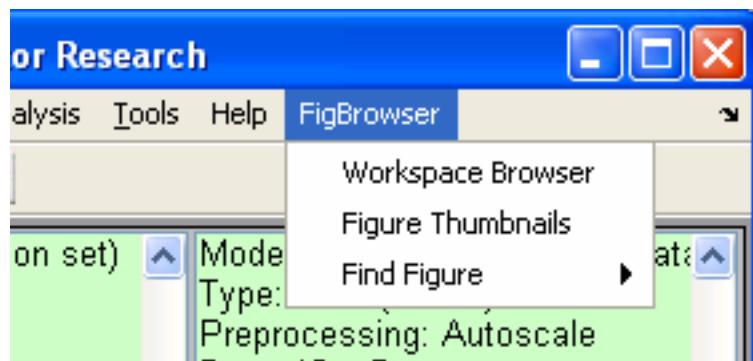
Figure 2-7. FigBrowser Menu; selecting **Figure Thumbnails** will open FigBrowser.
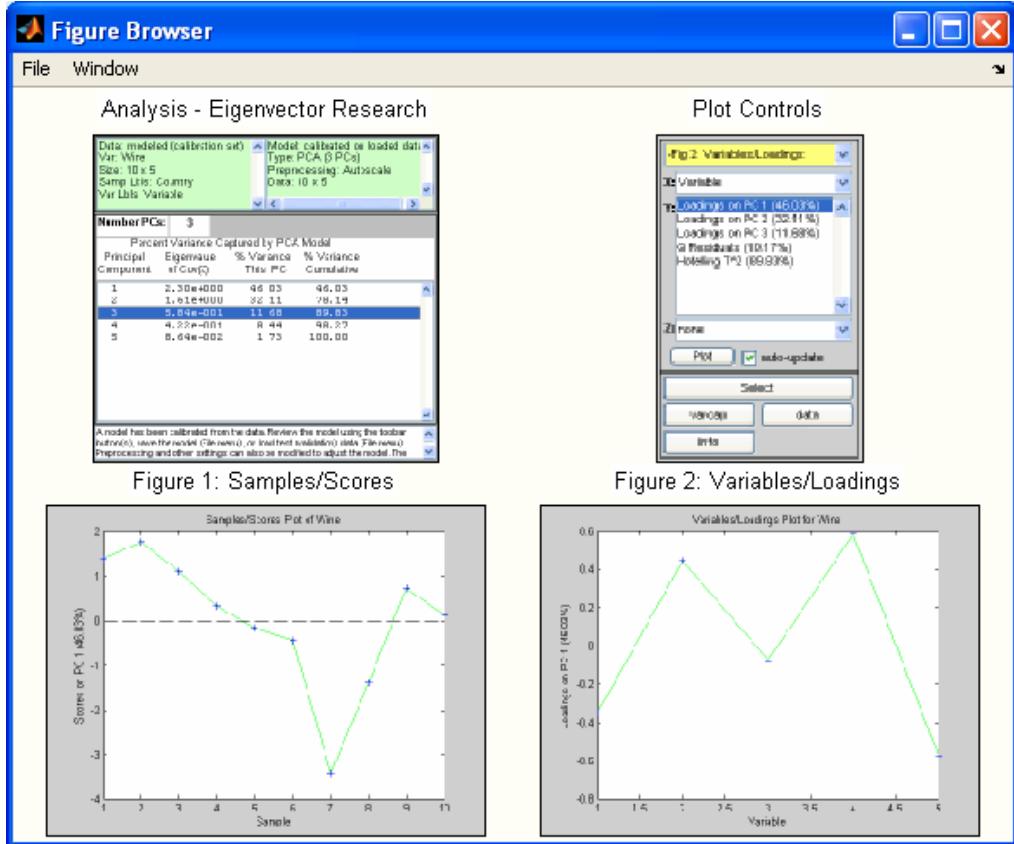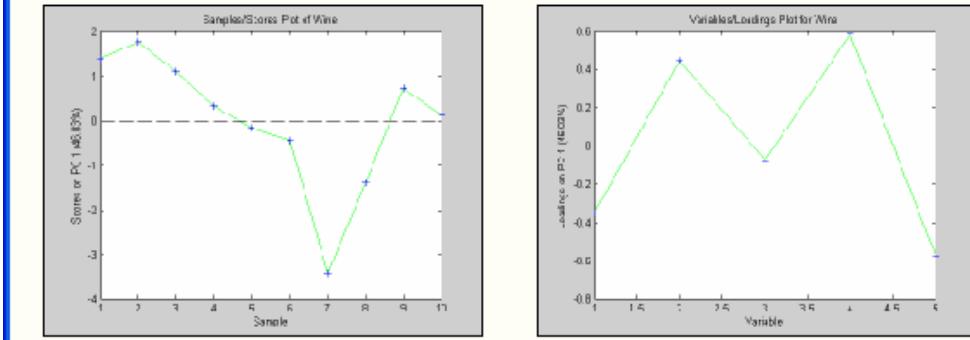
Figure 2-8. Figure Browser.

Clicking on a particular figure thumbnail will bring it to the front, make it the "current figure" in MATLAB, and then close the thumbnail window.

Analysis

The Analysis application provides a common interface for several popular PLS_Toolbox functions, including:

PCA	Purity	PARAFAC	PLS	PLSDA	MPCA
MCR	Cluster	PCR	SIMCA	MLR	

The interface allows the flexibility to switch between analysis methods (for a given type of data) and will help you manage your developed models. There are various useful tools integrated into the application that will be described below.

The Analysis interface can be started from **Browse** or from the command line using the generic command.

```
>> analysis
```

It can also be started with a default analysis method selected by typing the PLS_Toolbox command for the specific analysis of interest without any input arguments. For example, the command below starts the analysis interface preset to the MCR analysis method.

```
>> mcr
```

<u>Main Figure</u>

The main Analysis window (Figure 2-9) has a layout with four basic areas. The menu items allow access to common I/O functionality, data manipulation, and analysis set-up. The Toolbar contains buttons specific to a particular analysis method. The status windows show information for the currently loaded data and model. For analysis methods that generate statistics, the SSQ window will display statistics and allow you to manipulate the number of components or factors to be modeled. At the bottom of the figure is a **Help Window** that displays suggestions for the next step of an analysis. It is meant as a guide for novice users and can be turned off by right-clicking on the window.
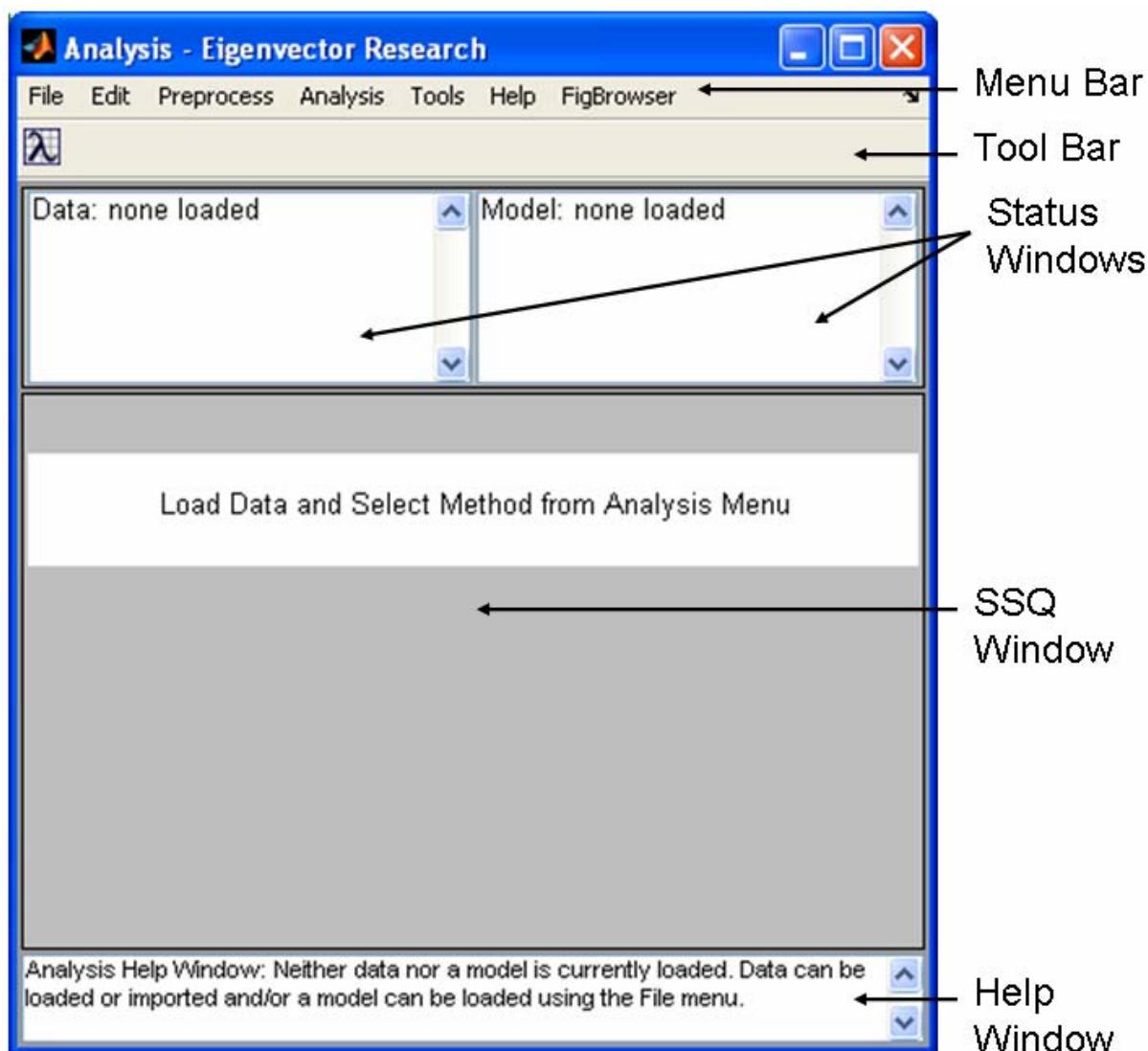
Figure 2-9. Main **Analysis** window.

Some menu items are available at all times, others will be disabled depending on the loaded data and model type. Notice that when no DataSet Object or model is loaded, all items except for loading functions are disabled in the menus (see next figure). As you load data and create models you'll find appropriate menu items enabled or disabled.

Menu Items - File

The **File** menu (Figure 2-10) contains functionality to load, save and clear data and models. Saving and loading occur through a common interface (see the next section). In general, items dealing with data will allow you to access either the X- or Y-block. The use of the X- and Y-blocks depends on the analysis method selected; some analysis methods do not use the Y-block. In all cases, the number of rows (samples) in the Y-block must match the number of rows (samples) in the X-block. Use **Load Data** to load

MATLAB-formatted variables from .mat files or the MATLAB workspace. If you choose **Load Data/Both**, you'll be prompted to load a Y-block after loading an X-block. **Import Data** will load data from sources outside the MATLAB environment, such as ThermoGalactic .spc, Microsoft Excel, or .txt files. **New Data** is used to create a DataSet Object of given size and initial value (*e.g.*, random values (rand), NaN, 0). Note that PLS_Toolbox and MATLAB also supply several different command line tools for importing and manipulating data. Often it can be useful to import data from the command line then load it into **Analysis** using the standard **Load Data** menu.

Several types of analyses use "options" to provide additional optional inputs to a function. These options are stored in structure arrays and can be loaded and saved similarly to models. They can also be edited via the **Edit** menu (see next section). See the documentation for the individual analysis method for more information on specific options.
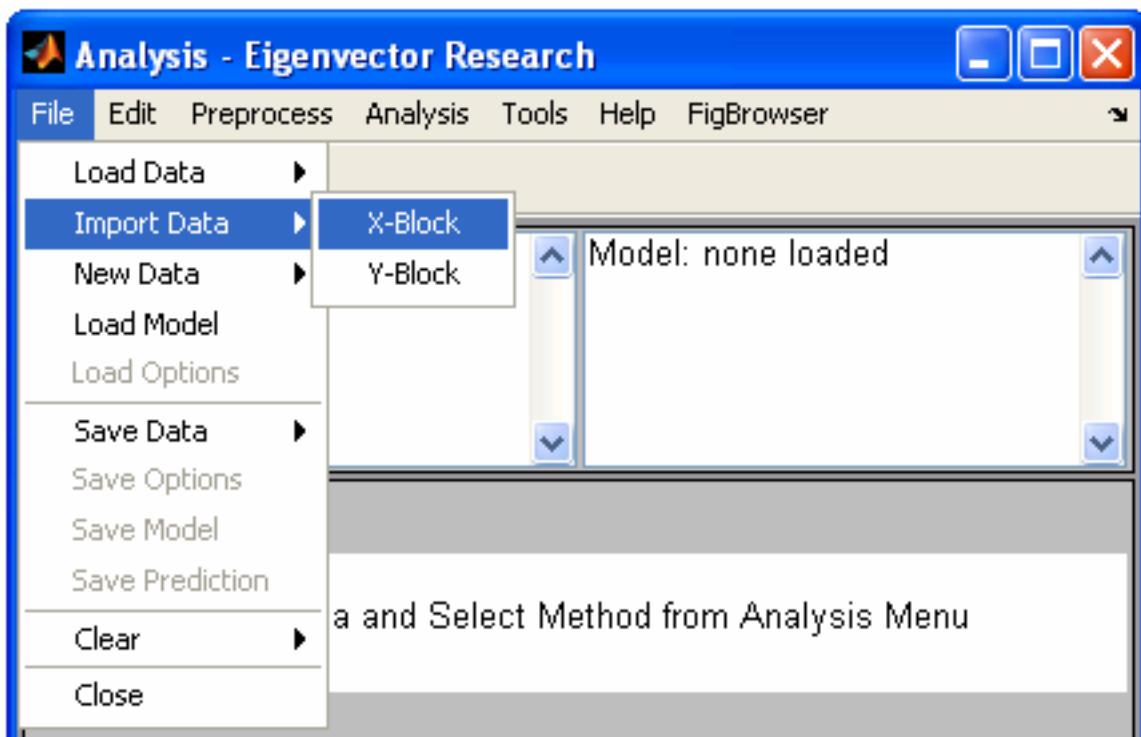
Figure 2-10. **File** menu.

The **Save Data** menu option saves data as a DataSet Object and saves Models and Predictions as MATLAB Structures (see the appendix entries for each of the items in the PLS_Toolbox manual for more information). When you **Clear** a model, all of the plots associated with that model are closed automatically. Likewise, if you clear data (X-block or Y-block) all plots associated with them will close. If data are overwritten, all open plots will be updated.

Once a model has been calculated, most analysis methods allow you to load new data to which you may then apply an existing model (*i.e.*, make a prediction using the model). Be aware that if you load new data to be applied to an existing model, the size of the new data must be the same as that of the old data or you will receive an error.

Once a model has been calculated, if the calibration data are cleared (or overwritten by loading new data), the model can no longer be modified. The same is true for a model which has been loaded from a file or the MATLAB workspace. To make any changes, you must create a new model by using the **File/Clear/Model** menu option.

Load and **Save** operations use a common interface that allows loading from either the MATLAB workspace or MATLAB-formatted (.mat) files. You can use the interface to switch between workspace and file modes using the button located in the lower left corner. The Workspace view allows you to save or load directly to/from the current MATLAB Workspace. The File view allows you to save or load directly to/from a .mat file.

In File view (Figure 2-11), the controls at the top of the window allow for standard folder navigation. The two list boxes, Files and Variables, show, respectively, the available files in the currently selected folder and the available variables in the currently selected file. Note that a .mat file can contain several variables and you can select one or more from the Variables list to load. When saving to a .mat file you must name both the file and the variable (*i.e.*, both the File and Variable text boxes must have values in them). Also notice that in the Files list a name preceded with "[ ]" indicates a folder. To navigate into any folder, either double-click the folder name in the listbox or select it and click the **Open** button.
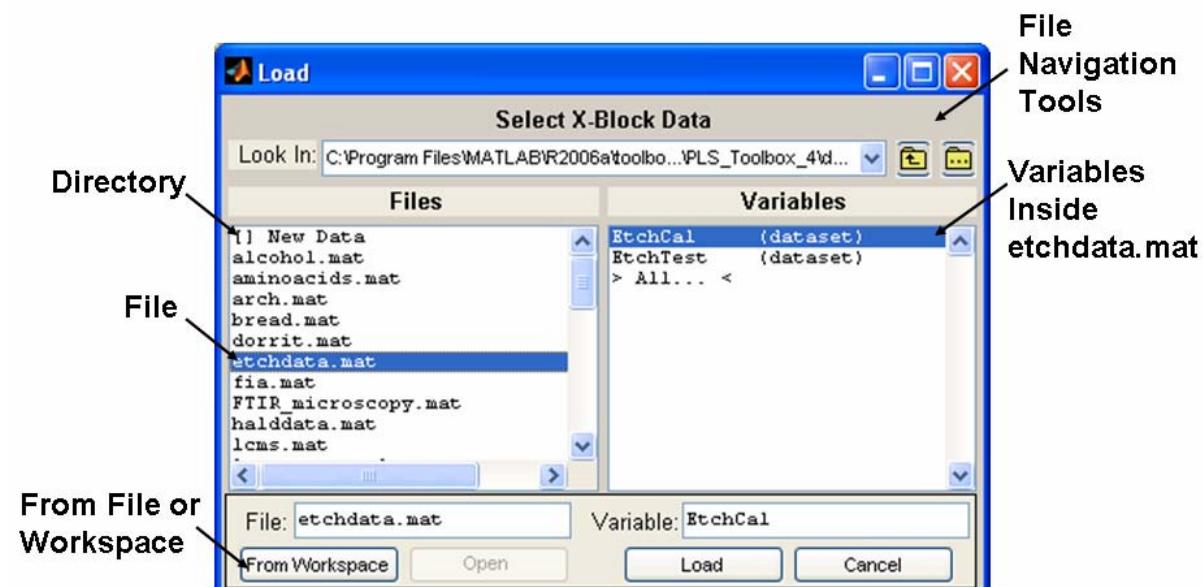
Figure 2-11. **Load** dialog box.

The **Edit** menu of the Analysis window (Figure 2-12) provides tools for viewing and manipulating loaded data. The **X-block Data** and **Y-block Data** options open the specific DataSet Object in a **DataSet Editor**. Selecting **Plot X-block** or **Plot Y-block** will open the DataSet Object with **PlotGUI** and display plots of general statistics and allow plotting of subsets of the data (see the **DataSet Editor** and **PlotGUI** sections later in this chapter for more information).

Select Y-Columns is used when the Y-block contains multiple columns. A list of available columns is presented from which you can choose which of the Y-block columns to use in the analysis. The top two selections from the **Options** submenu will open the Options GUI and allow you to adjust settings the current analysis or for the Analysis GUI itself. The **Preferences** selection will open a GUI for adjusting application "preferences" to override default options (set within a function). Users should be extremely careful if using the Preferences GUI, changes to a function's preferences will be persistent (even if MATLAB is exited) and no warnings will be shown.
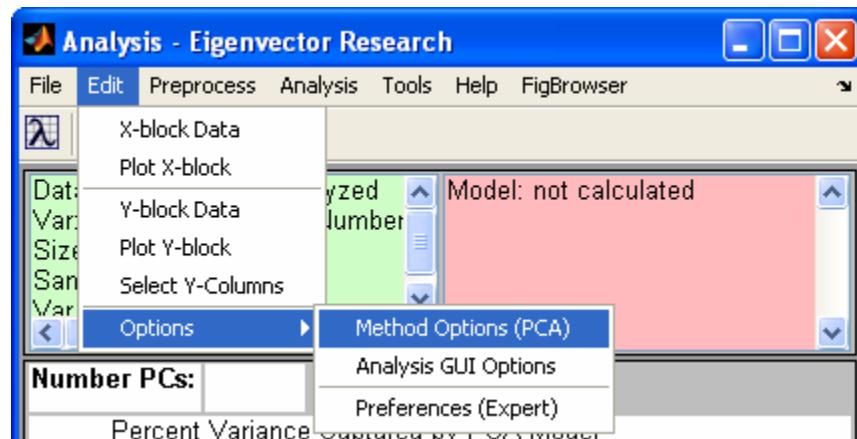
Figure 2-12. **Edit** menu.

Options GUI

Options provide additional <u>optional</u> inputs to a function. The inputs are stored in a MATLAB structure array and can be loaded, edited, and saved from the Analysis interface. The Options GUI is an interface into the Options structure.
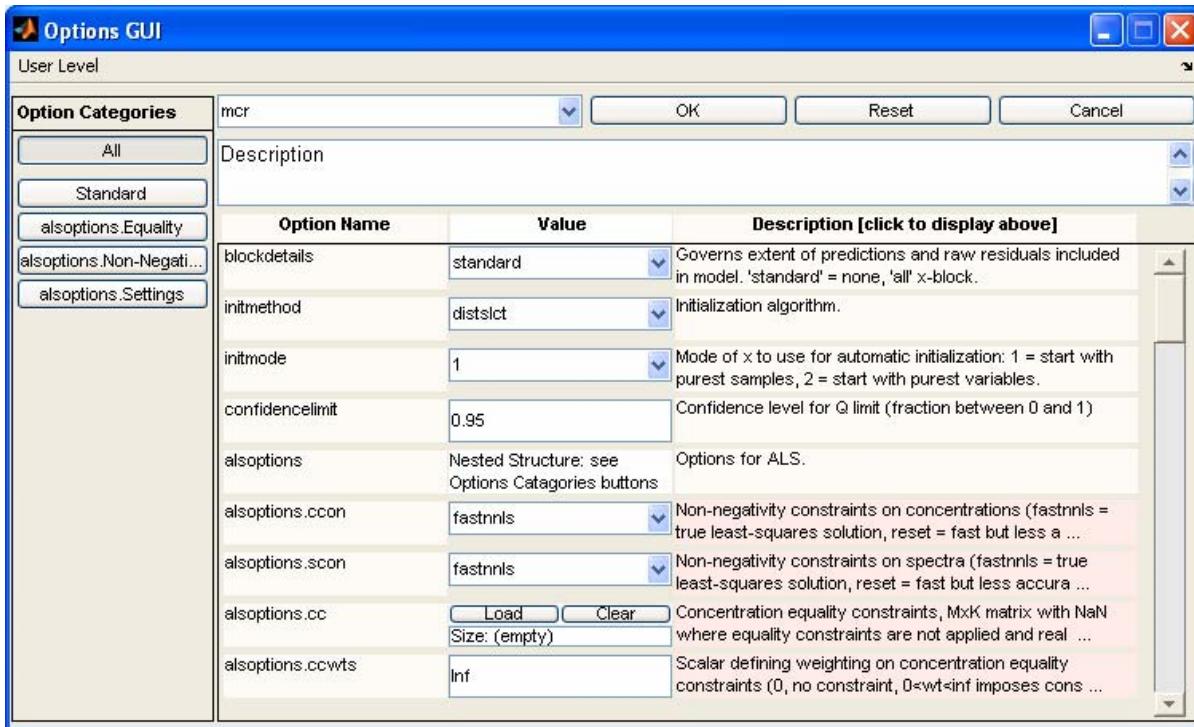
Figure 2-13. **Options** GUI window for MCR.

Within the **Options GUI** you have several ways to narrow down the options available for editing. The **User Level** menu will make available only the options that a particular type of user needs. If set to "advanced," all available options will be displayed. The **Options Categories** buttons display logical subsets of options to make it easier to view and modify options of interest. Substructures will also appear as buttons in the Options Categories list.

To change an option click on the appropriate box or pulldown menu in the **Value** list and enter or select the value you wish. Look at the **Description** box for a brief explanation of the options. If the box is pink, the explanation is longer than can fit in the box. Clicking on the box will display the complete contents in the scrollable Description area above the list.

Menu Items - Preprocess

The **Preprocess** menu (Figure 2-14) allows setting and viewing of preprocessing options. Each block has a submenu for setting common preprocessing methods directly or for accessing the **Custom Preprocessing** figure. After making a change to preprocessing, you will usually be required to recalculate the model (by clicking the **Calc** button). **View Preprocessed Data** displays the effects of the selected preprocessing on loaded data. The plot(s) are automatically updated to reflect any changes in preprocessing.
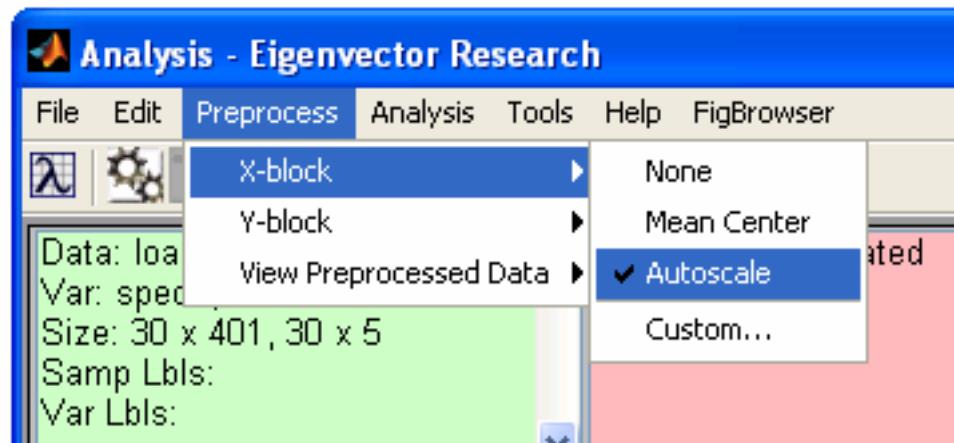
Figure 2-14. **Preprocess** menu.
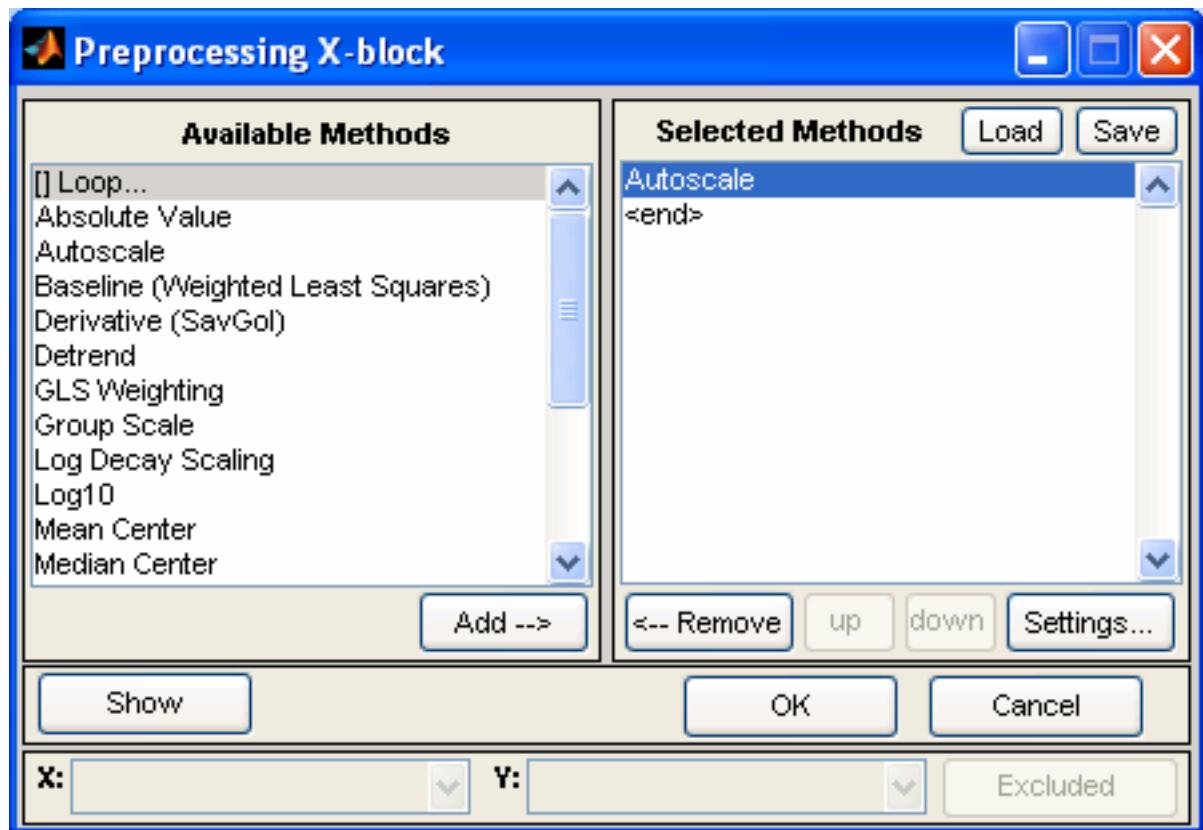
Figure 2-15. **Custom Preprocessing** window.

The **Custom Preprocessing** window (Figure 2-15) allows you to choose from a list of available preprocessing methods. After selecting a method from the available methods list, pressing the **Add** button will insert the selected method into the **Selected Methods** list on the right. Some methods will display an additional window for method specific settings when the item is added to the Selected Methods list. These settings can also be

28

modified by selecting the method in the Selected Methods window, then pressing the **Settings…** button.

The **Selected Methods** are order specific – that is, they get applied in order from top to bottom. The order of preprocessing can have a very significant effect on an analysis; this should be carefully considered in the development of a model.

Note that n-way data have different preprocessing methods than 2-way data, and care should be taken when switching between 2-way and n-way data. Again, you must recalculate the model after making any changes to preprocessing. You may close the preprocessing window (using the "X" button in the upper right corner of the figure) at any time; its settings are automatically saved after each addition.

You can load and save preprocessing settings from/to the MATLAB workspace and .mat files using the Custom Preprocessing window's **Load** button.

The **Show** button will display two plots side by side with the raw data on the left and the preprocessed data on the right (Figure 2-16). You can select the axis values using the drop-down menus and toggle the **Excluded** button to show excluded data.
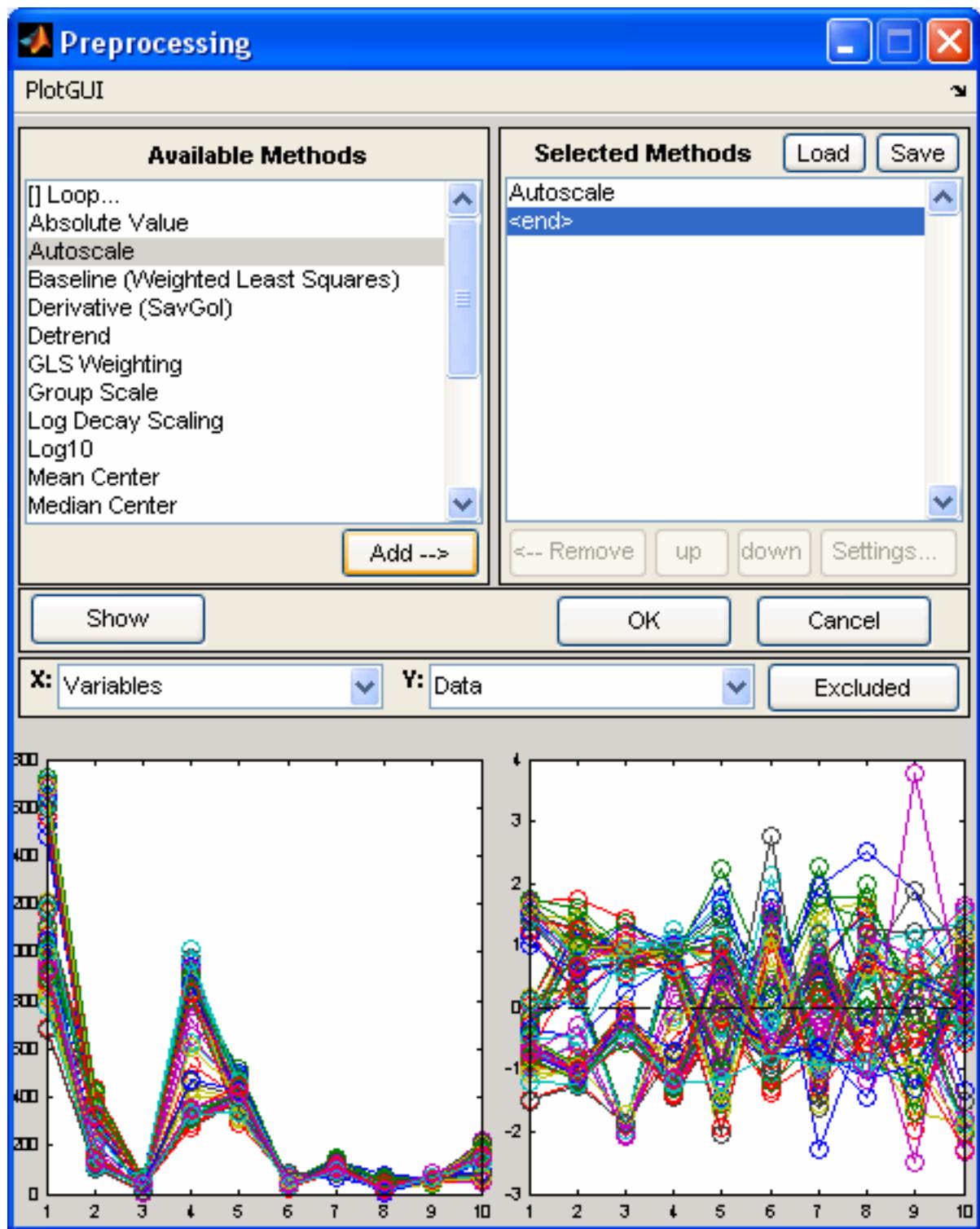
Figure 2-16. **Preprocessing** GUI with **Show** clicked.

The **Analysis** menu (Figure 2-17) displays a list of data analysis methods available in the interface. Only those methods that are valid for the currently loaded data will be enabled (*e.g.,* in the figure below, the `wine` demo DataSet Object is loaded and only five methods are available). Switching methods will cause any currently developed model to be cleared. If the model is unsaved you will be prompted to save the current model.

The methods available at any time depends on the number of data blocks loaded, the dimensionality of the data (2-way vs. n-way), and additional details in the DataSet Object. Methods that require both an X and a Y block (*e.g.,* PLS, PCR, …) will only be available if both blocks are loaded. Methods that require only an X-block are available if both X- and Y-blocks are loaded; however, they will only operate on the loaded X-block while ignoring the Y-block. SIMCA requires that the X-block contain classes for the samples (see the section on the **DataSet Editor** later in this chapter, and Chapter 16 for more information on DataSet Objects). PLSDA requires either classes for the X-block samples or a Y-block containing class assignments.
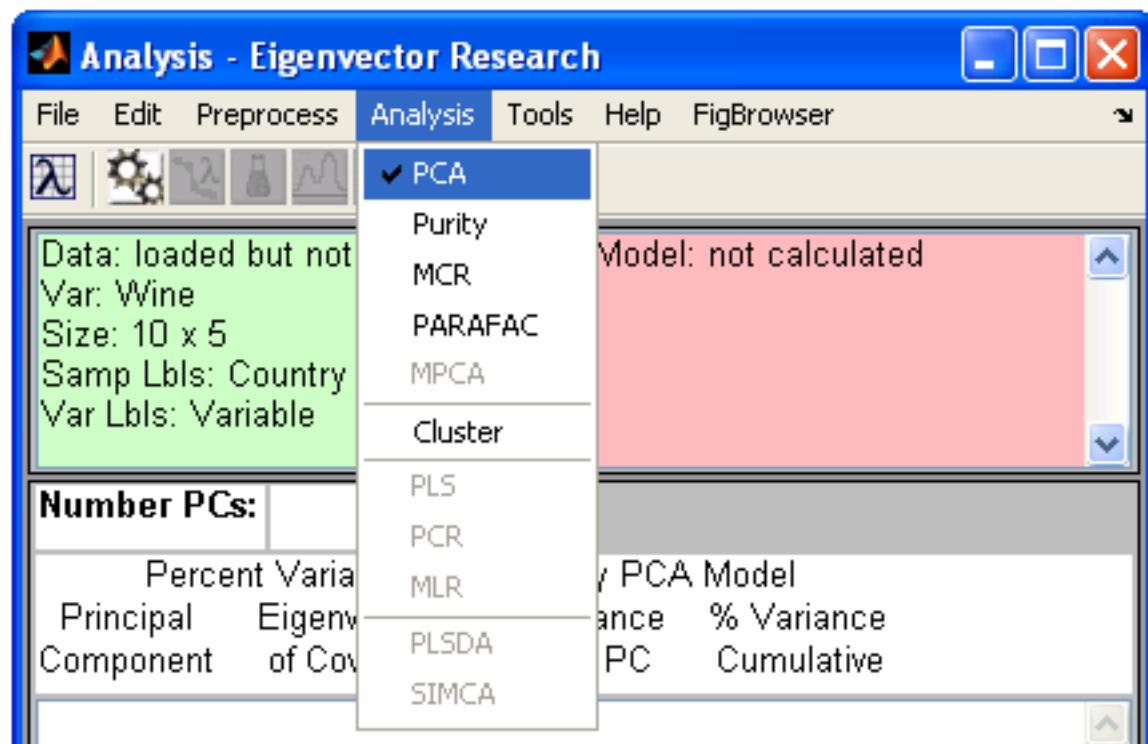
Figure 2-17. **Analysis** menu.

Menu Items - Tools

The **Tools** menu (Figure 2-18) shows utilities available for DataSet Objects and Models. **Cross-Validation** displays an interface for selecting and configuring a cross-validation

method (see `crossval` in the reference manual for more information). Cross-Validation is not available for all methods. **Show Model Details** displays model statistics and information in a window from which the user can easily copy the information. **Correlation Map** will open a figure containing a map of correlated variables. If there are less than 20 variables, they will be sorted, with the most correlated variables next to each other (see `crosscor` in the reference manual for more information). **Estimate Factor SNR** estimates the number of significant factors in multivariate data.
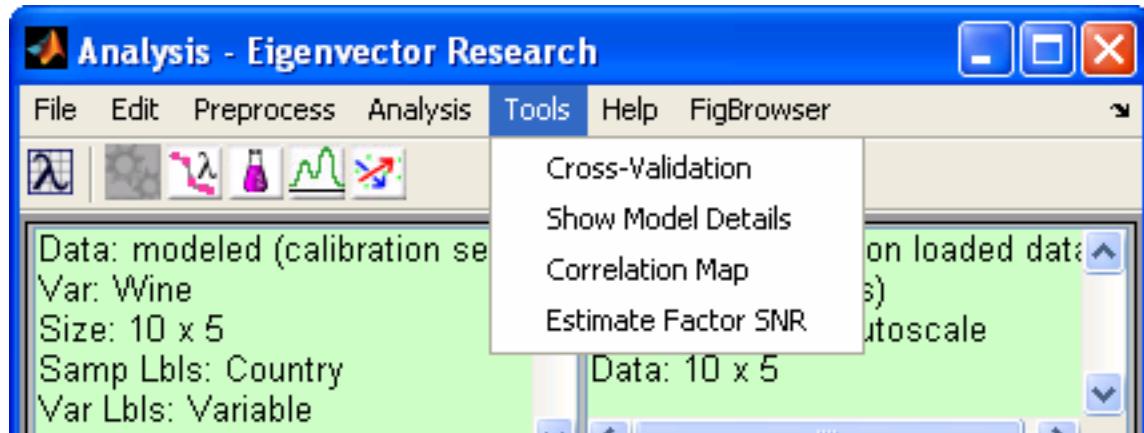
Figure 2-18. **Tools** menu.

Menu Items - Help

The **Help** menu (Figure 2-19) has several selections for PLS_Toolbox help and information. **PLS_Toolbox Help** is an interactive interface providing topic-specific assistance on PLS_Toolbox functions. The **PLS_Toolbox Browser** is a graphical interface for the Toolbox (see above; clicking the Eigenvector Research Lambda icon button on the toolbar will also open the Toolbox Browser). The Manual selections open various portions of this document. The **Online** selections will open your default browser to the EVRI homepage or FAQ page. **About PLS_Toolbox** provides version and installation information for MATLAB as well as PLS_Toolbox.
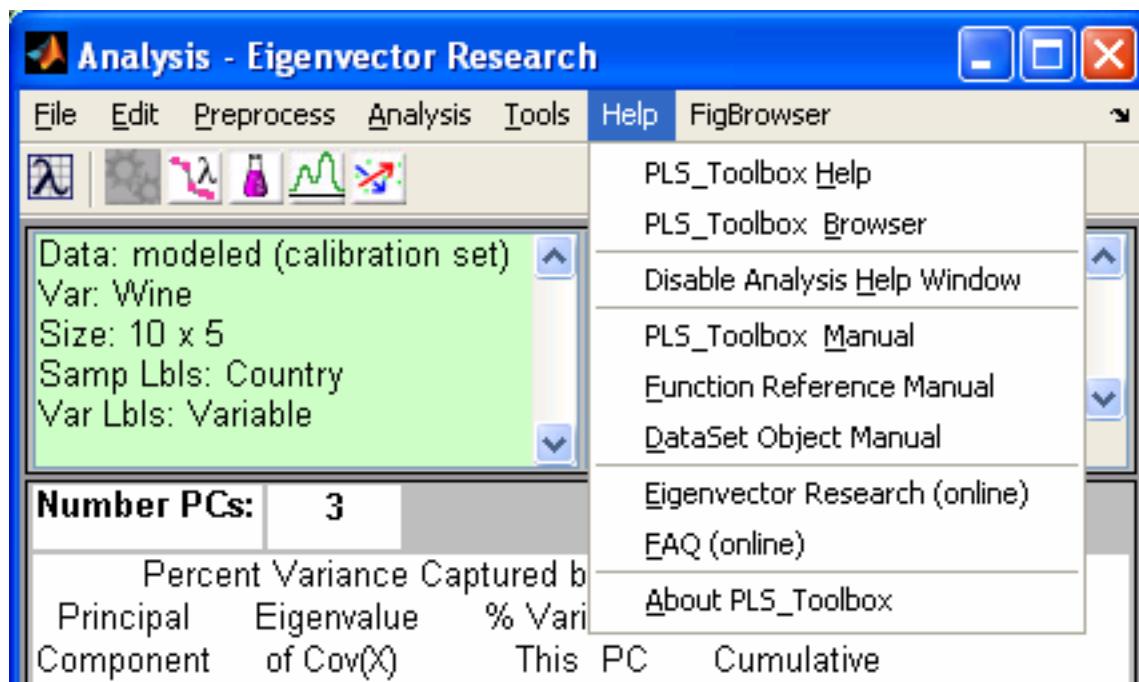
Figure 2-19. **Help** menu.

The Toolbar

The toolbar on the Analysis window (Figure 2-20) contains buttons to calculate and display models and data. The buttons available and their actions depend on the type of analysis method selected and individual buttons will be automatically enabled or disabled depending on the status of your analysis. For instance, when you first load data and choose an analysis, only the calculate button will be enabled. Holding the mouse cursor over the top of a particular button will display the **Tooltip** for that button. The Eigenvector Research **Lambda** icon button is always present in the toolbar and opens the PLS_Toolbox **Browser**.
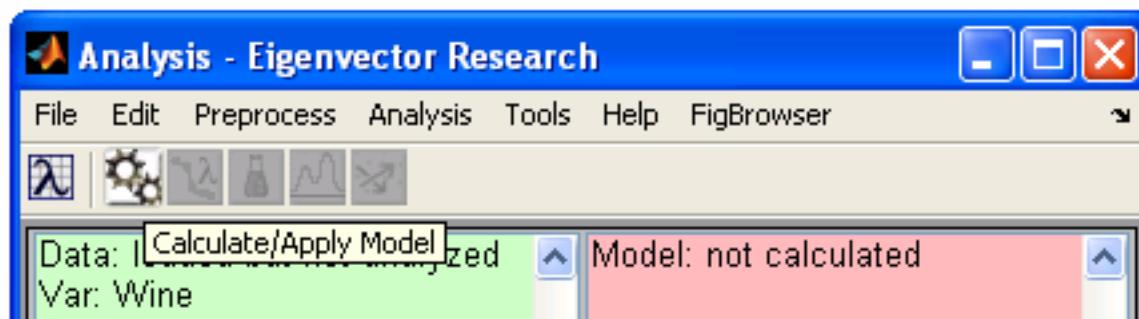
Figure 2-20. PCA, MCR, PLS and PCR toolbar with **Calculate** button tooltip.
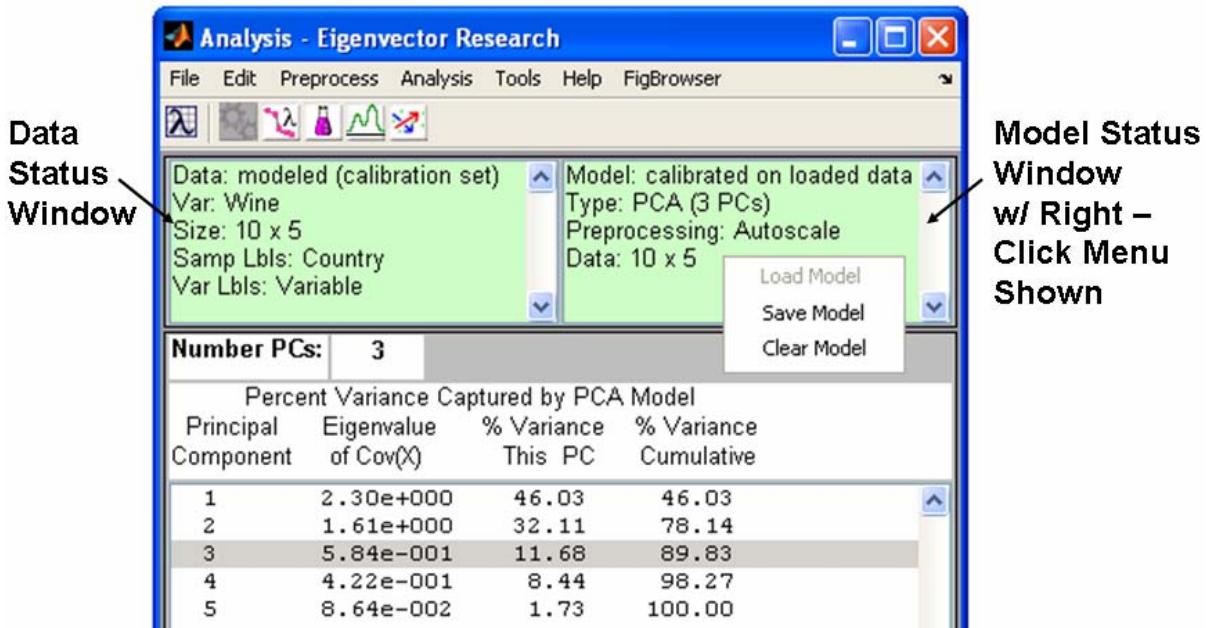
Figure 2-21. **Analysis** interface with status windows populated
(note right-click menu shown for model status window).

Status Windows

The status windows (Figure 2-21) show information on models and loaded data. Both windows are right- and left-click enabled. Left-clicking the **Data Status Window** will bring up the **DataSet Editor** with your current data (see the DataSet Editor section below for more information). Left-clicking the Model status window will display the **Show Model Details** window. Right-clicking either window will display a subset of the File and Edit menu items applicable to the window (see the Model Status Window right-click menu displayed above). If editing data in the DataSet editor, any changes made will be automatically updated in the loaded **DataSet,** but you will need to recalculate the model upon completion.
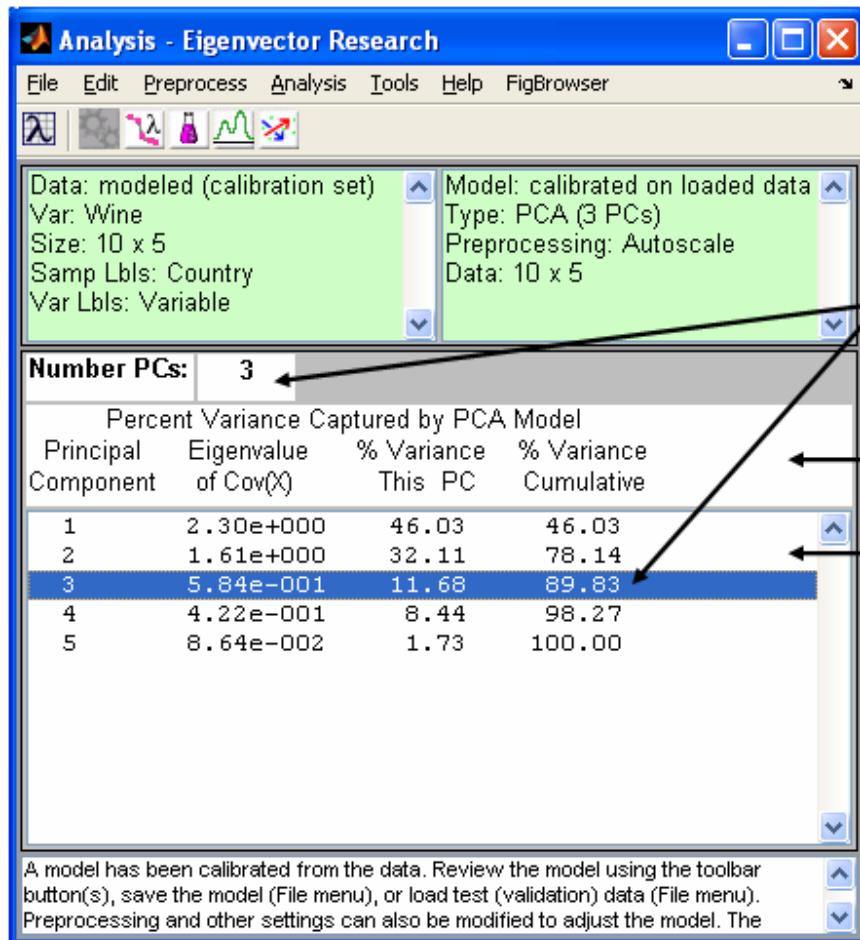
Figure 2-22. **Analysis** interface with SSQ table populated.

SSQ Window

The **SSQ Window** (Figure 2-22) interactively displays Variance Captured or other statistical information for models. The terminology and data displayed will change depending on the Analysis selected. To choose the number of components or factors for an Analysis you can click on the desired number in the **Variance Captured Data Table** (don't forget to recalculate when needed).

For some methods (*e.g.,* MCR and PARAFAC), models are not "nested" – that is, when you add or remove components, the other components in the model are affected by the addition or removal (this is not true of PCA, PCR or PLS models, in which adding or removing a component has no effect on the other components). In these methods, the SSQ table behaves slightly differently. Instead of obtaining an entire table of variance captured for all components, even those not included in the model, the variance captured for only the included components is given. Models with more or fewer components can be investigated by clicking on the appropriate number of components and clicking **Calculate**. (In the rare event that you need to exceed the default maximum number of factors (20), the Number PCs/Components box is active (editable) and you may enter a

larger number manually). Note that once a model with a given number of components is calculated, it is "cached" so that it can be recalled faster should you want to return to that model later. These models are indicated in the table by the label "<View Model>". Clicking on any of these lines followed by **Calculate** will automatically recall that model.

Describing the different analysis methods is beyond the scope of this chapter. For more information on the individual methods, please see Chapter 4.
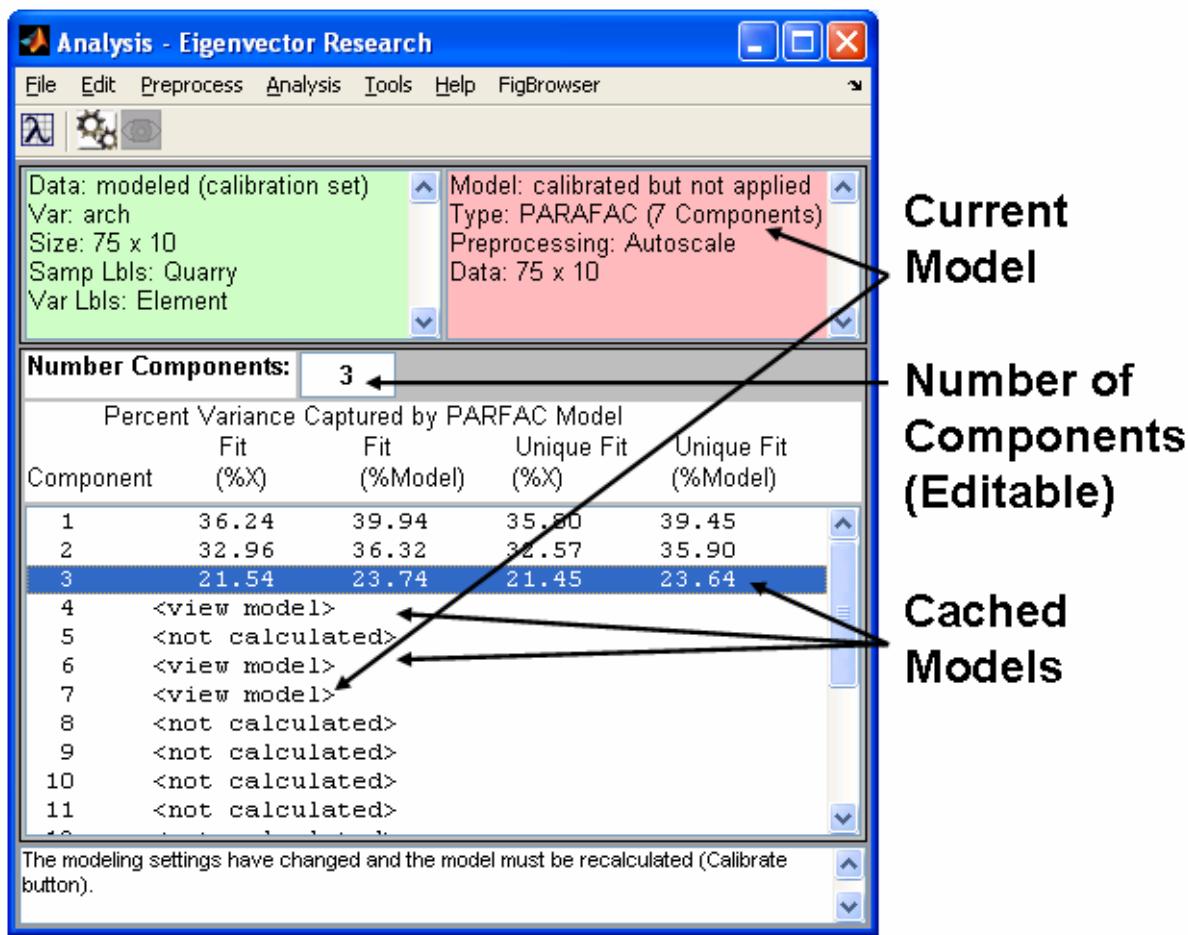
Figure 2-23. **Analysis** interface showing cached models for PARAFAC analysis.

The DataSet Editor

The **DataSet Editor** (DSE) (Figure 2-23) is an interface for editing the contents of a DataSet Object (see "Chapter 16: Advanced Software Information" for more technical information about DataSet Objects). Using the Editor can be easier and quicker than manipulating a DataSet Object from the command line. The demonstration below will run through some of the common functions of the DSE.

Start an empty DataSet Editorby using the MATLAB command below or by clicking the DataSet Editor icon in the Browser:

```
>> editds
```

Load the Wine DataSet Object using the Load command from the **File** menu. Navigate to the dems folder in your PLS_Toolbox folder to locate the Wine DataSet. (If you have already loaded a DataSet object into the MATLAB workspace, you can also double-click on the DataSet object in the MATLAB Workspace Browser to start the DSE and load the given DataSet object).

The Load, Save, and Import functions in the File menu are similar to those in the Analysis interface, allowing you to load or import data from a variety of sources. The DSE also permits concatenation of data by loading new data with modes that match one or more modes of the currently loaded data.

After loading the Wine DataSet Object, your editor should look similar to Figure 2-24. The default tab displayed is **Info**. Here we can see general information about the DataSet Object including the author, its size, and date created.
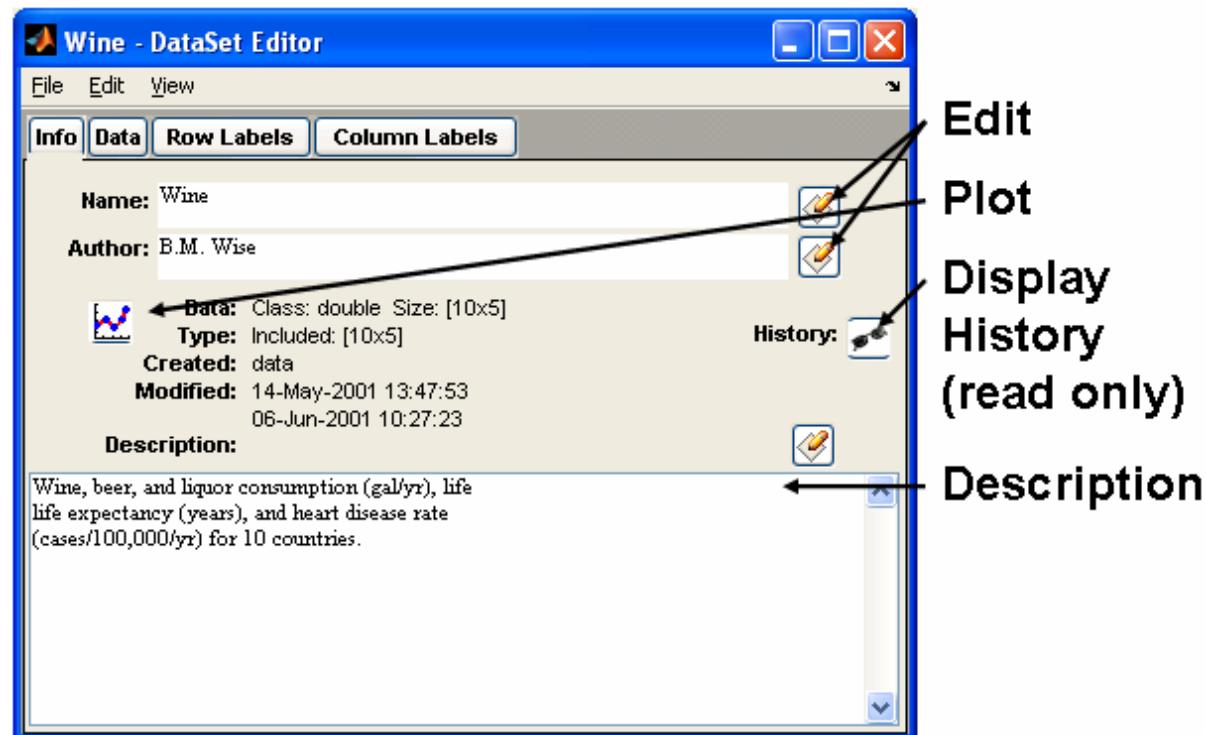
Figure 2-24. DataSet Editor default view.

Fields with the **Edit** button near them can be edited by clicking the button, editing the contents of the field, and then clicking **Accept** (as opposed to **Discard**) (Figure 2-25).

Try changing the "B." in the Author field to "Barry". Notice an asterisk appeared next to Wine in the title bar of the figure after you clicked **Accept**. This indicates there is unsaved data, so don't forget to **Save** your changes to a new DataSet Object via the **File** menu. Name your file and your variable "newwine". Keep in mind that if you save the new DataSet to the MATLAB workspace it will be deleted when you exit MATLAB. To retain it, you must save it to a file from either the DataSet Editor or from the MATLAB workspace.

Clicking the **Plot** button or selecting the **View/Plot** menu item will bring up a figure of the plotted data as well as a **Plot Controls** figure for manipulating the plot (see below for more information on **Plot GUI**).
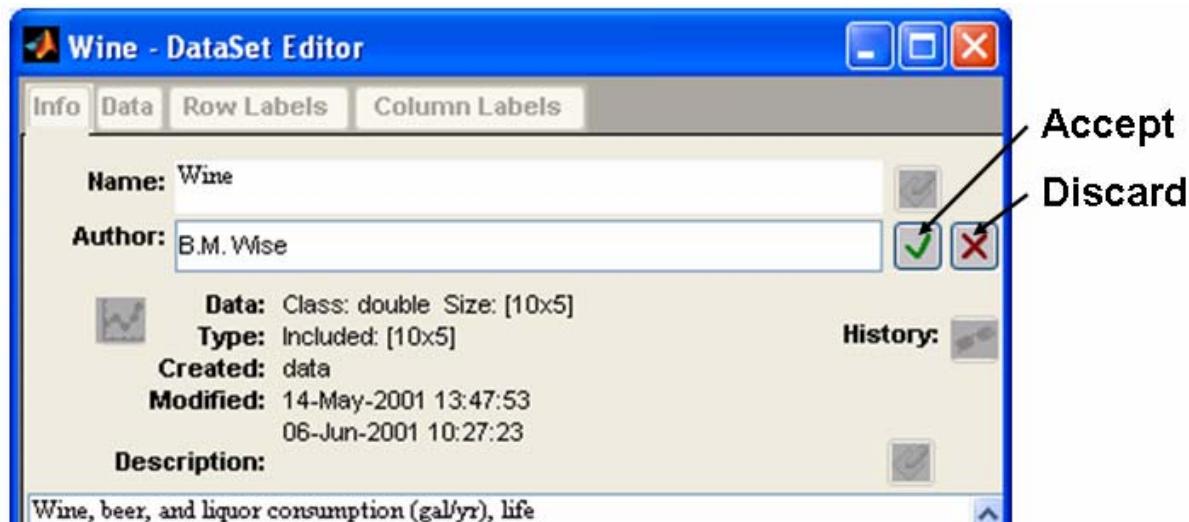
Figure 2-25. Editing a DataSet Object field.

The Data Tab

The Data tab (Figure 2-26) allows you to edit individual cells, include/exclude rows and columns, and to designate rows/columns as **Axis Scales**, **Classes**, or the **Include** field. For example, to exclude the Wine column, left-click the "Wine" column header, then right-click (Control-click on some systems) the same column header and select **Exclude Selected** from the menu. Applicable results (*e.g.*, changes in the include field or "Use as") will be reflected in the Mode tab.

The selections in the right-click menu can also be accessed via the **Edit** menu after selecting the column of interest. If more than one column or row is selected, the action will be performed on all selected columns and/or rows.

Other options for the selected column include:
- **Extract Data** to export the column(s) or row(s) to the workspace or a .mat file,
- **Copy** to make a copy of the selected column(s) or row(s) on the system clipboard (to copy into other programs),
- **Paste** to copy the contents of the clipboard into the selected column(s) or row(s),

38

- **Fill with value** changes all cells to value indicated,
- **Use as Axisscale / Class / Include** which copies the column(s) or row(s) into one of the label fields of the DataSet (see below).
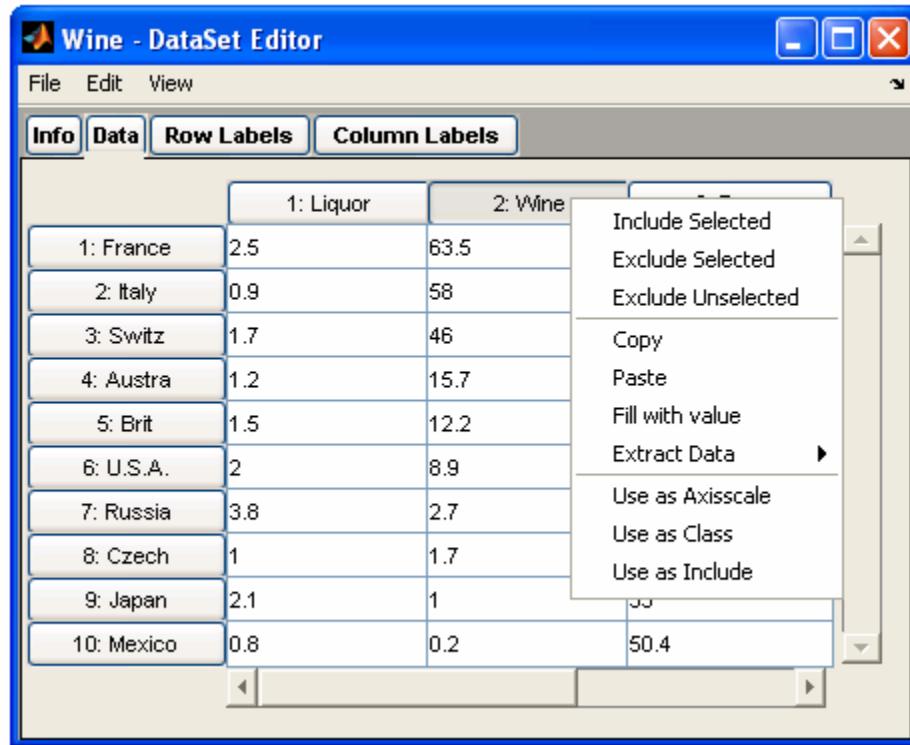
Figure 2-26. The right-click menu for a data column.

Mode Labels Tabs

The Mode Labels tabs allow you to enter information associated with the different *modes* of the data. In a typical two-way DataSet Object, mode 1 (*i.e.*, rows) is related to samples and mode 2 (*i.e.,* columns) is related to variables. In the Mode Labels tabs, you can set axis scales, classes, labels and the include field for each mode.

For example, after excluding the Wine column in the Data tab as described above, go to the **Mode 2 Labels** tab (Figure 2-27). You'll notice the **Incl.** field checkbox next to the Wine label is not checked. This is because you have just excluded it. Including/Excluding fields can just as easily be accomplished using the check boxes in the **Mode Labels** tabs. You can also directly edit the values in any of the fields here.

The DataSet Editor will allow you to load Labels, Axis Scales, and Classes from the **Mode Label** tabs directly from files or variables as long as the information being loaded is the correct size. This can be a useful tool when you have different data sources that use the same labels. Above we created a new Wine DataSet Object; now let's clear and

reload the Mode 2 Labels. First, right-click the **Label** header and select **Clear/Reset** (or select **Edit/Clear/Reset**). Next, right-click the **Label** header again and select **Load Label** (or select **File/Load Label**). This will open the load dialog figure and allow you to navigate to a .mat file or choose a variable from the workspace. Locate the Wine.mat file in the dems folder and click Load. The DataSet Editor will automatically extract and load the Mode 2 Labels from the original DataSet Object.
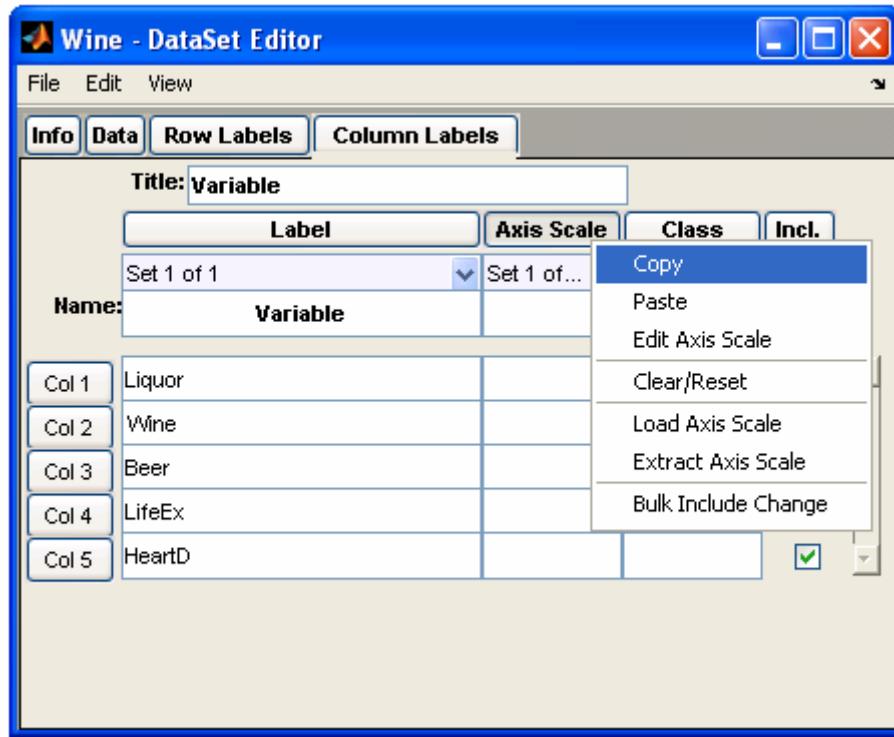
Figure 2-27. Mode 2 Label tab.

When loading from a DataSet object, the same field from the same mode will always be used. To load from a different mode, you must first **Extract** or **Copy** the contents from the source DataSet object and **Load** or **Paste** them into the target DataSet object. Note that you can always load or paste from a non-DataSet object, even when that information was copied from an external program such as Microsoft Excel.

From the **Mode Label** tabs you can also create multiple **Sets** of Labels, Axis Scales, and Classes. This can be useful if you find yourself needing to plot your data against two different axis scales; for instance, frequency and wavelength. To add an additional set, click on the set selection pull-down menu just below the column header buttons (This menu usually says "Set 1" as in Figure 2-27) and choose **New Set…** and finally confirm the creation of a new set. You can then enter values manually or select the column header button and Paste or Load all the values from the clipboard, workspace or file.

Using the **Edit** selection from the right-click menu will display the contents of the entire column of Label / Axisscale / Class / Include field in a list box. This can provide quicker

40

way of making changes to these fields. Labels can be copied, manipulated in Excel, then pasted back into the list.

The **Bulk Include Change** selection is also available from the menu. It allows a selection from a list box. You can use the shift and/or control keys while selecting an item in the box to make changes to the include field.

Other DataSet Editor Features

The DataSet Editor has many powerful data manipulation features. The Edit menu includes the following utilities:

- **Transpose** a DataSet object will switch columns and rows – but only for 2-way DataSet objects.

- **Hard-Delete Excluded** will permanently remove excluded data from a DataSet Object.

- **Exclude Excessive Missing** will automatically exclude rows or columns (or multi-dimensional indices) in which the number of missing data values (NaNs) exceeds the allowable amounts, as defined by the missing data replacement algorithm, `'mdcheck'`. This action can be used to remove samples or variables which are too sparse in information to be used in modeling.

- **Missing Data Map** (from the View menu) will provide a color map of missing data points (NaNs) in the data matrix. Elements which are not missing are shown in green, elements which are missing but could be replaced with the standard missing data replacement algorithm (`'mdcheck'`) are shown in yellow, and elements which are missing and cannot be replaced by the missing data replacement algorithm are shown in red.

- **Permute Modes** will allow you to change the order of modes of the data.

- **Concatenate** will give you the option to concatenate old and new data (if data are already loaded and new data are either Loaded or Imported through the DSE File menu). The old and new data are compared, and if they match in size in one or more modes, you will be given the option to concatenate the old and new data. By this method, you can build a larger DataSet Object from several smaller datasets.

In general, the DataSet Editor allows quick and easy access to the contents of a DataSet Object. It has been integrated into the Analysis interface (as shown earlier) so you can easily make changes to your data and recalculate your model without having to save and reload your data or go to the command line.

Viewing and Modifying DataSets with PlotGUI

The `'plotgui'` function is also useful when working with DataSet objects. This utility provides a graphical view of a DataSet object and allows graphical manipulation of the

include and `class` fields. The `'plotgui'` **Plot Controls** window can be invoked from the MATLAB command line by typing `plotgui`. It is also used by other PLS_Toolbox functions and can be accessed from any of a number of different interfaces including the workspace **Browser**.

PlotGUI is configured to have a single small controls interface, **Plot Controls**, which contains all of the tools necessary to manipulate a particular plot. At any time there may be several plots (figures) open under "control" of PlotGUI but only one Plot Controls window. Selecting a plot and clicking on its "gray space" (the gray margin area around the actual plot axes) will automatically bring the **Plot Controls** interface to the front.

At the top of the **Plot Controls** window is a **Figure Selector** pull-down menu, which indicates the current figure being controlled. Below this are three **Axis Menus**, one for each of the x, y and z axes of a plot. Before data are loaded, all of these menus will be empty. Data can be loaded into the GUI by using the **File/Load Data** menu in the **Plot Controls** window or by providing it in the command line instruction

» `plotgui(mydata)`

After loading data, a plot will appear and the pull-down **Axis Menus** will list the available columns of the loaded data. Changing the plot is accomplished by changing the selections on the **Axis Menus**. Selections from the y-axis menu are plotted against the selection from the x-axis menu. A three-dimensional plot can be created by selecting an item from the z-axis menu. If "auto-update" is checked, plots are automatically updated when new selections are made. Otherwise, the Plot button must be pressed after changing the axis menu selections.

Multiple y-axis items can be simultaneously plotted by holding down the **Control key** when making selections (As these plots can get confusing, a legend can be added to the plot by selecting **Insert/Legend** from the menus on the plot itself). In addition to the columns of the DataSet Object, the x-axis menu also allows plotting against the sample number (*i.e.,* row number) and any `axisscale` stored in the DataSet Object. In Figure 2-28, the Wine DataSet Object has been loaded and the Liquor, Wine, and Beer consumption values have been selected to plot against sample number (**Plot/Columns)**.

In addition to plotting the contents of the data field, `'plotgui'` can also display information from other DataSet fields. The **View** menu, shown in Figure 2-28, offers various options depending on the DataSet Object contents. The top section of this menu allows display of available labels, classes and excluded data (*i.e.,* columns or rows which have had their indices removed from the DataSet Object include field). A raw-text table of the plotted data can be displayed (**View/Table**) and axis lines (representing zero on each axis) can be added to the plot.

If labels and numbers on a plot are badly overlapping, they can be "decluttered" by selecting one of the options from the **View/Declutter Labels** menu. There are several levels of decluttering. In addition, if **Declutter/Selected Only** is checked, then labels will
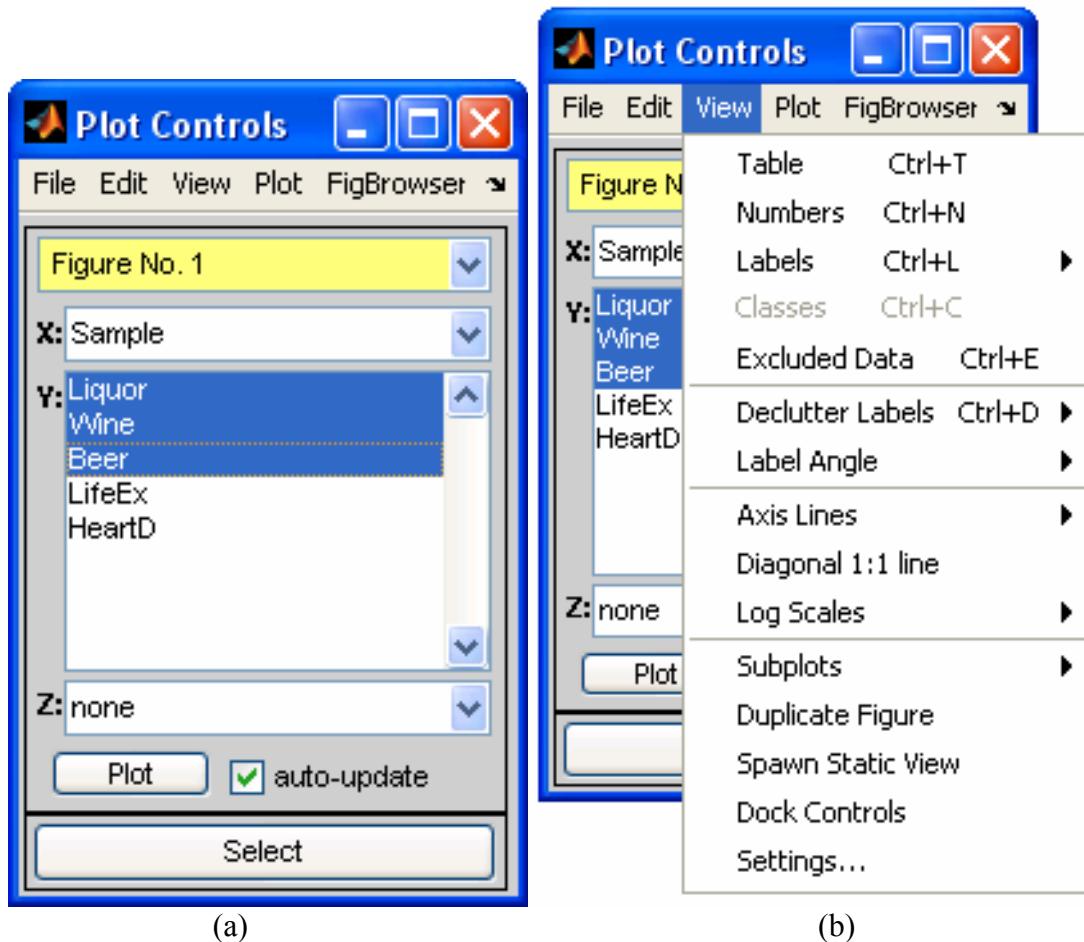
Figure 2-28. (a) **Plot Controls** with three columns selected from the Wine DataSet Object. (b) The **View** menu options with the Wine DataSet loaded.

be shown only for the points which are selected (see below) on a plot. If no points are selected, all labels are shown (after decluttering as desired).

The middle portion of the View menu adds various annotations for axes and selects optional log scaling for the axes.

The bottom part of the **View** menu contains various other options including creating a duplicate "linked" (see **Selections** below) copy of the current figure in a new window or spawning a static copy of the current plot (*i.e.,* a figure not controlled by `plotgui`). You can also create **Subplots** using the fly-out menu. To operate on a particular subplot just click on it first, then make selections with Plot Controls.

The **Plot** menu selects the mode of the DataSet Object from which the menus will select and plot data. By default this starts at the highest mode ("Columns" in this example) and, thus, the pull-down axis menus will contain an entry for each column in the DataSet Object. To plot rows of the DataSet Object, **Rows** should be selected from this menu, at which point the axis menus will display all the available rows. The **Data Summary**

selection allows plotting of various statistics from any mode (selected from the x-axis menu).

Selections: Assigning Classes

The **Select** button allows you to make a selection from the plotted data. The default selection mode is a standard rubber-band box in which one corner of a box is marked when the mouse button is pressed down and the opposite corner is indicated when the button is let back up. Any points inside the box will be selected. Different selection modes can be set through the **Edit/Selection Mode** menu. Points can be added to a previous selection by pressing **Select** again and holding down the Shift key while making the additional selection. In the same manner, points can be removed from a selection using the Control key while making a selection.

Figure 2-29 illustrates beer consumption versus sample number along with the country labels attached to each point. All the European countries have been selected. Selected points are usually shown in pink.
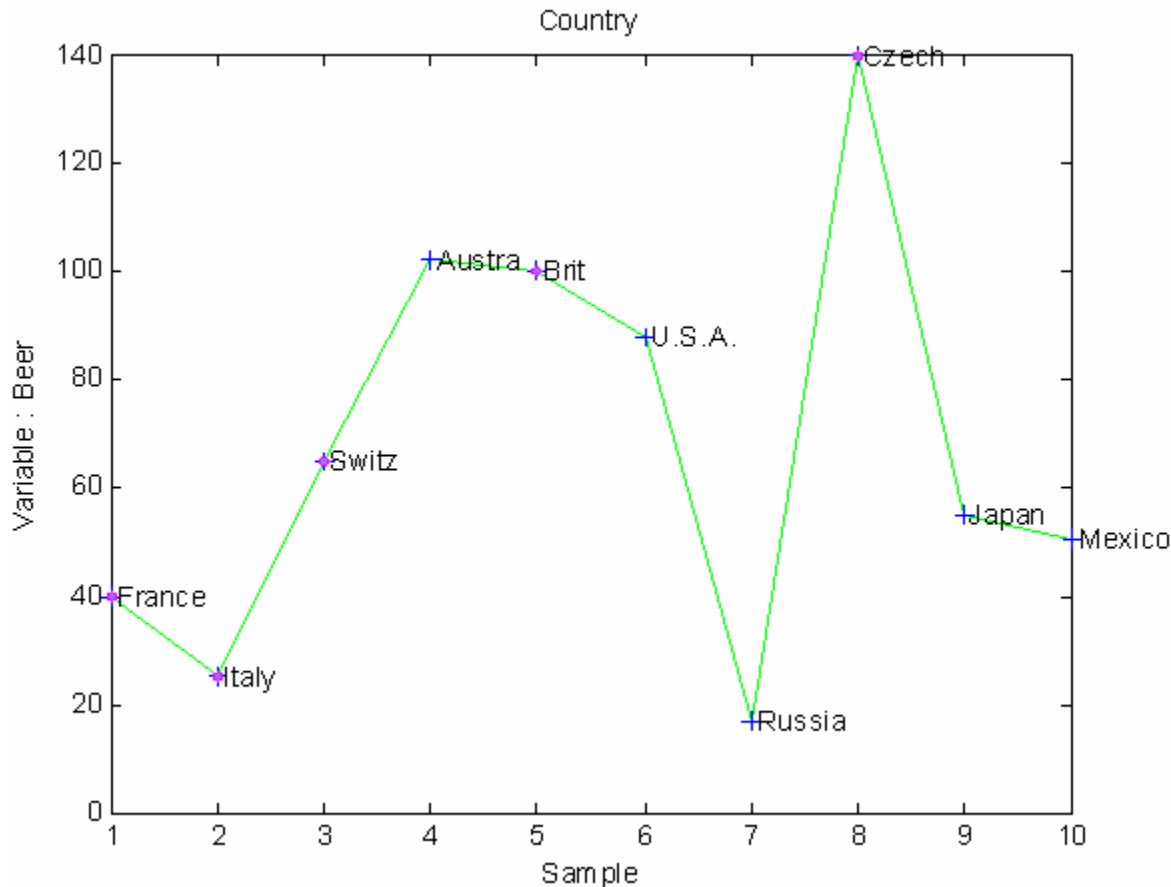
Figure 2-29. Plot of a single column (beer consumption) of the Wine DataSet Object with country labels and circles indicating selected (European) points.

When points are selected, they can be assigned a class by selecting **Edit/Set Class** (or right-clicking the selection and choosing **Set Class** from the menu) and entering the

desired class (if **View/Classes** is not turned on, it will be turned on automatically so you can see symbols representing the current classes for each point). In Figure 2-30, the European countries have been assigned to class 1, which appear as triangles. The remaining data are automatically assigned class 0 (zero) and shown as black circles.

Selections: Excluding Data

Selected points can be "excluded" by selecting **Edit/Exclude Selection**. When points are excluded, the row or column containing each point is removed from the `include` field of the DataSet object. Excluded data can only be viewed in plots if **View/Excluded Data** is selected. To re-include previously excluded data, turn on **View/Excluded Data**, select the points to re-include, then choose **Edit/Include Selection**.

Figure 2-31 demonstrates how the Wine data may be viewed by rows by selecting **Plot/Rows**. In this case row 1 (France) is selected. The Life Expectancy and Heart Disease variables have been excluded but **View/Excluded Data** is turned on so that the excluded data can be seen as dimmed points. We've also changed the "marker" style by using **View/Settings...** and setting the value to "o" (lower case letter o). If a PCA model were created from these data, it would be based only on the first three variables (consumption of beer, wine, and liquor).
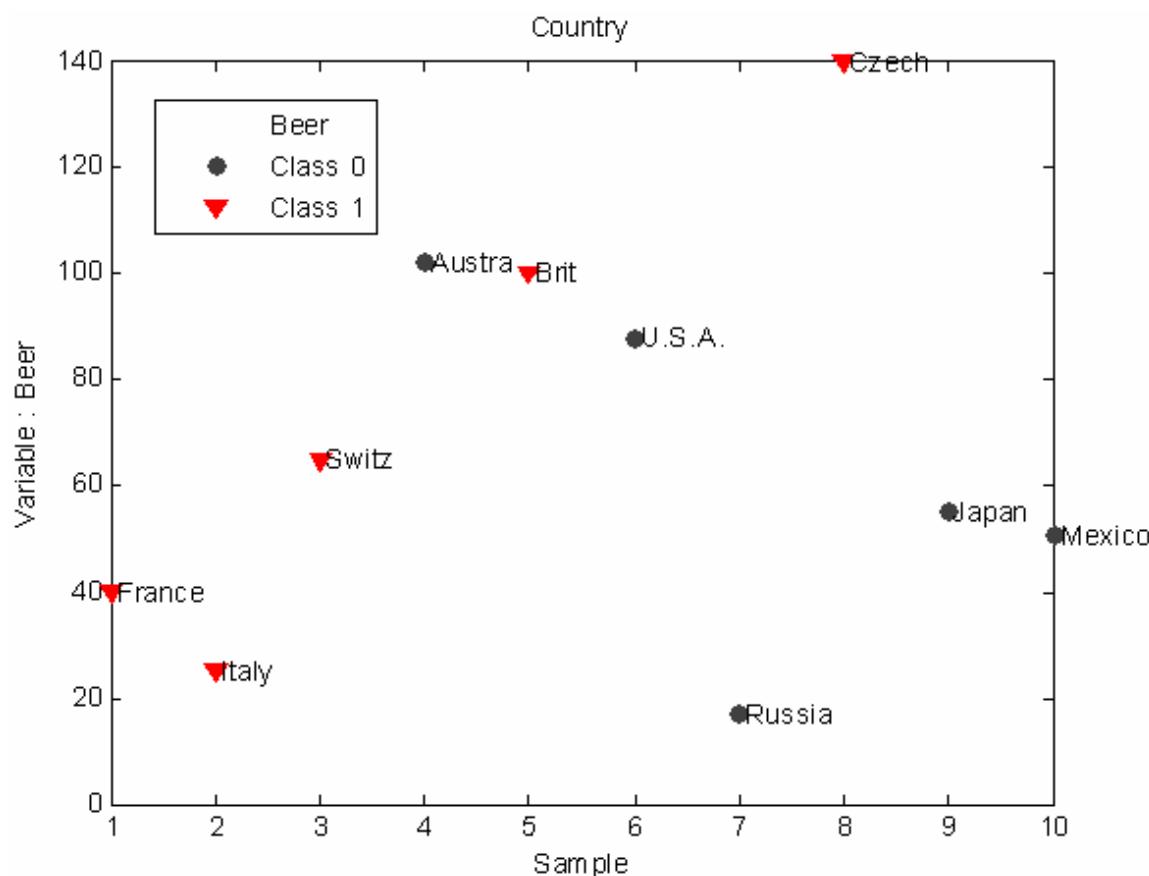
Figure 2-30. One column of the Wine DataSet with the European countries set as Class 1.

45
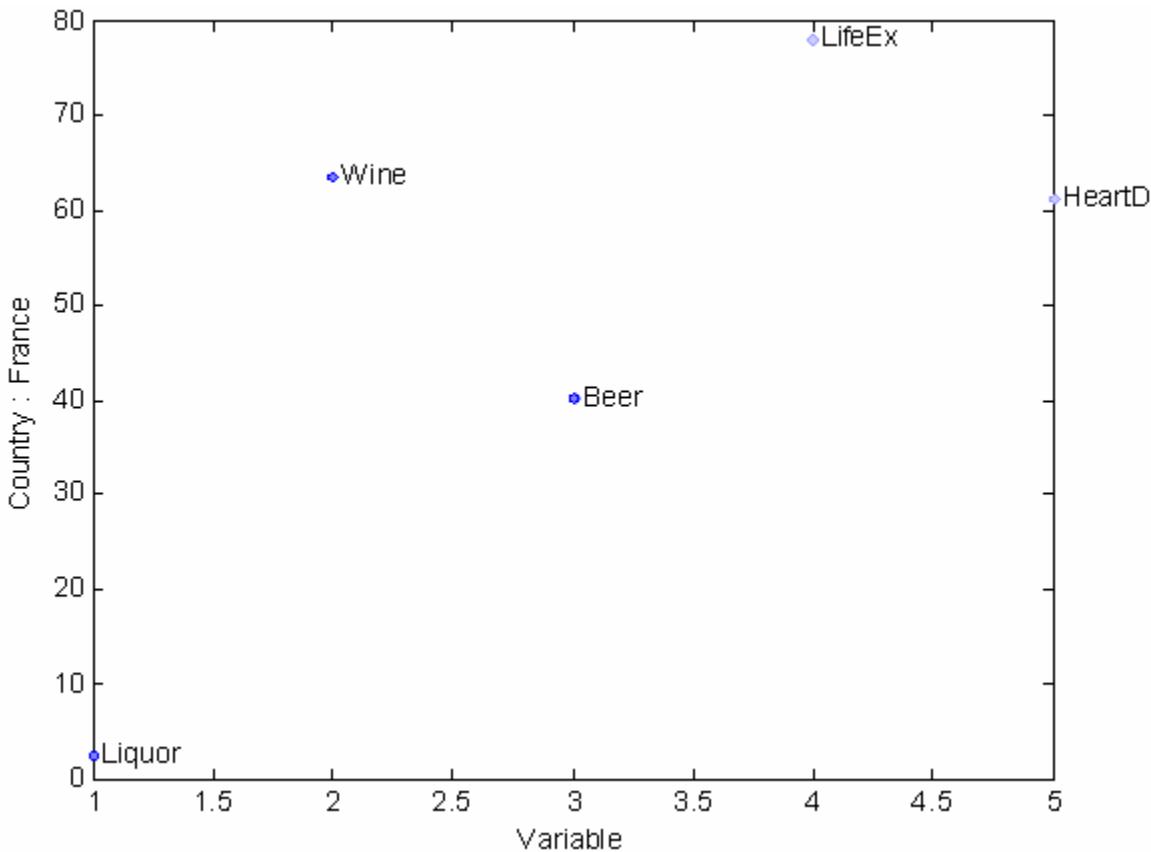
Figure 2-31. Wine DataSet row 1 (France) with the last two variables (life expectancy and heart disease) excluded, but viewed.

Exclusions can also be done on the currently *plotted* data (*i.e.*, the selection in the y-axis menu). The **Edit/Exclude Plotted** menu option will exclude the column(s) or row(s) currently selected in the y-axis menu. For example, selecting **Edit/Exclude Plotted Data** when the wine column is plotted would exclude the wine column from the DataSet Object. Likewise, selecting **Edit/Exclude Not Plotted** would exclude everything *except* wine from the DataSet Object. An excluded item will still appear in the y-axis menu but will have a double carrot symbol (>>) prior to the column or row label.

If changes are made to a dataset (*e.g,.* the `class` or `include` fields) using `plotgui`, these changes must be saved back to the MATLAB workspace (using **File/Save)** to use the modified DataSet Object in other routines. One exception to this is if the `plotgui` figure was invoked by another GUI such as **Analysis**. In this case, the GUI will handle the changes automatically.

These descriptions of the **DataSet Editor** and `plotgui` are intended to introduce you to manipulating the contents of DataSet Objects. More sophisticated manipulations of DataSet Objects can be performed at the command line. For more technical information on DataSet Objects, please see Chapter 16, Advanced Software Information

Getting Started with Solo and PLS_Toolbox GUIs

Loading Data from the Workspace into GUI Functions

Using the data loaded from Section 2.1, we can perform a PCA analysis of these data in a PLS_Toolbox GUI (Graphic User Interface). If you type the PLS_Toolbox command *pca*, MATLAB will open the **Analysis** GUI. This GUI is a generic interface to several analysis methods but when opened using the *pca* command it has the PCA method pre-selected in the Analysis menu. The details of PCA and other chemometric routines will be discussed later – here we intend only to introduce the reader to use of the GUIs. The initial window generated by the '*pca*' function is shown in Figure 2-32.
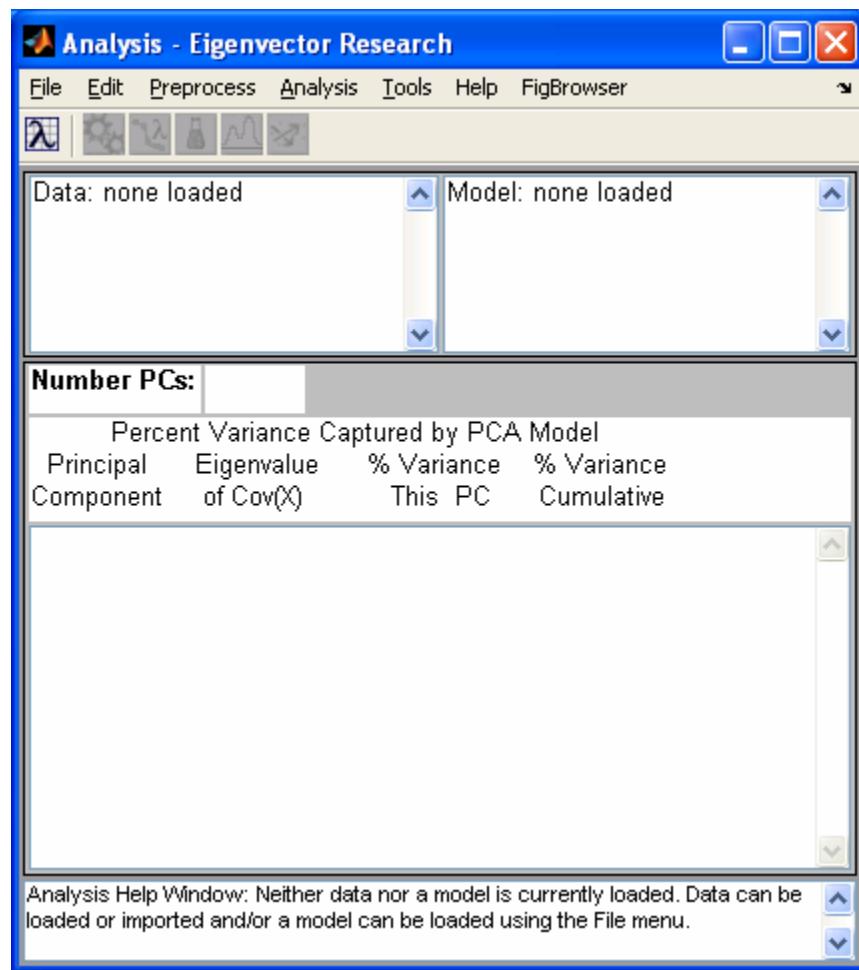
Figure 2-32. **Analysis** GUI set for PCA.

Data may be loaded using the **File/Load Data/X-Block** menu of the **Analysis** window and then selecting the numerical "data" matrix in the appearing **Load** window, shown in Figure 2-33, and clicking on the **Load** button.
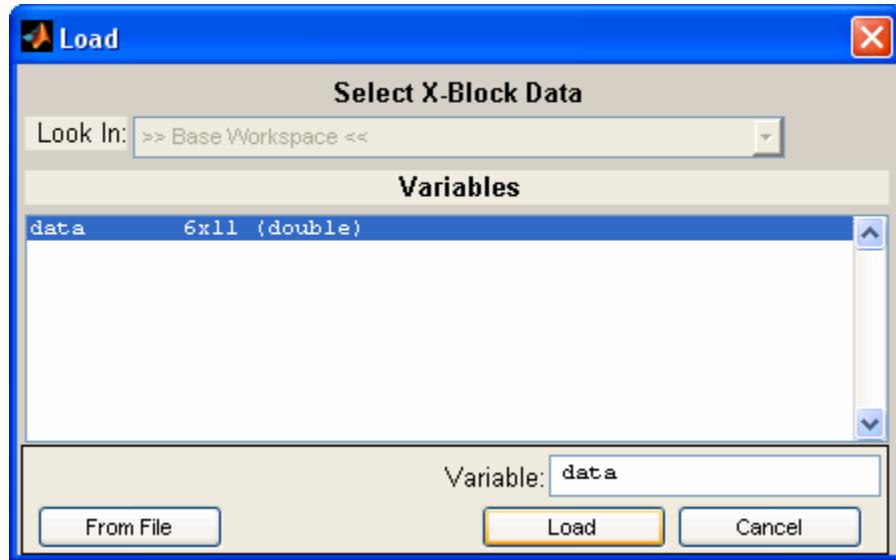
Figure 2-33. **Load** window from PCA tool.

When the data are loaded, the interface creates a DataSet Object out of them. You can now load the labels created above via the DataSet Editor by selecting **Edit/X-Block**. Go to the Row Labels (Mode 1 or Samples) tab and right click the **Label** button then select **Load Label**(Figure 2-34). This will bring up a **Load** window similar to before where you can select the SampleLabels cell matrix created above. Do the same for Column Labels (Mode 2 or Variables) then close the DataSet Editor by clicking on **File/Close** (changes are automatically saved).
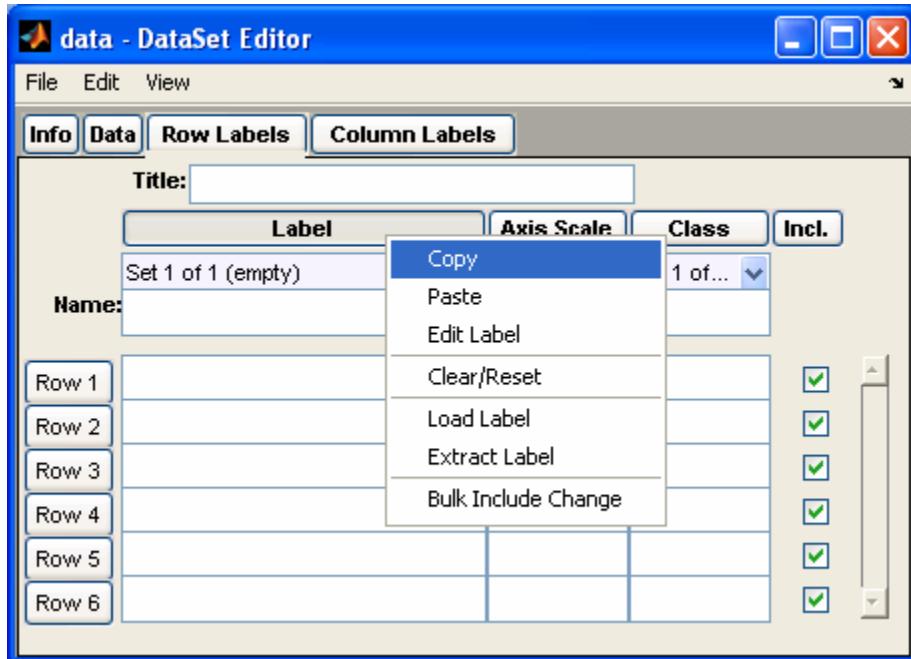
Figure 2-34. DataSet Editor on **Row Labels** tab with right-click menu.

48

Importing Data Directly into the GUI

Thus far in this example, we've used the MATLAB import tools to read Excel data into the Workspace and then load that data into Analysis. There is a quicker alternative. From the **File/Import Data/X-Block** menu selection in Analysis, one can import data directly. Several of the import functions will also attempt to intelligently build a DataSet Object with information available in the file. In the case of Redbeerdata.xls, the PLS_Toolbox Excel file reading functions are able to parse the data and labels directly into a DataSet Object without a manual step.
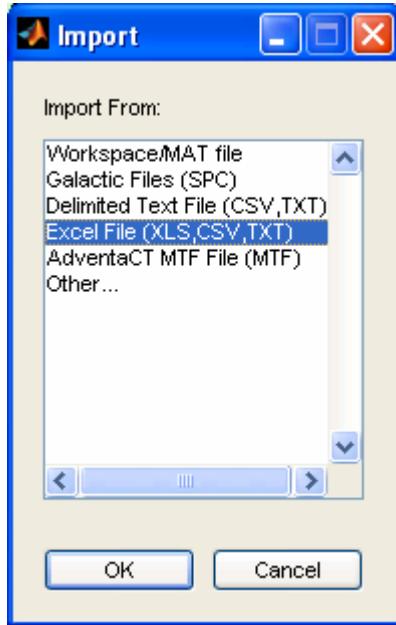
Figure 2-35. **Import** Window.

The import menu item is also available from the DataSet Editor and can be a quick and easy way of loading data from a file. In some cases the file parsing functions can't correctly interpret labels and data, so some pre-formatting may be necessary.

Examining Data in the GUI

Once the data has been loaded into the GUI, it can now be examined by selecting **Edit/Plot X-Block** in the **Analysis** window. Two windows will appear. The **X-data** window, shown in Figure 2-35, contains the desired graph, while the **Plot Controls** window, Figure 2-36, controls the axes and other contents of the graph. (Note: the Figure number assigned to plot windows depends upon the number and status of other figure windows, so may not always be the same for a particular type plot.)
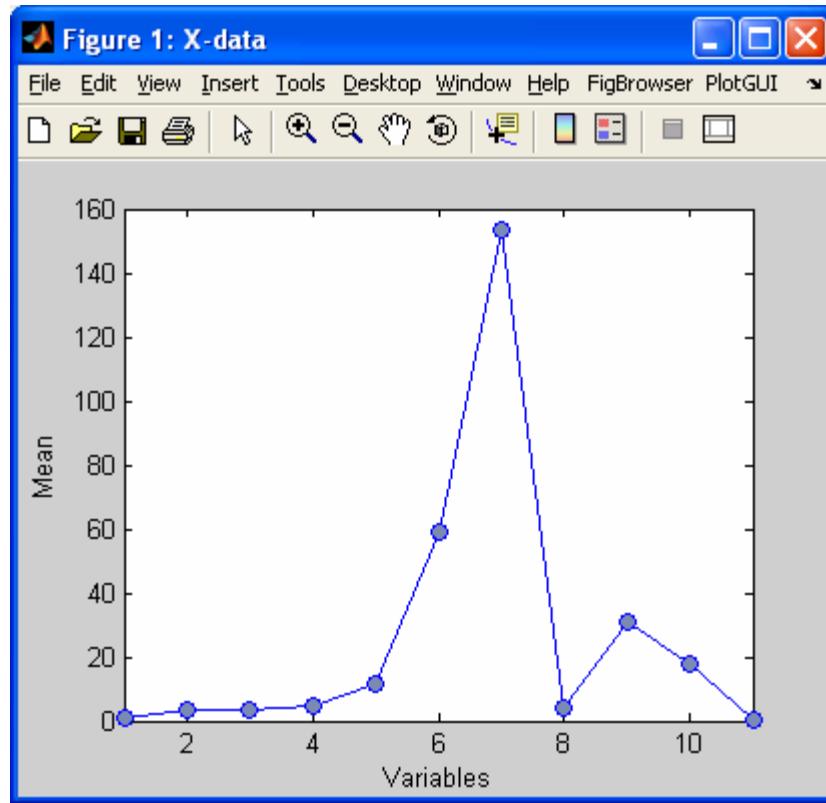
Figure 2-36. Raw data window from PCA window.

Notice that in Figure 2-36 the Y-axis is, (by default), the **Mean** of the variables. You may change the Y-axis to the data for all the variables by clicking on **Data** in the **Y:** menu in the **Plot Controls** window. Furthermore you may add labels to the variables by choosing **View/Labels** from the **Plot Controls** window. The result is shown in Figure 2-37. (Note: there is also a **View** menu in the **Figure** window. This menu serves other MATLAB figure functions.)
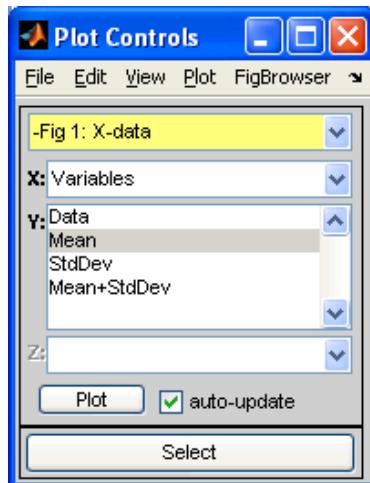
Figure 2-37. **Plot Controls** window from PCA tool.
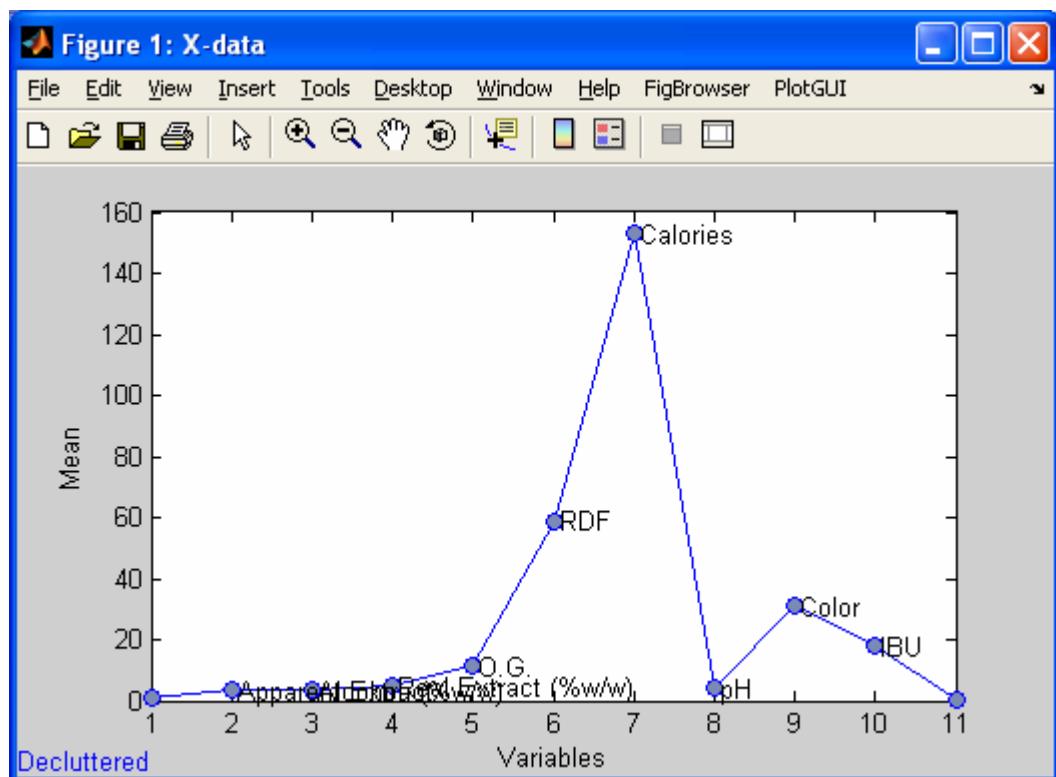
Figure 2-38. Plot of the red beer raw data from the PCA window.

If you wish to copy the Figure for pasting into other software for a report or presentation, choose **Edit/Copy Options...** in the menu of the **Raw Data** window, and select the format that you wish the copy function to use. Then choose **Edit/Copy Figure** (not **Edit/Copy**) from the menu of the **Raw Data** window. Alternatively, you can use the **File/Export Figure** menu selection in the **Plot Controls** to export the figure directly to Power Point or Word. Other choices in the **Raw Data** window menus will allow the user to modify the axes labels, font styles, axis limits, and many other properties of the plot.

You may use the tool bar at the top of the **Raw Data** window to do modifications of the graph such as zooming. For example, to zoom in on a particular part of the figure, click on the magnifying glass containing the plus (**+)** sign and, using the mouse, draw a rectangle over the region you wish to resize. This process may be repeated to further zoom into a section of the graph. You may zoom out by clicking on the magnifying glass with the minus (**–**) sign and then clicking on the graph as many times as necessary. You may add comments in the interior of the graph by selecting the **Insert\Text Box** menu item and drawing a box on the graph where a comment is to be added.

In summary, the **Plot Controls** window controls what data are plotted in the **Raw Data** window, while the **Raw Data** menus and tool bar control how the plot looks. You may close both of these windows by clicking on the **x** in the upper-right corner of the **Raw Data** window.

Viewing a PCA Model

Returning to the **Analysis** window, we can instruct the function to create a PCA model with two principal components by clicking on the **calc** button (the button with the gears pictured on it), selecting the second row of the **Percent Variance Captured by PCA Model** sub-window and finally clicking on the **calc** button again (Figure 2-39).
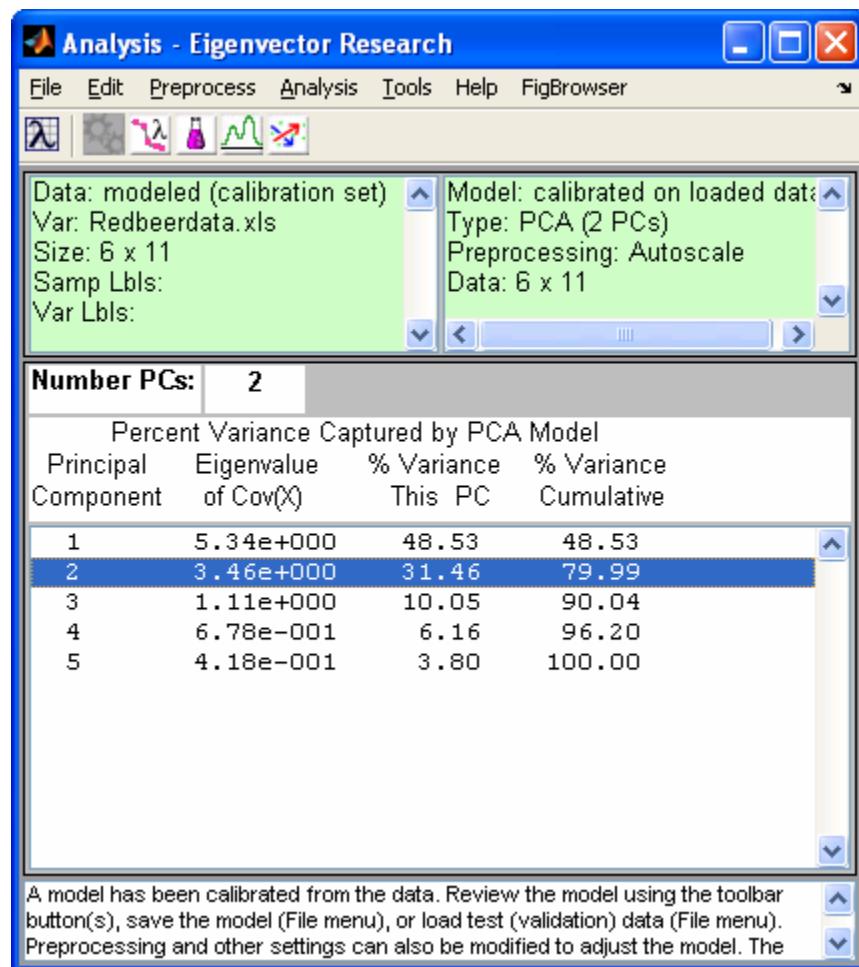
Figure 2-39. Beer data in **Analysis** window with two-component PCA model.

The additional buttons on the toolbar will then become active when the calculation is complete. Clicking on these will produce new figure windows along with a **Plot Controls** window. Clicking on **Plot Eigenvalues** (the button with a descending plot and a lambda symbol) will open an eigenvalue plot of the model.
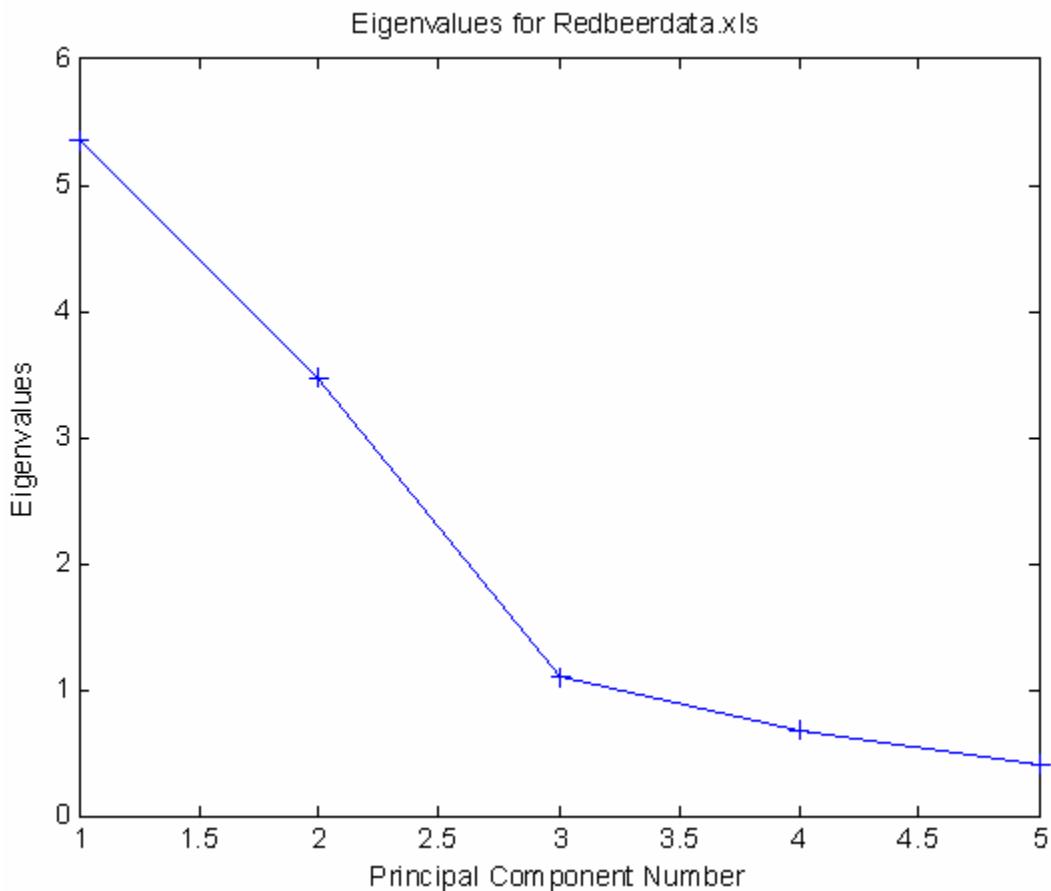
Figure 2-40. Eigenvalue plot suggesting two PCs.

The eigenvalue plot suggests a good model can be built using two principal components. Clicking on **Plot Scores** (the button with an Erlenmeyer flask on it) will open a scores plot. Let's look at a scores-scores plot. To do this, use the Plot Controls window to select **Scores on PC 1** for the X: axis and **Scores on PC 2** for the Y: axis. Next we'll want to add labels (View/Labels) and set the lable decluttering to zero so we can see all of the labels (**View/Declutter Labels/None**). You can move the individual labels by clicking and dragging them. The plot should look similar to Figure 2-41.
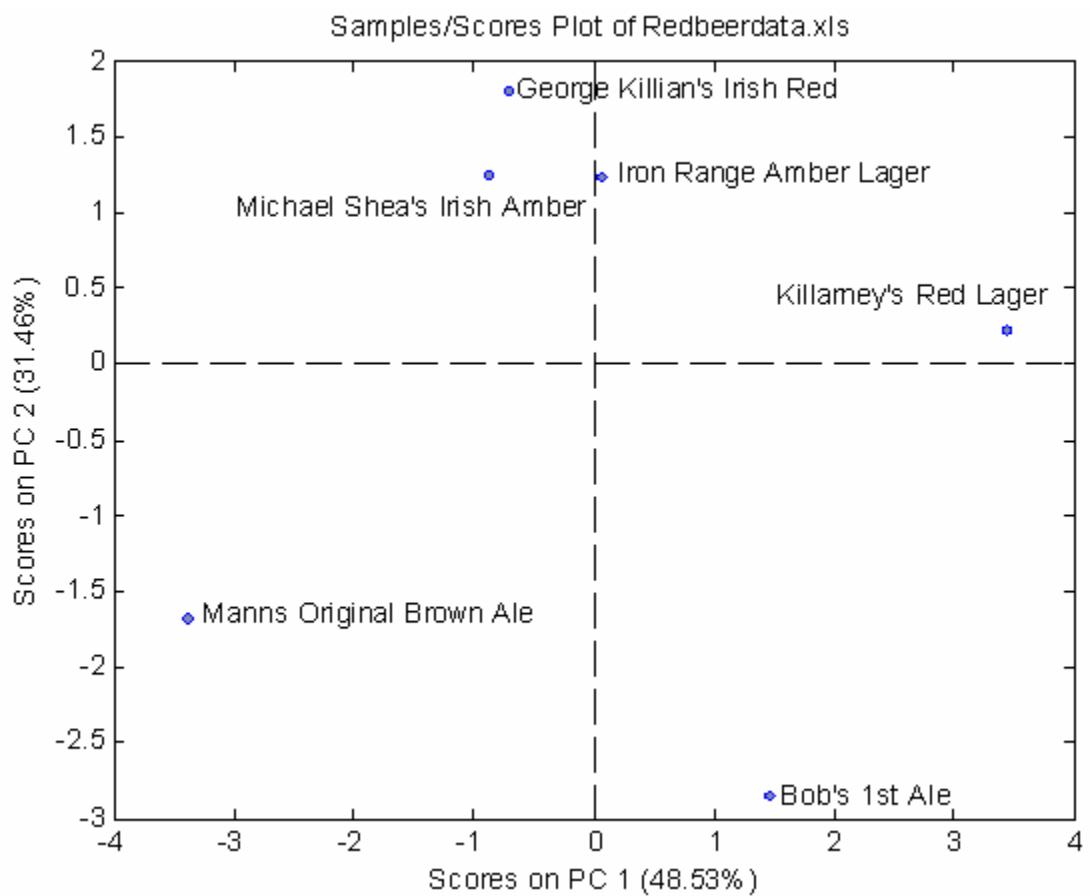
Figure 2-41. Scores plot PC1 vs. PC2 (declutter set to "none").

Here we can see that some of the samples group together while others seem to be quite different. Next, create a biplot by clicking on the button with crossing arrows. Go through the same steps as above for adding labels and moving individual labels to make a legible plot. The biplot should look similar to Figure 2-42.
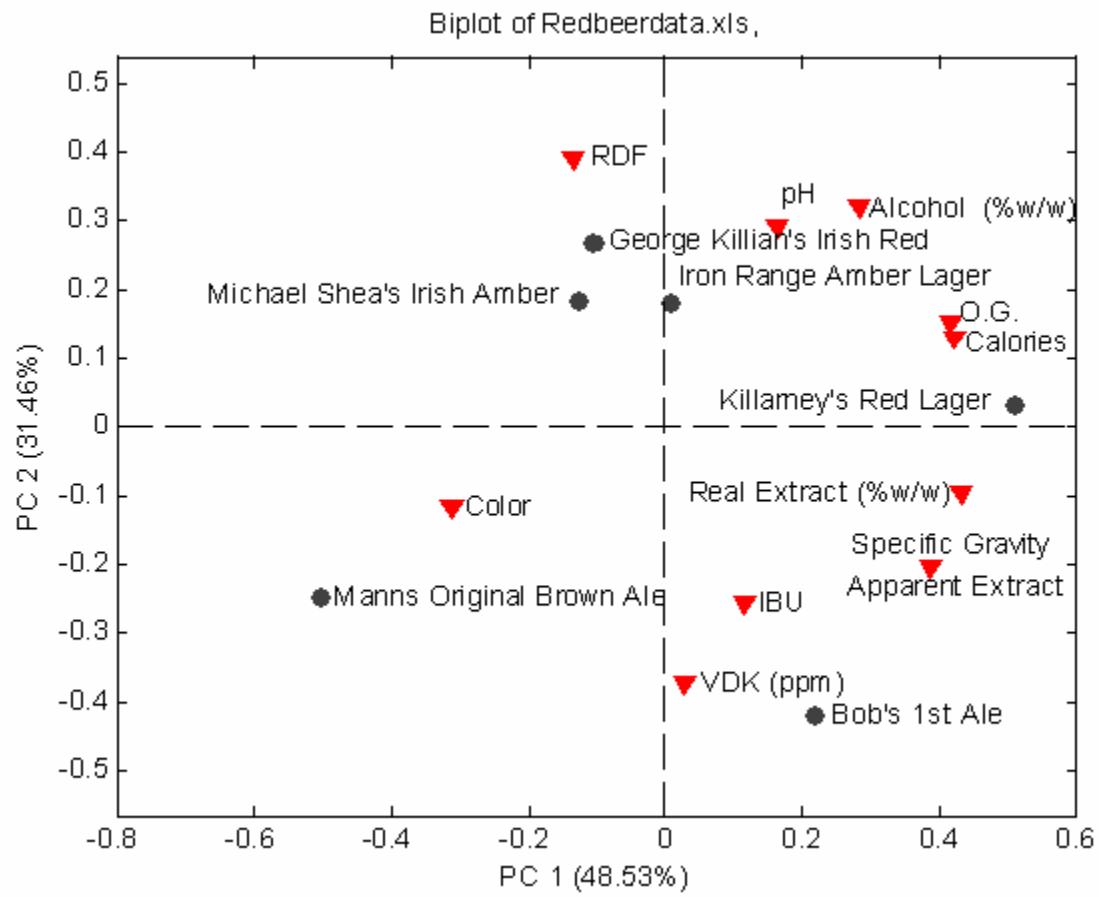
Figure 2-42. Biplot PC1 vs. PC2 (declutter set to "none").

Here we can see that the O.G. (original gravity) and Calories variables are highly correlated (appear very close to each other). We also see that Color and Manns Original Brown Ale seem to be correlated.

Let's look at a Loadings plot by clicking the button with a green double-peak plot. Again, choose PC 1 for the X axis and PC 2 for the Y axis and turn off decluttering and position labels as needed. The loadings plot should look similar to Figure 2-43.
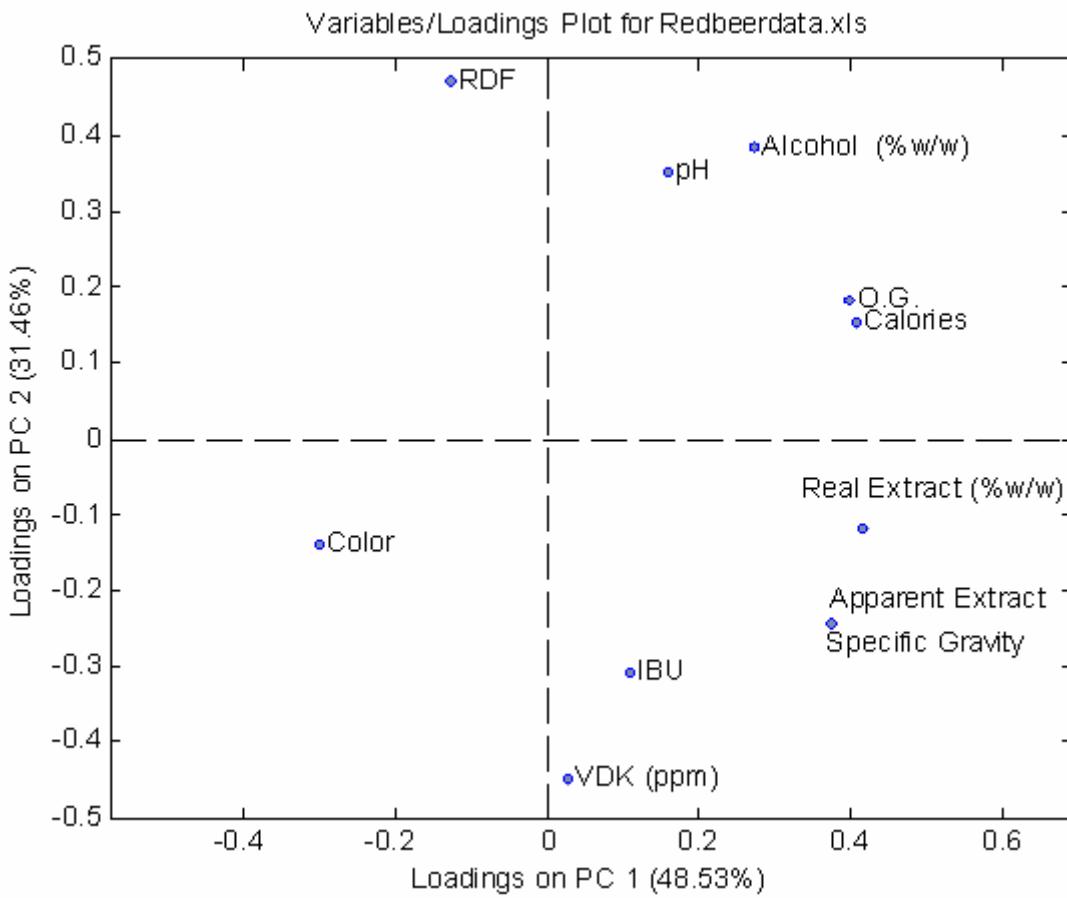
Figure 2-43. Loadings Plot PC1 vs. PC2 (declutter set to "none").

The Loadings plot shows the same variable information from the Biplot. We can see what variables seem to be correlated; for example, Alcohol and pH f.

Finally, let's look at a plot of Q vs. T-Squared plot. We'll leave the declutter on (light). Some of the labels won't be shown but we'll be able to see the plot more clearly.
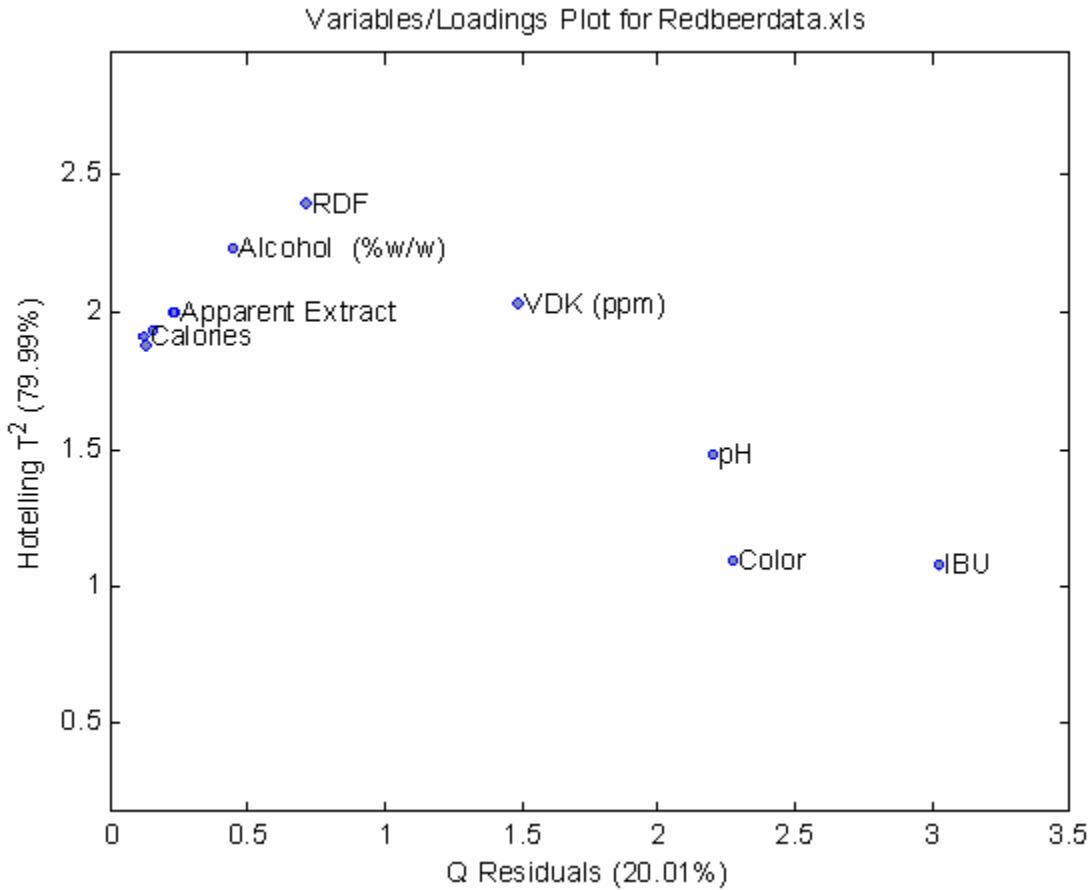
Figure 2-44. Q vs. T-Squared Plot (declutter set to "light").

We don't see any really unusual variables here; none of the points are far off on either axis. Now that we're reasonably happy with our two PC model we can save it.

Saving a PCA Model

Now that we have a model, it can be saved for future use. You may choose **File/Save Model** from the **Analysis** window **File** menu and give it a location and name. For now we shall save the model to the **MATLAB Workspace** as **beermodel**. The default will save the model to the MATLAB workspace, but you may choose to save the model to a file as well. Remember if you do not save the model to a file now or to a file after leaving the GUI, it will be lost when quitting MATLAB! If you loaded the data from a file in the GUI, you may also choose to save the data to the MATLAB workspace or to a file using the **File/Save Data** menu. You may now leave the GUI by selecting **File/close** from the main **PCA** window.

Examining a Structure Array in MATLAB

Typing 'whos' will show our original data and our new PCA model, beermodel.

```
» whos
  Name                    Size                    Bytes  Class

  SampleLabels            6x26                      312  char array
  VariablesLabels        11x19                      418  char array
  ans                     6x26                      312  char array
  beermodel               1x1                     14606  struct array
  data                    6x11                       528  double array
  textdata                8x12                      6226  cell array

Grand total is 2085 elements using 22402 bytes
```

Our model has been saved as a new kind of data class called a **structure array**. We can examine this new form by typing the name of the variable, beermodel.

```
» beermodel

beermodel =

        modeltype: 'PCA'
             name: {'data'}
             date: '25-Aug-2002'
             time: [2002 8 25 17 16 58.1980]
             info: 'Scores are in cell 1 of the loads field.'
            loads: {2x1 cell}
             tsqs: {2x1 cell}
       ssqresiduals: {2x1 cell}
      description: {3x1 cell}
           detail: [1x1 struct]
```

A structure array is a great way to keep associated data together. The model output by the PCA tool is composed of a large and varied set of data. We can examine these by indicating the subsection or **field** of the structure array with a period. For example, if we type:

```
» beermodel.modeltype

ans =

PCA
```

the response indicates that this is a PCA model. Some of the fields of our model have multiple parts. If we type:

58

```
» beermodel.loads
```

```
ans =
```

```
    [ 6x1 double]
    [11x1 double]
```

the response tells us that `beermodel.loads` contains both a 6 x 1 and an 11 x 1 double precision matrix. This field is a cell array. We can examine the second matrix in the cell array by typing:

```
» beermodel.loads{2}
```

```
ans =
```

```
     0.3747
     0.3747
     0.2724
     0.4164
     0.4003
    -0.1282
     0.4088
     0.1577
    -0.3001
     0.1101
     0.0271
```

Manually dissecting a model can lead to inconsistencies in the model structure, so it is recommended, should you need to use or examine your PCA model, that you first try using a GUI tool. You may start the PCA Tool by typing *pca* at the command prompt, and then load your saved model from either the **MATLAB Workspace** or from a saved file using the **File/Load Model** menu in the **PCA** window.

If you have not saved your model or data from the GUI, be sure to save it now from the **MATLAB Workspace**!

Creating a PLS Model

In this example we will create and inspect a PLS (Partial Least Squares Regression, Chapter 6) model. Use the following commands to load the Hald DataSet and start PLS:

```
>> load halddata
```

```
>> pls
```

Load both the x and y block data via the **File/Load Data/Both** menu and click the **Calc** button. Then select the first two latent variables and click the **Calc** button again to create a model using two latent variables (LVs) (Figure 2-45).
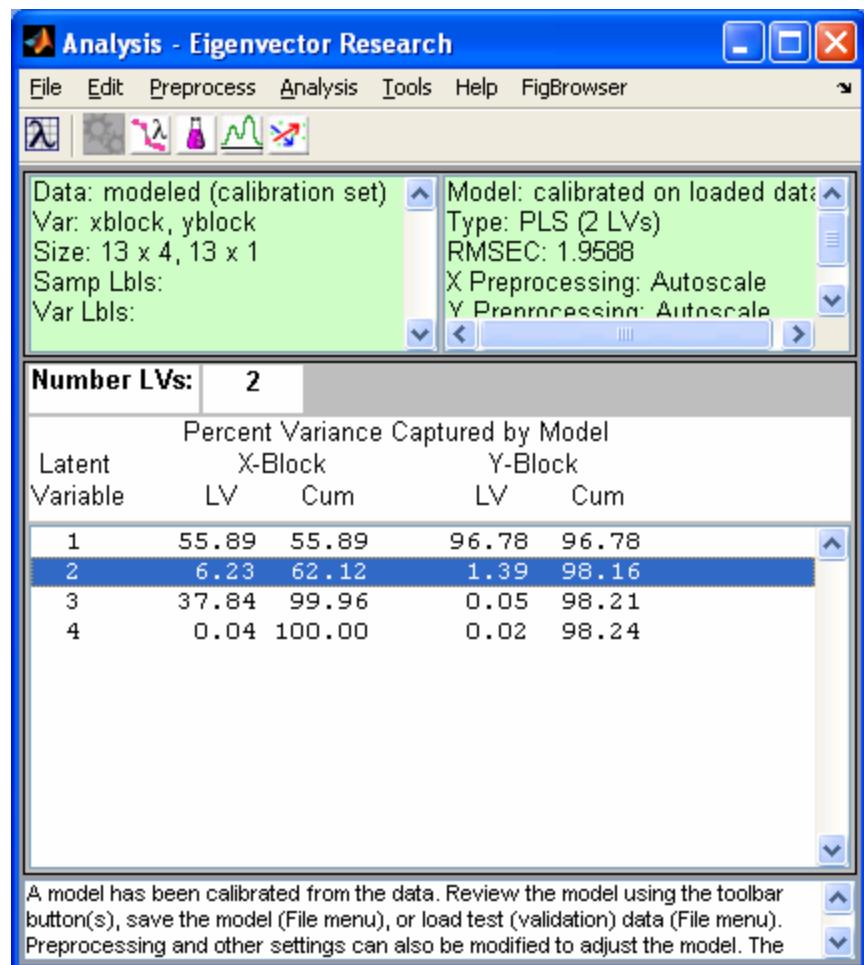
Figure 2-45. Two-LV model of Hald DataSet.

Now calculate the cross validation statistics for the model using **Tools/Cross-Validation**. Set the **Method** to "leave one out" (Figure 2-46). This will clear the model;press the **Calc** button again to re-calculate the model using cross-validation.
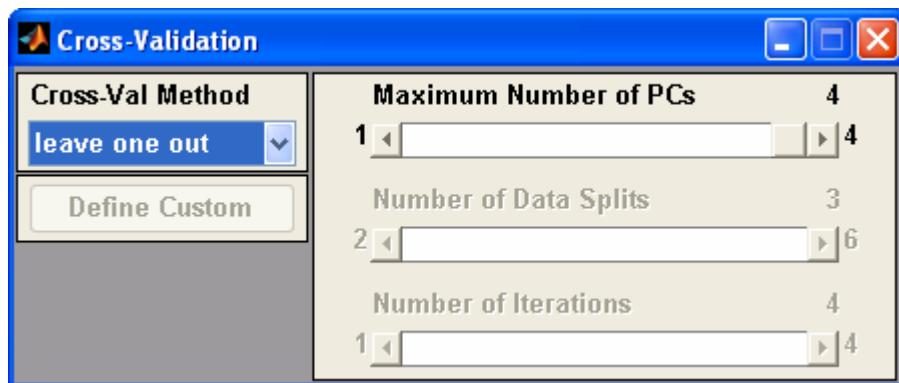
Figure 2-46. Cross-validation for two-LV model.

Now look at a scores-scores plot by clicking the **Scores** button and selecting LV1 for the X: axis and LV 2 for the Y: axis. Also add the sample numbers as labels to each point using the **View/Numbers** menu item (Figure 2-47).
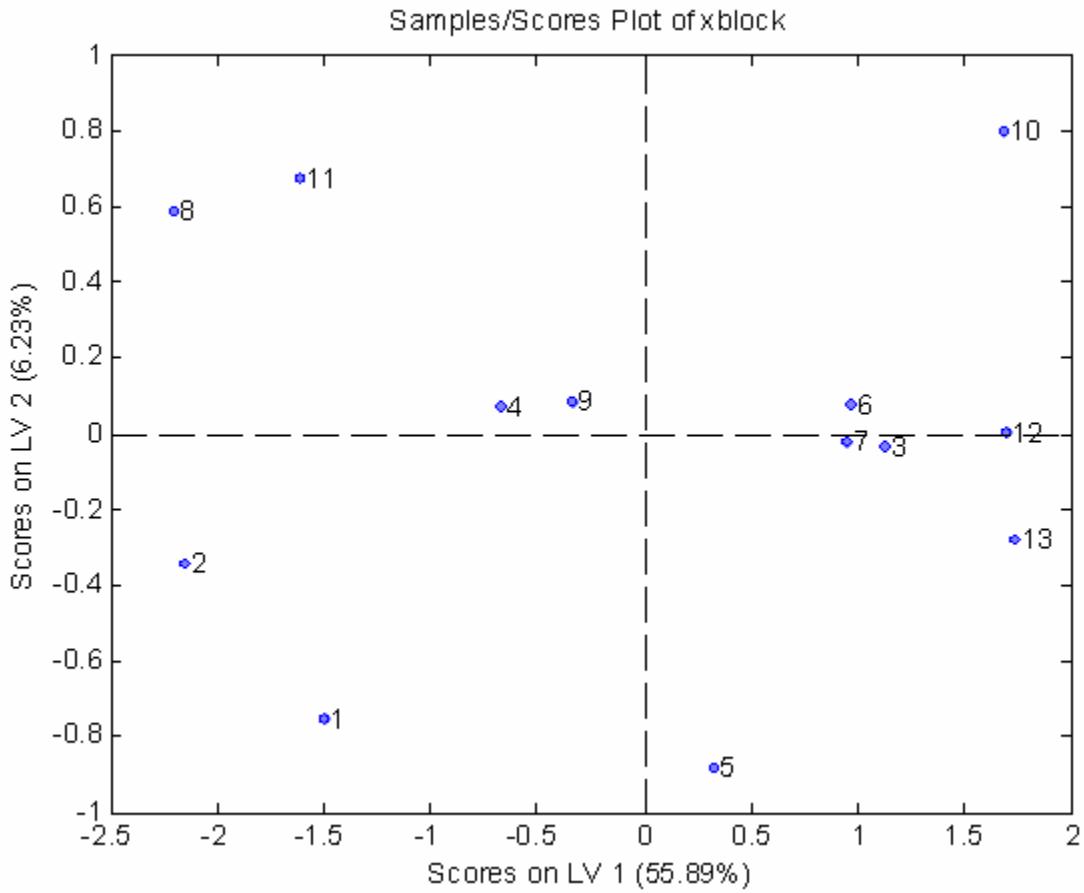
Figure 2-47. Scores plot LV1 vs. LV2 (declutter set to "none").

We see that samples 3, 6, and 7 seem to be related. Next, let's change the x-axis to "y-measured" and the y-axis to "y-predicted". Then add a legend showing the cross-validation statistics by right-clicking on the green y-predicted line and selecting **Show on figure**. Reposition the legend by clicking on it and dragging it to a new position (Figure 2-48).
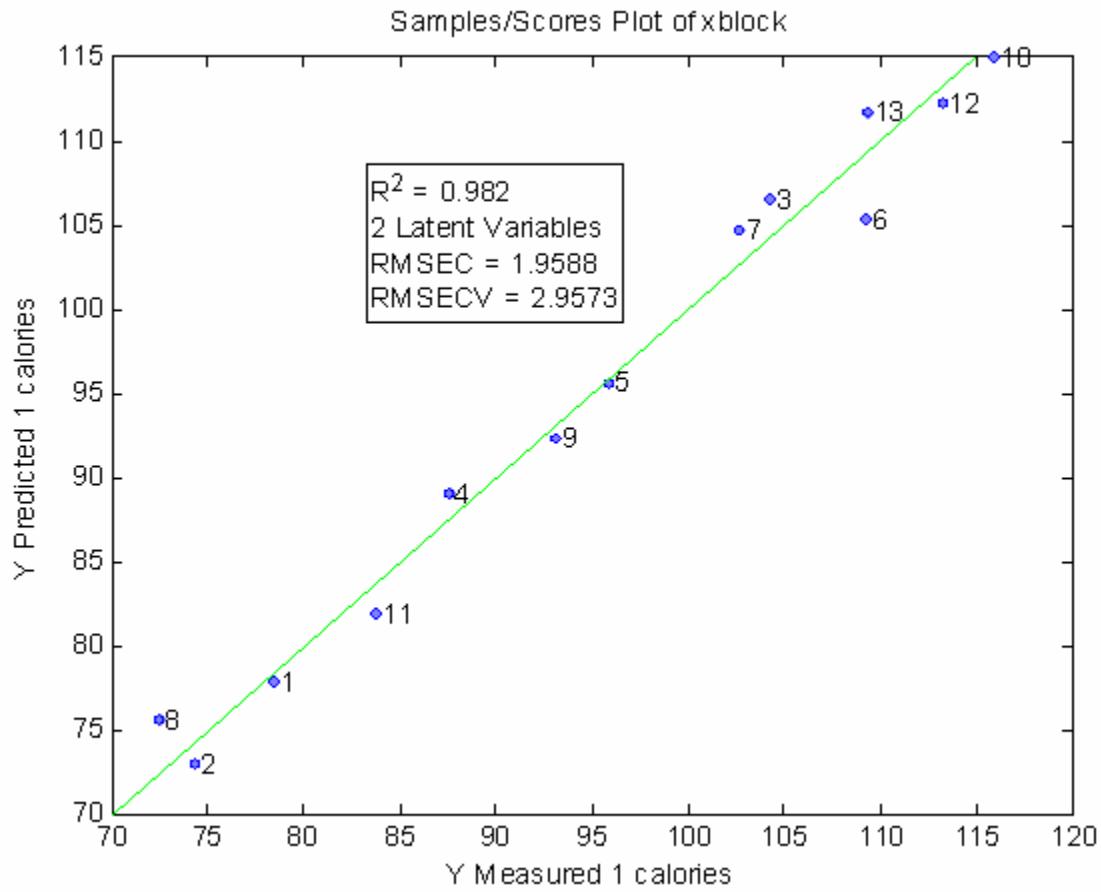
Figure 2-48. Y-measured vs. Y-predicted with Cross-Val legend.

It appears as if the model does capture the trend of the data, with a calibration error of roughly 2 calories.

Now, create a Loadings plot with LV 1 as the x-axis and LV 2 as the y-axis. Add labels using the **View** menu item from the Plot Controls (Figure 2-49).

62
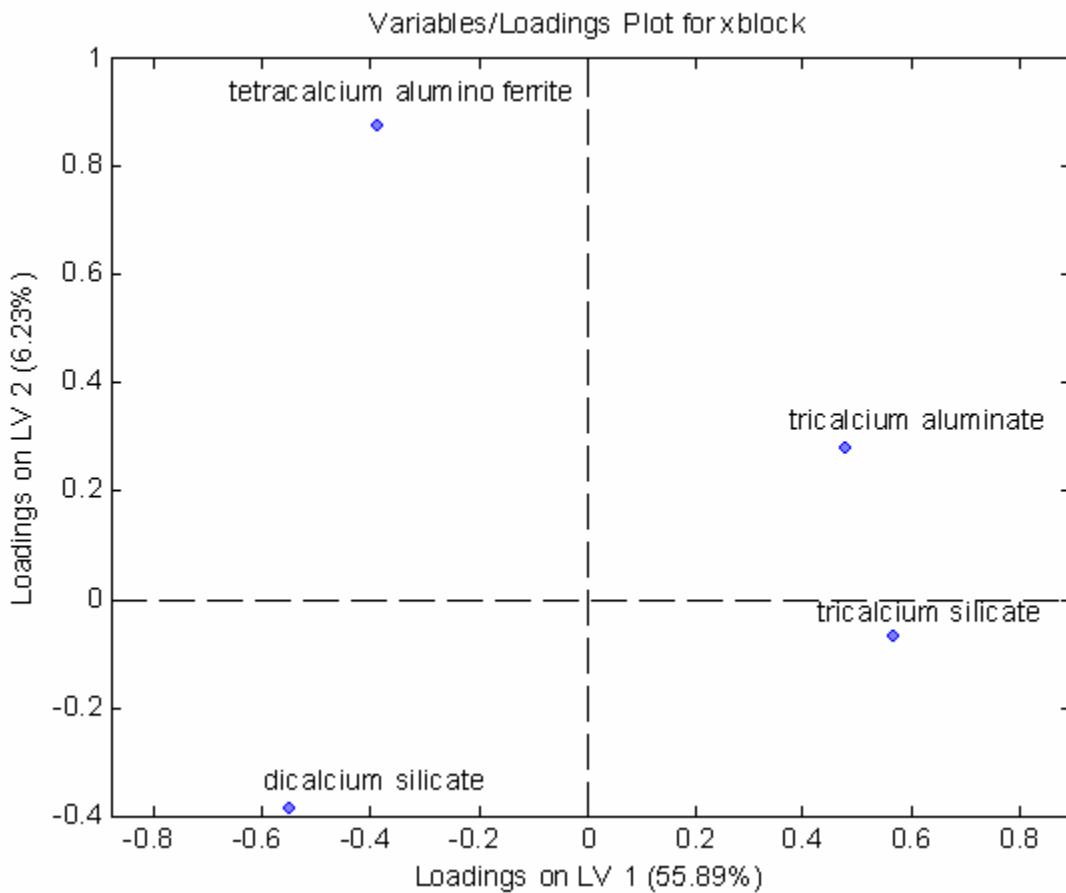
Figure 2-49. Loadings plot LV1 vs. LV2.

Here we see that none of the variables are highly correlated in both LV 1 and LV 2. We also that LV 2 does not capture much variance in tricalcium silicate.

Now look at the regression vector vs. variables by selecting **Variable** for the x-axis and **Reg Vector for Y 1 calories** for the y-axis in the Plot Controls (Figure 2-50). Add labels and adjust the axis to better see the plot using the following command:

```
>> axis([.5 4.5 -.55 .55])
```

Clicking on the y axis menu item in the **Plot Controls** again will reset the horizontal axis line correctly.
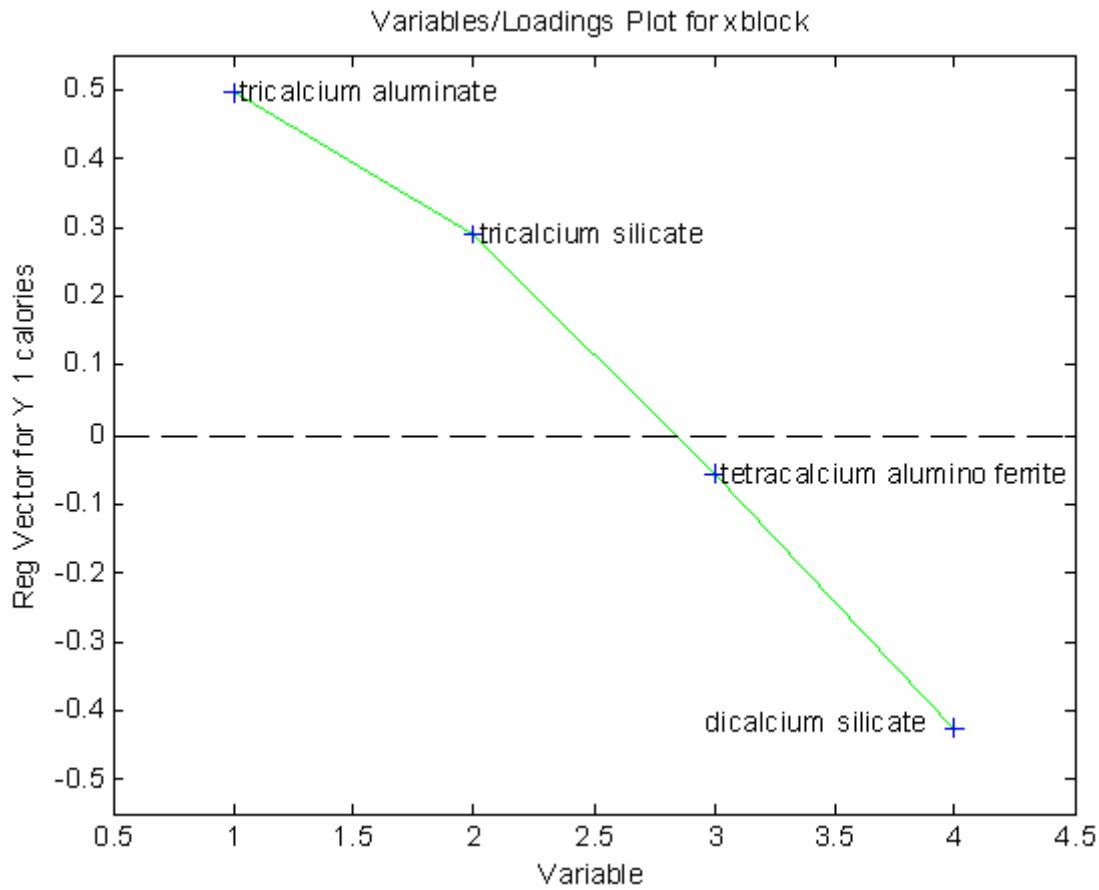
Figure 2-50. Regression vector vs. variable (axis adjusted from command line).

This plot suggests that increases in either of the first two variables will tend to increase the heat of reaction, while an increase in dicalcium silicate will tend to decrease the heat of reaction. Although the regression coefficient for the third variable (tetracalcium alumino ferrite) indicates that changes in that variable have little impact on the predicted heat of reaction, interpretation of regression coefficients can be complicated (see Partial Least Squares and Principal Component Regression topics in Chapter 6). The regression coefficients are best understood as the direction in the data which is parallel to the property of interest (heat of reaction in this case) and perpendicular to other effects observed in the data.

Finally, create a Q vs. T-squared plot (Figure 2-51) using the same procedure as with the PCA model from earlier in this chapter (see Figure 2-44).
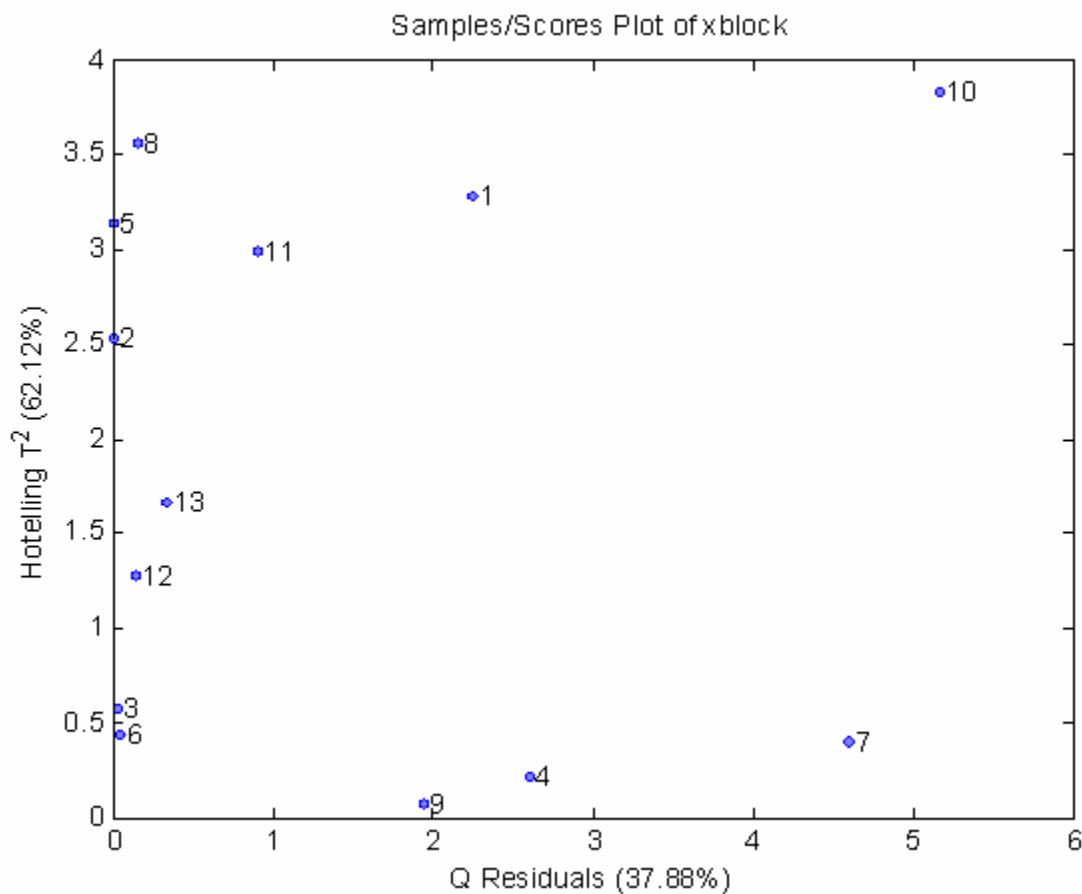
Figure 2-51. Plot of T-squared vs. Q.

Samples high in T-squared are described as having high leverage on the model, but none of the samples seem like they're "on their own" in either T-squared or Q.

This concludes our "quick start" section. We've shown how to load data, calculate a model, and create some of the typical plots used for PCA and PLS. In the next section we'll take a more detailed look at the user interfaces.

3. An Introduction to Linear Algebra

Linear algebra is the language of chemometrics. One cannot expect to truly understand most chemometric techniques without a basic understanding of linear algebra. This section reviews the basics of linear algebra and provides a foundation for the Chemometrics Tutorial section that follows. It is presented in a rather dense fashion: no proofs are given and there is often little discussion of the theoretical implications of the theorems and results presented. The goal has been to condense into as few pages as possible the aspects of linear algebra used in most chemometric methods. MATLAB commands for performing the operations listed are also included; the reader is encouraged to run the examples presented in the text. Those already familiar with linear algebra can easily skip this section. Other readers may find this section to be a good quick review. Those totally unfamiliar with linear algebra should consider spending some time with a linear algebra text. In particular, those by Gilbert Strang (see references) are particularly easy to read and understand. Several of the numerical examples in this section are adapted from Strang's *Linear Algebra and Its Applications, Second Edition* (Academic Press, 1980).

Scalars, Vectors and Matrices

A *scalar* is a mathematical quantity that is completely described by a single number. Scalar variables are generally denoted by lowercase letters. Examples of scalar variables include temperature, density, pressure and flow. In MATLAB, a value can be assigned to a scalar at the command line*:*

» a = 5;

Here we have used the semicolon operator to suppress the echo of the result. Without this semicolon MATLAB would display the result of the assignment:

» a = 5

a =

     5

A *vector* is a mathematical quantity that is completely described by its magnitude and direction. An example of a three dimensional column vector might be

$$\mathbf{b} = \begin{bmatrix} 4 \\ 3 \\ 5 \end{bmatrix} \qquad (3\text{-}1)$$

Vectors are generally denoted by bold lowercase letters. (In MATLAB no distinction is made between the notation for scalars, vectors and matrices: they can be upper or lower case and bold letters are not used.) In MATLAB, the vector above could be entered at the command in one of several ways. One way would be to enter the vector with an element on each line, like this:

```
» b = [4
3
5]

b =

        4
        3
        5
```

Another way to enter the vector would be to use the semicolon to tell MATLAB that each line was completed. For instance,

```
» b = [4; 3; 5];
```

produces the same result as above. Note that square bracketsgenerally indicate that the contents are a vector or matrix.

This vector is represented geometrically in Figure 3-1, where the three components 4, 3 and 5 are the coordinates of a point in three-dimensional space. Any vector **b** can be represented by a point in space; there is a perfect match between points and vectors. One can choose to think of a vector as the arrow, the point in space, or as the three numbers that describe the point. In a problem with 400 dimensions (such as in spectroscopy), it is probably easiest to consider the 400 numbers.

The transpose of a column vector is a row vector and vice-versa. The transpose is generally indicated by a superscript T, though in some instances, including MATLAB, an apostrophe (') will be used. For example:

$$\mathbf{b}^{\mathrm{T}} = [\ 4 \ \ 3 \ \ 5\ ] \quad\quad\quad\quad\quad (3\text{-}2)$$

In MATLAB, we could easily assign $\mathbf{b}^{\mathrm{T}}$ to another variable **c**, as follows:

```
» c = b'

c =

        4              3              5
```

A *matrix* is a rectangular array of scalars, or in some instances, algebraic expressions that evaluate to scalars. Matrices are said to be *m* by *n*, where *m* is the number of rows in the matrix and *n* is the number of columns. A 3 by 4 matrix is shown in Equation 3-3.

$$\mathbf{A} = \begin{bmatrix} 2 & 5 & 3 & 6 \\ 7 & 3 & 2 & 1 \\ 5 & 2 & 0 & 3 \end{bmatrix} \tag{3-3}$$

This matrix could be entered in MATLAB as follows:

```
» A = [2 5 3 6; 7 3 2 1; 5 2 0 3];
```
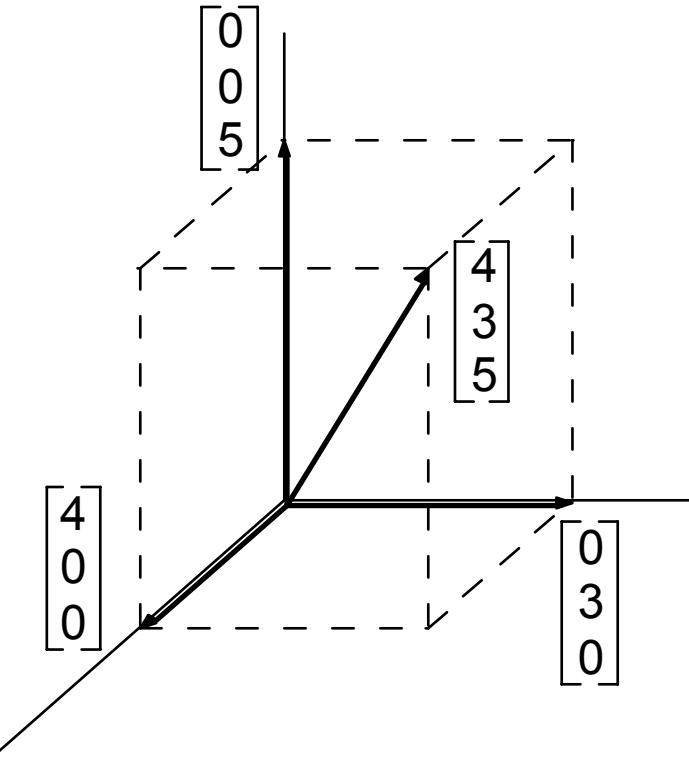

Figure 3-1. Geometric representation of the vector $[4\ 3\ 5]^{\mathrm{T}}$.

Matrices are usually denoted by bold uppercase letters. The elements of a matrix can be indicated by their row and column indices, for instance, $\mathbf{A}_{2,4} = 1$. We can index individual matrix elements in MATLAB in a similar way, for instance:

```
» A(2,4)

ans =

     1
```

Note that here we have used curved brackets. Curved brackets are used to index into matrices and in function calls to indicate a collection of input arguments.

The transpose operator "flips" a matrix along its diagonal elements, creating a new matrix with the ith row being equal to the jth column of the original matrix:

$$\mathbf{A}^{T} = \begin{bmatrix} 2 & 7 & 5 \\ 5 & 3 & 2 \\ 3 & 2 & 0 \\ 6 & 1 & 3 \end{bmatrix}$$ (3-4)

This would be done in MATLAB:

```
» A'

ans =

    2        7        5
    5        3        2
    3        2        0
    6        1        3
```

Vectors and scalars are special cases of matrices. A vector is a matrix with either one row or column. A scalar is a matrix with a single row and column.

Vector and Matrix Addition and Multiplication

Matrices can be added together provided that the dimensions are consistent; *i.e.,* both matrices must have the same number of rows and columns. To add two matrices together, simply add the corresponding elements. For instance:

$$\begin{bmatrix} 1 & 4 & 3 \\ 5 & 4 & 0 \end{bmatrix} + \begin{bmatrix} 2 & 4 & 1 \\ 2 & 6 & 3 \end{bmatrix} = \begin{bmatrix} 3 & 8 & 4 \\ 7 & 10 & 3 \end{bmatrix}$$ (3-5)

In MATLAB we might do this as follows:

```
» x = [1 4 3; 5 4 0];
» y = [2 4 1; 2 6 3];
» x + y

ans =

    3        8        4
    7       10        3
```

Note that if the matrices are not of consistent sizes, the addition will not be defined:

$$\begin{bmatrix} 1 & 4 & 3 \\ 5 & 4 & 0 \end{bmatrix} + \begin{bmatrix} 2 & 4 \\ 1 & 2 \\ 6 & 3 \end{bmatrix} = ??$$ (3-6)

If you try this in MATLAB, you will get the following:

70

```
» x = [1 4 3; 5 4 0]; y = [2 4; 1 2; 6 3];
» x + y
??? Error using ==> plus
Matrix dimensions must agree.
```

This is one of the most common error messages you will see when using MATLAB. It tells you that the operation you are attempting is not defined.

Vector and matrix addition is commutative and associative, so provided that **A**, **B** and **C** are matrices with the same number of rows and columns, then:

$$\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A} \tag{3-7}$$

$$(\mathbf{A} + \mathbf{B}) + \mathbf{C} = \mathbf{A} + (\mathbf{B} + \mathbf{C}) \tag{3-8}$$

Vectors and matrices can be multiplied by a scalar. For instance, if $c = 2$, then (using our previously defined **A**):

$$c\mathbf{A} = \begin{bmatrix} 4 & 10 & 6 & 12 \\ 14 & 6 & 4 & 2 \\ 10 & 4 & 0 & 6 \end{bmatrix}$$

Multiplication of a matrix by a scalar in MATLAB is done using the * operator:

```
» c = 2;
» c*A

ans =

     4          10          6          12
    14           6          4           2
    10           4          0           6
```

Note that scalar multiplication is commutative and associative, so if c and d are scalars:

$$c\mathbf{A} = \mathbf{A}c \tag{3-9}$$

$$(c + d)\mathbf{A} = c\mathbf{A} + d\mathbf{A} \tag{3-10}$$

Vectors can be multiplied together in two different ways. The most common vector multiplication is the *inner product*. For the inner product to be defined, the two vectors must have the same number of elements or *dimension*. The inner product is the sum over the products of corresponding elements. For instance, for two 3 element column vectors **a** and **b** with

$$\mathbf{a} = \begin{bmatrix} 2 \\ 5 \\ 1 \end{bmatrix} \text{ and } \mathbf{b} = \begin{bmatrix} 4 \\ 3 \\ 5 \end{bmatrix} \tag{3-11}$$

the inner product is

$$\mathbf{a}^T\mathbf{b} = \begin{bmatrix} 2 & 5 & 1 \end{bmatrix} \begin{bmatrix} 4 \\ 3 \\ 5 \end{bmatrix} = [2*4 + 5*3 + 1*5] = 28 \qquad (3\text{-}12)$$

Note that the inner product of two vectors produces a scalar result. In MATLAB, this example looks like:

```
» a = [2; 5; 1]; b = [4; 3; 5];
» a'*b

ans =

    28
```

The inner product occurs often in the physical sciences and is commonly referred to as the *dot product*. We will see it often in regression problems where we model a system property or output (such as a chemical concentration or quality variable) as the weighted sum of a number of different measurements.

The inner product is also used when calculating the length of a vector. The length of a vector is the square root of the sum of the squares of the vector coefficients (not to be confused with the number of elements or dimension of a vector). The length of a vector $\mathbf{a}$, denoted $\|\mathbf{a}\|$ (also known as the 2-norm of the vector), is the square root of the inner product of the vector with itself:

$$\|\mathbf{a}\| = \sqrt{\mathbf{a}^T\mathbf{a}} \qquad (3\text{-}13)$$

We could calculate the norm of the vector $\mathbf{a}$ above explicitly in MATLAB with the `sqrt` (square root) function. Alternately, we could use the `norm` function. Both methods are shown here:

```
» sqrt(a'*a)

ans =

    5.4772

» norm(a)

ans =

    5.4772
```

The vector *outer product* is encountered less often than the inner product, but will be important in *many* instances in chemometrics. Any two vectors of arbitrary dimension (number of elements) can be multiplied together in an outer product. The result will be an *m* by *n* matrix where *m* is the number of elements in the first vector and *n* is the number of elements in the second vector. As an example, take

$$\mathbf{a} = \begin{bmatrix} 2 \\ 5 \\ 1 \end{bmatrix} \text{ and } \mathbf{b} = \begin{bmatrix} 4 \\ 3 \\ 5 \\ 7 \\ 9 \end{bmatrix} \tag{3-14}$$

The outer product of **a** and **b** is then:

$$\mathbf{ab}^\mathrm{T} = \begin{bmatrix} 2 \\ 5 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 4 & 3 & 5 & 7 & 9 \end{bmatrix} = \begin{bmatrix} 2*4 & 2*3 & 2*5 & 2*7 & 2*9 \\ 5*4 & 5*3 & 5*5 & 5*7 & 5*9 \\ 1*4 & 1*3 & 1*5 & 1*7 & 1*9 \end{bmatrix}$$

$$= \begin{bmatrix} 8 & 6 & 10 & 14 & 18 \\ 20 & 15 & 25 & 35 & 45 \\ 4 & 3 & 5 & 7 & 9 \end{bmatrix} \tag{3-15}$$

In MATLAB this would be:

```
» a = [2 5 1]'; b = [4 3 5 7 9]';
» a*b'

ans =

    8      6     10     14     18
   20     15     25     35     45
    4      3      5      7      9
```

Here we used a slightly different method of entering a column vector: it was entered as the transpose of a row vector.

Two matrices **A** and **B** can be multiplied together, provided that the number of columns in **A** is equal to the number of rows in **B**. The result will be a matrix **C** that has as many rows as **A** and columns as **B**. Thus, one can multiply $\mathbf{A}_{mxn}$ by $\mathbf{B}_{nxp}$ and the result will be $\mathbf{C}_{mxp}$. The ijth element of **C** consists of the inner product of the ith row of **A** with the jth column of **B**. As an example, if

$$\mathbf{A} = \begin{bmatrix} 2 & 5 & 1 \\ 4 & 5 & 3 \end{bmatrix} \text{ and } \mathbf{B} = \begin{bmatrix} 4 & 3 & 5 & 7 \\ 9 & 5 & 3 & 4 \\ 5 & 3 & 6 & 7 \end{bmatrix} \tag{3-16}$$

then

$$\mathbf{AB} = \begin{bmatrix} 2*4+5*9+1*5 & 2*3+5*5+1*3 & 2*5+5*3+1*6 & 2*7+5*4+1*7 \\ 4*4+5*9+3*5 & 4*3+5*5+3*3 & 4*5+5*3+3*6 & 4*7+5*4+3*7 \end{bmatrix}$$

$$= \begin{bmatrix} 58 & 34 & 31 & 41 \\ 76 & 46 & 53 & 69 \end{bmatrix} \tag{3-17}$$

In MATLAB:

```
» A = [2 5 1; 4 5 3]; B = [4 3 5 7; 9 5 3 4; 5 3 6 7];
» A*B

ans =

   58    34    31    41
   76    46    53    69
```

Matrix multiplication is distributive and associative:

$$A(B + C) = AB + AC \tag{3-18}$$

$$(AB)C = A(BC) \tag{3-19}$$

but is not, in general, commutative:

$$AB \neq BA \tag{3-20}$$

Other useful matrix identities include the following:

$$(A^T)^T = A \tag{3-21}$$

$$(A + B)^T = A^T + B^T \tag{3-22}$$

$$(AB)^T = B^T A^T \tag{3-23}$$

Orthogonal and Orthonormal Vectors

Vectors are said to be *orthogonal* if their inner product is zero. The geometric interpretation of this is that they are at right angles to each other or perpendicular. Vectors are *orthonormal* if they are orthogonal and of unit length, *i.e,.* if their inner product with themselves equals 1. For an orthonormal set of column vectors v_i, with i = 1, 2, ... *n*, then

$$v_i^T v_j = \begin{cases} 0 \text{ for } i \neq j \\ 1 \text{ for } i = j \end{cases} \tag{3-24}$$

Note that it is impossible to have more than *n* orthonormal vectors in an n-dimensional space. For instance, in three dimensions, one can only have three vectors that are orthogonal, and thus, only three vectors can be orthonormal (although there are an infinite number of sets of three orthogonal vectors). Sets of orthonormal vectors can be thought of as new basis vectors for the space in which they are contained. Our conventional coordinate system in three dimensions consisting of the vectors $[1\ 0\ 0]^T$, $[0\ 1\ 0]^T$ and $[0\ 0\ 1]^T$ is the most common orthonormal basis set;, however, as we shall see when we consider Principal Components Analysis in the next chapter, it is not the only basis set, nor is it always the most convenient for describing real data.

74

Special Matrices

There are several special matrices that deserve some attention. The first is the *diagonal matrix*, which is a matrix whose only non-zero elements lie along the matrix diagonal; *i.e.,* the elements for which the row and column indices are equal are non-zero. A sample diagonal matrix **D** is shown here:

$$\mathbf{D} = \begin{bmatrix} 4 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 7 & 0 \end{bmatrix} \tag{3-25}$$

Diagonal matrices need not have the same number of rows as columns; the only requirement is that only the diagonal elements be non-zero. We shall see that diagonal matrices have additional properties which we can exploit.

Another special matrix of interest is the *identity matrix*, typically denoted as **I**. The identity matrix is always square (number of rows equals number of columns) and contains ones on the diagonal and zeros everywhere else. A 4 by 4 identity matrix is shown here

$$\mathbf{I}_{4x4} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{3-26}$$

Identity matrices can be created easily in MATLAB using the eye command. Here we create the 3 by 3 identity matrix:

```
» id = eye(3)

id =

     1     0     0
     0     1     0
     0     0     1
```

Any matrix multiplied by the identity matrix returns the original matrix (provided, of course, that the multiplication is defined). Thus, for a matrix $\mathbf{A}_{mxn}$ and identity matrix **I** of appropriate size

$$\mathbf{A}_{mxn}\mathbf{I}_{nxn} = \mathbf{I}_{mxm}\mathbf{A}_{mxn} = \mathbf{A}_{mxn} \tag{3-27}$$

The reader is encouraged to try this with some matrices in MATLAB.

A third type of special matrix is the symmetric matrix. Symmetric matrices must be square and have the property that they are equal to their transpose:

$$\mathbf{A} = \mathbf{A}^\mathrm{T} \tag{3-28}$$

Another way to say this is that $\mathbf{A}_{ij} = \mathbf{A}_{ji}$. We will see symmetric matrices turn up in many places in chemometrics. Covariance matrices, for example, are symmetric.

Gaussian Elimination: Solving Systems of Equations

Systems of equations arise in many scientific and engineering applications. Linear algebra was largely developed to solve these important problems. Gaussian elimination is the method that is consistently used to solve systems of equations. Consider the following system of three equations in three unknowns

$$\begin{bmatrix} 2b_1 & b_2 & b_3 \\ 4b_1 & b_2 & \\ -2b_1 & 2b_2 & b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -2 \\ 7 \end{bmatrix} \tag{3-29}$$

This system can also be written using matrix multiplication as follows:

$$\begin{bmatrix} 2 & 1 & 1 \\ 4 & 1 & 0 \\ -2 & 2 & 1 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -2 \\ 7 \end{bmatrix} \tag{3-30}$$

or simply as

$$\mathbf{Xb} = \mathbf{y} \tag{3-31}$$

where

$$\mathbf{X} = \begin{bmatrix} 2 & 1 & 1 \\ 4 & 1 & 0 \\ -2 & 2 & 1 \end{bmatrix}, \mathbf{b} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix}, \text{ and } \mathbf{y} = \begin{bmatrix} 1 \\ -2 \\ 7 \end{bmatrix} \tag{3-32}$$

The problem is to find the values of b_1, b_2 and b_3 that make the system of equations hold. To do this, we can apply Gaussian elimination. This process starts by subtracting a multiple of the first equation from the remaining equations so that b_1 is eliminated from them. We see here that subtracting 2 times the first equation from the second equation should eliminate b_1. Similarly, subtracting -1 times the first equation from the third equation will again eliminate b_1. The result after these first two operations is:

$$\begin{bmatrix} 2 & 1 & 1 \\ 0 & -1 & -2 \\ 0 & 3 & 2 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -4 \\ 8 \end{bmatrix} \tag{3-33}$$

The first coefficient in the first equation, 2, is known as the *pivot* in the first elimination step. We continue the process by eliminating b_2 in all equations after the second, which in this case is just the third equation. This is done by subtracting -3 times the second equation from the third equation to produce:

$$\begin{bmatrix} 2 & 1 & 1 \\ 0 & -1 & -2 \\ 0 & 0 & -4 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -4 \\ -4 \end{bmatrix} \qquad (3\text{-}34)$$

In this step, the second coefficient in the second equation, -1, was the pivot. This system can now be easily solved by *back-substitution*. It is apparent from the last equation that $b_3 = 1$. Substituting this into the second equation yields $-b_2 = -2$; thus, $b_2 = 2$. Substituting $b_3 = 1$ and $b_2 = 2$ into the first equation we find that $b_1 = -1$.

Gaussian elimination is done in MATLAB with the left division operator \ (for more information about \ type `help mldivide` at the command line, mldivide is the function name for \). Our example problem can be easily solved as follows:

```
» X = [2 1 1; 4 1 0; -2 2 1]; y = [1; -2; 7];
» b = X\y

b =

    -1
     2
     1
```

It is easy to see how this algorithm can be extended to a system of *n* equations in *n* unknowns. Multiples of the first equation are subtracted from the remaining equations to produce zero coefficients below the first pivot. Multiples of the second equation are then used to clear the coefficients below the second pivot, and so on. This is repeated until the last equation contains only the last unknown and can be easily solved. This result is substituted into the second to last equation to get the second to last unknown. This is repeated until the entire system is solved.

Singular Matrices and the Concept of Rank

Gaussian elimination appears straightforward enough; however, are there some conditions under which the algorithm may break down? It turns out that, yes, there are. Some of these conditions are easily fixed, while others are more serious. The most common problem occurs when one of the pivots is found to be zero. If this is the case, the coefficients below the pivot cannot be eliminated by subtracting a multiple of the pivot equation. Sometimes this is easily fixed: an equation from below the pivot equation with a non-zero coefficient in the pivot column can be swapped with the pivot equation and elimination can proceed. However, if all of the coefficients below the zero pivot are also zero, elimination cannot proceed. In this case, the matrix is called *singular* and there is no hope for a unique solution to the problem.

As an example, consider the following system of equations:

$$\begin{bmatrix} 1 & 3 & 2 \\ 2 & 6 & 9 \\ 3 & 9 & 8 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -4 \\ -4 \end{bmatrix} \qquad (3\text{-}35)$$

Elementary row operations can be used to produce the system:

$$\begin{bmatrix} 1 & 3 & 2 \\ 0 & 0 & 5 \\ 0 & 0 & 2 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -6 \\ -7 \end{bmatrix} \tag{3-36}$$

This system has no solution as the second equation requires that b_3 = -6/5 while the third equation requires that b_3 = -7/2. If we tried this problem in MATLAB we would see the following:

```
» X = [1 3 2; 2 6 9; 3 9 8]; y = [1; -4; -4];
» b = X\y
```

```
Warning: Matrix is singular to working precision.
```

```
b =

   -Inf
    Inf
   -3.5000
```

We will discuss the meaning of the warning message shortly.

On the other hand, if the right hand side of the system were changed so that we started with:

$$\begin{bmatrix} 1 & 3 & 2 \\ 2 & 6 & 9 \\ 3 & 9 & 8 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -8 \\ -1 \end{bmatrix} \tag{3-37}$$

This would be reduced by elementary row operations to:

$$\begin{bmatrix} 1 & 3 & 2 \\ 0 & 0 & 5 \\ 0 & 0 & 2 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -10 \\ -4 \end{bmatrix} \tag{3-38}$$

Note that the final two equations have the same solution, b_3 = -2. Substitution of this result into the first equation yields $b_1 + 3b_2 = 5$, which has infinitely many solutions. We can see that singular matrices can cause us to have no solution or infinitely many solutions and will generate warnings at the command line. If we do this problem in MATLAB we obtain:

```
» X = [1 3 2; 2 6 9; 3 9 8]; y = [1; -8; -1];
» b = X\y
```

Warning: Matrix is singular to working precision.

```
b =

  -Inf
   Inf
  -2.0000
```

The solution obtained agrees with the one we calculated above, b_3 = -2. There are an infinite number of solutions for b_1 and b_2. In this case MATLAB chose the -inf and inf, respectively.

Consider once again the matrix from our previous example and its reduced form:

$$\begin{bmatrix} 1 & 3 & 2 \\ 2 & 6 & 9 \\ 3 & 9 & 8 \end{bmatrix} \rightarrow \begin{bmatrix} 1 & 3 & 2 \\ 0 & 0 & 5 \\ 0 & 0 & 2 \end{bmatrix} \tag{3-39}$$

We could have taken the elimination one step further by subtracting 2/5 of the second equation from the third to produce:

$$\begin{bmatrix} 1 & 3 & 2 \\ 0 & 0 & 5 \\ 0 & 0 & 0 \end{bmatrix} \tag{3-40}$$

This is known as the *echelon form* of a matrix. It is necessarily upper triangular, that is, all non-zero entries are confined to be on, or above, the main diagonal (the pivots are the 1 in the first row and the 5 in the second row). The non-zero rows come first, and below each pivot is a column of zeros. Also, each pivot lies to the right of the pivot in the row above. The number of non-zero rows obtained by reducing a matrix to echelon form is the *rank* of the matrix. Note that this procedure can be done on any matrix; it need not be square. It can be shown that the rank of an *m* by *n* matrix has to be less than, or equal to, the lesser of *m* or *n*, i.e:.

$$\text{rank}(\mathbf{X}) \leq \min(m,n) \tag{3-41}$$

A matrix whose rank is equal to the lesser of *m* or *n* is said to be of *full rank*. If the rank is less than min(*m,n*), the matrix is *rank deficient* or *collinear*. MATLAB can be used to determine the rank of a matrix. In this case we get:

```
» rank(X)
```

```
ans =

     2
```

which is just what we expect based on the result shown in Equation 3-40.

Matrix Inverses

The *inverse* of matrix $\mathbf{A}$, $\mathbf{A}^{-1}$, is the matrix such that $\mathbf{AA}^{-1} = \mathbf{I}$ and $\mathbf{A}^{-1}\mathbf{A} = \mathbf{I}$. It is assumed here that $\mathbf{A}$, $\mathbf{A}^{-1}$ and $\mathbf{I}$ are all square and of the same dimension. Note, however, that $\mathbf{A}^{-1}$ might not exist. If it does, $\mathbf{A}$ is said to be *invertible*, and its inverse $\mathbf{A}^{-1}$ will be unique.

It can also be shown that the product of invertible matrices has an inverse, which is the product of the inverses in reverse order:

$$(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \tag{3-42}$$

This can be extended to hold with three or more matrices, for example:

$$(\mathbf{ABC})^{-1} = \mathbf{C}^{-1}\mathbf{B}^{-1}\mathbf{A}^{-1} \tag{3-43}$$

How do we find matrix inverses? We have already seen that we can perform elementary row operations to reduce a matrix $\mathbf{A}$ to an upper triangular echelon form. However, provided that the matrix $\mathbf{A}$ is nonsingular, this process can be continued to produce a diagonal matrix, and finally, the identity matrix. This same set of row operations, if performed on the identity matrix, produces the inverse of $\mathbf{A}$, $\mathbf{A}^{-1}$. Said another way, the same set of row operations that transform $\mathbf{A}$ to $\mathbf{I}$ transform $\mathbf{I}$ to $\mathbf{A}^{-1}$. This process is known as the *Gauss-Jordan method*.

Let us consider an example. Suppose that we want to find the inverse of

$$\mathbf{A} = \begin{bmatrix} 2 & 1 & 1 \\ 4 & 1 & 0 \\ -2 & 2 & 1 \end{bmatrix} \tag{3-44}$$

We will start by augmenting $\mathbf{A}$ with the identity matrix, then we will perform row operations to reduce $\mathbf{A}$ to echelon form:

$$\left[\begin{array}{ccc|ccc} 2 & 1 & 1 & 1 & 0 & 0 \\ 4 & 1 & 0 & 0 & 1 & 0 \\ -2 & 2 & 1 & 0 & 0 & 1 \end{array}\right] \rightarrow \left[\begin{array}{ccc|ccc} 2 & 1 & 1 & 1 & 0 & 0 \\ 0 & -1 & -2 & -2 & 1 & 0 \\ 0 & 0 & -4 & -5 & 3 & 1 \end{array}\right]$$

We now continue the operation by eliminating the coefficients above each of the pivots. This is done by subtracting the appropriate multiple of the third equation from the first two, then subtracting the second equation from the first:

$$\left[\begin{array}{ccc|ccc} 2 & 1 & 0 & \dfrac{-1}{4} & \dfrac{3}{4} & \dfrac{1}{4} \\ 0 & -1 & 0 & \dfrac{1}{2} & \dfrac{-1}{2} & \dfrac{-1}{2} \\ 0 & 0 & -4 & -5 & 3 & 1 \end{array}\right] \rightarrow \left[\begin{array}{ccc|ccc} 2 & 0 & 0 & \dfrac{1}{4} & \dfrac{1}{4} & \dfrac{-1}{4} \\ 0 & -1 & 0 & \dfrac{1}{2} & \dfrac{-1}{2} & \dfrac{-1}{2} \\ 0 & 0 & -4 & -5 & 3 & 1 \end{array}\right]$$

Finally, each equation is multiplied by the inverse of the diagonal to get to the identity matrix:

$$\begin{bmatrix} 1 & 0 & 0 & | & \dfrac{1}{8} & \dfrac{1}{8} & \dfrac{-1}{8} \\ 0 & 1 & 0 & | & \dfrac{-1}{2} & \dfrac{1}{2} & \dfrac{1}{2} \\ 0 & 0 & 1 & | & \dfrac{5}{4} & \dfrac{-3}{4} & \dfrac{-1}{4} \end{bmatrix} \tag{3-45}$$

The matrix on the right is $\mathbf{A}^{-1}$, the inverse of $\mathbf{A}$. Note that our algorithm would have failed if we had encountered an incurable zero pivot, *i.e,.* if $\mathbf{A}$ was singular. In fact, *a matrix is invertible if, and only if, it is nonsingular.*

This process can be repeated in MATLAB using the `rref` (reduced row echelon form) command. We start by creating the $\mathbf{A}$ matrix. We then augment it with the identity matrix using the `eye` command and use the `rref` function to create the reduced row echelon form. In the last step we verify that the 3 by 3 matrix on the right is the inverse of $\mathbf{A}$. (The result is presented here as fractions rather than decimals by setting the MATLAB command window display preference to "rational").

```
» A = [2 1 1; 4 1 0; -2 2 1];
» B = rref([A eye(3)])

B =

      1           0           0          1/8         1/8        -1/8
      0           1           0         -1/2         1/2         1/2
      0           0           1          5/4        -3/4        -1/4

» A*B(:,4:6)

ans =

      1           0           0
      0           1           0
      0           0           1
```

A simpler way of obtaining an inverse in MATLAB is to use the `inv` command:

```
» Ainv = inv(A)

Ainv =

     1/8         1/8        -1/8
    -1/2         1/2         1/2
     5/4        -3/4        -1/4
```

Another useful property of inverses is:

$$(\mathbf{A}^T)^{-1} = (\mathbf{A}^{-1})^T \tag{3-46}$$

We could also verify this for our example in MATLAB:

```
» inv(A') - inv(A)'

ans =

     0          0          0
     0          0          0
     0          0          0
```

Vector Spaces and Subspaces

Before continuing on, it is useful to introduce the concept of a *vector space*. The most important vector spaces are denoted $\mathbf{R}^1$, $\mathbf{R}^2$, $\mathbf{R}^3$, ...; there is one for every integer. The space $\mathbf{R}^n$ consists of all column vectors with n (real) components. The exponent n is said to be the *dimension* of the space. For instance, the $\mathbf{R}^3$ space can be thought of as our "usual" three-dimensional space: each component of the vector is one of the x, y or z axis coordinates. Likewise, $\mathbf{R}^2$ defines a planar space, such as the x-y plane. A *subspace* is a vector space that is contained within another. For instance, a plane within $\mathbf{R}^3$ defines a two dimensional subspace of $\mathbf{R}^3$, and is a vector space in its own right. In general, a subspace of a vector space is a subset of the space where the sum of any two vectors in the subspace is also in the subspace and any scalar multiple of a vector in the subspace is also in the subspace.

Linear Independence and Basis Sets

In a previous section we defined the rank of a matrix in a purely computational way: the number of non-zero pivots after a matrix had been reduced to echelon form. We are beginning to get the idea that rank and singularity are important concepts when working with systems of equations. To more fully explore these relationships, the concept of *linear independence* must be introduced. Given a set of vectors $\mathbf{v}_1$, $\mathbf{v}_2$, ... , $\mathbf{v}_k$, if all non-trivial combinations of the vectors are nonzero:

$$c_1\mathbf{v}_1 + c_2\mathbf{v}_2 + ... + c_k\mathbf{v}_k \neq 0 \quad \text{unless} \quad c_1 = c_2 = ... = c_k = 0 \tag{3-47}$$

then the vectors are *linearly independent*. Otherwise, at least one of the vectors is a linear combination of the other vectors and they are *linearly dependent*.

It is easy to visualize linear independence. For instance, any two vectors that are not scalar multiples of each other are linearly independent and define a plane. A third vector in that plane must be linearly dependent as it can be expressed as a weighted sum of the other two vectors. Likewise, any 4 vectors in $\mathbf{R}^3$ must be linearly dependent. Stated more formally, a set of k vectors in $\mathbf{R}^m$ must be linearly dependent if $k > m$. It is also true that the r nonzero

rows of an echelon matrix are linearly independent, and so are the r columns that contain the pivots.

A set of vectors $\mathbf{w}_1$, $\mathbf{w}_2$, ... , $\mathbf{w}_k$, in $\mathbf{R}^n$ is said to *span the space* if every vector $\mathbf{v}$ in $\mathbf{R}^n$ can be expressed as a linear combination of $\mathbf{w}$'s*:*

$$\mathbf{v} = c_1\mathbf{w}_1 + c_2\mathbf{w}_2 + ... + c_k\mathbf{w}_k \text{ for some } c_i. \qquad (3\text{-}48)$$

Note that for the set of $\mathbf{w}$'s to span $\mathbf{R}^n$ then $k \geq n$. A *basis* for a vector space is a set of vectors that are linearly independent and span the space. Note that the number of vectors in the basis must be equal to the dimension of the space. Any vector in the space can be specified as one and only one combination of the basis vectors. Any linearly independent set of vectors can be extended to a basis by adding (linearly independent) vectors so that the set spans the space. Likewise, any spanning set of vectors can be reduced to a basis by eliminating linearly dependent vectors.

Row Spaces, Column Spaces and Nullspaces

Suppose that $\mathbf{U}$ is the echelon matrix obtained by performing elimination on the m by n matrix $\mathbf{A}$. Recall that the rank r of $\mathbf{A}$ is equal to the number of nonzero rows of $\mathbf{U}$. Likewise, the dimension of the *row space* of $\mathbf{A}$ (the space spanned by the rows of $\mathbf{A}$), denoted $\mathrm{R}(\mathbf{A}^\mathrm{T})$, is equal to r, and the rows of $\mathbf{U}$ form a basis for the row space of $\mathbf{A}$, that is, they span the same space. This is true because elementary row operations leave the row space unchanged.

The *column space* of $\mathbf{A}$ (the space spanned by the columns of $\mathbf{A}$, also referred to as the range of $\mathbf{A}$), denoted $\mathrm{R}(\mathbf{A})$, also has dimension r. This implies that the number of independent columns in $\mathbf{A}$ equals the number of independent rows, r. A basis can be constructed for the column space of $\mathbf{A}$ by selecting the r columns of $\mathbf{U}$ that contain non-zero pivots.

The fact that the dimension of the row space is equal to the dimension of the column space is one of the most important theorems in linear algebra. This fact is often expressed simply as "row rank = column rank." This fact is generally not obvious for a random non-square matrix. For square matrices it implies that, if the rows are linearly independent, so are the columns. Note also that the column space of $\mathbf{A}$ is equal to the row space of $\mathbf{A}^\mathrm{T}$.

The *nullspace* of $\mathbf{A}$, $\mathrm{N}(\mathbf{A})$, is of dimension $n - r$. $\mathrm{N}(\mathbf{A})$ is the space of $\mathbf{R}^n$ not spanned by the rows of $\mathbf{A}$. Likewise, the nullspace of $\mathbf{A}^\mathrm{T}$, $\mathrm{N}(\mathbf{A}^\mathrm{T})$, (also known as the left nullspace of $\mathbf{A}$) has dimension $m - r$, and is the space of $\mathbf{R}^m$ not spanned by the columns of $\mathbf{A}$.

Orthogonality of Subspaces

Earlier we defined orthogonal vectors. Recall that any two vectors $\mathbf{v}$ and $\mathbf{w}$ are orthogonal if their inner product is zero. Two subspaces V and W can also be orthogonal, provided that every vector $\mathbf{v}$ in V is orthogonal to every vector $\mathbf{w}$ in W; *i.e.,* $\mathbf{v}^\mathrm{T}\mathbf{w} = 0$ for all $\mathbf{v}$ and $\mathbf{w}$.

Given the definition of orthogonality of subspaces, we can now state more clearly the properties of the row space, column space and nullspaces defined in the previous section. For

any *m* by *n* matrix $\mathbf{A}$, the nullspace $N(\mathbf{A})$ and the row space $R(\mathbf{A}^T)$ are orthogonal subspaces of $\mathbf{R}^n$. Likewise, the left nullspace $N(\mathbf{A}^T)$ and the column space $R(\mathbf{A})$ are orthogonal subspaces of $\mathbf{R}^m$.

The *orthogonal complement* of a subspace V of $\mathbf{R}^n$ is the space of all vectors orthogonal to V and is denoted $V^\perp$ (pronounced V perp).

Projections onto Lines

We will see in the next chapter that the projection of points onto lines is very important in many chemometric methods. In general, the projection problem is: given a vector $\mathbf{x}$ and a point defined by the vector $\mathbf{y}$, find the point $\mathbf{p}$ along the direction defined by $\mathbf{x}$ which is closest to $\mathbf{y}$. This is illustrated graphically in Figure 3-2. Finding this point $\mathbf{p}$ is relatively straightforward once we realize that $\mathbf{p}$ must be a scalar multiple of $\mathbf{x}$; *i.e.*, $\mathbf{p} = \hat{b}\,\mathbf{x}$, and that the line connecting $\mathbf{y}$ to $\mathbf{p}$ must be perpendicular to $\mathbf{x}$:

$$\mathbf{x}^T(\mathbf{y} - \hat{b}\,\mathbf{x}) = 0 \;\;\rightarrow\;\; \mathbf{x}^T\mathbf{y} = \hat{b}\,\mathbf{x}^T\mathbf{x} \;\;\rightarrow\;\; \hat{b} = \frac{\mathbf{x}^T\mathbf{y}}{\mathbf{x}^T\mathbf{x}} \qquad (3\text{-}49)$$

Therefore, the projection $\mathbf{p}$ of the point $\mathbf{y}$ onto the line spanned by the vector $\mathbf{x}$ is given by

$$\mathbf{p} = \hat{b}\,\mathbf{x} = \frac{\mathbf{x}^T\mathbf{y}}{\mathbf{x}^T\mathbf{x}}\,\mathbf{x} \qquad (3\text{-}50)$$
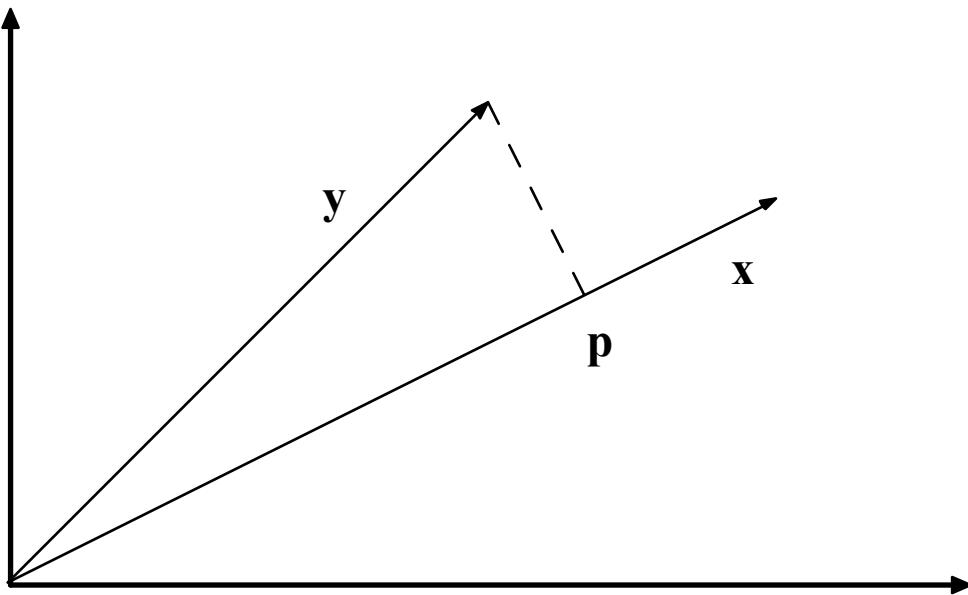
Figure 3-2. The projection of the vector $\mathbf{y}$ onto the vector $\mathbf{x}$.

84

The (squared) distance from **y** to **p** can also be calculated. The result is

$$\|\mathbf{y} - \mathbf{p}\|^2 = \frac{(\mathbf{y}^T\mathbf{y})(\mathbf{x}^T\mathbf{x})-(\mathbf{x}^T\mathbf{y})^2}{\mathbf{x}^T\mathbf{x}} \qquad (3\text{-}51)$$

We may also be interested in the projection of a point **y** onto a subspace. For instance, we may want to project the point onto the plane defined by two vectors, or an *n*-dimensional subspace defined by a collection of vectors; that is, a matrix. In this case, the vector **x** in the two equations above will become the matrix **X**, and the inner product $\mathbf{x}^T\mathbf{x}$ will become $\mathbf{X}^T\mathbf{X}$. If **X** is *m* by *n* and rank *r*, the matrix $\mathbf{X}^T\mathbf{X}$ is *n* by *n*, symmetric ($\mathbf{X}^T\mathbf{X} = (\mathbf{X}^T\mathbf{X})^T$) and also of rank *r*. Thus we see that if **X** has linearly independent columns, *and therefore* rank *r* = *n*, then $\mathbf{X}^T\mathbf{X}$ is nonsingular and therefore invertible. This is a very important result, as we shall see shortly.

Projections onto Subspaces and Least Squares

Previously we have considered solving **Xb** = **y** only for systems where there are the same number of equations as variables (*m* = *n*). This system either has a solution or it doesn't. We now consider the case of *m* > *n*, where we have more samples (rows) than variables (columns), with the possibility that the system of equations can be inconsistent; that is, there is no solution which makes the equality hold. In these cases, one can only solve the system such that the average error in the equations is minimized.

Consider for a moment the single variable case **xb** = **y** where there is more than one equation. The error is nothing more than the length of the vector **xb** - **y**, E = ‖**xb** - **y**‖. It is easier, however, to minimize the squared length:

$$\mathrm{E}^2 = (\mathbf{xb} - \mathbf{y})^T(\mathbf{xb} - \mathbf{y}) = \mathbf{x}^T\mathbf{x}b^2 - 2\mathbf{x}^T\mathbf{y}b + \mathbf{y}^T\mathbf{y} \qquad (3\text{-}52)$$

The minimum of this can be found by taking the derivative with respect to b and setting it to zero:

$$\frac{d\mathrm{E}^2}{db} = 2\mathbf{x}^T\mathbf{x}b - 2\mathbf{x}^T\mathbf{y} = 0 \qquad (3\text{-}53)$$

The least squares solution to the problem is then:

$$\hat{b} = \frac{\mathbf{x}^T\mathbf{y}}{\mathbf{x}^T\mathbf{x}} \qquad (3\text{-}54)$$

This is the same solution we obtained to the projection problem $\mathbf{p} = \hat{b}\,\mathbf{x}$ in Equation 3-49. Thus, requiring that the error vector be perpendicular to **x** gave the same result as the least squares approach. This suggests that we could solve systems in more than one variable by either geometry or calculus.

Consider now the system **Xb** = **y**, where **X** is *m* by *n*, *m* > *n*. Let us solve this system by requiring that **Xb̂** - **y** be perpendicular to the column space of **X**. For this to be true, each

vector in the column space of $\mathbf{X}$ must be perpendicular to $\mathbf{X\hat{b}}$ - $\mathbf{y}$. Each vector in the column space of $\mathbf{X}$, however, is expressible as a linear combination, say $\mathbf{c}$, of the columns of $\mathbf{X}$, $\mathbf{Xc}$. Thus, for all choices of $\mathbf{c}$,

$$(\mathbf{Xc})^T(\mathbf{X\hat{b}} - \mathbf{y}) = 0, \quad \text{or} \quad \mathbf{c}^T[\mathbf{X}^T\mathbf{X\hat{b}} - \mathbf{X}^T\mathbf{y}] = 0 \qquad (3\text{-}55)$$

There is only one way that this can be true for all $\mathbf{c}$: the vector in the brackets must be zero. Therefore, it must be true that

$$\mathbf{X}^T\mathbf{X\hat{b}} = \mathbf{X}^T\mathbf{y} \qquad (3\text{-}56)$$

These are known as the *normal equations* for least squares problems. We can now solve for $\mathbf{\hat{b}}$ by multiplying through by $(\mathbf{X}^T\mathbf{X})^{-1}$ to obtain:

$$\mathbf{\hat{b}} = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{y} \qquad (3\text{-}57)$$

The projection of $\mathbf{y}$ onto the column space of $\mathbf{X}$ is therefore

$$\mathbf{p} = \mathbf{X\hat{b}} = \mathbf{X}(\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{y} \qquad (3\text{-}58)$$

In chemometrics we commonly refer to $\mathbf{\hat{b}}$ as the regression vector. Often $\mathbf{X}$ consists of the matrix of m samples with n measured variables. The vector $\mathbf{y}$ consists of some property (such as a concentration or quality parameter) for the m samples. We then want to determine a $\mathbf{\hat{b}}$ that we can use with new samples, $\mathbf{X}_{new}$, to estimate their properties $\mathbf{\hat{y}}_{new}$:

$$\mathbf{\hat{y}}_{new} = \mathbf{X}_{new}\mathbf{\hat{b}} \qquad (3\text{-}59)$$

As an example, suppose we measured two variables, x_1 and x_2, on four samples, and also had a quality variable y. Our data would then be:

$$\mathbf{X} = \begin{bmatrix} 1 & 1 \\ 1 & 2 \\ 2 & 1 \\ 2 & 2 \end{bmatrix} \quad \text{and} \quad \mathbf{y} = \begin{bmatrix} 6 \\ 6 \\ 7 \\ 11 \end{bmatrix} \qquad (3\text{-}60)$$

We can determine a regression vector $\mathbf{\hat{b}}$ that relates the measured variables x_1 and x_2 to the quality variable y in MATLAB as follows:

```
» X = [1 1; 1 2; 2 1; 2 2]; y = [6 6 7 11]';
» b = inv(X'*X)*X'*y

b =

    3.0000
    2.0000
```

Thus, our model for estimating our quality variable is $y = 3x_1 + 2x_2$. In MATLAB, however, we can simplify this calculation by using the "left division" symbol \ instead of the `inv` operator and get the same result:

```
» b = X\y

b =

    3.0000
    2.0000
```

The $\hat{\mathbf{b}}$ can now be used to get **p**, the projection of **y** into **X**, and the difference between **y** and its projection into **X**, **d**:

```
» p = X*b

p =

     5
     7
     8
    10

» d = y-p

d =

     1
    -1
    -1
     1
```

We can also check to see if **d** is orthogonal to the columns of **X**. The simplest way to do this is to check the value of $\mathbf{X}^T\mathbf{d}$:

```
» X'*d

ans =

   1.0e-14 *

   -0.9770
   -0.9770
```

This gives us the inner product of each of the columns of **X** with **d**. We see that the values are very close to zero, the only difference from zero being due to machine round off error. Thus, **d** is orthogonal to the columns of **X**, as it should be.

Ill-conditioned Problems

We have now seen how to solve least squares problems in several variables. Once again, we might ask: "when might I expect this procedure to fail?" Based on our previous experience with the solution of m equations in m unknowns and the formation of inverses, we expect that the least squares procedure will fail when $\mathbf{X}$ is rank deficient, that is, when rank$(\mathbf{X}^T\mathbf{X}) < n$. However, what about when $\mathbf{X}$ is nearly rank deficient; that is, when one column of $\mathbf{X}$ is nearly a linear combination of the other columns? Let us consider such a system:

$$\mathbf{X} = \begin{bmatrix} 1 & 2 \\ 2 & 4 \\ 3 & 6 \\ 4 & 8.0001 \end{bmatrix} \quad \text{and} \quad \mathbf{y} = \begin{bmatrix} 2 \\ 4 \\ 6 \\ 8 \end{bmatrix} \tag{3-61}$$

Here the second column of $\mathbf{X}$ is almost, but not quite, twice the first column. In other words, $\mathbf{X}$ is close to being singular. We can now use MATLAB to estimate a regression vector $\hat{\mathbf{b}}$ for this problem:

```
» X = [1 2; 2 4; 3 6; 4 8.0001]; y = [2 4 6 8]';
» b = X\y

b =

    2
    0
```

Here we see that the system can be solved exactly by $y = 2x_1$. However, what would happen if the y data changed a very small amount? Consider changing the third element of y from 6 to 5.9999 and 6.0001. The following results:

```
» X = [1 2; 2 4; 3 6; 4 8.0001]; y = [2 4 6.0001 8]'; b = X\y

b =

    3.7143
   -0.8571

» X = [1 2; 2 4; 3 6; 4 8.0001]; y = [2 4 5.9999 8]'; b = X\y

b =

    0.2857
    0.8571
```

We see that the regression coefficients changed from $\hat{\mathbf{b}} = [3.7143 \ -0.8571]$ to $\hat{\mathbf{b}} = [0.2857 \ 0.8571]$ given this very small change in the data. This is an example of what happens in regression when the $\mathbf{X}$ matrix is very close to singular. Methods for dealing with these ill-conditioned problems will be discussed in the next section.

Projection Matrices

We saw previously that given the problem $\mathbf{Xb} = \mathbf{y}$, we could obtain the projection of $\mathbf{y}$ onto the columns of $\mathbf{X}$, $\mathbf{p}$, from:

$$\mathbf{p} = \mathbf{X}(\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{y} \qquad (3\text{-}62)$$

$$\mathbf{p} = \mathbf{Py} \qquad (3\text{-}63)$$

The quantity $\mathbf{X}(\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T$, which we shall denote $\mathbf{P}$, is a *projection matrix*. Projection matrices have two important properties: they are idempotent and symmetric. Thus

$$\mathbf{PP} = \mathbf{P}^2 = \mathbf{P} \qquad (3\text{-}64)$$

$$\mathbf{P}^T = \mathbf{P} \qquad (3\text{-}65)$$

It is easy to see that $\mathbf{P}$ must be idempotent: the first application of $\mathbf{P}$ projects $\mathbf{y}$ into $\mathbf{X}$. A second application won't change the result since $\mathbf{Py}$ will already be in the column space of $\mathbf{X}$.

Orthogonal and Orthonormal Bases

When we think of a basis for a space, such as the x-y plane, we normally think of an orthogonal basis; that is, we define our distances in the plane based on two directions that are perpendicular. Orthogonal basis sets, it turns out, are convenient from both a conceptual and mathematical perspective. Basis sets can be made even simpler by normalizing the basis vectors to unit length. The result is an orthonormal basis. An orthonormal basis, $\mathbf{v}_1, \mathbf{v}_2, ..., \mathbf{v}_k$ has the property that:

$$\mathbf{v}_i^T\mathbf{v}_j = \begin{cases} 0 \text{ for } i \neq j \\ 1 \text{ for } i = j \end{cases} \qquad (3\text{-}66)$$

Of course, we are most familiar with the standard basis, $\mathbf{v}_1 = [1\ 0\ ...\ 0]^T$, $\mathbf{v}_2 = [0\ 1\ ...\ 0]^T$, etc.; however, it is possible to construct an infinite number of orthonormal bases for any space of dimension 2 or greater by simply rotating the basis vectors while keeping them at right angles to each other.

Suppose for a moment that we are interested in projecting a vector $\mathbf{y}$ onto an $\mathbf{X}$ that consists of orthonormal columns. In this case, $\mathbf{X}^T\mathbf{X} = \mathbf{I}$, thus

$$\mathbf{P} = \mathbf{X}(\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T = \mathbf{XX}^T \qquad (3\text{-}67)$$

A square matrix with orthonormal columns is known as an *orthogonal matrix* (though orthonormal matrix would have been a better name). An orthogonal matrix $\mathbf{Q}$ has the following properties:

$$\mathbf{Q}^T\mathbf{Q} = \mathbf{I}, \quad \mathbf{QQ}^T = \mathbf{I}, \quad \text{and} \quad \mathbf{Q}^T = \mathbf{Q}^{-1} \qquad (3\text{-}68)$$

Furthermore, **Q** will also have orthonormal rows; if **Q** is an orthogonal matrix, so is **Q**^{T}. We will see this again shortly when we consider Principal Components Analysis (PCA) in the next section.

Pseudoinverses

We saw previously that we were not able to solve **Xb** = **y** using the "normal equations" in the case where the columns of **X** were not independent or collinear. But is that the best we can do? Are we simply forced to conclude that there is no solution to the problem? In fact, it is still possible to obtain a least squares solution to the problem. To do so, we must introduce the concept of the pseudoinverse, **X**$^+$, for a matrix **X** that is not invertible. The general situation when **X** is collinear is that there are many solutions to **Xb** = **y**. Which one should we choose? The one with minimum length of $\hat{\mathbf{b}}$, $\|\hat{\mathbf{b}}\|$. To get this, we require that the component of $\hat{\mathbf{b}}$ in the nullspace of **X** be zero, which is the same as saying that $\hat{\mathbf{b}}$ must lie in the row space of **X**. Thus, the optimal least squares solution to any **Xb** = **y** is $\hat{\mathbf{b}}$ such that:

$\mathbf{X}\hat{\mathbf{b}}$ equals the projection of **y** into the column space of **X**, and

$\hat{\mathbf{b}}$ lies in the row space of **X**.

We call the matrix that solves this problem the pseudoinverse **X**$^+$, where $\hat{\mathbf{b}}$ = **X**$^+$**y**. Note that when the columns of **X** are independent,

$$\mathbf{X}^+ = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T \tag{3-69}$$

This satisfies our requirements stated above. In the case where **X** is collinear, we must find another way to calculate **X**$^+$.

The Singular Value Decomposition

We now introduce the *singular value decomposition*, or SVD, which will allow us to obtain a general solution to the problem of finding pseudoinverses. Any *m* by *n* matrix **X** can be factored into

$$\mathbf{X} = \mathbf{USV}^T \tag{3-70}$$

where **U** is orthogonal and *m* by *m*, **V** is orthogonal and *n* by *n*, and **S** is *m* by *n* and diagonal. The non-zero entries of **S** are referred to as the *singular values* and decrease monotonically from the upper left to the lower right of **S**.

As an example of the SVD, let us consider the matrix

$$\mathbf{X} = \begin{bmatrix} 1 & 2 & 3 \\ 2 & 3 & 5 \\ 3 & 5 & 8 \\ 4 & 8 & 12 \end{bmatrix} \tag{3-71}$$

Here we have chosen **X** to be collinear: the third column is the sum of the first two columns. We can now use MATLAB to compute the SVD of **X**, and verify that the product of the **U**, **S** and **V**^{T} reproduces **X**.

```
» X = [1 2 3; 2 3 5; 3 5 8; 4 8 12];
» [U,S,V] = svd(X)

U =

    0.1935    0.1403   -0.9670    0.0885
    0.3184   -0.6426    0.0341    0.6961
    0.5119   -0.5022   -0.0341   -0.6961
    0.7740    0.5614    0.2503    0.1519

S =

   19.3318         0         0
         0    0.5301         0
         0         0    0.0000
         0         0         0

V =

    0.2825   -0.7661    0.5774
    0.5221    0.6277    0.5774
    0.8047   -0.1383   -0.5774

» U*S*V'

ans =

    1.0000    2.0000    3.0000
    2.0000    3.0000    5.0000
    3.0000    5.0000    8.0000
    4.0000    8.0000   12.0000
```

Note that **S** is diagonal, and that the diagonal elements decrease from upper left to lower right. In fact, the last singular value appears to be zero. Recall now that the inverse of a product is the product of the inverses in reverse order. This leads to an explicit formula for the pseudoinverse of **X**, **X**$^+$:

$$\mathbf{X}^+ = \mathbf{V}\mathbf{S}^+\mathbf{U}^T \tag{3-72}$$

Here we must be very careful in formation of $\mathbf{S}^+$. In practice, all singular values that are close to zero are set to zero in the inverse (the challenge comes with determining what constitutes "close to zero"). Alternately, one can think of this as truncation of the matrices $\mathbf{U}$, $\mathbf{S}$ and $\mathbf{V}$ where only the first r columns of $\mathbf{U}$ and $\mathbf{V}$ are retained, along with the first r rows and columns of $\mathbf{S}$, where $r = \text{rank}(\mathbf{X})$. In MATLAB, we see for our example:

```
» U(:,1:2)*S(1:2,1:2)*V(:,1:2)'

ans =

    1.0000    2.0000    3.0000
    2.0000    3.0000    5.0000
    3.0000    5.0000    8.0000
    4.0000    8.0000   12.0000
```

It is apparent that we only need the first two "factors" in the SVD to reproduce the original data. The inverse of $\mathbf{X}$, $\mathbf{X}^+$ can then be calculated from:

```
» Xinv = V(:,1:2)*inv(S(1:2,1:2))*U(:,1:2)'

Xinv =

   -0.2000    0.9333    0.7333   -0.8000
    0.1714   -0.7524   -0.5810    0.6857
   -0.0286    0.1810    0.1524   -0.1143
```

Note that this is same result as would be obtained from the MATLAB command `pinv`, which uses the SVD and sets all singular values that are within machine precision to zero:

```
» pinv(X)

ans =

   -0.2000    0.9333    0.7333   -0.8000
    0.1714   -0.7524   -0.5810    0.6857
   -0.0286    0.1810    0.1524   -0.1143
```

Let us now return to our ill-conditioned regression problem where

$$\mathbf{X} = \begin{bmatrix} 1 & 2 \\ 2 & 4 \\ 3 & 6 \\ 4 & 8.0001 \end{bmatrix} \quad \text{and} \quad \mathbf{y} = \begin{bmatrix} 2 \\ 4 \\ 6 \\ 8 \end{bmatrix} \tag{3-73}$$

92

Recall that a small change in the third element of **y** produced wildly different regression vectors. We can now repeat this problem assuming that the true rank of **X** is 1; that is, to within measurement accuracy the second column of **X** is a multiple of the first column. In MATLAB we would obtain:

```
» X = [1 2; 2 4; 3 6; 4 8.0001]; y = [2 4 6 8]';
» [U,S,V] = svd(X);
» Xinv = V(:,1)*inv(S(1,1))*U(:,1)'

Xinv =

    0.0067    0.0133    0.0200    0.0267
    0.0133    0.0267    0.0400    0.0533

» b = Xinv*y

b =

    0.4000
    0.8000
```

With this inverse, changing the third element of **y** would no longer change the result significantly:

```
» y = [2 4 5.9999 8]';
» b = Xinv*y

b =

    0.4000
    0.8000

» y = [2 4 6.0001 8]';
» b = Xinv*y

b =

    0.4000
    0.8000
```

Thus we see that the use of a pseudoinverse can enhance the stability of our calculations. In the next section we will see additional ways of forming pseudoinverses.

Conclusion

This introduction to linear algebra, while brief, should include most of what the reader needs to know in order to tackle the chemometrics literature. Interested readers are encouraged to consult one of the many texts on the subject for more detail on the methods, including proofs and additional examples.

4. Preface to the Tutorial Chapters

Although the tools found in PLS_Toolbox are applicable in a wide variety of applications, its main focus is chemometrics. Chemometrics is often thought of as a sub-discipline of chemistry, and in particular, analytical chemistry. However, "chemometric techniques" have been successfully applied in many areas, and in fact, many were "borrowed" from other disciplines to begin with. Problems that are most often thought of as being in the domain of the chemical engineer, *i.e.,* chemical processes, can also benefit from chemometric methods. PLS_Toolbox includes many functions that can be used in the chemical laboratory or process domain, as well as other non-chemical fields.

In the chapters that follow we provide a tutorial on many of the chemometric methods included with PLS_Toolbox, and illustrate the methods with some example problems in a variety of applications. This begins with basic data exploration and regression modeling and continues through a large number of techniques and applications.

Some Definitions

Before moving on to chemometric techniques, it is important that we define chemometrics. This has been a matter of debate in the technical community for some time; however, we choose the following definition: *Chemometrics is the science of relating measurements made on a chemical system to the state of the system via application of mathematical or statistical methods, and of designing optimal experiments for investigating chemical systems.* It is clear from the definition that chemometrics is a measurement science and is data-based. The goal of many chemometrics techniques is the efficient production of an empirical or semi-empirical model, derived from data, which is used to estimate one or more properties of a system from measurements. It is less obvious from the definition, perhaps, that chemical systems include those under observation in the laboratory, as well as those in the open environment, and chemical processes.

Beyond simply obtaining a model that provides useful predictions, chemometric techniques can also be used to obtain insight about a chemical system. This is illustrated in Figure 4-1. One typically starts with some *data* taken from a system. This data most often is in the form of a table (typically stored as a data file) which contains, for a number of samples, some measured properties of the samples. The measurements could be derived from spectroscopy or other analytical technique, from process measurements as a function of time, or from some other system. Without any further processing, such a table would be of little use; it is simply a record of measurements. One might then take the data table and calculate the means and variances of the variables, and perhaps look for any trends or correlations between variables. At this point, some *information* has been obtained about the system. By looking at additional data sets from the same system or perhaps designed experiments, one might obtain some *knowledge* about how the system functions, such as what peaks in a spectrum are related to a compound of interest or what manipulated process variables affect particular system outputs. Finally, one might combine this largely empirical knowledge of how the system operates with fundamental

principles from chemistry and physics to develop an *understanding* of the system. This understanding may lead to improvements in how the system is used and operated that are far more valuable than any changes made simply because of predictive models. It is for this reason that we emphasize tools that may be used to learn about chemical systems, rather than just provide "black box" models of them.

Chemical systems are typically multivariate, *i.e.,* multiple measurements are made simultaneously. Therefore, most chemometric methods fall under the class of statistical techniques known as multivariate analysis. Paraphrasing Anderson (1984), *multivariate statistical analysis is concerned with data that consists of multiple measurements on a number of individuals, objects or data samples*. The measurement and analysis of dependence between variables is fundamental to multivariate analysis.
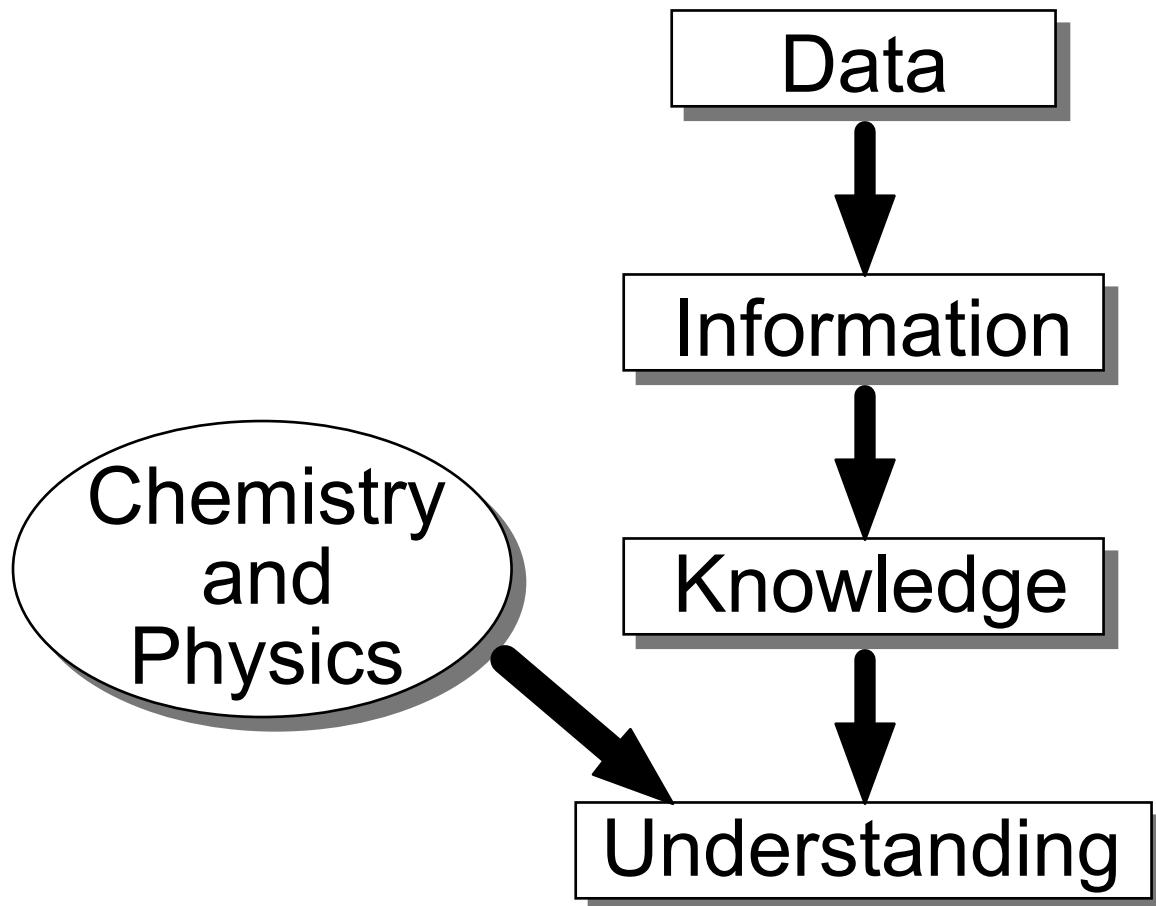
Figure 4-1. The information hierarchy.

Nomenclature and Conventions

In this tutorial scalars will be represented in lower case italic (*s*), vectors will be in bold lower case (**b**), and matrices (two-dimensional arrays) will be bold upper case (**X**). Arrays of dimension 3 or higher (*i.e.,* with three or more modes) will be denoted by underlined bold upper case letters (**D**). In two-way data matrices it will be assumed that

the rows of the matrix represent samples or observations and the columns represent variables. The transpose of $\mathbf{X}$ will be denoted $\mathbf{X}^T$. A vector $\mathbf{b}$ is assumed to be a column vector; row vectors are represented as transposes ($\mathbf{b}^T$).

5. Principal Components Analysis

Today's laboratory instruments produce a plethora of data. It is not uncommon for processes to have hundreds or thousands of measured variables. Some analytical instruments measure tens of thousands of variables. For instance, in a typical FTIR spectrometer, the absorbance is measured at over 10,000 frequencies. Chemical processes are becoming more heavily instrumented and the data are recorded more frequently (Wise *et al.,* 1990; Kresta *et al.,* 1991; Wise and Gallagher, 1996). This increase in instrumentation is creating a data overload, and the result is that a good deal of the data are "wasted;" that is, no useful information is obtained from them. The problem is one of both compression and extraction. Generally, there is a great deal of correlated or redundant information in laboratory and process measurements. This information must be compressed in a manner that retains the essential information and is more easily displayed than each of the variables individually. Also, essential information often lies not in any individual variable but in how the variables change with respect to one another; that is, how they co-vary. In this case, the information must be extracted from the data. Furthermore, in the presence of large amounts of noise, it would be desirable to take advantage of some sort of signal averaging.

Principal Components Analysis (PCA) (Jackson, 1981) is a favorite tool of chemometricians for data compression and information extraction. PCA finds combinations of variables, or *factors,* that describe major trends in the data. If **X** is a data matrix with *m* rows and *n* columns, and with each variable being a column and each sample a row, PCA decomposes X as the sum of *r* $\mathbf{t}_i$ and $\mathbf{p}_i$, where *r* is the rank of the matrix **X**:

$$\mathbf{X} = \mathbf{t}_1\mathbf{p}^T_1 + \mathbf{t}_2\mathbf{p}^T_2 + ... + \mathbf{t}_k\mathbf{p}^T_k + ... + \mathbf{t}_r\mathbf{p}^T_r \qquad (5\text{-}1)$$

Here *r* must be less than or equal to the smaller dimension of **X**, *i.e.,* $r \leq \min\{m,n\}$. The $\mathbf{t}_i$, $\mathbf{p}_i$ pairs are ordered by the amount of variance captured. The $\mathbf{t}_i$ vectors are known as *scores* and contain information on how the *samples* relate to each other. The $\mathbf{p}_i$ vectors are known as *loadings* and contain information on how the *variables* relate to each other. Generally the PCA model is truncated after *k* components and the remaining small variance factors are consolidated into a residual matrix E:

$$\mathbf{X} = \mathbf{t}_1\mathbf{p}^T_1 + \mathbf{t}_2\mathbf{p}^T_2 + ... + \mathbf{t}_k\mathbf{p}^T_k + \mathbf{E} \qquad (5\text{-}2)$$

While the form of Equation 5-2 may at first seem foreign, there are chemical systems that can be modeled with exactly the same equation. For example, if **X** were a number of absorbance spectra of mixtures which followed Beer's law (linear additivity), then the $\mathbf{t}_i$ could be replaced with concentrations and the $\mathbf{p}_i$ could be replaced with pure component spectra.

Mathematically, PCA relies upon an eigenvector decomposition of the covariance or correlation matrix of the process variables. For a given data matrix $\mathbf{X}$ with m rows and n columns, the covariance matrix of $\mathbf{X}$ is defined as

$$\text{cov}(\mathbf{X}) = \frac{\mathbf{X}^T\mathbf{X}}{m\text{-}1} \qquad (5\text{-}3)$$

provided that the columns of $\mathbf{X}$ have been "mean-centered" by subtracting off the original mean of each column. If the columns of $\mathbf{X}$ have been "autoscaled" (*i.e.,* adjusted to zero mean and unit variance by dividing each column by its standard deviation), Equation 5-1 gives the correlation matrix of $\mathbf{X}$. Unless otherwise noted, it is assumed that data are either mean-centered or autoscaled prior to analysis. In the PCA decomposition, the $\mathbf{p}_i$ vectors are *eigenvectors* of the covariance matrix; that is, for each $\mathbf{p}_i$

$$\text{cov}(\mathbf{X})\mathbf{p}_i = \lambda_i\,\mathbf{p}_i \qquad (5\text{-}4)$$

where λ_i is the *eigenvalue* associated with the eigenvector $\mathbf{p}_i$. The $\mathbf{t}_i$ form an orthogonal set ($\mathbf{t}_i^T\mathbf{t}_j = 0$ for $i \neq j$), while the $\mathbf{p}_i$ are orthonormal ($\mathbf{p}_i^T\mathbf{p}_j = 0$ for $i \neq j$, $\mathbf{p}_i^T\mathbf{p}_j = 1$ for $i = j$). Note that for $\mathbf{X}$ and any $\mathbf{t}_i$, $\mathbf{p}_i$ pair,

$$\mathbf{X}\mathbf{p}_i = \mathbf{t}_i \qquad (5\text{-}5)$$

that is, the score vector $\mathbf{t}_i$ is the linear combination of the original $\mathbf{X}$ variables defined by $\mathbf{p}_i$. Another way to look at this is that the $\mathbf{t}_i$ are the projections of $\mathbf{X}$ onto the $\mathbf{p}_i$. The $\mathbf{t}_i$, $\mathbf{p}_i$ pairs are arranged in descending order according to the associated λ_i. The λ_i are a measure of the amount of *variance* described by the $\mathbf{t}_i$, $\mathbf{p}_i$ pair. In this context, we can think of variance as *information*. Because the $\mathbf{t}_i$, $\mathbf{p}_i$ pairs are in descending order of λ_i, the first pair captures the largest amount of information of any pair in the decomposition. In fact, it can be shown that the $\mathbf{t}_1$, $\mathbf{p}_1$ pair captures the greatest amount of variation in the data that it is possible to capture with a linear factor, and that each subsequent pair captures the greatest possible amount of variance remaining after subtracting $\mathbf{t}_i\mathbf{p}^T_i$ from $\mathbf{X}$.

Generally it is found (and it is usually the objective) that the data can be adequately described using far fewer factors than original variables. Thus, the data overload problem can be solved by observing fewer scores (weighted sums of the original variables) than original variables, with no significant loss of information. It is also often found that PCA turns up combinations of variables that are useful descriptions, or even predictors, of particular events or phenomena. These combinations of variables are often more robust indicators of laboratory sample or process conditions than individual variables due to the signal averaging aspects of PCA.

Principal Components Analysis is shown graphically in Figure 5-1. Shown here are the values of three variables measured on a collection of samples. When plotted in three dimensions, it is apparent that the samples all lie on a plane and can be enclosed by an

ellipse. It is also apparent that the samples vary more along one axis of the ellipse than along the other. The first PC describes the direction of the greatest variation in the data set, which is the major axis of the ellipse. The second PC describes the direction of second greatest variation, which is the minor axis of the ellipse. In this case, a PCA model (the scores and loadings vectors and associated eigenvalues) with two principal components adequately describes all the variation in the measurements.
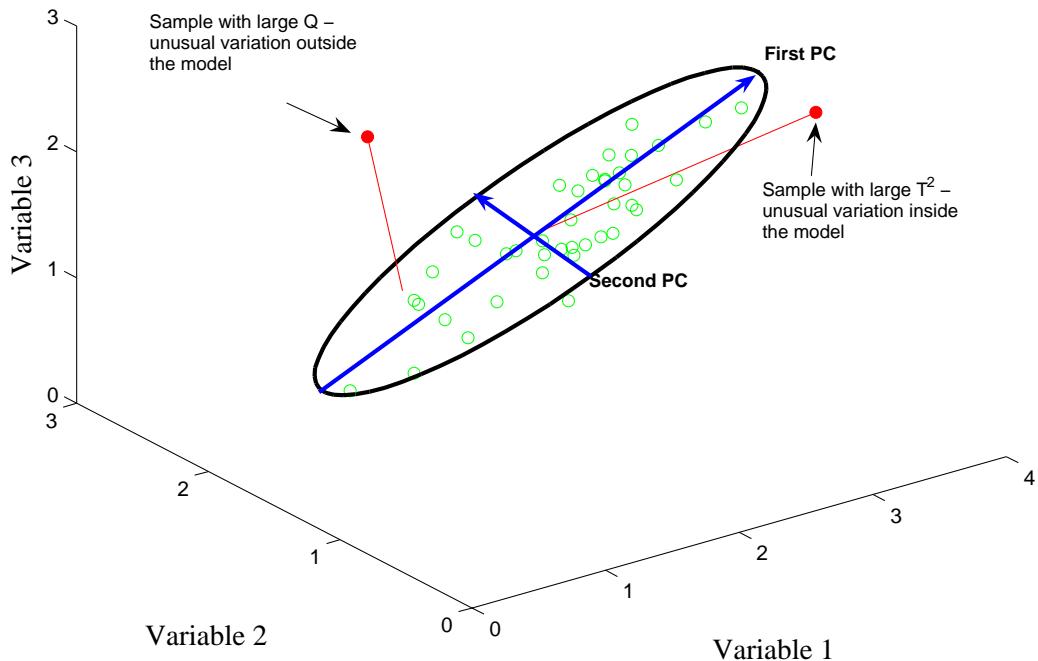
Figure 5-1. Graphical representation of Principal Components Analysis.

Statistics Associated with PCA Models

Scores (**t**) from PCA models have mean zero (assuming the data matrix **X** has been mean- centered prior to decomposition) with variance equal to their associated eigenvalue. Thus, if it is assumed that the scores are normally distributed, one can calculate confidence limits for the scores by applying the Student's t-distribution. Therefore, the limits on the scores for the ith PC for confidence limits $1-\alpha$ would be

$$t_{i,\alpha} = \pm \text{ sqrt}(\lambda_i)*t_{m-1,\alpha/2} \qquad (5\text{-}6)$$

where *m* is the number of samples and $t_{m-1,\alpha/2}$ corresponds to the probability point on the (single sided) t-distribution with m-1 degrees of freedom and area $\alpha/2$. A word of caution

regarding the use of confidence limits on scores is advised, however. If the underlying physical phenomena which are related to the scores are not a random process, the scores will not be normally distributed, violating the assumption of Equation 5-6. Examples of this include when some of the variables in a system are controlled, when the data come from a designed experiment, or when the data are clustered due to some underlying physical phenomena.

It is also possible to calculate a lack-of-fit statistic for PCA models, Q. Q is simply the sum of squares of each row (sample) of **E** (from Equation 5-2); *i.e.,* for the ith sample in **X**, $\mathbf{x_i}$:

$$Q_i = \mathbf{e_i}\mathbf{e_i}^T = \mathbf{x_i}(\mathbf{I} - \mathbf{P_k}\mathbf{P_k}^T)\mathbf{x_i}^T \tag{5-7}$$

where $\mathbf{e_i}$ is the ith row of **E**, $\mathbf{P_k}$ is the matrix of the k loadings vectors retained in the PCA model (where each vector is a column of $\mathbf{P_k}$) and **I** is the identity matrix of appropriate size (n by n). The Q statistic indicates how well each sample conforms to the PCA model. It is a measure of the difference, or *residual*, between a sample and its projection into the k principal components retained in the model.

A single row of the m by n **E** matrix, $\mathbf{e_i}$, represents the Q contributions for a given sample. The Q contributions show how much each variable contributes to the overall Q statistic for the sample while retaining the sign of the deviation in the given variable. Such contributions can be useful in identifying the variables which contribute most to a given sample's sum-squared residual error. Because the PCA model captures some variables more effectively than others, the residual variance may vary widely between variables. The residual variance for the jth variable is:

$$s_j^2 = \sum_{i=k+1}^{r} p_{ij}^2 \lambda_i \tag{5-8}$$

where p_{ij} is the loading of the jth variable in the ith PC (Wise et al., 1989). For the data from which the model was obtained, this relationship will be exact. If it is assumed that the eigenvalues of all the PCs not retained in the model are equal, then the variance in the residual of the jth variable can be estimated using only the PCs and the eigenvalues retained in the model from:

$$s_{j,est}^2 = \left(\sum_{i=k+1}^{r} \lambda_i \right)\left(1 - \sum_{i=1}^{k} p_{ij}^2 \right) \tag{5-9}$$

The sum of normalized squared scores, known as Hotelling's T^2 statistic, is a measure of the variation in each sample *within* the PCA model. T^2 is defined as

$$T_i^2 = \mathbf{t}_i \lambda^{-1} \mathbf{t}_i^T = \mathbf{x}_i \mathbf{P}_k \lambda^{-1} \mathbf{P}_k^T \mathbf{x}_i^T \tag{5-10}$$

102

where $\mathbf{t}_i$ refers to the ith row of $\mathbf{T}_k$, the m by k matrix of k scores vectors from the PCA model, and λ is a diagonal matrix containing the eigenvalues (λ_1 through λ_k) corresponding to k eigenvectors (principal components) retained in the model.

T^2 contributions describe how individual variables contribute to the Hotelling's T^2 value for a given sample. The contributions to T_i^2 for the ith sample, $\mathbf{t}_{con,i}$, is a 1 by k vector calculated from

$$\mathbf{t}_{con,i} = \mathbf{t}_i \lambda^{-1/2} \mathbf{P}_k^T = \mathbf{x}_i \mathbf{P}_k \lambda^{-1/2} \mathbf{P}_k^T \tag{5-11}$$

The term $\mathbf{t}_{con}$ can be considered a scaled version of the data within the PCA model. The data are scaled to equalize the variance captured by each PC. Note that this formulation for T^2 contributions has the property that the sum-squared contributions give T_i^2 for the given sample. That is,

$$T_i^2 = \mathbf{t}_{i,con} \mathbf{t}_{i,con}^T \tag{5-12}$$

Confidence limits can be established for the overall residual Q and T^2. Confidence limits can be calculated for Q, provided that all of the eigenvalues of the covariance matrix of $\mathbf{X}$, the λ_i, have been obtained (Jackson and Mudholkar, 1979)

$$Q_\alpha = \Theta_1 \left[\frac{c_\alpha \sqrt{2\Theta_2 h_0^2}}{\Theta_1} + 1 + \frac{\Theta_2 h_0 (h_0 - 1)}{\Theta_1^2} \right]^{\frac{1}{h_0}} \tag{5-13}$$

where

$$\Theta_i = \sum_{j=k+1}^{n} \lambda_j^i \text{ for i} = 1, 2, 3 \tag{5-14}$$

and

$$h_0 = 1 - \frac{2\Theta_1 \Theta_3}{3\Theta_2^2} \tag{5-15}$$

In Equation 5-13, c_α is the standard normal deviate corresponding to the upper $(1-\alpha)$ percentile. In Equation 5-14, k is the number of principal components retained in the model and n is the total number of principal components. Thus, n is less than or equal to the smaller of the number of variables or samples in $\mathbf{X}$. It is much more likely that residual Q will behave "normally" as opposed to the scores. This is because Q is a measure of the non-deterministic variation in a system, *i.e.*, the variation remaining after the deterministic variation has been removed.

Statistical confidence limits for the values for T2 can be calculated by means of the F-distribution as follows:

$$T^2_{k,m,\alpha} = \frac{k(m-1)}{m-k} F_{k,m-k,\alpha}$$

(5-16)

Here *m* is the number of samples used to develop the PCA model and *k* is the number of principal component vectors retained in the model.

Some discussion of the geometric interpretation of Q and T2 is perhaps in order. As noted above, Q is a measure of the variation of the data outside of the principal components included in the PCA model. Going back to the data in Figure 5-1, Q is a measure of the distance off the plane containing the ellipse; in fact, $\sqrt{Q}$ *is* the Euclidean distance of the data point from the plane formed by the two-component model. A sample with a large Q is shown on the upper left side of the figure. This sample is out of the plane of the model (although its projection into the model is not unusual). The Q limit defines a distance off the plane that is considered unusual based on the data used to form the PCA model. T2, on the other hand, is a measure of the distance from the multivariate mean (the intersection of the PCs in the figure) to the projection of the sample onto the two principal components. The T2 limit defines an ellipse on the plane within which the data normally project. A sample with a large T2 value (but small Q) is shown on the upper right side of Figure 5-1.

Note that the calculated confidence limits on Q and T2 make some assumptions regarding the distribution of the data; specifically, that they are multivariate normal. Clearly, data are often not normally distributed. How can we get away with this assumption? The central limit theorem states that sums of several different groups will tend to be normally distributed, regardless of the probability distribution of the individual groups (Anderson, 1984; Box *et al.*, 1978). This suggests that factor-based methods such as PCA will tend to produce measures that are more normally-distributed than the original data. This assumption still breaks down in some instances, particularly for T2 statistics where the data are clustered or otherwise oddly distributed due to some non-normal root cause. However, residual statistics are surprisingly well-behaved in a very wide variety of cases.

A Word About Centering and Scaling

It was mentioned above that PCA is generally applied to data that have been mean-centered. Mean-centering translates the axes of the coordinate system to the center of gravity, or centroid, of the data. In Figure 5-1, this is the point where the two PCs cross. Without mean-centering, the first PC for the data in Figure 5-1 would go from the origin, (at the very front of the figure) to the center of the data. This direction may or may not be a useful description of variation in the system. In some systems one might expect the various "factors" in the data to have a zero intercept. An example is spectroscopy, where a concentration of zero corresponds to zero absorbance. In this instance, forcing the PCA to include zero by not mean-centering may be a reasonable thing to do. In other systems where the zero point of the measurement scale is arbitrary (*e.g.,* temperature measured in

degrees Celsius) the first PC may not provide a useful description of variation in the system and will further complicate the analysis because subsequent PCs are constrained to be orthogonal to the first one. In the example shown in Figure 5-1, it is easy to see that factors that are orthogonal to a line between zero and the data mean are not at all descriptive of the true nature of the data.

Variance scaling, such as autoscaling (which mean-centers and scales the columns to unit variance), may be appropriate in systems where the variables have different units; for example, temperature, pressure and concentration. Principal Components Analysis attempts to capture variation. Numerically, a variation in temperature between 1000 and 1100 C is much greater than a variation in concentration between 0.01 and 0.1 M. However, the effect of each of these variables on the system of interest may be very similar, and the information content of the temperature data is not inherently greater. For that reason, it may be advisable to autoscale the data. This approach essentially puts all variables on an equal basis in the analysis. In other systems where all of the variables have the same units, such as spectroscopy, mean-centering may be the appropriate choice because one has a reason to believe that variables with a great deal of variation are actually more important; that is, they contain more information about the system under observation than those with small variation.

PCA Example I: The Wine Data Set

Now that we have some background in PCA, we can use the technique with a relatively simple data set to see how it works. The data in Table 5-1 were published in Time Magazine in January, 1996. The data show the beer, wine and liquor consumption (liters per year), life expectancy (years) and heart disease rate (cases per 100,000 per year) for the 10 countries listed. The data are plotted in Figure 5-2 (using the MATLAB `bar3` function). It is apparent from the table that there are some significant trends in the data. For instance, Russia has the highest liquor consumption, lowest beer consumption, lowest life expectancy, and highest heart disease rate.

Table 5-1. The Wine data set.

	liquor consumption liter/year	wine consumption liter/year	beer consumption liter/year	life expectancy years	heart disease rate cases/10e5/yr
France	2.5	63.5	40.1	78	61.1
Italy	0.9	58.0	25.1	78	94.1
Switzerland	1.7	46.0	65.0	78	106.4
Australia	1.2	15.7	102.1	78	173.0
Great Britain	1.5	12.2	100.0	77	199.7
United States	2.0	8.9	87.8	76	176.0
Russia	3.8	2.7	17.1	69	373.6
Czech Republic	1.0	1.7	140.0	73	283.7
Japan	2.1	1.0	55.0	79	34.7
Mexico	0.8	0.2	50.4	73	36.4
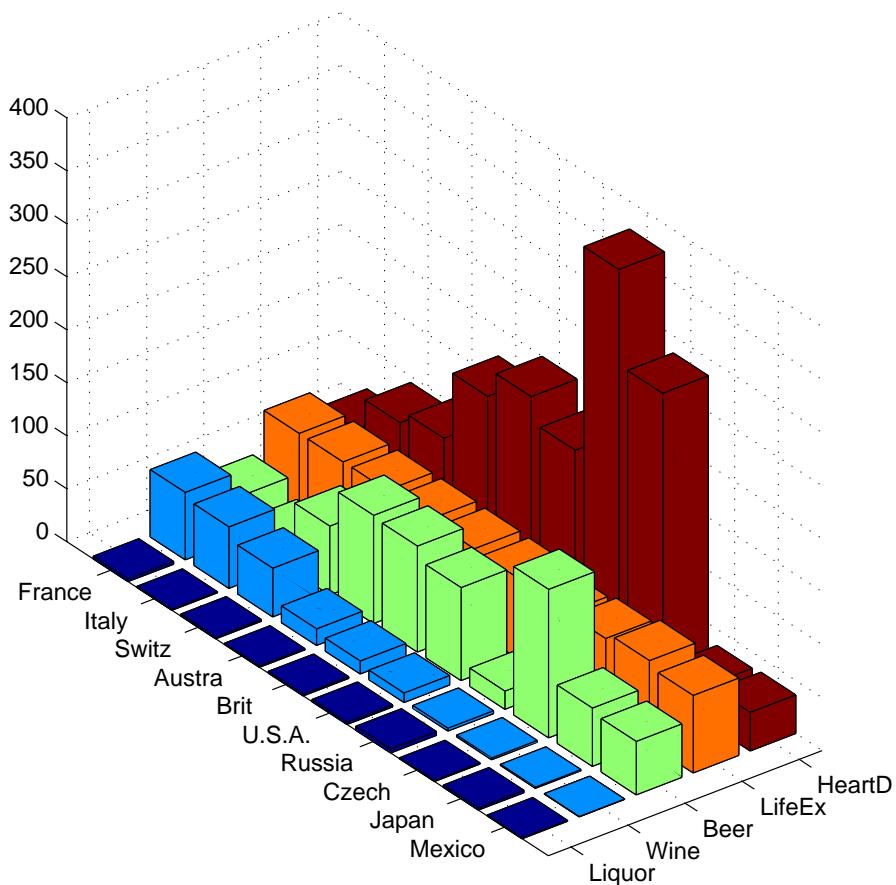
Figure 5-2. Raw data from Wine data set.

Are the there any other trends in the wine data? Principal Components Analysis will be used to investigate this more fully. To get started, execute the following commands at the MATLAB prompt:

```
» load wine
» pca
```

This will open the PLS_Toolbox Analysis GUI with PCA pre-selected in the **Analysis** menu (Figure 5-3). The wine data can now be loaded into the Analysis GUI by selecting the **Load Data/X-Block** option under the **File** menu; the variable to load is the DataSet Object called wine. This DataSet Object contains labels for the variables and samples, as well as other information about the data. At this point, the data have been loaded but not analyzed. Before analyzing, we should consider how the data should be preprocessed. There are several preprocessing options listed under the **Preprocess/X-Block** menu: none, mean centering, autoscaling, and custom (the default is autoscaling). How should we scale these data? One hint is that the variables have different units: liters/year, years and cases/person-year. Furthermore, is drinking one liter of hard liquor equivalent to drinking a liter of beer? Probably not. This suggests that autoscaling would be a good choice.

Once the scaling selection is made, a PCA model can be calculated by pressing the **Calculate** button. The number of principal components can then be selected by clicking on the table and highlighting the line with the last chosen PC. In this case, we will choose two PCs (more on how to select the number of PCs later), then click on the **Calculate** button to activate the choice. At this point, the Analysis GUI window should look identical to the one shown in Figure 5-3. From the table we see that our two-component model captures more than 78% of the variance in the data, which suggests that the data are fairly well correlated. However, what is the structure in the data set?
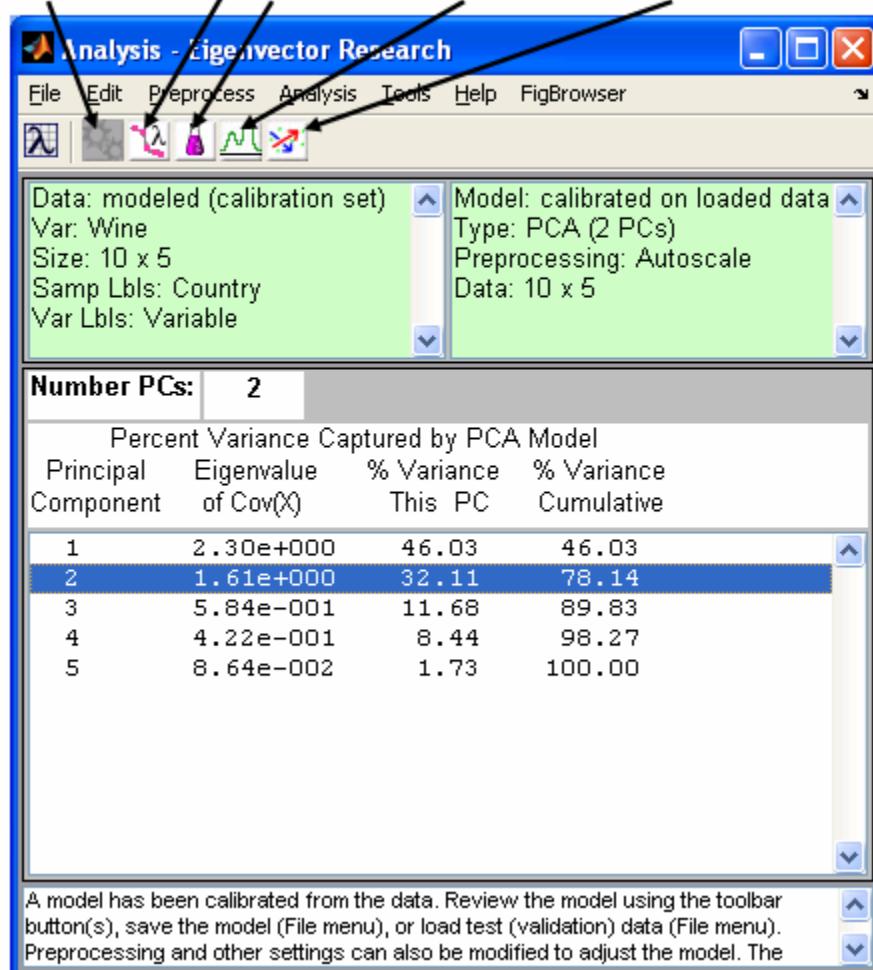
Figure 5-3. Wine data loaded and analyzed with PCA.

We can get a quick idea of the relationships between samples by clicking on the **Scores** button, which will create a **Plot Controls** window, as shown in Figure 5-4, and a window containing a plot of the scores on the first PC (not shown). We can now create a plot of the scores on the second PC versus scores on the first PC using the **Plot Controls**, as follows: select **scores on PC 1** from the drop down menu to the right of the **X:**; select **scores on PC 2** by highlighting it in the box to the right of the **Y:**. Add labels to the plot by selecting **View/Labels/Country**. Add reference lines by selecting **View/Axis Lines/All**. This should create the plot shown in Figure 5-5. From this we see that Russia, in the lower left quadrant, is the most unique country in this data set (at least with regard to the variables measured). The distance between Russia and its nearest neighbor is further than that between Russia and any other country on the plot. We also see a trend that stretches from the Czech Republic to France. We expect that countries with similar

scores should be similar. For instance, the U.S., Britain, Australia and Mexico are all close together, implying that they are similar.

The scores plot shows us about the relationship between samples. What about the relationships between variables? This information can be obtained from a loadings plot. Click on the **Loads** button in the main **Analysis** window. This will create a plot of loadings on the first PC (not shown) and will change the contents of the **Plot Controls** window to reflect that it is now controlling the Loadings plot. Select **Loadings on PC 1** from the drop down menu to the right of the **X:**, and select **Loadings on PC 2** by highlighting it in the box to the right of the **Y:**. Add labels to the plot by selecting **View/Labels/variable**. Add reference lines by selecting **View/Axis Lines/All**. This should create the plot shown in Figure 5-6.
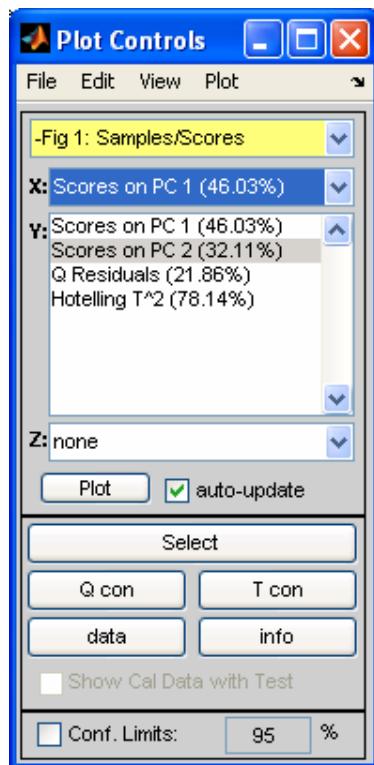
Figure 5-4. Plot Controls window.
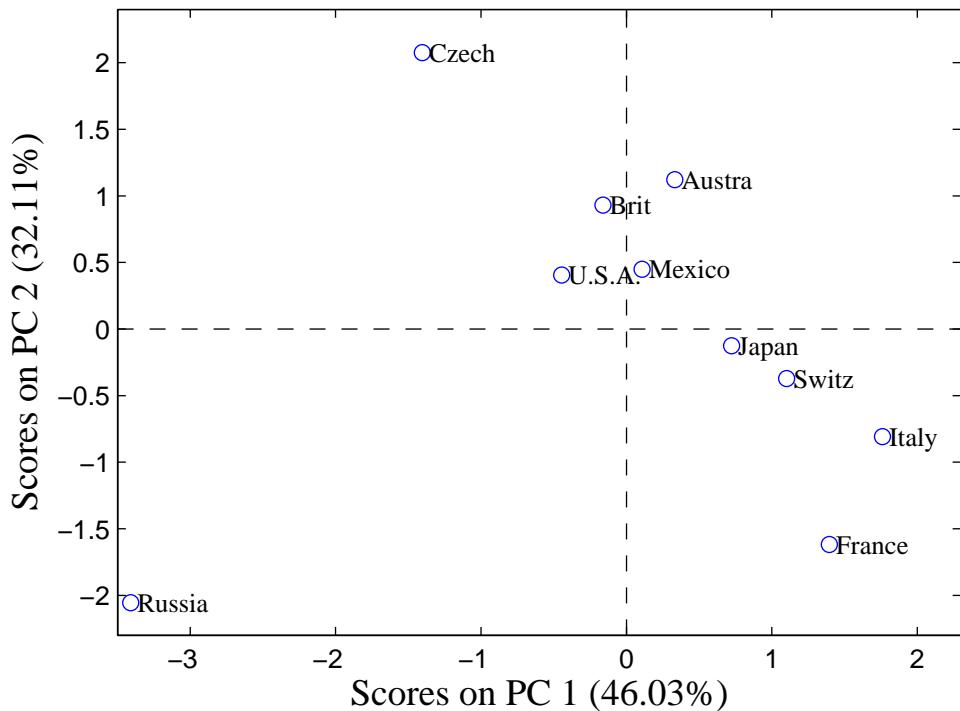
Figure 5-5. Scores plot from Principal Components Analysis of the Wine data.
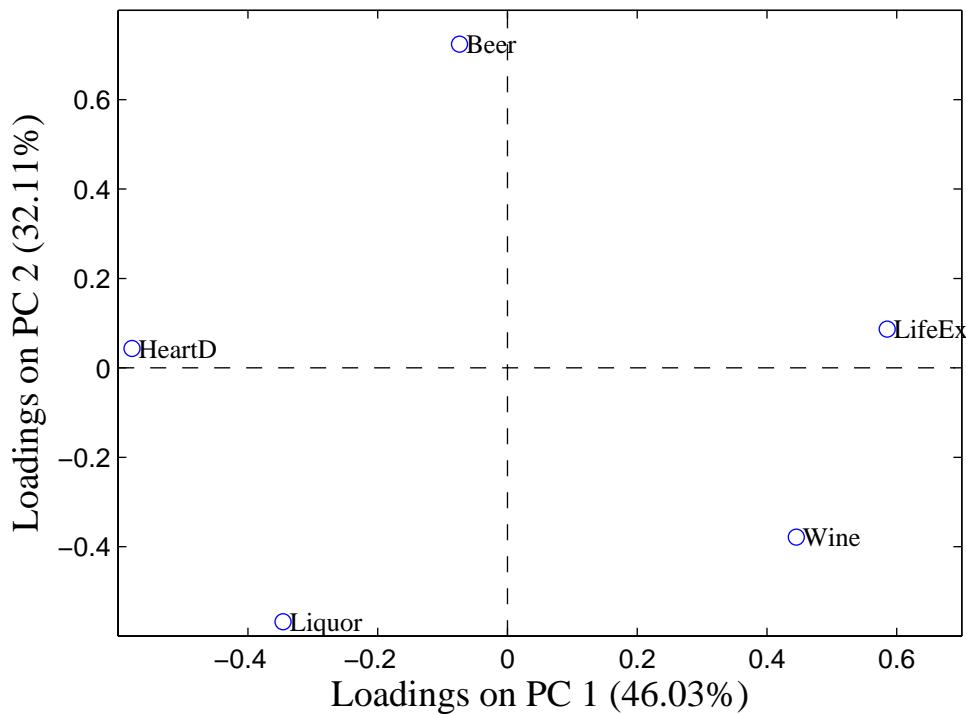
Figure 5-6. Loadings plot from Principal Components Analysis of the Wine data.

The loadings plot in Figure 5-6 shows that none of the variables are very similar (no variables are very close to each other on the plot); however, there are some interesting things to note. Variables which load most significantly into the first PC are life expectancy and heart disease rate; these are the variables which are furthest from zero in the left-right direction on the plot. They load with opposite signs, which indicates that they are anti-correlated. (It makes some sense that life expectancy varies inversely with heart disease rate.) We also see that wine has a positive loading on the first PC, and liquor has a negative loading. This suggests that wine is somewhat positively correlated with life expectancy; likewise, liquor is somewhat positively correlated with heart disease. Along the second PC direction, we see that beer loads positively and liquor and wine load negatively. Considering beer, wine and liquor on the two PCs simultaneously, we see a sort of ternary diagram with each variable at the point of a triangle. This suggests a sort of "name your poison" type of phenomenon; countries apparently tend to trade one of these vices for others, but the sum of the three tends to remain constant.

At this point, we might ask, which variables are responsible for the differences between the countries? This information comes from considering the scores and loadings simultaneously. For instance, we might want to know what it is that makes Russia unique. Russia has a negative score on the first PC and a negative score on the second. Thus, we look to the loadings plot to see what variables would give us this condition. Increasing the liquor consumption tends to move a sample down and to the left, while increasing the heart disease rate tends to move it to the left. Decreasing beer consumption moves a sample down; decreasing life expectancy moves it to the left. Changes in wine consumption move samples from upper left to lower right, which is orthogonal to the direction from the origin of the scores plot to Russia. Thus we would say that Russia tends towards high liquor consumption, low beer consumption, a high heart disease rate and low life expectancy. This is confirmed by the original data table.

In a similar way we can determine which variables are responsible for the "trend" from the Czech Republic to France. As a sample moves from upper left to lower right, heart disease and beer consumption decrease while life expectancy and wine consumption increase. Thus, we expect France to have high wine consumption and life expectancy with low heart disease and beer consumption. For the Czech Republic the opposite should be true. This is indeed confirmed by the original data table.

Another, sometimes more convenient, way to look at scores and loading plots is to use a biplot, which is a combined scores and loadings plot. It allows for easy interpretation of which variables are responsible for the observed differences in the sample scores. Click on the **Biplot** button in the main **Analysis** window, then use the **Plot Controls** to add labels and axes to the plot. The result is shown in Figure 5-7. For examples with few variables and samples, biplots can be very convenient.
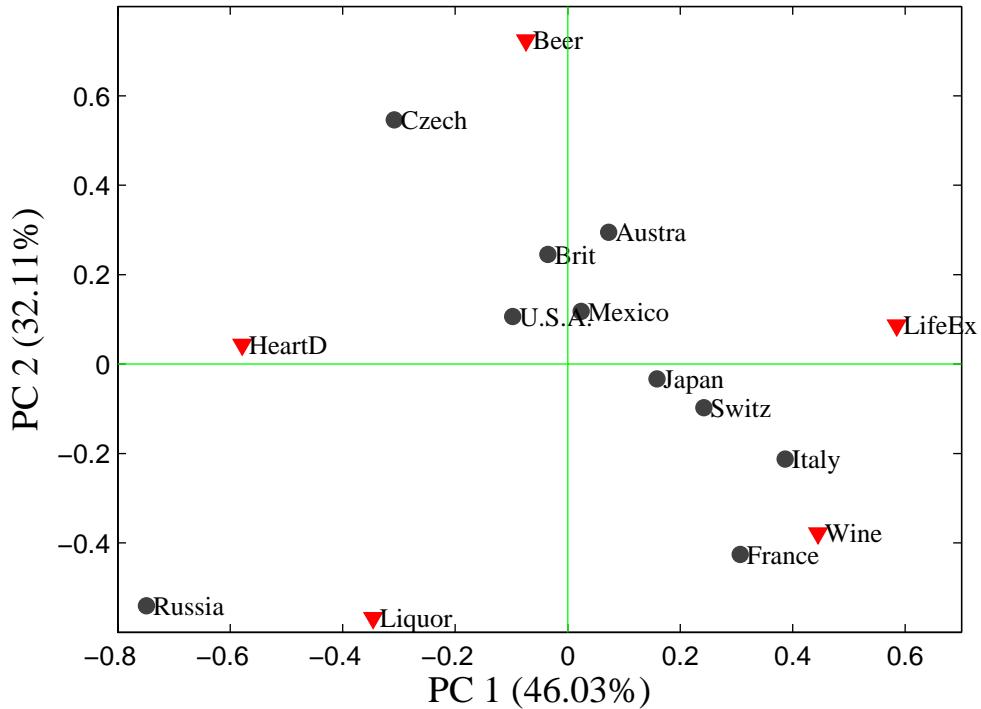
Figure 5-7. Biplot from Principal Components Analysis of the Wine data.

The scores plot obtained in Figure 5-5 suggests some similarity between groups of countries, *e.g.,* the U.S., Britain, Australia and, surprisingly, Mexico. Is this really the case? We can check on this by looking at the sample residuals. In the **Plot Controls** window, select **Scores** in the uppermost menu. (If you have closed the scores figure, you must regenerate it first by clicking the **Scores** button in the main **Analysis** window.) For the X axis select **Sample** and for the Y axis select **Q Residuals**. (Add labels using the **View** menu if necessary.) The result should look like Figure 5-8. Here we see that Mexico, is not well described by the PCA model. This indicates that, even though it projects close to U.S., Australia and Britain, Mexico is actually a relatively long way off the plane formed by the two PC model.
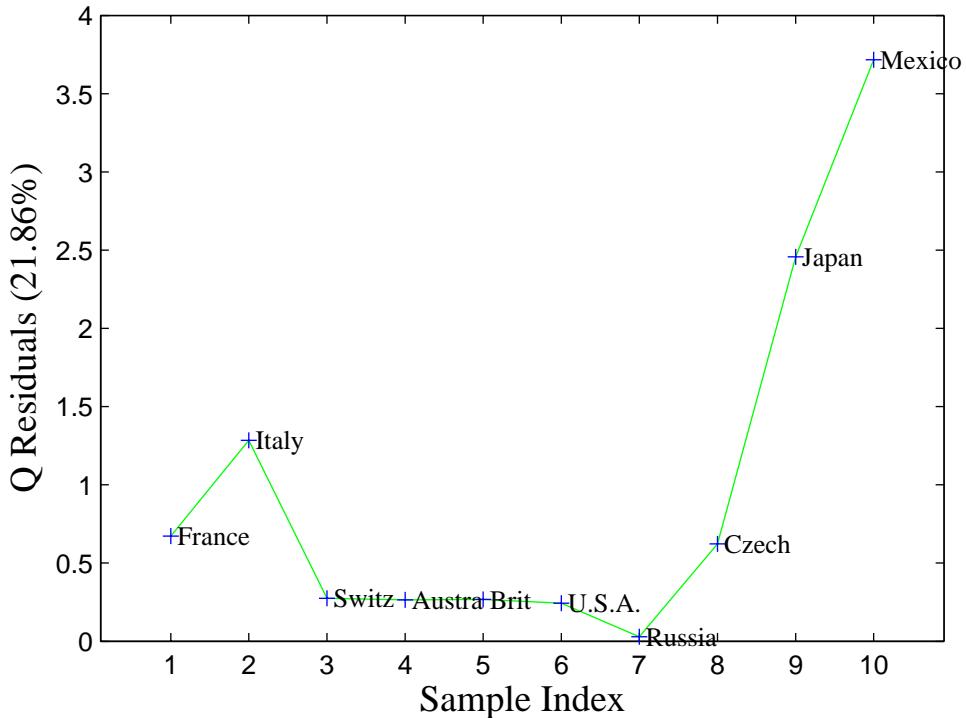
Figure 5-8. Sample Q residuals for two-PC model of Wine data.

What combination of variables causes Mexico to have this large residual? In other words, in what direction does a sample move to change the conditions from a country like the U.S. to one like Mexico? The answer can be obtained by looking at the contributions to the Q residual. This is just a bar graph of the row of **E** from Equation 5-2 corresponding to Mexico. To get the Q contributions for Mexico, select **Scores** in the **Plot Controls** window if it is not already selected. Click on the **Q con** button, then click on the Mexico sample in the scores plot. This will produce the plot shown in Figure 5-9 (you may have to change limits on the axes via the **Edit/Axes Properties…** menu on the figure to produce this exact plot). Here it can be seen that Mexico is low in all variables simultaneously. Again, this can be confirmed by consulting the original data table.

In summary, PCA of the wine data suggests that, over the countries considered, wine consumption appears to be correlated with life expectancy and decreased heart disease rate. Is this the whole story? Unfortunately not. PCA does not imply causality, it only looks for correlation. It does not say that wine consumption causes longevity any more than it says that longevity causes wine consumption. It should also be noted that there are many factors that are not at all represented in this data set. For instance, when this data set was acquired, Russia certainly did not have the health care infrastructure of many of the other countries, but this is not accounted for in any way. Dietary factors and heredity are also not considered. However, in spite of its limitations, this simple analysis largely agrees with what medical researchers are learning about wine consumption and health.
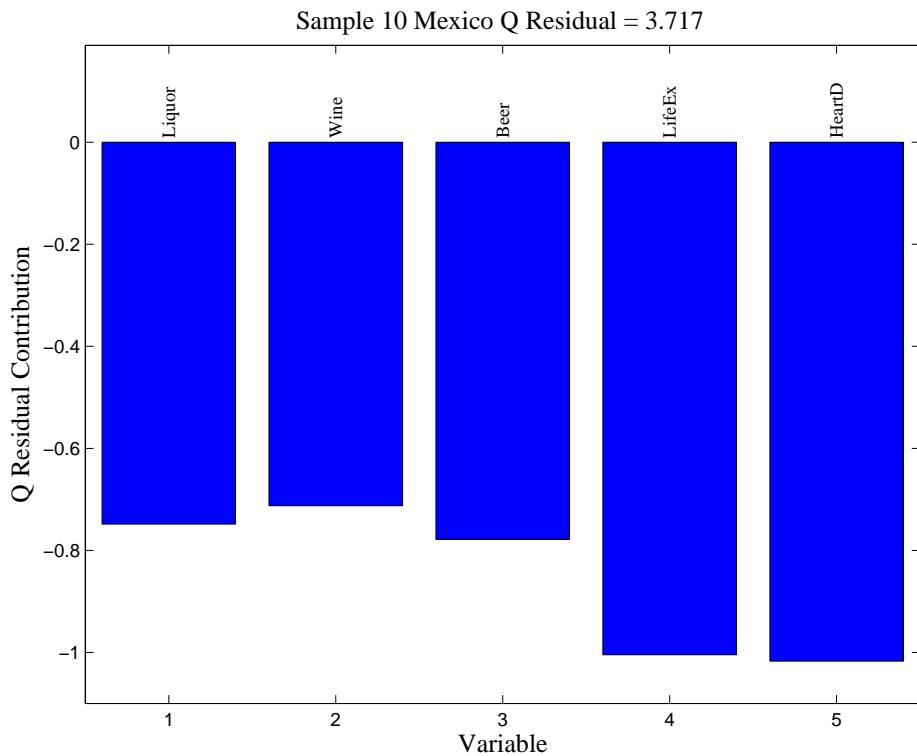
Figure 5-9. Q residual contributions for Mexico.

PCA Example II: Application to a Chemical Process

We now consider the use of PCA on data produced by a continuous chemical process, in this case a Slurry-Fed Ceramic Melter (SFCM) test system (Wise *et al.,* 1991). In this process, nuclear waste from fuel reprocessing is combined with glass-forming materials. This slurry is fed into a high temperature glass melter, the SFCM, producing a stable vitrified product for disposal in a long-term repository. These data are available in the PLS_Toolbox file `replacedata.mat`. Raw data from the process, consisting of temperatures in 20 locations within the melter and the molten glass level, are shown in Figure 5-10. The temperatures are measured at ten levels in each of two vertical thermowells that are inserted into the molten glass pool. (The variables are arranged in the data set so that variables 1 to 10 are from the bottom to the top of thermowell number 1, and variables 11 to 20 are from the bottom to the top of thermowell number 2; variable 21 is the molten glass level.) It is immediately apparent from Figure 5-10 that there is a great deal of correlation in the data. Many of the variables appear to follow a sawtooth pattern.

A Principal Components Analysis can be initiated on these data by executing the following commands at the MATLAB prompt:

```
» load replacedata
» pca
```

114

The first command loads the data set into the MATLAB workspace. The second command launches the **Analysis** GUI pre-set for PCA. The user can now load the data into the **Analysis** GUI using the **File/Load Data/X-Block** menu. Specifically, we want to load the variable named `repcal`.
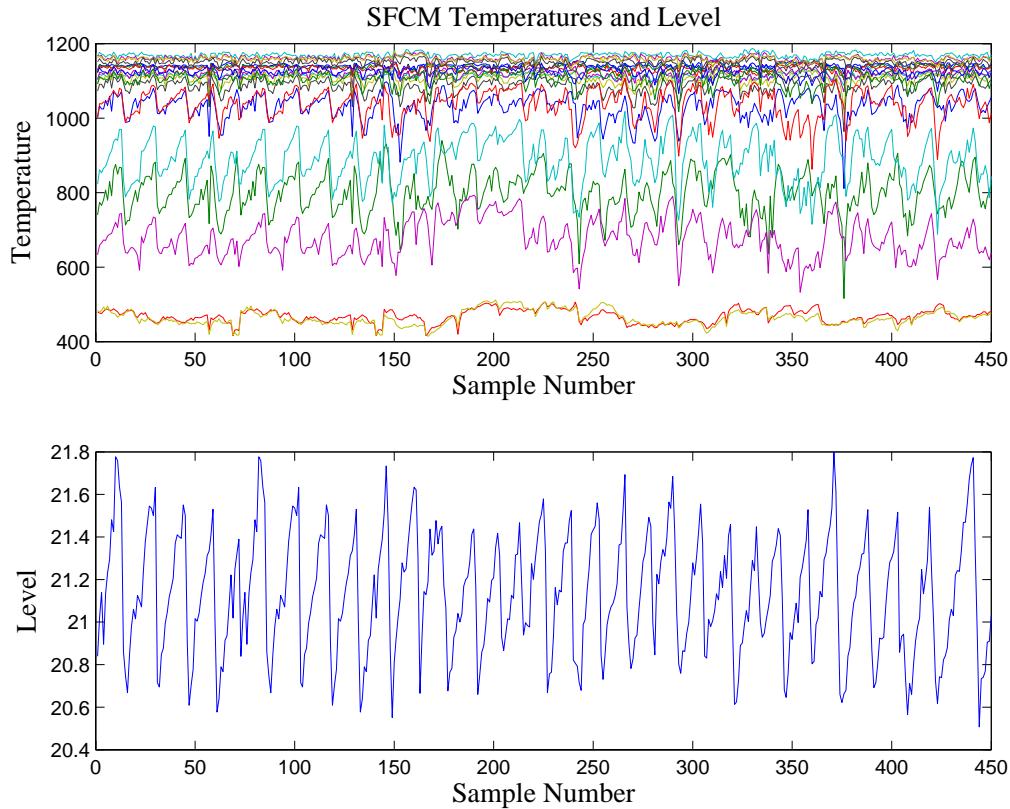
Figure 5-10. Raw temperature and level data from SFCM process.

As in the wine example, the first decision to be made is the choice of scaling options. If these were only temperature data, (where all the variables had the same units and where variables with larger variance were expected to be more important), an argument could be made for mean-centering the data. In this case, the inclusion of a level measurement argues for autoscaling, which is the default preprocessing option. Thus, the model can be built by simply clicking on the **Calculate** button, which produces the window shown in Figure 5-11. The Percent Variance Captured Table shows that the first two PCs capture substantial amounts of the variation in the model, with 36% and 30%, respectively.

Choosing the Number of Factors in a PCA Model

Once the scaling option is decided, one must determine the number of PCs to retain in the model. Unfortunately a foolproof method for automating the choice has yet to be discovered. Instead, the choice must be made based upon a few rules of thumb and the user's knowledge of the data.
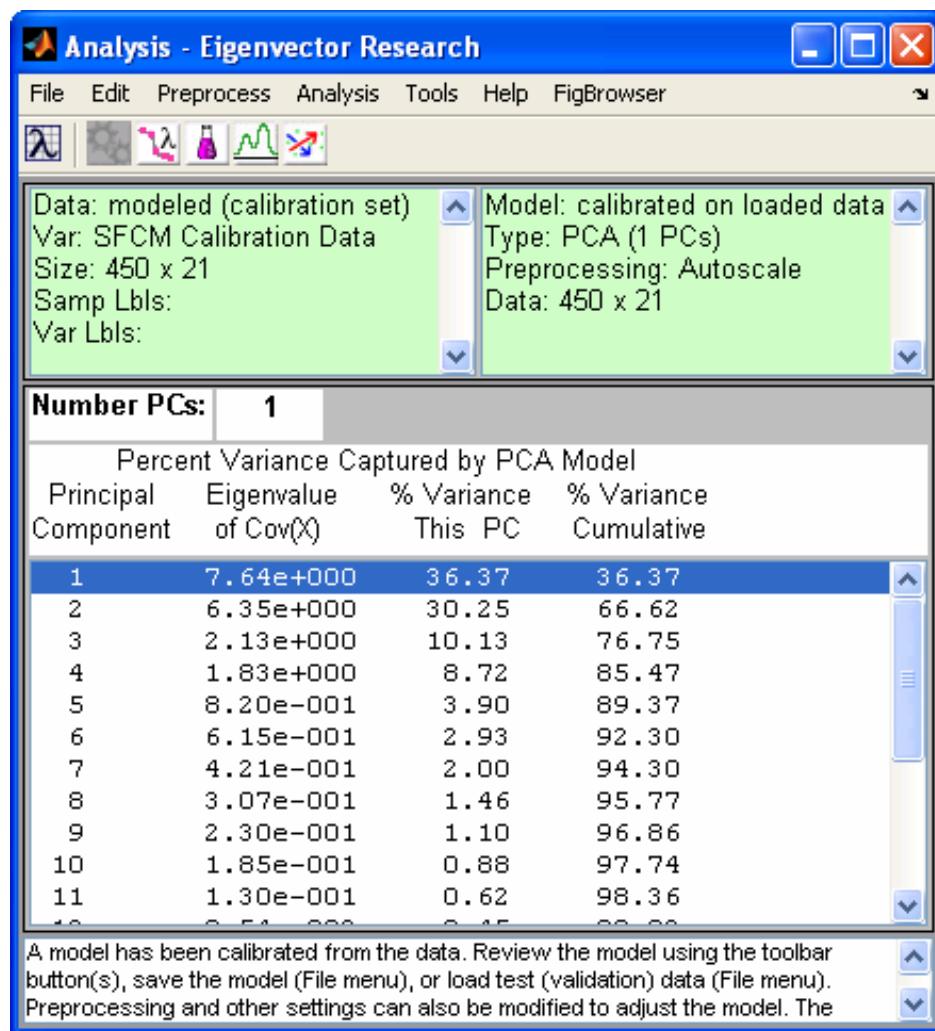
Figure 5-11. Analysis GUI with PCA model of Replacedata.

It is generally useful to list the eigenvalues in a table along with the percentage of the variance that each PC captures, as shown in Figure 5-11. It is also a good idea to plot the eigenvalues. This can be done in the **Analysis** window by clicking on the **Plot Eigenvalues/RMSECV** (descending plot and a lambda symbol) button, which for our example problem produces the plot shown in Figure 5-12. When looking at the plot of eigenvalues, one looks for a "knee" (on the right-hand side) in the line. It can also be helpful to look at the eigenvalues starting from the smallest ones and going back to the larger, looking for a sudden jump in the values. It can be seen in Figure 5-12 that the eigenvalues get gradually larger until number 5 is reached, then there is a sudden jump up to number 4. This is perhaps more apparent in the table in Figure 5-11, where one can see how the ratio of successive eigenvalues varies. Note how eigenvalue 4 is larger than eigenvalue 5 by a factor of ~2.2, but eigenvalue 5 is larger than eigenvalue 6 by a factor of only ~1.3. This suggests that it may be appropriate to choose four PCs for the model.

The eigenvalues themselves can be considered when choosing number of factors, provided the data have been autoscaled. In this case, the eigenvalues will sum to the

116

number of variables, and eigenvalues can be interpreted as the number of original variables each PC is worth. For instance, the first PC captures as much variance as over 7.5 original variables, while the second captures as much variance as 6 original variables. A good rule of thumb is that any PC with an eigenvalue less than 1 is probably not describing any systematic variance in the system and should likely not be included in the model. Eigenvalues greater than 2 usually are describing systematic variation (except in some instances where the number of variables is very large relative to the number of samples). Eigenvalues between 1 and 2 must be evaluated on a case-by-case basis using the other rules given in this section.

Eigenvalues of similar size should be retained or eliminated together. In our example, this rule suggests that PCs 3 and 4, with eigenvalues of 2.1 and 1.8, should either stay or go together. The reasoning is that in these instances, there is nearly equal variance in two directions, and the individual PCs are rotationally ambiguous; that is, any rotation of the pair of PCs spanning the same space is an equally valid representation of the data. Thus, eliminating only one of them is essentially arbitrary. PC number 5 has an eigenvalue of 0.82, and all subsequent eigenvalues are, of course, smaller, suggesting they should not be included.
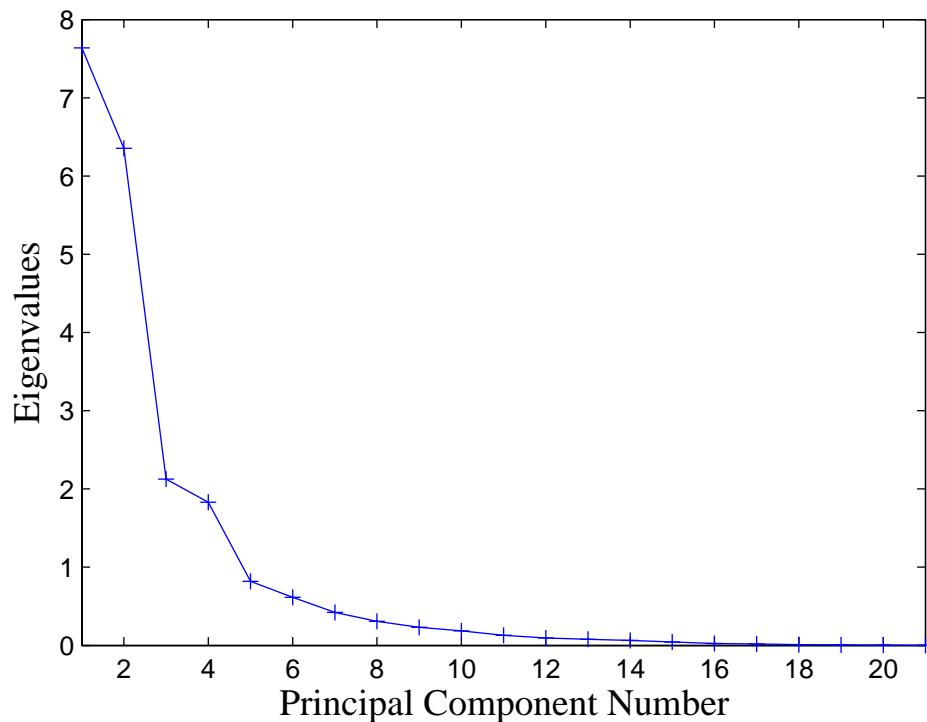
Figure 5-12. Eigenvalues from SFCM data in repdata.mat file.

It is also possible to choose the number of PCs based on cross-validation. In this procedure, the data set is divided into a number of equal size segments. A PCA model is then built on all but one of the segments. The model is then used to estimate variables that are left out of the data (Wise and Ricker, 1991). The error for this "reconstruction" is then plotted as a function of the number of PCs used. Generally this is presented as the

root-mean-square error of cross-validation (RMSECV). As PCs which describe large amounts of systematic variance are added to the model the error should decrease. When PCs describing only small noise variance are added, the error should increase.

Cross-validation can be performed in the **Analysis** window by selecting **Tools/Cross-Validation**, which opens the Cross-Validation window as shown in Figure 5-13. The parameters for the cross-validation can be set using this window. In these data, which are a time series, it makes the most sense to break the data into contiguous blocks (more on this later). The default setting of breaking the data into 10 blocks is chosen, and up to 15 PCs are to be calculated. Cross-validation is performed by pressing the **Calculate** button in the main window. After the calculations are complete, the RMSECV curve can be viewed by pressing the **Plot Eigenvalues/RMSECV** button then selecting **RMSECV** in the **Plot Controls** window. The result of this is shown in Figure 5-14, which shows the Predictive Residual Error Sum of Squares or PRESS value for the data as function of the number of PCs. This is an indication of how well the data can be reconstructed from the PCs. This indicates that the minimum reconstruction error was at seven PCs. However, the decrease after four PCs was relatively modest.
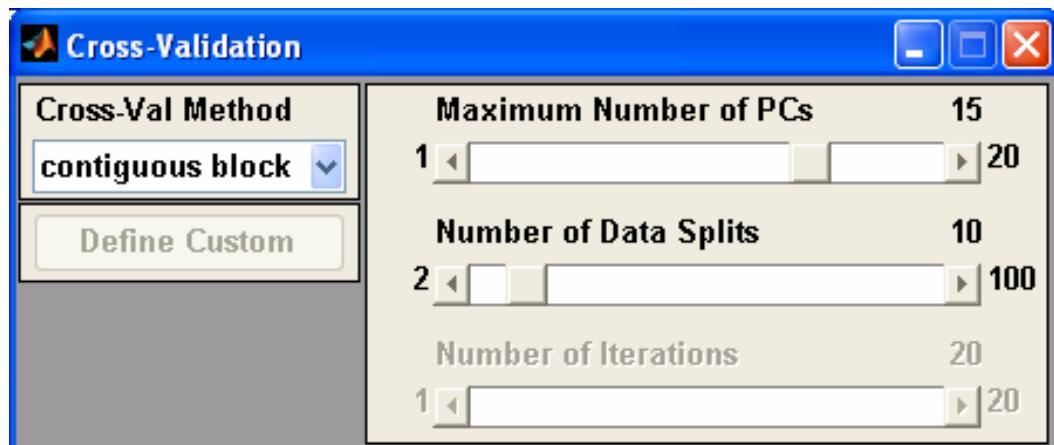
Figure 5-13. Cross-Validation Window.

In this instance, the absolute and relative sizes of the eigenvalues suggest that four PCs should be retained. The cross-validation suggests that up to seven PCs might be best; however, most of the improvement in error is achieved before five PCs. Together, these results suggest four PCs for the final model.

If these rules of thumb were all we had to go on, the choice of the number of PCs would still not be easy in many cases. One should also consider the amount of "left over" variation in the data as compared to the expected level of noise or other non-deterministic variation. In this example, four PCs capture over 85% of the variation. One might ask whether it is reasonable to expect 15% non-deterministic variance in the system, *i.e.,* what is the noise level?
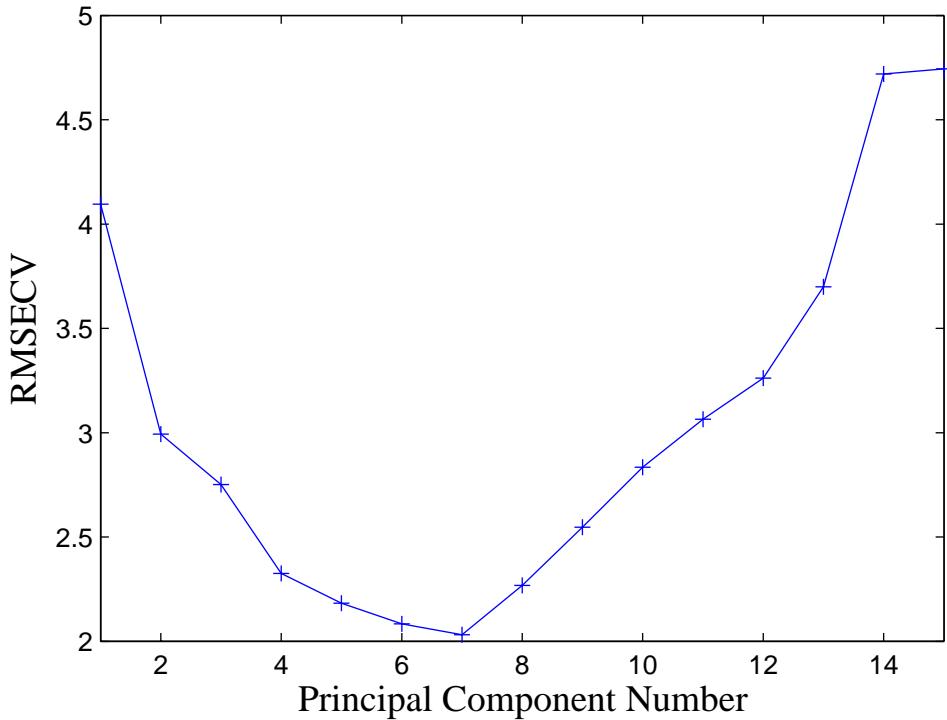
Figure 5-14. Cross-validation PRESS curve for SFCM data in replacedata.mat file.

When determining the number of PCs to retain, one should also look at the scores and loadings. In many problems it can be expected that many variables in the data set will be quite correlated. This can be because of spatial relationships (for example, temperature sensors that are close to each other should be related) or frequency relationships (for example, absorbances at nearby frequencies should be related). Because of these types of relationships, the loadings for the first few PCs will often be "smooth" or group the variables in a way that makes physical sense. PCs descriptive of noise, however, will typically appear random. This is an indication that these PCs do not describe physically significant variations. Likewise, one may expect that the scores should indicate similarities in the samples. In our example, these similarities may be due to the dynamic nature of the data and the fact that the data should be correlated in time. When the scores become random, it is probable that they are capturing non-deterministic variation.

In this example, the number of PCs can be set to 4 by clicking on the fourth PC in the table then pressing the **Calculate** button.

Viewing and Interpreting the Model

Once a preliminary model has been obtained the user can now explore the data by viewing the scores, which show the relationship between samples, and the loadings, which show the relationships between variables.

The first principal component scores for the SFCM data are shown in Figure 5-15 and the corresponding loadings are shown in Figure 5-16. Note how all the temperatures on the

left load positively while all the temperatures on the right load negatively. Thus, the scores capture the difference between the temperatures on the left and right side of the melter, which apparently varies randomly over time. The sawtooth nature of many of the process variables, which is attributable to changes in the level in the molten glass pool, is captured in the second PC. The level is a controlled variable and its affect on the scores is readily apparent. The scores and loadings for the second PC are shown in Figures 5-17 and 5-18. Examination of the loadings indicates that the variables that contribute most strongly to the sawtooth trend are those near the surface of the molten glass pool, variables 7–9 and 15–19. The third and fourth PCs (not shown) are harder to interpret. Recall that each PC is constrained to be orthogonal to all previous PCs. This constraint can make interpretation of the loadings and scores for PCs progressively more difficult as the number of PCs increases.

Multivariate Statistical Process Control

Once a PCA model is developed, it can be combined with tools and techniques from univariate statistical process control (SPC) to form multivariate statistical process control (MSPC) tools (Jackson, 1979; Wise *et al.,* 1990, 1991). Control limits can be placed on the process scores, "sum of scores" T^2, and residual Q. Limits can also be placed on the residuals of individual variables (single columns of **E**) though this will not be addressed here. There are multivariate analogs to Shewart, range, and CUSUM charts (Box *et al.*, 1978). When used for MSPC purposes, PCA models have the additional advantage that the new scores variables produced, which are linear combinations of the original variables, are generally more normally-distributed than the original variables themselves. In our case, we are typically sampling a large number of variables when we form the PCA scores and thus we would expect the scores, which, like a mean, are a weighted sum, to be approximately normally-distributed. A word of caution is advised here, however. In some instances, if score values are associated with a controlled variable (such as the level of the SFCM in the example above) we would not expect the scores to be normally-distributed.
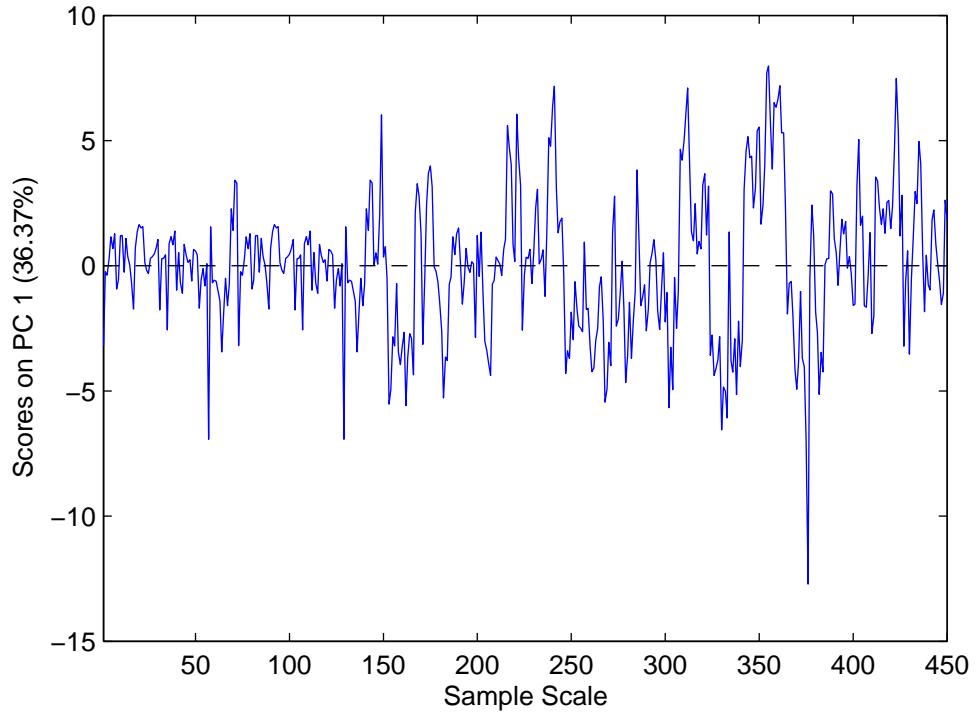
Figure 5-15. Scores on the first PC of the SFCM data.
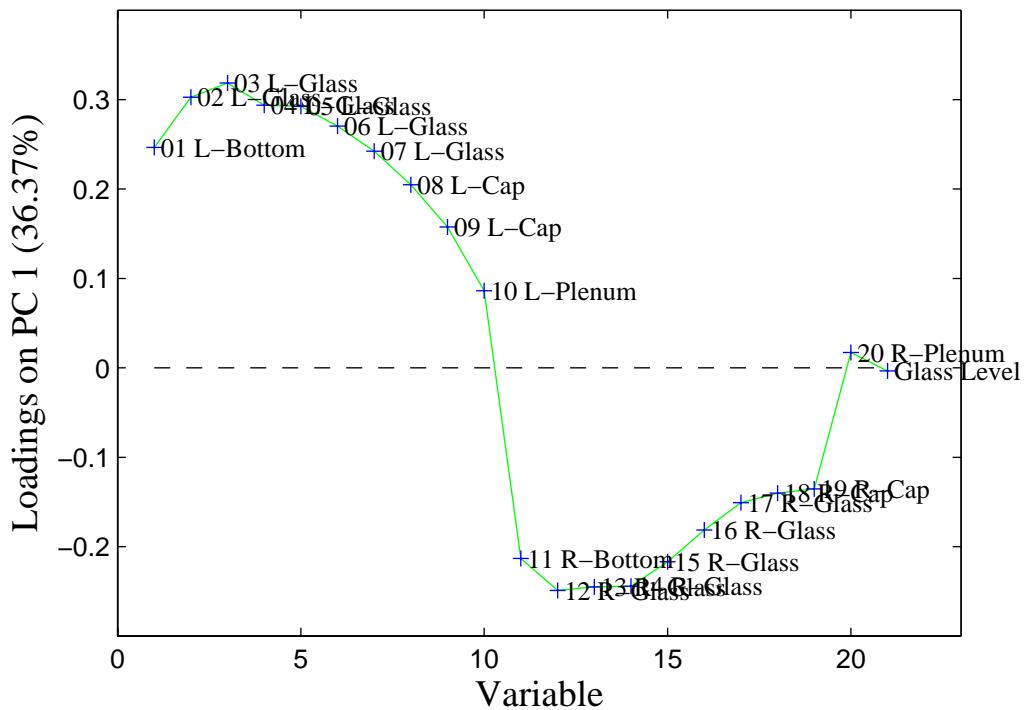
Figure 5-16. Loadings for the first PC of the SFCM data.
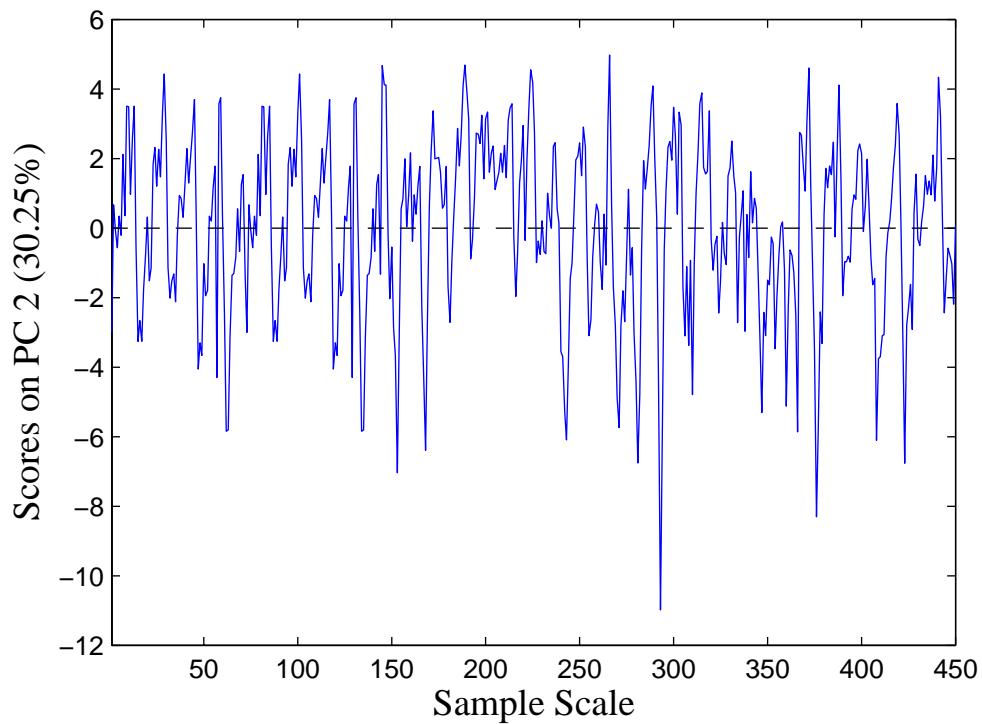
Figure 5-17. Scores on the second PC of the SFCM data.
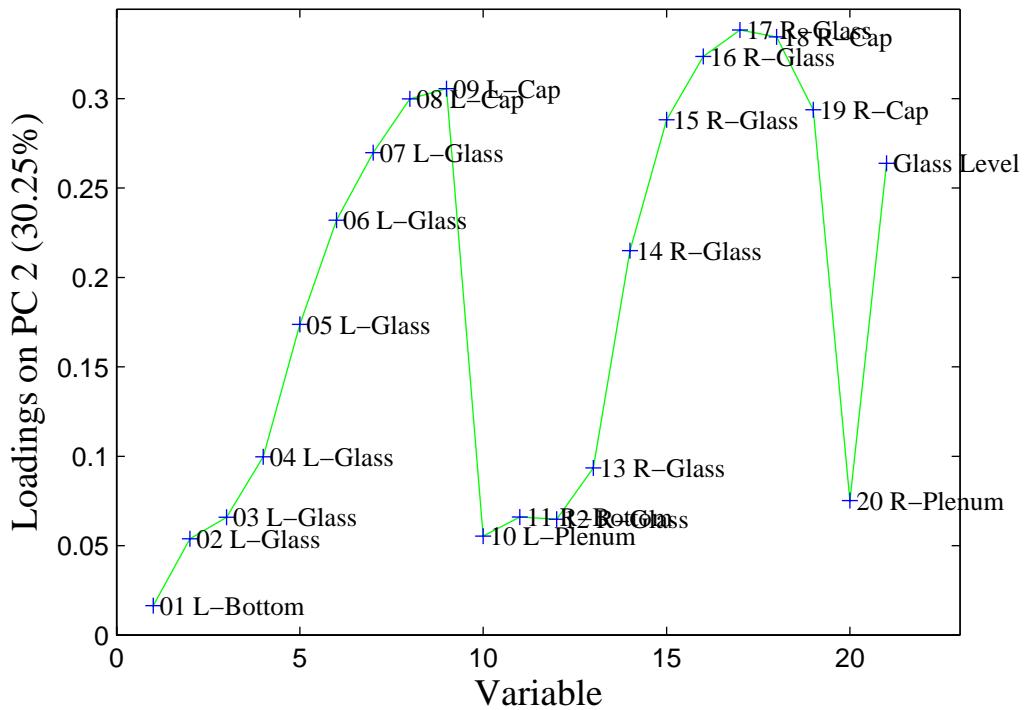
Figure 5-18. Loadings for the second PC of the SFCM data.

122

The variance captured by the PCA model in each original variable can be viewed by clicking the **varcap** button in the **Plot Controls** window when Loadings are selected in the top menu. The resulting stacked bar chart is shown in Figure 5-19. Here it can be seen that the PCA model captures from ~60% to ~93% of the variance in all of the variables. The plot also shows how the variance is captured by each PC. For instance, PC1 (dark blue) captures the most variation in the lower temperatures (2-6 and 12-16), while the second PC (light blue) captures mostly variation in the area where the feed meets the molten glass, known an the cold cap (7-9, 17-19) and in the level (21). The fourth PC (dark brown) captures variation in the plenum variables (10 and 20).
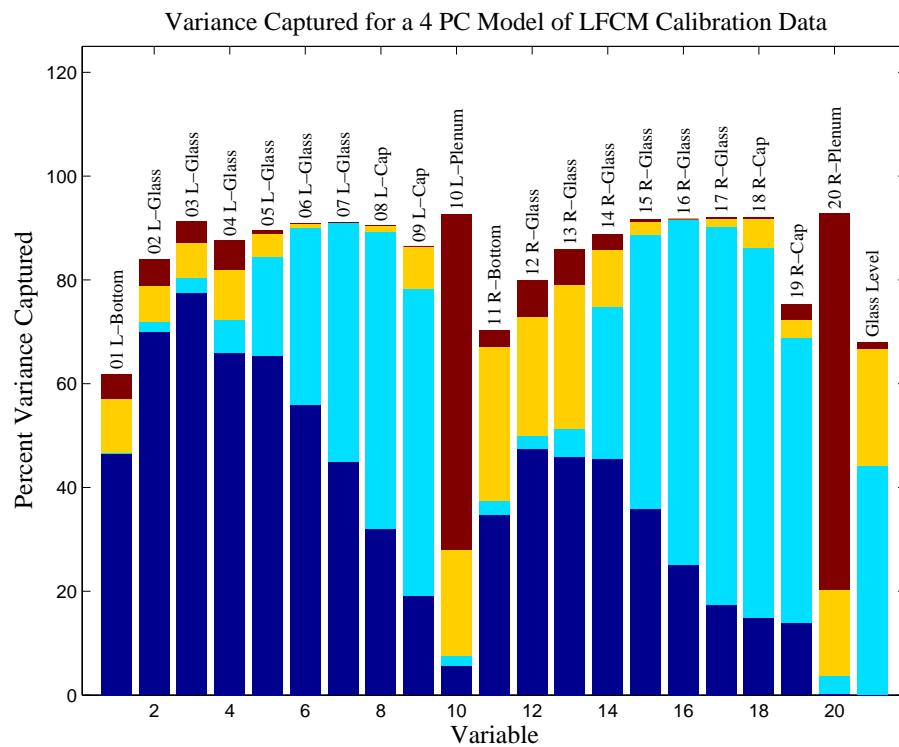
Figure 5-19. Variance captured for each variable in four-PC model.

A theoretical connection exists between PCA and state space models typically used by the process control community for describing the dynamics of a chemical process. Much literature is available concerning the state-space formalism (see, for instance, Åstrom and Wittenmark, 1984; or Kwakernaak and Sivan, 1972); however, it is useful to provide a brief introduction here. Consider a linear, time-invariant, discrete, state-space process model:

$$\mathbf{x}(k+1) = \mathbf{\Phi}\mathbf{x}(k) + \mathbf{\Gamma}\mathbf{u}(k) + \upsilon(k) \qquad (5\text{-}14)$$

$$\mathbf{y}(k) = \mathbf{C}\mathbf{x}(k) + \mathbf{e}(k) \qquad (5\text{-}15)$$

where $\mathbf{x}(k)$ is the n by 1 state vector at sampling period k, $\mathbf{u}(k)$ is the r by 1 vector of process inputs and $\mathbf{y}(k)$ is the p by 1 vector of process measurements. The vector $\upsilon(k)$

represents the state noise or disturbance input to the process; $\mathbf{e}(k)$ is measurement noise. The $\mathbf{\Phi}$, $\mathbf{\Gamma}$, and $\mathbf{C}$ matrices are assumed constant. Equation 5-14 shows that the process state at time $k+1$ is a function of the state, process inputs and disturbances at time k. Equation 5-15 shows that the process measurements are related to the process states and measurement noise.

It has been shown that, for processes where there are more measurements than states, *i.e.,* when there are more elements in $\mathbf{y}$ than $\mathbf{x}$, variations in the process states appear primarily as variations in the PCA scores, while noise mainly affects the residuals (Wise *et al.,* 1990). This allows one to consider only the noise properties of the system when deriving limits on PCA residuals; the dynamics of the process need not be considered explicitly. The rapid increase in the availability of process analytical instrumentation has drastically increased the instances of processes having more measurements than (significant) states.

MSPC Example

As an example of using a PCA model for MSPC we return now to the SFCM data, which includes two test data sets, `reptest1` and `reptest2`. The PCA model just developed can be easily applied to the test data. First, the calibration data must be cleared by selecting **File/Clear/X and Y Blocks** in the **Analysis** window. The new data can then be loaded using the **File/Load Data/X-Block** menu and selecting `reptest1` in the dialog box. The model is then applied to the new data by clicking the **Calculate** button. Scores from the new data can now be viewed by clicking the **Scores** button and selecting the desired plot in the **Plot Controls** window. Note that the default is to show the new scores along with the scores from the original data. This option can be changed by toggling the **Show Cal Data with Test** checkbox on the Plot Controls window.

As an example, a scores plot which includes the calibration and test data can be produced by pressing the **Scores** button and selecting PCs 1 and 2 in the **Plot Controls** window. Axes lines can be added by selecting **View/Axis Lines/All** in the **Plot Controls** window. A 99% confidence ellipse can be added by checking the **Conf. Limits** box in the **Plot Controls** window and indicating 99% in the text box. The results of performing this operation are shown in Figure 5-20. Note that the calibration data are shown as black circles while the new data are indicated by red circles. From this plot it is apparent that the new data conform to the old data as far as its projection onto the first two PCs is concerned. This is certainly not the whole story, however, as we shall see.

When applying an existing model to new data, the single most useful plot is usually the Q residuals for the new samples. This plot tells if the new samples fit the existing model. The Q residuals for the new samples can be obtained by selecting Q residuals in the **Plot Controls** window when **Scores** is selected in the uppermost menu (X axis). Figure 5-21 shows a Q residuals plot of only the new samples (the **Show Cal Data with Test** checkbox has been unchecked). Note that the 99% confidence limit has been added to the plot. It is apparent that there is some sort of excursion around sample 50, the Q residuals get very large and stay that way. What variables are responsible for this deviation from normal behavior? This information can be obtained by consulting the Q contributions by

clicking on the **Q con** button in the **Plot Controls** window then clicking on the point of interest. The Q contributions are shown for sample 50 in Figure 5-22. (Note that you may have to adjust axes limits by using the **Edit/Axes Properties…** in the **Q Residual Contributions** plot window to get the exact plot shown.) These contributions suggest that thermocouple number 5 has gone bad, reading higher than it should. Samples 51-54 have similar residuals (not shown). It is interesting to check sample 33 to see if it was an early indication of the failure of sensor 5. The residuals for it are shown in Figure 5-23. Clearly, it is not the same sensor failure, but another type of process anomaly.
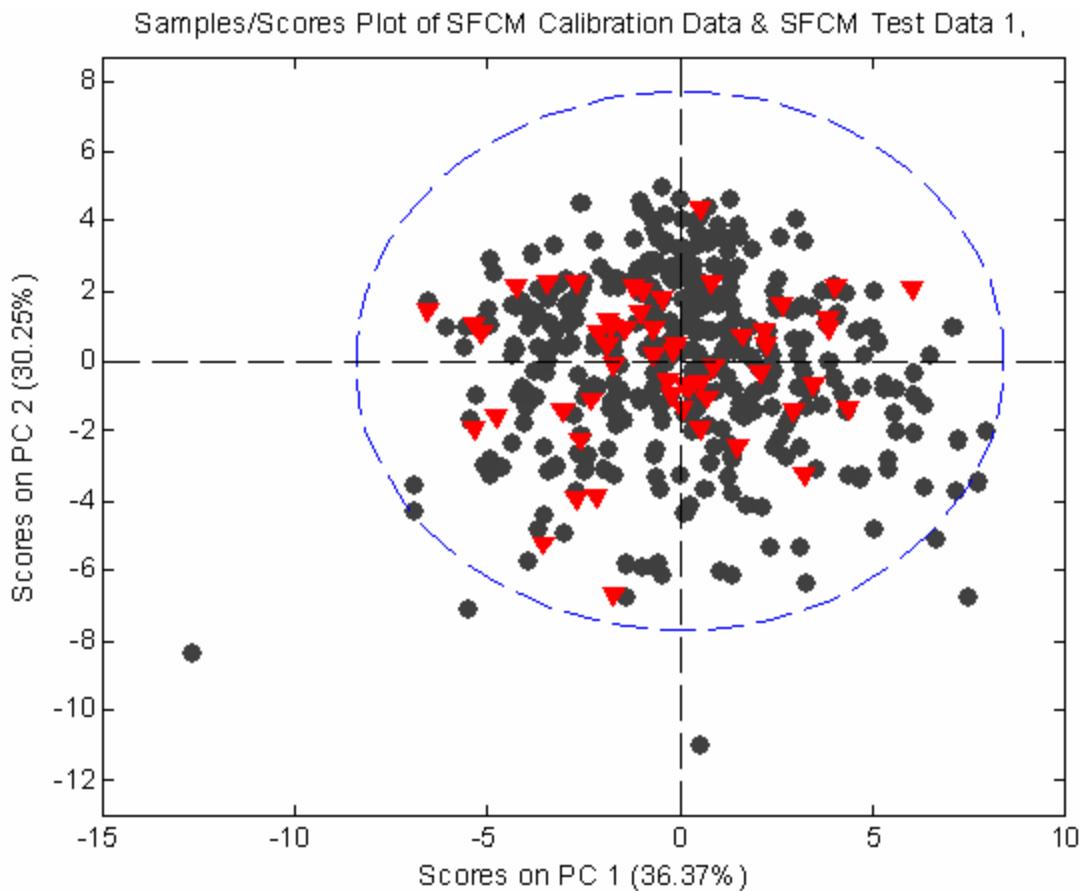
Figure 5-20. Scores plot of SFCM data showing new data with calibration data.
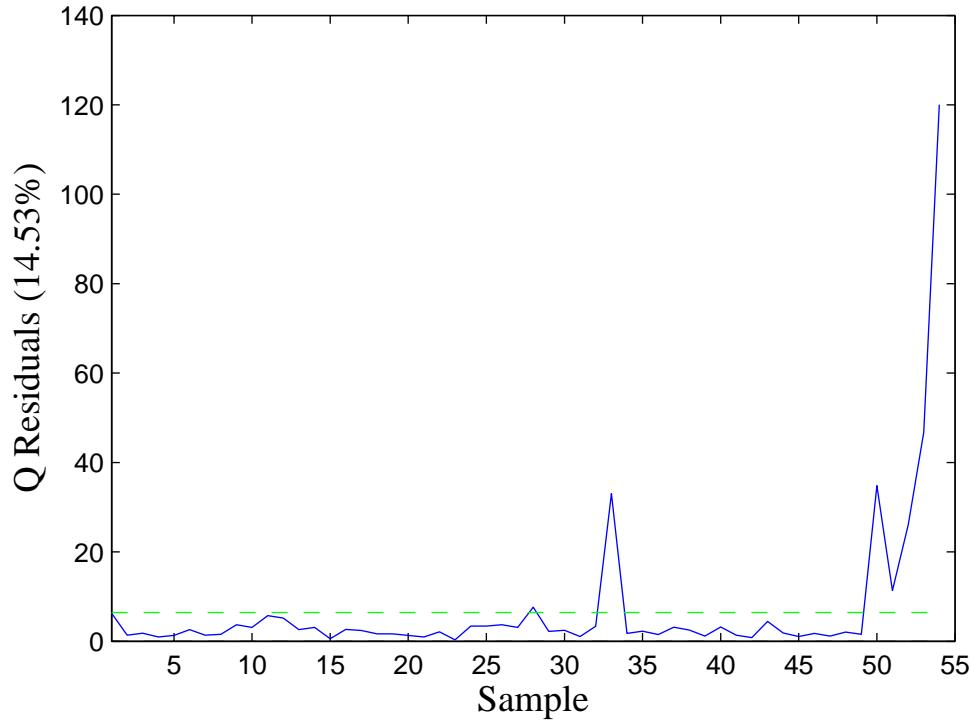
Figure 5-21. Q residuals for test samples from SFCM data set.
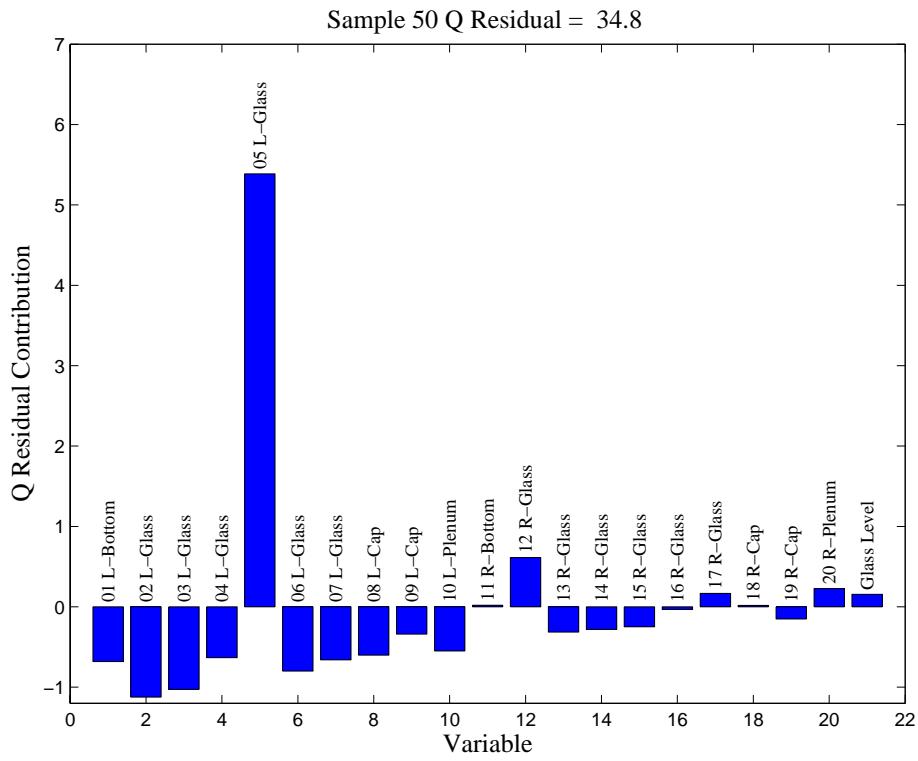
Figure 5-22. Contributions of the residuals to sample 50 in SFCM test data.

126
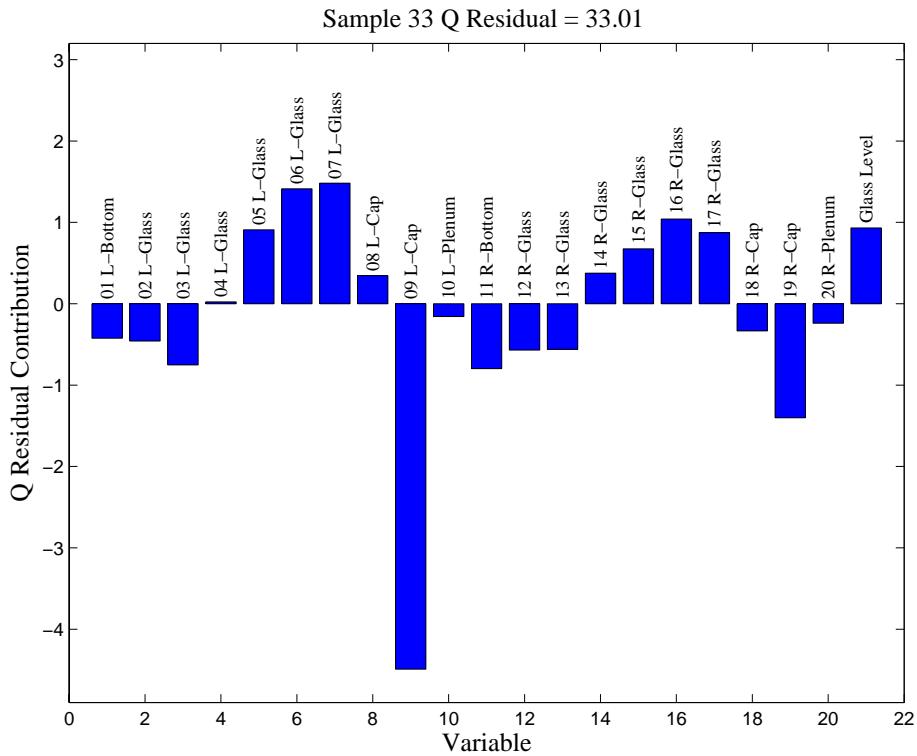
Figure 5-23. Contributions of the residuals to sample 33 in SFCM test data.

If desired, confidence limits can be calculated for the residuals and the contribution plots can be normalized so that equal residuals are of equal significance (Wise *et al.,* 1990). (Look for this in a future edition of the toolbox.)

PCA Summary

Principal Components Analysis is a widely used technique for exploring and modeling multivariate data. It provides an interpretable model of a data set. A PCA model consists of the following parts:

- a mean vector, used for centering the data
- a vector of standard deviations or other factor, used for variance scaling the data
- a set of loadings, which describe directions of variations in the data and show the relationships between the variables
- a set of scores, which show relationships between the samples
- a set of eigenvalues, which give the amount of variance in each of the loading directions

Statistical limits can be calculated for the model scores, T^2, and Q residuals and individual residuals given the eigenvalues and number of samples in the data.

New data can be compared with an existing PCA model by:

- subtracting the original mean from the data
- scaling the data with the original standard deviations or other factor
- projecting the new centered and scaled data onto the loadings to get new scores, T^2 and residual values
- comparing the scores, T^2 values, Q residuals and individual residuals to their previously determined limits

All of these steps are done automatically when using the Analysis tool

The concepts and mathematics used in Principal Components Analysis are common to many other multivariate techniques. Thus, a good understanding of the technique forms a good foundation for many other chemometric methods.

Multi-Way PCA

The PCA method outlined above takes no explicit account of the ordered nature of the data set, *i.e.,* the fact that the data were collected in a sequential manner. Reordering the samples would produce identical results. There are methods that explicitly consider that the data set is ordered. These are referred to as multi-way methods because the data are usually organized into time-ordered blocks that are each representative of a single sample or process run. The blocks are then arranged into multi-way matrices. Multi-way methods are particularly useful for the analysis of batch process data and analytical data where a response is being measured as a function of two or more parameters. Examples include gas chromatography/mass spectrometry (GC-MS), where the response in ion counts arriving at the detector is measured as a function of GC retention time and mass/charge. There are many other "hyphenated" analytical techniques which produce a matrix of data for each sample.

Consider the three-dimensional data array shown in the top of Figure 5-24. A data matrix of this type would be typical of a series of runs of a batch process (or a series of samples from a second order analytical technique such as GC-MS). Here there are $j = 1, 2, ..., J$ variables measured at times $k = 1, 2, ..., K$ throughout the batch. Similar data will exist on $i = 1, 2, ..., I$ runs of the batch process. The data can be summarized in the three dimensional ($I \times J \times K$) array **X**. Different batch runs (samples) are arranged along the vertical side, different process measurements (variables) along the horizontal side, and time recedes into the figure. Each horizontal slice through the array is a ($J \times K$) matrix representing the time history for all variables of a batch of a particular batch or sample. Each vertical slice made parallel to the front face of the cube is a ($I \times J$) matrix representing the values of all the variables in all the batches taken at a common time. A vertical slice made parallel to the side of the cube (the time axis) would represent a ($I \times K$) matrix of all the time histories of a single variable for all the batches.

There are several methods for decomposing the array **X** (Geladi, 1989). These methods include the Tri-Linear Decomposition (TLD) (Sanchez and Kowalski, 1990; Booksh *et al.,* 1994), Parallel Factor Analysis (PARAFAC) (Smilde and Doornbos, 1991; Smilde *et*

al., 1994), and Tucker models (Kroonenberg and de Leeuw, 1980). Each of the decomposition methods places different constraints on the resulting matrices and vectors. Here, we will consider one of the more straightforward approaches, that of multi-way PCA (MPCA) (Wold *et al.,* 1987, Wise *et al.*, 1999).
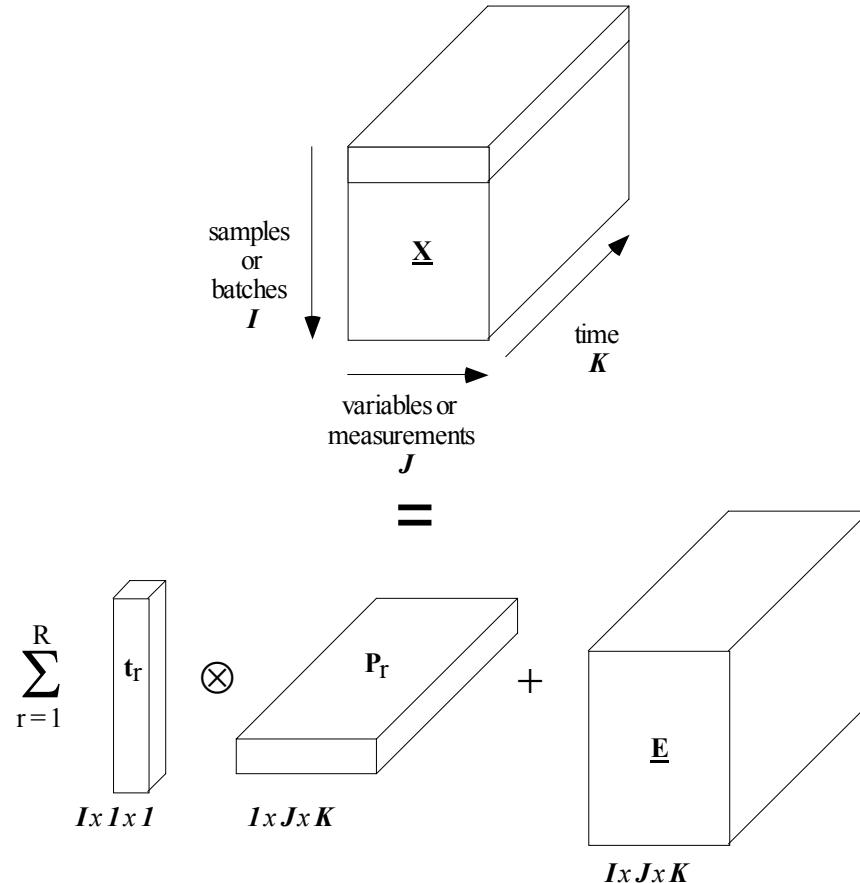
Figure 5-24. Three-dimensional data array and multi-way PCA decomposition.

MPCA is statistically and algorithmically consistent with PCA and has the same goals and benefits (Nomikos and MacGregor, 1994). In MPCA, the array $\underline{\mathbf{X}}$ is decomposed as the summation of the product of score vectors ($\mathbf{t}$) and loading matrices ($\mathbf{P}$) plus a residual array $\underline{\mathbf{E}}$ that is minimized in a least-squares sense.

$$\mathbf{X} = \sum_{r=1}^{R} \mathbf{t}_r \otimes \mathbf{P}_r + \mathbf{E} \qquad (5\text{-}16)$$

Here $\otimes$ is the outer product operator. This decomposition, shown graphically at the bottom of Figure 5-24, is done in accordance with the principles of PCA and separates the data in an optimal way into two parts. The noise or residual part $\underline{\mathbf{E}}$ is as small as possible and is associated with non-deterministic variation in the data. The systematic part, the sum of the $\mathbf{t}_r \otimes \mathbf{P}_r$, expresses the deterministic variation as one part ($\mathbf{t}$) related only to batches and a second part ($\mathbf{P}$) related to variables and their time variation.

MPCA is equivalent to performing PCA on a large two-dimensional matrix formed by unfolding the three-way array $\underline{\mathbf{X}}$ in one of six possible ways, only three of which are essentially different. For example, one might unfold $\underline{\mathbf{X}}$ in such a way as to put each of its vertical slices (I x J) side by side to the right, starting with the slice corresponding to the first time interval. The resulting two-dimensional matrix has dimensions ($I \times JK$). This particular unfolding allows one to analyze variability among batches or samples in $\underline{\mathbf{X}}$ by summarizing information in the data with respect to variables and their time variation. A mathematically-equivalent unfolding would be to take slices off the side of $\underline{\mathbf{X}}$ and place them down the time axis, which also forms a matrix with dimensions ($I \times JK$). (The latter unfolding orders the matrix with the history of each variable kept together, while the former orders the matrix with the all the measurements taken at the same time kept together.) One might also be interested in unfolding $\underline{\mathbf{X}}$ in other ways; however, the unfolding shown in Figure 5-24 (and the equivalent unfolding mentioned above) are the only ways that keep batch (sample)-specific information separate from time and variable information.

The MPCA algorithm proceeds as shown in Figure 5-25. First the matrix is unfolded in one of the two equivalent ways described above. Each column of the resulting matrix is then mean-centered and, if appropriate, scaled to unit variance (autoscaled). An eigenvector decomposition as described in Equations 5-1 and 5-2 is then applied to the unfolded $\underline{\mathbf{X}}$. Each of the $\mathbf{p}$, however, is really an unfolded version of the loadings matrix $\mathbf{P}_r$. After the $\mathbf{p}$ are obtained, the $\mathbf{P}_r$ can be obtained by reversing the unfolding procedure. In a similar manner, the three way array $\underline{\mathbf{E}}$ can be formed by folding the PCA residual matrix $\mathbf{E}$. The Q and T^2 statistics can be calculated using the unfolded solution as shown in Equations 5-7 and 5-10.

This version of MPCA explains the variation of measured variables about their average trajectories. Subtracting the average trajectory from each variable (accomplished by mean-centering the columns of the unfolded matrix $\mathbf{X}$) removes the major nonlinear behavior of the process. The ith elements of the $\mathbf{t}$-score vectors correspond to the ith batch (sample) and summarize the overall variation in this batch with respect to the other batches in the database over the entire history of the batch. The $\mathbf{P}$ loading matrices summarize the time variation of the measured variables about their average trajectories. The elements of $\mathbf{P}$ are the weights, which when applied to each variable at each time interval within a batch, give the $\mathbf{t}$ scores for that batch.

130
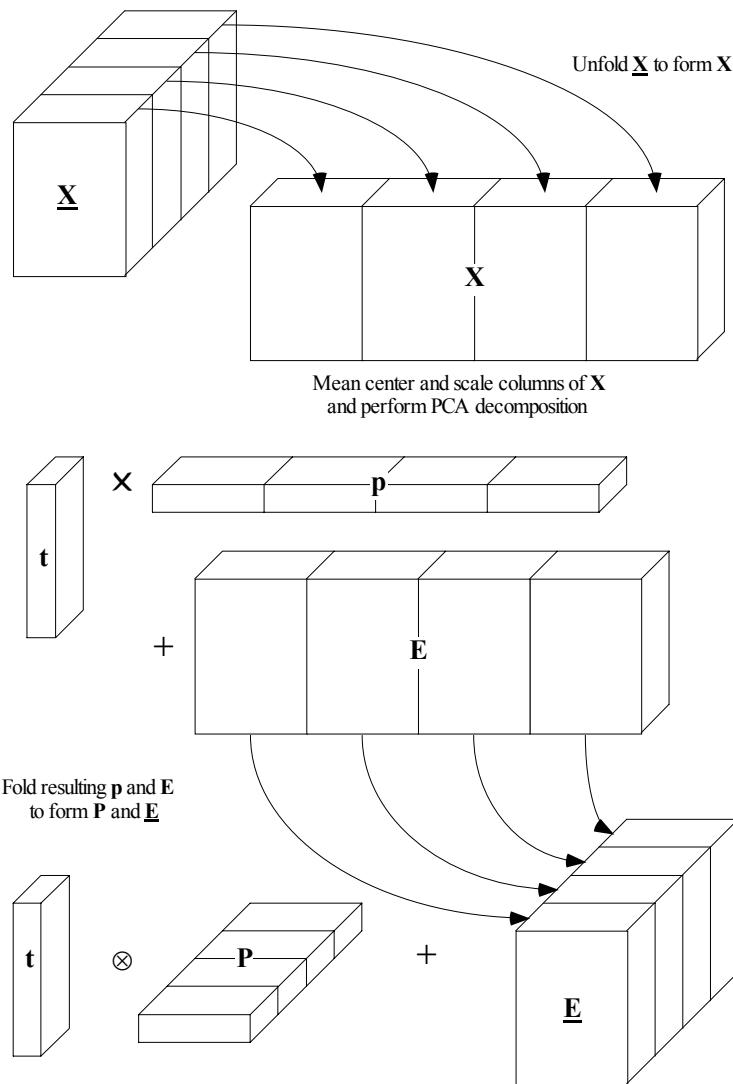
Figure 5-25. Algorithm for performing MPCA.

Example of MPCA

As an example of MPCA, consider the problem of monitoring the manufacture of semiconductors (Gallagher *et al.*, 1997; Wise *et al.*, 1997, White *et al.*, 1997). There are many steps in this process; here we will focus on an Al-stack etch process performed on the commercially available Lam 9600 plasma etch tool. The goal of this process is to etch the TiN/Al - 0.5% Cu/TiN/oxide stack with an inductively coupled BCl_3/Cl_2 plasma. Data from machine state sensors were collected during wafer processing. The machine data consist of 40 process setpoints and measured and controlled variables sampled at 1 second intervals during the etch. These are engineering variables, such as chamber pressure and RF power. In this example, twelve non-setpoint process variables with some normal variation will be used for monitoring, as shown in Table 5-2. Also, the physics of the problem suggest that these variables should be relevant to process and final product state. These data are available in the `etchdata.mat` file included with PLS_Toolbox.

Table 5-2. Machine state variables used for process monitoring.

1	Endpoint A Detector	7	RF Impedance
2	Chamber Pressure	8	TCP Tuner
3	RF Tuner	9	TCP Phase Error
4	RF Load	10	TCP Reflected Power
5	RF Phase Error	11	TCP Load
6	RF Power	12	Vat Valve

A series of three experiments were performed where faults were intentionally induced by changing the TCP power, RF power, pressure, Cl_2 or BCl_3 flow rate, and He chuck pressure. Data from 127 wafers with 20 induced faults are available from these three experiments.

To make the test more representative of an actual sensor failure, the analysis was done with "reset" values: the controlled variable which was changed was reset to have the same mean as its normal baseline value, so that it would look normal in the data file. For example, if the induced fault was a change of the TCP power from 350 to 400 watts, the data file value of the TCP power was reset from a mean of 400 back to 350 by addition of a constant bias. The resulting data look as if the controller was seeing a biased sensor for TCP power and adjusting accordingly; TCP power would appear normal, but it would not be. The effect of a TCP power offset, however, should be evident (we hope) in the remaining process variables because the apparent relationship between the TCP power and the remaining variables should be different.

The 'mpca' function can be used to start the analysis interface to develop an MPCA model of the normal data. Here the data for the 107 normal wafers have been arranged as a 80 (time steps) by 12 (variables) by 107 (wafers) matrix. Note that in MPCA, the third mode is the default sample mode (largely for historical reasons). This is in contrast to the analysis of 2-way arrays, where the first dimension is the sample dimension. For other multi-way functions in PLS_Toolbox (PARAFAC, Tucker and NPLS), the convention is also that the first dimension is the sample dimension. In all these methods, however, the sample mode can be redefined through options.samplemode. A reasonable way to scale the data is to use group scaling. In this instance, the mean trajectory is subtracted out of the data but the same variance scaling is used for the entire history of each variable. An MPCA model can be formed by executing

```
» load etchdata
```

```
» mpca
```

The first command loads the data set into the MATLAB workspace. The second command launches the **Analysis** GUI pre-set for MPCA. The user can now load the EtchCal data into the **Analysis** GUI using the **File/Load Data/X-Block** menu. When MPCA is selected, the **Analysis** GUI will default to group scaling, so building a model is as simple as clicking the **Calculate** button. The function will display the variance captured table shown in Table 5-3 and allow the user to explore the scores and loadings

132

plots via the **Plot Controls** window. Here it looks as though two PCs would be appropriate based on the distribution of the eigenvalues. A two component model can be formed by selecting the second line in the variance captured table and clicking the **Calculate** button

At first it seems that a model which only captures 46% of the variation in the process is not a particularly good one. However, it must be remembered that in MPCA the mean trajectory models a great deal of normal process variation, and this mean is extracted before calculating the PCA model of the unfolded data.

Table 5-3. Percent variance captured by MPCA model

Principal Component Number	Eigenvalue of Cov(X)	% Variance Captured This PC	% Variance Captured Total
1	3.96e+000	33.03	33.03
2	1.51e+000	12.59	45.61
3	3.03e-001	2.53	48.14
4	2.88e-001	2.40	50.54
5	1.95e-001	1.63	52.16
6	1.86e-001	1.55	53.71
7	1.59e-001	1.33	55.04
8	1.44e-001	1.20	56.24
9	1.26e-001	1.05	57.29
10	1.23e-001	1.02	58.31

The scores from the MPCA model can be plotted by clicking the **Scores** button on the main **Analysis** GUI. This will generate a **Plot Controls** window. Select **Scores on PC1** in the **X:** menu and **Scores on PC2** in the **Y:** menu. The result of this operation is shown in Figure 5-27. We have also used the `legend` command to add the legend on the figure as follows:

```
» legend('  ','Exp 29','Exp 31','Exp 33')
```

It can be seen that the calibration data are clustered according to which experiment the data are from. The experiments were run at widely spaced intervals (many weeks) and system drift is obvious.

The loadings for the MPCA model can be explored by clicking the **Loads** button on the main analysis interface, which will generate a **Plot Controls** window. Note that the loadings from MPCA can be quite complex as there is a loading coefficient for each combination of variable and time step. The default plot shows the loadings on the first PC, as shown in Figure 5-26. Here each line on the plot represents a variable trajectory for the first PC. Individual variables can be plotted by clicking **Explore** in the lower right hand corner of the **Plot Controls** window.
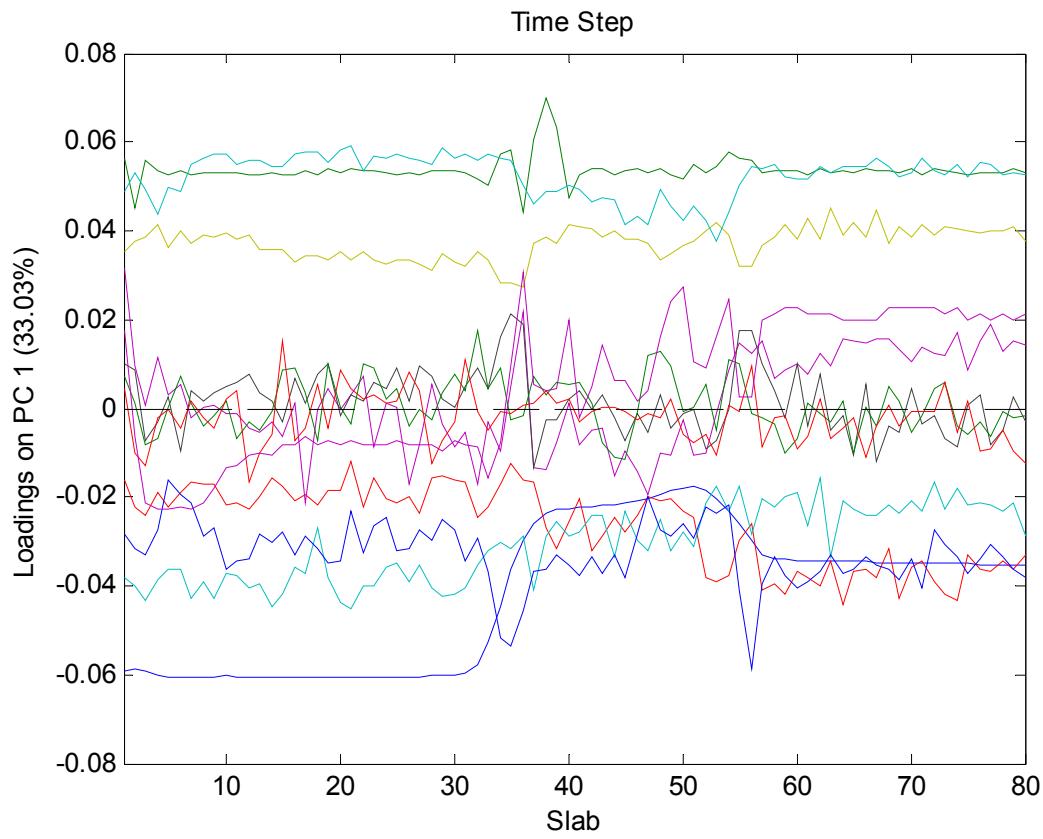
Figure 5-26. Loading plot for wafer calibration data.

The MPCA model can be applied to new data in the **Analysis** GUI as follows: select **File/Clear/X and Y Blocks**, then **File/Load/X-Block**, and select the EtchTest data. Click the **Calculate** button to apply the model to the data. The scores of the test data on the calibration data can be viewed by clicking the **Scores** button which brings up the **Plot Controls** window. This window can be used to produce a scores plot with both the calibration and test data. Such a result is shown in Figure 5-28. This figure shows the scores from the new test wafers with the induced faults with the limits based on the calibration data. Note that if you toggle the **Show Cal Data with Test** check box on and off you see that only a few of the test wafers are outside the control limits on these first two PCs. The residuals, however, show a different story. Figure 5-29 shows the Q residuals for the test wafers with 95% limits. This figure was produced by first selecting the calibration data samples using the **Select** button in the **Plot Controls**. A good view to work from is **Scores on the First PC** versus **sample** (not shown). Multiple selections can be made by holding down the shift key on subsequent selections. The selected calibration samples are then excluded by choosing **Edit/Exclude Selection** in the **Plot Controls** window. Most of the wafers are out, or nearly out, as we would hope. This suggests that MPCA would be a good tool for detecting faults in batch systems. Additional specificity can be obtained if models are built on the individual experiments.

134
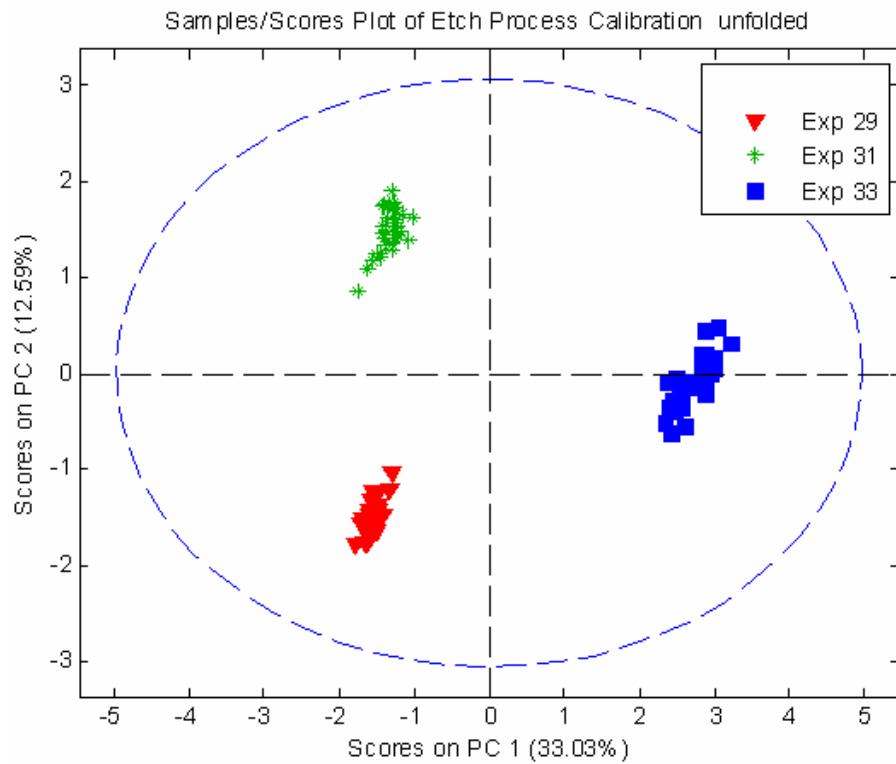
Figure 5-27. Scores on first two PCs for wafer calibration data.
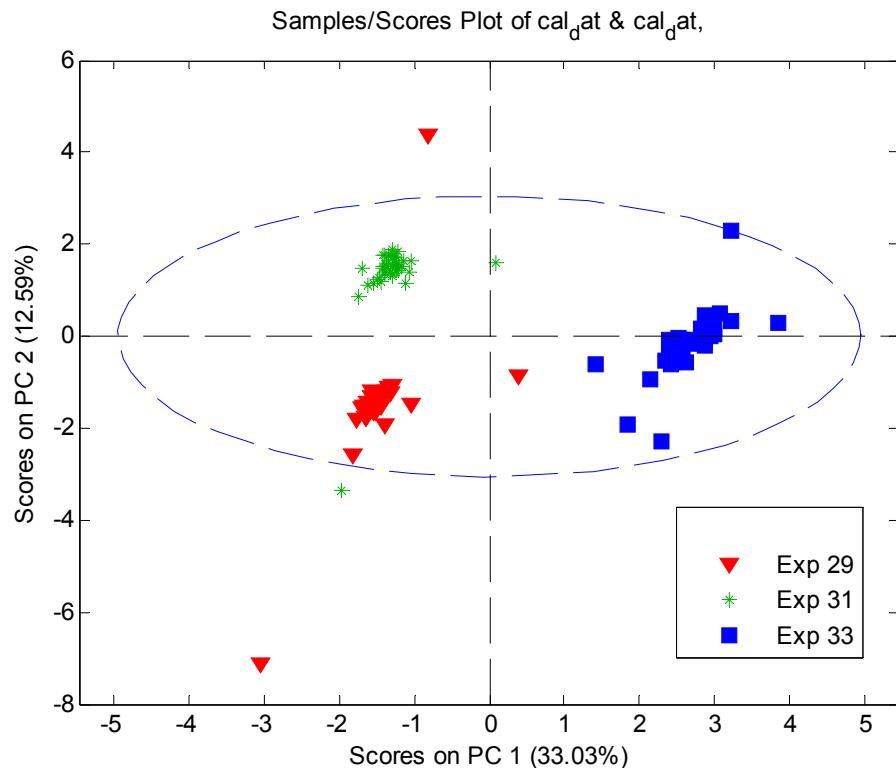
Figure 5-28. Scores on first two PCs for wafer test data.
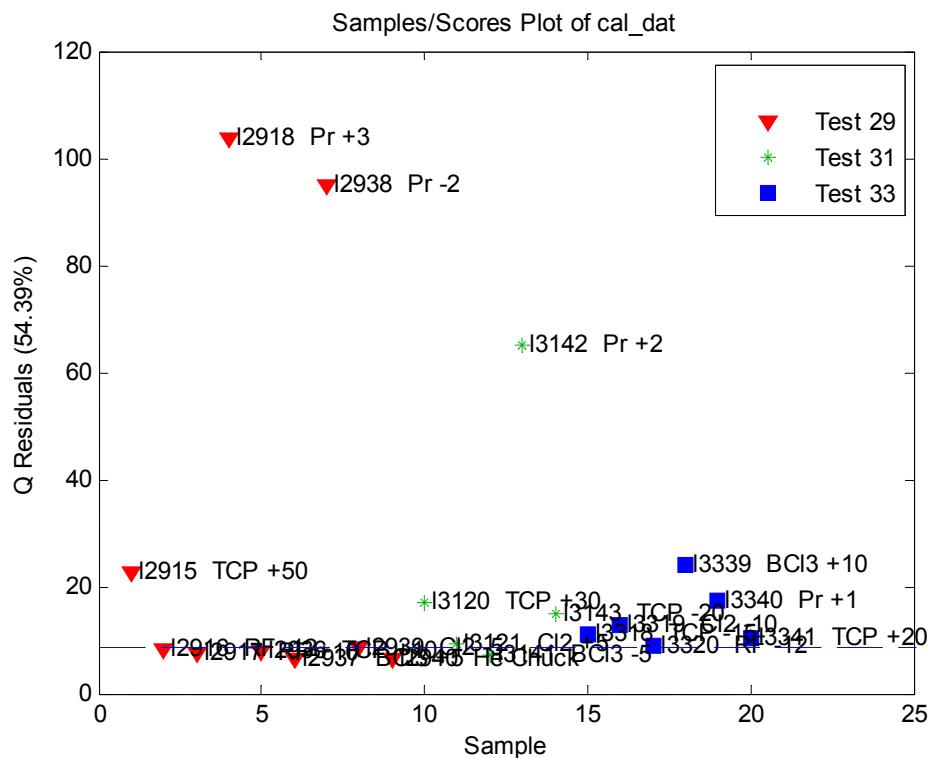
Figure 5-29. MPCA Q residuals for test wafers.

6. Multivariate Regression

Multivariate Calibration

In years past, process measurements consisted primarily of traditional "engineering" variables such as temperature, pressure, flow rate, and electrical power. In distillation control, for example, although the aim was to achieve a specific concentration of product in the overhead stream, the column was controlled based upon pressure and temperature measurements. Later, the advent of on-line spectrometers provided a means to make even better estimates of chemical composition. All of these measurements are indirect and rely on the ability to develop a model that relates the set of measured variables to the chemical composition of the system (or another, unmeasured, property or state of interest). The development of so-called regression models is the focus of this section. Although often used in spectroscopic applications (because of the large amount of information available in spectroscopic data), the techniques to be discussed have application to a wide range of data sources and properties-of-interest.

Classical Least Squares

The Classical Least Squares (CLS) model assumes that measurements are the weighted sum of linearly independent signals (see, for instance, Erickson *et al.*, 1992). In spectroscopy, for example, the CLS model assumes that measured spectra are the sum of pure component spectra weighted by the concentration of the analytes. Thus, the model is:

$$\mathbf{x} = \mathbf{p}\, \mathbf{S} \qquad\qquad (6\text{-}1)$$

where $\mathbf{x}$ is the measured response vector, $\mathbf{S}$ is the matrix of pure component responses and $\mathbf{p}$ is the vector containing the weights (*i.e.,* concentrations) of the analytes. Generally, given the vector of measurements, $\mathbf{x}$, one would like to know $\mathbf{p}$, the degree to which each component contributes to the overall measurement. $\mathbf{p}$ can be determined from

$$\mathbf{p} = \mathbf{x}\, \mathbf{S}^{+} \qquad\qquad (6\text{-}2)$$

where $\mathbf{S}^{+}$ is the pseudoinverse of $\mathbf{S}$, defined for CLS as:

$$\mathbf{S}^{+} = \mathbf{S}^{T}(\mathbf{S}\mathbf{S}^{T})^{-1} \qquad\qquad (6\text{-}3)$$

The main disadvantage of CLS is that the pure responses $\mathbf{S}$ of all spectrally-active components must either be known *a priori* or estimated using known concentrations of all spectrally-active components. These estimates must include any minor components that may not be of interest themselves but may contribute to the measured signal. Given a matrix of concentrations $\mathbf{C}$ and measured spectra $\mathbf{X}$, an estimate of the pure component spectra $\mathbf{S}_{est}$ can be obtained from

$$\mathbf{S}_{est} = (\mathbf{C}^{T}\mathbf{C})^{-1}\mathbf{C}^{T}\mathbf{X} \qquad\qquad (6\text{-}4)$$

In Equation 6-4, note that the concentration profiles of all spectrally-active species must be linearly independent (otherwise $(\mathbf{C}^T\mathbf{C})^{-1}$ would not exist, and the pure component spectra $\mathbf{S}_{est}$ cannot be estimated). Likewise, in Equation 6-3, note that the pure component responses must also be linearly independent (otherwise, $(\mathbf{SS}^T)^{-1}$ does not exist, and $\mathbf{S}^+$ cannot be calculated). In the more practical case where the pure component responses are nearly collinear, $\mathbf{S}^+$ can be calculated, but will be rather unstable, in that it may change a great deal given small changes in the estimates of the pure responses due to noise or other interferences. In this case, estimates of $\mathbf{p}$ obtained by Equation 6-2 may not be very accurate.

The CLS procedure may be demonstrated using the `nir_data.mat` file in PLS_Toolbox. The file contains measured near-infrared absorbance spectra of thirty simulated gasoline samples that were prepared from five pure components. An estimate of the pure component spectra can be obtained from the mixture spectra `spec1` and the concentration matrix `conc` as follows:

```
» load nir_data
» cspec = spec1(1:25,:);
» cconc = conc(1:25,:);
» tspec = spec1(26:30,:);
» tconc = conc(26:30,:);
» purespec = inv(cconc.data'*cconc.data)*cconc.data'*cspec.data;
» plot(spec1.axisscale{2},purespec);
```

The estimate of the pure component spectra obtained (`purespec`, or $\mathbf{S}_{est}$ in Equation 6-4) is shown in Figure 6-1. The matrix of pure component spectra can then be used to estimate concentrations of the analytes in the remaining five samples as follows:

```
» cpred = inv(purespec*purespec')*purespec*tspec.data';
» plot(tconc.data,cpred','+');
```

138
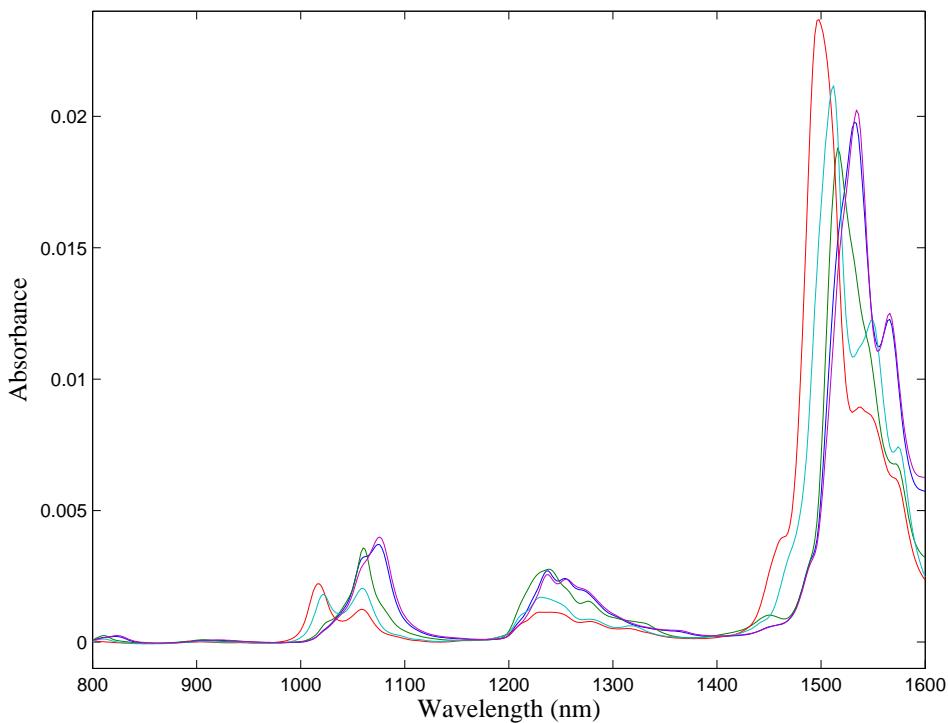
Figure 6-1. Estimate of pure component spectra from NIR spectra of simulated gasoline samples.

The actual versus predicted concentrations are shown in Figure 6-2. In this case, the predictions are quite good. If, however, the concentrations of one of the analytes in the calibration spectra is not known, the predictions will suffer considerably. The reader is encouraged to try this by, for example, excluding one or more of the five columns in the pure component concentration matrix conc before calculating the pure component spectra. As will be shown below, unknown concentrations are not a problem with inverse least squares (ILS) methods.

Inverse Least Squares

It is possible to get around the problem of having to know or estimate **S** by using an inverse least squares (ILS) model. ILS assumes that a regression vector **b** can be used to determine a property of the system y from the measured variables **x** (a row vector, such as a spectrum). Thus, the ILS model is

$$\mathbf{x}\,\mathbf{b} = y \qquad\qquad (6\text{-}5)$$

Compare this inverse model to the classical model in Equation 6-1. In the classical model, responses are expressed as a function of pure component concentrations (**p**), whereas the inverse model expresses a single concentration (y) as a function of the responses. Note that the inverse model formulation is more widely applicable than the classical (CLS) case, for at least two reasons: 1) only the value of the property of interest (y) needs to be known, and 2) this property is not restricted to being a component concentration property.

The regression vector **b** must be determined using a collection of measurements **X** and the known values of the property of interest, **y**. Thus, **b** is estimated from

$$\mathbf{b} = \mathbf{X}^{+}\mathbf{y} \qquad\qquad (6\text{-}6)$$

where $\mathbf{X}^{+}$ is the pseudoinverse of **X**. There are many ways to determine a pseudoinverse, but perhaps the most common is Multiple Linear Regression (MLR, also known as ordinary least squares, OLS). In this case, $\mathbf{X}^{+}$ is defined by

$$\mathbf{X}^{+} = (\mathbf{X}^{\mathrm{T}}\mathbf{X})^{-1}\mathbf{X}^{\mathrm{T}} \qquad\qquad (6\text{-}7)$$
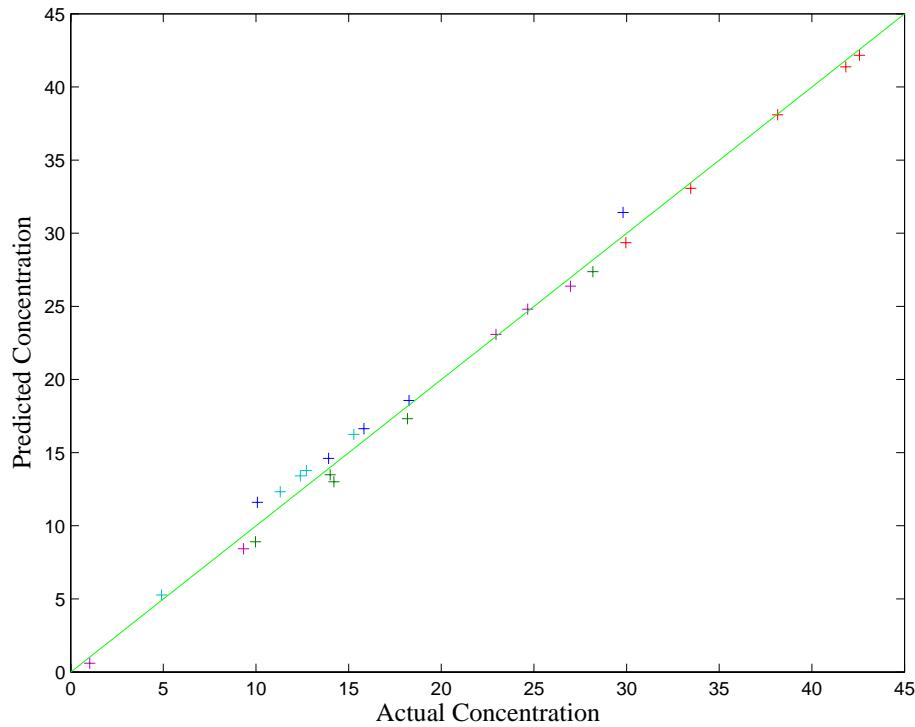
Figure 6-2. Actual versus predicted concentrations of simulated gasoline samples from NIR spectra.

Unfortunately, this approach often fails in practice because of collinearity of some or all of the response variables in **X** (*e.g.*, some columns of **X** (variables) are linear combinations of other columns), or because **X** contains fewer samples than variables (fewer rows than columns). In either of these cases, $(\mathbf{X}^{\mathrm{T}}\mathbf{X})^{-1}$ would not exist. For example, typical spectroscopy calibration problems are extremely ill-conditioned due to a high degree of correlation between absorbances at adjacent wavelengths. Also, the number of wavelength channels offered by the spectrometer is typically greater than the number of calibration samples that are available. In such a case, any attempt to use more wavelengths than samples to build an MLR model would result in an underdetermined situation, where there are an insufficient number of samples to estimate the regression coefficients of all of the wavelengths.

In most real systems, exact collinearity of variables in **X** is rather rare, due to the presence of random experimental noise. Nonetheless, when Equation 6-7 is used with systems that produce nearly collinear data, the solution for **b** is highly unstable, in that very small perturbations in the original data (for example, from noise or experimental error) cause the method to produce wildly different results. The use of highly collinear variables in MLR also increases the possibility of overfitting the model, meaning that the calibration may fit the data very well, but fails when used to predict the properties of new samples. As a result, an important practical aspect of the MLR method is the selection of response variables to be included in **X**, such that collinearity is avoided.

MLR Example

As noted in the introduction to this section, the possible applications of regression methods go beyond the spectral calibration problem. In one such example of MLR, we will develop a regression model that will enable estimation of the level of molten glass in the Slurry-Fed Ceramic Melter (SFCM) using temperatures measured in the SFCM (See the chapter on PCA for more information about these data). In this example, the temperatures and the level of the molten glass take the place of spectral response variables and concentration, respectively. The twenty SFCM temperatures, shown in Figure 5-11, will serve as the predictor variables in this problem, as they will be used to predict the molten glass level. As noted previously, the measured temperatures rise and fall with the glass level, which is a controlled variable. A model relating temperatures to level would serve as a backup to the level measuring instrument, which is a pneumatic device.

The SFCM temperature and molten glass level data are stored in the file `plsdata.mat`. The file contains 300 calibration or "training" samples (`xblock1` and `yblock1`) and 200 test samples (`xblock2` and `yblock2`). A simple model relating temperature to level can be created using MLR. First we will load the data into MATLAB and delete a few samples that are known outliers as follows:

```
» load plsdata
» x = delsamps(xblock1,[73 167 188 278 279]);
» y = delsamps(yblock1,[73 167 188 278 279]);
```

Note that we deleted the samples from both the predictor (`xblock1`) and predicted variables (`yblock1`). The variables are then mean-centered and a regression vector is calculated:

```
» [mx,xmns] = mncn(x.data);
» [my,ymns] = mncn(y.data);
» bmlr = mx\my;
```

Here we have used the backslash "left division" operator in MATLAB to obtain the regression vector `bmlr`. This is equivalent to forming the MLR pseudoinverse (Equation 6-7). With the regression vector and mean-centering parameters in hand, we can now apply the model to a new data set in order to assess its performance. Model application

involves first scaling the new predictor variables, applying the model's regression coefficients, and then re-scaling the result, as follows:

```
» sx = scale(xblock2.data,xmns);
» ymlr = sx*bmlr;
» symlr = rescale(ymlr,ymns);
» plot(1:200,yblock2.data,'-g',1:200,symlr,'-or')
```

A plot of the measured and predicted level is shown in Figure 6-3. Except for a period after samples 150 and 175, the predictions look very good. As we will see in the following sections, however, it may be possible to do somewhat better using other regression techniques, such as PCR and PLS.

Principal Components Regression

It was mentioned earlier that regression by MLR suffers from two different problems: 1) the relative abundance of response variables relative to the number of available calibration samples (for the typical spectral calibration problem), which leads to an underdetermined situation, and 2) the possibility of collinearity of the response variables in **X**, which leads to unstable matrix inversions and unstable regression results. Principal Components Regression (PCR) is one way to deal with both of these problems (see, for example, Næs and Martens, 1988; Martens and Næs, 1989; Geladi and Esbensen, 1991; Höskuldsson, 1996). Instead of regressing the properties of interest (*e.g.*, concentrations, or molten glass level) onto a set of the original response variables (*e.g.*, spectral response variables, or temperatures), the properties are regressed onto the principal component scores of the measured variables, (which, by definition, are orthogonal, and thereforewell-conditioned). Thus, the pseudoinverse of the response data matrix, $\mathbf{X}^+$, is estimated as

$$\mathbf{X}^+ = \mathbf{P} \ (\mathbf{T}^T\mathbf{T})^{-1} \ \mathbf{T}^T \qquad\qquad (6\text{-}8)$$

Compared to the estimation of the pseudoinverse for MLR (Equation 6-7), this operation is much more stable, due to the orthogonality of the principal component scores (**T**) and loadings (**P**). Furthermore, the underdetermined problem in MLR is addressed by the fact that the maximum possible number of principal components (PCs) is equal to the lesser of the number of response variables and the number of calibration samples, and, as a result, can never be greater than the number of calibration samples.

Because it directly addressesthe collinearity problem, PCR can be said to be less susceptible to overfitting than MLR. However, one could still overfit a PCR model, through the retention of too many PCs. Therefore, as in PCA, an important part of PCR is the determination of the optimal number of principal components to retain in the model. In contrast to a PCA model, however, the purpose of a PCR regression model is to predict the properties of interest for new samples. As a result, we would like to determine the number of PCs that optimizes the predictive ability of the model. The appropriate number of PCs is typically determined by cross-validation, which involves a procedure where the available data are split sample-wise into a training and a test set. The prediction residual

error on the test set samples is then determined as a function of the number of PCs retained in the PCR model. This procedure is usually repeated several times, using different sample subset selections for training and test sets, such that each sample in the original data set is part of a test set at least once. A plot of the total "composite" prediction error over all the test sets as a function of the number of PCs retained in the model is then used to determine the optimal number of PCs.

For problems in which there are more samples than variables, a PCR model that retains the maximum possible number of PCs (which is equal to the number of variables) is identical to the MLR model built using the same set of response variables. In a sense, the PCR model "converges" to the MLR model as PCs are added. However, in real applications, it is almost always the case that the optimal number of PCs to retain in the model is much fewer than the maximum.
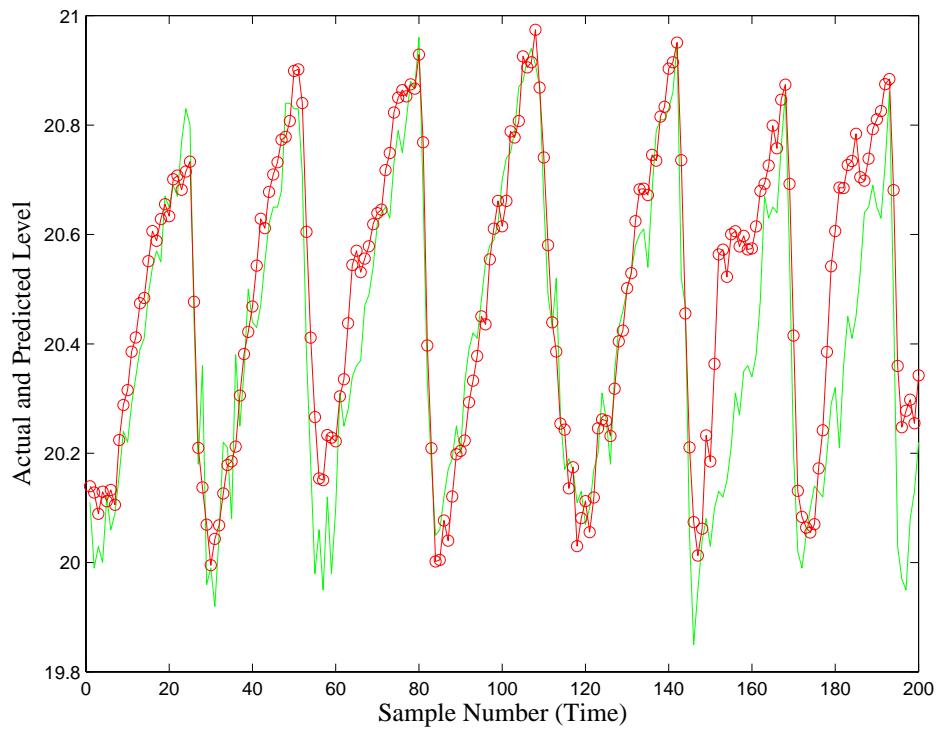
Figure 6-3. Actual and predicted glass level for SFCM data test set.

Application of PCR

As an example, we will return to the SFCM temperature and glass level data (`plsdata`) that were used to demonstrate MLR. We must first decide how to split the available data for cross-validation to determine the optimum number of PCs to retain in the PCR model. When many training samples are available, a good rule of thumb is to use the square root of the number of samples for the number of repetitions of the cross- validation procedure, up to a maximum of ten repetitions. With 295 samples in the training set, this rule would lead to ten repetitions.

We must also decide how to select the test sets for each repetition of the cross-validation procedure. One possibility would be to form each test set using every 10th sample in the data set. However, when dealing with data from a dynamic system (where the samples in the data matrix correspond to sequential points in time), this can be rather dangerous, because it is often the case that noise in such a system is not random with time; the variation due to noise on the nth sample is correlated to the noise on the $n+1$th sample. Thus, if the cross-validation test sets were chosen using every 10th sample, noise in the test data might be highly correlated with noise in the training data, which would "bias" the cross-validation results towards suggesting the retention of PCs that explain only noise (*i.e.*, overfitting). Instead, when dealing with time series data produced by a dynamic system, it is better to choose contiguous blocks of data for the test sets, where the length of the block is longer than the settling time of the process. In our case, it is convenient to use ten "block-wise" training sets of about thirty samples each. With these cross-validation settings, the first test set will contain samples 1 to 30, the second will contain samples 31 to 60, and so on.

The **Analysis** GUI in PLS_Toolbox can be used to perform cross-validation and build PCR (and PLS) models. Start the tool by typing `pcr` at the MATLAB prompt, which will start the **Analysis** GUI in the PCR mode. The data can be loaded into the tool by selecting **File/Load Data/Both** in the main **Analysis** window. The user will be prompted for X-block (predictor) and Y-block (predicted) variables. Here we will use the DataSet Objects x and y, created previously.

Now that the data are loaded, we need to decide how to preprocess the data for modeling. Because the response (temperature) variables with the greatest variance in this data set also appear to be correlated to the molten glass level, we'll choose to mean-center (rather than autoscale) the data by selecting **Preprocess/X-block/Mean Center** in the main **Analysis** window. (Note that the scaling for Y is irrelevant if there is only one Y variable, as is the case here.) If desired, a preliminary model can now be built by clicking the **Calculate** button.
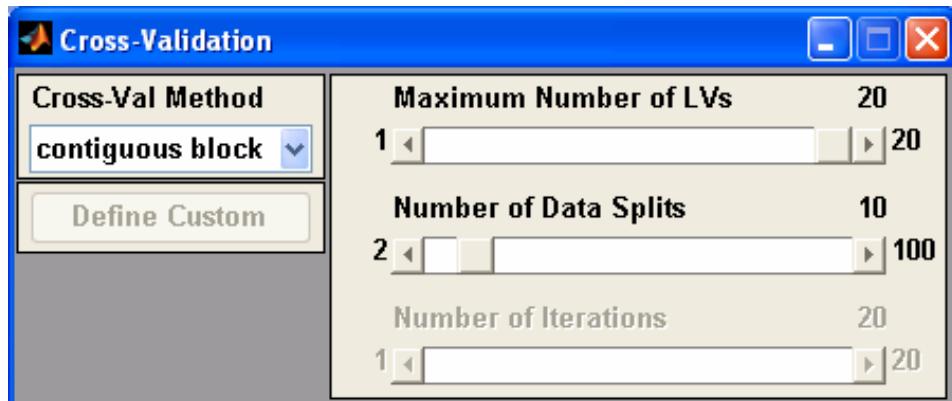
Figure 6-4. Cross-validation window.

144

We must now decide how to cross-validate the model. Select **Tools/Cross-Validation** from the menu to open an additional window where the cross-validation parameters can be set, as shown in Figure 6-4. Here we will choose to split the data into ten contiguous block-wise subsets, and to calculate all twenty PCs. Once this selection is made, the user can close the cross-validation window, go back to the main **Analysis** window and press **Calculate** to cross-validate the model. The variance captured by the PCR model of the temperature/level data then appears in the main Analysis window (Figure 6-5).
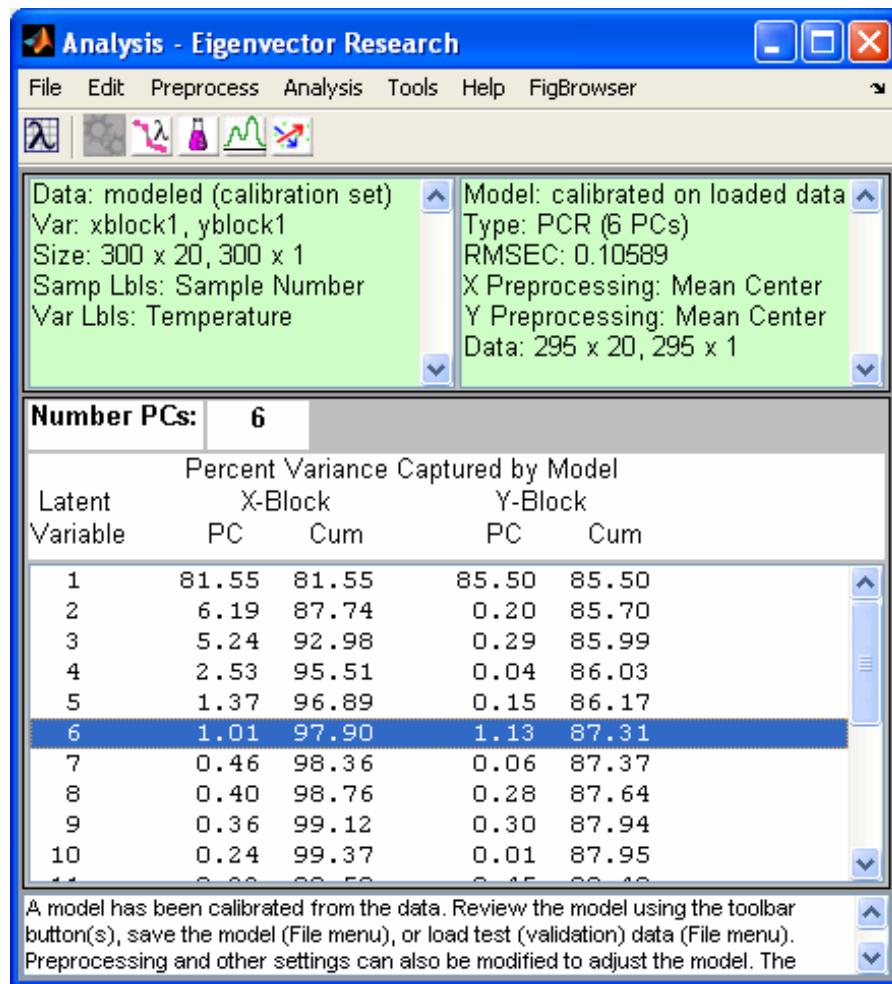
Figure 6-5. Analysis GUI with PCR model.

Now that the PCR model and the cross-validation results have been computed, one can view the cross-validation results by clicking on the **Plot Eigenvalues/RMSECV** button. This action brings up a **Plot Controls** window, which can be used to set up and manipulate all plots that involve general model statistics. A common plot that is used to analyze cross-validation results is called the "Predicted Residual Error Sum of Squares" (or PRESS) plot, shown in Figure 6-6. This plot can be obtained by selecting **Principal Component Number** for **X:** and **RMSECV** for **Y:** in the **Plot Controls** window. The Root Mean Square Error of Cross-validation (RMSECV) is a "composite" prediction

error obtained over all repetitions of the cross-validation procedure. Note how the RMSECV has several local minima and a global minimum at eleven PCs.

The choice of the number of factors to retain in the PCR model can be somewhat problematic under these conditions. Reasonable choices would include six, eight, or eleven PCs, as these all produce low RMSECV values. A good rule of thumb is to not include additional factors unless they improve the RMSECV by at least 2%. Thus, we would definitely choose eight PCs over eleven PCs since the reduction in RMSECV from eight to eleven PCs is very small. Our choice is now between six and eight PCs. At this point, it might help to consider the percent X and Y variance captured in the PCR model (in the main **Analysis** window) for making a final determination. Note that PCs 7 and higher capture less than 0.5% of the variance in both the predictor (X) variables and the predicted (Y) variable. A second good rule of thumb is that, when building predictive models, one should strive to use a model with the lowest possible complexity. In this context, complexity refers to the number of PCs in the PCR model. Given this situation, where a model with six PCs and a model with eight PCs capture essentially the same amount of both X and Y variance, this rule suggests that a model with six PCs would be the best choice. Thus, we choose six PCs for construction of the final model using all 295 training samples. This is done by clicking on the sixth line of the variance captured table in the **Analysis** window and then clicking the **Calculate** button, which will update the PCR model to include six PCs. Scores and loadings for PCs 1 through 6 can be viewed using the toolbar buttons across the top of the main window, along with scores versus actual and fitted y values.
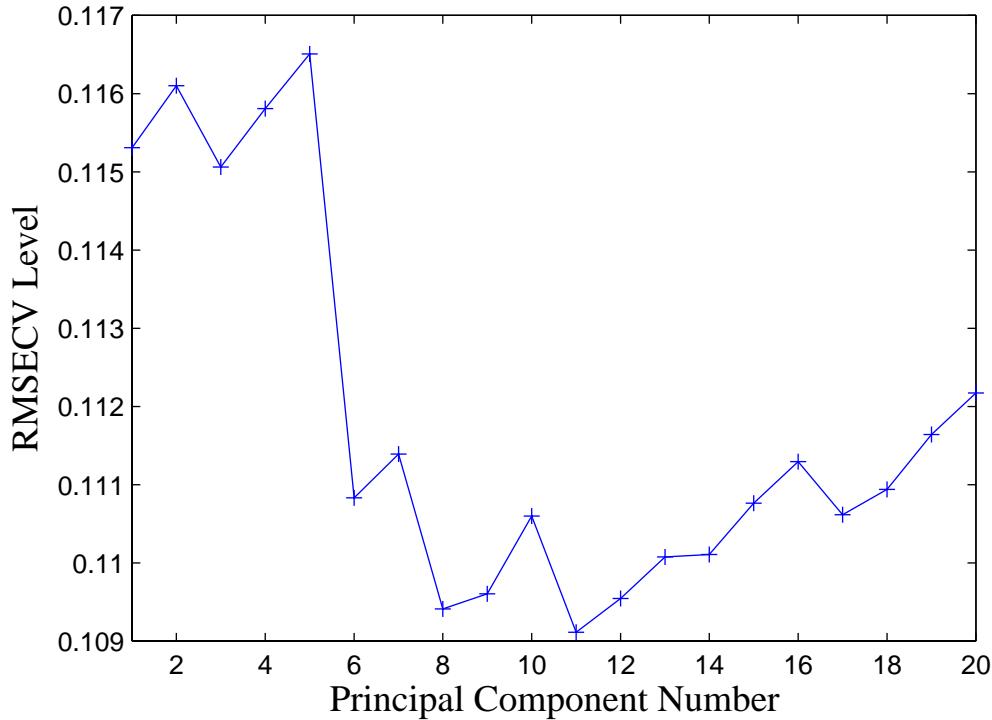
Figure 6-6. PCR RMSECV for melter data example.

The model can be saved by selecting **File/Save Model**, which opens a **Save Model** dialog box, and entering a name. Note that the default is to save the model to the MATLAB workspace. Any model saved to the workspace will be lost whenever the workspace is cleared; for example, when MATLAB is shut down. Alternatively, the model can be saved directly to a file by clicking the **To File** button on the lower left of the **Save Model** dialog box. This action would prompt the user to input both a file name (for the .mat file that will be saved) and a name for the model structure that will reside in that .mat file.

Returning to the RMSECV plot for the final PCR model (Figure 6-6), note that some PCs in the final model (specifically, PCs 2, 4 and 5) actually result in an increase in the model's estimated prediction error. This result suggests that these specific PCs, although they help explain variation in the X variables (temperatures), are not relevant for prediction of the molten glass level. In the next section, we will look at a technique that will help us avoid these irrelevant factors.

Partial Least Squares

Partial Least Squares (PLS) regression (Wold *et al.*, 1984; Geladi and Kowalski, 1986; Lorber *et al.*, 1987; Martens and Næs, 1989; Höskuldsson, 1996) is related to both PCR and MLR, and can be thought of as occupying a middle ground between them. PCR finds factors that capture the greatest amount of variance in the predictor (X) variables (*e.g.,* spectra or the temperatures in the previous example). MLR seeks to find a single factor that best correlates predictor (X) variables with predicted (Y) variables (*e.g.,* concentrations or level). PLS attempts to find factors which both capture variance *and* achieve correlation. We commonly say that PLS attempts to maximize *covariance*, and this is the explicit objective of the SIMPLS algorithm for PLS.

There are several ways to calculate PLS model parameters (see, for example, de Jong, 1993). Perhaps the most intuitive method is known as NIPALS (Non-Iterative PArtial Least Squares). NIPALS calculates scores **T** and loadings **P** (similar to those used in PCR), and an additional set of vectors known as weights, **W** (with the same dimensionality as the loadings **P**). The addition of weights in PLS is required to maintain orthogonal scores.

Both the NIPALS and SIMPLS algorithms for PLS also work when there is more than one predicted variable (**Y**). In such cases of multiple Y-variables, scores **U** and loadings **Q** matrices are also calculated for the **Y**-block. A vector of "inner-relationship" coefficients, **b**, which relate the **X**- and **Y**-block scores, must also be calculated.

Using NIPALS, the scores, weights, loadings and inner-coefficients are calculated sequentially. The PLS decomposition is started by selecting one column of **Y**, $\mathbf{y}_j$, as the starting estimate for $\mathbf{u}_1$. Usually the column of **Y** with the greatest variance is chosen. Of course, in the case of univariate **y**, $\mathbf{u}_1 = \mathbf{y}$. Starting in the **X** data block:

$$\mathbf{w}_1 = \frac{\mathbf{X}^T\mathbf{u}_1}{\|\mathbf{X}^T\mathbf{u}_1\|}$$

(6-9)

$$\mathbf{t}_1 = \mathbf{Xw}_1 \qquad\qquad (6\text{-}10)$$

In the **y** data block:

$$\mathbf{q}_1 = \frac{\mathbf{Y}^T\mathbf{t}_1}{\|\mathbf{Y}^T\mathbf{t}_1\|} \qquad\qquad (6\text{-}11)$$

$$\mathbf{u}_1 = \mathbf{Yq}_1 \qquad\qquad (6\text{-}12)$$

Convergence is then checked by comparing $\mathbf{t}_1$ in Equation 6-10 with the value from the previous iteration. If they are equal within rounding error, the algorithm proceeds to Equation 6-13 below. If they are not, the algorithm returns to Equation 6-9, using the $\mathbf{u}_1$ obtained previously from Equation 6-12. If the **Y**-block is univariate, Equations 6-11 and 6-12 can be omitted, $\mathbf{q}_1$ can be set to 1, and no iteration is required.

The **X** data block loadings are then calculated, and the scores and weights are rescaled accordingly:

$$\mathbf{p}_1 = \frac{\mathbf{X}^T\mathbf{t}_1}{\|\mathbf{t}_1^T\mathbf{t}_1\|} \qquad\qquad (6\text{-}13)$$

$$\mathbf{p}_{1new} = \frac{\mathbf{p}_{1old}}{\|\mathbf{p}_{1old}\|} \qquad\qquad (6\text{-}14)$$

$$\mathbf{t}_{1new} = \mathbf{t}_{1old}\,\|\mathbf{p}_{1old}\| \qquad\qquad (6\text{-}15)$$

$$\mathbf{w}_{1new} = \mathbf{w}_{1old}\,\|\mathbf{p}_{1old}\| \qquad\qquad (6\text{-}16)$$

The regression coefficient (b) for the inner relation is then calculated:

$$b_1 = \frac{\mathbf{u}_1^T\mathbf{t}_1}{\mathbf{t}_1^T\mathbf{t}_1} \qquad\qquad (6\text{-}17)$$

After the scores and loadings have been calculated for the first factor (which is commonly called a Latent Variable in PLS), the **X**- and **Y**-block residuals are calculated as follows:

$$\mathbf{E}_1 = \mathbf{X} - \mathbf{t}_1\mathbf{p}_1{}^T \qquad\qquad (6\text{-}18)$$

$$\mathbf{F}_1 = \mathbf{Y} - b_1\mathbf{t}_1\mathbf{q}_1{}^T \qquad\qquad (6\text{-}19)$$

The entire procedure is now repeated for the next latent variable, starting with Equation 6-9. However, **X** and **Y** in Equations 6-9 through 6-12 are replaced with their residuals $\mathbf{E}_1$ and $\mathbf{F}_1$, respectively, and all subscripts are incremented by one.

148

It can be shown that PLS forms the matrix inverse defined by:

$$\mathbf{X}^+ = \mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1}(\mathbf{T}^T\mathbf{T})^{-1}\mathbf{T}^T \tag{6-20}$$

where the $\mathbf{W}$, $\mathbf{P}$, and $\mathbf{T}$ are as calculated above. Compare this expression for the pseudoinverse of the response data matrix, $\mathbf{X}^+$, to the equivalent expressions for MLR and PCR, in Equations 6-7 and 6-8, respectively. Also, note that the scores and loadings calculated in PLS are *not* the same as those calculated in PCA and PCR. They can be thought of, however, as PCA scores and loadings that have been rotated in a manner that makes them more relevant for predicting $\mathbf{y}$. As in PCR, the PLS model converges to the MLR solution if the maximum possible number of latent variables is retained in the model.

Alternatively, it can be shown that the first PLS weight vector is given by the eigenvector of $\mathbf{X}^T\mathbf{Y}\mathbf{Y}^T\mathbf{X}$ that is associated with the largest eigenvalue; *i.e.,*

$$\lambda\mathbf{w}_1 = \mathbf{X}^T\mathbf{Y}\mathbf{Y}^T\mathbf{X}\mathbf{w}_1 \tag{6-21}$$

Based on this equation, another algorithm for calculating PLS models, called SIMPLS, was developed by Sijmen de Jong (1993). This method relies on orthogonalization of a Krylof sequence to calculate the PLS weights, which is very non-intuitive but very fast and accurate. SIMPLS gives the exact same result as NIPALS PLS for univariate $\mathbf{y}$, but a slightly different solution for multivariate $\mathbf{Y}$. There is some evidence that this solution is actually slightly superior to the NIPALS PLS solution because it maximizes the covariance criterion, whereas NIPALS does not. Primarily because of its speed, SIMPLS is the default PLS algorithm used in PLS_Toolbox. However, NIPALS is available as an option. For more on SIMPLS-related algorithms, see de Jong, Wise and Ricker (2001).

If the PLS algorithm appears intimidating, do not despair. The important thing to remember is that PLS attempts to find factors (called Latent Variables) that maximize the amount of variation explained in $\mathbf{X}$ that is relevant for predicting $\mathbf{Y}$. This is in contrast to PCR, where the factors (called Principal Components) are selected solely based on the amount of variation that they explain in $\mathbf{X}$.

Because of the unique relationship between weights and loadings in a PLS model, the calculation of scores for new data does not simply involve a projection onto the loadings, as it does with PCR or PCA (i.e., $\mathbf{T}_{new} = \mathbf{X}_{new}\mathbf{P}$) . Given new data, $\mathbf{X}_{new}$, the scores for these new samples are instead calculated using:

$$\mathbf{T}_{new} = \mathbf{X}_{new}\mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1} \tag{6-22}$$

Like PCR and MLR, prediction of the y-values for new data is accomplished using Equation 6-5.

Application of PLS

PLS can be applied to our example problem of developing a model that relates the SFCM temperatures to the molten glass level. As before, we will divide the 295 samples available for training ten times, leaving a contiguous block of about thirty samples out each time. Once again, the cross-validation can be done with the **Analysis** GUI by selecting PLS in the **Analysis** menu of the main **Analysis** window. By default, PLS_Toolbox uses SIMPLS algorithm for PLS. However, the NIPALS algorithm can be performed from the command line, or specified for use in the **Analysis** window by going to **Edit/Options** in the **Analysis** window menu when "PLS" is specified under the "Analysis" menu. The interface is shown in Figure 6-7, including the variance captured table.
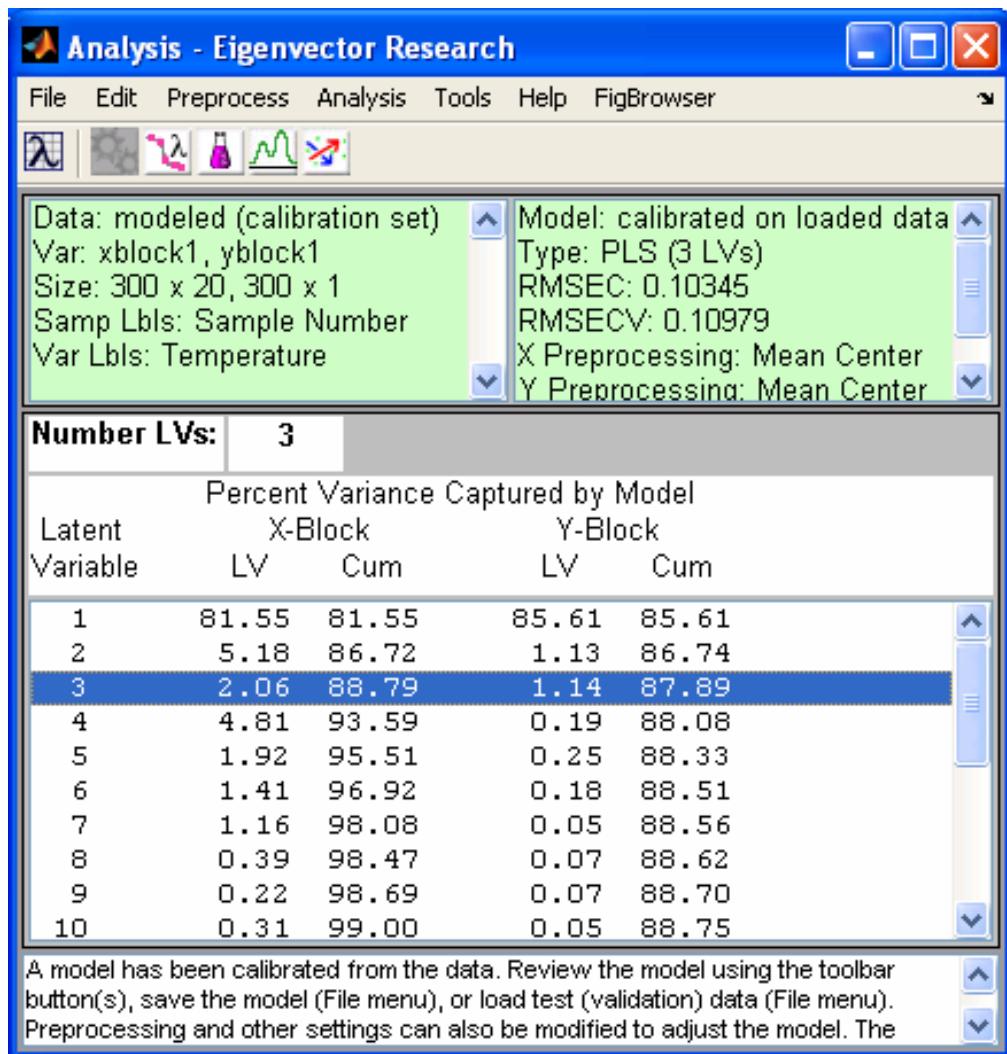
Figure 6-7. Analysis window showing PLS model.

Figure 6-8 shows the RMSECV versus number of LVs for the PLS model. Note how the RMSECV goes through an obvious minimum at four LVs, as opposed to the eleven PCs

used in the PCR model (Figure 6-6). This is typical of the behavior of PLS relative to PCR. Because PLS attempts to find factors that describe variance (like PCR) *and* achieve correlation (like MLR), PLS models tend to "converge" to the MLR solution faster than PCR models. For the same number of factors, they also tend to capture more of the relevant information in **X** (*i.e.*, the variance which is predictive of **Y**), which results in minimum RMSECV at a smaller number of factors.

Recalling our two rules of thumb with regard to selecting the optimal number of factors (namely, to only choose additional factors when the RMSECV improves by at least 2%, and to choose as few factors as possible), a three-LV PLS model makes a good final choice. This choice is also supported by the variance captured in **Y** as shown in Figure 6-7. The user can select three LVs for the model by clicking on the third line of the variance captured table, and then clicking the **Calculate** button.

As mentioned above, there are often factors in PCR models which do not contribute positively to the predictive ability of the model (*e.g.*, factors 2, 4, and 5 in our PCR example; see Figure 6-6). This happens in PCR because the factors (the PCs) are chosen without consideration of how they relate to the predicted variable. This happens much less frequently in PLS because the factors (the latent variables) *are* chosen with regard to how correlated the factor scores are to the predicted variable.

One could form an "altered" PCR model by leaving out these seemingly irrelevant factors. The technique of Correlation PCR does this by re-ordering the factors in order of Y-block variance captured. Most research results, however, have not shown convincingly that this is a good thing to do. Although reordering the factors allows selection of only those which provide the most significant Y-block information, it rarely provides a model which does as well as a PLS model. In fact, Correlation PCR will only do better when the Y-block measurements contain a significant amount of noise or other errors which "distract" the PLS algorithm. Interestingly, under these conditions it is also virtually impossible to prove that Correlation PCR is doing better.
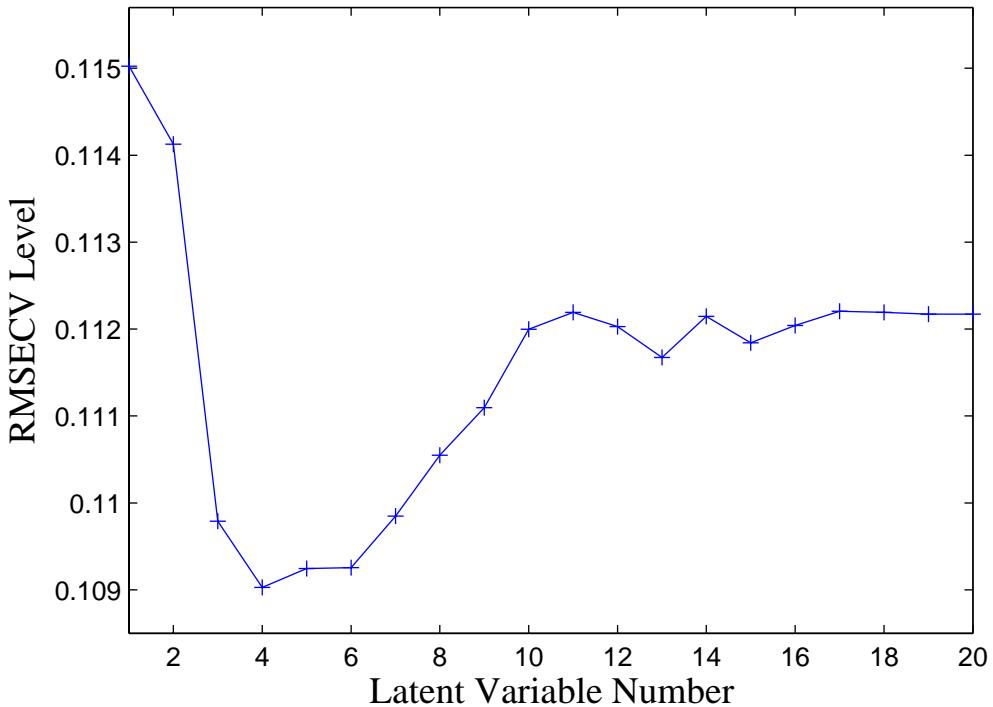
Figure 6-8. RMSECV for PLS on SFCM data.

We can compare the regression vectors calculated by PLS and PCR (not Correlation PCR) with the regression vector calculated by MLR, as shown in Figure 6-9. (In the model structure that is saved via the **File/Save Model** command in the **Analysis** window, the regression vectors are stored in the model.reg field.) It can be seen that the MLR regression coefficients vary considerably from variable to variable, switching from positive to negative and back several times. This "ringing" in the coefficients is typical of models produced by MLR when the problem is ill-conditioned due to the covariance of the data. Note how the PLS and PCR models have coefficients that are muchsmoother. In fact, the PLS and PCR models make more sense from a physical standpoint. Because of the close physical proximity of the temperature sensors in this system, we would expect adjacent sensors to respond similarly, and therefore would not expect the relationships between adjacent sensors and the level to be opposite of one another, as the MLR model coefficients suggest. Also, prior engineering knowledge of the SFCM system predicts that the molten glass level changes should have the largest effect on variables 6–8 and 16–18. These variables have the largest coefficients in the PLS and PCR models, which makes good physical sense. In contrast, the largest coefficients in the MLR model are where the PLS and PCR coefficients are very close to zero. These results suggest that the MLR model might be overfit, in that it is attempting to explain noise in the temperature data that is coincidentally correlated to the level.
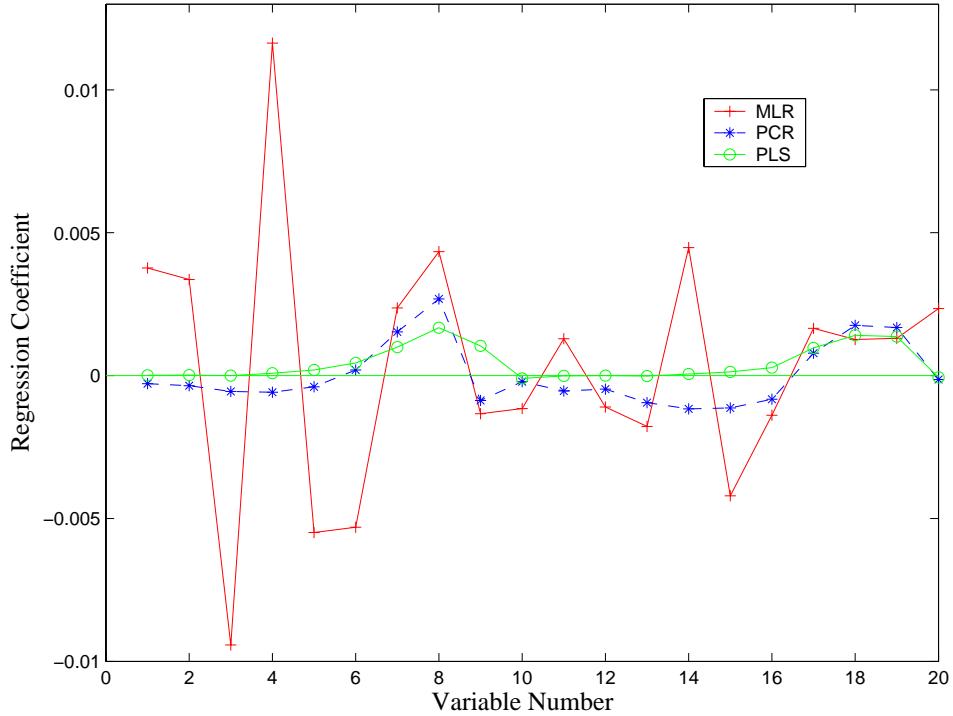
Figure 6-9. Regression coefficients in MLR, PCR, and PLS models of SFCM data.

Ridge Regression

Ridge regression (RR), essentially a modification of the MLR method, is another technique for dealing with ill-conditioned data. Ridge regression gets its name because a constant is added to the "ridge" of the covariance matrix in the process of forming the pseudoinverse:

$$\mathbf{X}^+ = (\mathbf{X}^T\mathbf{X} + \mathbf{I}\Theta)^{-1}\,\mathbf{X}^T \qquad\qquad (6\text{-}23)$$

Note the difference between this expression of the pseudoinverse and that of the MLR method in Equation 6-7. The addition of the constant Θ to the ridge has the effect of making a potentially ill-conditioned covariance matrix ($\mathbf{X}^T\mathbf{X}$) "look" more like the identity matrix, which is a perfectly-conditioned matrix. As a result, this addition stabilizes the values of the coefficients determined from the regression. It also has the effect of shrinking the coefficients (*i.e.*, decreasing their magnitude). It has been shown (Draper and Smith, 1981) that the regression vector calculated from ridge regression is the least squares solution subject to the constraint that the vector is confined to a sphere centered around the origin. Thus, in some sense, RR assumes that the regression coefficients are more likely to be small (near zero) than large. Note that it is also possible to impose a non-spherical constraint on the regression vector by using a specific diagonal matrix instead of the identity matrix in Equation 6-23. This is often useful when one knows that certain coefficients are more likely to be close to zero than others.

Ridge regression is also used quite often when one is concerned with the values of the regression coefficients themselves, rather than in prediction. If one can derive needed information from the coefficients themselves, RR can be an appropriate choice.

The trick in ridge regression is to determine the optimum value of Θ for developing a predictive model. A common statistical method was outlined by Hoerl *et al.* (1975). It is also possible to determine the optimum value through cross-validation.

Application of Ridge Regression

As an example of the use of ridge regression, we will now revisit the SFCM data used in the examples of PCR and PLS. We will use the PLS_Toolbox functions `ridge`, which uses the method of Hoerl and Kennard, and `ridgecv`, which uses cross-validation to develop RR models. We will consider values of the ridge constant (Θ) from 0 to 0.015 at thirty-one different levels, so that we can see the effect of Θ on the coefficients. For cross-validation, we will split the data ten ways (please see the function help files or the reference manual for input/output specifications).

```
» [brr1,theta1] = ridge(mx,my,0.015,31);
» [brr2,theta2,cumpress] = ridgecv(mx,my,0.015,31,10);
```

The regression coefficients are shown as a function of the ridge parameter in Figure 6-10. Note how the values shrink as the value of Θ is increased. The value of the ridge parameter using the method of Hoerl and Kennard is 0.0074, while the value determined using the cross-validation procedure outlined above is 0.0073. The regression coefficients are compared with those determined from MLR in Figure 6-11. Note how the regression coefficients have been shrunk in RR as compared to MLR, but are still quite similar to the MLR solution, in a qualitative sense.
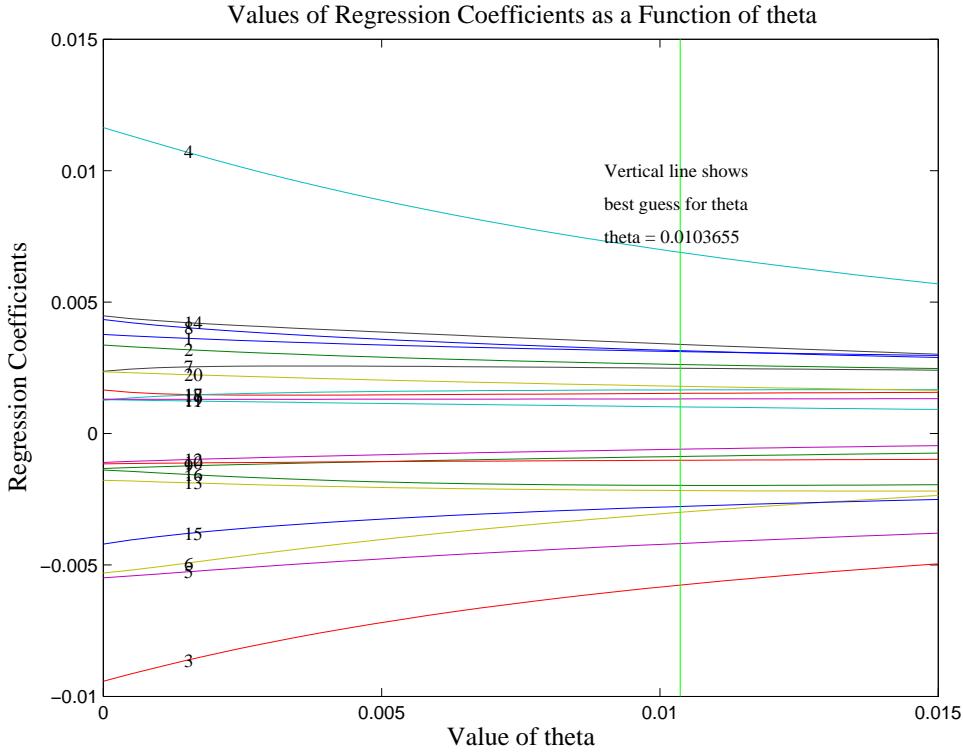
Figure 6-10. Value of the regression coefficients as a function of Θ for SFCM data.

Comparison of Regression Models on SFCM Example

Of course, in the SFCM example, the real reason for forming the regression models is to make predictions of the SFCM level given the temperatures in the event of a failure of the level instrument, or to provide a redundant check on the performance of the instrument. Thus, the best test of the models is their ability to predict the level given new temperature measurements.

Before comparing the predictive ability of the models, it is useful to review several quality measures. In all of the measures considered, we are attempting to estimate the average deviation of the model from the data. The root-mean-square error of calibration (RMSEC) tells us about the fit of the model to the calibration data. It is defined as:

$$\text{RMSEC} = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{n}} \tag{6-24}$$

where the $\widehat{y}_i$ are the values of the predicted variable when all samples are included in the model formation and n is the number of calibration samples. RMSEC is a measure of how well the model fits the data.

155
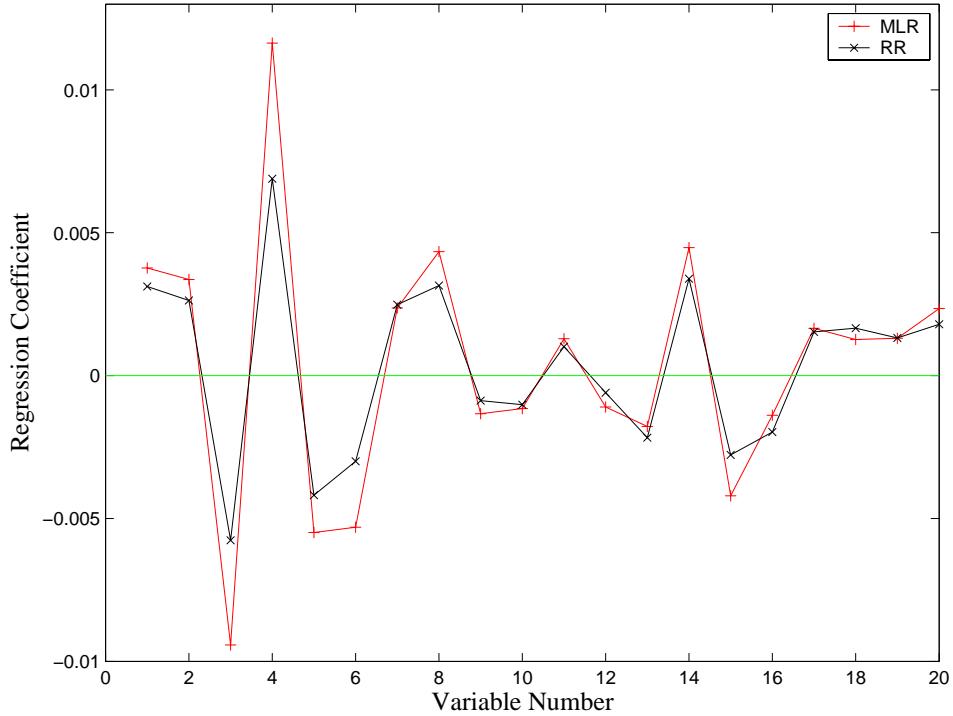
Figure 6-11. Regression coefficients in MLR and RR models of SFCM data.

This is in contrast to the previously mentioned root-mean-square error of cross-validation (RMSECV) which is a measure of a model's ability to predict samples that were not used to build the model. The RMSECV can also be defined using Equation 6-24, where the $\widehat{y}_i$ corresponds to predictions for samples that were not included in the model formulation. Another measure that was mentioned in the cross-validation discussion, the Predicted Residual Error Sum of Squares (or PRESS), is related to the RMSECV as follows:

$$\text{RMSECV}_k = \sqrt{\frac{\text{PRESS}_k}{n}}$$

$$(6\text{-}25)$$

where k refers to the number of factors (PCs, LVs) used in the model, and n is the number of calibration samples. PRESS_k is the sum of squared prediction errors for the model which includes k factors. Of course, the exact value of RMSECV depends not only on k, but on how the cross-validation test sets were formed. It is also common to calculate PRESS, and thus RMSECV, for a "leave one out" cross-validation (*i.e.*, where each sample is left out of the model formulation and predicted once).

The RMSECV and PRESS measures typically refer to cross-validation experiments, where the existing calibration data set is split into different training and test sets in an effort to assess how a model built using all of the calibration data would perform when applied to new data. Alternatively, one could designate a completely independent prediction set of samples that have known Y values, so that such an assessment can be done directly, In this case, one can calculate a root-mean-square error of prediction (RMSEP) when the model is applied to new data. RMSEP is calculated exactly as in

Equation 6-24, except that the estimates $\hat{y}_i$ refer to samples in the independent prediction set, which were not involved in either model building or cross-validation.

The MLR, PCR, PLS, and RR models developed for the SFCM example can now be compared using the measures just introduced. Predictions can be made in the **Analysis** window by loading new X-block data, then clicking **Calculate**. The predictions can be saved to the workspace (or to a file) by selecting **File/Save Prediction**. This information is summarized in Table 6-1. An independent data set of 200 samples not used for model building was used for the calculation of RMSEP.

Table 6-1. Comparison of RMSEC, RMSECV and RMSEP on MLR, PCR, PLS and RR models of SFCM temperature and level data.

	MLR	PCR	PLS	RR
RMSEC	0.0991	0.1059	0.1034	0.0996
RMSECV	0.1122	0.1108	0.1098	0.1122
RMSEP	0.1496	0.1366	0.1396	0.1471

Note how the MLR model shows the smallest value for RMSEC, the error of *calibration*. This indicates that, as expected, the MLR model fits the data best. Note, however, from the RMSECV that the MLR does not predict the best, even for samples within the original calibration data. The PLS model produces the lowest cross-validation error (RMSECV). For the prediction on new samples, the PCR model outperforms the other models, with PLS a close second. In practice, PCR and PLS generally have similar performance; the main advantage of PLS is often computational speed. In addition, PLS models generally require fewer factors than PCR models for the same set of data (see next section), which has advantages in both model implementation and model interpretation.

It should be evident from the comparison of models that *fit* and *prediction* are entirely different aspects of a model's performance. If prediction is the goal, a model should be built with this criterion in mind. The calculation of PRESS from a cross-validation procedure is one way to measure a model's predictive ability.

Detecting and Dealing with Outliers

Recall that in the previous examples where we used MLR, PCR, PLS and RR to model the SFCM data, we started by removing outliers from the data. We'll now re-work the problem from the beginning, with all of the data included. Load the `plsdata.mat` file and start **Analysis** preset to PLS by typing `pls` at the prompt. Load the `xblock1` and `yblock1` DataSet Objects into the **Analysis** window. Select mean-centering for the X-block by selecting **Preprocess/X-block/Mean Center**. Calculate a preliminary model by pressing **Calculate**. Select 3 LVs by clicking the 3rd line of the variance captured table, and then click **Calculate**. The **Analysis** interface should now match the one shown in Figure 6-12.

Click the **Scores** button and use the **Plot Controls** window to make a plot of the **Scores on LV 2** versus **Scores on LV 1**. Add axis lines with the **Plot Controls** window **View/Axis Lines/All** menu. Add 95% confidence limits by checking the box in the **Plot Controls** window. The resulting scores plot should look like Figure 6-13. This scores plot is the first indication that there may be unusual samples in the data. We can find out more about the sample in the upper left of this scores plot by clicking **info** in the **Plot Controls** window and then clicking on the point in the plot. Information about the sample that corresponds to that point comes up in a separate window, as shown in Figure 6-14.
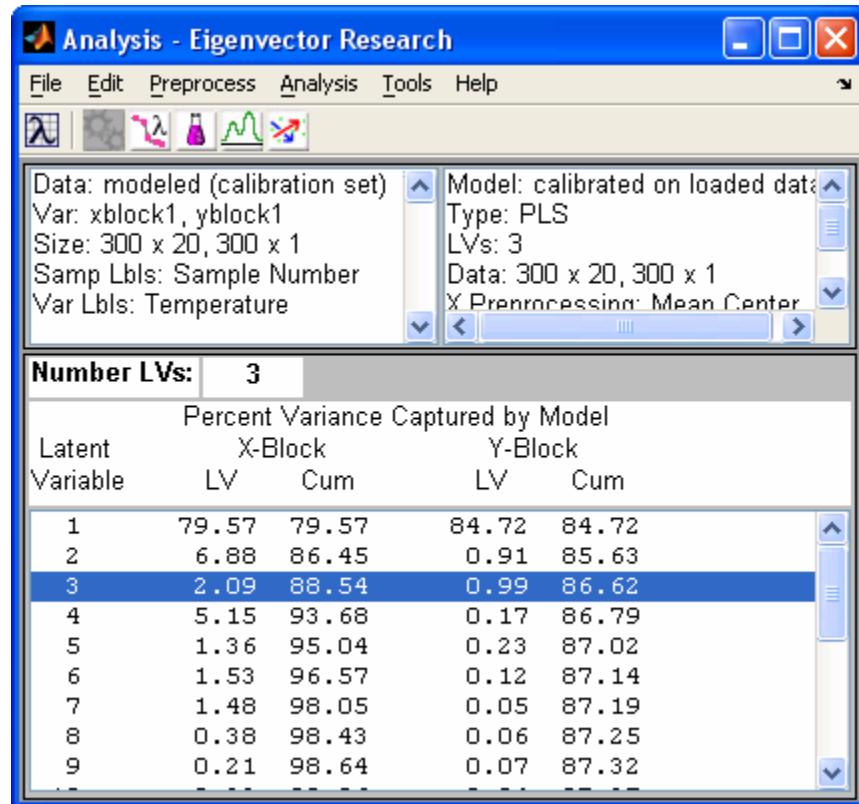
Figure 6-12. Analysis window showing PLS model of SFCM data.

158
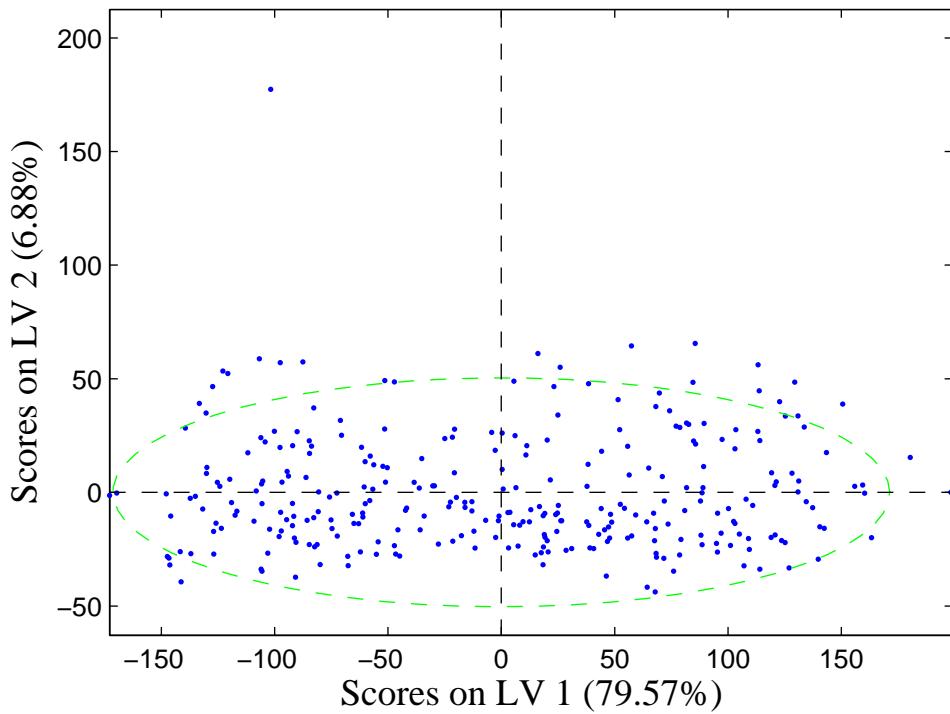
Figure 6-13. Scores plot from SFCM data with outliers included.
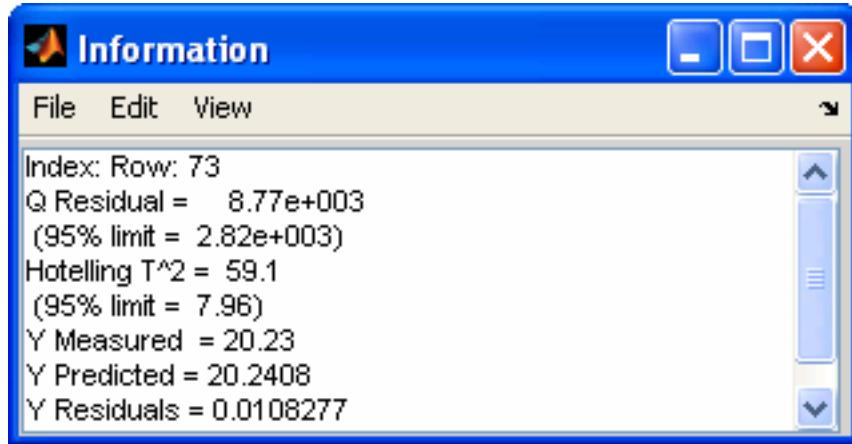
Figure 6-14. Information window for sample 73.

The information window indicates that Sample 73 is indeed unusual, with very large Q Residual and T^2 values compared to the 95% limits. Thus, plots of all the available PLS scores, as well as plots of the sample-wise Hotelling T^2 and Q Residual statistics, can be quite useful for detecting samples that are unusual due to "extreme" values in their X data. Similarly, plots of the available PLS loadings, and variable-wise T^2 and Q statistics (obtained by clicking on the **Loadings** button on the **Analysis** window) can be useful for determining unusual X-variables.

In PLS (and PCR) regression, one can also look for sample outliers in the predicted (Y) data, using the **Y Studentized Residual** versus **Leverage** plot, which can be made by

selecting the proper options in the **Plot Controls** window. In the example, this plot should look like Figure 6-15. Note that, in this plot, the samples that were excluded from the original analyses of these data are highlighted, which indicates that they have been selected. In order to select samples, first click on the **Select** button on the **Plot Controls** window, then use the rubber band box on the figure to select them. Multiple selections can be made by holding down the shift key.
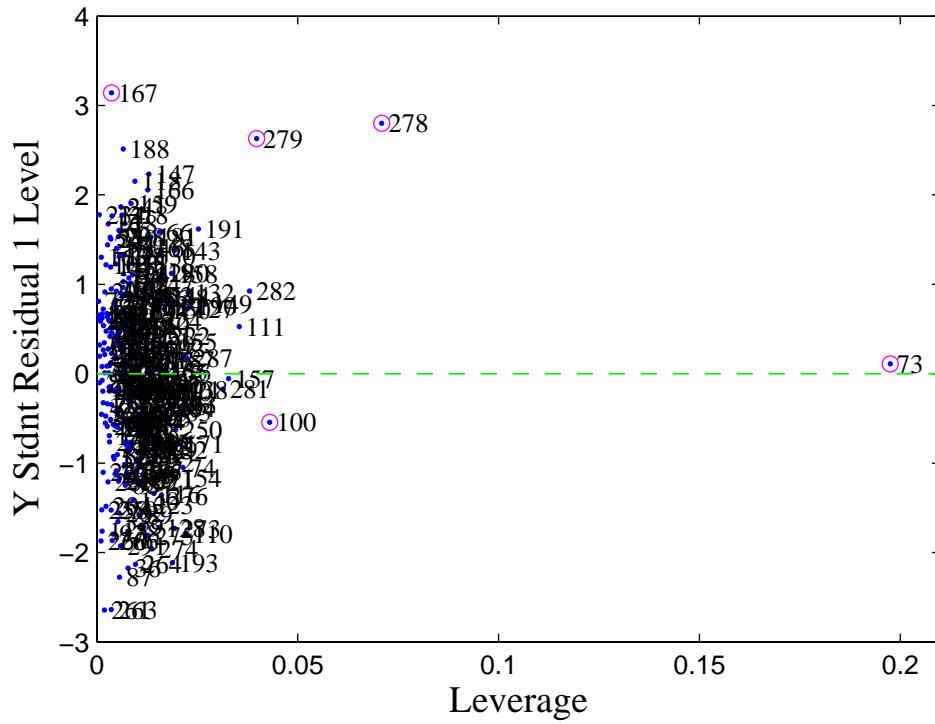
Figure 6-15. Studentized residuals versus leverage for SFCM data.

Leverage defines the influence that a given sample will have on a model, and is related to the Hotelling T^2 value. The studentized residual is an indication of the lack of fit of the y-value of a sample. To "studentize" something means to make it mean zero and unit variance. Thus, the X-axis scale on Figure 6-15 can be interpreted as the number of standard deviations of error in a sample's y-value. The upper-most sample, number 167, has an error with a standard deviation of greater than 3, which is quite large. This suggests that the "known" y-value associated with this sample may be in error, as there is no other indication that this sample is unusual (see, for instance, where this sample falls on a plot of Q versus T^2).

The right-most sample, number 73, has a very high leverage, but a very low studentized Y Residual . Although this sample has a rather unique profile of temperature readings (X-values), when compared to all the other samples, the PLS model is still able to sufficiently predict its level (Y-value). In general, samples with very high leverage also tend to have very low calibration residuals, because they have influenced the model so greatly.

160

The most unusual sample in this data set is probably number 278, as it has both a very high leverage and a high residual. This suggests that the sample could have a lot of "bad" influence on the model, due to both its very unique temperature readings (X-values) and the relative inability of the PLS model to predict its level (Y-value). This can be checked by making a plot of **Y CV Residual** versus **Y Residual** using the **Plot Controls** window. The result is shown in Figure 6-16, where a line of slope 1 has been added by executing *dp* at the command line. Sample 278 is the uppermost sample on the plot, and is also the sample with the greatest deviation from the line. Not only does this sample have one of the largest Y-residuals (distance of the point from the origin in this plot), but it also has the largest difference between its calibration residual (where it is included in the model formation) and its cross-validation residual (where it is not included in the model formation). This result further suggests that this sample does not "fit" well with the rest of the data, with respect to both its X-data and its Y-data. Note that it is normal for points on this plot to have a slope slightly greater than 1, as samples generally have a smaller calibration residual than cross-validation residual.
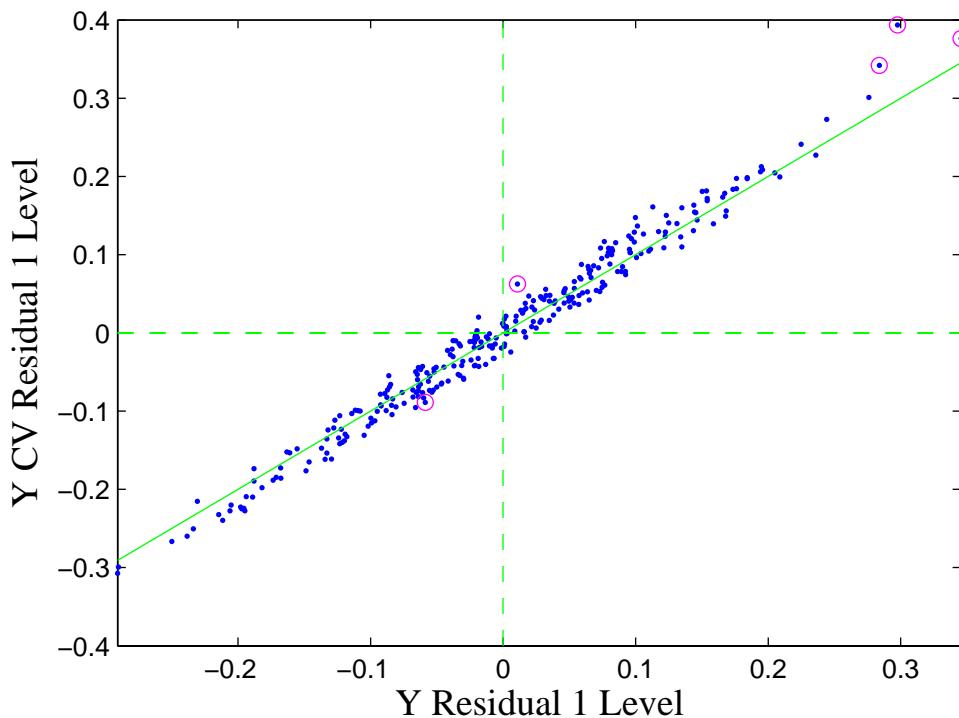
Figure 6-16. Cross-validated Y residual versus Y calibration residual.

Now that we have identified a number of unusual samples, the question becomes: what do we do with them? In this example, the answer is fairly obvious, because we have plenty of normal samples and the unusual samples appear to be the result of either abnormal conditions in the SFCM or errors in the reference (level) values. This suggests that we can delete the samples with little fear that, in doing so, we will eliminate critical information from the model. This choice is not always so simple, however. In many cases, unusual samples represent perfectly normal process states that are merely underrepresented, and the better choice would be retain these samples, and attempt to

collect more samples that are similar to them. Generally, the choice of whether or not to remove an outlier must be made based not only on the statistics involved but on the knowledge and experience of the user.

In this case, the model can easily be rebuilt without the suspect samples by selecting them, as we have already done, then choosing **Edit/Exclude Selection** in the **Plot Controls** window when the **Scores** are the active figure. Note that this causes the model information to disappear from the main Analysis window, because the data it was based on have been edited. The model can now be rebuilt without the suspect data.

Continuum Regression

PCR, PLS and MLR have all been unified under the single technique Continuum Regression (CR) (Stone and Brooks, 1990; Wise and Ricker, 1993, de Jong, Wise and Ricker, 2001). CR is a continuously adjustable technique which encompasses PLS and includes PCR and MLR at opposite ends of the continuum, as shown in Figure 6-17. When using CR, cross-validation must be done to determine both the number of factors and the technique within the continuum that produces the optimum model (*i.e.,* the model that predicts most accurately when used with new data).
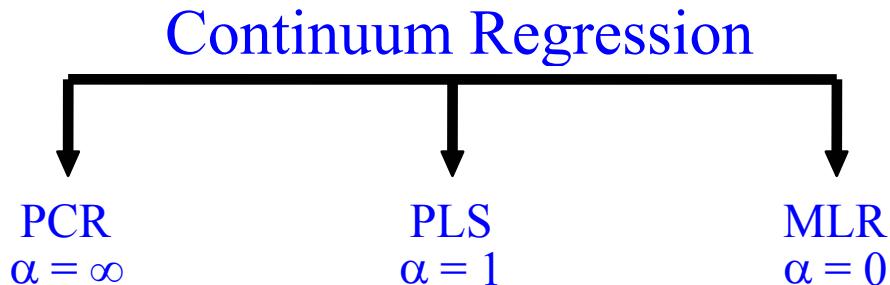
Figure 6-17. Relationship between PCR, PLS, MLR and CR.

There are several interesting implementations of CR. Here we will consider a method that is fairly easily understood, though not particularly efficient. The first step in the CR method is to perform a singular value decomposition (SVD) on the matrix of predictor variables **X** (m by n)

$$\mathbf{X} = \mathbf{U}\,\mathbf{S}\,\mathbf{V}^{\mathrm{T}} \qquad\qquad (6\text{-}26)$$

where **U** (m by m) and **V** (n by n) are orthonormal matrices and **S** (m by n) is diagonal (*i.e.,* zero everywhere except on the matrix diagonal). The elements of **S** are known as the *singular values,* and are placed in **S** in descending order (*i.e.,* $s_{11} \geq s_{22} \geq s_{33}$ and so on). The SVD is closely related to PCA. In fact, the eigenvectors or loadings **P** are identical to **V**, that is:

$$\mathbf{V} = \mathbf{P} \qquad\qquad (6\text{-}27)$$

The relation between the PCA scores $\mathbf{T}$ and the SVD model parameters $\mathbf{U}$ and $\mathbf{S}$ is

$$\mathbf{U\,S} = \mathbf{T} \qquad\qquad (6\text{-}28)$$

In fact, the PCA model proposed in Equation 5-2 can be written as

$$\mathbf{X} = \mathbf{T}_k\mathbf{P}_k^{\mathrm{T}} + \mathbf{E} = \mathbf{U}_k\mathbf{S}_k\mathbf{V}_k^{\mathrm{T}} + \mathbf{E} \qquad\qquad (6\text{-}29)$$

The next step in CR is to form the matrix $\mathbf{S}^\alpha$ by taking each of the singular values to the desired power, α. The new $\mathbf{X}$ block, defined as $\mathbf{X}^\alpha$, is then formed as follows:

$$\mathbf{X}^\alpha = \mathbf{U\,S}^\alpha\,\mathbf{V}^{\mathrm{T}} \qquad\qquad (6\text{-}30)$$

The PLS algorithm described earlier can now be used along with the matrix inverse defined by Equation 6-20 to produce a regression vector, $\mathbf{r}$, for any number of latent variables desired. That is

$$\mathbf{r} = \mathbf{W}(\mathbf{P}^{\mathrm{T}}\mathbf{W})^{-1}(\mathbf{T}^{\mathrm{T}}\mathbf{T})^{-1}\mathbf{T}^{\mathrm{T}}\mathbf{y} \qquad\qquad (6\text{-}31)$$

The regression vector obtained is not properly scaled because of the re-scaled $\mathbf{X}$ block. Any regression vector, $\mathbf{r}$, can be re-scaled, however, by projecting it onto the SVD basis set $\mathbf{V}$ and multiplying by the ratios of the singular values used in Equation 6-19 to the original singular values calculated in Equation 6-26. Thus:

$$\mathbf{r}_{\mathrm{scl}} = \mathbf{r\,V\,S}_{\mathrm{scl}}\,\mathbf{V}^{\mathrm{T}} \qquad\qquad (6\text{-}32)$$

where

$$\mathbf{S}_{\mathrm{scl}} = \mathbf{S}^\alpha\,./\,\mathbf{S} \qquad\qquad (6\text{-}33)$$

where the symbol "./" indicates term-by-term division of the non-zero elements of the singular value matrices.

The continuum regression algorithm converges, mathematically at least, to the PCR solution for large α and to MLR for $\alpha = 0$. In practice, there are some numerical difficulties encountered when taking the singular values to high powers. The CR algorithms included in PLS_Toolbox are typically stable up to a power of ~8, depending upon the problem. However, at this power, the solution has essentially converged to the PCR solution and obtaining a solution for higher powers is of little use.

The CR algorithm described above can be understood in terms of "stretching" the space of the predictor variables. When the singular values are taken to a power greater than 1, the resulting matrix $\mathbf{X}^\alpha$ is stretched relative to $\mathbf{X}$ in such a way the directions of greatest variance in $\mathbf{X}$ have even greater relative variance in $\mathbf{X}^\alpha$; that is, the rich get richer and the poor get poorer. Because PLS attempts to capture variance along with correlation, making the $\mathbf{X}$ matrix more "directional" causes the PLS algorithm to produce latent variables that are more closely aligned with the principal components of the original $\mathbf{X}$.

As the power m goes to 0, $\mathbf{X}^\alpha$ becomes less directional, with all directions coming closer to having equal variance. With no "preferred" direction for capturing variance, the PLS algorithm will capture correlation only, producing the MLR solution.

The application of CR to the SFCM temperature and level data will serve as our example. Cross-validation was used to find the optimal model within the CR parameter space. The powers investigated spanned the range of 0.25 to 4. The crcvrnd function was used to cross-validate using a 10-way split of the data, a single iteration, and twenty latent variables as follows (please see reference section for explanation of input/output syntax):

```
» powers = 10.^[-1:.05:1];
» [press,fiterr,minlvp,b] = crcvrnd(mx,my,10,1,20,powers,1);
```

The resulting PRESS surface is plotted in Figure 6-18. Inspection of this PRESS surface would probably lead one to select the PLS model originally chosen. There is a clear area of good models near the PLS model with four latent variables.
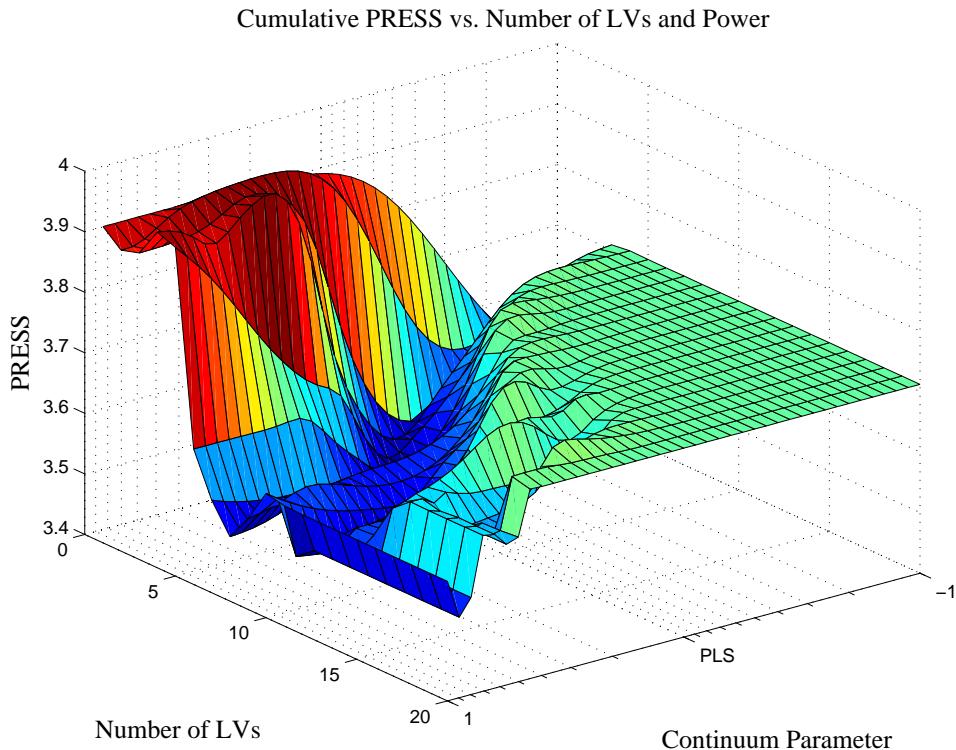
Figure 6-18. Continuum Regression cross-validation PRESS surface for SFCM data.

We can also look at the CR prediction error surface, which is shown in Figure 6-19. Here we see that the model with power = 4 and six LVs is a very good model. This model is nearly equivalent to our PCR model with six PCs. The very best model on the test set was at a power of 0.595 with two LVs. This model had an RMSEP of 0.1362 compared to 0.1366 for our six-PC PCR model and 0.1396 for our three-LV PLS model. (Although this difference is probably not statistically significant, it is consistent with experience.)

164

Much work remains to be done with CR. The example here exemplifies some of the problems with selection of a final model. In some instances the selection will be fairly clear, and often, the best models are found at powers above or below 1. The `crcvrnd` function can be used to do repeated cross-validations using different orderings of the data set. Often this will produce smoother, more interpretable PRESS surfaces. The authors of PLS_Toolbox would be very interested in hearing about your experience with CR.
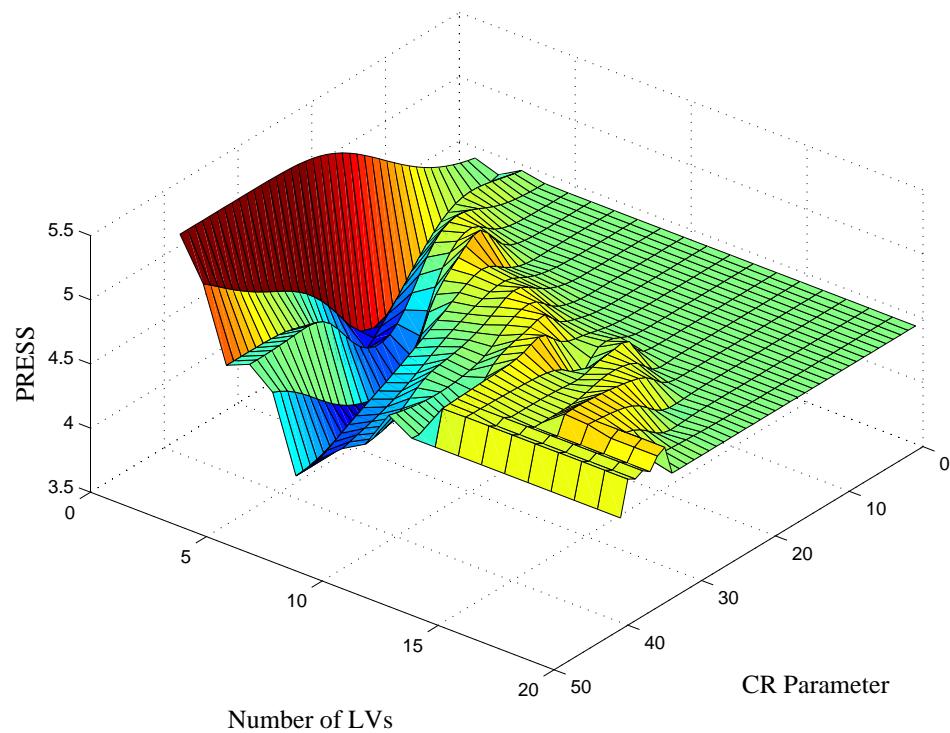
Figure 6-19. Continuum Regression prediction PRESS surface for SFCM data.

7. Advanced Preprocessing

So far, we have dealt with only basic preprocessing of data for use in PCA and regression, including centering and variance scaling. Often, however, it is useful to do other types of preprocessing, such as taking derivatives of spectra. Preprocessing is, in general, the modification of data done before building a model or otherwise analyzing those data. The purposes of preprocessing are to linearize the response of the variables and to remove extraneous sources of variation (variance) which are not of interest in the analysis. Linearization is often important because (1) many modeling methods expect linear response and, (2) in general, linear responses are easier to model than non-linear ones. Similarly, interfering sources of variance can cause increased difficulty in modeling. Interfering variance appears in almost all real data because of systematic errors present in experiments. This unwanted variance will require the model to work harder (expend degrees of freedom) to isolate the variance of interest from the interfering variance.

A variety of preprocessing methods are available in PLS_Toolbox. This chapter describes some basic information on the methods available to the user both in the Preprocessing GUI and from the corresponding command line functions. Advanced users are encouraged to read the help documentation for the command line functions and for the functions referenced under "See also" therein.

Preprocessing GUI

Many tools in PLS_Toolbox allow for a number of advanced preprocessing techniques to be used through the `preprocess` function. This can be accessed from the **Analysis** window by selecting **Preprocess/X-Block/Custom** or **Y-Block/Custom**, which brings up the interface shown in Figure 7-1. Techniques may be selected from the list on the left and moved into the list to execute on the right. Some techniques have adjustable parameters which can be viewed and modified by selecting the preprocessing step in the Selected Methods list and clicking on **Settings….** The settings for the method will be displayed in a dialog box. As an example, the **Savitzky-Golay** derivative preprocessing settings consist of the window width, polynomial order, and derivative order. In **Autoscale** an optional scaling offset can be used to avoid "blowing up" the noise on variables with very little variance.
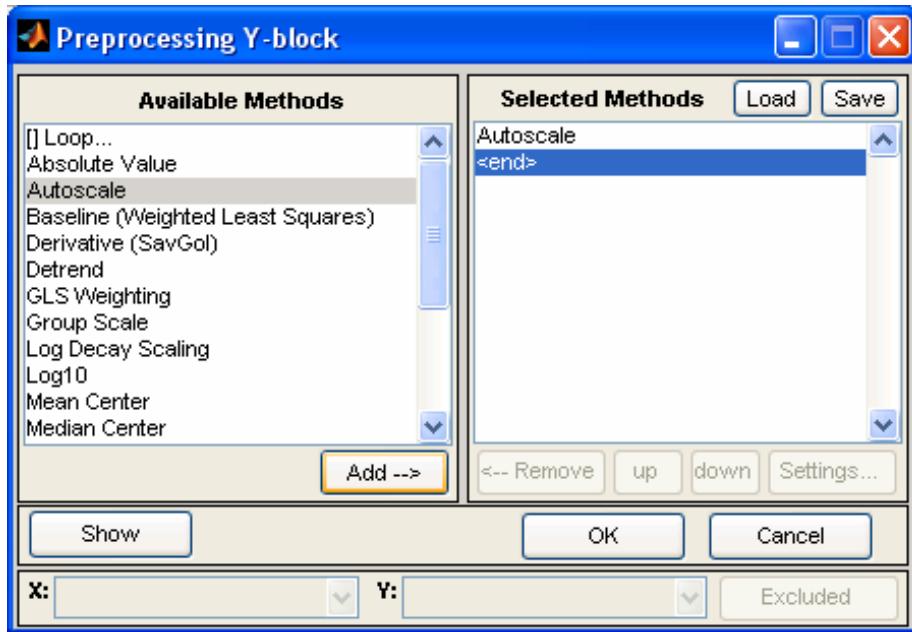
Figure 7-1. Advanced Preprocessing interface.

It is also important to specify the order in which preprocessing steps are to be done. For instance, in some pattern recognition problems, it would be natural to normalize the responses to vectors of unit length, then autoscale the results prior to performing PCA. The order of preprocessing steps can be changed by selecting a step in the Selected Methods list and clicking the **up** or **down** buttons to change the method's position in the list. See the discussion below for more information on order in preprocessing.

The `preprocess` function can also be invoked from the command line as follows:

```
» s = preprocess;
```

which will bring up the interface shown in Figure 7-1. After the preprocessing steps are selected and parameterized, click OK to close the interface. A structure describing the preprocessing will be stored in `s`. This structure may be passed to command line calls for tools such as `pca` and `pls` as part of their options structure, allowing for the easy integration of advanced preprocessing with user-defined scripts.

Notes about Preprocessing Order

Given the wide variety of preprocessing options available and the goals of each, it is of particular interest to consider the order in which preprocessing is applied. This order is completely customizable by the user, but there are some basic rules to follow.

In general, it is desirable to perform "row-wise" (sample-based) methods prior to any "column-wise" (variable-based) methods.

168

A row-wise method is one that acts on each sample one at a time (see, for example, normalization and derivatization, below). These methods are typically used to remove unwanted variance from individual samples. The effect on any individual sample is independent of the other samples in the data.

In contrast, column-wise methods act on variables of the data (see, for example, centering and scaling). These methods numerically prepare the data for modeling and are thus usually the last methods applied before modeling. These methods often assume that any variance in the data is of interest and use and, as such, is important.

During the following discussion, notes will be included with each topic when there is a deviation or special case in the order that it might be applied.

Noise, Offset, and Baseline Filtering

A variety of methods exist to remove high- or low-frequency interferences (where frequency is defined as change from variable to variable). These interferences, often described as noise (high frequency) or background (low frequency) are common in many measurements but can often be corrected by taking advantage of the relationship between variables in a data set. In many cases, variables which are "next to" each other in the data matrix (adjacent columns) are related to each other and contain similar information. These noise, offset, and baseline filtering methods utilize this relationship to remove these types of interferences.

Noise, offset, and baseline filtering methods are usually performed fairly early in the sequence of preprocessing methods. The signal being removed from each sample is assumed to be only interference and is generally not useful for numerical analyses. One exception to this is when normalization is also being performed. In these cases, it sometimes occurs that a background or offset being removed is fairly constant in response and is, therefore, useful in correcting for scaling errors. For more information, see the normalization methods described below.

Note that these methods are not relevant when working with variables which do not have this similarity, such as process variables, genetic markers, or other highly selective or discrete variables. For such variables, use of multivariate filtering methods (described later) may be of use for removing interferences.

Smoothing (SavGol)

Smoothing is a low-pass filter used for removing high-frequency noise from samples. Often used on spectra, this operation is done separately on each row of the data matrix and acts on adjacent variables. Smoothing assumes that variables which are near to each other in the data matrix (*i.e.*, adjacent columns) are related to each other and contain similar information which can be averaged together to reduce noise without significant loss of the signal of interest.

The smoothing implemented in PLS_Toolbox is the Savitzky-Golay (SavGol) algorithm (Savitzky and Golay, 1964). The algorithm essentially fits individual polynomials to windows around each point in the spectrum. These polynomials are then used to smooth the data. The algorithm requires selection of both the size of the window (filter width) and the order of the polynomial. The larger the window and lower the polynomial order, the more smoothing that occurs. Typically, the window should be on the order of, or smaller than, the nominal width of non-noise features.. Note that the same algorithm is used for derivatives (see below) and can be converted from one into the other by changing the derivative order setting.

From the command line, this method is performed using the `savgol` function.

Derivative (SavGol)

Derivatives are a common method used to remove unimportant baseline signal from samples by taking the derivative of the measured responses with respect to the variable number (index) or other relevant axis scale (wavelength, wavenumbers, etc.) Derivatives are a form of high-pass filter and frequency-dependent scaling and are often used when lower-frequency (*i.e.*, smooth and broad) features such as baselines are interferences and higher-frequency (*i.e.*, sharp and narrow) features contain the signal of interest. This method should be used only when the variables are strongly related to each other and adjacent variables contain similar correlated signal.

The simplest form of derivative is a point-difference first derivative, in which each variable (point) in a sample is subtracted from its immediate neighboring variable (point). This subtraction removes the signal which is the same between the two variables and leaves only the part of the signal which is different. When performed on an entire sample, a first derivative effectively removes any offset from the sample and de-emphasizes lower-frequency signals. A second derivative would be calculated by repeating the process, which will further accentuate higher-frequency features.

Because derivatives de-emphasize lower frequencies and emphasize higher frequencies, they tend to accentuate noise (high frequency signal). For this reason, the Savitzky-Golay algorithm is often used to simultaneously smooth the data as it takes the derivative, greatly improving the utility of derivatized data. For details on the Savitzky-Golay algorithm, see the description for the smoothing method, above.

As with smoothing, the Savitzky-Golay derivativization algorithm requires selection of the size of the window (filter width), the order of the polynomial, and the order of the derivative. The larger the window and lower the polynomial order, the more smoothing that occurs. Typically, the window should be on the order of, or smaller than, the nominal width of non-noise features which should not be smoothed. Note that the same algorithm is used for simple smoothing (see above) and can be converted from one into the other by changing the derivative order setting.

An important aspect of derivatives is that they are linear operators, and as such, do not affect any linear relationships within the data. For instance, taking the derivative of

absorbance spectra does not change the linear relationship between those data and chemical concentrations.

Figure 7-2 shows the results of first and second derivativization on the near-IR spectra of corn. Notice that taking the first derivative has removed the predominant background variation from the original data. The smaller variations remaining are due to the chemical differences between samples.
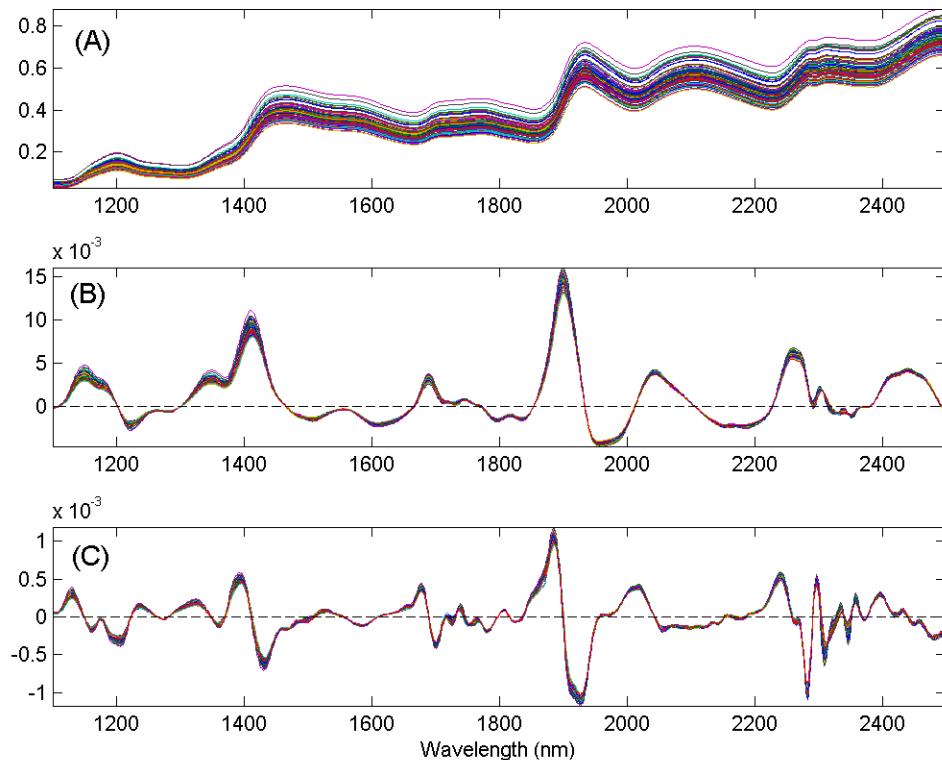
Figure 7-2. NIR spectra of corn (A), the first derivative of the spectra (B), and the second derivative of the spectra (C).

Note that at the end-points (and at excluded regions) of the variables, limited information is available to fit a polynomial. The SavGol algorithm approximates the polynomial in these regions, which may introduce some unusual features, particularly when the variable-to-variable slope is large near an edge. In these cases, it is preferable to exclude some variables (*e.g.*, the same number of variables as the window width) at the edges.

From the command line, this method is performed using the `savgol` function.

Detrend
In cases where a constant, linear, or curved offset is present, the Detrend method can sometimes be used to remove these effects (see, for example, Barnes et al., 1989).

Detrend fits a polynomial of a given order to the entire sample and simply subtracts this polynomial. Note that this algorithm does not fit only baseline points in the sample, but fits the polynomial to all points, baseline and signal. As such, this method is very simple to use, but tends to work only when the largest source of signal in each sample is background interference.

In measurements where the variation of interest (net analyte signal) is a reasonably significant portion of the variance, Detrend tends to remove variations which are useful to modeling and may even create non-linear responses from otherwise linear ones. In addition, the fact that an individual polynomial is fit to each spectrum may increase the amount of interfering variance in a data set. Due to these reasons, use of Detrend is recommended only when the overall signal is dominated by backgrounds which are generally the same shape and are not greatly influenced by chemical or physical processes of interest. In general, derivatives tend to be far more amenable to use before multivariate analysis.

Figure 7-3 shows the effect of Detrend on the corn near-IR data. Note that the general linear offset is removed from all spectra, giving a mean intensity of zero for each spectrum.
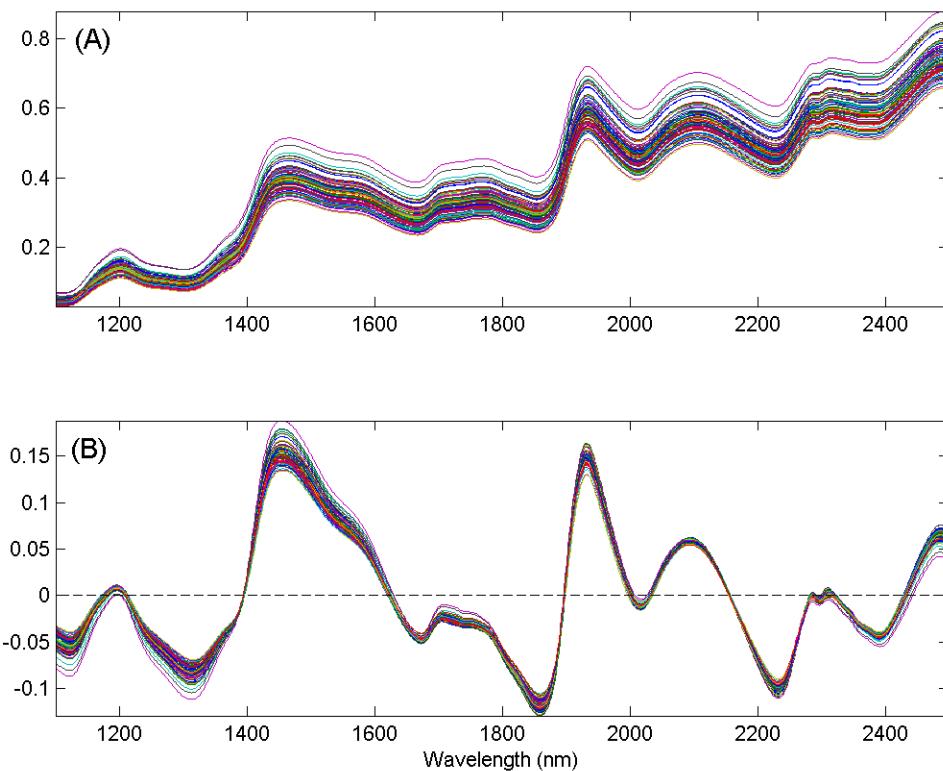
Figure 7-3. The effect of first-order detrending on the corn near-IR spectral data. The original data are shown in (A) and the detrended data in (B).

172

The single setting for Detrend is the order of polynomial to fit to the data.

From the command line, there is no specific function to perform Detrend (although there is a MATLAB function of the same name). However, this method can be performed using the `baseline` function by indicating that all points in the spectrum are to be used in the baseline calculation.

Baseline (Weighted Least Squares)

Another method for automatically removing baseline offsets from data is the Baseline (Weighted Least Squares) preprocessing method. This method is typically used in spectroscopic applications where the signal in some variables is due only to baseline (background). These variables serve as good references for how much background should be removed from nearby variables. The Weighted Least Squares (WLS) baseline algorithm uses an automatic approach to determine which points are most likely due to baseline alone. It does this by iteratively fitting a baseline to each spectrum and determining which variables are clearly above the baseline (*i.e.*, signal) and which are below the baseline. The points below the baseline are assumed to be more significant in fitting the baseline to the spectrum. This method is also called asymmetric weighted least squares. The net effect is an automatic removal of background while avoiding the creation of highly negative peaks.

Typically, the baseline is approximated by some low-order polynomial (adjustable through the settings), but a specific baseline reference (or even better, multiple baseline references) can be supplied. These references are referred to as the baseline "basis." When specific references are provided as the basis, the background will be removed by subtracting some amount of each of these references to obtain a low background result without negative peaks.

When using a polynomial to approximate the baseline, care should be taken in selecting the order of the polynomial. It is possible to introduce additional unwanted variance in a data set by using a polynomial of larger order (*e.g.*, greater than 2) particularly if a polynomial gives a poor approximation of the background shape. This can increase the rank of a data matrix. In general, baseline subtraction in this manner is not as numerically safe as using derivatives, although the interpretation of the resulting spectra and loadings (for example) may be easier.

There are a number of settings which can be used to modify the behavior of the WLS Baseline method. At the "Novice" user level (see User Level menu in the WLS Baseline settings window), the order of the polynomial can be selected or a basis (reference background spectra) can be loaded. If a basis is loaded, the polynomial order setting is ignored.

At the "Intermediate" user level, several additional settings can be modified including the selection of two different weight modes, various settings for the weight modes, and the "trbflag" which allows fitting of a baseline to either the top or the bottom of data (top is used when peaks are negative-going from an overall baseline shape). In addition, several

settings for ending criteria can be changed. At the "Advanced" user level, additional advanced settings can be accessed, if desired. See the `wlsbaseline` function for more information on the intermediate and advanced baseline options.

An example of the WLS Baseline method is shown in Figure 7-4. The top plot shows the original spectra with obvious, significant baseline contributions. The bottom plot shows the same spectra following WLS Baseline application using a second-order polynomial baseline. Although some baseline features remain after baselining, the narrow Raman features are much more significant contributor to the remaining signal.
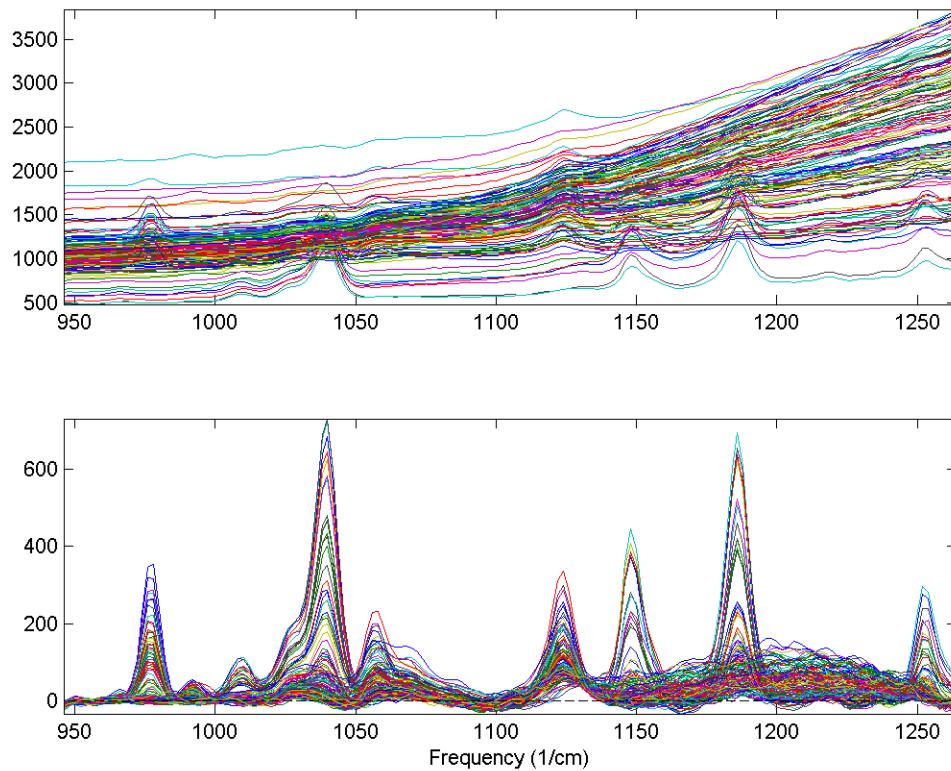
Figure 7-4. Effect of Weighted Least Squares (WLS) Baselining on Raman spectra. The original data (top plot) and baseline corrected data (bottom plot) are shown.

From the command line, this method is performed using the `wlsbaseline` function. There is also a method called `baseline` which can be used to manually select the baseline points that will be used to fit a polynomial to each spectrum. The manual selection method is faster and less prone to introduction of variance, but requires more knowledge on the part of the user as to what areas of the spectra are truly baseline. In addition, there is a windowed version of the WLS baseline algorithm called `baselinew`. This algorithm fits an individual polynomial to multiple windows across a spectrum and is better at handling unusually shaped baselines, but requires the selection of an appropriate window size.

174

Sample Normalization

In many analytical methods, the variables measured for a given sample are subject to overall scaling or gain effects. That is, all (or maybe just a portion of) the variables measured for a given sample are increased or decreased from their true value by a multiplicative factor. Each sample can, in these situations, experience a different level of multiplicative scaling.

In spectroscopic applications, scaling differences arise from pathlength effects, scattering effects, source or detector variations, or other general instrumental sensitivity effects (see, for example, Martens and Næs, 1989). Similar effects can be seen in other measurement systems due to physical or chemical effects (*e.g.*, decreased activity of a contrast reagent or physical positioning of a sample relative to a sensor). In these cases, it is often the relative value of variables which should be used when doing multivariate modeling rather than the absolute measured value. Essentially, one attempts to use an internal standard or other pseudo-constant reference value to correct for the scaling effects.

The sample normalization preprocessing methods attempt to correct for these kinds of effects by identifying some aspect of each sample which should be essentially constant from one sample to the next, and correcting the scaling of all variables based on this characteristic. The ability of a normalization method to correct for multiplicative effects depends on how well one can separate the scaling effects which are due to properties of interest (*e.g.*, concentration) from the interfering systematic effects.

Normalization also helps give all samples an equal impact on the model. Without normalization, some samples may have such severe multiplicative scaling effects that they will not be significant contributors to the variance and, as a result, will not be considered important by many multivariate techniques.

When creating discriminant analysis models such as PLS-DA or SIMCA models, normalization is done if the relationship between variables, and not the absolute magnitude of the response, is the most important aspect of the data for identifying a species (*e.g.*, the concentration of a chemical isn't important, just the fact that it is there in a detectable quantity). Use of normalization in these conditions should be considered after evaluating how the variables' response changes for the different classes of interest. Models with and without normalization should be compared.

Typically, normalization should be performed before any centering or scaling or other column-wise preprocessing steps and after baseline or offset removal (see above regarding these preprocessing methods). The presence of baseline or offsets can impede correction of multiplicative effects. The effect of normalization prior to background removal will, in these cases, not improve model results and may deteriorate model performance.

One exception to this guideline of preprocessing order is when the baseline or background is very consistent from sample to sample and, therefore, provides a very useful reference for normalization. This can sometimes be seen in near-infrared

spectroscopy in the cases where the overall background shape is due to general solvent or matrix vibrations. In these cases, normalization before background subtraction may provide improved models. In any case, cross-validation results can be compared for models with the normalization and background removal steps in either order and the best selected.

A second exception is when normalization is used after a scaling step (such as autoscaling). This should be used when autoscaling emphasizes features which may be useful in normalization. This reversal of normalization and scaling is sometimes done in discriminant analysis applications.

<u>Normalize</u>

Simple normalization of each sample is a common approach to the multiplicative scaling problem. The Normalize preprocessing method calculates one of several different metrics using all the variables of each sample. Possibilities include:

Name	Description	Equation*
1-Norm	Normalize to (divide each variable by) the sum of the absolute value of all variables for the given sample. Returns a vector with unit area (area = 1) "under the curve."	$w_i = \sum_{j=1}^{n} \left| x_{i,j} \right|$
2-Norm	Normalize to the sum of the squared value of all variables for the given sample. Returns a vector of unit length (length = 1). A form of weighted normalization where larger values are weighted more heavily in the scaling.	$w_i = \sum_{j=1}^{n} x_{i,j}^{2}$
Inf-Norm	Normalize to the maximum value observed for all variables for the given sample. Returns a vector with unit maximum value. Weighted normalization where only the largest value is considered in the scaling.	$w_i = Max(\mathbf{x}_i)$

* Where, in each case, w_i is the normalization weight for sample i, $\mathbf{x}_i$ is the vector of observed values for the given sample, j is the variable number, and n is the total number of variables (columns of $\mathbf{x}$).

The weight calculated for a given sample is then used to calculate the normalized sample, $\mathbf{x}_{i,norm}$, using:

$$\mathbf{x}_{i,norm} = \mathbf{x}_i w_i^{-1} \qquad (7\text{-}1)$$

176

An example using the 1-norm on near infrared spectra is shown in Figure 7-5. These spectra were measured as 20 replicates of 5 synthetic mixtures of gluten and starch (Martens, Nielsen, and Engelsen, 2003) In the original data (top plot), the five concentrations of gluten and starch are not discernable because of multiplicative and baseline effects among the 20 replicate measurements of each mixture. After normalization using a 1-norm (bottom plot), the five mixtures are clearly observed in groups of 20 replicate measurements each.
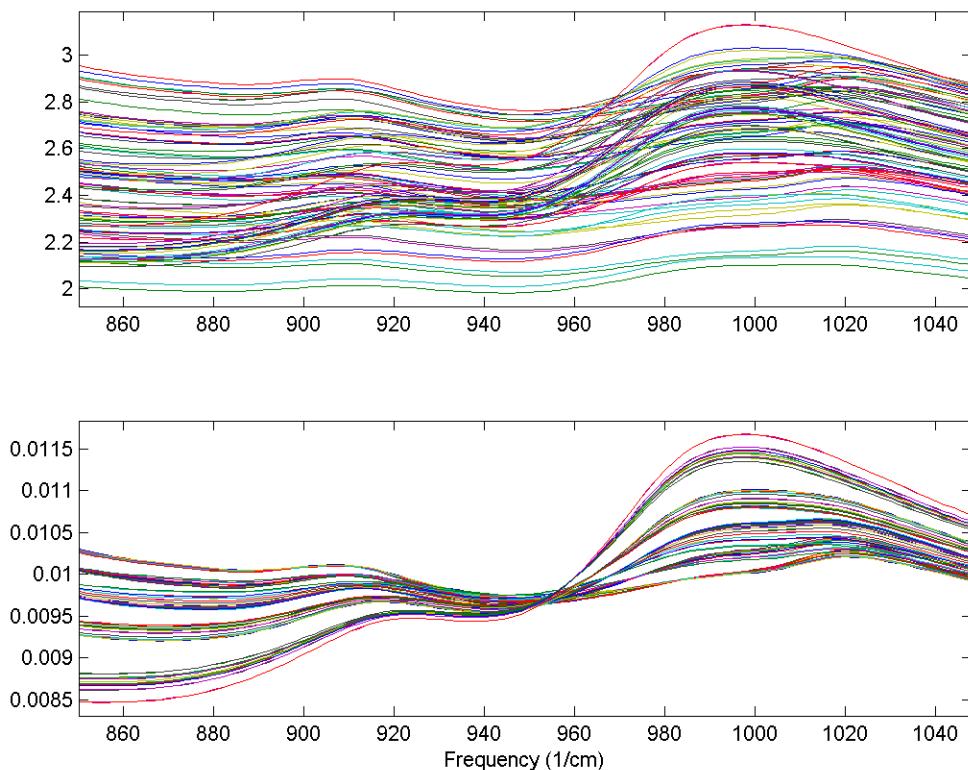
Figure 7-5. Effect of normalization on near-IR spectra of five synthetic gluten and starch mixtures. Original spectra (top plot) and spectra after 1-norm normalization (bottom plot) are shown.

From the **Preprocessing** GUI, the only setting associated with this method is the type of normalization (1-norm, 2-norm or inf-norm). There is currently no option to perform this normalization based on anything other than all selected variables.

From the command line, this method is performed using the `normaliz` function (note the unusual spelling of the function).

SNV (Standard Normal Variate)

Unlike the simple 1-Norm Normalize described above, the Standard Normal Variate (SNV) normalization method is a weighted normalization (*i.e.*, not all points contribute to the normalization equally). SNV calculates the standard deviation of all the pooled variables for the given sample (see for example Barnes et al., 1989). The entire sample is then normalized by this value, thus giving the sample a unit standard deviation (s = 1). Note that this procedure also includes a zero-order detrend (subtraction of the individual mean value from each spectrum - see discussion of detrending, above), and also that this is different from mean centering (described later). The equations used by the algorithm are the mean and standard deviation equations:

$$\bar{x}_i = \frac{\sum_{j=1}^{n} x_{i,j}}{n} \tag{7-2}$$

$$w_i = \sqrt{\frac{\sum_{j=1}^{n} \left(x_{i,j} - \bar{x}_i\right)^2}{(n-1)} + \delta^{-1}} \tag{7-3}$$

where n is the number of variables, $x_{i,j}$, is the value of the jth variable for the ith sample, and δ is a user-definable offset. The user-definable offset can be used to avoid over-normalizing samples which have near zero standard deviation. The default value for this offset is zero, indicating that samples will be normalized by their unweighted standard deviation. The selection of δ is dependent on the scale of the variables. A setting near the expected noise level (in the variables' units) is a good approximation.

This normalization approach is weighted towards considering the values that deviate from the individual sample mean more heavily than values near the mean. Consider the example Raman spectrum in Figure 7-6. The horizontal line at intensity 0.73 indicates the mean of the spectrum. The dashed lines at 1.38 and 0.08 indicate one standard deviation away from the mean. In general, the normalization weighting for this sample is driven by how far all the points deviate from the mean of 0.73. Considering the square term in equation 7-3 and the histogram on the left of Figure 7-6, it is clear that the high intensity points will contribute greatly to this normalization.
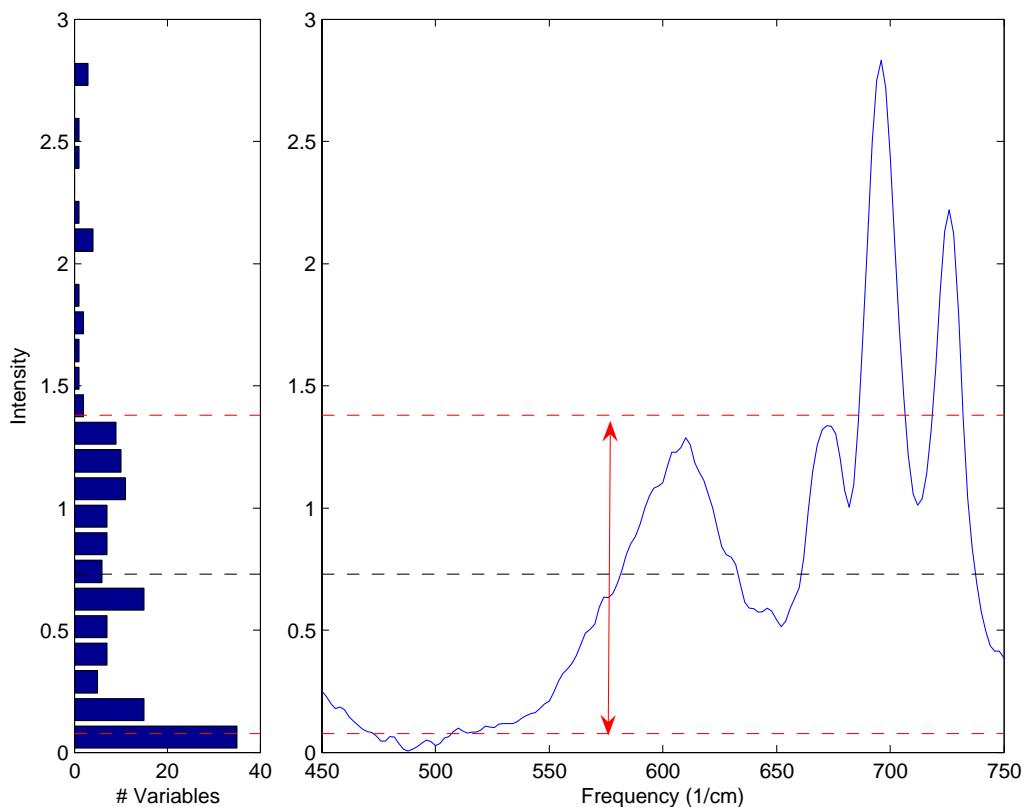
Figure 7-6. Example Raman spectrum (right plot) and corresponding intensity histogram (left plot). The mean of the spectrum is shown as a dashed line at intensity 0.73; one standard deviation above and below this mean are shown at intensities 1.38 and 0.08 and indicated by the arrow.

This approach is a very empirical normalization method in that one seldom expects that variables for a given sample should deviate about their mean in a normal distribution with unit variance (except in the case where the primary contribution to most of the variables is noise and the variables are all in the same units). When much of the signal in a sample is the same in all samples, this method can do very well. However, in cases where the overall signal changes significantly from sample to sample, problems may occur. In fact, it is quite possible that this normalization can lead to non-linear responses to what were otherwise linear responses. SNV should be carefully compared to other normalization methods for quantitative models.

Figure 7-7 shows the result of SNV on the gluten and starch mixtures described earlier. Comparing the SNV results to the original spectra and 1-norm spectra shown in Figure 7-5, it is obvious that SNV gives tighter groupings of the replicate measurements. In fact, SNV was originally developed for NIR data of this sort, and it behaves well with this kind of response.
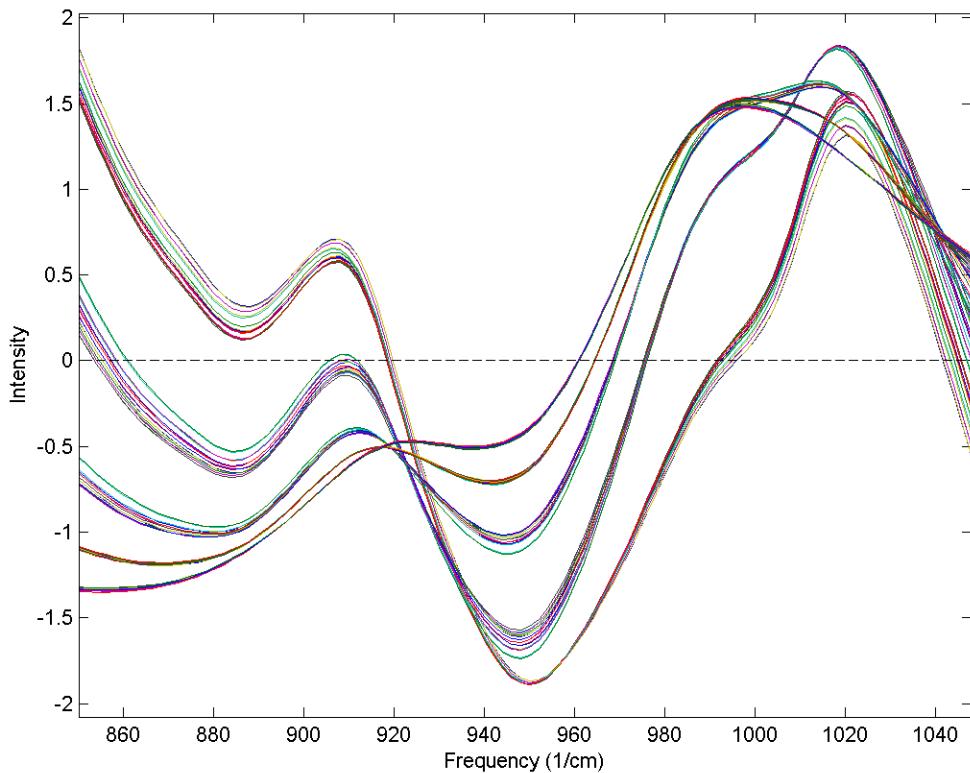
Figure 7-7. Effect of SNV normalization on near-IR spectra measured of five synthetic gluten and starch mixtures.

From the **Preprocessing** GUI, the only setting associated with this method is the offset. There is currently no option to perform this normalization based on anything other than all selected variables.

From the command line, this method is performed using the snv function.

MSC (mean)

Multiplicative signal correction (MSC) is a relatively simple processing step that attempts to account for scaling effects and offset (baseline) effects (Martens and Næs, 1989). This correction is achieved by regressing a measured spectrum against a reference spectrum and then correcting the measured spectrum using the slope (and possibly intercept) of this fit. Specifically, MSC follows this procedure: Define **x** as a column vector corresponding to a spectrum to be standardized and **r** as a vector corresponding to the reference spectrum (often this is the mean spectrum of the calibration data set). The vectors are most often mean-centered according to:

$$\mathbf{x}_c = \mathbf{x} - \bar{x}\mathbf{1}$$
(7-4)

$$\mathbf{r}_c = \mathbf{r} - \bar{r}\mathbf{1}$$
(7-5)

where $\mathbf{x}_c$ and $\mathbf{r}_c$ are the mean centered vectors, $\overline{x}$ and $\overline{r}$ are the respective means, and **1** is a vector of ones. The unknown multiplicative factor b is determined using :

$$\mathbf{r}_c b = \mathbf{x}_c \tag{7-6}$$

$$b = (\mathbf{r}_c^T \mathbf{r}_c)^{-1} \mathbf{r}_c^T \mathbf{x}_c \tag{7-7}$$

and the corrected spectrum $\hat{\mathbf{x}}$ is then given by:

$$\hat{\mathbf{x}} = \mathbf{x}_c / b + \overline{r}\mathbf{1} \tag{7-8}$$

Figure 7-8 shows an example of MSC using NIR spectra of synthetic gasoline samples with added baseline and scaling effects. The spectra with artificial baseline and scaling effects are shown in the top plot. The corrected spectra are shown in the bottom plot. The corrected spectra were brought to within 0.03 absorbance units of the original spectra (not shown).
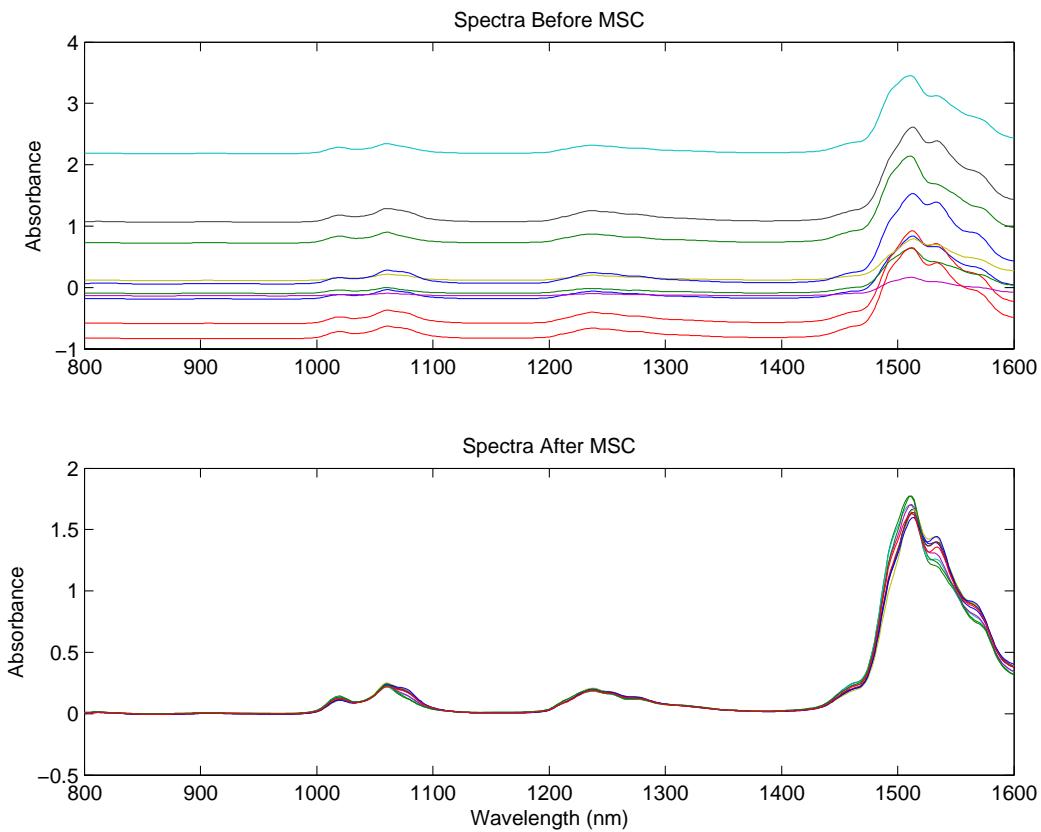
Figure 7-8. Example of Multiplicative Scatter Correction of artificial baseline and scaling effects.

The simulated baseline addition and subsequent correction can be done using the following commands:

```
» bspec = spec1.data(21:30,:);
» for i = 1:10, bspec(i,:) = bspec(i,:)*rand(1) + randn(1); end
» [sx,alpha,beta] = mscorr(bspec,mean(spec1.data(1:20,:)));
```

The first line creates a matrix of ten spectra. The second multiplies them by a random number between 0 and 1 and adds a random offset. The function `mscorr` is then used to correct the spectra using the mean of the first twenty spectra as the reference. The outputs of `mscorr` are the corrected spectra (`sx`), and the intercepts (`alpha`), and slope (`beta`) for the fit of each spectrum to the reference.

From the **Preprocessing** GUI, there are two settings which can be modified: intercept and spectral mode. The intercept option controls whether or not the intercept (*i.e.*, $\bar{r}$ in equation 7-8) is used. The spectral mode setting defaults to 2 and can only be modified when x is a multiway matrix. This setting defines the data mode which is associated with the spectral dimension (*i.e.*, the mode which should be used in the regression). There is currently no option to perform this normalization based on anything other than all selected variables.

From the command line, this method is performed using the `mscorr` function.

Simple Mathematical Operations

Two preprocessing methods involve simple mathematical operations which are used to linearize or otherwise modify certain kinds of data.

Absolute Value

The absolute value method is used to remove any sign information from the data. Although unusual, this method may be useful following a derivative or other method which creates negative values. Such correction can allow the use of non-negativity constraints, or simply improve interpretability of derivatized spectra. It should be noted, however, that an absolute value following any method which centers data (such as mean- or median-centering) may create a non-linear response and complicate modeling.

There are no settings associated with this preprocessing method. The command line function to perform this operation is the MATLAB command `abs`.

Log10

A base 10 logarithm (that is, $X_p = \log_{10} X$) can be used whenever the response of the data is linear to the function 10^X. Note that negative values will become undefined values (`NaN` = Not a Number). Most modeling algorithms will attempt to replace these values

with their least-biasing value. As such, the use of an absolute value preprocessing step prior to a Log10 step may be necessary to avoid problems during modeling.

There are no settings associated with this preprocessing method. The command line function to perform this operation is the MATLAB command `log10`.

Variable Centering

As discussed previously in this tutorial, many preprocessing methods are based on the variance in the data. Such techniques should generally be provided with data which are centered relative to some reference point. Centering is generically defined as

$$\mathbf{X}_c = \mathbf{X} - \mathbf{1}\bar{\mathbf{x}}$$
(7-9)

where $\bar{\mathbf{x}}$ is a vector representing the reference point for each variable, $\mathbf{1}$ is a column-vector of ones, and $\mathbf{X}_c$ represents the centered data. Often the reference point is the mean of the data. Interpretation of loadings and samples from models built on centered data is done relative to this reference point. For example, when centering is used before calculating a PCA model, the resultant eigenvalues can be interpreted as variance captured by each principal component. Without centering, the eigenvalues include both variance and the sum-squared mean of each variable.

In most cases, centering and/or scaling (see next section) will be the last method in a series of preprocessing methods. When other preprocessing methods are being used, they are usually performed prior to a centering and/or scaling method.

Mean-Center

One of the most common preprocessing methods, mean-centering calculates the mean of each column and subtracts this from the column. Another way of interpreting mean-centered data is that, after mean-centering, each row of the mean-centered data includes only how that row differs from the average sample in the original data matrix.

In the **Preprocessing** GUI, this method has no adjustable settings. From the command line, this method is achieved using the `mncn` function.

For more information on the use of mean-centering, see the discussion on Principal Components Analysis in Chapter 5.

Median-Center

The median-centering preprocessing method is very similar to mean-centering except that the reference point is the median of each column rather than the mean. This is considered one of the "robust" preprocessing methods in that it is not as influenced by outliers (unusual samples) in the data.

In the **Preprocessing** GUI, this method has no adjustable settings. From the command line, this method is performed using the medcn function.

Variable Scaling

Variable scaling is another very common method used with multivariate analysis techniques. Many techniques assume that the magnitude of a measurement is proportional to its importance and that the level of noise is similar in all variables. When variables have significantly different scales simply because they are in different units, the magnitude of the values is not necessarily proportional to the information content. Likewise, scale is also an issue when some variables contain more noise than other variables.

Variable scaling helps address these problems by scaling each variable (column) of a data matrix by some value. The scaling for each variable is presumed to give that variable's information content an equal standing with the other variables. In general this is performed by

$$\mathbf{X}_S = \mathbf{X}\mathbf{S} \qquad\qquad (7\text{-}10)$$

where $\mathbf{S}$ is a diagonal matrix of the scaling factors and $\mathbf{X}_S$ is a matrix of the scaled data. Note that in some cases, scaling will be combined with a centering step, described above.

If scaling is being used, it will be, in general, the final method applied prior to model calculation.

Autoscale

This is an exceptionally common preprocessing method which uses mean-centering followed by dividing each column (variable) by the standard deviation of the column. That is, the diagonal of the matrix $\mathbf{S}$ in equation 7-10 is equal to the inverse of the standard deviation for each column. The result is that each column of $\mathbf{X}_S$ has a mean of zero and a standard deviation of one.

This approach is a valid approach to correcting for different variable scaling and units if the predominant source of variance in each variable is signal rather than noise. Under these conditions, each variable will be scaled such that its useful signal has an equal footing with other variables' signal. However, if a given variable has significant contributions from noise (*i.e.*, a low signal-to-noise ratio) or has a standard deviation near zero, then autoscaling will cause this variable's noise to have an equal footing with the signal in other variables. This variable may then adversely influence the model. Under these conditions, excluding such variables or using the offset parameter (described below) is recommended.

Autoscaling includes an adjustable parameter "offset" which is added to each column's standard deviation prior to scaling. When offset is non-zero, the diagonal of the matrix $\mathbf{S}$

184

in equation 7-10 is equal to $(s + \text{offset})^{-1}$ where s is the vector of standard deviations for each column of X. The offset is useful for de-emphasizing variables which have a standard deviation near zero. By setting the offset to some small value, variables which have standard deviations near or at that level are not as heavily up-scaled. This effectively reduces their influence on a model. The exact level for the offset is largely dependent on the scale and noise level of the data. The default value of offset is zero.

In the **Preprocessing** GUI, this method has one adjustable setting for the scaling offset. From the command line, this method is performed using the `auto` function.

For more information on the use of autoscaling, see the discussion on Principal Components Analysis in Chapter 5.

Group Scale

Similar to autoscaling, group scaling performs scaling based on standard deviations. Group scaling is often used when the data consist of several equal-sized blocks of variables. Each block contains variables in some given unit of measure, but different blocks use different units. This kind of situation occurs in Multiway Principal Components Analysis (MPCA).

Group scale is performed by splitting the variables into a predefined number of equally-sized blocks and scaling each block by the grand mean of their standard deviations. For each block, the standard deviations for each variable in a block are calculated and the mean of those standard deviations is used to scale all columns in the block. The same procedure is repeated for each block of variables. The group scale method does assume that all blocks have an equal number of columns. Group scaling when different numbers of variables are in each group can only be done by hand at the MATLAB command line.

In the **Preprocessing** GUI, this method has one adjustable parameter indicating the number of blocks to split the variables into. If set to zero, the GUI will attempt to infer the number of blocks from the size of the original data (if a three-way matrix). From the command line, this method is performed using the `gscale` function.

Log Decay Scaling

Log decay scaling is typically used in Mass Spectrometry (MS) and is a first-principle alternative to autoscaling for MS data. The scaling is based on the assumption that, in some types of instrumentation, the sensitivity of the instrument is roughly logarithmically proportional to the size of the mass fragment. The larger the mass, the less sensitive the instrument and the lower the counts for the given mass. Log decay scaling attempts to correct for this insensitivity to larger masses by scaling each mass by a continuously decreasing log function of the form:

$$s_i = e^{-i/n\tau} \qquad (7\text{-}11)$$

where s_i is the scaling for variable i (sorted in order of increasing mass), n is the total number of variables and τ (tau) is an adjustable parameter defining the differential scaling of early masses to later masses. The smaller the value for τ, the more the larger masses are up-scaled relative to the smaller masses. Selection of τ largely depends on the instrumentation and the insensitivity to larger masses. The default value for τ is 0.3.

Note that, unlike autoscaling, this method does not mean-center the data.

In the **Preprocessing** GUI, this method allows for adjustment of τ in the settings. From the command line, this method is performed using the logdecay function.

Sqrt Mean Scale

In many cases, the goal of scaling is to adjust the magnitude of each variable so that the level of noise is equal in all variables. In cases where the noise is approximately proportional to the square root of the signal in each variable, the square root mean scaling (sqrt mean scale) approach can be used. This method scales each variable by the square root of the mean of the variable. If the predominant noise source is truly proportional to the square root of the signal, this effectively corrects all variables to the same level of noise.

This method has been used effectively to correct Mass Spectra (Keenan and Kotula, 2004) but is also valid in other spectroscopies or measurements where noise is likely to be shot-noise limited (low light luminescence and Raman spectroscopies, for example). Note that, unlike autoscaling, this method does not mean-center the data.

In the **Preprocessing** GUI, there are no adjustable parameters. There is no equivalent method at the command line, but this scaling can be emulated using the commands:

```
>> [junk,mx] = mncn(x);
>> sx = sqrt(mx);
>> data = scale(x,sx*0,sx);
```

Multiway Centering and Scaling

When handling multi-way data (that is, data sets which have three or more modes), there are two specialized centering and scaling methods which can be used: multiway center and multiway scale. The details of how these methods work is beyond the scope of this chapter but details can be obtained from the multiway methods chapter (Chapter 10) and from the help for the npreprocess command. The basic information on these methods is given below.

Note that when used together, multiway centering and scaling may need to be done iteratively if a true convergence is to be reached. The following general guidelines can be applied:

186

1. Centering across one mode tends to disturb scaling across all modes (except for particular scaling where the scaling is independent of the level/offset/center, such as in autoscaling.)
2. Scaling within a mode disturbs centering across the same mode but not across other modes.
3. Scaling affects scaling in other modes.

More details of these considerations can be found in Bro and Smilde, 2003.

Multiway Center

Performs centering across one or more modes of a multiway array. The result is a matrix which has a mean of zero for the given mode(s). In the **Preprocessing** GUI, the only setting defines which mode or modes should be centered. The npreprocess function can be used to perform this method at the command line.

Multiway Scale

Performs scaling of one or more modes of a multiway array. In the **Preprocessing** GUI, the only setting defines which mode or modes should be scaled. The npreprocess function can be used to perform this method at the command line.

Multivariate Filtering

In some cases, there is insufficient selectivity in the variables to easily remove things like backgrounds or other signals which are interferences to a multivariate model. In these cases, using multivariate filtering methods before model calibration may help simplify the end model. Multivariate filters identify some unwanted covariance structure (*i.e.*, how variables change together) and remove these sources of variance from the data prior to calibration or prediction. In a simple way, these filters can be viewed as pattern filters in that they remove certain patterns among the variables. The resulting data contain only those covariance patterns which passed through the filter and are, ideally, useful or interesting in the context of the model.

Identification of the patterns to filter can be based on a number of different criteria. The full discussion of multivariate filtering methods is outside the scope of this chapter, but it is worth noting that these methods can be very powerful for calibration transfer and instrument standardization problems, as well as for filtering out other differences between measurements which should otherwise be the same (*e.g.*, differences in the same sample due to changes with time, or differences within a class of items being used in a classification problem).

One common method to identify the multivariate filter "target" uses the Y-block of a multivariate regression problem. This Y-block contains the quantitative (or qualitative) values for each sample and, theoretically, samples with the same value in the Y-block should have the same covariance structure (*i.e.*, they should be similar in a multivariate

fashion). A multivariate filter can be created which attempts to remove differences between samples with similar y-values. This filter should reduce the complexity of any regression model needed to predict these data. Put in mathematical terms, the multivariate filter removes signals in the X-block (measured responses) which are orthogonal to the Y-block (property of interest).

Two multivariate filtering methods are provided in the **Preprocessing** GUI: Orthogonal Signal Correction (OSC) and Generalized Least Squares Weighting (GLSW). In the context of the **Preprocessing** GUI, both methods require a Y-block and are thus only relevant in the context of regression models. Additionally, as of the current version of PLS_Toolbox, the GUI access to these functions only permits their use to orthogonalize to a Y-block, not for calibration transfer applications. From the command line, however, both of these functions can also be used for calibration transfer or other filtering tasks. For more information on these uses, please see the calibration transfer and instrument standardization chapter of this manual.

OSC (Orthogonal Signal Correction)

Orthogonal Signal Correction (Sjöblom et al., 1998) removes variance in the X-block which is orthogonal to the Y-block. Such variance is identified as some number of factors (described as components) of the X-block which have been made orthogonal to the Y-block. When applying this preprocessing to new data, the same directions are removed from the new data prior to applying the model.

The algorithm starts by identifying the first principal component (PC) of the X-block. Next, the loading is rotated to make the scores be orthogonal to the Y-block. This loading represents a feature which is not influenced by changes in the property of interest described in the Y-block. Once the rotation is complete, a PLS model is created which can predict these orthogonal scores from the X-block. The number of components in the PLS model is adjusted to achieve a given level of captured variance for the orthogonal scores. Finally, the weights, loadings, and predicted scores are used to remove the given orthogonal component, and are also set aside for use when applying OSC to a new unknown sample. This entire process can then be repeated on the "deflated" X-block (the X-block with the previously-identified orthogonal component removed) for any given number of components. Each cycle results in additional PLS weights and loadings being added to the total that will be used when applying to new data.

There are three settings for the OSC preprocessing method: number of components, number of iterations, and tolerance level. The number of components defines how many times the entire process will be performed. The number of iterations defines how many cycles will be used to rotate the initial PC loading to be as orthogonal to Y as possible. The tolerance level defines the percent variance that must be captured by the PLS model(s) of the orthogonalized scores.

In the **Preprocessing** GUI, this method allows for adjustment of the settings identified above. From the command line, this method is performed using the `osccalc` and `oscapp` functions.

188

GLS Weighting

Generalized Least Squares Weighting (GLSW) calculates a filter matrix based on the differences between pairs or groups of samples which should otherwise be similar.

In the case of a calibration transfer problem, similar samples would be data from the same samples measured on two different instruments or on the same instrument at two different points in time. The goal of GLSW is to down-weight the differences between the two instruments and, therefore, make them appear more similar. A regression model built from GLSW-filtered data can be used on either instrument after applying the filtering to any measured spectrum. Although this specific application of GLSW is not covered by this chapter, the description below gives the mathematical basis of this use.

GLSW can also be used prior to building a regression model in order to remove variance from the X-block which is mostly orthogonal to the Y-block. This application of GLSW is similar to OSC (see above), and such filtering can allow a regression model to achieve a required error of calibration and prediction using fewer latent variables. In this context, GLSW uses samples with similar Y-block values to identify the sources of variance to down-weight.

In both cases, a single adjustable parameter, α, defines how strongly GLSW downweights interferences. Adjusting α towards larger values (typically above 0.001) decreases the effect of the filter. Smaller αs (typically 0.001 and below) apply more filtering.

Algorithm. The GLSW algorithm will be described here for the calibration transfer application (because it is simpler to visualize) and then the use of GLSW in regression multivariate filtering will be described. In either case, the approach involves the calculation of a covariance matrix from the differences between similar samples. In the case of calibration transfer problems, this difference is defined as the numerical difference between the two groups of mean-centered transfer samples. Given two sample matrices, $\mathbf{X}_1$ and $\mathbf{X}_2$, the data are mean-centered and the difference calculated:

$$\mathbf{X}_{1,mc} = \mathbf{X}_1 - \mathbf{1}\bar{\mathbf{x}}_1 \qquad\qquad (7\text{-}12)$$

$$\mathbf{X}_{2,mc} = \mathbf{X}_2 - \mathbf{1}\bar{\mathbf{x}}_2 \qquad\qquad (7\text{-}13)$$

$$\mathbf{X}_d = \mathbf{X}_2 - \mathbf{X}_1 \qquad\qquad (7\text{-}14)$$

where **1** is a vector of ones equal in length to the number of rows in $\mathbf{X}_1$, $\bar{\mathbf{x}}_1$ is the mean of all rows of $\mathbf{X}_1$, and $\bar{\mathbf{x}}_2$ is the mean of all rows of $\mathbf{X}_2$. Note that this requires that $\mathbf{X}_1$ and $\mathbf{X}_2$ are arranged such that the rows are in the same order in terms of samples measured on the two instruments.

The next step is to calculate the covariance matrix, $\mathbf{C}$:

$$\mathbf{C} = \mathbf{X}_d^T \mathbf{X}_d \qquad (7\text{-}15)$$

followed by the singular-value decomposition of the matrix, which produces the left eigenvectors, $\mathbf{V}$, and the diagonal matrix of singular values, $\mathbf{S}$:

$$\mathbf{C} = \mathbf{V}\mathbf{S}^2\mathbf{V}^T \qquad (7\text{-}16)$$

Next, a weighted, ridged version of the singular values is calculated

$$\mathbf{D} = \sqrt{\frac{\mathbf{S}^2}{\alpha} + \mathbf{1}}_D \qquad (7\text{-}17)$$

where $\mathbf{1}_D$ is a diagonal matrix of ones of appropriate size and α is the weighting parameter mentioned above. The scale of the weighting parameter depends on the scale of the variance in $\mathbf{X}_d$. Finally, the inverse of these weighted eigenvalues are used to calculate the filtering matrix.

$$\mathbf{G} = \mathbf{V}\mathbf{D}^{-1}\mathbf{V}^T \qquad (7\text{-}18)$$

This multivariate filtering matrix can be used by simply projecting a sample into the matrix. The result of this projection is that correlations present in the original covariance matrix are down-weighted (to the extent defined by α). The filtering matrix is used both on the original calibration data prior to model calibration, and any future new data prior to application of the regression model.

The choice of α depends on the scale of the original values but also how similar the interferences are to the net analyte signal. If the interferences are similar to the variance necessary to the analytical measurement, then α will need to be higher in order to keep from removing analytically useful variance. However, a higher α will decrease the extent to which interferences are down-weighted. In practice, values between 1 and 0.0001 are often used.

When using GLSW to filter out X-block variance which is orthogonal to a Y-block, a different approach is used to calculate the difference matrix, $\mathbf{X}_d$. In this situation we have only one X-block, $\mathbf{X}$, of measured calibration samples, but we also have a Y-block, $\mathbf{y}$ (here defined only for a single column-vector), of reference measurements. To a first approximation, the Y-block can be considered a description of the similarity between samples. Samples with similar y values should have similar values in the X-block.

In order to identify the differences between samples with similar y values, the rows of the X- and Y-blocks are first sorted in order of increasing y value. This puts samples with similar values near each other in the matrix. Next, the difference between proximate samples is determined by calculating the derivative of each column of the X-block. These derivatives are calculated using a 5-point, first-order, Savitzky-Golay first derivative

(note that a first-order polynomial derivative is essentially a block-average derivative including smoothing and derivatizing simultaneously). This derivativization yields a matrix, $\mathbf{X}_d$, in which each sample (row) is an average of the difference between it and the four samples most similar to it. A similar derivative is calculated for the sorted Y-block, yielding vector $\mathbf{y}_d$, a measure of how different the y values are for each group of 5 samples.

At this point, $\mathbf{X}_d$ could be used in equation 7-15 to calculate the covariance matrix of differences. However, some of the calculated differences (rows) may have been done on groups of samples with significantly different y values. These rows contain features which are correlated to the Y-block and should not be removed by GLS. To avoid this, the individual rows of $\mathbf{X}_d$ need to be reweighted by converting the sorted Y-block differences into a diagonal reweighting matrix, $\mathbf{W}$, in which the ith diagonal element, w_i, is calculated from the rearranged equation

$$\log_2 w_i = -\mathbf{y}_{d,i} s_{yd} \qquad (7\text{-}19)$$

The value $\mathbf{y}_{d,i}$ is the ith element of the $\mathbf{y}_d$ vector, and s_{yd} is the standard deviation of y-value differences:

$$s_{yd} = \sqrt{\sum_{i=1}^{m} \frac{(y_{d,i} - \overline{y}_d)^2}{m-1}} \qquad (7\text{-}20)$$

The reweighting matrix is then used along with $\mathbf{X}_d$ to form the covariance matrix

$$\mathbf{C} = \mathbf{X}_d{}^T \mathbf{W}^2 \mathbf{X}_d \qquad (7\text{-}21)$$

which is then used in equations 7-16 through 7-18 as described above.

In the **Preprocessing** GUI, the GLSW method allows for adjustment of the weighting parameter, α. From the command line, this method is performed using the `glsw` function, which also permits a number of other modes of application (including identification of "classes" of similar samples).

8. Classification

Often, data sets consist of samples that belong to several different groups or "classes." Classes may differ for many reasons, including variations in sample preparation, differences in chemical compound type (aromatic, aliphatic, carbonyl, etc.), or variations in process state (startup, normal, particular faults, etc.). A variety of methods have been developed for classifying samples based on measured responses.

Methods that attempt to identify groups or classes without using pre-established class memberships are known as *cluster analysis* or *unsupervised pattern recognition*. Methods that use known class memberships are generally called *classification* or *supervised pattern recognition*. As we will demonstrate, classification of new unknown samples can be accomplished either manually using unsupervised methods or in an automated manner using supervised techniques.

Distance Measures in Cluster Analysis and Classification

Most cluster analysis methods are based on the assumption that samples that are close together in the measurement space are similar and therefore likely to belong to the same class. There are however, many ways of defining distance between samples. The most common is simple Euclidean distance, where the distance d_{ij} between samples $\mathbf{x}_i$ and $\mathbf{x}_j$ is defined as

$$d_{ij} = \sqrt{\left(\mathbf{x}_i - \mathbf{x}_j\right)\left(\mathbf{x}_i - \mathbf{x}_j\right)^{\mathrm{T}}} \qquad (8\text{-}1)$$

which is simply the square root of the sum of squared differences between the samples. Preprocessing, such as autoscaling, is often used prior to calculating the distance. Distance may also be defined based on PCA scores instead of on the raw data. This is in essence a noise-filtered estimate of the distance, as the deviations between samples in dimensions not included in the model are not considered. In this case, the distance d_{ij} between samples $\mathbf{x}_i$ and $\mathbf{x}_j$ with scores $\mathbf{t}_i$ and $\mathbf{t}_j$ (note that $\mathbf{t}_i$ and $\mathbf{t}_j$ are 1 x k vectors containing the scores on all PCs of the model for samples $\mathbf{x}_i$ and $\mathbf{x}_j$) is defined as

$$d_{ij} = \sqrt{\left(\mathbf{t}_i - \mathbf{t}_j\right)\left(\mathbf{t}_i - \mathbf{t}_j\right)^{\mathrm{T}}} \qquad (8\text{-}2)$$

It is also possible to define the distance based on principal component scores adjusted to unit variance. This is analogous to the T^2 statistic given in Equation 5-10. In this case the distance in Equation 8-2 is weighted by the inverse of the eigenvalues, λ:

$$d_{ij} = \sqrt{\left(\mathbf{t}_i - \mathbf{t}_j\right)\lambda^{-1}\left(\mathbf{t}_i - \mathbf{t}_j\right)^{\mathrm{T}}} \qquad (8\text{-}3)$$

The distance measure defined in Equation 8-3 is one type of Mahalanobis distance. A Mahalanobis distance accounts for the fact that, in many data sets, variation in some directions is much larger in some directions than in others. Therefore, distance in some

directions is more significant than distance in other directions. This is illustrated graphically in Figure 8-1, which shows a data set (the stars) with lines representing constant Euclidean and Mahalanobis distances from the centroid. If these lines represented class boundaries, the data point shown as the sun would be clearly outside the Mahalanobis line, but would be inside a Euclidean distance line (especially if it were expanded to encompass all the data points).
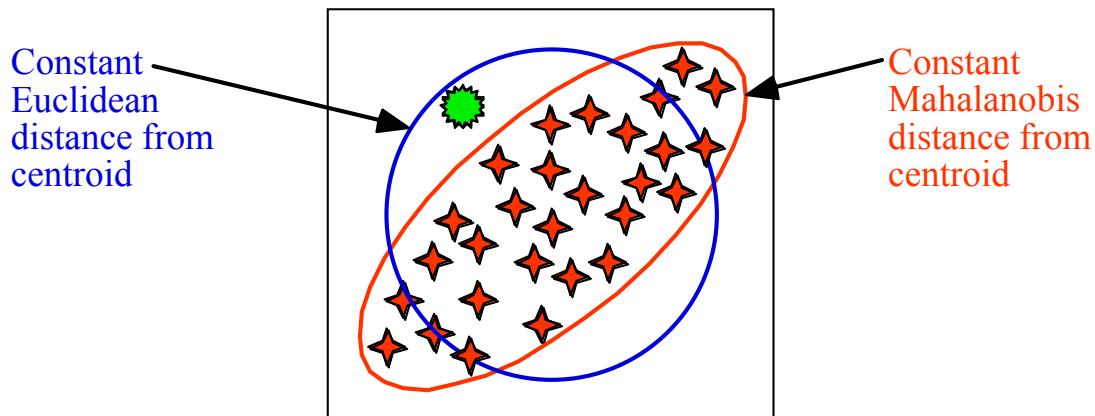
Figure 8-1. Contrast between Mahalanobis and Euclidean distance measures.

It is also possible to define a Mahalanobis distance based on the raw data. In this case

$$d_{ij} = \sqrt{\left(\mathbf{x}_i - \mathbf{x}_j \right) \mathbf{C}^{-1} \left(\mathbf{x}_i - \mathbf{x}_j \right)^T}$$

(8-4)

where $\mathbf{C}$ is the covariance matrix of the data (defined in Equation 5-3). In this case, all dimensions in the data are considered when calculating a distance. This measure is not recommended for high-dimensional data sets with strong covariance because it overemphasizes dimensions where the variation is due mainly to noise.

Cluster Analysis and Dendrograms

In cluster analysis, each sample is initially assumed to be a lone cluster. All of the distances between samples are then calculated via one of the methods shown above, and the samples with the smallest distance are found and linked together. The procedure is repeated and the samples with the next closest distance are found and linked. The results are often displayed as a connection dendrogram. An example of this is shown in Figure 8-2. Here the group of samples (with two measured parameters x_1 and x_2) are linked together, starting with the closest two, numbers 4 and 5, followed by the next closest samples, 1 and 2. Sample 6 is then linked to sample 5, which is already linked to sample 4, and so on. The results are shown in the dendrogram at right. The vertical bars indicate which samples or groups are linked, while the horizontal position of the bar indicates the length of the link, *i.e.*, the distance between the linked samples or groups.

194
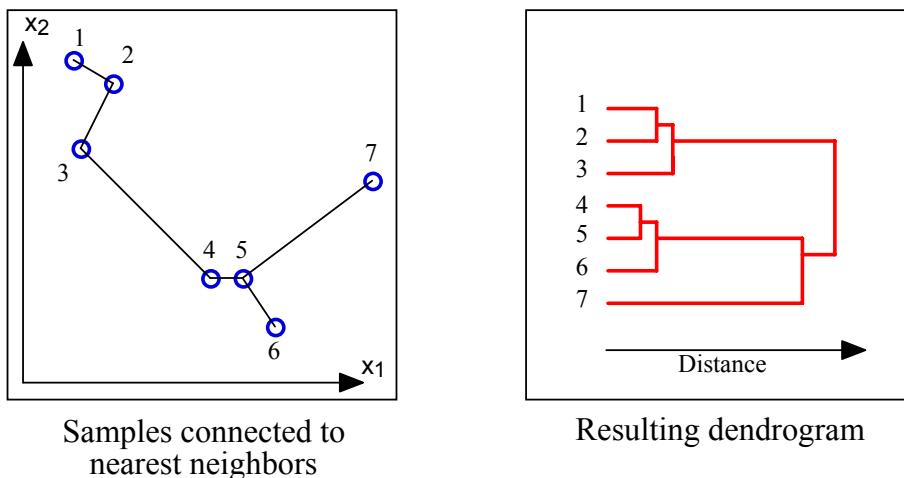
Figure 8-2. Example of linking in cluster analysis and resulting dendrogram.

In the example shown above, the distance between two groups of points was defined as the distance between the nearest neighbors of the two groups. For instance, the distance between samples 3 and 4 was used as the distance between the group of samples 1-3 and the group of samples 4-7, because samples 3 and 4 were the nearest neighbors of the two groups. There are other ways to define the distance between two groups. The most common of these is the centroid method, where the distance between two groups is the distance between either the center of mass or the average of the groups.

The clusters can be defined from the dendrogram by placing a vertical line across it and moving it up and down the distance scale. For any given distance, the number of clusters with all points within that distance is the number of lines in the dendrogram that intersect the vertical line. In our example, a vertical line placed in the middle of the dendrogram would indicate three clusters, two of which consisted of three samples each (1-3 and 4-6) and a remaining lone sample (7).

An Example of Cluster Analysis and Comparison with PCA

As an example of cluster analysis we now consider the "Arch" data set. This data set consists of the analysis of 75 obsidian samples from four known quarries (samples 1-63) and artifacts from archeological digs of unknown origin (samples 64-75). The samples were analyzed for the concentration of 10 metals, (Fe, Ti, Ba, Ca, K, Mn, Rb, Sr, Y, and Zr), via X-ray fluorescence. The goal of this exercise will be to determine from which class (*i.e.,* quarry) each of the unknown samples comes.

Start the "Analysis" tool by typing `analysis` at the command line, and load in the Arch.mat data from the PLS_Toolbox/Dems folder. Build a preliminary PCA model of the data by selecting **PCA** from the **Analysis** menu and clicking the **Calculate** button (gears), leaving the preprocessing set to the default, autoscaling. Specify a model with four principal components by clicking on the fourth line of the variance captured table and again clicking the **Calculate** button. A nice view of the data can be obtained by

clicking the **Scores** button and plotting Scores on PC1 on the x-axis and Scores on PC2 on the y-axis. The result should look like Figure 8-3 below. The samples from known quarries are identified with labels beginning with K, SH, ANA and BL. Unknown samples are labeled s1-s12 and are shown as filled dark grey circles. It is evident that samples from each of the quarries cluster together.
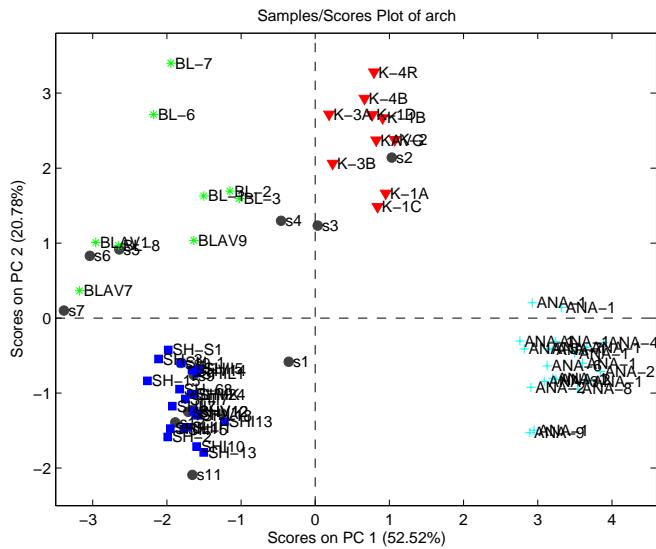
Figure 8-3. Scores on first two principal components of Arch data.

We would now like to produce a dendrogram view of these data. However, before we proceed, we will exclude the unknown samples from the analysis. This is easily done from a scores plot of Sample Number on the x-axis versus Score on PC1 on the y-axis. Click the **Select** button in **Plot Controls** window and make a rubber-band box around the last twelve samples (dark grey circles). In the **Plot Controls** window, select **Exclude Selection** from the **Edit** menu. From the **Analysis** menu select **Cluster**, then click **Calculate**. Accept the defaults and click **Execute**. The result should look like Figure 8-4, which shows a dendrogram of the samples from known quarries. The vertical line was added by executing the command vline(2.7,'--g'). Note how the samples from each quarry are perfectly grouped in the dendrogram, with each group coming off a single branch to the left of the vertical dashed line, in spite of the fact that the known class information of the samples was not used in the calculation of the dendrogram.
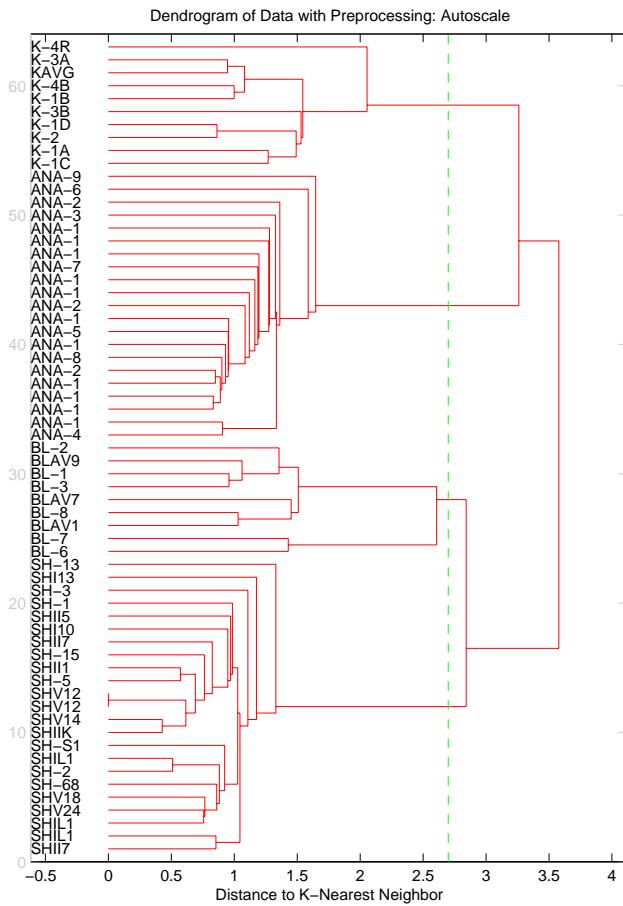
Figure 8-4. Dendrogram of samples from known quarries in Arch data.

Classification by k-Nearest Neighbor and by Inspection in PCA

The success of the dendrogram tells us that all samples of a given class (quarry) have as their nearest neighbors samples from the same class. This gives us some confidence that we should be able to assign the class of unknown samples by determining the class of their nearest known neighbor or neighbors. This leads us to the classification method k-nearest neighbor, or kNN (Sharaf, 1986). In kNN the class of a sample is determined by the class of its single nearest neighbor (k = 1) or by a vote of a small (generally odd) number of its nearest neighbors (k = 3, 5, …). An example of this is shown in Figure 8-5. Here the unknown sample is the square. Its three nearest neighbors consist of two plusses and one X; thus, it would be assigned to the class of plusses.
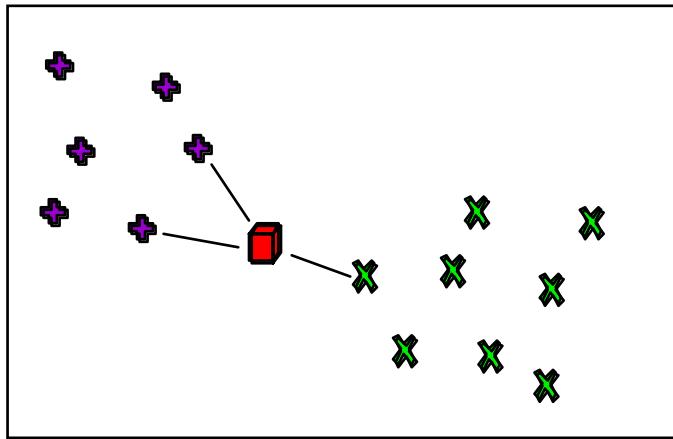
Figure 8-5. Classification by kNN.

The class of the unknown samples can be determined by running the command line function knn. Inputs are the known samples, the test samples, and a flag to indicate that autoscaling will be used. The results are shown below

```
>> pclass = knn(arch(1:63,:),arch(64:end,:),1);
```

Unknown Number	Unknown Label	Class Number	Nearest Neighbor
1	s1	3	SHV24
2	s2	1	KAVG
3	s3	1	K-1C
4	s4	1	K-3A
5	s5	2	BLAV1
6	s6	2	BL-8
7	s7	2	BLAV1
8	s8	3	SHI10
9	s9	3	SH-1
10	s10	3	SH-1
11	s11	3	SH-5
12	s12	3	SHI10

The classification largely agrees with what we might expect from observation of the principal component scores plot. The samples that are hard to classify from the PCA scores plot are s1, s3 and s4. The first unknown, s1, is far from any of the groups, but it does appear to be somewhat closer to class 3, the SH samples. Samples s3 and s4 are assigned to K (class 1) by kNN, but appear to be equally close to the K and BL (class 2) groups in Figure 8-3.

Is there a way that we might further explore the data and assign classes using PCA? Recall that we have so far looked only at the scores on the first two principal components. Are any of the other PCs useful for classification? It is easy to determine this by plotting the scores on each of the PCs individually versus sample number, or by

198

doing cross-plots of the scores. It is clear from Figure 8-3 that PCs 1 and 2 are describing differences between the quarries. What about PC 3, shown in Figure 8-6? This PC appears to be describing a variation in the data that doesn't have anything to do with the quarry, as the sample scores do not appear to be at all correlated with quarry. What about PC 4, shown in Figure 8-7? On this PC the scores from BL quarry are negative while those from K and SH are positive or near zero. Thus it appears that PC 4 is useful in discriminating the quarries.
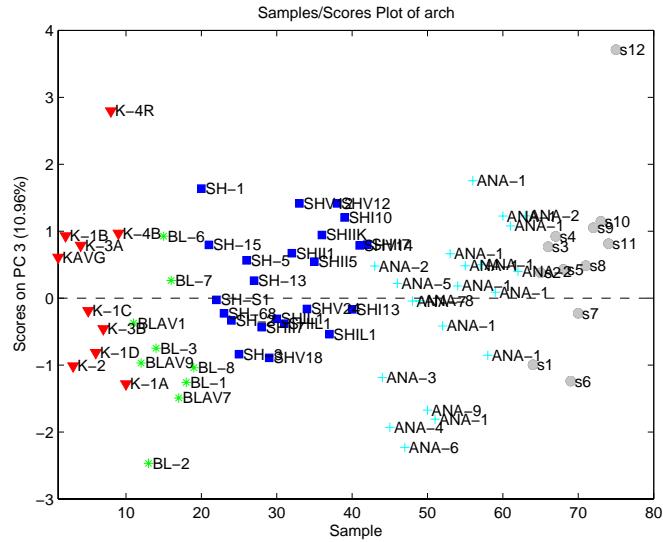
Figure 8-6. Scores on PC 3 of Arch data.
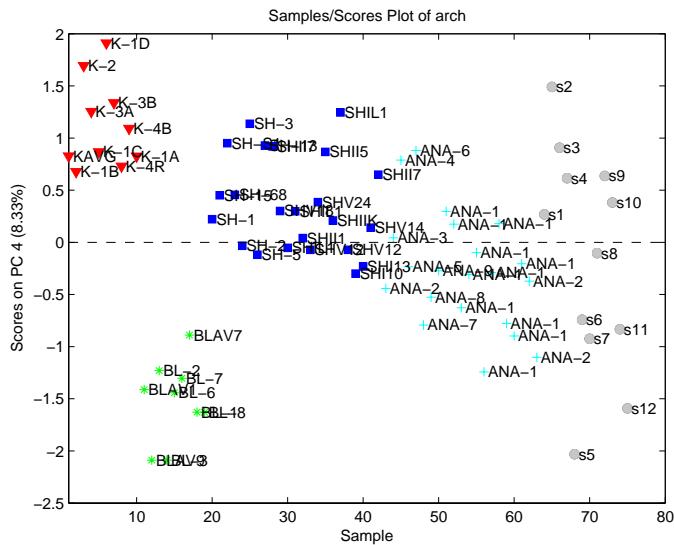
Figure 8-7. Scores on PC 4 of Arch data.

A plot of the scores on PC 4 versus PC 1 (along with PC 2 versus PC 1, Figure 8-3), can now be used to determine the source of samples s1, s3 and s4 (Figure 8-8). Sample s1

remains close to the SH group in the PC 4 versus PC1 plot, so the assignment to the SH group from kNN appears appropriate. Similarly, samples s3 and s4 remain close to the K class, suggesting the classification from kNN is correct.
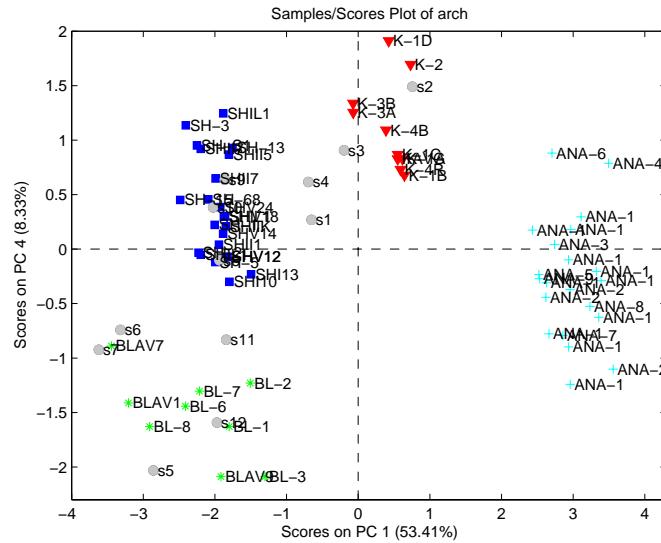
Figure 8-8. Scores of PC4 versus PC1 of Arch data.

In this example we have shown how samples may be classified by the very simple technique of kNN. Our classifications were confirmed by inspection of a PCA model. While kNN can be a very useful classification method in many circumstances, there is much that it doesn't give you. In particular, there is no information in the kNN model concerning what variables are useful in separating classes from each other. The PCA model we generated, however, contains much of this information in the loadings. The reader is encouraged to use the loadings in the Arch example to determine what variables are responsible for separating the classes.

SIMCA

We have observed that PCA is a very useful tool for identifying if samples are the same or different, and what variables are responsible. We also know that a PCA model is a description of a data set that includes statistical limits and accounts for the fact that variation in some directions is larger than in others. However, there is no guarantee that a given PCA model of multiple classes will be useful for differentiating the classes. This is because the class information was not used in the construction of the model; the PCA model just attempts to describe the overall variation in the data. So how can we use PCA in a way that utilizes the properties of the models but incorporates information about the classes of the calibration data? The answer to this is SIMCA. There is some disagreement about the source of the acronym, (Soft Independent Method of Class Analogy, Standard Isolinear Method of Class Assignment, etc.) but there is consensus on the details of the method (Wold, 1976).

A SIMCA model consists of a collection of PCA models, one for each class in the data set. This is shown graphically in Figure 8-9. Each class can have a different number of principal components; the number depends on the data in the class. Each PCA sub-model contains all the usual parts of a PCA model: mean vector, scaling information, preprocessing such as smoothing and derivatizing, etc.
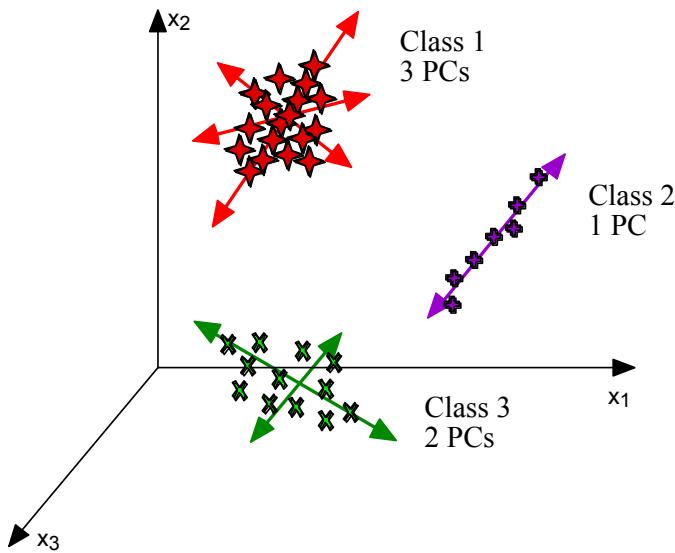
Figure 8-9. Graphical representation of a SIMCA model.

As an example of SIMCA, we now return to the Arch data from the previous example. Start the **Analysis** GUI, choose **File/Load Data/X-block** and load the data from the PLS_Toolbox/Dems folder. Select **SIMCA** from the **Analysis** menu, then click the **Show SIMCA model builder** button (the button with the hammer on it). The window shown in Figure 8-10 should appear. The available classes in the data set are shown on the left. Note that the unknown samples, which are listed as Class 0 in the arch DataSet Object, are not listed, as the tool assumes that samples of unknown class are listed as class 0.

Figure 8-10. SIMCA Model Builder window.

Start the model building process by selecting 1 from the Available Classes list then clicking **Fit Model**. (Note that it is possible to build a model on combined classes as well as individual classes.) A PCA model of the Class 1 samples appears in the main **Analysis GUI** window. This model can now be developed in the usual way—the number of PCs in the model can be selected, the preprocessing can be changed, etc. (In our example we'll leave the preprocessing set to the default autoscaling.) The samples from the classes not being modeled, as well as any unknown samples, will be projected onto the class model under construction. An example of this projection is shown in Figure 8-11, which shows the model of Class 1, the K class, as triangles. The unknown samples are the filled circles with labels s1-s12. (The labels were made to appear only on these samples by first selecting them from a plot of PC1 versus sample number, then selecting **View/Labels** in the **Plot Controls** window.) A 95% ellipse was created by selecting **Conf. Limits** in the **Plot Controls** window. As expected, the samples upon which the model was built fall near the center of the plot within the 95% ellipse. Sample s2 falls within the scores limit, and samples s3 and s4 are close (if the limit is adjusted to 99%, these samples fall inside).
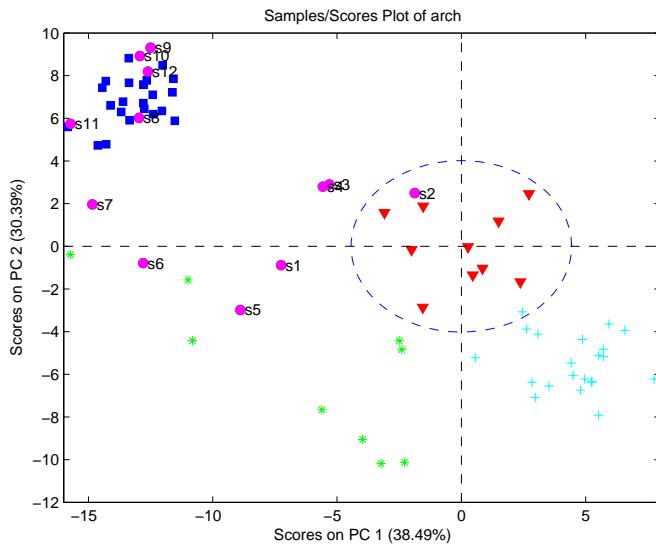
Figure 8-11. Arch data projected onto model of class 1 (K).

It is also useful to look at the T^2 versus Q for the data on the model of Class 1, as shown in Figure 8-12. Here the axes have been changed to logarithmic scales by selecting **View/Log Scales/All** in the **Plot Controls** window. Samples s2 and s3 are close to the 95% Q limit, while other samples are much further away.
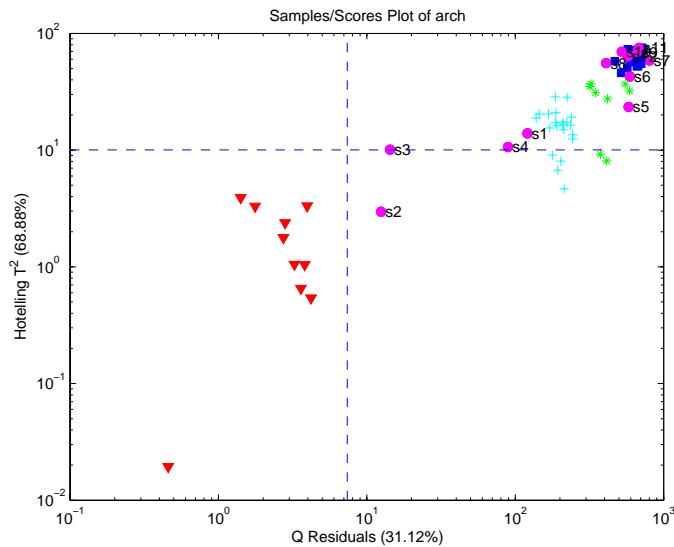
Figure 8-12. T^2 versus Q for all the Arch data on the model of class 1 (K).

Once the PCA model of class 1 is finalized, it may be added to the SIMCA model by clicking the **Add Model** arrow in the **SIMCA Model Builder** window. The next class can then be selected and the procedure repeated. For this example, all PCA models were constructed with two principal components except for class 3, the SH class, which was built with one component. Once all the models are built, click on **Assemble SIMCA**

Model in the **SIMCA Model Builder** window. To apply the SIMCA model to the calibration data and the unknown samples, click the **Calculate** button (the button with the gears on it) in the main **Analysis** GUI window.

To get a quick view of the results, click the **Samples/Scores** button and plot "Nearest Class" versus sample number. This should produce the plot shown in Figure 8-13. Note that all samples are nearest to their respective class. Labels can be added to the unknowns only by selecting them and turning labels on in the **Plot Controls/View** menu. A zoomed-in view focusing on the unknowns is shown in Figure 8-14. Except for sample s1, the assignments agree well with the classification by inspection and kNN results above. Note that the plots show the nearest class. The nearest class to a sample is defined as the class model which results in a minimum distance of the sample i to model j, d_{ij}:

$$d_{ij} = \sqrt{\left(Q_r\right)^2 + \left(T_r^2\right)^2}$$

(8-5)

with reduced Q:

$$Q_r = \frac{Q}{Q_{0.95}}$$

(8-6)

where $Q_{0.95}$ is the 95% confidence interval for the model under consideration, and reduced T^2:

$$T_r^2 = \frac{T^2}{T_{0.95}^2}$$

(8-7)

with a similarly defined $T^2_{0.95}$. This distance measure gives equal weighting to distance in the model space (T^2) and residual space (Q). Use of reduced Q and T^2 allows direct comparison of the values of specific samples on different SIMCA submodels. Without the use of these reduced statistics, each model's T^2 and Q values would be on very different numerical scales and not easily comparable.

Inspection of the reduced Q and T^2 plots (not shown) reveals that many of the samples are not within the 95% limits of the classes.
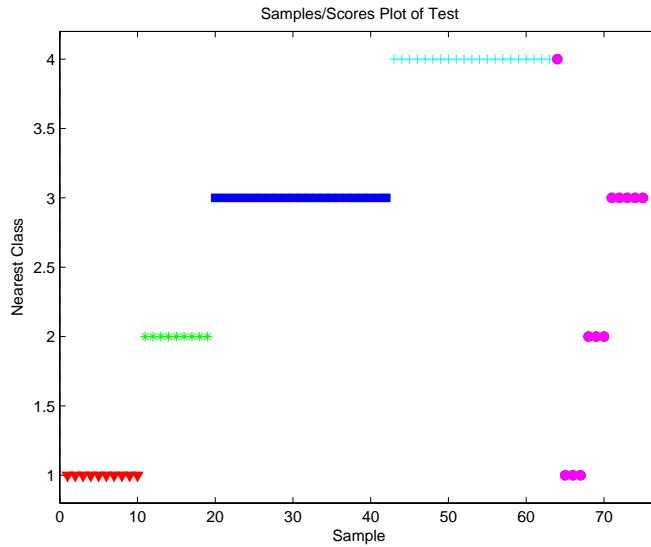
Figure 8-13. Nearest classes to SIMCA submodels for Arch samples.
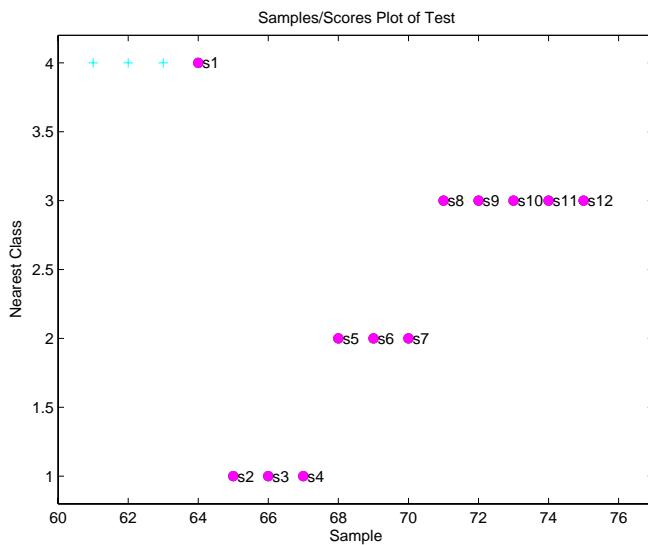
Figure 8-14. Nearest classes to SIMCA submodels for unknown Arch samples.

PLS-DA

While SIMCA is often a very useful classification tool, it does have drawbacks, the main one of these being that the PCA submodels in SIMCA are computed with the goal of capturing variation within each class. No attempt is made to identify directions in the data space that discriminate classes directly. We now consider a classification method that addresses this issue directly: Partial Least Squares Discriminant Analysis (PLS-DA). The attentive reader will note that the goal of PLS-DA is very similar to that of another

common discrimination technique called Linear Discriminant Analysis (LDA). In fact, Barker and Rayens (2003) have shown that PLS-DA is essentially the inverse-least-squares approach to LDA and produces essentially the same result but with the noise reduction and variable selection advantages of PLS.

In PLS-DA we will use PLS to develop a model that predicts the class number for each sample. In a data set with just two classes, it is easy to see how we might set up a y variable which indicates if the samples are in one of the classes by setting it to 1 if it is in the class and 0 if it is not. The model, of course, will not predict either a 1 or 0 perfectly, so a limit must be set, say 0.5, above which the sample is estimated as a 1 and below which it is estimated as a 0.

But what if there are more than two classes? It would be possible to set up a y variable with the class numbered 1, 2 or 3. However, this would imply that class 2 is somehow in between class 1 and class 3, which likely is not the case. The solution to this is to create a Y-block with a variable for each class. A 1 indicates a sample belongs to a class, and a 0 indicates that it does not. PLS for multivariate Y can now be performed.

As an example of PLS-DA, we now return to the Arch data set. Load the arch.mat file into the **Analysis** GUI by selecting **File/Load/X-block** in the main **Analysis GUI** window. Under the **Analysis** menu select **PLS-DA**. Set up cross-validation by selecting **Cross-Validation** from the **Tools** menu. In the **Cross-Validation** window that appears, select **Venetian Blinds** under the **Cross-Val Method** menu. The defaults of 9 splits of the data and 10 LVs can be left as they are. Click the **Calculate** button (the gears) in the main **Analysis** GUI window. The result should look like the window shown in Figure 8-15.

The number of latent variables (LVs) to retain in the model must now be specified. Click on the **Stats** button (the button with the pink graph and lambda symbol). The RMSECV curves for each of the four class variables in the Y-block can viewed by control-clicking each of the curves in the **Plot Controls** window. A legend can be added by clicking the legend icon on the plot. The result should look like Figure 8-16. It is apparent that the RMSECV for all the class variables level out after three LVs, except for class 1, which continues down slightly. Based on this, selecting three LVs for the overall model appears prudent. A selection of three LVs is also supported by the Variance Captured table. Select three LVs by clicking the third line of the Variance Captured table and then clicking the **Calculate** button.
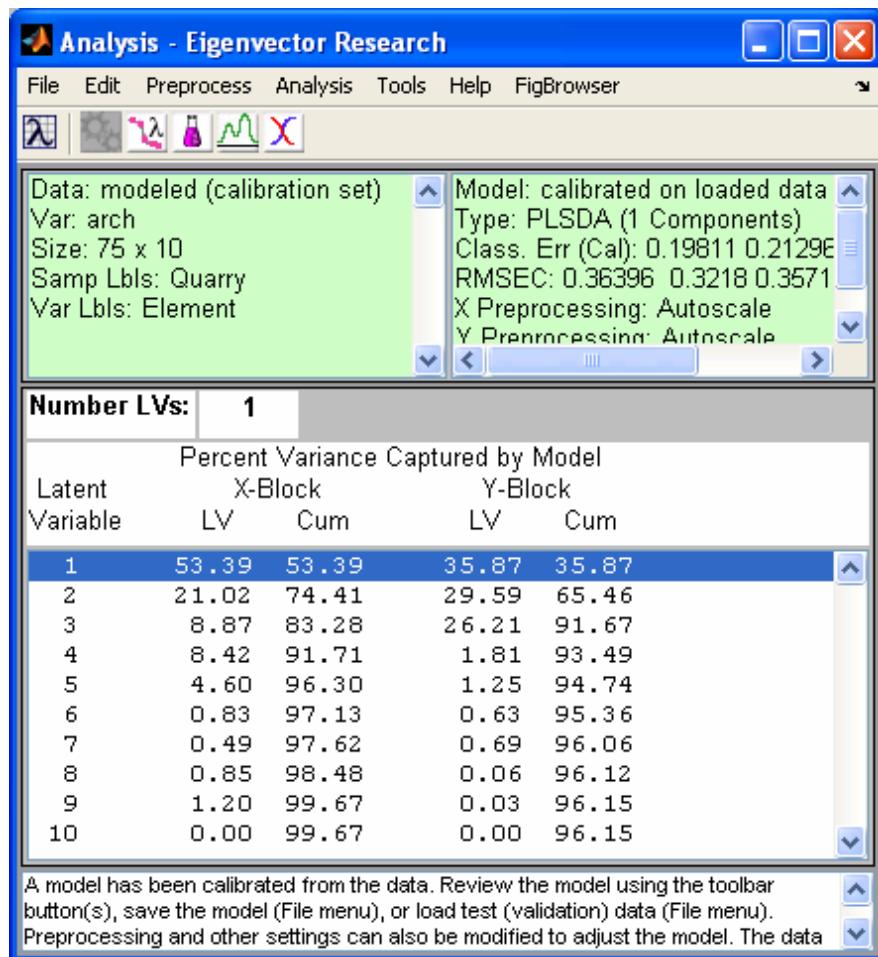
Figure 8-15. Analysis GUI main window with PLS-DA model of Arch data.
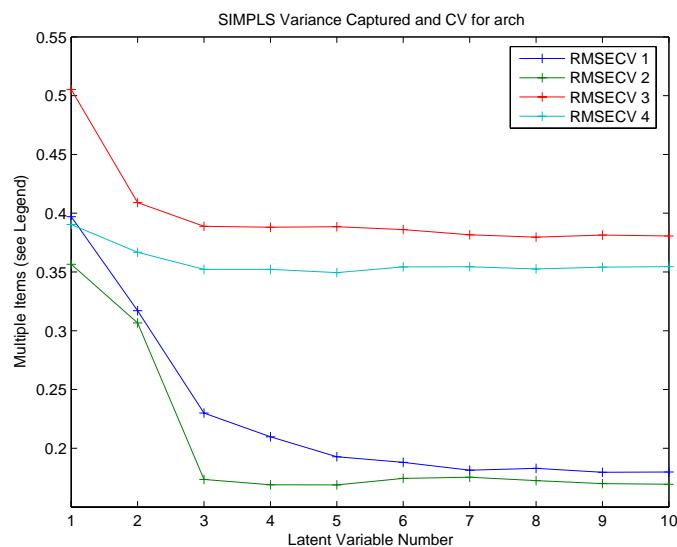
Figure 8-16. RMSECV for classes in PLS-DA model of Arch data.

Other aspects of the PLS-DA model may now be explored. Click the **Samples/Scores** button, and use the **Plot Controls** window to view the sample scores and the predictions for all of the samples, including the unknowns, for each of the classes. For instance, it is possible to view the predictions for class 1 (K) by selecting **Y Predicted 1 (Class 1)** from the Y menu. The result for the three-LV PLS-DA model is shown in Figure 8-17. The calculated threshold is shown as the horizontal red dashed line at approximately 0.35. The threshold is estimated using Bayes' Theorem and the available data in order to minimize total errors (see the `plsdthres` function for more details).

Note that one of the BL samples (green stars) is predicted to be a Class 1 (K). Changing the model to four LVs corrects this, and appears to have little impact on any of the other class identifications (Figure 8-18). Note that samples s2-s4 are predicted to be class 1 (K). Samples s5-s7 are predicted as class 2 (BL), and samples s7-s12 are predicted to be class 3 (SH). Note that sample S7 is predicted to belong to both the BL and SH class (in both the three-LV and four-LV models). Sample s1 is not predicted to belong to any model.

The Bayesian threshold calculation assumes that the predicted y values follow a distribution similar to what will be observed for future samples. Using these estimated distributions, a threshold is selected at the point where the two estimated distributions cross; this is the y-value at which the number of false positives and false negatives should be minimized for future predictions. This calculation assumes that the distribution of predicted y-values for a class is approximately normal. Small numbers of samples in any class may bias the threshold. Similar calculations can be done on cross-validated or test-set y-predictions to verify future performance of the selected threshold. In addition, examination of the observed distribution of y-values is also warranted. This can be done by examining the ROC and Threshold plots.
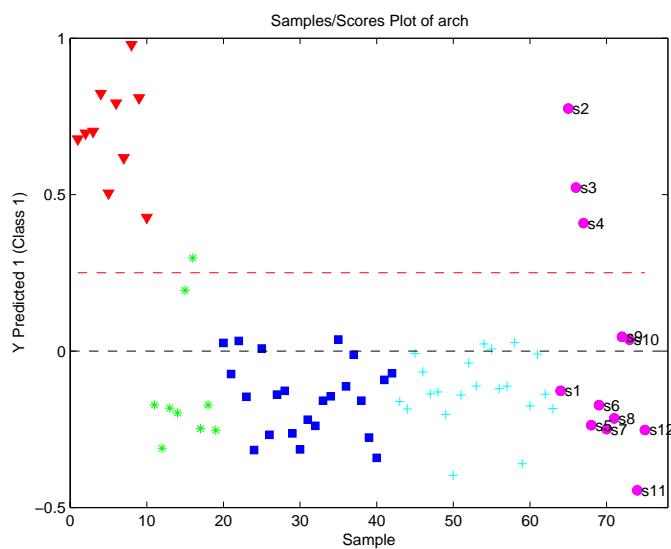
Figure 8-17. PLS-DA three-LV model predictions for class 1 (K).
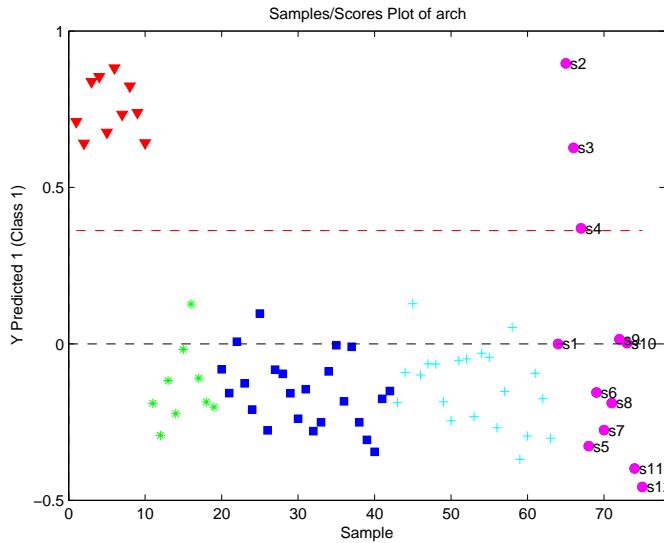
Figure 8-18. PLS-DA four-LV model predictions for class 1 (K).

The overall sensitivity and specificity of the model can be accessed by selecting the **View/Show Model Details** menu in the **Analysis** GUI or using the `modlrder` function at the command line. In these results, the sensitivity and specificity is reported for each of the four classes as well as both calibration (self-prediction) and cross-validation results. In this case, all are reported as perfect (no errors):

```
Modeled Class: 1 2 3 4
Sensitivity (Cal): 1.000 1.000 1.000 1.000
Specificity (Cal): 1.000 1.000 1.000 1.000
Sensitivity (CV):  1.000 1.000 1.000 1.000
Specificity (CV):  1.000 1.000 1.000 1.000
```

These values (which, in this case, indicate no errors in either calibration or cross-validation) can be converted into "fractional error" by subtracting each from 1.

Sensitivity and specificity can also be viewed in a graphical form referred to as a Receiver Operating Characteristics Curve (ROC curve) by selecting the **ROC curves** button in the **Analysis** GUI toolbar. The result of this is shown in Figure 8-19. The sensitivity versus specificity for each of the four class models are shown on the left. Each plot shows the specificity of the model (number of samples predicted as not in the class divided by actual number not in the class) versus the sensitivity (number of samples predicted as in the class divided by number actually in the class) as a function of selected threshold. A curve which reaches the upper left corner implies that at some threshold, the specificity could be perfect (1) without loss of sensitivity (dropping below 1). The threshold selected by the PLSDA algorithm is shown as a red circle on each of the estimated and cross-validated curves.
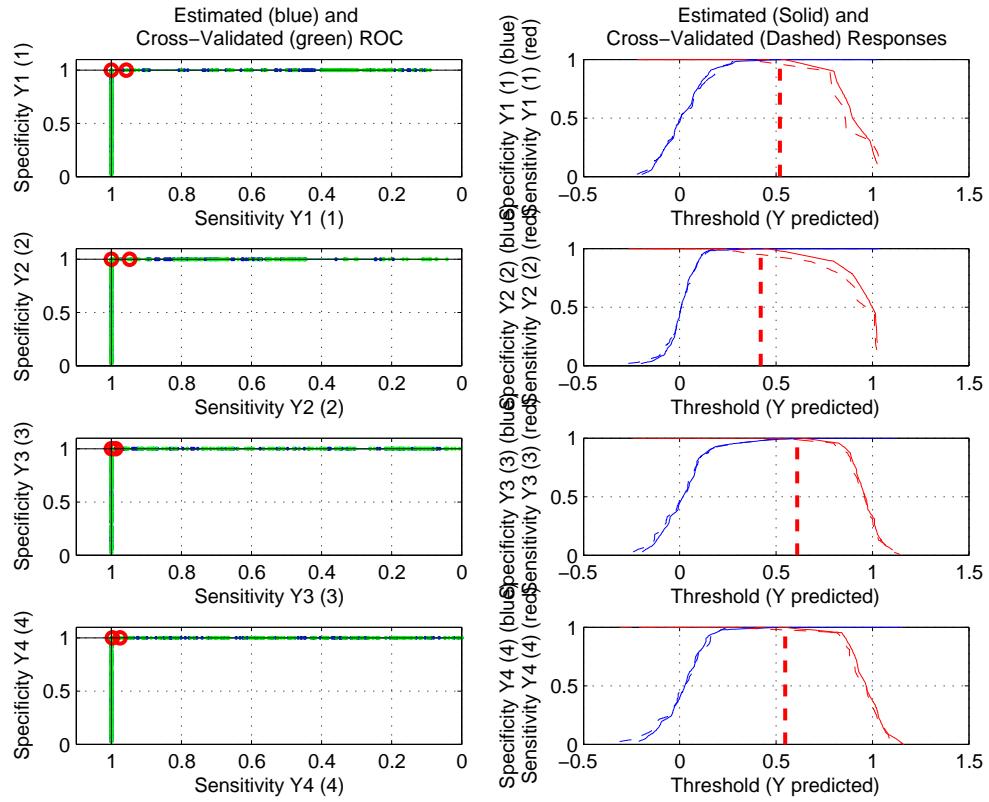
Figure 8-19. Receiver Operating Characteristic curves (left) and threshold plots (right) for PLS-DA model of Arch data.

The figures on the right show the sensitivity and specificity as the threshold value is varied. Ideally, these lines cross while still at a value of 1. Crossing below a value of 1 indicates that, as the threshold is increased, sensitivity begins to suffer (drops below 1) before the model is completely specific. The vertical dashed red line indicates the threshold selected by the PLSDA algorithm. This is the threshold used to calculate the sensitivity and specificity reported in the model details. The point that the vertical threshold line crosses the solid red line in any given plot is the calibration sensitivity, and the point where the threshold line crosses the dashed red line is the cross-validation sensitivity. Similarly, the point where the threshold line crosses the solid blue line is the calibration specificity and the point where the threshold line crosses the dashed blue lineis the cross-validation specificity.

It should be noted that the curves in both sets of plots are estimated based on interpolation between measured values. It is not unlikely that, as in this example, the ROC curves show a slightly different sensitivity and specificity result than that given in the model details. The **Model Details** results are the exact sensitivity and specificity determined from the modeled samples. The ROC curve results are the estimated results given a larger, similarly distributed set of samples.

Based on the results shown in Figure 8-19, the PLS-DA model of Arch is nearly a complete success based on calibration and cross-validation using data with known classes. The only real issue is sample s7, which is predicted to belong to both the BL and SH class with approximately equal probability. Inspection of a PCA of the data as well as scores from the PLS-DA model suggests that this sample is much more likely to be BL rather than SH. It is possible to add non-linear terms to the model by augmenting the original data with squares and cross terms of the data. If this is done, the classification of s7 is BL.

A detailed treatment of the PLS-DA technique is given by Barker and Rayens (2003). In addition, an example of its use was given by Musumarra (2004).

212

9. Curve Resolution and Mixture Analysis

PCA is perhaps the most commonly used factor analysis technique; however, it is not the only one. In this chapter, additional factor-based techniques are considered that are useful for extracting information from a data set. While techniques such as PCA calculate factors based on mathematical properties such as capturing maximum variance and orthogonality, the factors are often difficult to interpret because they are generally not directly related to chemical properties. For example, PCA loadings of a data set of measured spectra generally are not pure component spectra. Instead, the loadings are typically linear combinations of pure analyte spectra that have positive and negative intensities. Factor analysis techniques discussed in this chapter are aimed at estimating factors that have desirable properties from a chemical point of view and are easier to interpret.

The first two sections of this chapter discuss evolving factor analysis (EFA) and evolving window factor analysis (EWFA). These two techniques are appropriate for data that are naturally ordered or have continuity, and can be used to find an initial estimate of the range of existence of analytes in an evolving system. This discussion is followed by a section on multivariate curve resolution (MCR). MCR examples utilize EFA results to initialize the algorithm for an evolving data set. MCR is also known as self-modeling curve resolution (SMCR) and end member extraction. The MCR section introduces the mathematical model for the technique as well as the constrained alternating least squares algorithm (ALS). Although ALS is not the only algorithm used in MCR, it is one of the most common. It is one of several algorithms available that solve the objective function in a constrained least squares sense.

A related technique, discussed after MCR, is self-modeling mixture analysis (SMA). The objectives and mathematical models of MCR and SMA are similar; they both typically decompose a data matrix into the outer product of non-negative factors. The difference is that SMA is appropriate for data sets that are not evolving or naturally ordered in time. In fact, SMA algorithms can be applied to data sets that have continuity, but techniques specifically designed to take data ordering into account are often not useful for data that does not have continuity. The SMA section introduces purity-based methods. These algorithms are based on geometric arguments regarding data that are naturally decomposed into the outer product of non-negative factors. These algorithms tend to be fast and work very well when the data are highly selective. However, purity-based algorithms do not generally find a solution in a least squares sense and are not as amenable to the inclusion of constraints. Therefore, purity-based methods are very popular for obtaining (and inspecting) an initial solution that is followed by an algorithm that allows for a constrained least squares solution.

Evolving Factor Analysis

Evolving Factor Analysis (EFA) is one method applied to data that are naturally ordered; for example, data produced by dynamic systems. Like multi-way principal components analysis (MPCA), EFA considers the ordered nature of the data set explicitly. EFA is a general technique for analysis of multivariate data that have an intrinsic order (Keller and Massart, 1992). Like PCA, EFA can be used to determine how many "factors" are present in a data set; that is, how many independent sources of variation exist. Additionally, EFA can be used to determine where in a data set the factors first appear and where they disappear.

The fundamental idea of EFA is to follow the singular values of a data matrix as rows (samples) are added. Given a data matrix $\mathbf{X}$ (usually not mean-centered when performing EFA) with m samples and n variables, the singular value of the first row (sample) is determined. Next, the singular values for the first two rows are calculated, followed by the first three rows, and so on until all m samples have been considered. Since the number of samples considered, and thus the number of factors, evolves as the method proceeds, the technique is known as EFA. Of course, the number of non-zero singular values can never be greater than the lesser of the number of rows and columns in the sub-matrix considered. It is also customary to do EFA in the reverse direction, *i.e.,* determine the singular values starting from the last row in the matrix and working upwards until all rows have been considered.

Once the singular values have been determined, they (or their logarithms, since they usually span many orders of magnitude) can be plotted versus the ordered variable (*e.g.,* time). As new factors enter the data, new significant singular values will rise from the baseline of small singular values associated with noise in the data. Working in the reverse direction, significant singular values will rise from the baseline when factors disappear from the data matrix.

EFA Example

As an example of EFA, consider the semiconductor etch process again (see the previous description of the data set in Chapter 5). Optical Emission Spectroscopy (OES) was used to measure the plasma during etch. Initially, there is only the BCl_3/Cl_2 etch gas in the reactor. When the plasma is ignited, the first layer of aluminum begins to etch away. Once the aluminum is gone, the titanium nitride (TiN) is uncovered and begins to etch away. When the TiN layer is gone, the plasma is in contact with only the silicon oxide layer, which is nearly non-reactive. A set of idealized concentration profiles is shown for this process in Figure 9-1, along with a set of pure component spectra (obtained using MCR, discussed below).

Of course, the pure component spectra are not observed directly. Instead the measured mixture spectra are observed as a function of time, as shown in Figure 9-2. These data can be found in the `oesdata.mat` file. Note that the data are stored as a DataSet Object of type 'batch.' Three etch runs are stored, each with a different number of time steps. To accommodate the different number of time steps (number of rows), the data are stored as

214
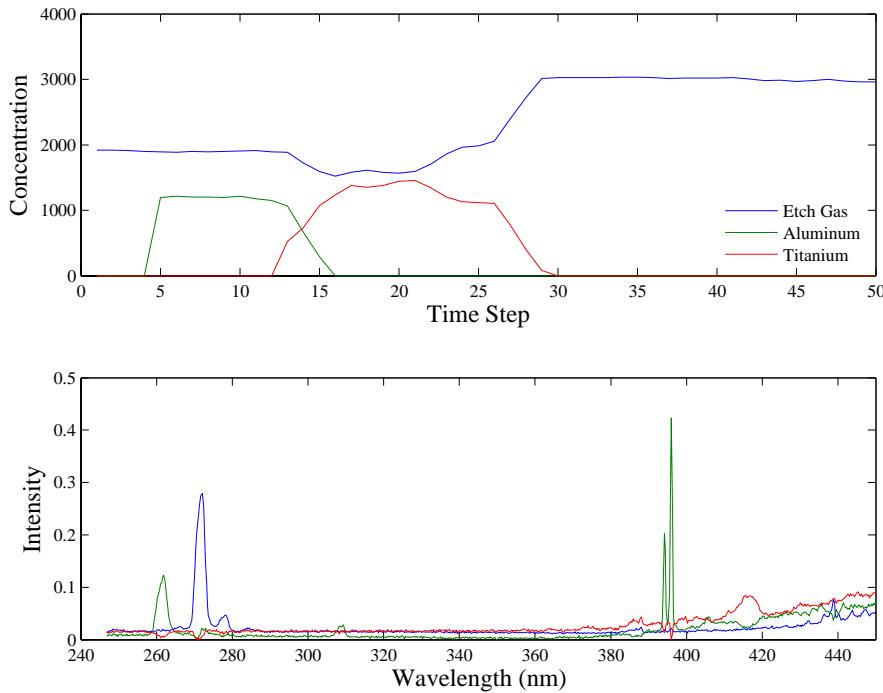
Figure 9-1. Concentration profiles and pure component spectra for EFA example.

a cell array in the `oesdata.data` field. If the data followed the idealized concentration profiles of Figure 9-1, the results of EFA would be as shown in Figure 9-3. In the forward analysis, a large singular value exists from the very beginning, a result of the presence of the etch gas. As Aluminum (Al) begins to etch, another singular value is added. A third singular value rises from the baseline as TiN begins to etch. In the reverse direction, all that remains at the end of the run is etch gas. As the TiN etch ends, a singular value rises from the baseline. Finally, a third singular value emerges as the Al etch ends.

Unfortunately, in reacting systems, evolving factor analysis is seldom this simple (though it can be in chromatography and other analytical applications where a separation step precedes the spectroscopic measurement). Figure 9-4 shows the results of EFA on actual OES data from the first wafer in the data set. Evolving factor analysis can be applied to this data using the `evolvfa` function as follows:

```
» load oesdata;
» [egf,egr] = evolvfa(oesdata.data{1});
```

Here the input is the matrix of spectra from the first batch and the outputs are the forward and reverse singular values. The results are shown in Figure 9-4. In this example, both etch gas and Al are present at the beginning of the run. A second singular value is

observed when the Al disappears; that is, when it starts to vary independently from the etch gas. A fourth minor component is also observed.
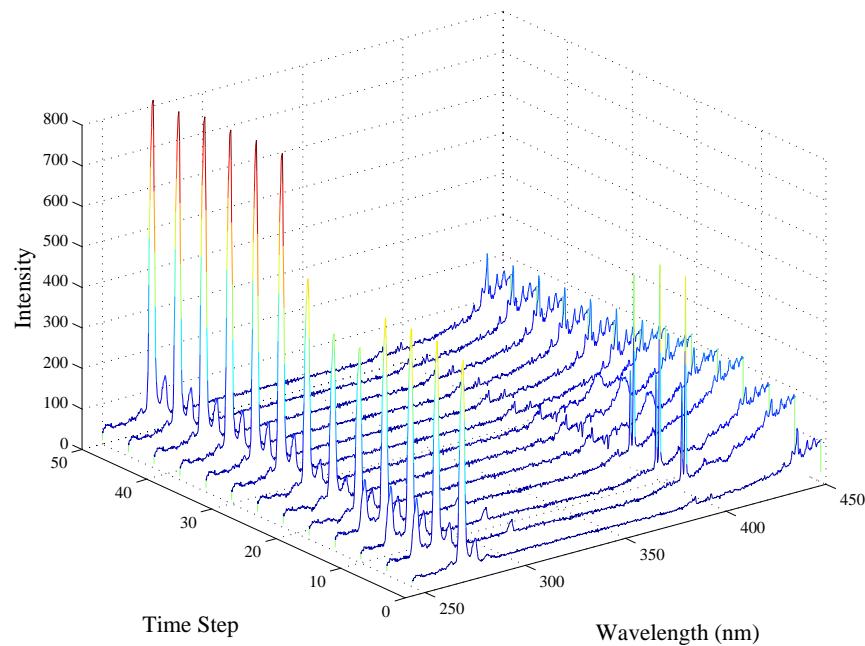
Figure 9-2. Optical emission spectra as a function of time.
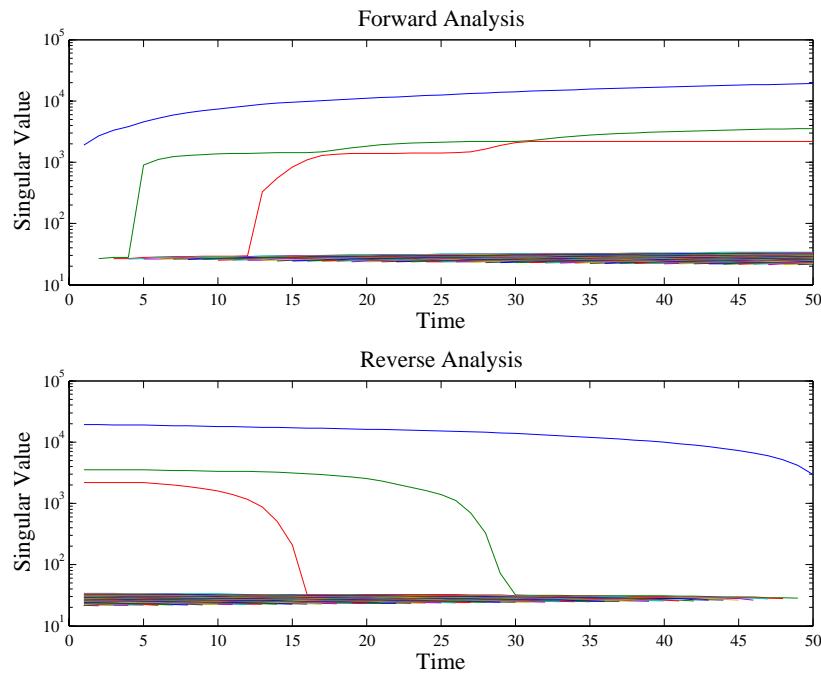
Figure 9-3. Evolving factor analysis of idealized OES from etch process.
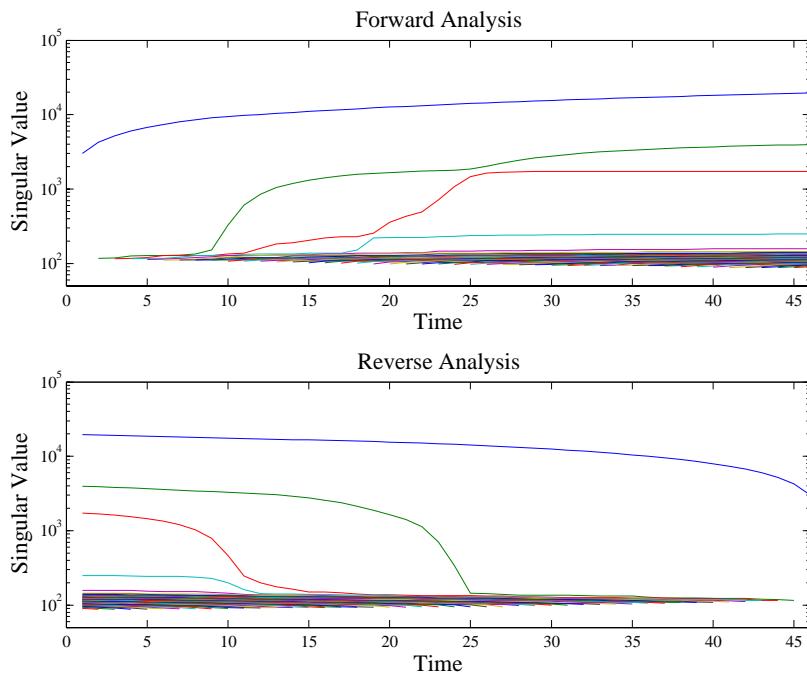
Figure 9-4. Evolving factor analysis of actual OES from etch process.

In summary, EFA provides important information concerning the times of existence of independently varying factors in the data set. This may be used to identify when analytes enter a reactor, or when process disturbances or instrument failures occur. However, interpretation of EFA profiles can be complicated when ranges of existence are highly overlapped.

Evolving Window Factor Analysis

Evolving Window Factor Analysis (EWFA) is closely related to EFA and can sometimes be used to resolve ambiguities concerning the range of existence of factors in a data set. EWFA tracks the singular values of a moving window in a data set. For instance, with a window width of $2j+1$ samples, i is incremented $i=1,\ldots,m$ and the singular values of samples $i-j$ to $i+j$ are calculated. As in EFA, the singular values are plotted as a function of index number i. The result is an indication of the number of independently varying factors in each window.

Consideration must be given to the window width used in EWFA. The window should be narrow enough to isolate factors which exist in different parts of the data record, but sufficiently wide to enhance the signal-to-noise obtained by including multiple spectra. At times the choice is not easy; however, it is a simple matter to try several window widths and examine the results. One suggestion is to use EFA first to find out how many factors are present in the entire data set, then use a window width that is one sample larger than the number of factors.

<u>Example of EWFA</u>

As an example of EWFA, the OES data from the semiconductor etch process is used again. EWFA can be performed on the first wafer of the `oesdata.mat` file using the `ewfa` function as follows:

```
» load oesdata;
» eigs = ewfa(oesdata.data{1},7);
```

In this example, the window width was set to 7 and the results are shown in Figure 9-5. Singular values for the windows near the ends of the record with a width less than 7 are shown as dashed lines. It is clearly seen that there is only a single source of variation at both ends of the data record (though we know that at the beginning it is both Al and etch gas). There are three sources of variation centered around sample 12 and two sources around sample 23. Given our knowledge of the process, it is a good guess that the two factors centered around sample 23 are etch gas and TiN. What about around sample 12? Based on the EFA, we know that there are four factors total in the data set. The three factors must be etch gas, Al, and an unknown fourth component. Multivariate Curve Resolution may help us determine its origin.

Multivariate Curve Resolution

EFA and EWFA provide important information regarding the system; namely, the total number of factors present and their times of appearance and disappearance. However, it would be impossible to identify the compounds based on this information alone (additional information is necessary). Nonetheless, the results of EFA do provide a starting point for the determination of the concentration profiles and pure component spectra. Techniques for obtaining this additional information are known as Multivariate Curve Resolution (MCR), or Self Modeling Curve Resolution (SMCR) (see Jiang and Ozaki, 2002; Tauler *et al.,* 1993a,b, 1994, 1995, 1998; Massart *et al.,* 1998; Hamilton and Gemperline, 1990; Sánchez *et al.,* 1997). MCR has also been referred to as End Member Extraction.
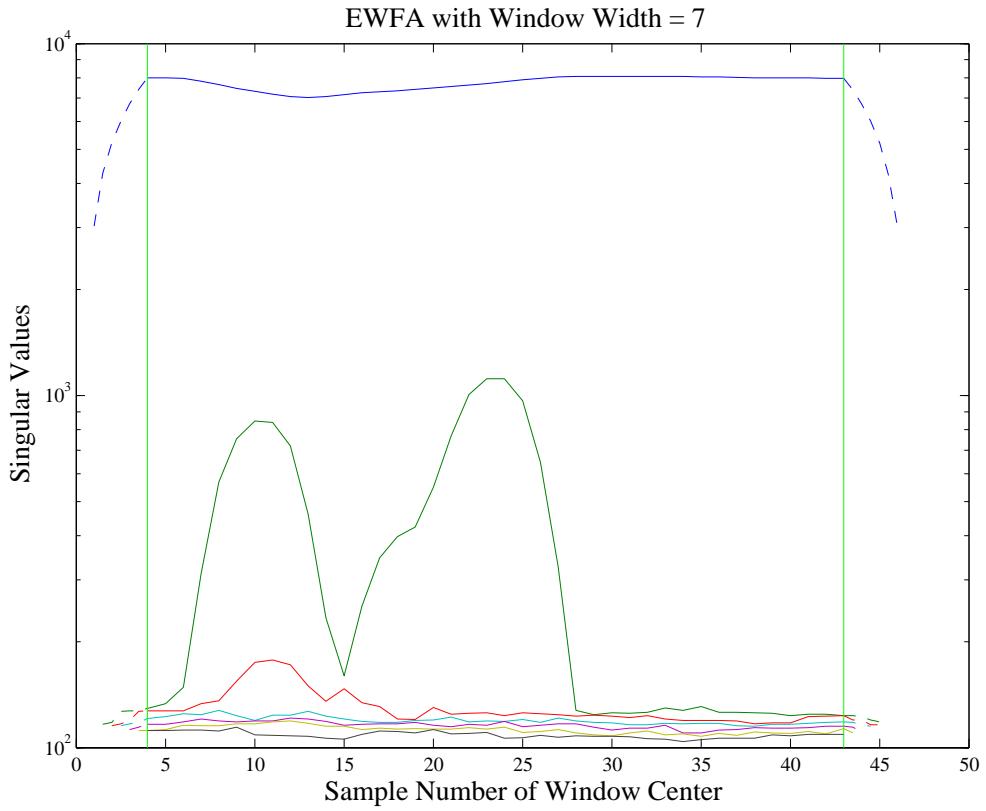
Figure 9-5. Evolving window factor analysis of actual OES from etch process.

The objective of MCR is to extract concentration profiles and pure component spectra with as few assumptions about the data as possible. Given an $m \times n$ data matrix $\mathbf{X}$ (not mean-centered) that is the product of a $m \times k$ matrix of concentration profiles $\mathbf{C}$, and a $n \times k$ matrix of pure component spectra $\mathbf{S}$, where k is the number of analytes,

$$\mathbf{X} = \mathbf{CS}^T + \mathbf{E} \qquad (9\text{-}1)$$

the goal is to obtain physically meaningful $\mathbf{C}$ and $\mathbf{S}$. Obviously this cannot be obtained directly from a principal components analysis (PCA) decomposition of $\mathbf{X}$ without additional information because the equation:

$$\mathbf{X}_{est} = \mathbf{TP}^T = \mathbf{TRR}^{-1}\mathbf{P}^T = \mathbf{CS}^T \qquad (9\text{-}2)$$

where

$$\mathbf{X} = \mathbf{X}_{est} + \mathbf{E} = \mathbf{TP}^T + \mathbf{E} \qquad (9\text{-}3)$$

has an infinite number of solutions for any arbitrary invertible k by k transformation matrix $\mathbf{R}$, resulting in a rotational and intensity ambiguity for $\mathbf{C}$ and $\mathbf{S}$ if no other information is known. Here $\mathbf{T}$ is a m by k matrix of scores with orthogonal columns,

and $\mathbf{P}$ is a n by k matrix of orthonormal loadings also referred to as "abstract factors" (Malinowski, 1991).

Fortunately, more information *is* typically available. In particular, both concentrations and spectra are necessarily non-negative. Using this constraint, it is often possible to extract the pure component spectra through a procedure of alternating and constrained least squares optimization. For example, non-negativity is a sufficient constraint if there is sufficient selectivity in the data (Manne, 1995; Tauler, 2001; Gemperline and Cash, 2003). Starting with the results of the EFA, it is possible to obtain an initial estimate of the concentration profiles, or at least, the range of existence in the data set of each component. These concentration profiles are used as initial estimates in the constrained and alternating least squares optimization. At each iteration of the optimization, a new estimate of the spectra matrix $\mathbf{S}$ and of the concentration profiles $\mathbf{C}$ is obtained. Iteration between the following two equations is performed:

$$\mathbf{S}^T = \mathbf{C}^{+T}\mathbf{X}_{est} \tag{9-4}$$

$$\mathbf{C} = \mathbf{X}_{est}\mathbf{S}^+ \tag{9-5}$$

where $\mathbf{C}^+ = \mathbf{C}\left(\mathbf{C}^T\mathbf{C}\right)^{-1}$ and $\mathbf{S}^+ = \mathbf{S}\left(\mathbf{S}^T\mathbf{S}\right)^{-1}$ are pseudoinverses of the matrices $\mathbf{C}$ and $\mathbf{S}$ respectively. If non-negativity constraints are implemented, Equations (9-4) and (9-5) are solved subject to these constraints. Equality constraints, such as forcing the concentration of a particular analyte to zero or some known value, can also be imposed. Selection of the correct number of components when originally calculating $\mathbf{X}_{est}$ (see Equation 9-3) is important. Selecting too few components will cause small-variance components to be undetectable. Although the original unfiltered data, $\mathbf{X}$, can be used, use of $\mathbf{X}_{est}$ can improve the stability of the pseudoinverse calculations, since $\mathbf{X}_{est}$ is a noise-filtered estimate of $\mathbf{X}$.

The constrained alternating least squares algorithm discussed above is commonly used. However, other algorithms that have similar objectives to those stated for MCR above are also used (see Tomasi *et al.*, 2006; Paatero,1997; Berman *et al.*, 2005). It should be noted that there is typically an intensity ambiguity in the MCR results, *i.e.*, an ambiguity in the absolute magnitude of the concentration profiles and pure component spectra. For example, if $\mathbf{D}$ is an arbitrary k by k invertible diagonal matrix then

$$\mathbf{X}_{est} = \mathbf{C}\mathbf{S}^T = \mathbf{C}\mathbf{D}\mathbf{D}^{-1}\mathbf{S}^T \ . \tag{9-6}$$

If, however, the concentration of a component is known at any point within the data (*e.g.*, by including standards), it is possible to resolve the ambiguity for that particular component. However, when non-zero equality constraints for a concentration profile and/or spectrum are unavailable, the estimated spectrum $\mathbf{s}_k$ is constrained to be of unit length such that $\mathbf{s}_k^T\mathbf{s}_k = 1$ (otherwise a solution might wander about aimlessly without improving the fit). If additional information is known about the problem, it is possible to

incorporate it into the iteration procedure as a constraint. For instance, it is often assumed that the concentration profiles are unimodal. In other cases, closure or a known stoichiometry may be used. When additional known (correct) constraints are used, the quality of the solution obtained generally improves. The most common constraints are non-negativity that can be applied using hard (Bro and de Jong, 1997) or soft (Gemperline and Cash, 2003) methods. Other constraints can include hard modeling or functional constraints (see de Juan et al., 2000; Gurden et al., 2001; Gallagher et al., 2003).

As mentioned above, good solutions for **C** and **S** can be obtained when good selectivity exists. However, as the selectivity decreases, the estimates can become poor. This is a result of a rotational ambiguity [Gemperline, 1999; Tauler, 2001). For example, if **R** is an arbitrary invertible non-diagonal matrix then

$$\mathbf{X}_{est} = \mathbf{CS}^T = \mathbf{CRR}^{-1}\mathbf{S}^T \ . \tag{9-7}$$

Note: Users should be aware of the potential for multiplicative [Equation (9-6)] and rotational [Equation (9-7)] ambiguities and not over-interpret results from MCR. Utilizing additional correct constraints can reduce ambiguities in the solution; however, multiplicative ambiguities mean that **C** and **S** are in arbitrary units. In a perfect world, **C** and **S** would be proportional to true concentrations and spectra (at unit concentration and pathlength); however, rotational ambiguities can make concentration profiles and spectra look different from the true underlying factors. To emphasize these potential problems, **C** will be referred to as "contributions" instead of "concentrations" in the remainder of this chapter. The columns of the matrix **S** will still be referred to as spectra and/or pure component spectra.

It is also possible to combine data sets from different process runs (or analytical runs) simply by augmented matrices as follows:

$$\mathbf{X} = \begin{bmatrix} \mathbf{X}_1 \\ \mathbf{X}_2 \\ \vdots \\ \mathbf{X}_P \end{bmatrix} = \begin{bmatrix} \mathbf{C}_1 \\ \mathbf{C}_2 \\ \vdots \\ \mathbf{C}_P \end{bmatrix} \mathbf{S}^T + \begin{bmatrix} \mathbf{E}_1 \\ \mathbf{E}_2 \\ \vdots \\ \mathbf{E}_P \end{bmatrix} \tag{9-8}$$

where $\mathbf{X}_p$ are the ordered data for each of the $p = 1,\ldots,P$ process runs and the $\mathbf{C}_p$ are the associated contribution profiles from the runs. Combining data from different runs, and/or measured standards, may also contribute to the stability of the solutions obtained. Augmented matrices of standard analytes can be included to improve selectivity and allow MCR to be used for quantification (see Tauler, 1995; de Juan et al., 1998; Tauler et al., 1998; de Juan et al., 2001).

Example of Multivariate Curve Resolution

As an example of MCR, the data used in the EFA example discussed above are used. Recall that the approximate range of existence of each component present in the data was determined using EFA. Due to its small size, the fourth component in this data set is difficult to estimate; therefore, in the first attempt, only the first three components are estimated. It is expected that these data can be decomposed as non-negative concentrations times non-negative spectra, and the default optional constraint for `mcr` and its low level decomposition function `als`. is non-negativity for $\mathbf{C}$ and $\mathbf{S}$. The `als` function is used in this example.

The first step in the MCR decomposition is to generate an initial estimate of the contribution profiles, `c0` (or spectra). In this case there is reason to believe that the BCl_3/Cl_2 etch gas is present for the entire run. Al, however, is only present at the beginning, and TiN should only be present in the middle. Thus, an initial estimate is constructed using the expected range of existence of the analytes as follows:

```
» dat = oesdata.data{1};
» c0         = zeros(46,3);
» c0(:,1)    = 1;
» c0(1:12,2) = 1;
» c0(9:24,3) = 1;
```

The MCR decomposition can be performed using the `als` function as follows:

```
» [c,s] = als(dat,c0);
Non-Negativity on C (Fast Least-Squares)
Non-Negativity on S (Fast Least-Squares)
Terminated based on maximum iterations
Elapsed time: 18.3 seconds
Residual (RMSE) 7.956991e+002
Unmodelled Variance is 0.158656 percent
```

The resulting estimates for the contribution profiles and pure component spectra are shown in Figure 9-6. The residuals are also plotted as a function of time and wavelength (Figure 9-7). Figure 9-6 looks close to the expected result; however, the third analyte (TiN) has non-zero values in the first nine time steps. This was not expected based on the way the layers are applied to the semiconductor. Additionally, the residuals are high in the contribution profile about where EFA suggested the fourth component might exist. Contribution constraints can be used to eliminate non-zero estimates for the TiN where it is expected to have zero contributions. Constraint matrices are constructed using desired numerical values where constraints are to be applied, and `NaNs` in locations where there are no constraints. This is done as follows:
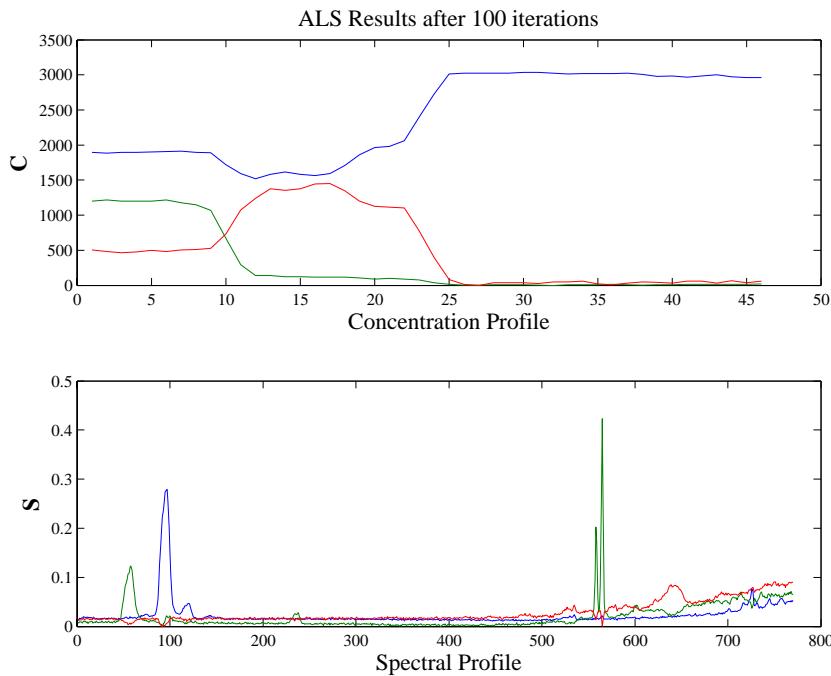
Figure 9-6. Results from MCR of OES from etch process with non-negative constraints and three factors: etch gas (blue), Al (green), TiN (red).

```
» options = als('options');
» options.cc          = zeros(46,3)*NaN;
» options.cc(15:end,2) = 0;
» options.cc(1:8,3)    = 0;
» [c,s] = als(dat,c0,options);
Non-Negativity on C (Fast Least-Squares)
Non-Negativity on S (Fast Least-Squares)
Hard Equality Constraints on C: component(s) 2  3
Terminated based on maximum iterations
Elapsed time: 16.8 seconds
Residual (RMSE) 7.966828e+002
Unmodelled Variance is 0.159048 percent
```

The first command above generates a default options structure, and the following commands fill in the contributions constraints matrix options.cc. Note that options.cc is the same size as the expected output c, *i.e.,* it is $m \times k$. The results from running als with the constraints are shown in Figure 9-8. In the contribution estimates, the etch gas is the upper line. The Al curve starts positive then goes to zero, while the TiN starts at zero, peaks, and returns to zero.

Next, we use the als function to estimate the contribution profiles and the spectra for the OES data with four factors. The contributions of the Al and TiN were constrained to be

zero in ranges suggested by the initial MCR results. A fourth component was constrained to be zero in the range of time steps 1 to 7 and 15 to 46.
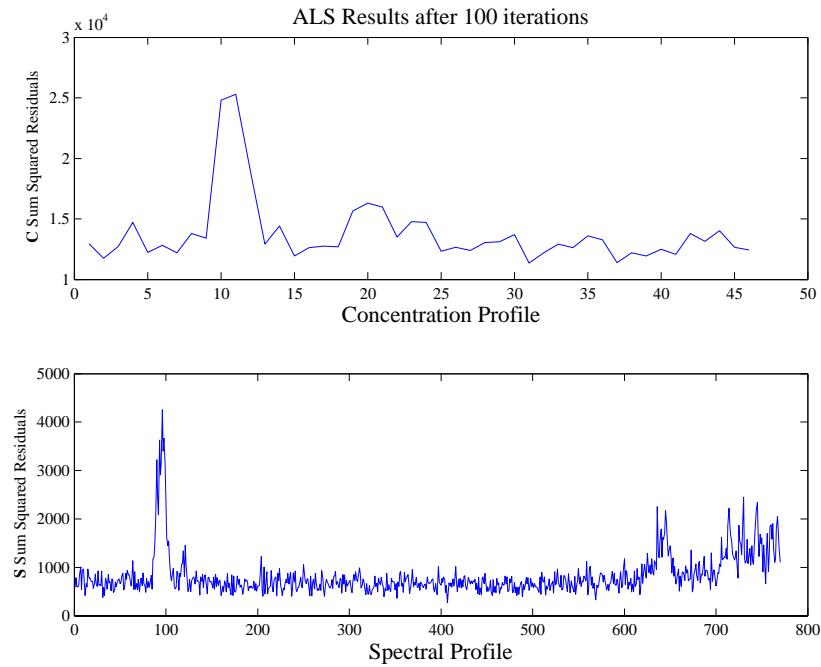
Figure 9-7. Residuals corresponding to the analysis shown in Figure 9-6.
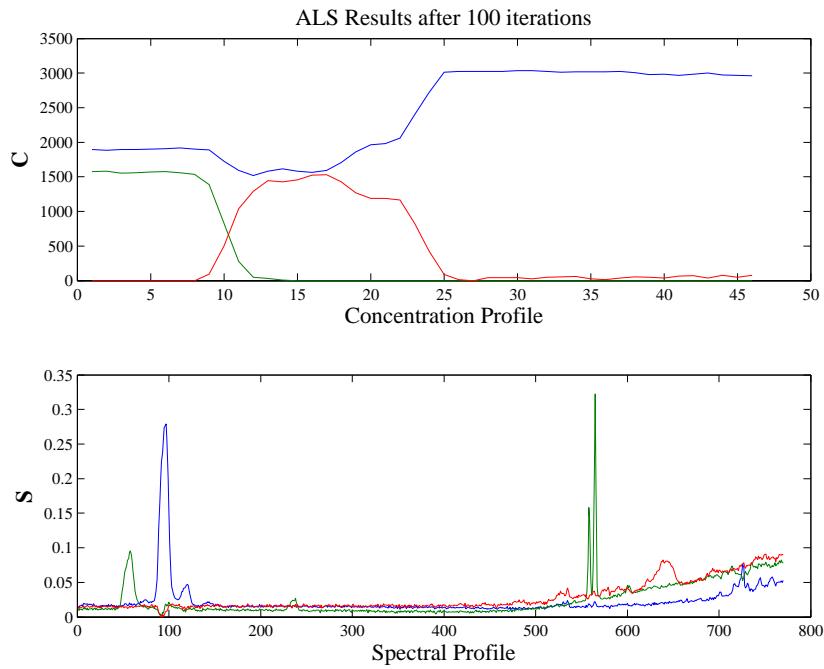
Figure 9-8. Results from MCR of OES with equality constraints: etch gas (blue), Al (green), TiN (red).

```
» load oesdata
» dat        = oesdata.data{1};
» c0         = zeros(46,4);
» c0(:,1)    = 1;
» c0(1:12,2) = 1;
» c0(9:24,3) = 1;
» c0(5:20,4) = 1;
» options    = als('options');
» options.cc             = zeros(46,3)*NaN;
» options.cc(15:end,2) = 0;
» options.cc(1:8,3)    = 0;
» options.cc(:,4)       = NaN;
» options.cc([1:7 15:end],4) = 0;
» [c,s] = als(dat,c0,options);
Non-Negativity on C (Fast Least-Squares)
Non-Negativity on S (Fast Least-Squares)
Hard Equality Constraints on C: component(s) 2  3  4
Terminated based on maximum iterations
Elapsed time: 17.1 seconds
Residual (RMSE) 7.611437e+002
Unmodelled Variance is 0.145175 percent
```

The result after 100 iterations is shown in Figure 9-9. In this case, the contribution profiles for the etch gas, Al, and TiN conform very well to those suggested by the major peaks in the spectra. The fourth component appears to be a background addition. Note that, based on residuals (not shown), the fit of this model to the data is only slightly better than a fit using three components, and may not be justified.
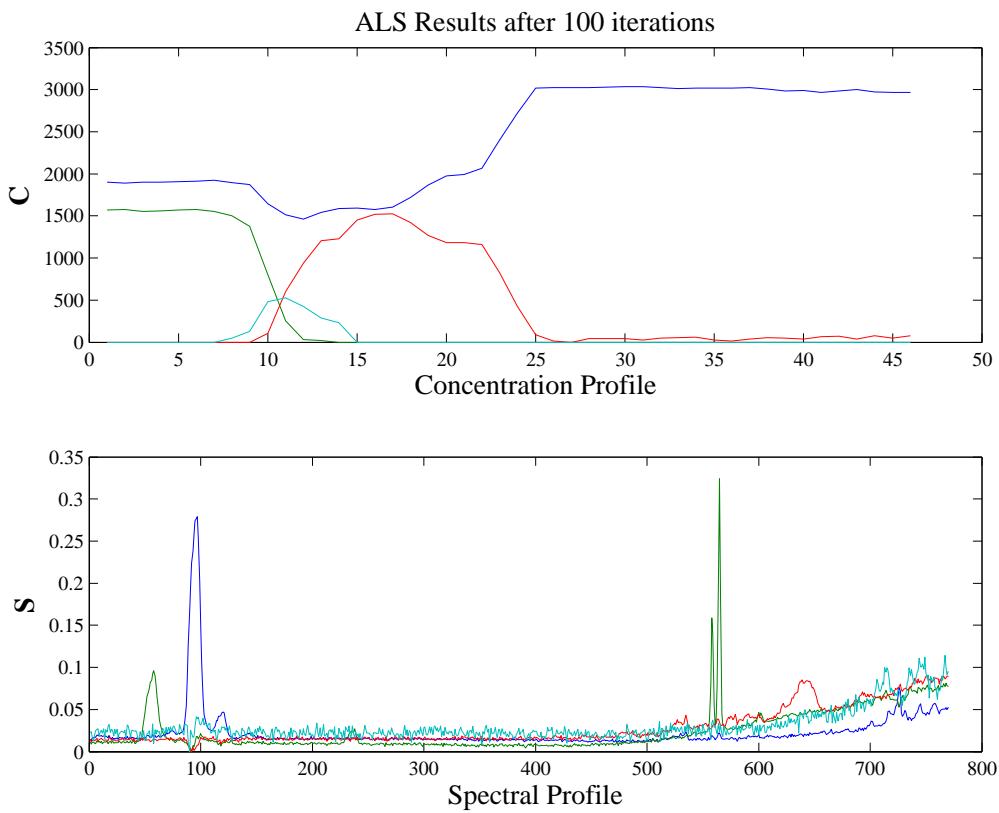
Figure 9-9. Results from MCR estimate of four factors from OES data: etch gas (blue), Al (green), TiN (red), unknown fourth factor (cyan).

This example is a fairly typical example of an MCR analysis. Often, the initial results using only non-negative constraints, and without equality constraints, are not particularly satisfactory. Additional effort is required to identify and apply the correct constraints to obtain a good solution. This effort is required because, in many instances, the true underlying factors cannot be determined based on non-negativity alone. In some cases, infinitely many solutions can satisfy non-negativity and fit the data equally well.

Self-Modeling Mixture Analysis

Techniques to resolve (decompose) spectral data sets into spectra and their contributions were originally known under the term self-modeling curve resolution. In this section, discrimination is made between techniques that rely on continuity in the data and techniques that do not. Techniques that rely on continuity will be referred to as self-modeling curve resolution (SMCR) or multivariate curve resolution (MCR). Techniques that do not rely on continuity, the subject of this section, will be referred to as self-modeling mixture analysis (SMA). This section has two parts. The first part is a tutorial that explains the mathematical principles and MATLAB code to perform self-modeling mixture analysis. The focus of the explanation is based on a geometrical representation. The second part of the tutorial explains how to use the software with a variety of data sets.

If the reader is familiar with the pure variable concept, he or she can go directly to the Tutorial of Purity Model Builder, where the use of the program is explained.

<u>Tutorial of mathematical principles</u>

This tutorial will describe the pure variable method for self-modeling mixture analysis (SMA). Self-modeling mixture analysis is a series of algorithms to resolve (decompose) spectral mixture data into pure component spectra and their contributions without using prior information about the mixtures. A truly pure variable, *e.g.,* the response at a specific wavenumber for IR spectra, or an m/z value for mass spectra, is a variable that has intensity contributions from only one of the components of the mixtures. Therefore, a truly pure variable is one that is selective for only a single analyte. This tutorial aims to give a good understanding of the pure variable method using a minimal amount of mathematics. Furthermore, this tutorial is not meant to present a literature overview.

Purity-based methods can be applied in an automated sense with minimal user intervention. However, an important aspect of the method presented here is that it can be used interactively, allowing users to guide the solution. This is often necessary because in a practical environment, spectral data sets are generally not based on a careful experimental design; samples often originate from a manufacturing process with only a single or very few samples available; or spectra shift due to temperature changes during the manufacturing of materials. The latter can result in problems for kinetic modeling. It is difficult to generate algorithms that automatically deal with all these problems and often human guidance is required. An interactive approach enables the user to account for deviations from the ideal mixture model and implement chemical and physical knowledge into the SMA decomposition.

Pure variable methods are often used to initialize other algorithms such as the ALS algorithm discussed above (see Windig et al., 2002; Windig et al., 2005; Gallagher et al., 2003a; Gallagher et al., 2003b).

<u>Pure Variable Concept</u>

As mentioned above, SMA resolves (decomposes) mixture data into pure component spectra and contributions without using prior information about the mixtures. The model is based on Equation (9-1) and is illustrated in Figure 9-10.
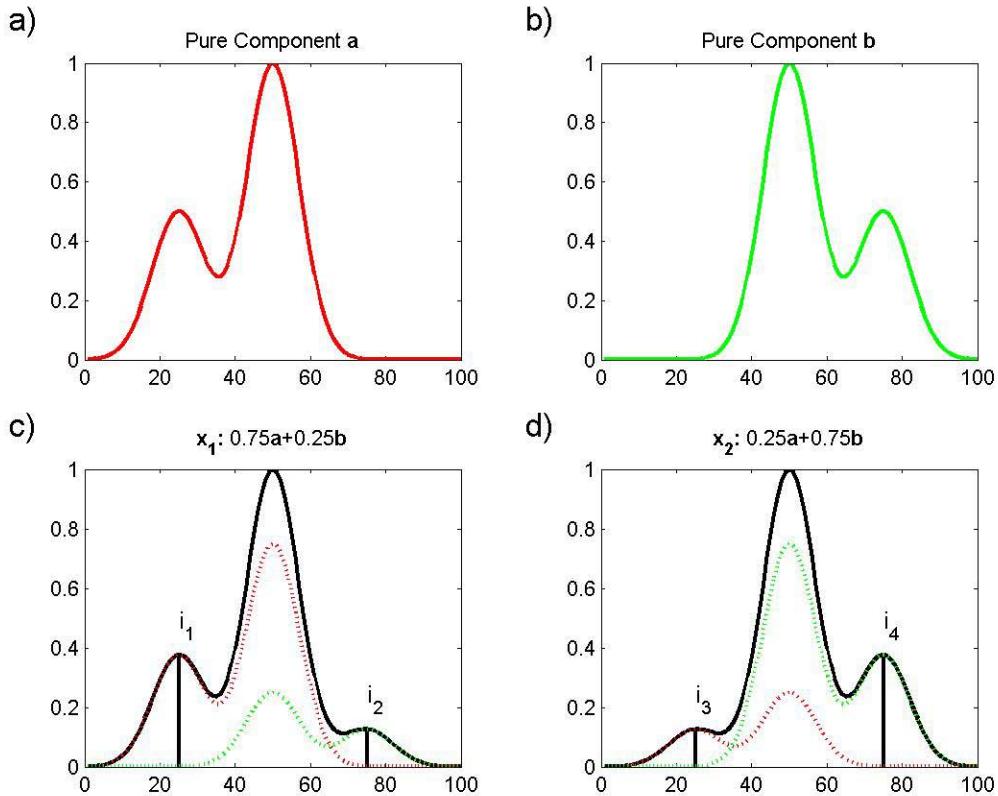
Figure 9-10. Panels (a) and (b) show spectra **a** and **b** of pure components A and B. Panels (c) and (d) show mixtures of these two components, $\mathbf{x}_1$ and $\mathbf{x}_2$. Since **a** has a peak around 25, where **b** does not have a peak, the intensity at 25 in $\mathbf{x}_1$ is a measure of the amount of **a** in $\mathbf{x}_1$. As a result, variable 25 is a pure variable for **a**. Similarly variable 75 is a pure variable for **b**.

In Figure 9-10a, the $1x100$ spectrum **a** of pure component A is given. In Figure 9-10b, the $1x100$ spectrum **b** of pure component B is given. In Figure 9-10c a $1x100$ mixture $\mathbf{x}_1$ of these two components is given (solid line). The mixture spectrum $\mathbf{x}_1$ in Figure 9-10c contains a 75% contribution of component A, indicated with a dotted line, and a 25% contribution of component B, also indicated with a dotted line. The $1x100$ mixture spectrum $\mathbf{x}_2$ in Figure 9-10d contains a 25% contribution of **a** and 75% contribution of **b**. Purity-based self-modeling mixture analysis has the following task: given only the mixture spectra in Figure 9-10c and 9-10d, 1) estimate the pure component spectra in Figure 9-10a and 9-10b; and 2) calculate their contributions in the mixture spectra (the numbers in the headers of Figure 9-10c and 9-10d). The term "contributions" is used instead of "concentrations" since, at best, we can only expect values that are proportional to concentrations (please see the discussion in the previous section regarding multiplicative and rotational ambiguities). To obtain concentrations in usable units, at least one calibration sample is necessary.

228

To show that the task stated above can be completed, the pure variable concept needs to be introduced. In the spectrum in Figure 9-10c, the line labeled i_1 is at a pure variable of component A, since only component A has intensity at that variable, and component B does not. Similarly, the line labeled i_2 in Figure 9-10c is at a pure variable for component B. The lines labeled i_3 and i_4 in Figure 9-10d are at the same pure variables. It is important to realize that the variable is pure for a certain component with respect to all other components. As a consequence, the purity of a variable is not just a function of a certain component, but also of all other components in the mixture.

Before continuing, it must be realized that not just variable 25 is pure for $\mathbf{a}$; variables 1 through 25 are all pure for $\mathbf{a}$, and variables 75 through 100 are all pure for $\mathbf{b}$. Variables at 25 and 75 were chosen because they are pure *and* they have a relatively high intensity.

When the pure variables are known (how to determine the pure variables without knowing the pure component spectra will be explained later), it is possible to calculate the spectra of the pure components as rationalized by the following equations.

$$i_1\mathbf{a} + i_2\mathbf{b} = \mathbf{x}_1$$
$$i_3\mathbf{a} + i_4\mathbf{b} = \mathbf{x}_2$$

(9-9)

$$\begin{bmatrix} i_1 & i_2 \\ i_3 & i_4 \end{bmatrix} \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \end{bmatrix} = \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \end{bmatrix}$$

(9-10)

In Equations (9-9) and (9-10), i_1 represents the intensity at the pure variable of the unknown component $\mathbf{a}$, and i_2 represents the intensity at the pure variable of the unknown component $\mathbf{b}$. Since i_1 and i_2 are intensities at pure variables, they are proportional to the concentrations of the unknowns $\mathbf{a}$ and $\mathbf{b}$.

What the equations state is that an amount i_1 of the unknown $\mathbf{a}$ plus an amount i_2 of the unknown $\mathbf{b}$ result in the first mixture spectrum $\mathbf{x}_1$. Similarly, the second equation represents the composition of the second mixture spectrum. The variables i_1, i_2, i_3, i_4, $\mathbf{x}_1$ and $\mathbf{x}_2$ are known and desired unknowns are $\mathbf{a}$ and $\mathbf{b}$. As a consequence there are two equations with two unknowns, which can be solved.

It must be realized that the above description is a simplification of the decomposition problem, since $\mathbf{a}$, $\mathbf{b}$, $\mathbf{x}_1$ and $\mathbf{x}_2$ are not single numbers, but series of numbers, *i.e.,* vectors. It could be envisioned that there is one set of equations for each of the 100 channels in the spectra. Also the matrix of coefficients often has more than two rows (there are more mixtures than unknown components); therefore, least squares solutions are needed in practice (since the system of equations is over-determined). At this point, the intent is to show the reader the principle that it is possible to estimate the unknown spectra, once the pure variables are known. MATLAB code to solve these problems is given below.

Since knowledge of the pure variables holds the key to the pure component spectra, determination of the pure variables is a valid approach for SMA. To resolve a mixture data set with the pure variable approach, pure variables must be present. This means that spectral channels must exist that are selective for each of the components present. If the variables are not pure, results will likely not represent pure component spectra but instead will be linear combinations of them (*i.e.*, the results may be hampered by a rotational ambiguity). However, as is shown later, second derivative data can often be used to enhance selectivity. As will be shown below, pure variables have properties that make it possible to determine them by simple means.

Determination of Pure Variables from Pure Component Spectra

In Figures 9-11a and 9-11b, the pure components **a** and **b** are shown and the pure variables are indicated by symbols. Although **a** and **b** are shown as continuous profiles, they are defined by discrete values. Points representing **a** and **b** are plotted in Figure 9-11c. The x-axis represents contributions of **a** and the y-axis represents contributions of **b**. By definition the contributions of pure A and pure B are 1 and a mixture of 50% **a** and 50% **b** lies on the line between the points **a** and **b**. The plotted points at [0,1] and [1,0] represent the pure spectra.

Points representing spectral variables can also be plotted. For example, in Figure 9-11d Variable 25 (also indicated with a triangle in Figure 9-11a) has a value of about [0.5 0]. Values for all 100 variables are plotted in Figure 9-11d. For the techniques discussed here, the actual position of the variable points is not important, but the direction from the origin is important. Therefore, each of the $j = 1,\ldots,100$ variables are normalized to unit length. The results are plotted in Figure 9-11e.

As can be seen in Figure 9-11e, the pure variables lie on the x and y-axis, which is not surprising considering the definition of pure variables. All the variables that are not pure are *bracketed* by the pure variables since all mixture variables (*i.e.*, non-pure variables) have positive contributions from **a** and **b.** This is a crucial property of spectral mixtures: a mixture consists of positive spectra and positive contributions. In Figure 9-11e the direction of the pure variables points coincides with the pure spectrum points. This seems to make sense, but as we will see below, it is not that simple.
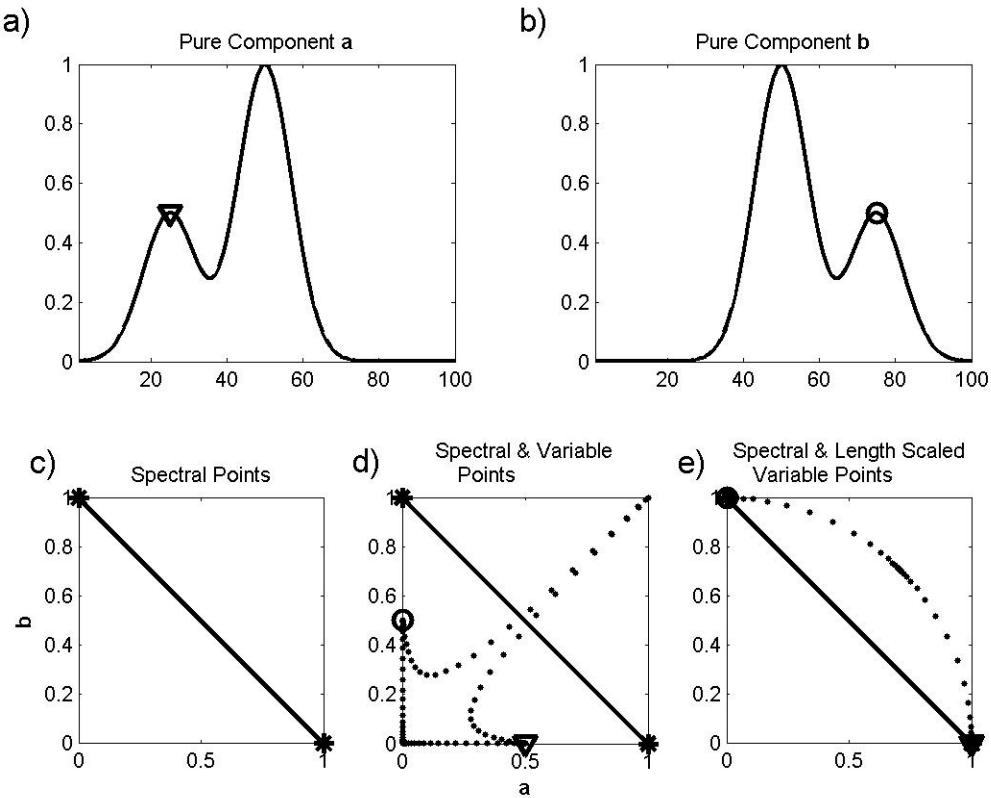
Figure 9-11. The values for the two pure components **a** and **b** in (a) and (b) results in (c). Plotting the spectral variables in addition results in (d). Scaling to unit length of the axes results in (e). Pure variables are indicated with symbols.

Determination of Pure Variables from Mixture Spectra

The example in Figure 9-11 is overly simple because the pure component spectra were used for these plots. What happens when only mixture spectra are available? This is shown in Figure 9-12. Figures 9-12c-e show plots of mixture spectra x_2 versus x_1. The good news is that the pure variables still have the property that they bracket all other variables, *i.e.*, the pure variables are on the exterior of the data set. To display the properties in Figure 9-12 better, a slightly different version is shown in Figure 9-13. The figure is essentially the same, but the spectral points are labeled with their mixture composition.

231
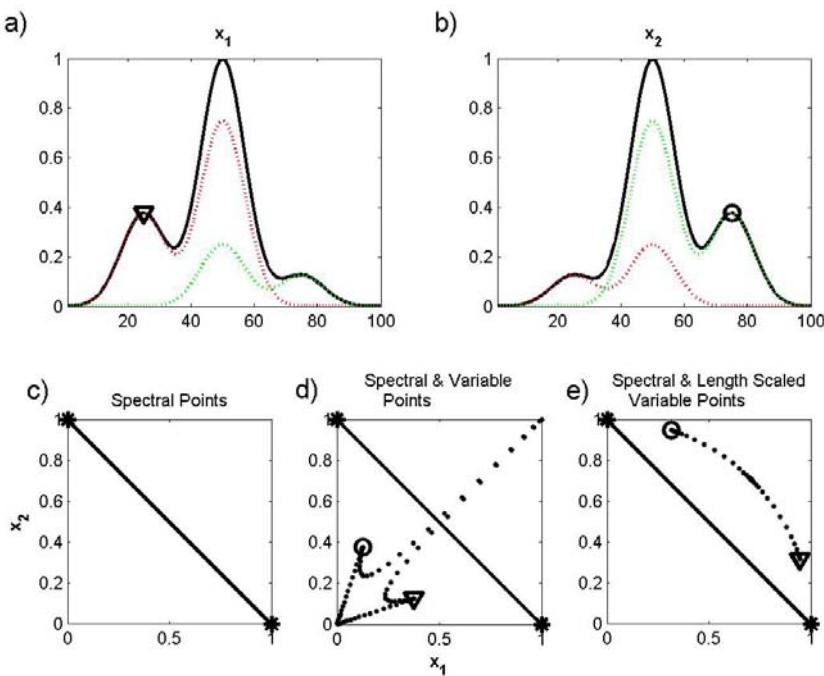
Figure 9-12. Mixture spectra $\mathbf{x}_1$ (a) and $\mathbf{x}_2$ (b) (the true unknown pure component spectra are the dashed lines in panels). The pure variables, indicated with a circle and a triangle, bracket all the other variables (d) and (e).
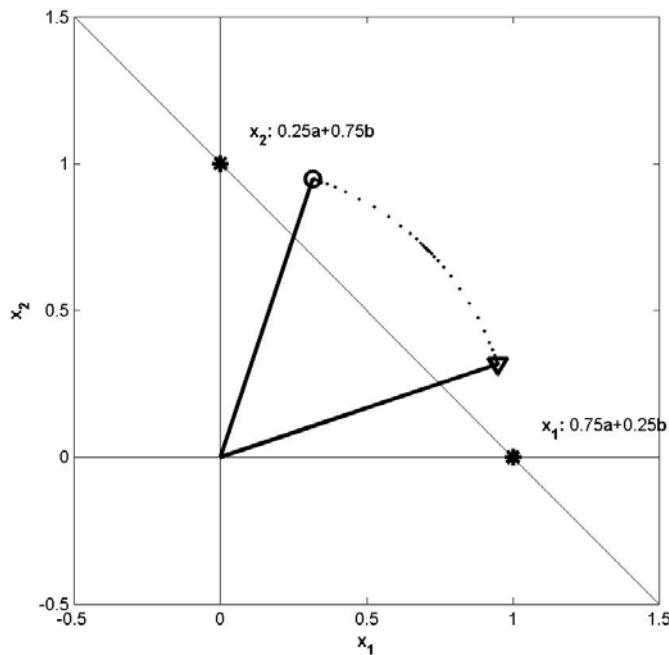
Figure 9-13. The same plot as in Figure 9-12d, but now with vectors representing the pure variables. The two stars indicate the mixture spectra from Figure 9-12a,b. All other possible mixtures lie in a line through these two stars.

Next the spectra of the pure components **a** and **b** are determined under the assumption that i_1, i_2, i_3, i_4, $\mathbf{x}_1$, and $\mathbf{x}_2$ are known and recognizing that the difference $\Delta \mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2$ is $\Delta \mathbf{x} = 0.5\mathbf{a} - 0.5\mathbf{b}$. This result can be used to give $\mathbf{a} = \mathbf{x}_1 + 0.5\Delta \mathbf{x}$ and $\mathbf{b} = \mathbf{x}_2 - 0.5\Delta \mathbf{x}$. [A general solution can be obtained by performing elementary row operations on Equation (9-10) (see Chapter 3, Introduction to Linear Algebra, for details); however, when the number of rows in the coefficient matrix is larger than the number of unknowns least squares is used. The solution for **a** represents a lengthening of $\mathbf{x}_1$ by half the distance between the two mixtures (see Figure 9-14). Note that the spectral points representing the pure spectra do not coincide with the spectral points of the pure variables! Also, the estimates of **a** and **b** are at unknown concentrations (and pathlength) and, as a result, are often normalized to unit length. At first glance it might appear that the estimated **a** has negative intensities because it is below the horizontal x-axis. However, it should be remembered that the x- and y-axes correspond to mixtures and $\mathbf{a} = (1 + 0.25)\mathbf{x}_1 - 0.25\mathbf{x}_2$.
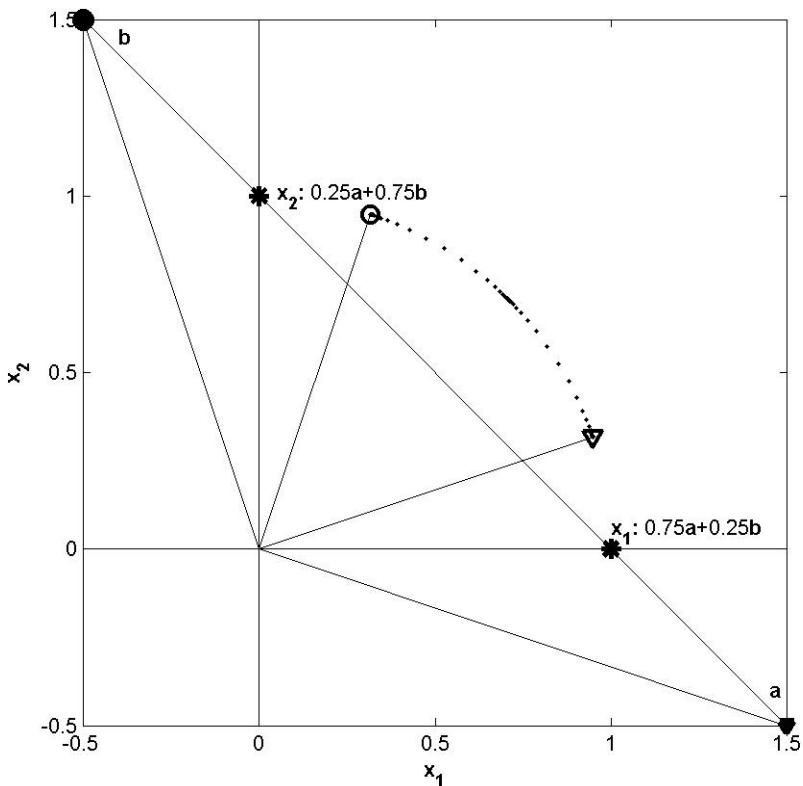
Figure 9-14. The same plot as in Figure 9-13, but now the points representing the pure spectra have been added, labeled with **a** and **b**, respectively. The two stars indicating the mixture spectra from Figure 9-12a and b. All other possible mixtures lie in a line through these two stars.

Determination of Pure Component Spectra from Pure Variables

In an effort to be more clear, Figure 9-14 is explored in more detail. An interactive MATLAB function `purvarmixturedemo` is available to reproduce the results in Figure 9-

15. These spectra (also calculated and displayed by the `purvarmixturedemo` function) are based on the original variables, not the variables scaled to unit length. In Figure 9-15a the direction of the $\mathbf{x}_1$ axis shows, not surprisingly, the spectrum of mixture $\mathbf{x}_1$. At first thought, it might be expected that plotting the spectrum in the direction of the pure variable axis $\mathbf{a}$ that the pure component spectrum of $\mathbf{a}$ would result (see Figure 9-15b). However, the spectrum is not the pure component spectrum of $\mathbf{a}$ but is instead a mixture spectrum. Changing the direction further (Figure 9-15c) shows another mixture spectrum (as should be expected because this direction is interior to the pure variables). This is clearly the wrong direction for finding the spectrum of pure $\mathbf{a}$. Moving away from the center clock-wise yields the spectrum of $\mathbf{a}$ (Figure 9-15d). This direction corresponds with the previously determined spectral point of $\mathbf{a}$ (Figure 9-14). Moving further in the clock-wise direction gives a spectrum with negative intensities (Figure 9-15e). In this case, the negative values suggest an incorrect direction.
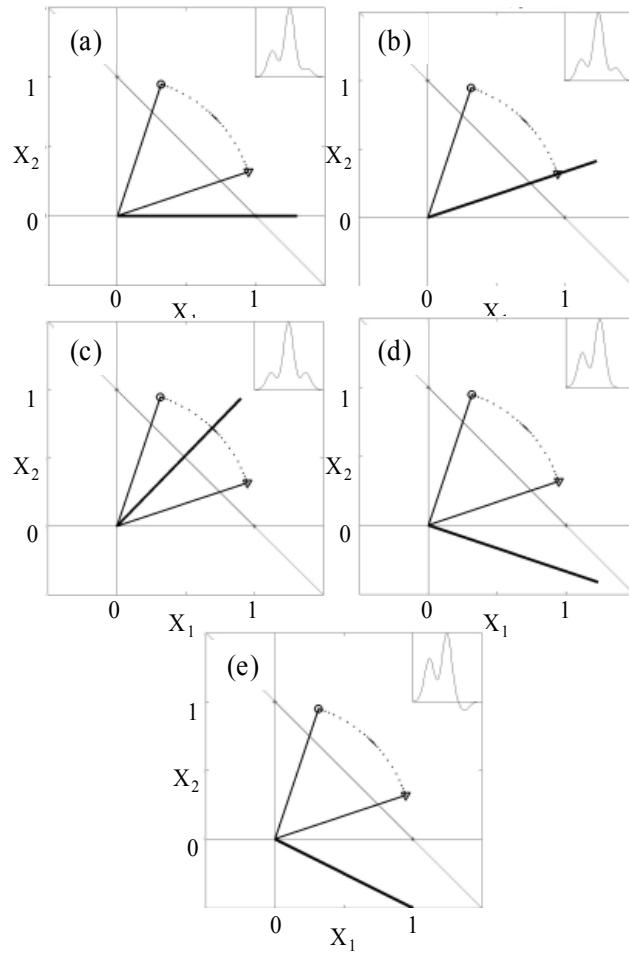
Figure 9-15. Similar plot as in Figure 9-14, but with different estimates of the pure component spectrum for $\mathbf{a}$. The two stars indicating the mixture spectra from Figure 9-12a,b. All other possible mixtures lie between these two stars.

SMA attempts to answer the following question: what determines the direction corresponding to pure component $\mathbf{a}$ when information used to plot the spectral point $\mathbf{a}$

234

in Figure 9-14 is unavailable? The answer lies in the pure variable concept. *The spectral point of* **a** *must not have signal from* **b**. This is the definition of a pure variable or selective variable: a selective variable is one that includes signal from only a single analyte and has signal free from interferences. As a result, the direction of the spectrum of **a** is orthogonal to the pure variable of **b**. Closer inspection of Figure 9-14d shows that this is indeed the case. Similarly, the spectrum of **b** can be found, as indicated with a solid circle in Figure 9-15.

To summarize the principle of the pure (selective) variable refer back to Figure 9-14.

a) Pure variables (indicated with an open circle and an open triangle) bracket all other variables i.e., selective variables are on the exterior of the data set.

b) Pure spectrum directions for each analyte are orthogonal to pure variable directions of all remaining analytes and interferences.

MATLAB Code for Pure Variable Method

The question now is how to put all these pictures in a workable algorithm. To demonstrate the algorithm, a more realistic data set will be created of a mixture of two components. The first data set is `purvardata,` which does not contain noise. The second data set is `purvardata_noise`, which contains the same spectra with added noise. A plot of the two pure components and the contributions of these components in the mixtures is given in Figure 9-16.
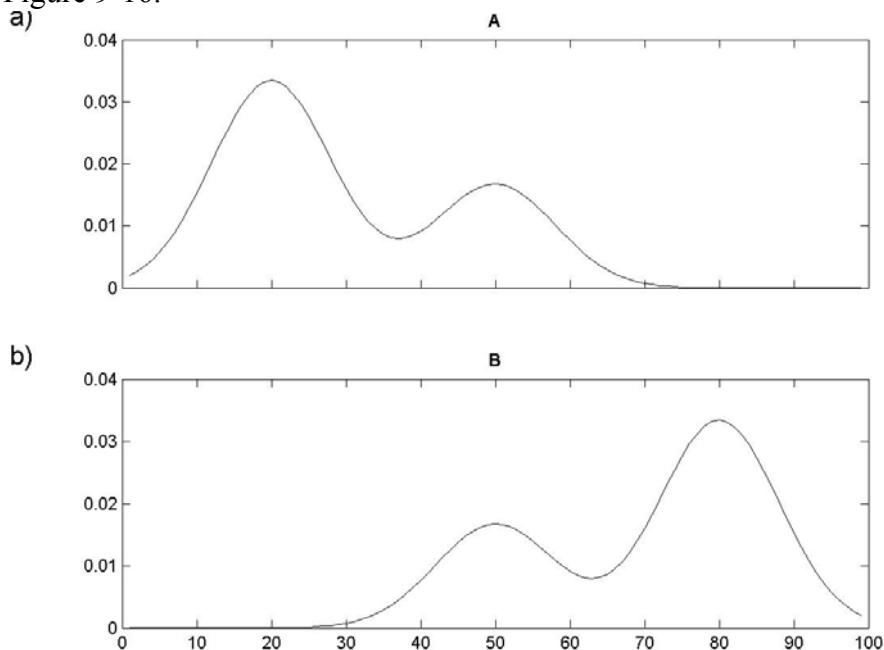
Figure 9-16. The components A and B from which the data sets have been constructed, using the contributions listed below.

Contributions	
A	**B**
0.3	0.7
0.4	0.6
0.5	0.5
0.6	0.4
0.7	0.3
0.8	0.2

The noise-free spectra and spectra with noise are shown in Figure 9-17. Noise was added as a uniform random distribution between +0.00025 and –0.00025, which is approximately $\pm 1\%$ of the maximum intensity.

a)

b)
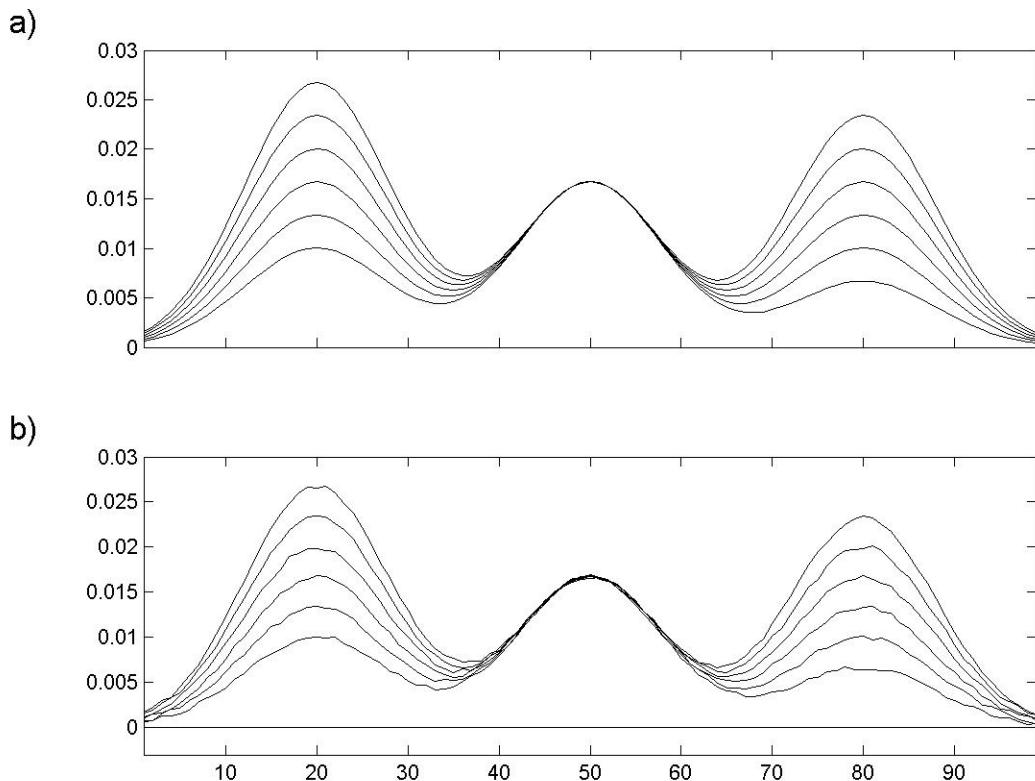
Figure 9-17. The demonstration data sets: (a) without noise, (b) with added noise.

To determine the first pure variable, the objective is to find one variable that brackets all the others (that is, a variable that is on the exterior of the data space). To do this, a

reference vector is first established. For this example, a vector with ones is used (the data set mean could also be used). The angle between this vector and all the other variables in the data set can be found using the MATLAB function subspace. Since it is common to work with degrees instead of radians, the output is converted to degrees. The first pure variable is found by determining the variable with the largest angle with the reference vector of ones using the following MATLAB commands:

```
>> load purvardata
>> [nrows,ncols] = size(data);
>> for i=1:ncols
>>   angle0(i) = subspace(data.data(:,i),ones(nrows,1));
>> end
>> angle0 = 180*angle0/pi;
>> [dummy,pure_variable_index] = max(angle0)
dummy =
    20.7826
pure_variable_index =
    99
```

The first pure variable is at index 99, although variable 75 might have been expected. It is not yet known which component the first pure variable corresponds to. Although variable 75 seems more appropriate than 99, "purity" as calculated here does not depend on intensity, so variable 99 is expected to have less overlap with the other component. A plot of the angle and a star indicating the pure variable is shown in Figure 9-18a, which is based on the following MATLAB command.

```
>> subplot(4,1,1),   plot(data.axisscale{2},angle0, ...
data.axisscale{2}(pure_variable_index),angle(pure_variable_index),'k*')
```

The same plot can be made for the data set purvardata_noise using the commands given above, with the exception that the first line is:

```
>> load purvardata_noise
```

A plot of the known contributions for both data sets is based on the following MATLAB command (Figure 9-18 c and d):

```
>> plot(data.userdata.purint(:,2),...
  data.data(:,pure_variable_index),'*k')
```

As can be observed in Figure 9-18b and d, the noise causes problems for the estimation of the pure variable. Although the estimated pure variable is the same for the noiseless and the noisy data set in this case, this is not typical. The problem lies in the fact that pure variables bracket all other variables. In other words, the pure variables are the most independent variables. Since noise is by definition independent of the signal, a noisy variable behaves like a pure variable. This can be observed by comparing Figure 9-18a and b. Although the variables 80-99 are basically equally pure in (a), the low intensity variables (with relatively higher noise) tend to get a higher purity in (b).
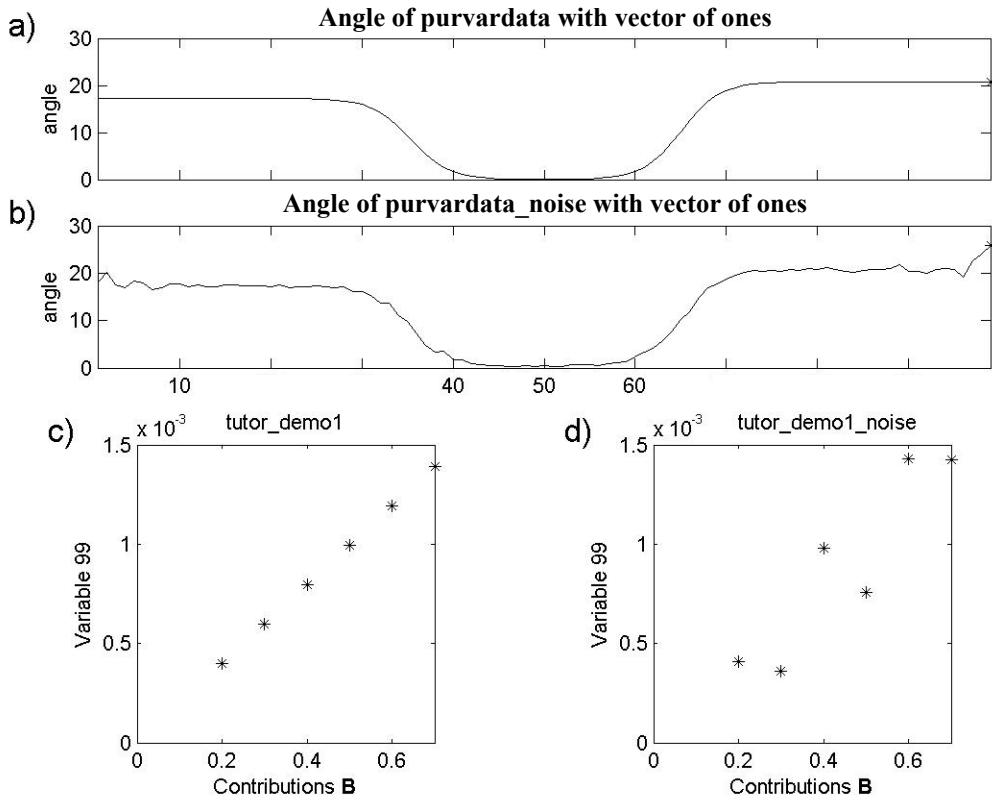
Figure 9-18. A plot of the angle of a variable from a vector of ones: (a) noiseless data set and (b) data set with added noise. The original contributions of B are plotted for the pure variables for the noiseless data set (c) and for the data set with noise (d).

Since, in general, low-intensity variables contain low signal-to-noise, a correction factor needs to be developed. The signal-to-noise is generally inversely related to the measured value, leading to the following proposed noise correction factor:

```
>> load purvardata_noise
>> offset = 3;
>> mean_data = mean(data.data);
>> max_mean_data = max(mean_data);
>> offset_relative = (offset/100)*max_mean_data;
>> correction_factor = mean_data./(mean_data+offset_relative);
```

The correction factor is plotted in Figure 9-19a and is multiplied by the angles calculated above prior to estimating pure variables.

```
>> angle_corrected = correction_factor.*angle0;
```

For variables with a high mean value, the correction factor is near one and will have little effect on the estimated angle. For variables with a low mean value, the offset will be

238

significant; as a consequence, the correction factor will be small. The result is that the estimated angle for these variables is decreased, making them appear "less pure." The corrected angles are plotted in Figure 9-19b with the maximum indicated. As can be observed in Figure 9-19c, the correction results in a pure variable that is not dominated by noise.

```
>> pure_variable_index = find(angle_corrected == max(angle_corrected));
>> plot(data.axisscale{2}, angle_corrected,...
        data.axisscale{2}(pure_variable_index),...
         angle_corrected(pure_variable_index), 'k* ')
>> plot(data.userdata.purint(:,2),...
        data.data(:,pure_variable_index),'*k');
```
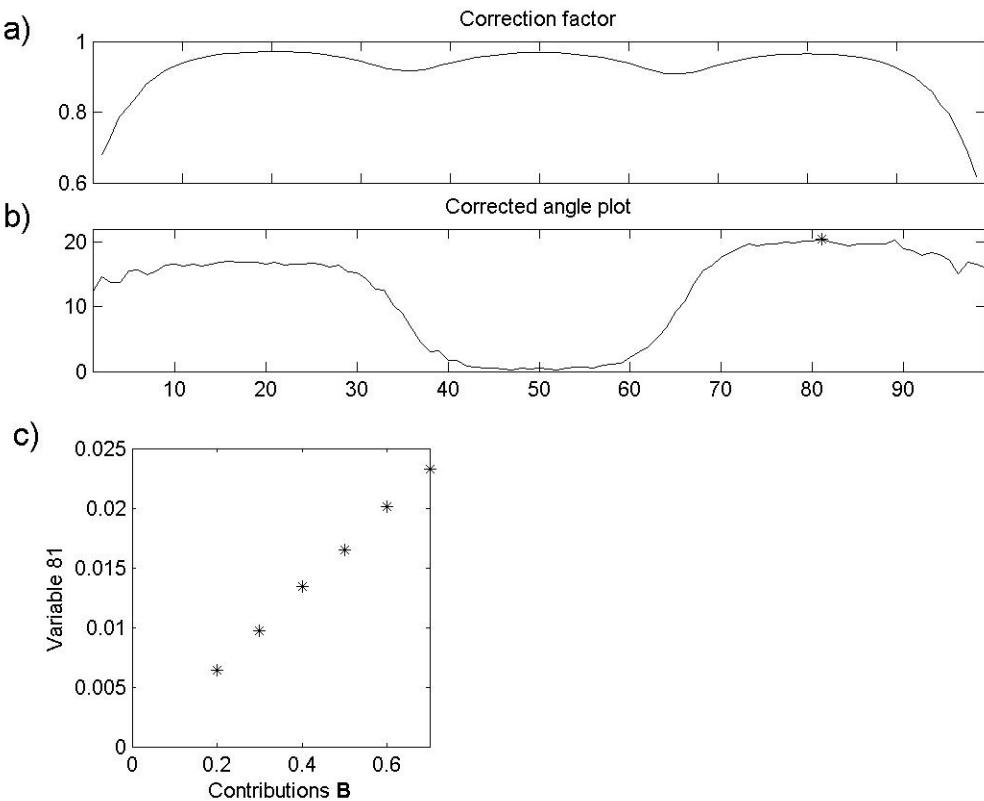

Figure 9-19. The correction factor (a) and the corrected angle plot in (b). The contributions of B versus the contributions of the pure variable are given in (c).

At this point in the analysis, one pure variable has been determined. Note that the angle spectrum has limited similarity to the original spectra in the data set and the angles do not reflect the original intensity of the variables. To create a spectrum that reflects the intensities in the original data, variables are multiplied by their length (two-norm) given by:

```
>> length_data = sqrt(sum(data.data.*data.data));
```

In Figure 9-20, the angle spectrum (a) is shown with the length (two-norm) spectrum next to it (b). Each value in the "length spectrum" is the corrected angle value multiplied by the corresponding two-norm..

```
>> angle_corrected_length = angle_corrected.*length_data;
>> plot(data.axisscale{2},angle_corrected_length,...
        data.axisscale{2}(pure_variable_index),...
         angle_corrected_length(pure_variable_index),'k* ')
```

The second pure variable is the variable with the largest angle from the first estimated pure variable calculated as follows:

```
>> for i=1:ncols
>>   angle0(i) = (180/pi)*subspace(data.data(:,i), ...
>>                   data.data(:,pure_variable_index));
>> end
>> angle_corrected = correction_factor.*angle0;
>> pure_variable_index = [pure_variable_index;
>>                   find(angle_corrected == max(angle_corrected))]

pure_variable_index =

    81
    21
```

The result of the pure variable selection is shown in Figure 9-20c and d. Two pure variables have now been estimated, and these define a plane, as any two vectors do. When the next angle spectrum is calculated, the subspace command searches for a third pure variable, which has the largest angle with this plane. Repeating the MATLAB commands immediately listed above yields

```
pure_variable_index =

    81
    21
    99
```

The results are shown in Figure 9-20e and f. It is obvious from these results that there are only two pure variables present because both the estimated angle and the length spectrum are small. After selecting two pure variables, only noise is present.
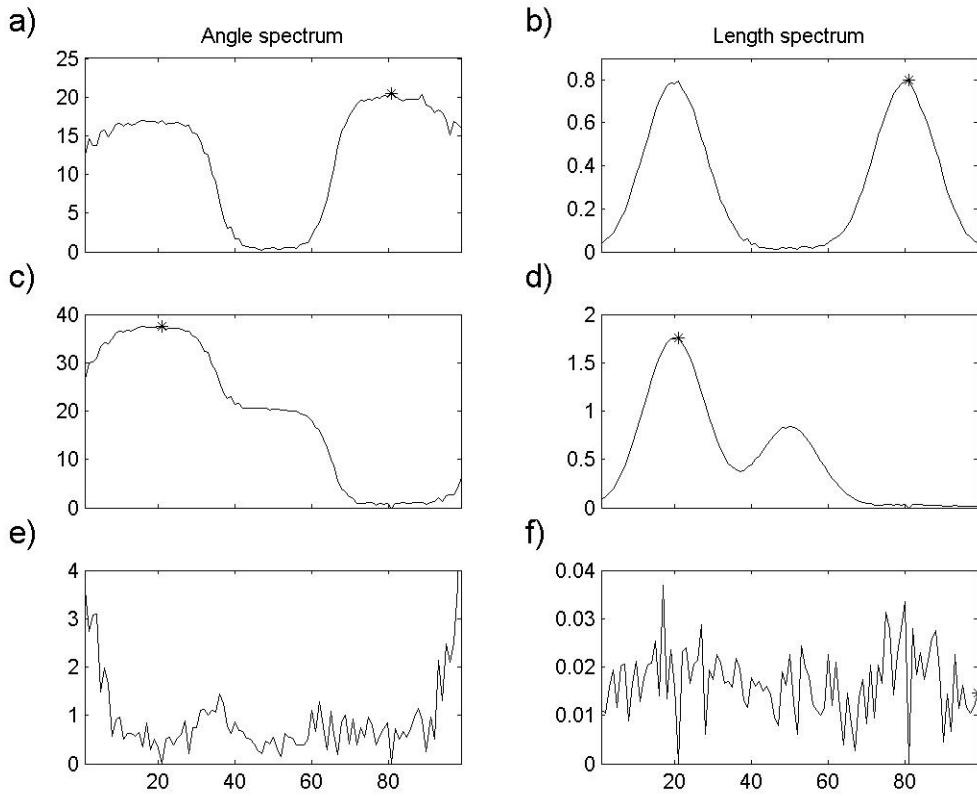
Figure 9-20. The successive series of angle spectra and length spectra. The pure variables are indicated with a star: 81 (a,b), 21 (c,d), and 99 (e,f).

At this point, it has been determined that the data set has two pure variables. Next estimates of the pure component spectra and contributions are obtained. For this we'll put Equations (9-9) and (9-10) into a more formal form. Equation (9-1) is rewritten:

$$\mathbf{X} = \mathbf{C}\mathbf{S}^T + \mathbf{E} \qquad (9\text{-}11)$$

where $\mathbf{X}$ is a $m \times n$ matrix of the original data with the spectra in rows, $\mathbf{C}$ is a $m \times k$ matrix of contributions, and $\mathbf{S}$ is a $n \times k$ matrix with columns corresponding to pure component spectra. k is the number of analytes present in the data matrix; it is the number of pure variables estimated. In the pure variable technique, an estimate of $\mathbf{C}$ is obtained by taking the columns of $\mathbf{X}$ that represent pure variables, and for clarity the notation $\hat{\mathbf{C}}$ will be used for this. (Recall that the values of the pure variables are not concentrations; they are proportional to concentrations, and are referred to as contributions.) The $m \times n$ matrix $\mathbf{E}$ represents the residual error, which is minimized in the least squares equations shown below.

The purity technique estimates $\hat{\mathbf{C}}$ from the columns of $\mathbf{X}$ and both are known. The next step estimates $\hat{\mathbf{S}}$ from

$$\hat{\mathbf{S}}^T = \hat{\mathbf{C}}^{+T}\mathbf{X} \qquad (9\text{-}12)$$

241

where $\hat{\mathbf{C}}^+ = \hat{\mathbf{C}}\left(\hat{\mathbf{C}}^T\hat{\mathbf{C}}\right)^{-1}$ with the property $\hat{\mathbf{C}}^{+T}\hat{\mathbf{C}} = \mathbf{I}$. In the next step, the contributions are now calculated from $\hat{\mathbf{S}}$ from

$$\tilde{\mathbf{C}} = \mathbf{X}\hat{\mathbf{S}}^+ \qquad\qquad (9\text{-}13)$$

where $\hat{\mathbf{S}}^+ = \hat{\mathbf{S}}\left(\hat{\mathbf{S}}^T\hat{\mathbf{S}}\right)^{-1}$. This step reduces the noise in the contributions and this procedure corresponds to a single iteration of the ALS algorithm discussed above. We can implement this procedure on the data from the example above using MATLAB. The pure variable indices obtained above were:

```
>> pure_variable_index = [81 21];
```

First, these are extracted from the data matrix to a matrix `purint` that corresponds to $\hat{\mathbf{C}}$.

```
>> purint = data.data(:,pure_variable_index);
```

To calculate the pure spectra $\hat{\mathbf{S}}^T$ we use the following command and assign the pure spectra to the matrix `purspec`:

```
>> purspec = pinv(purint)*data.data;
```

Next, the spectra are normalized to unit length. In terms of Figure 9-15, the direction of the pure spectra are known, *i.e.*, the pure spectrum axes, but what's needed is where the pure spectrum axis intersects the mixture line. This is simply done by normalizing the spectra to a total intensity of 1:

```
>> purspec = normaliz(purspec);
```

The matrix `purint` corresponding to $\hat{\mathbf{C}}$ is estimated from `purspec`:

```
>> purint = data.data*pinv(purspec);
```

The estimated `purint` is based on normalized data in the least squares calculation, and is expected to have less noise then the original pure variables. The following commands are the basis for Figure 9-21.

```
>> subplot(2,2,1);plot(data.axisscale{2},purspec(1,:),'k');
>> subplot(2,2,2);plot(data.axisscale{2},purspec(2,:),'k');
>> subplot(2,2,3);plot(data.userdata.purint(:,2),purint(:,1),'*k');
>> subplot(2,2,4);plot(data.userdata.purint(:,1),purint(:,2),'*k');
```
The procedure outlined above showed all the calculations needed for the purity technique. To learn more about the pure variable method, type `purityengine demo` or `purity demo` at the command line.
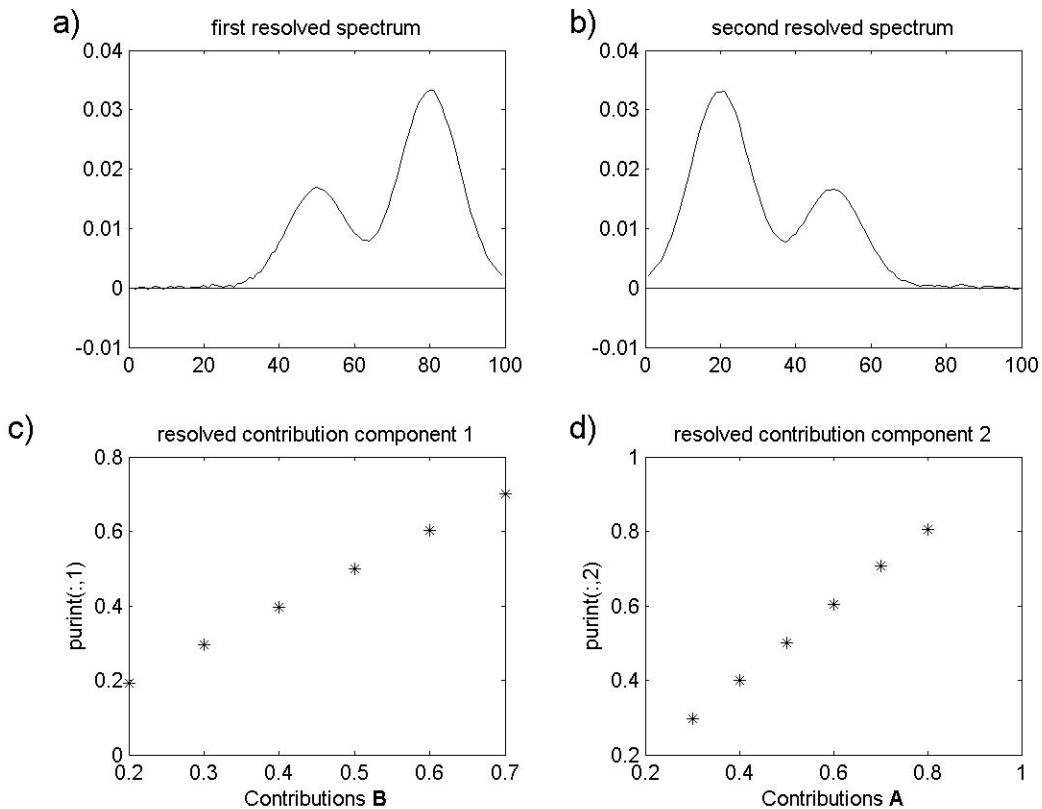
Figure 9-21. Resolved spectra (a) and (b), and resolved contributions (c) and (d).

Tutorial for Purity Model Builder

This tutorial is limited at this point to showing the use of Purity in the **Analysis** GUI. Familiarity with the purity concept is assumed. A summary of concepts:

a) A pure variable (*e.g.*, a wavenumber) is a variable that has contributions from only one component.

b) The values of a pure variable are directly proportional to the concentrations of the associated component. As a consequence, when all pure variables are known the spectra of the pure components can be calculated.

c) The purity programs demonstrated here determine the pure variables in a stepwise interactive manner: when the user sets a pure variable, the intensities of the variables associated with that component will diminish proportionally

Four different uses of the program will be demonstrated. Before using this tutorial one should first run:

```
>> puritydemo
```

It is important to do this, since more information is given about the data files. Furthermore, reference spectra are plotted in the demonstration which are needed to judge the solutions.

In the text below, the variables or spectra selected by the program are referred to as pure variables or pure spectra. Although these variables/spectra are the purest mathematically, this does not mean that they are pure from a chemical point of view. When the pure variables/spectra are chemically pure, the terms **proper pure variable** and **proper pure spectrum** will be used.

The Purity Model Builder Interface is spawned from the **Analysis** window using the **Show Purity Model Builder** button in the toolbar. After loading new data into the **Analysis** window, it will be the only button enabled. Clicking it will bring up the "Model Builder" interface. Initially the interface will have one toolbar and a **Purity** menu (see Figure 9-22). If either of the derivative buttons is clicked, a second toolbar will appear with buttons specific to the additional plots generated. Table 9-1 describes the function of each button/menu selection.

Table 9-1. List of Purity GUI menu items and buttons.

Name	Description
Menu	
Transpose	Transpose matrix to get pure spectra rather than pure variables.
Inactivate	Inactivate Selected/Zoomed Area of Purity Spectrum. Colors selected portion of x-axis red and ignores area when determines the maximum in the purity spectrum.
Reactivate	Reactivate Selected/Zoomed Area of Purity Spectrum. Undo Inactivate.
Max	Set Cursor to Maximum Purity Value(s).
Plot Spectrum	Plot of original spectra and (if available) the reconstructed data.
Resolve	Resolve spectra and contributions for selected pure variables.
Continuous/Discrete	This determines if the plot is continuous, discrete of bar. The default is continuous for rows (variable plots) and continuous for columns (spectrum plots). This is indicated in the figure, left top, as cc. Pressing the button goes through all the combinations of continuous, discrete and bar.
Accept	Load model back into Analysis and close Purity Model Builder.
Conventional (top) Toolbar	
Set Pure Variable	Set Pure Variable at cursor.
Reset	Remove last variable. Undo result of 'Set Pure Variable'
Plot at Cursor	Plot Variable At Cursor
Cursor	Manually move cursor to new location.
Increase Offset	Down weight variables.
Decrease Offset	Up weight variables.
Window Derivative Increase	Increase derivative window. Will create second set of plots if not already displayed.
Window Derivative Decrease	Decrease derivative window. Will create second set of plots if not already displayed.
Derivative (bottom) Toolbar [not displayed in default view]	
Set	Same as above but acting on derivative plots.
Increase Offset	Same as above but acting on derivative plots.
Decrease Offset	Same as above but acting on derivative plots.

The examples below cover interaction with the "Model Builder" interface. Once a model has been resolved, it can be loaded back into the Analysis window using the **Accept** selection from the **Purity** menu. One can then further explore and use the model.

Note: Purity is an entirely new method to PLS_Toolbox. As such, not all tools in the Analysis interface are compatible with Purity models.

Example: Raman Spectra of Time-Resolved Reaction

To get started, load the demonstration data and open the Analysis interface using the following commands:

```
>> load raman_time_resolved
>> analysis
```

The next step is to load the demo data into the **Analysis** window using **File/Load Data/X-Block**. The demonstration data set contains time-resolved Raman spectroscopic data of four components. Next, go to the **Analysis** menu and select **Purity**. Click on the **Perform Purity Analysis** button in the **Analysis** window toolbar (gears icon) to bring up the **Purity Model Builder** GUI (Figure 9-22). The top spectrum is the length spectrum, which has the same units as the original spectra and therefore is easily to relate to the original. The second spectrum is the purity spectrum, of which the maximum indicates the purest variable in the data set.
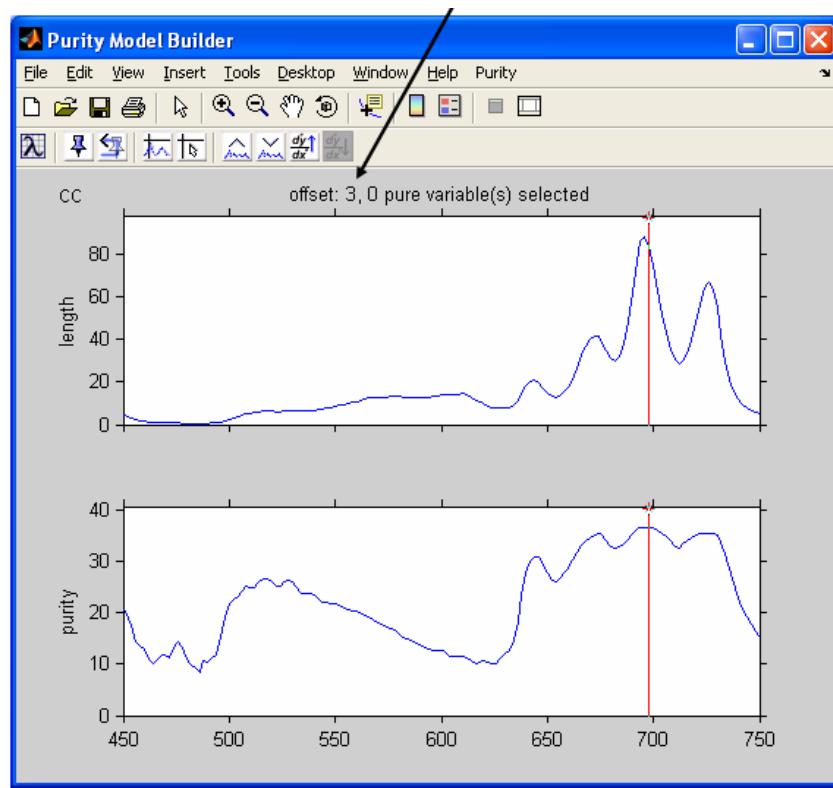
Figure 9-22. The main figure for interactive Purity analysis. Offset is shown in axis title.

The first part of the demonstration will show the effect of the offset, which is a noise correction factor. The offset is shown above the length spectrum. Its current value is 3.

246

By clicking on the 'Decrease Offset' button three times, the offset is changed to the value 0, which results in Figure 9-23.
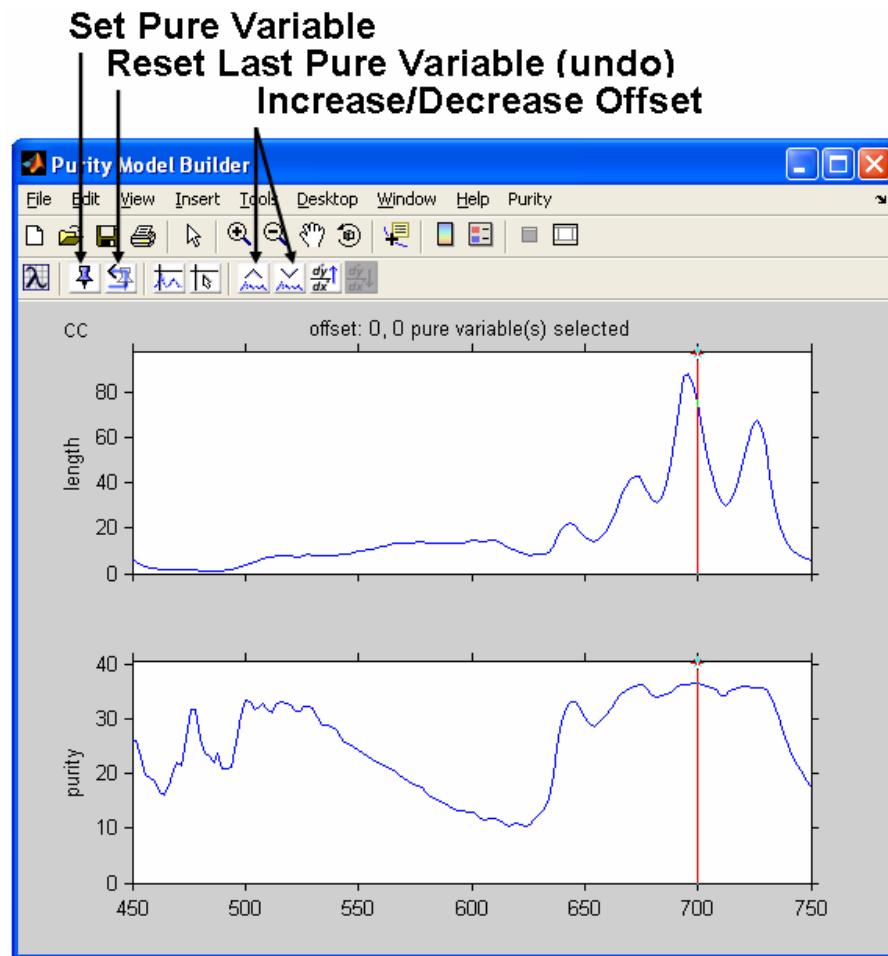
Figure 9-23. Offset decreased to zero.

The first pure variable, indicated by the cursor, is accepted by clicking the **Set Pure Variable** button (the tack icon); clicking it again will set the second pure variable and result in Figure 9-24. The previously-selected pure variables are indicated with green markers.
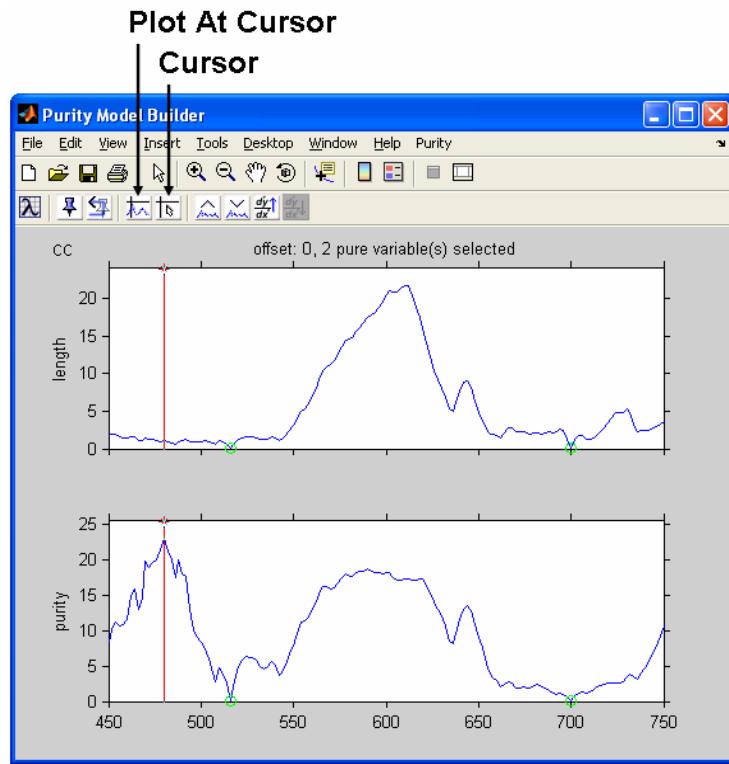
Figure 9-24. Two pure variables set (indicated by green marker).

Close and Return
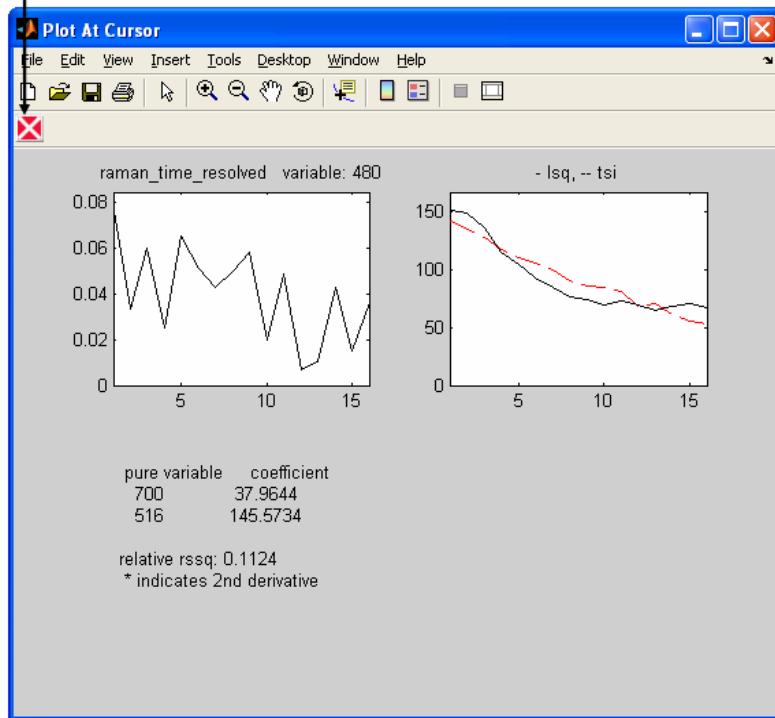
Figure 9-25. Plot of third pure variable.

The pure variable indicated in the figure above by the red cursor is not a good pure variable. As can be judged from the length spectrum, this is a low intensity variable. A plot of this variable also shows its noisy character. This plot can be obtained by clicking the option **Plot At Cursor** (Figure 9-25).

Next to a plot of the variable at the cursor (left plot) is a plot of the total signal of all the spectra (as a function of spectrum number) and the least squares approximation of the pure variables set that best reproduces the total signal so far. It is obvious that two pure variables are not enough. The coefficients of the pure variables to obtain the best least squares approximation are also listed. When the proper number of pure variables has been chosen, the total signal should be reproduced properly and all the coefficients should be positive.

Figure 9-25 shows the noisy character of the variable at the cursor position. This represents a problem with the pure variable approach. Pure variables are the most linearly independent variables, but so are noise variables. An approach to avoid this spectral region is by inactivating it. First we return to the main figure by clicking on 'return' (the red "X" icon). Inactivation is done as follows:
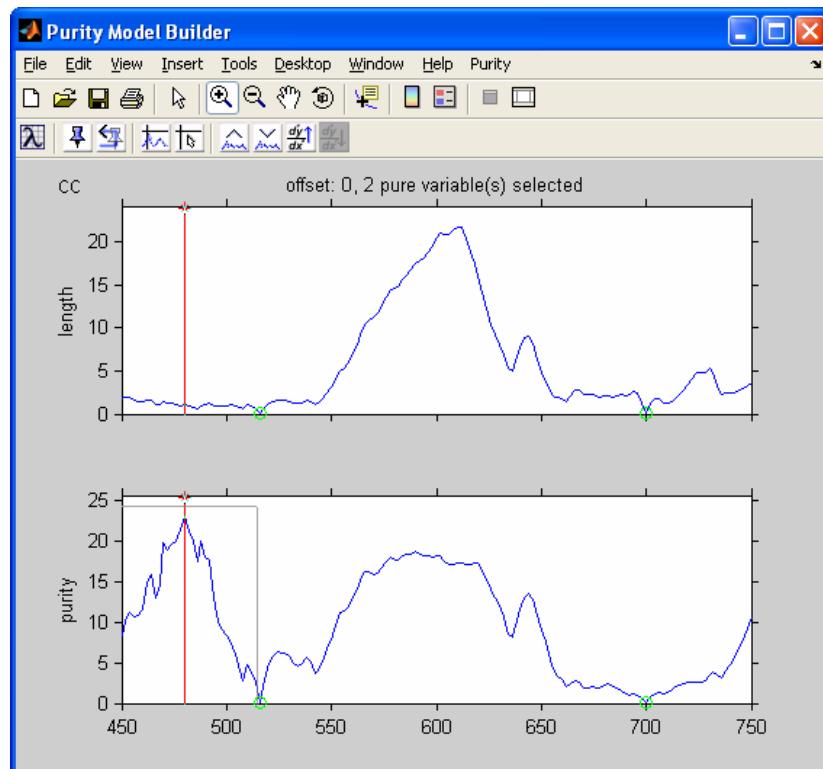
Figure 9-26. Zooming in on third pure variable.

a) Use the MATLAB figure toolbar to activate zoom and draw a rubber band box as indicated in Figure 9-26. The figure will zoom into this part (not shown).

b) Select **Inactivate** from the **Purity** menu (as shown in Figure 9-27).

The result is shown in Figure 9-27, where the x-axis of the area we zoomed is colored red. The result of this is that this area is ignored when the program determines the maximum in the purity spectrum. In this way we can ignore problematic regions in the spectrum, such as this noisy low-intensity area.
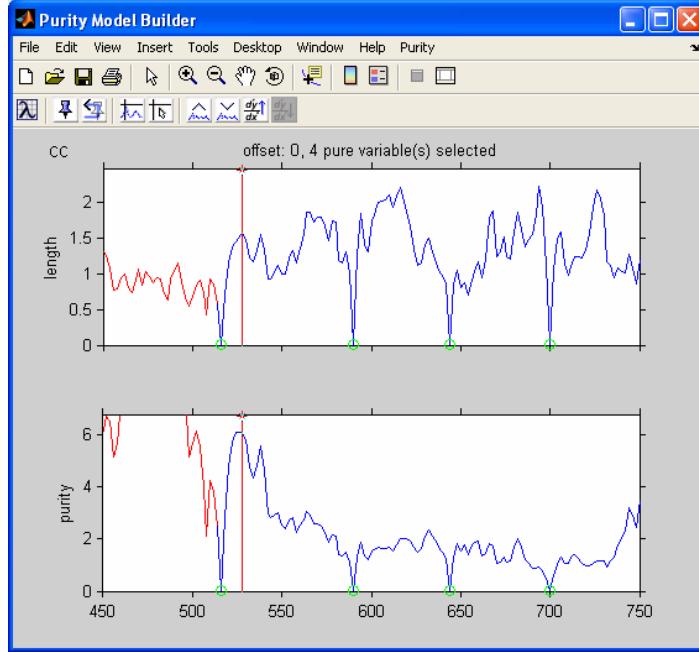
Figure 9-27. Inactivated region and menu.
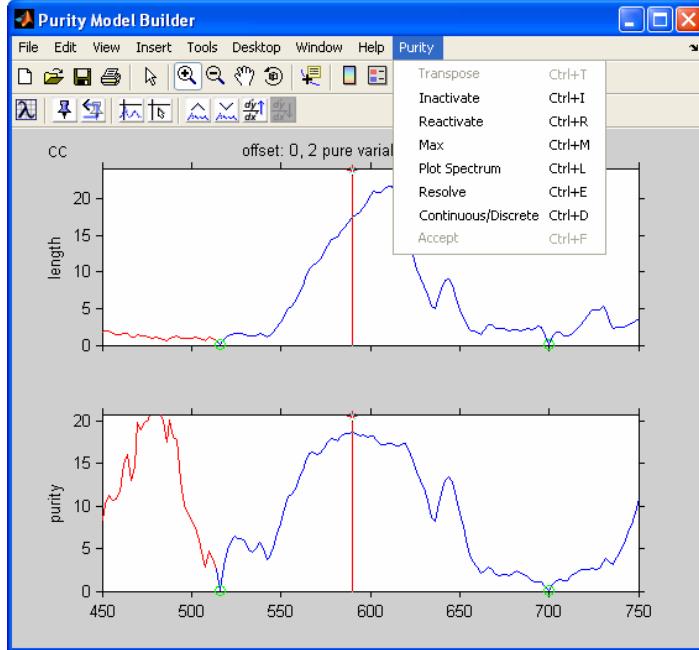
Figure 9-28. Four pure variables set. No remaining spectral information.

The program will automatically go to the new maximum (the same can be achieved by selecting **Max** from the **Purity** menu). Then accept the pure variable indicated by the

program by clicking on **Set Pure Variable**. Set the next pure variable by clicking the button again and the result will be Figure 9-28, which shows that there is no spectral information present anymore. The **Plot At Cursor** plot in Figure 9-29 shows that the total signal is reproduced properly with the four pure variables and the coefficients are positive.
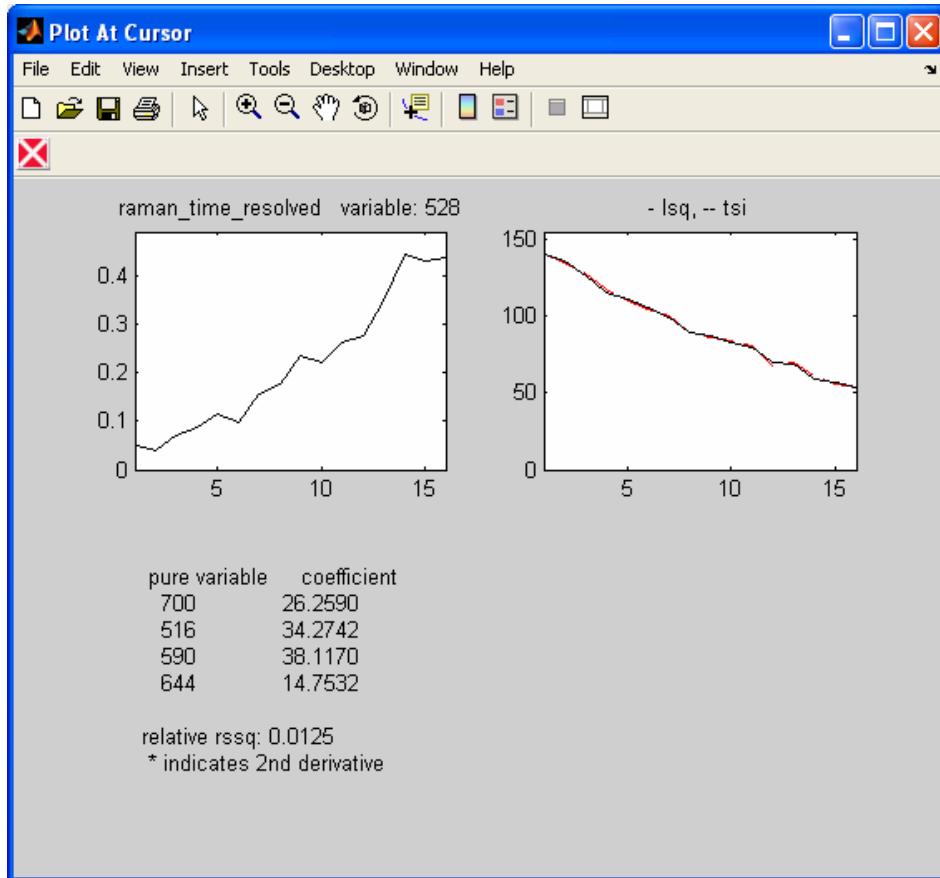
Figure 9-29. Plot at cursor for current pure variable, showing that four pure variables reproduce the signal properly.

It may seem confusing that the current variable at the cursor does not represent noise. One has to keep in mind that after selecting the proper number of pure variables, one will have a noisy purity spectrum. The position of the maximum is basically random, so the variables at the maximum in the purity spectrum basically do not have any meaning from a purity point of view.

After concluding that four pure variables describe the data set, the data set can be resolved after we return to the main figure by clicking on **Return**. We now resolve the data set by selecting **Resolve** from the **Purity** menu. This results in the resolved spectra in Figure 9-30. Clicking on the **Next** button (blue arrow icon) in the figure results in the resolved contribution profiles in Figure 9-31.
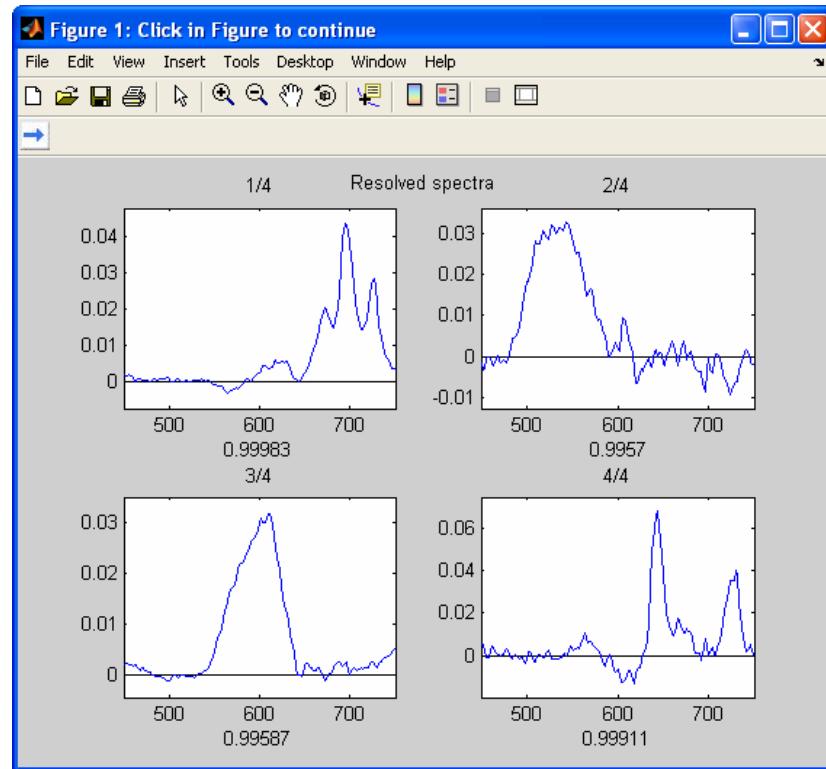
Figure 9-30. Resolved spectra.
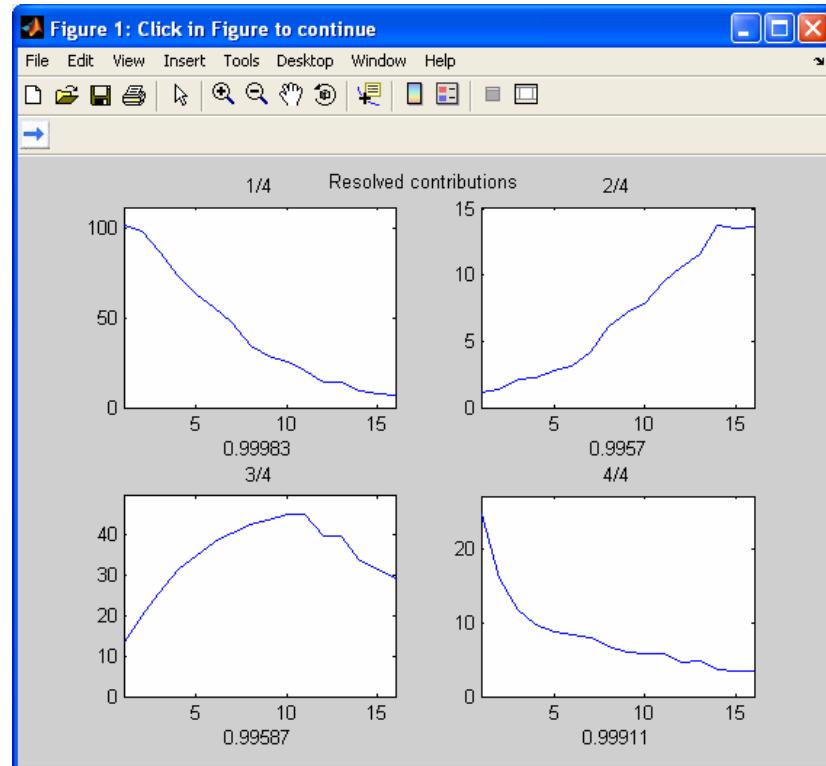
Figure 9-31. Resolved contributions.

252

Clicking the **Next** button again will return to the previous length and purity spectrum (Purity Model Builder). Clicking twice on the **Reset Last Variable** button resets the last two pure variables. We now zoom again into the area we just inactivated (colored red), as indicated in Figure 9-32.
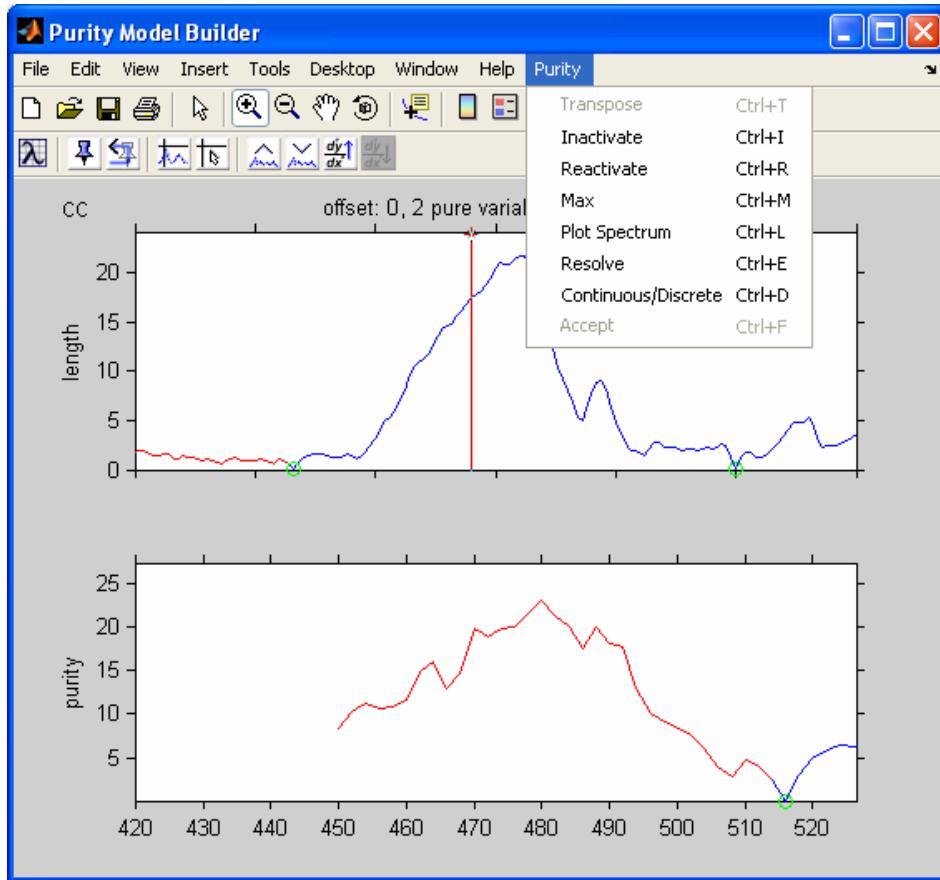
Figure 9-32. Reactivating selected area.

Reactivate the selected area by selecting **Reactivate** from the Purity menu. The figure should now look similar to Figure 9-24; the cursor automatically moves to the maximum.

We will now show an alternative to inactivating the region of 450-520 cm^{-1}. In order to correct problems with low-intensity variables, we can down-weight them by using the offset. By increasing the offset, the problematic area is decreased in intensity and the pure variable becomes acceptable. We increase the offset to 3 using the **Increase Offset** button, which is a good default value for the offset, followed by using the **Reset Last Variable** button twice, which results in Figure 9-33.
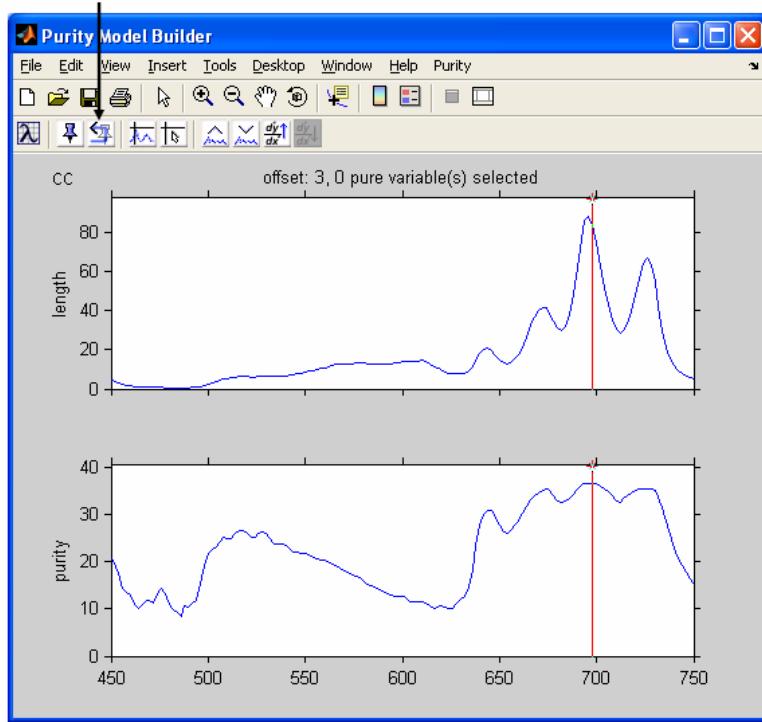
Figure 9-33. Offset equals 3 with no pure variables selected.
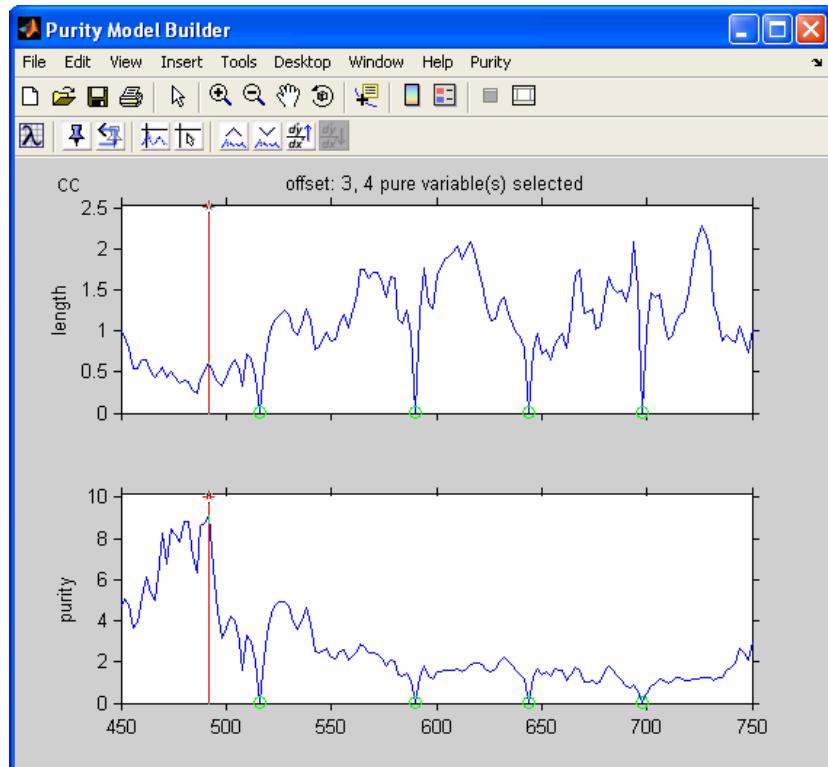
Figure 9-34. Four pure variables selected with offset at 3.

When we accept the first four pure variables now, by clicking the **Set Pure Variable** button four times, we obtain Figure 9-34, with no problems with low intensity variables.

After determining the pure variables, selecting **Resolve** from the **Purity** menu results in resolved spectra and contributions very similar to those shown in Figures 9-30 and 9-31 above.

A final check of the solution can be done by selecting **Plot Spectrum** from the **Purity** menu. This results in a plot of the original spectra, the spectra reconstructed from the resolved contribution profiles and spectra, and the differences between the two. See Figure 9-35.
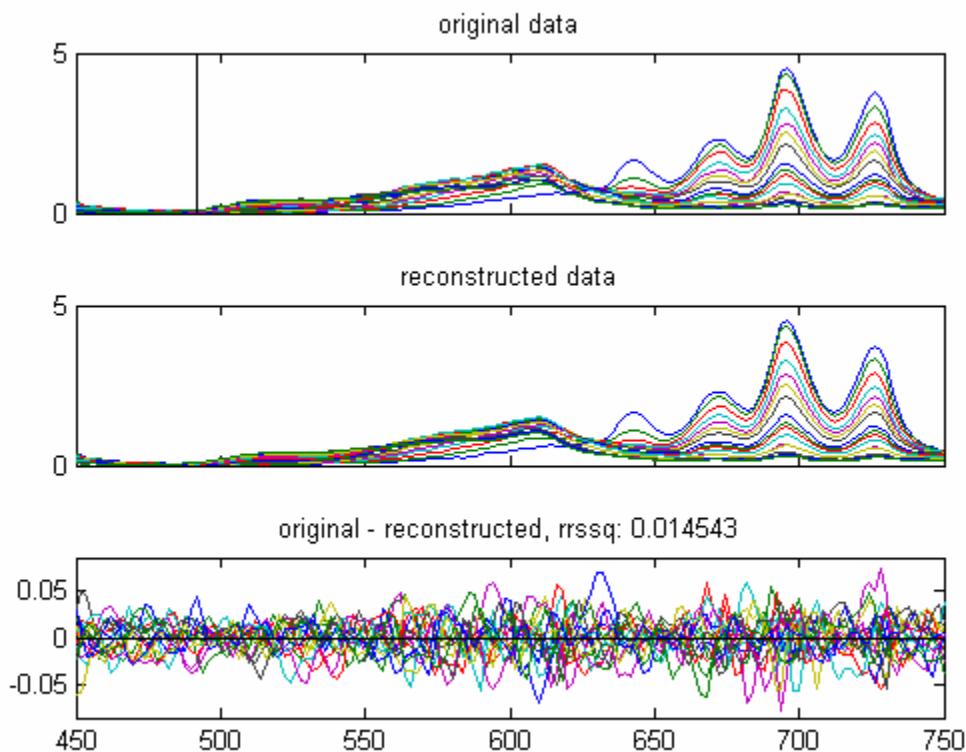
Figure 9-35. Plot of original, resolved, and difference spectra.

The rrssq value is a relative measure for the differences between the reconstructed and the original data set. In this case the difference is approximately 1.5%, which is a very good value.

FTIR Microscopy Example

This example uses FTIR microscopy spectra of a three-layer polymer laminate. We shall explore the use of second derivative pure variables.

Load the data and start the interface:

```
>> load FTIR_microscopy
>> purity
```

Note: One can start the **Analysis** interface pre-selected to Purity by simply typing `purity` at the command line.
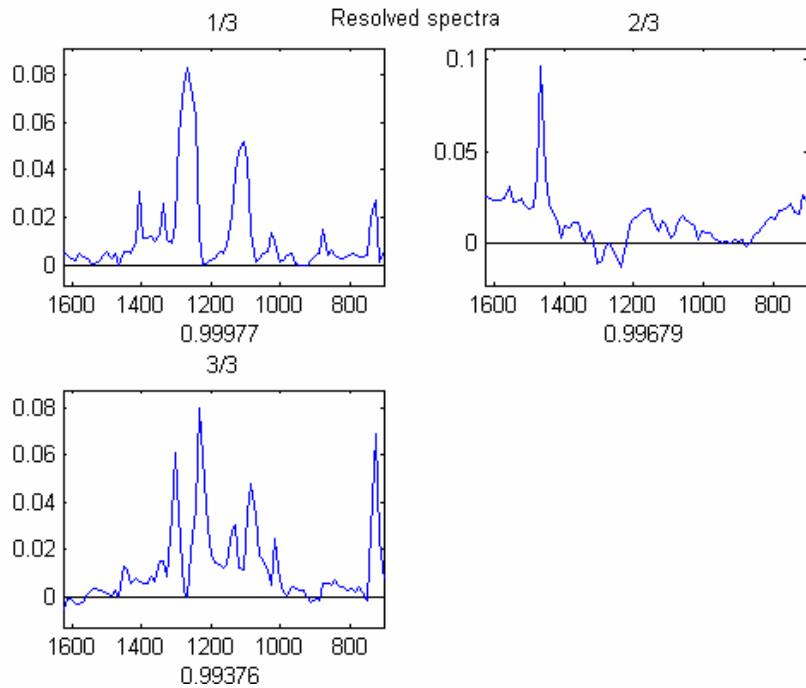
Figure 9-36. Resolved spectra for FTIR example.
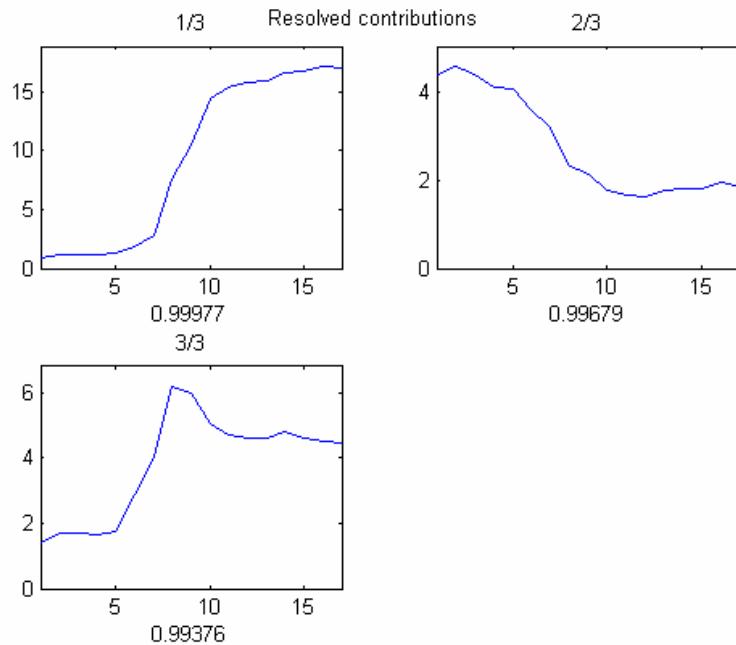
Figure 9-37. Resolved contributions for FTIR example.

Resolve three components in the same fashion as in the first example using the default settings. This will result in the resolved spectra and contribution profiles in Figures 9-36 and 9-37.

The resolved contribution profiles clearly indicate that the pure variables are not proper (for more information, run `purity demo`). After returning to the main program, we first reset the three pure variables by clicking on the button **Reset Last Variable** three times. Next we will use second derivative spectra by clicking the **Window Derivative Increase** button four times. The smoothing window for the Savitzky-Golay procedure for calculating second derivative spectra now has a size of 9, as is listed at the top of the length spectrum (see Figure 9-38).
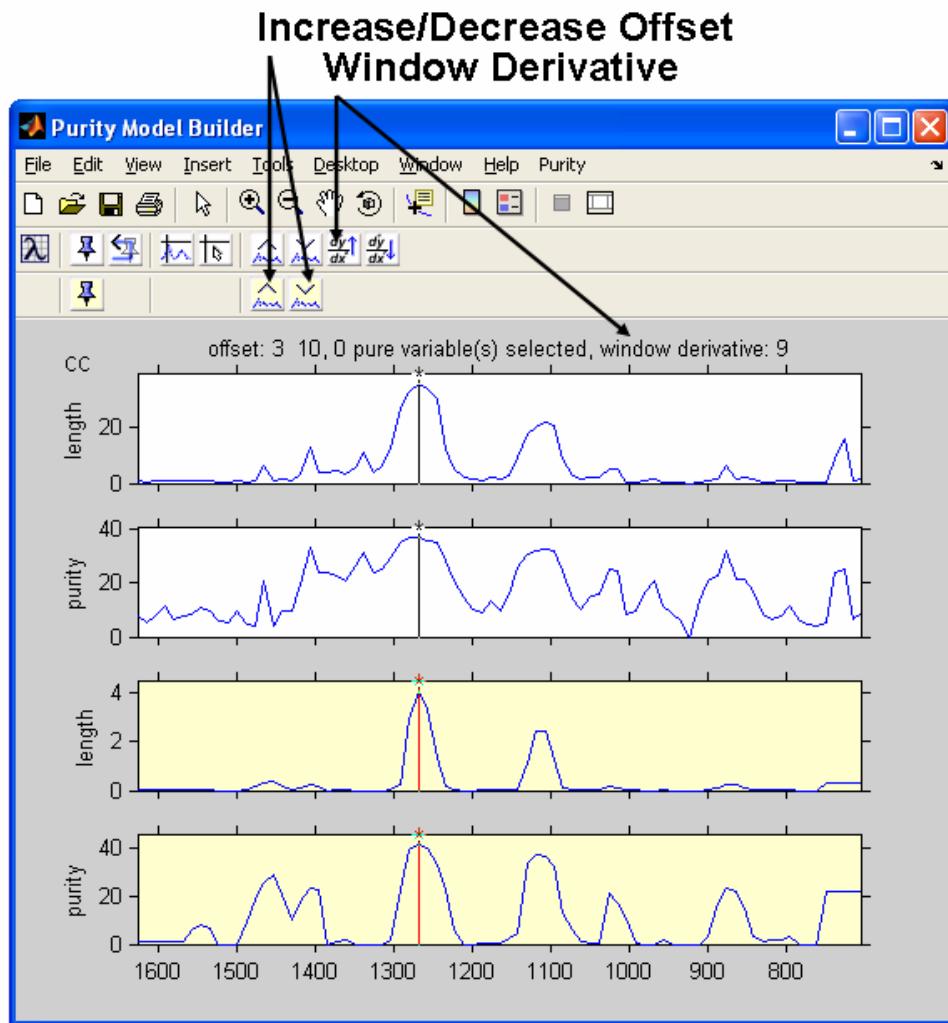
Figure 9-38. Savitzky-Golay window increased four times.

The major differences in the figure when in Window Derivative mode are:

a) Both the conventional and the second derivative data are shown.

b) There are two series of buttons (two toolbars) for setting pure variables and increase/decrease offset. The buttons and plots dealing with derivative data have a yellow hue.

c) For the offset, two values are listed. The first one is for the conventional data, the second one is for the second derivative data.

We will click three times on **Set Pure Variable** in the bottom series of buttons. Resolving the data results in Figures 9-39 and 9-40, which are the correct results.
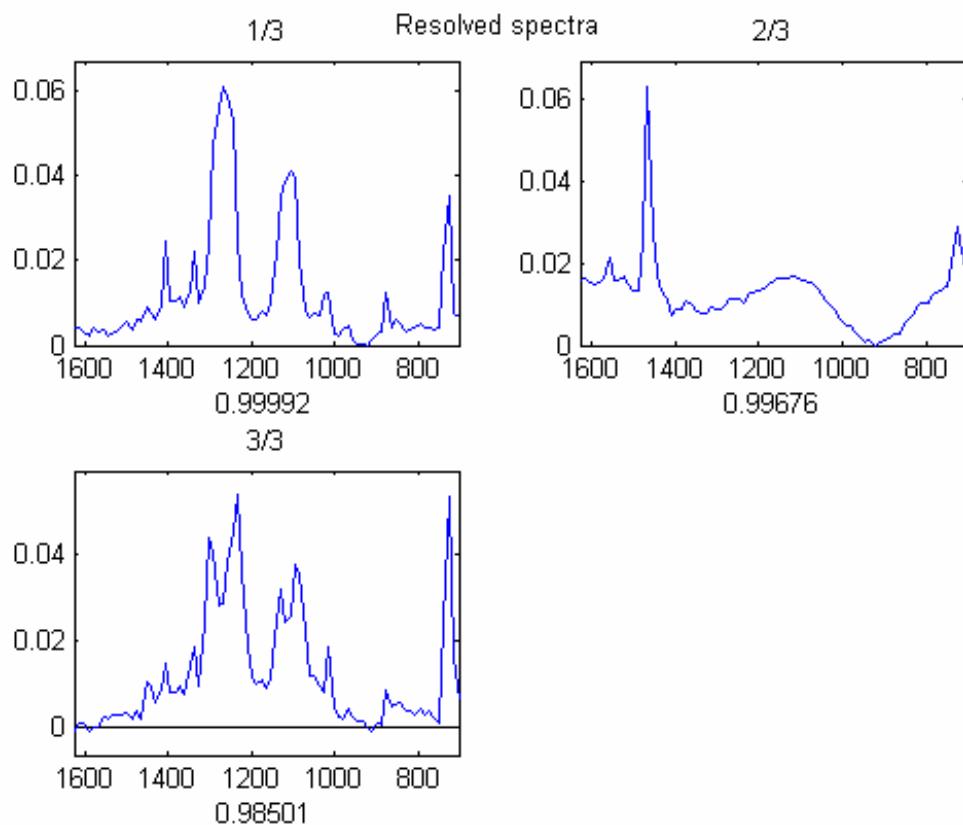
Figure 9-39. Resolved spectra for FTIR example.

258
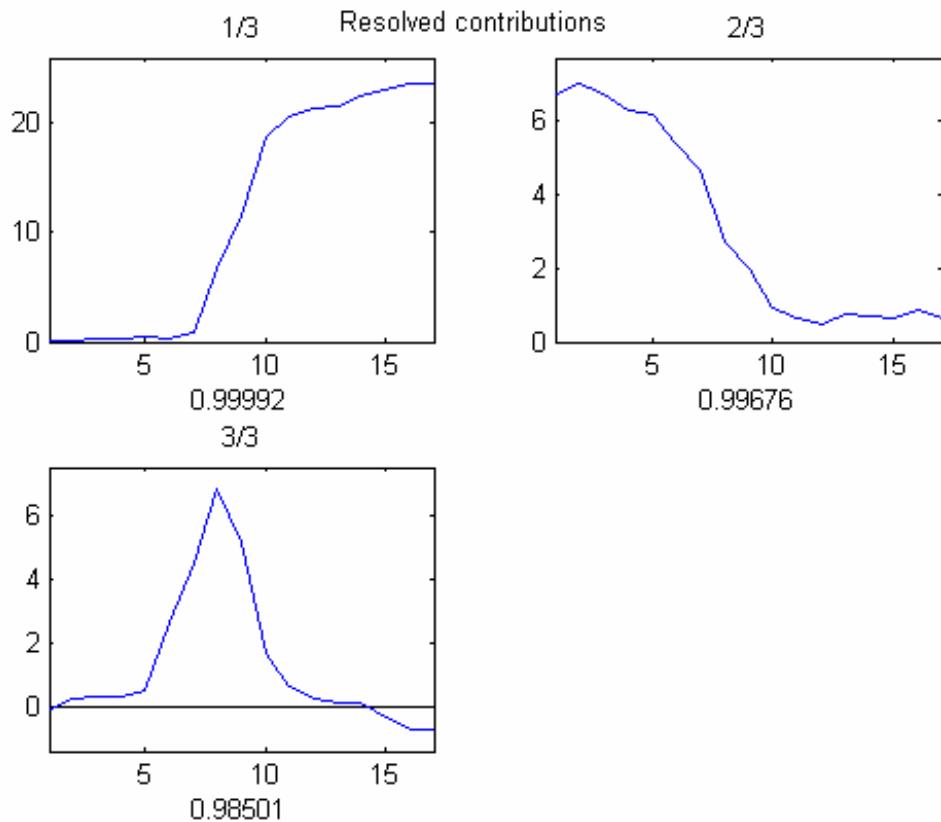
Figure 9-40. Resolved contributions for FTIR example.

Raman Spectra Combined Example

This example combines the use of conventional and second derivative pure variables.

Load the data and start the interface:

```
>> load raman_dust_particles
>> purity
```
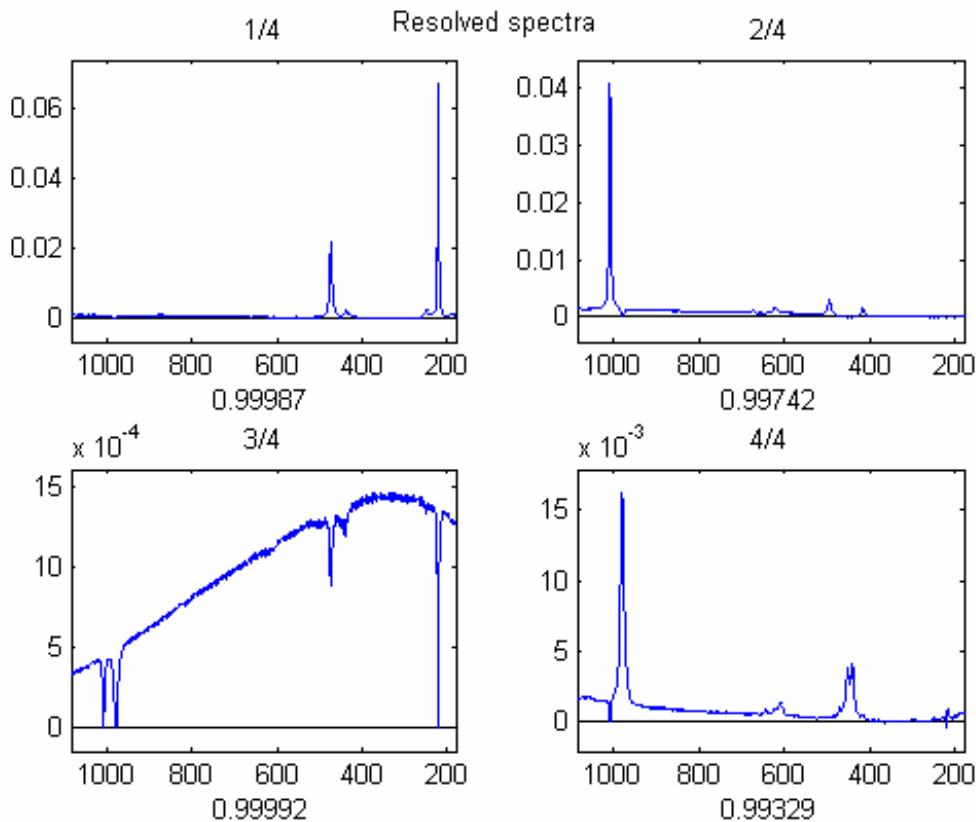
Figure 9-41. Resolved spectra.

This example has narrow peaks, identifying the components of the mixtures, and a broad baseline caused by fluorescence. Using the conventional data and extracting four components (the three components in the mixture, plus the baseline) results in the resolved spectra in Figure 9-41.

The third resolved component is the baseline, on which the resolved components reflect negatively. Using just the second derivative does not resolve the data properly, mainly because the broad baseline in not present in the second derivative data. A combination of the conventional and second derivative pure variables needs to be used. For this we reset all the pure variables and, using the **Windows Derivative Increase** button several times, we set the derivative window equal to 9. Since spectra with a baseline such as these have a high "natural" offset, it is best to set the offset for the conventional data to zero using the n **Decrease Offset** button on the top toolbar (see Figure 9-42).
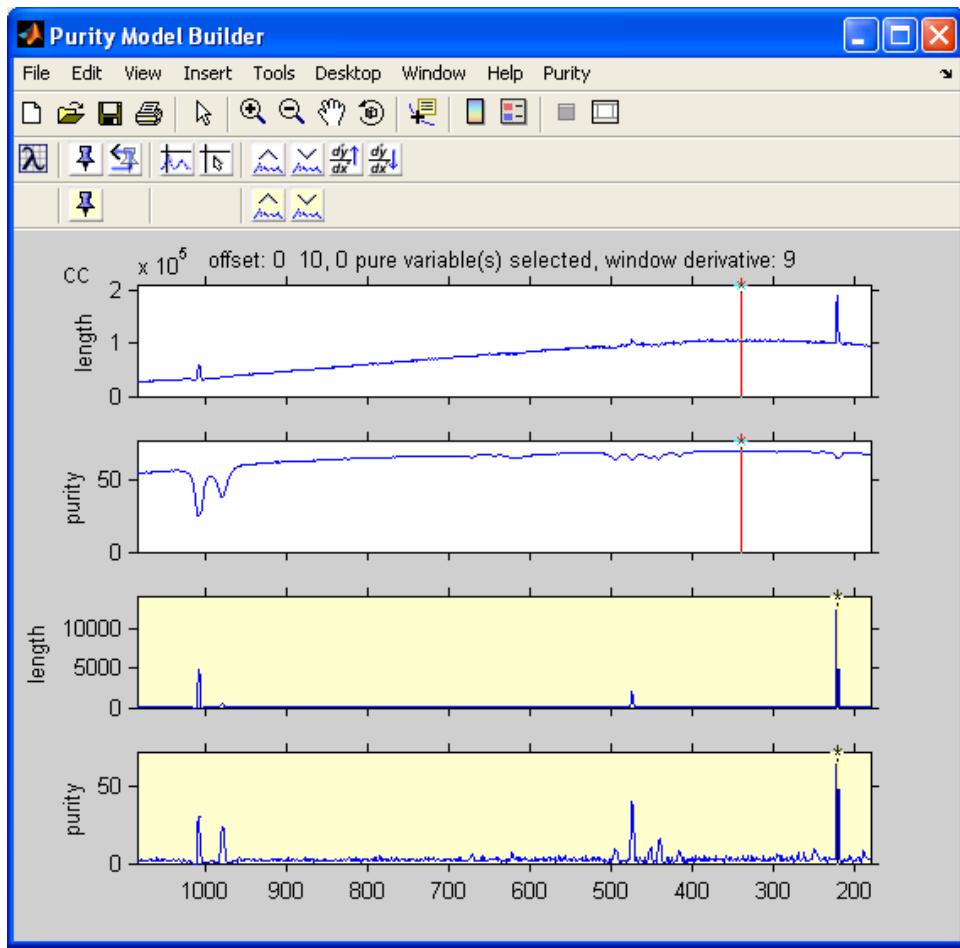
Figure 9-42. Window derivative set to 9 and offset decreased to zero.

We can now set the first four pure variables "suggested" by the program (indicated by the red colored cursor). The first pure variable is conventional (the red cursor appears in the top two plots in the figure), the other three pure variables are second derivative (the red cursor appears in the bottom two plots; remember to set these pure variables using the derivative (bottom) toolbar, resulting in the resolved spectra in Figure 9-43.
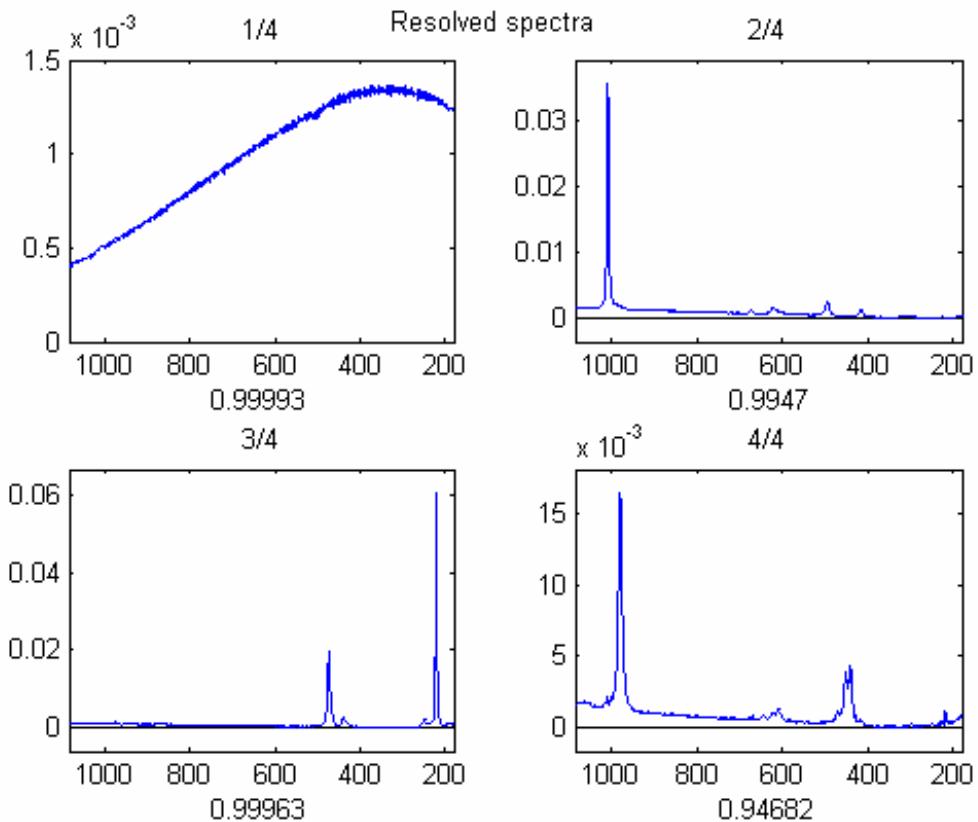
Figure 9-43. Resolved spectra with conventional and second derivative pure variables.

The results show a well-defined background spectrum and the three resolved components. However, there is still a problem in the resolved components with some baseline contributions, especially in the fourth resolved component. Therefore, we will try to extract an additional baseline component. The pure variable in the conventional spectrum is at a peak which we already have chosen as a pure variable in the 2nd derivative data. Therefore, we inactivate this area and obtain the next pure variable in the conventional spectrum. Zoom in on the area shown by the red peak in Figure 9-44, select **Inactivate** from the **Purity** menu, and then the cursor will automatically move to the new max.

262
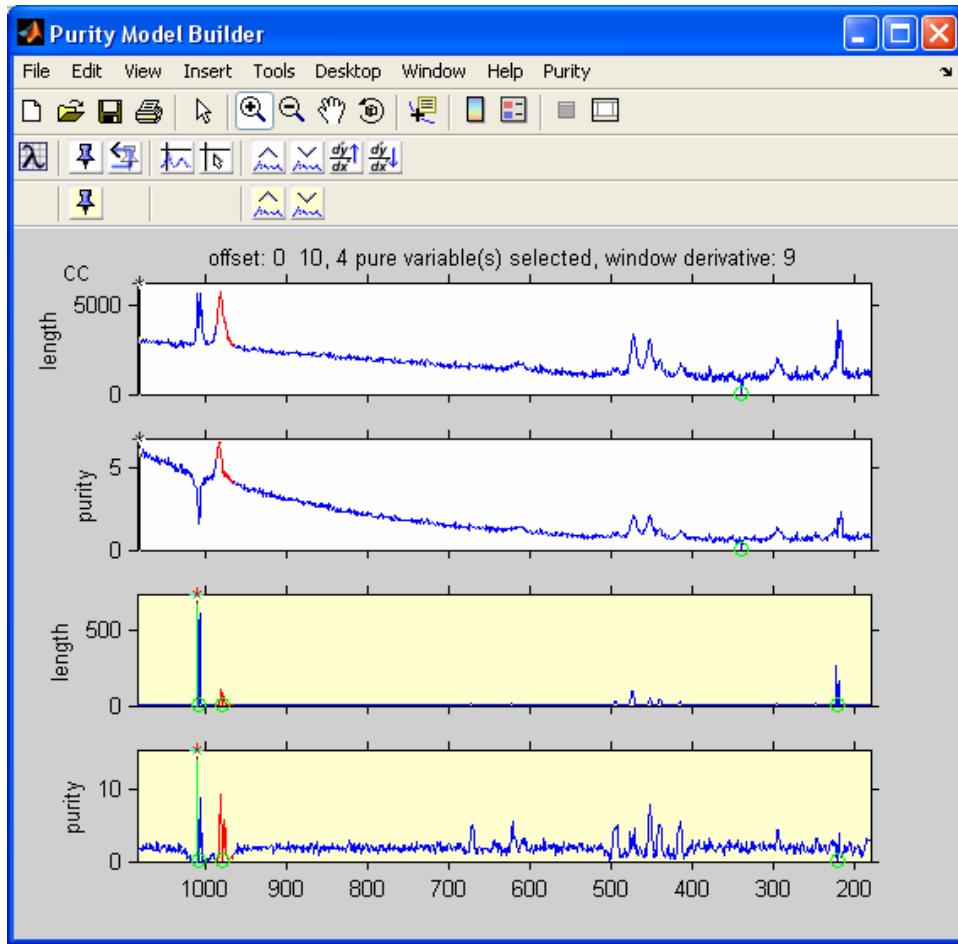
Figure 9-44. Inactivating area and selecting new pure variable.

The pure variable indicated in the conventional data is a good candidate for the background spectrum and is "set" using the conventional (top) toolbar. Please note that the pure variable in the second derivative spectra has a higher value (the cursor is red), but based on visual inspection it was decided to select the conventional pure variable. The high purity value in the second derivative data was caused by a residual of a previously selected pure variable, which can be caused by slight peak shifts or which can be an artifact of the use of second derivative spectra. More information can be found in the literature.

The resolved results are shown in Figures 9-45 and 9-46. It is clear that the background contribution in the resolved component spectra is minimized.
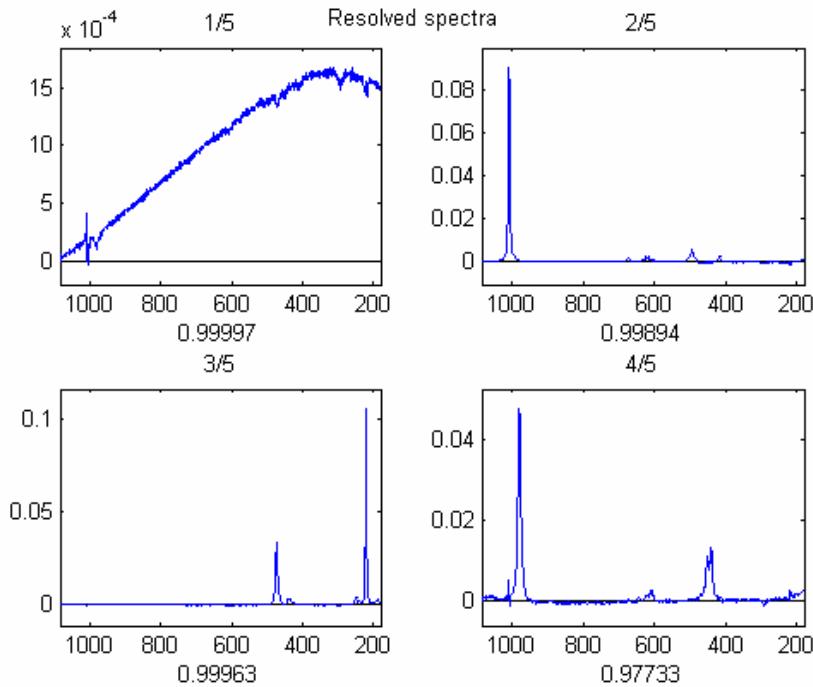
Figure 9-45. Resolved spectra.
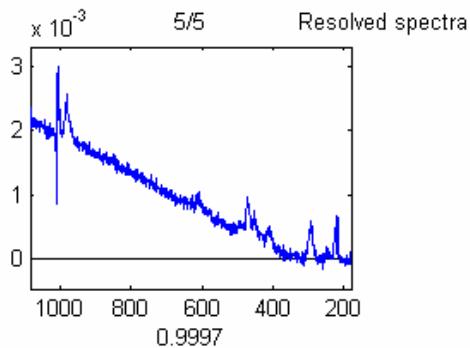
Figure 9-46. Fifth resolved spectrum.

MS Time-Resolved Example

This example demonstrates a pure spectrum to pure variable solution. Load the data and start the interface:

```
>> load MS_time_resolved
>> purity
```

For MS (mass spectroscopy) data, the pure variable approach is not always easy to apply. Due to the discontinuous character of the mass spectral data, it is not easy to judge

visually whether a spectrum represents noise or signal. Furthermore, the programs that compress the profile data into centroid data often introduce problems. However, MS data often do have pure variables. A way around the problems with pure variables is first determining the pure spectra, followed by deriving the pure variables from the pure spectrum solution.
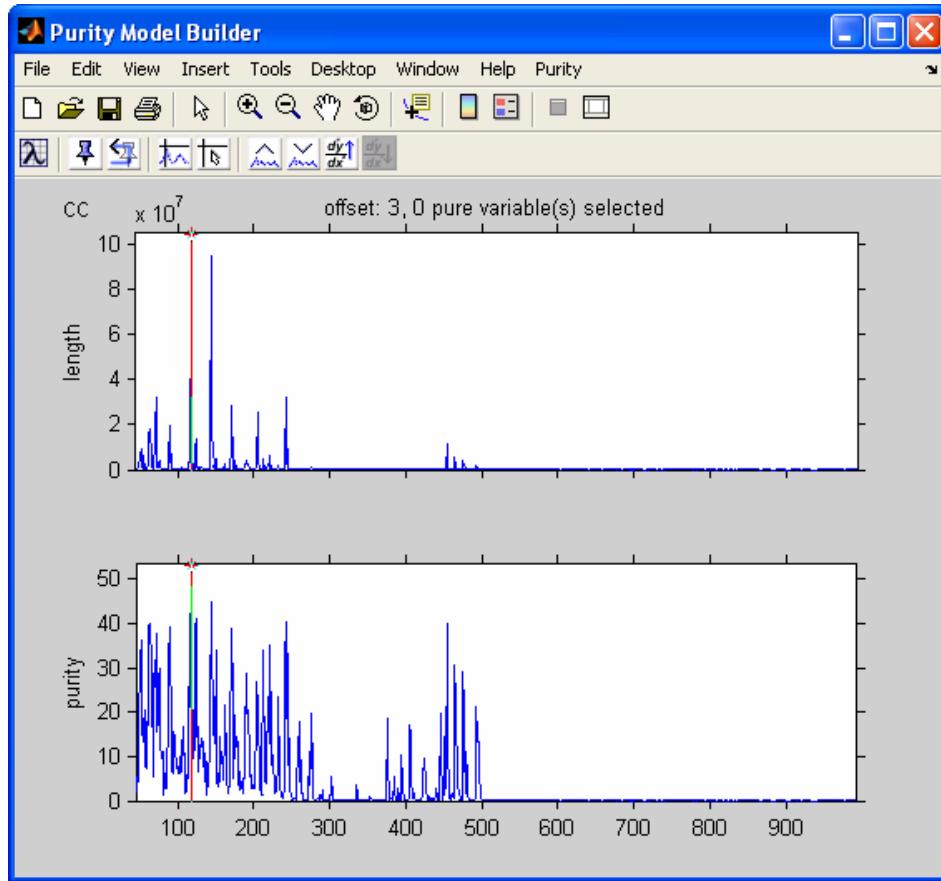
Figure 9-47. Time-resolved MS data loaded into the Purity Model Builder.

We want to analyze the pure spectra instead of the pure variables; this can be achieved by basically transposing the matrix. This is done by selecting **Transpose** from the **Purity** menu, resulting in Figure 9-48.
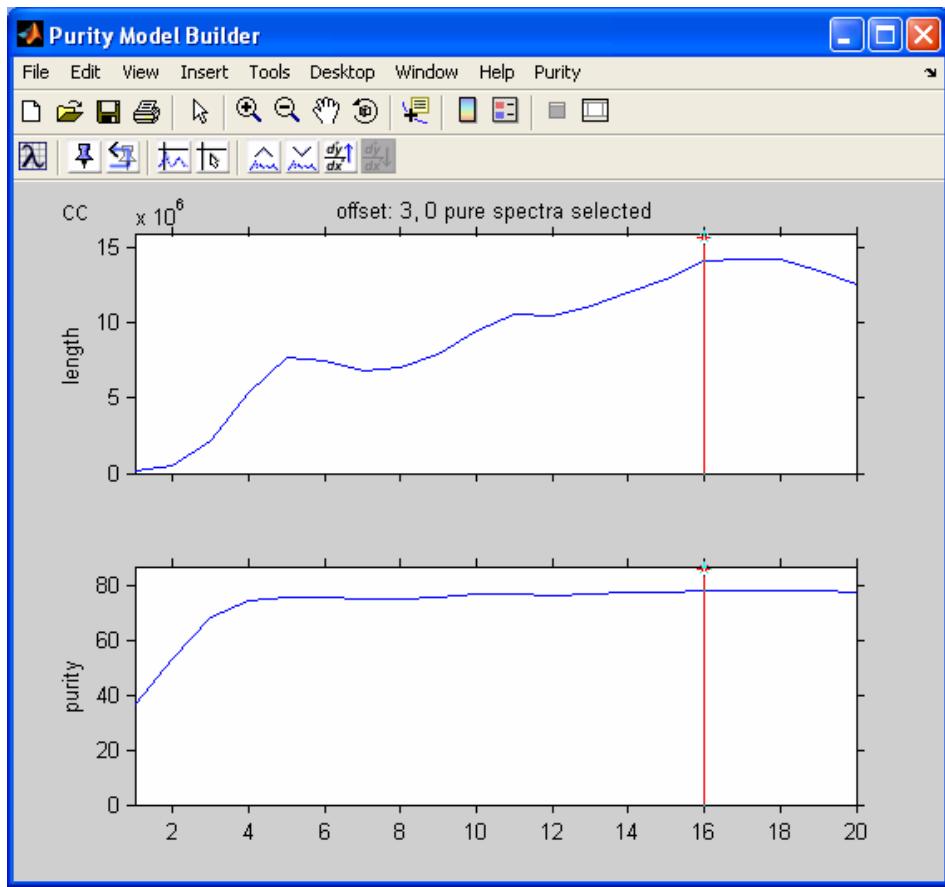
Figure 9-48. Transposed data.

After setting three pure spectra and selecting **Resolve**, we see a window asking us if we want to calculate the pure variable solution after calculating the pure spectrum solution. We also see the following statement:

"Reminder: offset change for pure variable calculations may be desirable."

The reason is the following. The offset is used for both the determination of the pure spectra and the pure variables. The appropriate offset may be different for the variables and the spectra. For example, if no low noise level intensity spectra are present, the offset value of zero can be used for the pure spectra (this would work for this example). However, a zero value for the determination of the pure variables is likely to give problems because of noisy variables. Therefore, one might change the zero value for the offset used to determine the pure spectra to 3 prior to the pure variable resolution step. We will not change the offset for this example.

After answering the question with **Yes**, the resolved results appear (Figure 9-49).

266
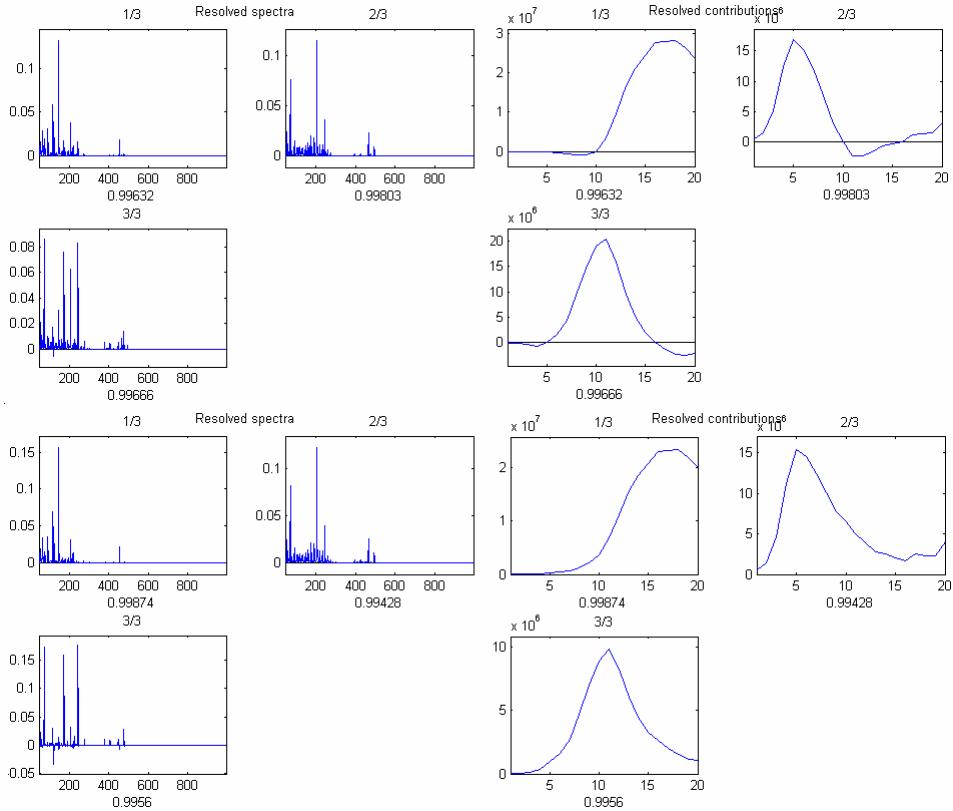
Figure 9-49. Resolved results for the time-resolved MS example.

Interactive Programs for Variable Selection Using Hyphenated Techniques

Introduction

This section describes the interactive programs to analyze MS data from hyphenated techniques. There are two programs. The first program, `coda_dw_interactive`, selects the best mass chromatogram based on the smoothness. The second program, `comparelcms_sim_interactive`, extracts differences between highly related samples, *e.g.*, different batches of the same material of which one batch is problematic.

CODA_DW_INTERACTIVE

To start the program, type:

» `coda_dw_interactive`

The dialog box to read the file comes up. Locate the file `lcms.mat` in the `dems` folder of your PLS_Toolbox installation. Alternatively, the file `lcms.mat` can be loaded in the work space prior to starting the program and then read into the program.
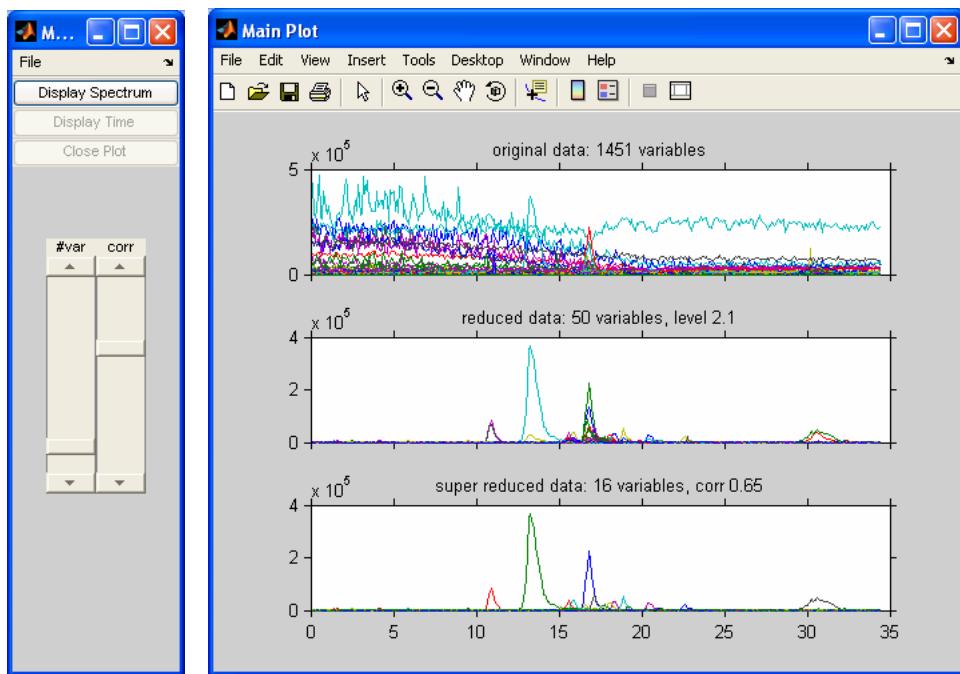
Figure 9-50. lcms.mat demonstration DataSet Object at default settings.

After reading in this file the windows in Figure 9-50 will appear. The top plot, in the **Main Plot** window, shows an overlay plot with all the mass chromatograms. As the title shows, there are 1451 chromatograms.

The second (middle) plot shows the variable selection of the algorithm. We refer to this as the reduced data. It is clear that only 'good' chromatograms are shown here. As the header shows, there are only 50 chromatograms which represent all the chemically significant information. Also listed in the header is the Durbin-Watson criterion (with a default value of less than 2.1).

In the second plot, there are generally several correlated chromatograms. The third plot shows the results when correlated chromatograms are deleted. We refer to this as the super-reduced data. In this case only 16 chromatograms are necessary to describe all the significant chemical information, as is listed in the title. The correlation level, also shown in the title, is 0.65. All the variables with a correlation of greater than 0.65 are deleted; increasing the correlation level would delete fewer chromatograms.

There are two sliders in the figure's **Main Menu**. The slider with the title **#var** determines how many variables will be displayed in the reduced data in the second plot. The variables are ranked by their quality, which is based on their value for the Durbin-Watson criterion. When we increase the slider value to 75 chromatograms (this is listed in the title of the reduced data), which is equivalent to a level for the value for the Durbin-Watson criterion of 2.4, variables of a lower quality will be included (see Figure 9-51).

268
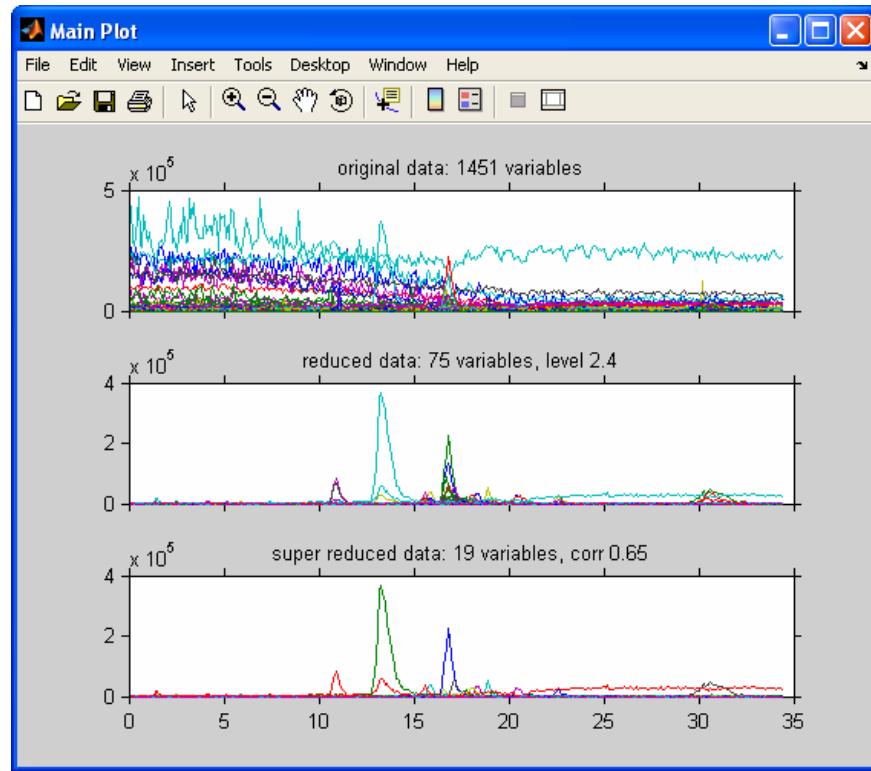
Figure 9-51. Number of variables increased to 75
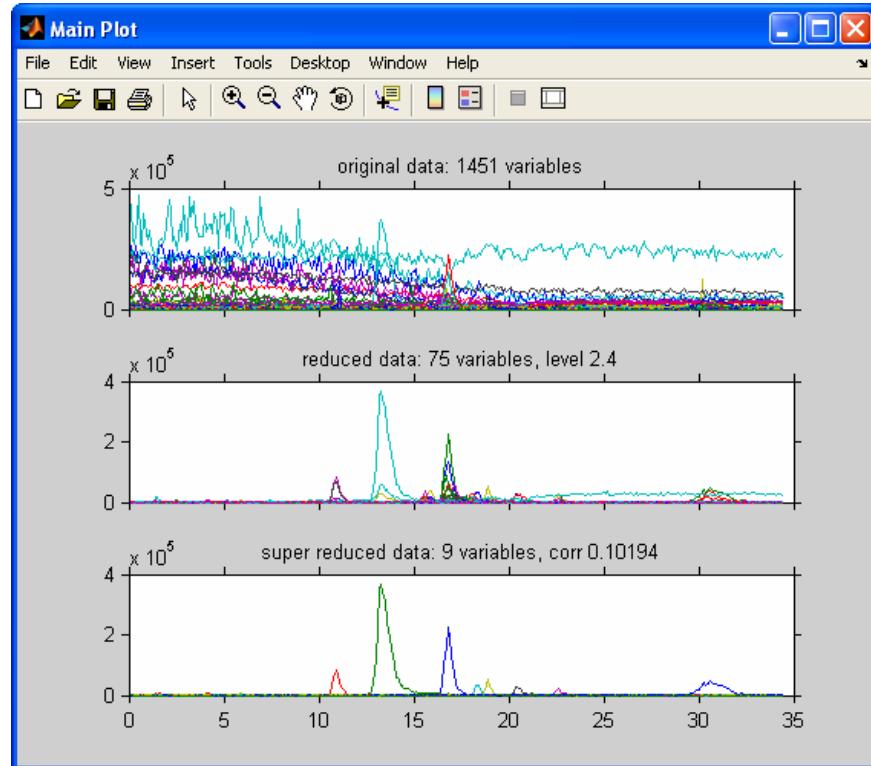
Figure 9-52. Correlation threshold set to 0.1

A change of the **corr** slider will result in changes in the third plot. A change to the value 0.10 (listed in the title of the super-reduced data) will delete too many variables, as we can see in Figure 9-52. In practice, a starting value of 0.65 appears to be appropriate.

In practice one can make some changes in the **#var** slider to accommodate the data reduction the researcher is interested in. The changes in the **corr** slider are secondary. Its only purpose is to show a simplified version of the second figure. Once the appropriate results have been obtained it is possible to plot spectra at any point in the chromatogram which we will demonstrate below.

When we want to select a chromatographic peak, it may be necessary to zoom in on the data. For this, the MATLAB zoom button can be used. Although any of the three plots can be used, Figure 9-53 shows the results of zooming in on the third plot of the super-reduced data.
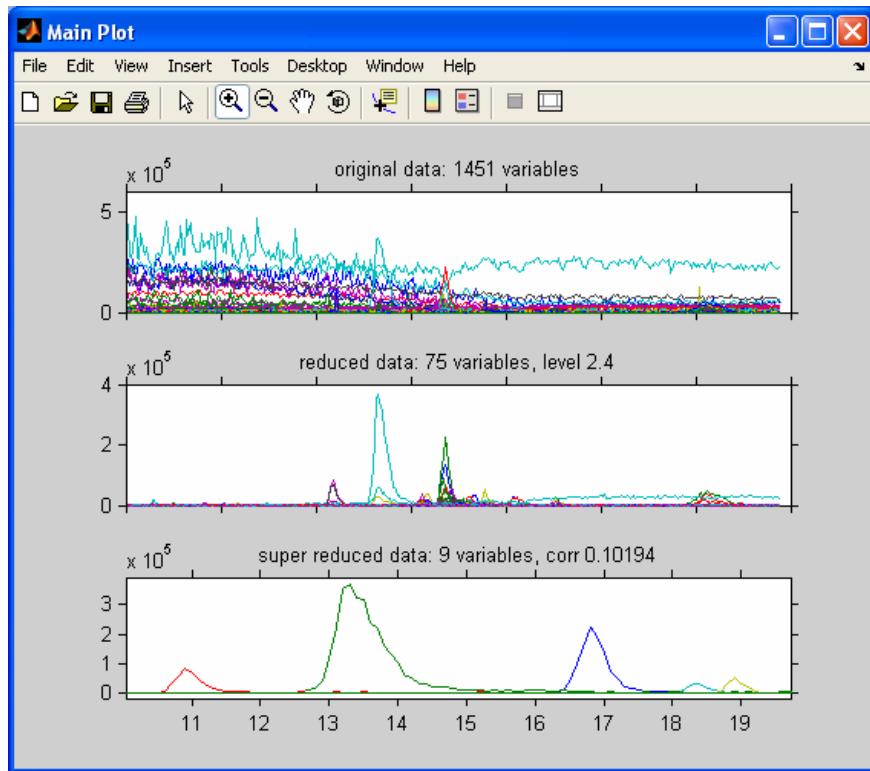
Figure 9-53. Zoomed in on super-reduced plot (third plot).
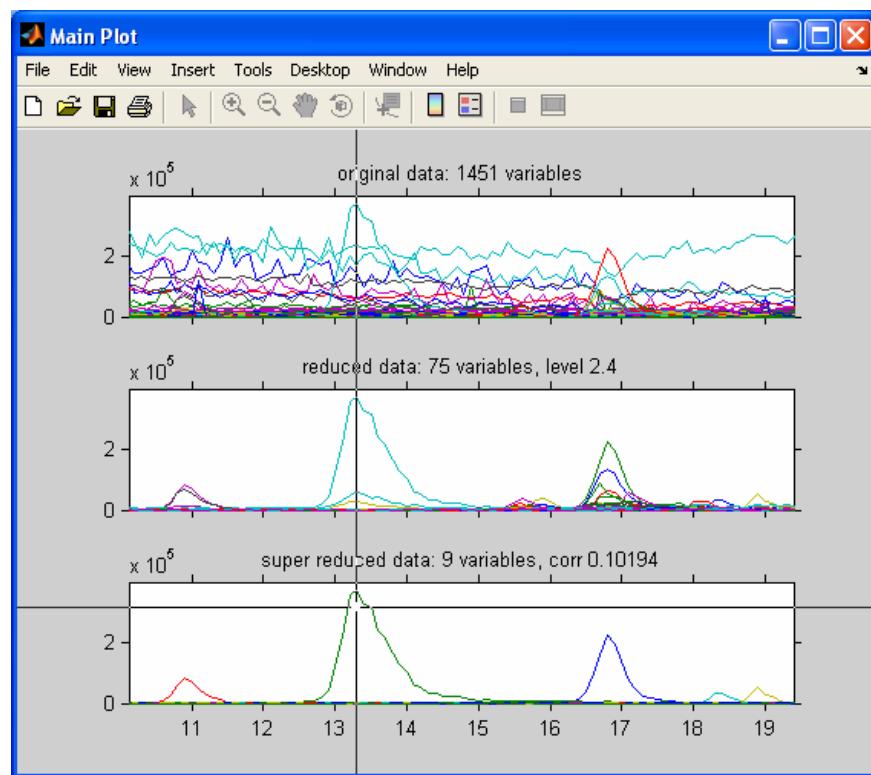
Figure 9-54. Selecting green peak
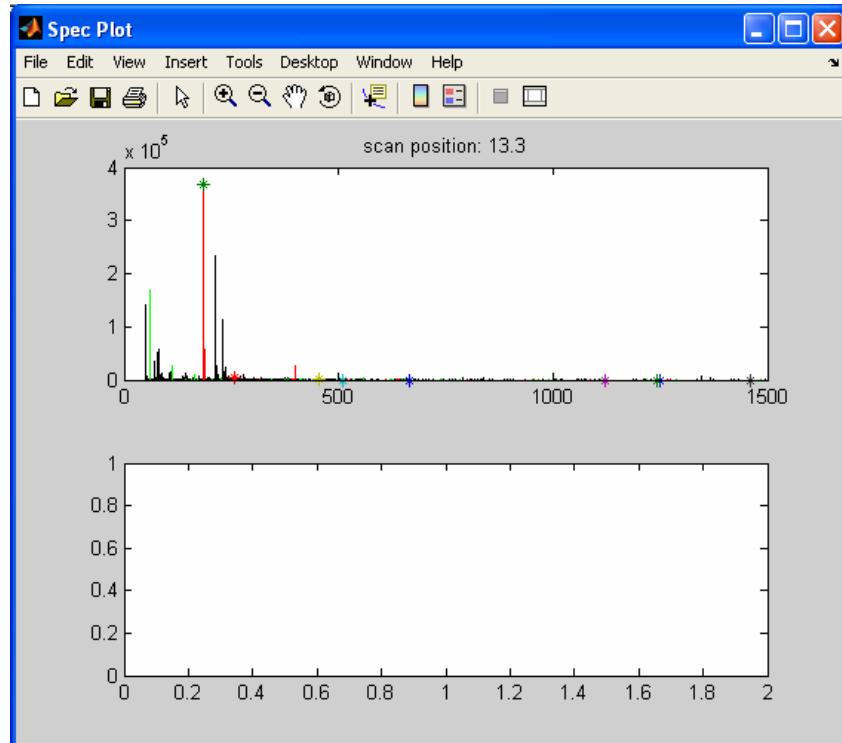
Figure 9-55. Initial spectrum plot.

When we want to select a peak to obtain the spectrum at that retention time, we choose the **Display Spectrum** button. This synchronizes all of the plots to the zoomed plot. We put the cross-hair on the green peak in the bottom plot as indicated in Figure 9-54. Clicking while the cross-hair is in that position results in Figure 9-55.

The spectrum shown here is the spectrum at the retention time we selected. This is the original data with the following color-coding added:

- The (in this case 50) best-quality masses selected by the algorithm are colored red in the bar plot.
- When the *n* best quality masses have been selected and colored in red, the best quality masses (*n*+1) to 2*n* are colored in green.
- The super-reduced masses are marked with colored stars. The colors of the stars correspond with the colors of the super-reduced mass chromatograms.

Since we selected a green super-reduced chromatogram (Figure 9-54), the red bar has a green star on top (Figure 9-55). So the mass with the green star should be the same as the green chromatogram in the super-reduced plot. We can check this, but because of the resolution of the plot we will first zoom in using the regular zoom capabilities of MATLAB by clicking on the ⊕ button and drawing a rectangular box around the mass of interest. Now we will select the mass with the green star by first clicking the **Display Time** button from the **Main Menu** figure, which results in a cross hair, followed by positioning it on the mass of interest and left-clicking (Figure 9-56).
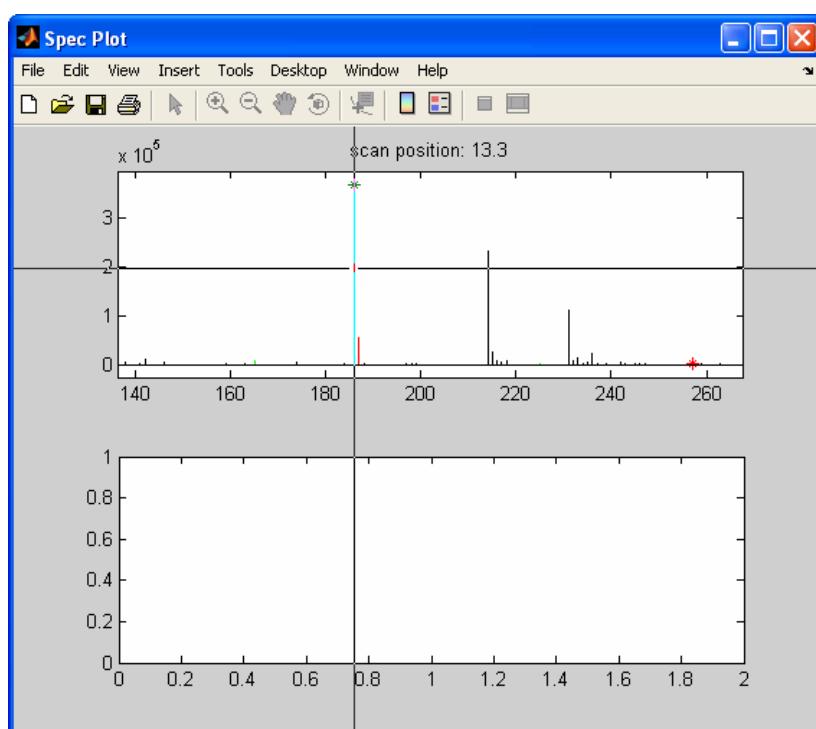
Figure 9-56. Selecting mass of green chromatogram.

When we click the mouse we see the following (see Figure 9-57):

- The chromatogram of the selected mass is plotted.
- The mass is labeled.

The plot of the chromatogram is straightforward. For the labeling of the mass spectrum, several other features are possible after clicking the **Display Time** button:

- A mass can be labeled by clicking on the mass of interest.
- In order to achieve a more appropriate labeling one can click on the mass of interest, keep the mouse button down and drag the cursor to a more appropriate position for the labeling. Releasing the button shows the label at the last position.
- A label of a mass can be deleted by selecting that mass again and dragging the cursor outside the plot onto the gray-space of the figure before releasing it.
- Before the **Display Time** button is selected, the MATLAB zoom capabilities are available.
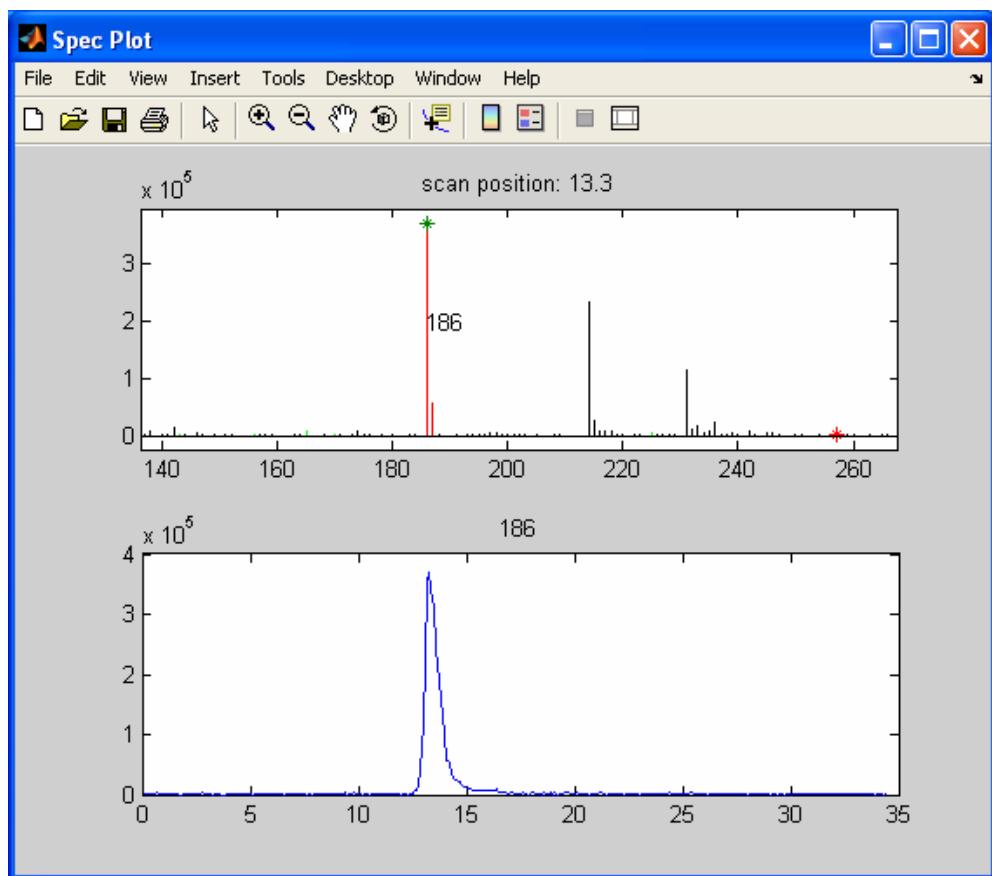
Figure 9-57. Zoomed at green peak mass with peak 186 selected.

This section showed all the options in the `coda_dw_interactive` program. Keep in mind that the sliders become inactive as soon as you select a spectrum (by clicking **Display Spectrum**) and will remain inactive until you close the **Spec Plot**.

COMPARELCMS_SIM_INTERACTIVE

To start the program type:

» `comparelcms_sim_interactive`

Locate the following 3 files in the `dems` folder of your PLS_Toolbox installation:
`lcms_compare1.mat`
`lcms_compare2.mat`
`lcms_compare3.mat`

As shown before, the files can also be loaded into the workspace prior to running the program and read from there.

These three files represent batches of the same material. The first data set is a good batch, the second data set is a bad batch and the third data set is a batch with some problems. The goal is to extract the differences.

After reading in these files, the windows in Figures 9-58 and 9-59 appear.
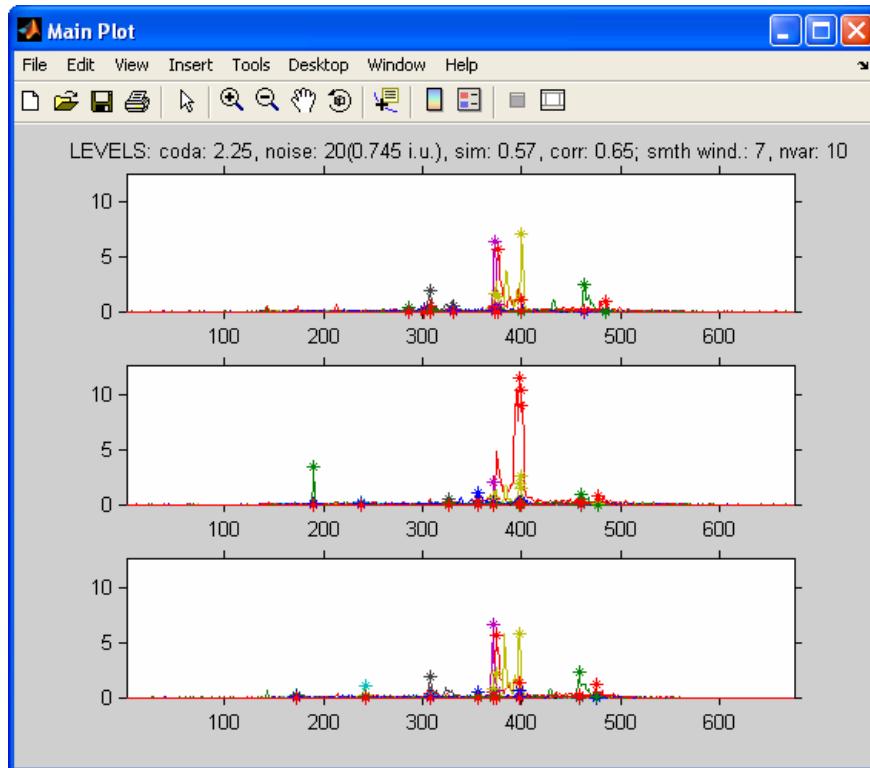
Figure 9-58. Default view of demo data
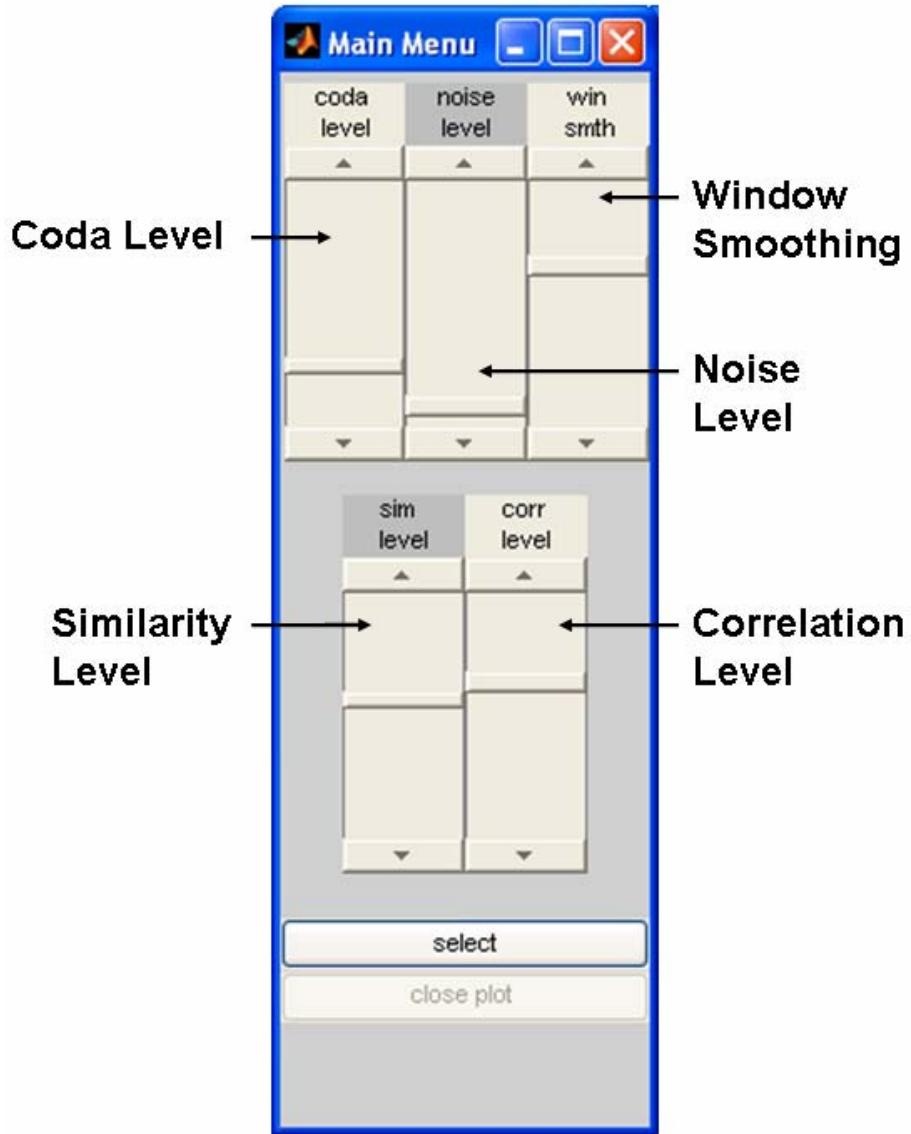
Figure 9-59. Default settings of main menu for `coda_dw_interactive` program.

The three plots show the super-reduced results of the differences between the data sets. The algorithm has several steps:

a) Data reduction using `coda_dw`, which is set by slider **coda level**. The level is shown in the header of the top plot. The default value is 2.25.

b) Low intensity variables can be eliminated by using the slider **noise level**. It is defined (as listed in the title) by 'counts', where one count is the lowest intensity change in the data. The default is 20. The corresponding intensity units are listed in parentheses (0.745 i.u. in this example).

c) After this initial data reduction we compare the chromatograms. Since some tolerance for small peak shifts must be present, the data are smoothed with a simple seven-point averaging filter. The window size can be changed with the slider **win smth**.

d) The smoothed data are compared and a similarity coefficient is calculated with values between zero and one. We only want to see the chromatograms that are dissimilar, so the value should be low: the lower the value, the fewer chromatograms are shown. The default value is 0.57, as listed in the title.

e) As described in the tutorial for coda_wq, the resulting chromatograms may have several mass chromatograms for a single component. The data are "super-reduced" by deleting highly correlated chromatograms. The correlation level for the procedure is set with the slider **corr level**. The higher its value, the more chromatograms will be left in.

In practice, one would start increasing the slider **coda level** to see if other peaks show up, or lower it when too many noise variables show up. The slider **noise level** is intuitive, so changing it need not be discussed. The level of the **win smth** slider depends on the quality of the instrumental analysis and generally should not be changed. The slider **sim level** determines the level of differences we will see and varying it seems appropriate. The slider **corr level** will be constant for most applications.

To give an example, one might want to know what the super-reduced coda_dw results look like. In this case one sets the slider **sim level** to its maximum value of one. In this case all super-reduced mass chromatograms will be shown (Figure 9-60). One can see that the full y-scale in Figure 9-60 is about 60, while the full scale in Figure 9-58 is about 12. Comparing these figures shows that it is difficult to extract the differences between the different samples by visual means only.
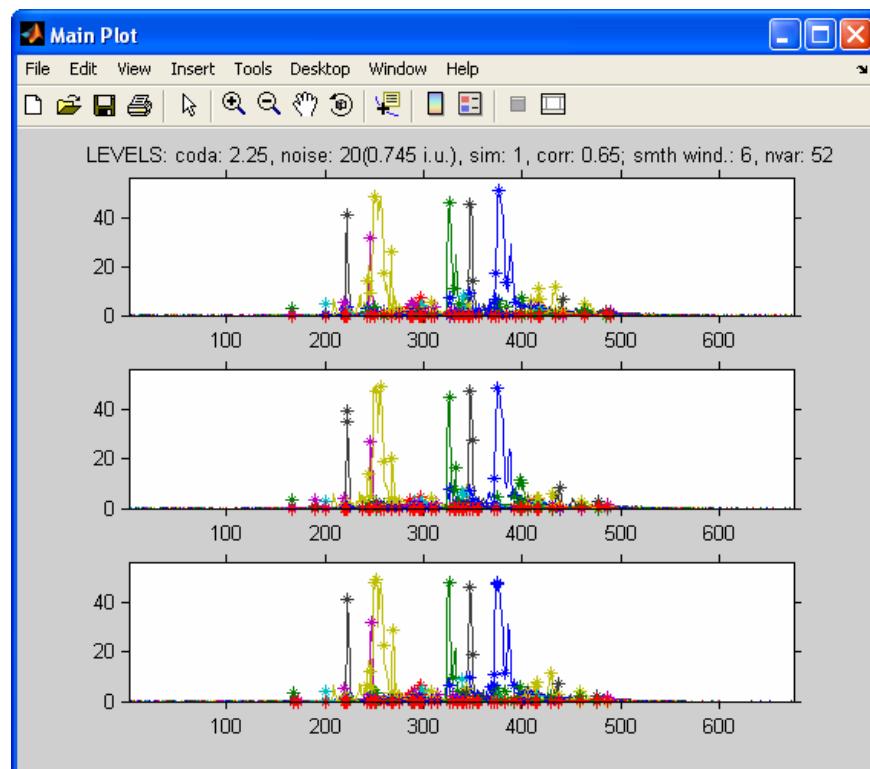
Figure 9-60. Sim level set to 1.

276

When we go back to the settings in the original configuration in Figure 9-58, (restart the program to get the same color coding), we can pick a chromatographic peak at a certain retention time and display the spectra.

When we want to select a chromatographic peak it may be necessary to zoom in on the data. For this, the MATLAB zoom button ![zoom button] can be used. Zooming in to the central part of the chromatograms (we use the third plot here, but other ones can be used too) results in Figure 9-61.
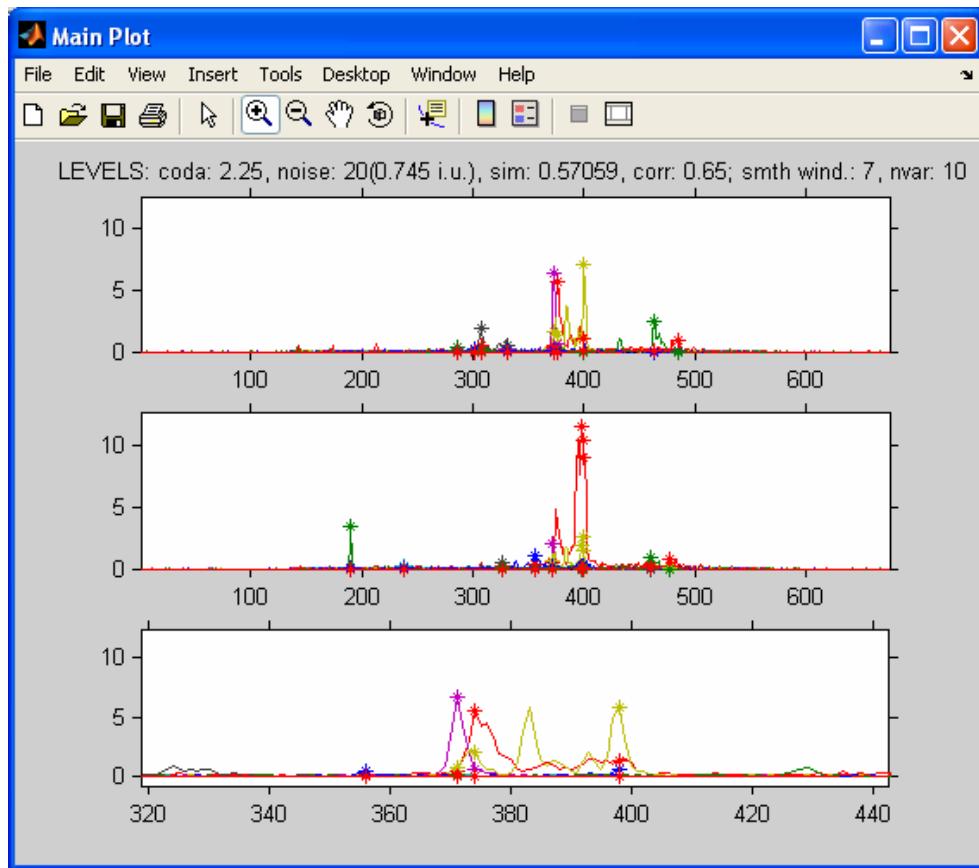
Figure 9-61. Zoomed in on third plot.
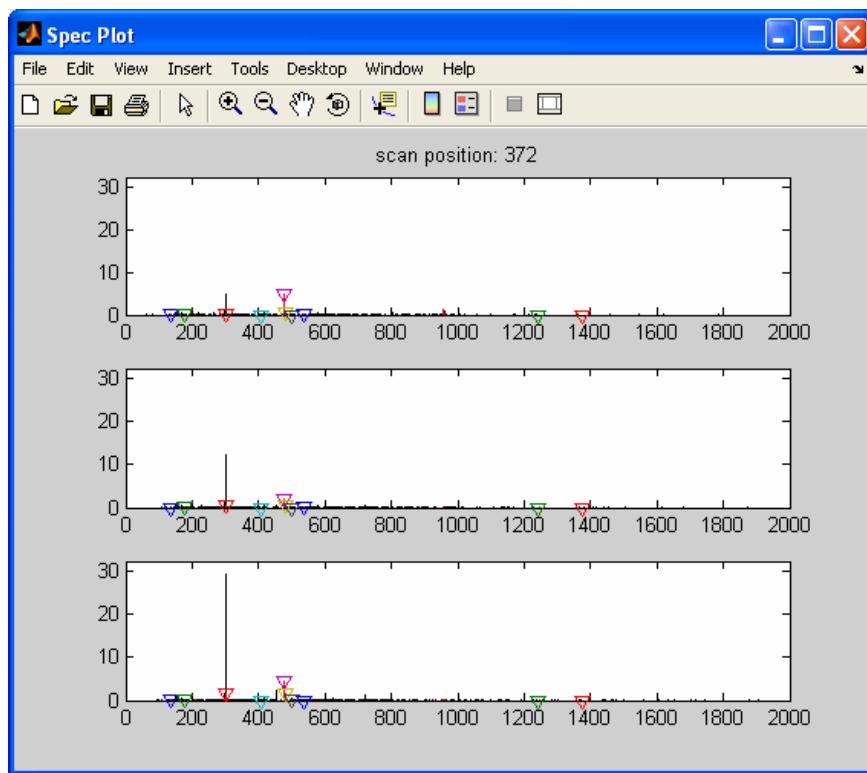
Figure 9-62. Spectrum at specified retention time (index 372).

When we want to select a peak to obtain the spectrum at that retention time, we click the button **select**. This results in synchronizing all the plots to the zoomed plot. If we put the cross-hair on the purple peak around 370 and left-click, a figure resembling Figure 9-62 will appear. The spectrum shown here is the spectrum at the retention time we selected. This is the original data with the following color coding added:

a) The chromatograms with a similarity of less than 0.57 (**sim level** slider) are colored red.
b) The super-reduced masses are marked with colored triangles. The colors of the stars correspond with the colors of the super-reduced mass chromatograms.

Since we selected a purple super-reduced chromatogram (the purple peak at around 370 from Figure 9-61), it is shown with a purple triangle on top of the red bar (Figure 9-62). So, the mass with the purple triangle should be the same as the purple chromatogram in the super-reduced plot. We can check this but, because of the resolution of the plot, we will first need to zoom using the regular zoom capabilities of MATLAB. So we click on the ⊕ button and draw a rectangular box around the mass of interest (although we can zoom on any of the three plots, use the third plot again); the results should look like Figure 9-63. Now we will select the mass with the purple triangle by using the **select** button, which results in a cross hair for clicking on the mass of interest (Figure 9-63). When we click the mouse we see the chromatograms of selected mass plotted (see Figure 9-64).
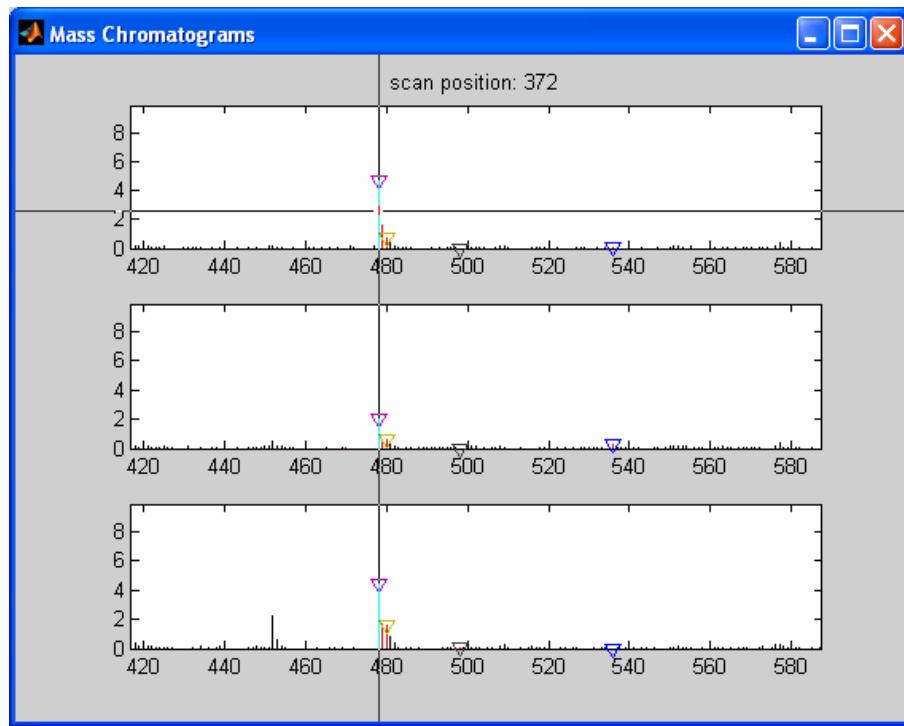
Figure 9-63. Selecting spectrum profile for index 372 (zoomed from Figure 9-64).
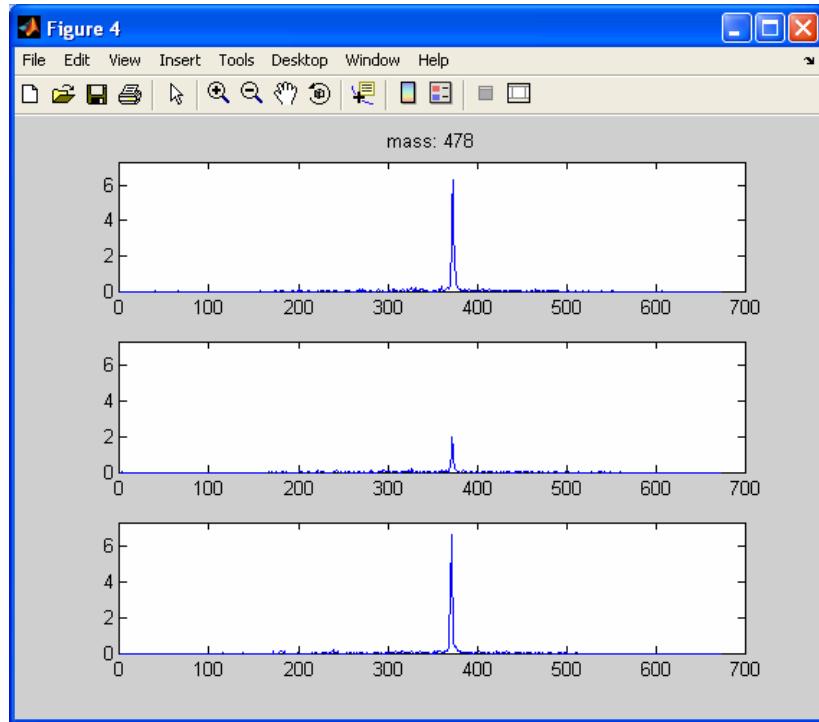
Figure 9-64. Profile for mass 478.

This section discussed all the options in the `comparelcms_sim_interactive` program. We can either select another mass in the same spectrum or close the figure and select another chromatographic peak. When we are working with the plot with the mass spectra, the sliders are inactivated. Closing all but the **Main Plot** will reactivate the sliders for further exploration.

10. Multi-way Methods

Multi-way data

In some situations, data have a more complex structure than usual. Most multivariate methods are suited for handling matrices, which can be considered to be tables of data. But imagine that you have, for example, a situation where for each sample the measurements are held in a matrix. When more than one sample is measured, the structure of the data is more appropriately held in a 'box' of data. Such data are called *multi-way* data. If each sample yields a matrix of size $J \times K$ and there are I samples, then an $I \times J \times K$ three-way array is obtained. In PLS_Toolbox there are a number of tools available for analyzing such data.

Generalized Rank Annihilation Method

One of the earliest applications of multi-way methods in chemistry addressed the situation where there are two samples only. It has been shown that the Generalized Rank Annihilation Method (GRAM) can be used to determine the magnitude of a single input (*e.g.*, concentration of an analyte of interest) in a multiple input response $\mathbf{N}_m$ given the response $\mathbf{N}_c$ of a calibration sample of known input magnitude (Sanchez, 1988) where

$$\mathbf{N}_c = \mathbf{X}\mathbf{C}_c\mathbf{Y}^T + \mathbf{E} \tag{10-1}$$

where $\mathbf{X}$ and $\mathbf{Y}$ are the profiles in each of the two orders and $\mathbf{C}_c$ is a diagonal matrix of concentrations. This leads to the generalized eigenvalue/eigenvector problem

$$\mathbf{N}_c\mathbf{Z}\mathbf{C}_m = \mathbf{N}_m\mathbf{Z}\mathbf{C}_c \tag{10-2}$$

where $\mathbf{Z}$ is a matrix of eigenvectors. Several algorithms have been proposed for performing the GRAM procedure. The state-of-the-art appears to be the method proposed by Wilson (1989), which projects the generally rectangular response matrices $\mathbf{N}_c$ and $\mathbf{N}_m$ into square matrices $\mathbf{A}$ and $\mathbf{B}$ and then solves

$$\mathbf{AZ} = \mathbf{BZ\Lambda} \tag{10-3}$$

using the QZ algorithm developed by Moler and Stewart (1973) and later refined by Ward (1975). In Equation 10-3, $\mathbf{\Lambda}$ is a diagonal matrix consisting of ratios of concentrations of analytes in the test and calibration samples.

GRAM is a relatively straightforward method and has utility in a large number of applications; many second-order analytical methods, such as GC-MS, are bilinear, *i.e.*, the data can be modeled as the outer product of concentration profiles and pure component spectra. The major problem with GRAM is that, in many systems, the concentration profiles change due to drift in the analytical system(for example, changes in the GC column in a GC-MS). These shifts can degrade the solutions from GRAM rapidly. Early implementations of GRAM led to non-meaningful imaginary solutions.

Modifications to the original GRAM algorithm (Shousong *et al.*, 1993), however, have rectified this problem and have led to significantly improved factor estimates.

An Example with GRAM

Willem Windig identified a technique for which GRAM works beautifully: time-decay Nuclear Magnetic Resonance. In time-decay NMR, a system is given a magnetic pulse and then the NMR spectra are observed as they decay. Different species decay exponentially with different half-lives. Windig recognized that, because the decay curves are exponential, the profile for a single component is the same within a single scale factor, regardless of the time slice one looks at. Different analytes, however, have different profiles, because of their different half lives. Thus, one can use GRAM to decompose a single matrix by inputting slightly different slices of the original matrix.

We will demonstrate GRAM using `nmr_data.mat` file in the PLS_Toolbox. The data consist of a 20 by 1176 matrix of time-decay NMR spectra of photographic film. The raw data are plotted in Figure 10-1. GRAM can be used to extract the pure component spectra and time decay profiles using the `gram` function as follows:

```
» a = nmrdata.data(1:19,:);
» b = nmrdata.data(2:20,:);
» nmrscl = nmrdata.axisscale{2};
» [ord1,ord2,ssq,aeigs,beigs] = gram(a,b,3,1:19,nmrscl);
```
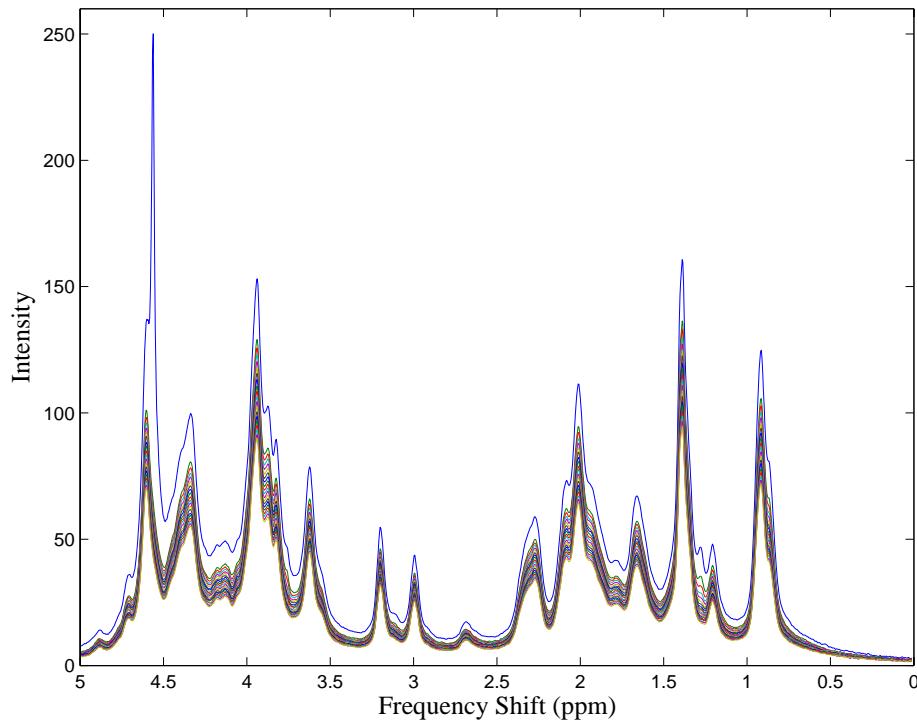

Figure 10-1. Time-decay NMR data of photographic film from nmr_data.mat.

282

In this sequence of commands, the first nineteen samples of the data are assigned to matrix `a,` while the second nineteen are assigned to `b`. The `gram` function is used to estimate three factors. Scales for plotting against are also defined. The results from GRAM are shown in Table 10-1 which gives the eigenvalues for each matrix and their ratios. The percent values listed give the relative sizes of the eigenvalues for comparison purposes. The profiles in each of the orders are shown in Figure 10-2.

Table 10-1. Results from GRAM: eigenvalues of A and B matrices.

```
Comp       ____Matrix__A____         ____Matrix__B____         Ratio
Number     Eigenval      %           Eigenval      %            A/B
1     4.68e+02      8.05        4.40e+00      0.08        106.43
2     5.23e+03     89.89        5.12e+03     98.24          1.02
3     1.20e+02      2.06        8.75e+01      1.68          1.37
```

The analyte that decays very rapidly and has the peak at ~4.5 ppm is water. The other two analytes are the gel and the backing of the photographic film. One of these decays much more rapidly than the other. Note that the spectra of the two are quite highly overlapped. Thus, the ability to solve for them directly with GRAM is potentially very useful.
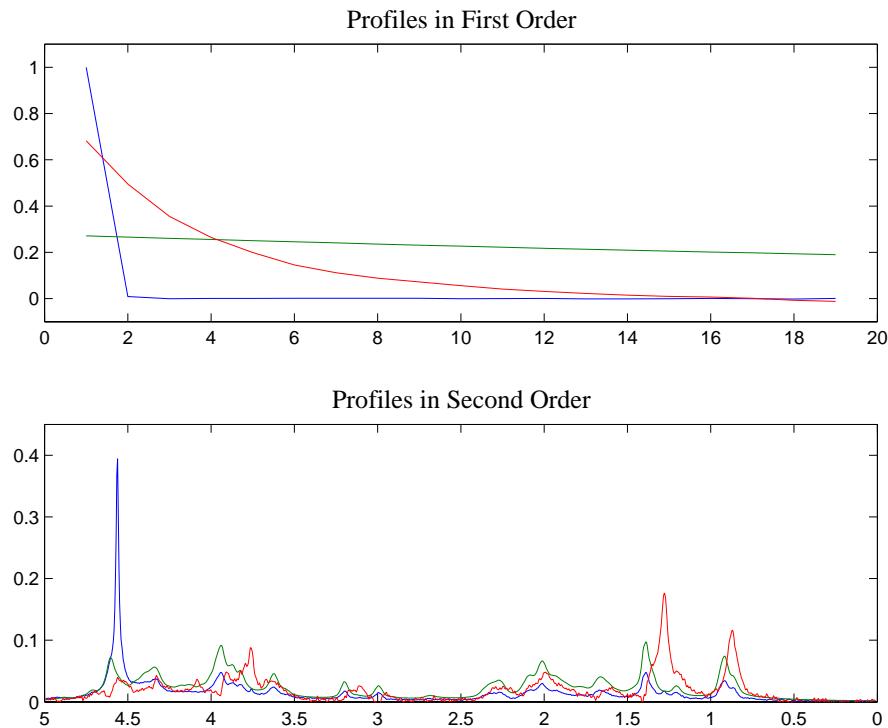
Figure 10-2. GRAM results showing "concentration" and spectral profiles.

PARAFAC

While GRAM solves the problem

$$\mathbf{N}_k = \mathbf{X}\mathbf{C}_k\mathbf{Y}^T + \mathbf{E}_k, \; k=1,..,K \qquad (10\text{-}4)$$

for two samples ($K = 2$), it was later realized that a multi-way model for general K exists. This is PARallel FACtor analysis, PARAFAC, which was developed in 1970 by R. Harshman and independently the same year by Carroll and Chang. The notation usually adopted in three-way modeling (Kiers, 2000) states Equation 10-4 as

$$\mathbf{X}_k = \mathbf{A}\mathbf{D}_k\mathbf{B}^T + \mathbf{E}_k, \; k=1,..,K \qquad (10\text{-}5)$$

where $\mathbf{X}_k$ is an $I{\times}J$ matrix and $\mathbf{A}$ ($I{\times}R$), $\mathbf{B}$ ($J{\times}R$), $\mathbf{C}$ ($K{\times}R$). The matrix $\mathbf{D}$ is an $R{\times}R$ diagonal matrix that holds the kth row of $\mathbf{C}$ in its diagonal. For all Ks considered simultaneously, the data are held in a three-way array $\underline{\mathbf{X}}$ of size $I{\times}J{\times}K$ (see Figure 5-24) and the submatrices $\mathbf{X}_k$ are also referred to as frontal slabs.

Written in scalar notation, the model is

$$x_{ijk} = \sum_{r=1}^{R} A_{ir}B_{jr}C_{kr} + e_{ijk} \qquad (10\text{-}6)$$

While Equation 10-5 appears to indicate that the model is not symmetric in the way the different modes (row, columns and so-called tubes) are handled, Equation 10-6 shows that the model is very similar to PCA and indeed does treat the different modes in the same manner. It is merely the matrix notation of the three-way array in Equation 10-5 that obscures the symmetry. Comparing the scalar representation with PCA, it is seen that for data where $K = 1$, *i.e.,* where there is only one slab, the model degenerates to a bilinear model.

To obtain some intuition on what this PARAFAC model represents, several different interpretations are offered in the following examples.

Imagine a matrix $\mathbf{X}_1$ obtained from a single run of a chromatographic system with spectral detection. The analytes are all present at unit concentration. Assuming linearity and additivity, this matrix can be decomposed into

$$\mathbf{X}_1 = \mathbf{A}\mathbf{B}^T + \mathbf{E}_1 \qquad (10\text{-}7)$$

where $\mathbf{A}$ is holding the pure analyte elution profiles in each column and $\mathbf{B}$ the corresponding spectra. Imagine further that a new sample $\mathbf{X}_2$ is taken. It contains the same analytes, but in different concentrations. The above model is not able to model the data, but by slightly modifying it by scaling each component with the concentration of the analyte, we get

$$\mathbf{X}_2 = \mathbf{A}\mathbf{D}_2\mathbf{B}^T + \mathbf{E}_2 \qquad (10\text{-}8)$$

where the matrix $\mathbf{D}_2$ holds the concentrations on the diagonal. Thus, this new matrix is described by the same factors ($\mathbf{A}$ and $\mathbf{B}$) only in different proportions. This is the idea in PARallel FACtor analysis – PARAFAC. The idea came from earlier investigations on how to rotate PCA-like components optimally (Cattell 1944), but has shown to be useful in a number of different settings.

The most astonishing feature of PARAFAC, compared to PCA, is that PARAFAC is unique up to scaling and permutation. Scaling ambiguity means that a column of $\mathbf{A}$ may be scaled by any α, as long as the corresponding column of $\mathbf{B}$ or $\mathbf{C}$ is scaled inversely, *i.e.*, by $1/\alpha$. The permutation ambiguity simply states that you may call component one component two and vice versa. Apart from these trivial ambiguities, the PARAFAC model is unique; there is only one solution to this model. Compared to the non-uniqueness of a bilinear model (see, for example, Equation 9-2), this uniqueness is the direct reason for much of the popularity of PARAFAC. If the measured data follow a PARAFAC model, the underlying parameters of the model can be estimated without any rotational ambiguity. For example, for the above-mentioned chromatographic data, a correctly-specified PARAFAC model will directly provide estimates of the individual elution profiles, analyte spectra and concentrations (with the exception that the scaling is ambiguous).

Example of Applying PARAFAC

As an example of applying PARAFAC, consider excitation-emission fluorescence of a number of amino acids: Tryptophan (Trp), Tyrosine (Tyr), and Phenylalanine (Phe). The `aminoacids.mat` file contains data for five samples. Data from single sample, number 4, is shown in Figure 10-3. Unlike the first three samples in the data, which are pure components, this sample is a mixture of all three amino acids.
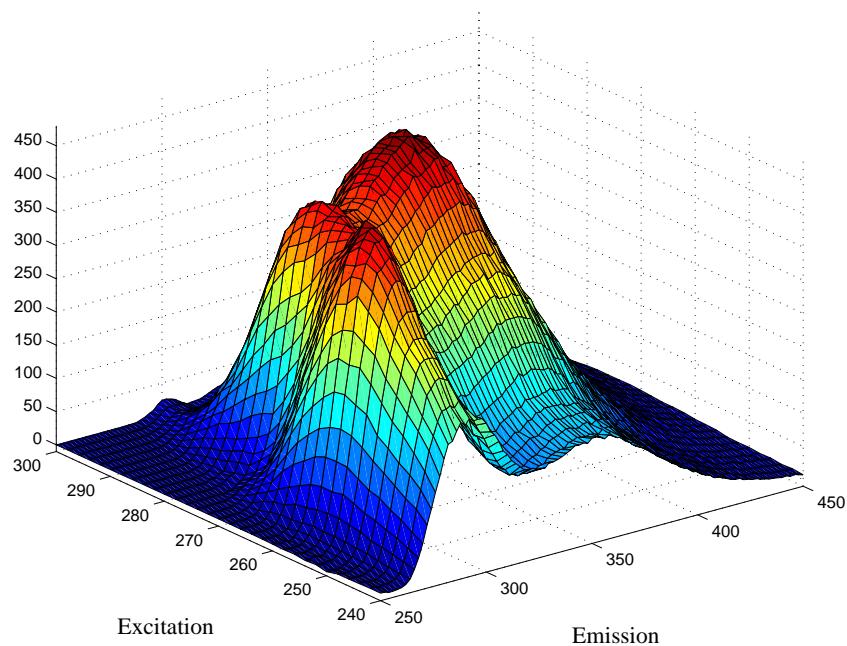
Figure 10-3. Sample 4 from amino acids data set.

A PARAFAC model of the data may be easily created with the `parafac` function as follows:

```
» load aminoacids
» model = parafac(X,3);

 Fitting PARAFAC ...
 Input: 3-way 5 x 201 x 61 array
 A 3-component model will be fitted
 Mode 1:  Unconstrained
 Mode 2:  Unconstrained
 Mode 3:  Unconstrained
 Convergence criteria:
 Relative change in fit : 1e-06
 Absolute change in fit : 1e-06
 Maximum iterations      : 10000
 Maximum time            :   1h; 0s.
 Algorithm : ALS
 No missing values
 Using fast approximation for initialization (ATLD)

    Iteration    Rel. Change       Abs. Change          sum-sq residuals
        37    0.0000009174       1.3257991418        1445117.4161680976

 Iterations terminated based on relative change in fit error
```

Note that the number of iterations required and the exact residuals may be different when executed at different times. PARAFAC is set to use random starting points in the solution for the model. The `parafac` function produces the GUI shown in the screen shot in Figure 10-4, providing an easy way to view the parameters in the PARAFAC model and a number of useful diagnostics.
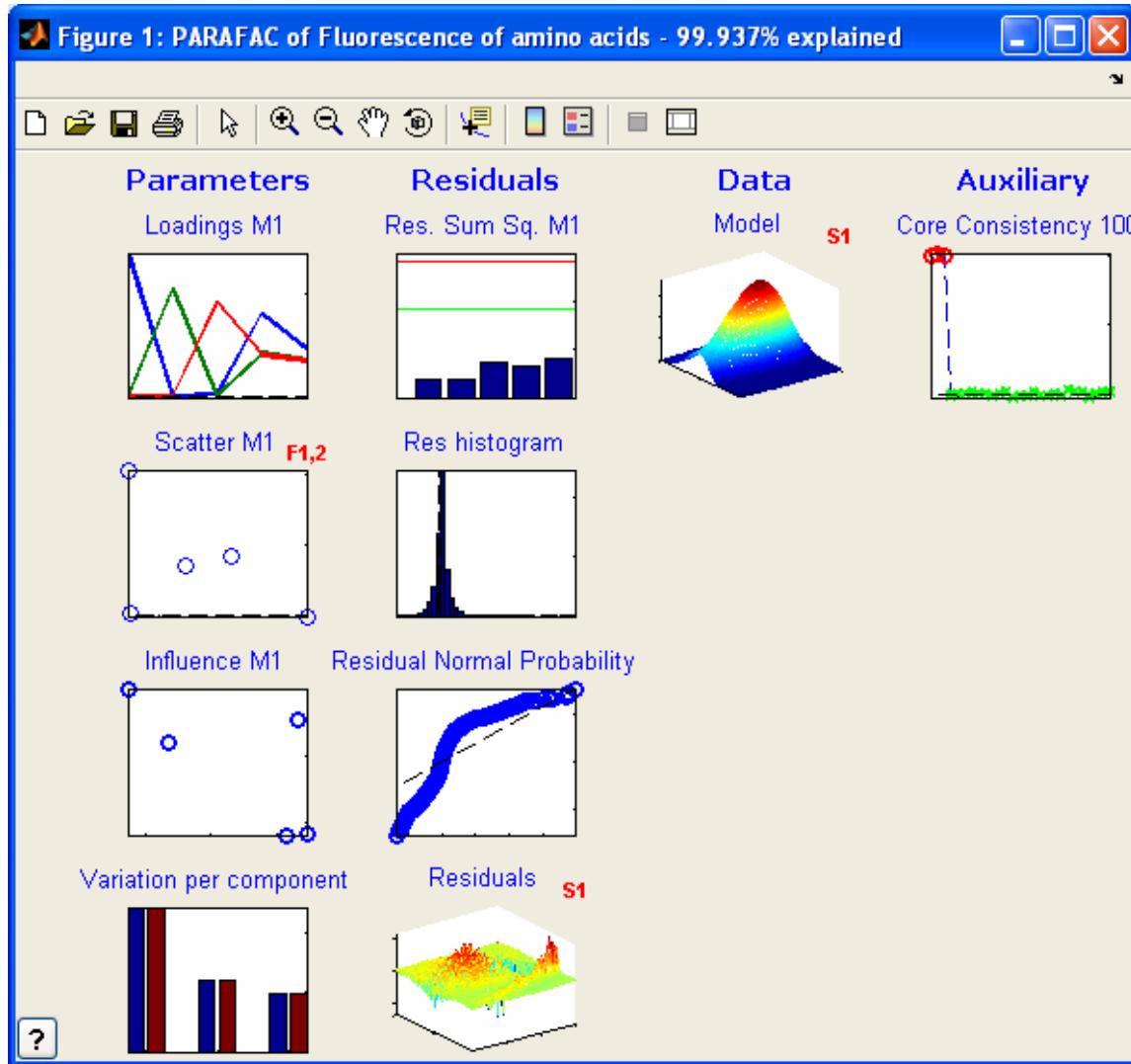
Figure 10-4. PARAFAC output.

Exploring the PARAFAC Model

A PARAFAC model may be explored using the interface shown in Figure 10-4, which is produced by the `parafac` function. The interface changes the display and produces additional information in the following ways:

- Click on the title of each plot to see a description of the plot.
- Click on the white background of the plot to change the mode plotted.
- Click on red text to change the sample or factor plotted.
- Right-click (control-click in OS-X) to spawn the figure.

As an example, the loading in each of the modes can be viewed in the upper left window. It is common to refer to contributions in all factors as loadings; the term **scores** is not typically used for PARAFAC. The initial view shows the loadings in the first mode. This view can be changed by clicking any of the axes or the white background of the figure. The figure changes to the loadings in the second mode, then in the third mode, then returns to the first mode. Scatter plots of the loadings for each factor within a mode are produced in the plot immediately below the loadings plots. For instance, the loadings of the first two factors in the first mode may be plotted against each other. The mode may be changed by clicking the axes, while the factors may be changed by clicking the red text.

Different views of the residuals are given in the second column of figures. Residuals are shown as a function of the index in each mode in the first plot. Again, the mode viewed can be changed by clicking the axes. The second residuals plot shows a histogram of all of the residuals, and their normality is evaluated in the third plot. The residuals of individual samples may be reviewed in the fourth residuals plot.

The individual samples may be viewed in the third column. The fourth column contains a diagnostic which is useful for evaluating the validity of the model: the core consistency check. This involves calculating a Tucker core using the loadings from the PARAFAC model. This Tucker core relates all possible combinations of the factors in each of the modes to each other (*e.g.,* second factor, first mode; third factor, second mode; first factor, third mode). If the model is valid, the Tucker model will produce values close to one for each of the PARAFAC factors (same factor in each mode), but values close to zero for cross factors (different factors in each mode).

Using the PARAFAC interface to review the amino acids model, we see that the model appears to be quite good. The loadings window shows that all the loadings are positive, as expected for this type of data, and the core consistency is quite good.

PLS_Toolbox contains additional tools for multi-way decompositions that are useful when the data are not as ideally trilinear as the amino acids example. For instance, PARAFAC2 may be used when one of the sample axes stretches, or when samples have different numbers of time steps. Tucker models are useful when single factors in some modes are related to two or more factors in other modes. These models are described in the sections that follow.

The Tucker3 Model

The Tucker3 model, or three-way PCA model, is one of the most basic three-way models used in chemometrics. It originates from psychometrics from the pioneering work of Ledyard Tucker (1964). The algorithmic solution for estimating the model was later

substantially improved by Kroonenberg and de Leeuw (1980) and later by ten Berge *et al.* (1987).

To explain the Tucker3 model, it is most convenient to start with a PCA model and then see how that can be extended appropriately. Given an $I \times J$ matrix $\mathbf{X}_k$, an R-component PCA model of the matrix can be written

$$\mathbf{X}_k = \mathbf{AB}^T + \mathbf{E} \qquad (10\text{-}9)$$

The matrix $\mathbf{A}$ will hold the scores (loadings in the first mode) and $\mathbf{B}$ the loadings (loadings in the second mode). If both the scores and loadings are normalized to a sum-of-squares of one, then the variance can be kept separately by introducing a diagonal matrix $\mathbf{G}$. Thus, instead of the above, we now write the model as

$$\mathbf{X}_k = \mathbf{AGB}^T + \mathbf{E} \qquad (10\text{-}10)$$

where it is noted that the actual content of $\mathbf{A}$ has changed because the norm of each column is now held in the diagonal of $\mathbf{G}$. This representation of a PCA model is similar to the truncated singular value decomposition described in Chapter 7, Introduction To Linear Algebra ; the matrix $\mathbf{G}$ corresponding to the singular value matrix is called the *core*. In order to prepare the two-way representation for the extension to higher orders, two further modifications are needed.

The first modification is to allow for off-diagonal values in $\mathbf{G}$. It is worth considering in detail the implications of such a modification. Usually, the components of a PCA model are taken in pairs: score one and loading one, score two and loading two, etc. However, allowing for off-diagonals in $\mathbf{G}$ means that the model of the data is not only given by such pairs. Also the 'interactions' of vectors have to be taken into account. For example, a two-component PCA model with diagonal $\mathbf{G}$ would read

$$\mathbf{X}_k = g_{11}\mathbf{a}_1\mathbf{b}_1^{\ T} + g_{22}\mathbf{a}_2\mathbf{b}_2^{\ T} + \mathbf{E} \qquad (10\text{-}11)$$

whereas with interactions, the corresponding model reads

$$\mathbf{X}_k = g_{11}\mathbf{a}_1\mathbf{b}_1^{\ T} + g_{22}\mathbf{a}_2\mathbf{b}_2^{\ T} + g_{12}\mathbf{a}_1\mathbf{b}_2^{\ T} + g_{21}\mathbf{a}_2\mathbf{b}_1^{\ T} + \mathbf{E} \qquad (10\text{-}12)$$

The first score vector interacts with the *second* loading vector (and vice versa) and the contribution of the interaction is given by the element g_{12}. This added flexibility does not actually provide better fit for a two-way model, but it does so when going to three- or higher-way models.

The second important modification of the PCA model is to allow for a different number of components in the two modes. Imagine that a spectral data set consists of different amounts of five different analytes, each with different spectra. However, two of the analytes covary, so that the rank of the matrix is only four. Ideally, it would be possible to model the data using four score (concentration) vectors and five loading (pure spectra) vectors, and then handle the fact that two of the analytes have the same concentrations by adjusting the core $\mathbf{G}$ accordingly. The core would then have to be of size 4×5 to allow for

the different number of components and if the first two loading columns would correspond to the first score column, then **G** could be written:

$$\mathbf{G} = \begin{vmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{vmatrix} \qquad (10\text{-}13)$$

Using four score vectors in **A** and five loadings vectors held in **B**, the model of **X** would then read:

$$\mathbf{X}_k = g_{11}\mathbf{a}_1\mathbf{b}_1^{\mathrm{T}} + g_{12}\mathbf{a}_1\mathbf{b}_2^{\mathrm{T}} + g_{23}\mathbf{a}_2\mathbf{b}_3^{\mathrm{T}} + g_{34}\mathbf{a}_3\mathbf{b}_4^{\mathrm{T}} + g_{45}\mathbf{a}_4\mathbf{b}_5^{\mathrm{T}} + \mathbf{E} \quad (10\text{-}14)$$

As can be seen, the use of a non-quadratic core makes it possible to handle different numbers of components in the different modes. As for the non-diagonal core, the introduction of a different number of components does not usually provide a better fit in two-way analysis, but makes a difference in three- or higher-way models.

The Tucker3 model is a simple extension of the above-mentioned two-way model to the three-way case. A Tucker3 model of an $I \times J \times K$ array $\underline{\mathbf{X}}$ is given by three component matrices **A**, **B** and **C** and a three-way core array $\underline{\mathbf{G}}$. Whereas a PCA model is defined by a single number of components, three such numbers have to be defined in a Tucker3 model. The numbers are called R_A, R_B, and R_C, respectively, and they define the number of columns in **A**, **B** and **C**, respectively. The core array $\underline{\mathbf{G}}$ is of size $R_A \times R_B \times R_C$ and, just as in the two-way model, each entry defines the magnitude of the corresponding set of column vectors in **A**, **B** and **C**. Using scalar notation, the model can be written

$$x_{ijk} = \sum_{r_A}^{R_A} \sum_{r_B}^{R_B} \sum_{r_C}^{R_C} g_{r_A r_B r_C} a_{i r_A} b_{j r_B} c_{k r_C} + e_{ijk} \qquad (10\text{-}15)$$

This is very similar to Equation 10-6, above. The most often used way of stating the Tucker3 model is by using matrix notation and unfolding the data:

$$\mathbf{X}^{(I \times JK)} = \mathbf{A} \mathbf{G}^{(R_A \times R_B R_C)} (\mathbf{C} \otimes \mathbf{B})^{\mathrm{T}} \qquad (10\text{-}16)$$

where $\mathbf{X}^{(I \times JK)}$ is the three-way array unfolded (matricized) into an $I \times JK$ matrix, and where the core array is rearranged similarly.

The number three in the name Tucker3 is describing that all three modes are reduced. It is possible to fit a model where only two modes are reduced which would then correspond to a Tucker2 model. If only one mode is reduced (Tucker1), the model corresponds to a normal PCA model of the data rearranged into a matrix, *i.e.*, what is typically referred to (somewhat erroneously) as a multi-way PCA (MPCA) model. If the Tucker model is applied to a four-way data set and all modes are reduced, then the appropriate name for that model would be a Tucker4 model.

290

Example of Tucker3

Nørgaard and Ridder (1994) have investigated a problem of measuring samples with three different analytes on a flow injection analysis (FIA) system where a pH-gradient is imposed. A carrier stream containing a Britton-Robinson buffer of pH 4.5 was continuously injected into the system with a flow of 0.375 mL/min. The 77 µL of sample and 770 µL of reagent (Britton-Robinson buffer pH 11.4) were injected simultaneously into the system by a six-port valve, and the absorbance was detected by a diode-array detector (HP 8452A) from 250 to 450 nm in two-nanometer intervals. The absorption spectrum was determined every second, 89 times during one injection. By the use of both a carrier and a reagent, a pH gradient is induced over the sample plug from pH 4.5 to 11.4. The three analytes present in the samples are 2-, 3-, and 4-hydroxy-benzaldehyde (HBA). All three analytes have different absorption spectra depending on whether they are in their acidic or basic form. Twelve samples of different constitution are measured as shown in Table 10-2. Thus the data set is a 12 (samples) × 100 (wavelengths) × 89 (times) array. The time mode of dimension 89 is also a pH profile due to the pH-gradient.

For each sample, a landscape is obtained showing the spectra for all times, or, conversely, the time profiles for all wavelengths. An example landscape is shown in Figure 10-5. It is characteristic of FIA that there is no physical separation of the samples. All analytes have the same dilution profile due to dispersion, *i.e.*, all analytes will have total time profiles that are the same shape.

Table 10-2. Concentrations of 2HBA, 3HBA, and 4HBA in the twelve samples.

Sample	2HBA	3HBA	4HBA
1	0.05	0.05	0.06
2	0.05	0.10	0.04
3	0.05	0.10	0.06
4	0.10	0.05	0.04
5	0.10	0.10	0.04
6	0.10	0.10	0.06
7	0.00	0.10	0.04
8	0.00	0.10	0.06
9	0.05	0.00	0.06
10	0.10	0.00	0.06
11	0.05	0.10	0.00
12	0.10	0.05	0.00
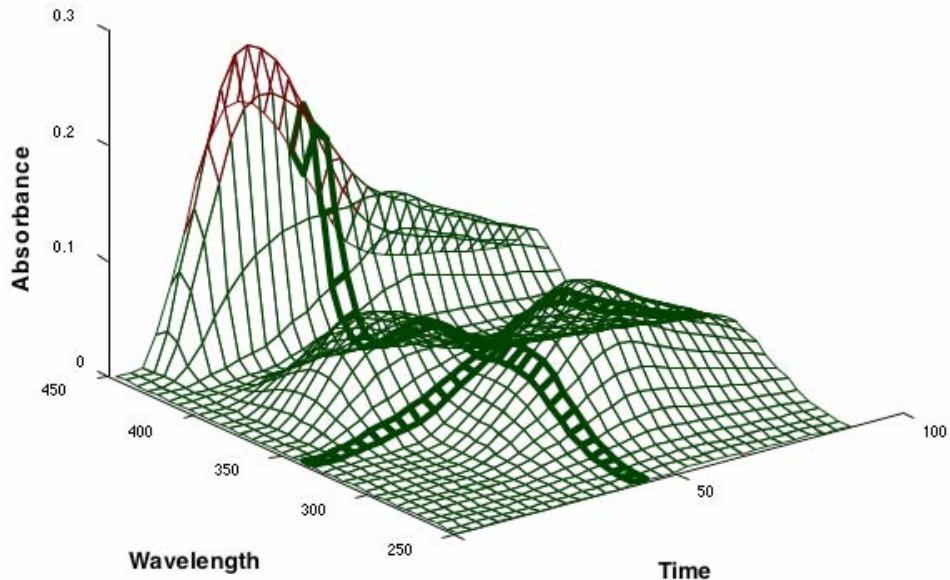
Figure 10-5. FIA landscape from HBA data.

The time-profile thus maintains its shape at all wavelengths for all samples and for all analytes. The total profile is the profile actually detected by the photometer and is the sum of the profiles of protonated and deprotonated analytes. Due to the pH gradient, and depending on the pK_a of a given analyte, the analyte will show up with different amounts of its acidic and basic form at different times, and hence will have different acidic and basic profiles in the sample plug. In the figure above these profiles are shown for one analyte. The first part of the sample plug, *i.e.*, the earliest measurements of a sample, is dominated by deprotonated analytes, while the end of the sample plug is dominated by protonated analytes.

Due to these special conditions, it is expected that the rank of the data will be different in the different modes. For example, three concentration (sample) variations are expected due to the three different analytes. As each analyte has both an acidic and a basic spectrum, we can expect six different spectral variations. Likewise, there are six profiles in the temporal mode, but, as the time-profiles have closure, these six underlying profiles will only span a four-dimensional subspace. More details on these matters can be found in Bro (1998).

To investigate the variations in the data empirically, an 8×8×8 Tucker3 model was fit.

```
» load fia;
» model=tucker(FIA,[8 8 8]);
```

Before looking into the model in detail, the core array was investigated. First the core was rotated to maximum variance in order to concentrate the variance on as few elements of the core as possible.

```
» rotatedcore = coreanal(model,'maxvar');
```

And the most significant entries of this core are listed as

```
» coreanal(rotatedcore.core,'list',30);
```

```
          ANALYSIS OF  8 x 8 x 8 CORE ARRAY
          (Comp /Value /Squared /FractionVar /SummedFraction)
```

[1, 1, 1]	-18.91	357.47	84.65%	84.65%
[1, 2, 2]	-5.88	34.59	8.19%	92.84%
[2, 3, 1]	3.78	14.31	3.39%	96.23%
[2, 4, 2]	-2.65	7.02	1.66%	97.89%
[2, 2, 1]	-1.56	2.44	0.58%	98.47%
[3, 2, 1]	1.23	1.50	0.36%	98.82%
[2, 2, 2]	-1.12	1.26	0.30%	99.12%
[2, 1, 2]	-0.91	0.83	0.20%	99.32%
[1, 4, 3]	-0.80	0.64	0.15%	99.47%
[3, 5, 1]	-0.72	0.52	0.12%	99.59%
[3, 4, 1]	-0.51	0.26	0.06%	99.65%
[3, 2, 2]	0.46	0.21	0.05%	99.70%
[2, 3, 2]	0.42	0.18	0.04%	99.74%
[3, 5, 2]	-0.42	0.18	0.04%	99.79%
[1, 3, 2]	0.34	0.12	0.03%	99.81%
[3, 6, 2]	0.34	0.12	0.03%	99.84%
[2, 2, 3]	-0.33	0.11	0.03%	99.87%
[3, 4, 2]	-0.28	0.08	0.02%	99.88%
[4, 1, 3]	-0.27	0.07	0.02%	99.90%
[1, 3, 3]	0.22	0.05	0.01%	99.91%
[1, 7, 3]	-0.18	0.03	0.01%	99.92%
[4, 1, 4]	-0.18	0.03	0.01%	99.93%
[3, 1, 2]	-0.16	0.02	0.01%	99.93%
[5, 1, 2]	-0.15	0.02	0.01%	99.94%

[2, 4, 1]	-0.14	0.02	0.00%	99.94%
[1, 6, 3]	-0.14	0.02	0.00%	99.95%
[1, 3, 4]	-0.13	0.02	0.00%	99.95%
[3, 3, 2]	0.13	0.02	0.00%	99.96%
[4, 2, 4]	0.11	0.01	0.00%	99.96%
[4, 2, 3]	0.11	0.01	0.00%	99.96%

The elements in the core are shown according to the amount of variation the corresponding component combinations explain. Looking at the first 16 most important components (highlighted in gray), it is observed that in the first sample mode, only three of the eight components appear. In the third temporal mode, only three components occur, but in the second spectral mode, six different components occur. The lack of four significant components in the temporal mode can well be explained by the fact that all underlying time-profiles are very similar, and hence difficult to distinguish. Apart from this, the model does seem to confirm the *a priori* assumptions.

Based on these results, a 3×6×3 component Tucker3 model is fitted to the data. The scores are shown in Figure 10-6 after rotating them towards the reference concentrations. As can be seen, the scores are found to be very similar to the reference concentrations.
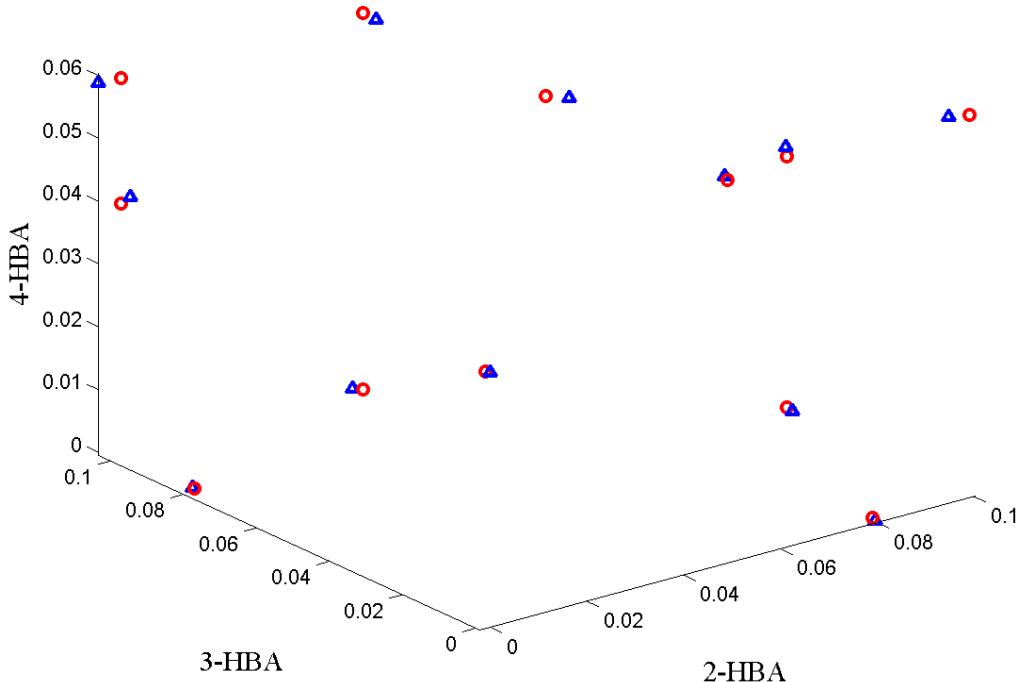
Figure 10-6. Scores (blue triangles) after rotating the 12×3 score matrix towards the matrix of reference concentrations (red circles).

PARAFAC2

A more exotic, yet very useful, model is the so-called PARAFAC2 model, developed in 1972 by R. A. Harshman (1972). A feasible algorithm was not developed before 1999 (Kiers, ten Berge and Bro, 1999). In some cases a data set—ideally trilinear—does not conform to the PARAFAC model. The reason can be sampling problems or physical artifacts. Another problem occurs when the slabs of the array are not of the same row (or column) dimension. An example could be that in a longitudinal analysis, certain subjects did not go along all the way (some persons dropped from the experiment before the analysis ended, some batches were stopped due to breakdown, etc.). It turns out that both the problem of axis shifts and varying axis dimensions can, in certain cases, be appropriately handled with the use of the PARAFAC2 model.

Consider a chromatographic data set obtained with spectral detection of some sort, very generally structured as elution time × wavelength × run/sample. In many situations such a data set will be well suited for a PARAFAC model. Fitting a PARAFAC model will give the parameters $\mathbf{A}$ ($\mathbf{a}_r$ being the elution profile or chromatogram of analyte r), $\mathbf{B}$ ($\mathbf{b}_f$ being the estimated spectrum of analyte the profile or chromatogram of analyte r), and $\mathbf{C}$ (c_{kr} being the relative concentration of analyte r in sample k). If there are shifts in retention time from run to run, the PARAFAC model can give misleading results, because the PARAFAC model assumes that the profile of each analyte ($\mathbf{a}_r$) is the same in every run. Instead of forcing the data into the PARAFAC model, it is possible to define a model that does not require the chromatographic profiles to be identical from run to run, but allows for some sort of deviation. The PARAFAC2 model is one way of doing so.

The PARAFAC model can be written

$$\mathbf{X}_k = \mathbf{A}\mathbf{D}_k\mathbf{B}^\mathrm{T}, \; k = 1, ..., K \qquad\qquad (10\text{-}17)$$

disregarding noise. For the above chromatographic data, $\mathbf{X}_k$ would be the measurements from one chromatographic run. Instead of modeling the $\mathbf{X}_k$ matrices directly, consider a model of an array consisting of the matrices $\mathbf{X}_k^\mathrm{T}\mathbf{X}_k$. Assuming first that the PARAFAC model is valid, then for the cross-product array it holds that:

$$\mathbf{X}_k\mathbf{X}_k^\mathrm{T} = (\mathbf{A}\mathbf{D}_k\mathbf{B}^\mathrm{T})^\mathrm{T}(\mathbf{A}\mathbf{D}_k\mathbf{B}^\mathrm{T}) = \mathbf{B}\mathbf{D}_k\mathbf{A}^\mathrm{T}\mathbf{A}\mathbf{D}_k\mathbf{B}^\mathrm{T} = \mathbf{B}\mathbf{D}_k\mathbf{G}\mathbf{D}_k\mathbf{B}^\mathrm{T}, \qquad (10\text{-}18)$$

$$k = 1, ..., K, \text{ and where } \mathbf{G} = \mathbf{A}^\mathrm{T}\mathbf{A}.$$

If the model $\mathbf{B}\mathbf{D}_k\mathbf{G}\mathbf{D}_k\mathbf{B}^\mathrm{T}$ is fit to the three-way array of cross-product matrices ($\mathbf{X}_k^\mathrm{T}\mathbf{X}_k$), then it is seen that 1) the individual $\mathbf{X}_k$ can have a different number of columns and 2) the matrix $\mathbf{A}$ need not be the same in every slab $\mathbf{X}_k$ as long as $\mathbf{A}^\mathrm{T}\mathbf{A}$ is the same ($\mathbf{A}$ is not estimated directly, only $\mathbf{G}$).

In the chromatographic example, the implication is that $\mathbf{B}$ (spectrum estimates) and $\mathbf{C}$ (concentration estimates) should be the same irrespective of elution time, but the chromatographic profiles need not be the same in every experiment. Only the covariance or crossproduct matrix of the profile loading matrix should be the same, in order to conform to the PARAFAC2 model. This is less restrictive than requiring that the profiles

be identical as in the PARAFAC model, but it is difficult to see directly what types of deviations from the trilinear model are then allowed. Kiers *et al.* (1999) have shown that requiring $\mathbf{G} = \mathbf{A}^T\mathbf{A}$ is equivalent to assuming the model:

$$\mathbf{X}_k = \mathbf{P}_k\mathbf{H}\mathbf{D}_k\mathbf{B}^T + \mathbf{E}_k, \ k = 1, ..., K \qquad (10\text{-}19)$$

where $\mathbf{H}$ is an $R{\times}R$ matrix, $\mathbf{D}_k$ and $\mathbf{B}$ are defined as before, and the matrix $\mathbf{P}_k$ ($I{\times}R$) is a columnwise orthonormal matrix. Thus, for every slab, $\mathbf{X}_k$, an individual set of loadings $\mathbf{A}_k = \mathbf{P}_k\mathbf{H}$ is estimated. Because these loadings are required to have the structure $\mathbf{P}_k\mathbf{H}$ it follows that for any k:

$$\mathbf{A}_k{}^T\mathbf{A}_k = (\mathbf{P}_k\mathbf{H})^T(\mathbf{P}_k\mathbf{H}) = \mathbf{H}^T\mathbf{P}_k{}^T\mathbf{P}_k\mathbf{H} = \mathbf{H}^T\mathbf{H} = \mathbf{G} \qquad (10\text{-}20)$$

because $\mathbf{P}_k{}^T\mathbf{P}_k = \mathbf{I}$. Thus, even though $\mathbf{A}_k$ differ from sample to sample, $\mathbf{A}_k{}^T\mathbf{A}_k$ is constant as long as each $\mathbf{A}_k$ can be modeled as $\mathbf{P}_k\mathbf{H}$.

The above model is called the (directly-fitted) PARAFAC2 model. For chromatographic data, the problem of shifts in retention time can be modeled by the PARAFAC2 model, if the data are measured such that a baseline is present both before and after the appearance of the peaks. Also, overlapping peaks must, at least approximately, be shifted similarly. However, even though the PARAFAC2 model cannot model the kind of deviation present in the data perfectly, using PARAFAC2 instead of merely PARAFAC can still be helpful. Typically, if the data are too complex for the PARAFAC model, using the less-restrictive PARAFAC2 will at least partly remedy the problem, yet still enable a unique approximate model of the data. And, in any case, the result from PARAFAC2 can give an indication as to whether PARAFAC is applicable, because, for trilinear data, the PARAFAC2 model should provide approximately the same results as PARAFAC. So if the results differ markedly, this is a clear indication that the added flexibility of PARAFAC2 is needed to handle the variation in the data appropriately.

An important aspect of the PARAFAC2 model is that, like PARAFAC, it is unique in certain cases. The conditions for uniqueness of the PARAFAC2 model have been much less studied than the uniqueness of the PARAFAC model. Harshman and Lundy (1996) and ten Berge and Kiers (1996) give certain results on when uniqueness can be expected.

Multilinear Partial Least Squares, N-PLS

To generalize the PLS approach to multi-way data, a general multilinear PLS (N-PLS) regression model has been developed (Bro 1996, Smilde 1997, de Jong 1998, Bro *et al.* 2001).

In the three-way version of PLS, the three-way array of independent variables is decomposed into a trilinear model similar to the PARAFAC model; however, for N-PLS, the model is not fitted in a least squares sense but seeks, in accordance with the philosophy of PLS, to describe the covariance of the dependent and the independent variables. This is achieved by simultaneously fitting a multilinear model of the dependent

variables, a (bi-) linear model of the independent variables, and a regression model relating the two decomposition models.

Unlike two-way PLS, there are only loading weights in NPLS. In two-way PLS, additional loadings are introduced to maintain orthogonal scores. However, a similar trick is not possible in multi-way modeling; therefore, the additional loadings are not introduced. This also means that, as opposed to the most common two-way PLS algorithms, NPLS models do not have orthogonal scores.

Another difference from two-way PLS is that the model of the X data is more complicated to calculate because a Tucker3-like core has to be included. This core is calculated after the scores, weights and regression coefficients are all determined and is only introduced to provide appropriate X-residuals for outlier detection and other purposes. Thus, the interpretation of the NPLS model of X is usually performed as for a PARAFAC model.

11. Variable Selection

Genetic Algorithms for Variable Selection

Genetic algorithm variable selection is a technique that helps identify a subset of the measured variables that are, for a given problem, the most useful for a precise and accurate regression model. The earlier discussion of multivariate regression describes how multiple variables can be used together to better predict a separate quantity and how the expected relationship between the measured variables can be used to identify outliers and other faults (through Q residuals and Hotelling's T^2). Many regression problems benefit from the multivariate advantages of more precise predictions and outlier detection. In some cases, however, some variables may be expensive or difficult to measure (expensive variables) and others may contain noise or interfering signal which may actually deteriorate the accuracy and/or precision of a regression model (noisy variables). In these cases, it can be advantageous to discard some variables.

Noisy variables can sometimes be identified with knowledge of the measurement technique being used. If a given sensor is known to be highly susceptible to noise and/or responds very little to the changes of interest in a system, it can often be discarded. Similarly, spectral data often include regions in which the instrumentation has very poor sensitivity and the species of interest have little to no response. These regions can often be discarded, thus improving a model. Sometimes, however, the choice of what variables to discard is not as clear.

Expensive variables pose a similar dilemma. Although many variables may be of use in a prediction, time, money, or other engineering considerations may preclude measuring all the variables originally considered for a regression model. In these cases, it is useful to identify a subset of the variables that allows sufficient prediction accuracy and precision while minimizing the number of variables to be measured.

Although there are a variety of variable selection methods, genetic algorithms (GA) provide a straightforward method based on a "survival of the fittest" approach to modeling data.

Genetic Algorithm Theory

Given an X-block of predictor data and a Y-block of values to be predicted, one can choose a random subset of variables from X and, through the use of cross-validation and any of the regression methods described earlier, determine the root-mean-square error of cross validation (RMSECV) obtained when using only that subset of variables in a regression model. Genetic algorithms use this approach iteratively to locate the variable subset (or subsets) which gives the lowest RMSECV.
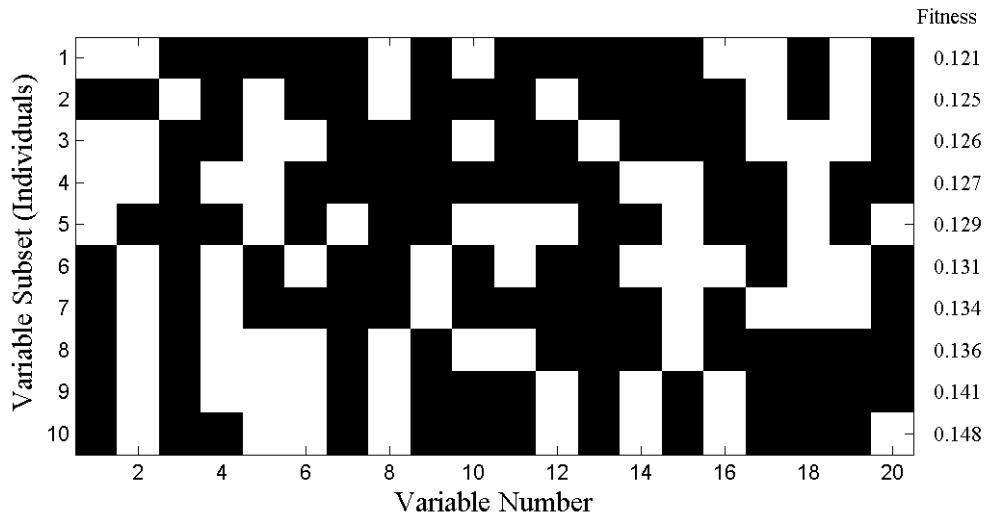
Figure 11-1. Map of selected variables for 10 of 64 individuals (white square indicates a selected variable)

The first step of the GA is to generate a large number (*e.g.*, 32, 64, 128) of random selections of the variables and calculate the RMSECV for each of the given subsets. When using factor-based regression methods (*e.g.*, PLS) the maximum number of allowed factors in a model is limited, and the RMSECV used is the lowest obtained using up to that limit.

Each subset of variables is called an *individual* and the yes/no flags indicating which variables are used by that individual is the *gene* for that individual. The pool of all tested individuals is the *population*. The RMSECV values, described as the *fitness* of the individual, indicate how predictive each individual's selection of variables is for the Y-block. Because of varying levels of noise and interference in the variables, the fitness of the different individuals in the population will extend over some range of values. Figure 11-1 shows ten out of a total of 64 variable subsets and resultant RMSECV values for the slurry-fed ceramic melter data (see Chapter 5 for a description of these data).

The RMSECV results for all of the individuals can also be examined as a function of the number of included variables. Figure 11-2 shows the results obtained from an example population for the SFCM data. Also shown is the median of all individual RMSECV fits (dotted line) and the RMSECV obtained using all the variables (dashed line). Note that at this point, many of the individuals performed worse than when all the variables were used.

The second step in the GA is selection. The individuals with fitness greater than the median fitness (*i.e.*, all models above the dotted line in Figure 11-2) are discarded. The remaining individuals used variables which, for one reason or another, provided a lower RMSECV – a better fit to the data. At this point, the population has been shrunk to half its original size. To replace the discarded individuals, the GA "breeds" the retained individuals.
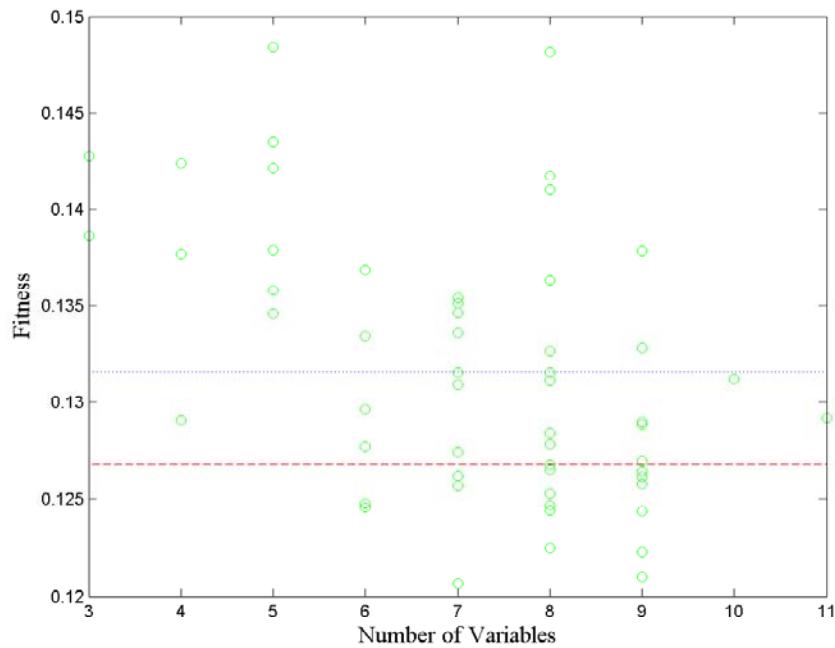
Figure 11-2. Fitness (RMSECV) versus the number of variables used by each individual.

In PLS_Toolbox, breeding is done by one of two methods: single or double cross-over. In single cross-over, the genes from two random individuals are split at some random point in the gene. The first part of the gene from individual A is swapped with the first part of the gene from individual B, and the two hybrid genes form two new individuals (C and D) for the population. This is shown schematically in Figure 11-3. Double cross-over breeding (also shown in the figure) is very similar to single cross-over except that two random points in the gene are selected and the middle portions of the two genes are swapped. The biggest practical difference is that double cross-over usually produces new individuals with less change from the original parent genes. Put in terms of selected variables, double cross-over typically creates new variable subsets which more-closely match the variables included in one parent or the other.

After adding the new individuals to the population, all the individuals' genes are given a chance for random mutation. This allows for a finite chance of adding or removing the use of variables that might be over- or under-represented in the population (See variable 13 in Figure 11-1 for an example of an underrepresented variable).
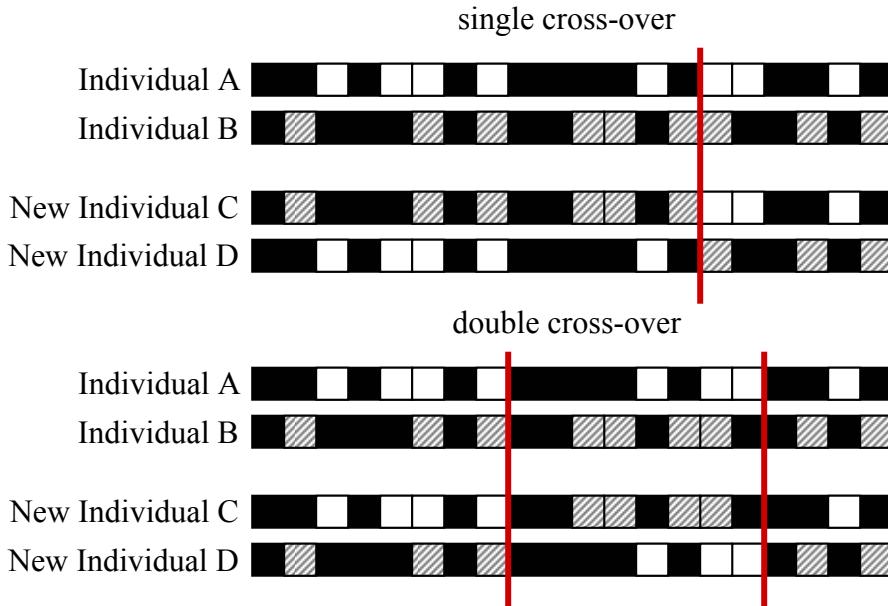
Figure 11-3. Schematic of single and double cross-over breeding.

Finally, after all the individuals have been paired and bred, the population returns to the original size and the process can continue again at the fitness evaluation step. The entire process is:

1. Generate random variable subsets
2. Evaluate each individual subset of selected variables for fitness to predict Y
3. Discard worse half of individuals
4. Breed remaining individuals
5. Allow for mutation
6. Repeat steps 2-5 until ending criteria are met

The GA will finish (a) after a finite number of iterations or (b) after some percentage of the individuals in the population are using identical variable subsets. Individuals using noisy variables will tend to be discarded; thus, the variables used by those individuals will become less represented in the overall gene population. Likewise, less noisy variables will become more and more represented. Depending on the number of variables and the rate of mutation, many of the individuals will eventually contain the same genes.

Practical GA Considerations

One of the biggest risks in GA variable selection is over-fitting. It is possible that the variables selected may be particularly good for generating a model for the given data, but may not be useful for future data. This is particularly problematic when analyzing data with smaller numbers of samples. Although the GA uses a modified version of cross-validation to help avoid this (see below), it is generally recommended that these guidelines be followed:

1. Keep the ending criteria sensitive. The more iterations which occur, the more feedback the GA will have from the cross-validation information, and thus the more likely the over-fitting,
2. Use random cross-validation and multiple iterations if practical,
3. Repeat the GA run multiple times and watch for general trends, and
4. When analyzing data with many variables and fewer samples (short-fat problems), set the window width (see below) to a larger value to use blocks of variables and keep the maximum number of latent variables low.

In PLS_Toolbox, genetic algorithm variable selection is performed using one of two functions, the **Genetic Algorithm** GUI (`genalg`), or the command-line version (`gaselectr`). If the GUI is used, data must first be loaded using the **File/Load Data** menu. If any preprocessing should be used, this can be set using the **Preprocess** menu.

In either the GUI or the command-line routine is used, various GA settings need to be specified. In the GUI, these settings are selected using graphical controls (see Figure 11-4); in the command-line interface, the settings are selected via an options structure. The following describes the settings and gives the name of the appropriate options field in parenthesis.

- **Size of Population** (`popsize`) – The larger the population size, the more time required for each iteration. Larger populations do, however, provide a better representation of different variable combinations. One alternative to using a large population size is to use multiple replicate runs (reps); this, however, does not allow for interbreeding between potentially useful gene mixtures.
- **Window Width** (`windowwidth`) – When adjacent variables contain correlated information, or the end use of the variable selection is to include or exclude adjacent variables together as a block (*e.g.*, lower-resolution measurement), the original variables can be grouped together and included or excluded in "blocks". Window width indicates how many adjacent variables should be grouped together at a time. The grouping starts with the first variable and the subsequent (windowwidth-1) variables.
- **% Initial Terms** (`initialterms`) – Specifies the approximate number of variables (terms) included in the initial variable subsets. Starting with fewer initial terms will make the identification of useful variables more difficult, but will bias the end solution towards models with fewer variables. See also **Target**.
- **Target Min/Max** (`target`) **and Penalty slope (**`penaltyslope`**)** – These settings are used together to guide the algorithm towards a solution with a given number (or percentage) of included variables. To use this feature, first set some level of penalty slope to enable the **Target Min/Max** edit boxes. Prior to discarding the unfit individuals, each individual is tested for the total number of variables used. Any individual using more variables than the Target Max or less than the Target Min will be penalized by increasing the RMSECV fitness, based on the number of variables above or below the limits times the penalty slope:

$$\text{RMSECV}' = \text{RMSECV}(1+\rho n) \qquad\qquad (11\text{-}1)$$

where ρ is the penalty slope and n is the number of variables the individual used above or below the target range. The result is that an individual with a good fit but using too many or too few variables will be more likely to be discarded, unless the fit is unusually better than that of other individuals. In the GUI, the penalty slope must first be selected, then the target range.

Target range can be specified in absolute number of variables or in percentage of total variables, based on the % checkbox to the right of the target. In the options structure, the percentage is specified using the `targetpct` field. A value of 1 (a checked checkbox in the GUI) indicates that target is specified in percent.

- **Max Generations** (`maxgenerations`) **and Percent at Convergence (**`convergence`**)** – Specify the ending criteria as described earlier. Lower settings for both will help avoid over-fitting of data. It is sometimes useful to perform many replicate runs with a lower setting for maximum generations.
- **Mutation rate** (`mutationrate`) – The higher the mutation rate, the more chance of including underrepresented variables or excluding over-represented variables.
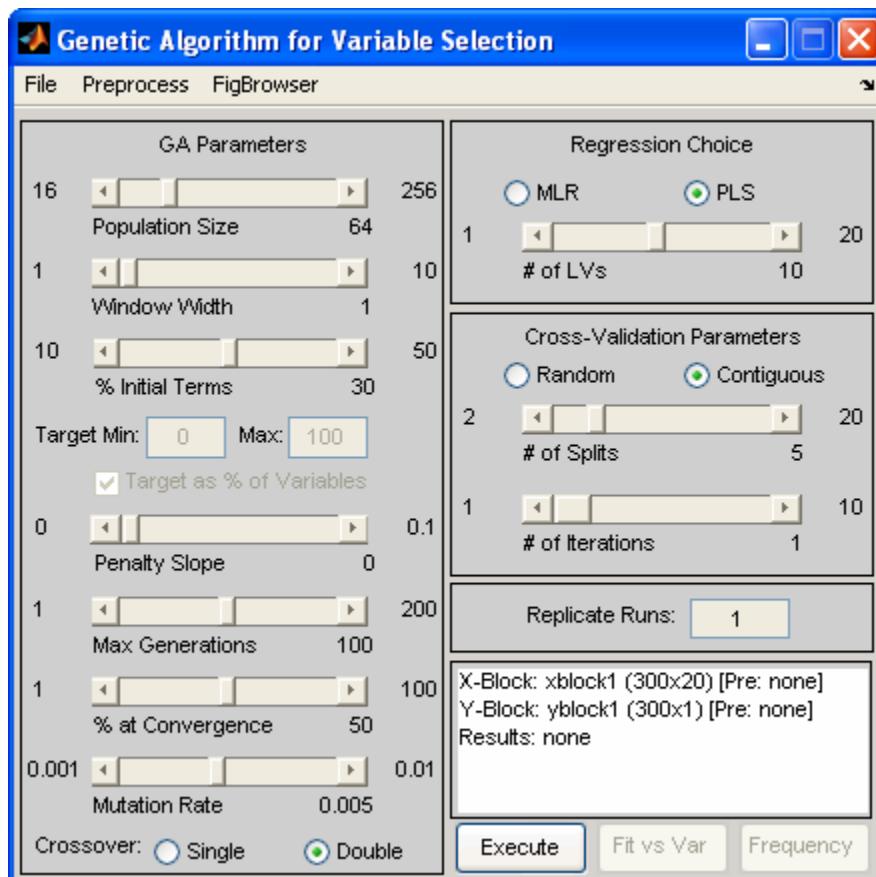
Figure 11-4. GUI interface used to specify GA settings.

- **Regression Choice** (`algorithm`) **and # of LVs** (`ncomp`) – Specifies the regression method as **MLR** (use all selected variables) or **PLS** (use latent variables derived from selected variables). The number of LVs slider (or `ncomp` option) specifies the maximum number of latent variables which can be used in a PLS model. This should generally be kept near the number of LVs necessary to accurately model the data and should be no more than absolutely necessary (to avoid overfitting).
- **Cross-Validation settings** (`cv, split, iter`) – Selects the type and number of splits and iterations to be used for cross-validation. Note that the contiguous block cross-validation used by GA is slightly modified from that used in standard cross-validation. Although the samples are still selected and left-out in contiguous blocks, the starting position of the first block shifts randomly through the data. This helps reduce the likelihood of over-fitting.
- **Replicate Runs** (`reps`) – This specifies the number of times the GA should be run using the specified conditions. The results of each cycle will be concatenated together and will appear together in the results plots, as described below.

The settings can be saved from the GUI for use as an options structure in the command-line function by selecting **File/Save Settings** and specifying a variable to which the options should be saved.

After the settings have been specified as desired, the analysis can be started in the GUI by selecting **Execute**. From the command line, executing `gaselctr` will start the analysis with the given settings: `gaselctr(x,y,options)`

Analysis of GA Results

During the analysis, a four-plot figure will be provided and the command window will display the progress of the GA run. An example is shown in Figure 11-5. The top left plot indicates the fitness vs. number of included variables for each member of the current population. The RMSECV obtained using all variables will be shown as a dashed horizontal line. If target and penalty slope are being used, the penalized fitness will be shown as red dots along with the actual fitness as the usual green circles.

The top right plot shows the trend of the average fitness (top line) and the best fitness (bottom line) with generation number. The horizontal dashed line is the RMSECV obtained using all variables. The best fitness represents how well the best model is doing. As the population begins to become more similar, the best and average fitness lines converge. If neither line is changing much, the GA has either reached a consensus of selected variables or the equivalent solutions with different selected variables.

The bottom right plot shows the change with each generation in the average number of variables used by each individual in the population. When min/max targets are not being used, this plot shows the natural trend towards some number of required variables. With min/max targeting, the plot indicates how well the target is being met, on average.

The bottom left plot indicates the total number of times each variable is used in the population. Variables which are used more are usually more useful in the regression.

Variables which show up less are less useful. Note, however, that depending on the population size, mutation rate, and total number of generations, the frequency of inclusion of any given variable may be biased. It is best to compare frequency of usage with multiple replicates or large, young populations.
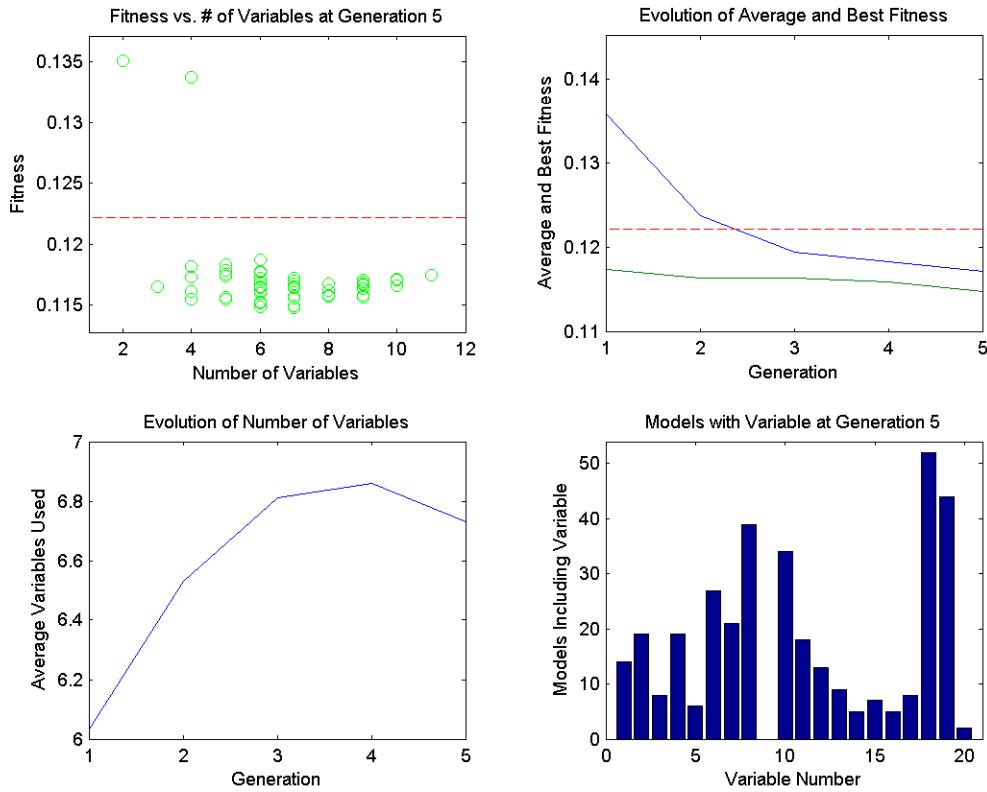
Figure 11-5. Example of diagnostic plots shown during GA run.

It is generally true that the entire set of selected variables should be considered as a whole as opposed to considering each variable as useful on its own. This is because a variable may only be helpful to prediction when used in conjunction with other variables included in an individual variable subset.

Once the analysis is done, two additional plot buttons will be available on the GUI: **Fit vs. Var** (Fitness versus Number of Variables) and **Frequency**. These two buttons return results similar to the top left and bottom right plots, respectively, in Figure 11-5. However, they include the compiled results from all replicate runs.

Fit vs. Var includes some additional information and can be used to look for trends in variable usage. Initially, you are presented with a plot of fitness of each individual versus the number of included variables. Use the mouse to select some range of the individuals (for example, if you wish to examine only models using more variables, select only these individuals from the plot). Next, a plot indicating variable usage, color coded by resulting

RMSECV, will be shown. For reference, the mean of the raw data is overlaid on the plot of included variables.

Figure 11-6 shows an example of a **Fit vs. Var** variable usage plot for the SFCM data. The variable usage plot is most useful to identify trends. If inclusion of a given variable tends to improve the RMSECV, the inclusion marks for this variable will tend to appear towards the bottom of the figure. Conversely, a variable which tends to degrade the RMSECV will tend to appear towards the top of the figure. If a variable doesn't show up at all, it is likely to be not useful and if it is used in all the models, it is probably more useful.

It is very important, however, to consider the range of RMSECVs observed through the models. In many cases, the final RMSECV values will be very similar for the individual models, and, as such, the differences in selected variables are not important. If, however, the GA run is stopped early, when a large range in RMSECV exists, more general trends can be observed. Figure 11-6, for example, shows the results of 135 models after only three generations. It can be clearly seen that variable 9 is harmful to good RMSECV while variable 11 is not useful but not harmful.
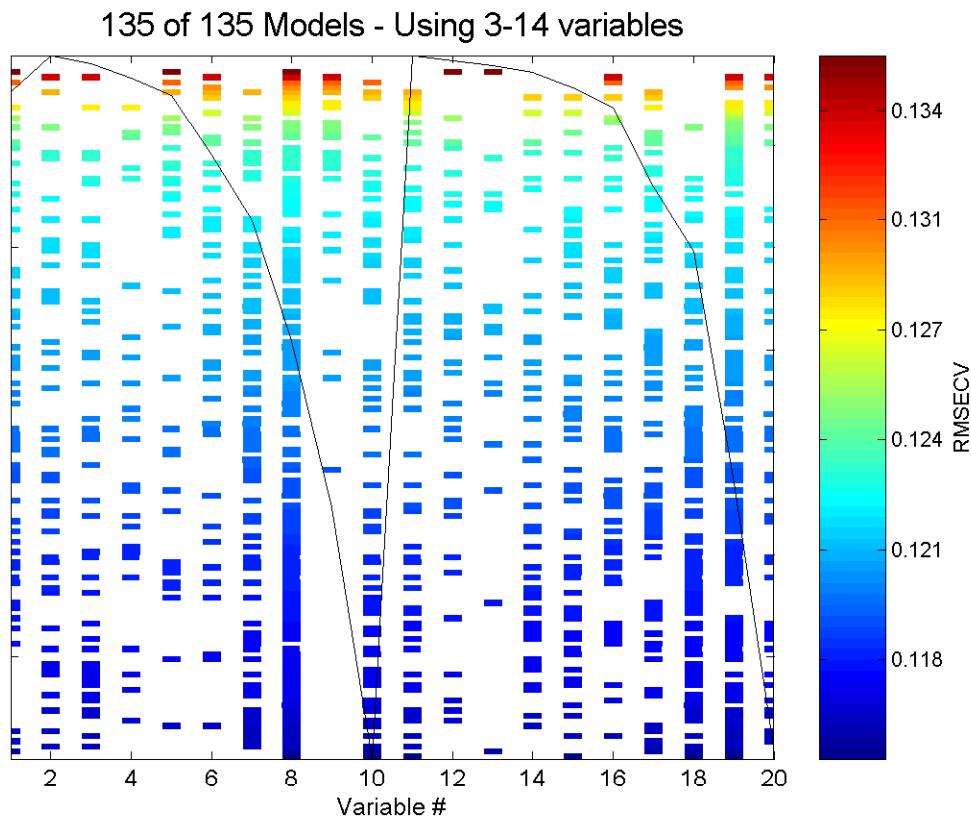
Figure 11-6. Example of Fit vs. Var plot for SFCM data.
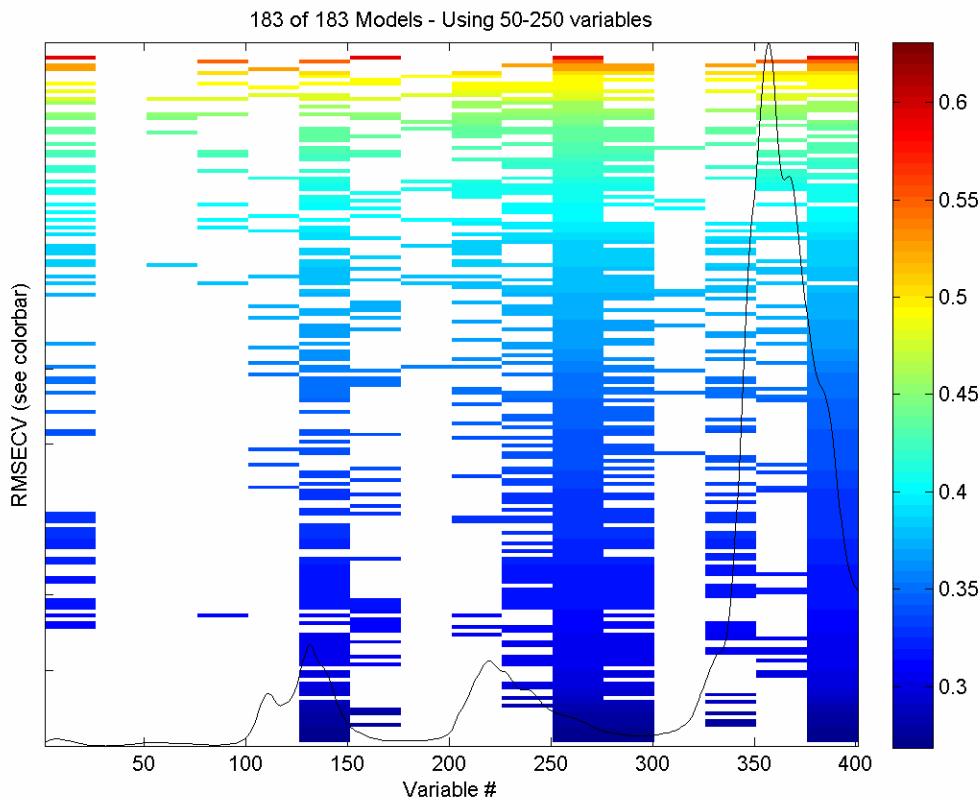
Figure 11-7. Example of Fit vs. Var plot for NIR spectra of simulated gasoline.

A second example of fit as a function of variables-used is shown in Figure 11-7. This is for prediction of the first of five components used for the gasoline simulant discussed in Chapter 6. The X-block is the spec1 dataset in the nir_data.mat file and the Y-block is the first column of the conc dataset. For this run, the window width was set to 25 variables, the maximum number of latent variables was set at five, and the analysis was repeated for a total of six replicate runs; otherwise, all other settings were at their default value.

Note that the RMSECV covers a fairly large range from just under 0.3% (absolute error in concentration as weight/weight %) to just above 0.6%, so the worst of these models are twice as bad as the best models at predicting the concentration. Nearly all models use the windows of variables centered at 138, 263, 288, and 388. Very few models, and almost none of the best models, use variables at 38, 63, 88, 138, 188, or 338. These variable windows are either not useful or are actually detrimental to the prediction of the concentration of this component. It can be seen that the selected regions fall on or near the spectral peaks of the mean spectrum, overlaid for reference on the plot.

Once a GA run is complete, the X-block data can be re-saved with only the selected variables (those used for the model with lowest RMSECV). The menu option **File/Save Best/as Dataset** will save the X-block data with the include field set to only the selected variables. To save only the selected variables as a standard array (*i.e.*, not in DataSet

308

Object format), use **File/Save Best/as Matrix**. This will save only the selected variables of the data as a simple array object. Either of these can be read into the **Analysis** GUI and used in further modeling.

The results and statistics of the GA run can also be saved as a structure by selecting **File/Save Results** and specifying a variable name. This structure contains various fields including the RMSECV for each final model in the `rmsecv` field, and the variables selected for each of those models as a binary representation (1 = selected) in the `icol` field. The first row of `icol` corresponds to the first entry in `rmsecv`.

Interval PLS (IPLS) for Variable Selection

Similar to the Genetic Algorithm (GA) described above, Interval PLS (IPLS) selects a subset of variables which will give superior prediction compared to using all the variables in a data set. Unlike the GA, IPLS does a sequential, exhaustive search for the best variable or combination of variables. Furthermore, it can be operated in "forward" mode, where intervals are successively included in the analysis, or in "reverse" mode, where intervals are successively removed from the analysis.

The "interval" in IPLS can be either a single variable or a "window" of adjacent variables (as might be used with spectroscopically-correlated or time-correlated variables, where adjacent variables are related to each other). In this discussion, we will refer to an "interval" with the understanding that this may include one ore more variables.

In forward mode, IPLS starts by creating individual PLS models, each using only one of the pre-defined variable intervals. This is similar to what is shown in Figure 11-1, except that only one of the individual intervals can be "on" at a time. If there are 100 intervals defined for a given data set, the first step calculates 100 models (one for each interval). Cross-validation is performed for each of these models and the interval which provides the lowest model root-mean-square error of cross-validation (RMSECV) is selected. This is the best single-interval model and the first selected interval, I_1.

If only one interval is desired, the algorithm can stop at this point returning the one selected interval. If, however, more than one interval is desired (to increase information available to the model and maybe, thereby, improve performance), additional cycles can be performed. In the second cycle, the first selected interval is used in all models but is combined with each of the other remaining intervals, one at a time, when creating a new set of new PLS models. Again using RMSECV, the best combination of two intervals (I_1 and one additional interval, I_2) is determined. Note that the first selected interval can not change at this point. This is repeated for as many intervals as requested (up to I_n).

Reverse mode of IPLS works in an opposite manner to forward mode. All intervals are initially included in the models, and the algorithm selects a single interval to discard. The interval which, when excluded, produced a model with the best RMSECV is selected for permanent exclusion. This is the "worst" interval, I_1. If the user has selected that more than one interval should be excluded, subsequent cycles discard the next worst intervals based on improved RMSECV when each interval is discarded.

Practical IPLS Considerations

The total number of intervals to include or drop (number of cycles to perform) depends on various factors, including but not limited to:

- The expected complexity of the system being modeled – the more complex (*e.g.,* non-linear) the data, the more intervals usually needed.

- The amount of data reduction necessary – if only a fixed number of variables can be measured in the final experiment, the number of intervals should be limited.

- The distribution of information in the variables – the more distributed the information, the more intervals needed for a good model.

One method to select the best number of intervals is to cross-validate by repeating the variable selection using different sub-sets of the data. There is no automatic implementation of this approach in PLS_Toolbox. However, the IPLS algorithm does allow one to indicate that the algorithm should continue to add (or remove) intervals until the RMSECV does not improve. This can give a rough estimate of the total number of useful intervals. If multiple runs with different sub-sets of the data are done using this feature, it can give an estimate of the likely "best" number of intervals.

Another consideration is interval "overlap". Variables in the data can be split in a number of ways.

- Intervals can each contain a single variable, thereby allowing single-variable selection.

- Intervals can contain a unique range or "window" of variables where each variable exists in only one interval.

- Intervals can contain overlapping ranges of variables where variables may be included in two or more intervals and can be included by selecting any of those intervals.

The decision on which approach to use depends on the uniqueness of information in the variables of the data and how complex their relationships are. If variables are unique in their information content, single-variable intervals may be the best approach. If adjacent variables contain correlated or complementary information, intervals which contain ranges of variables may provide improved signal-to-noise, increased speed of variable selection, and decreased chance of over-fitting (that is, selecting variables which work well on the calibration data but not necessarily on any data for the given system).

In contrast, although allowing overlapping intervals may seem as though it provides the advantages of increased signal-to-noise and modeling complexity, it may also lead to over-fitting. The difference between two adjacent windows becomes only the variables on the edges of the windows (those which are dropped or added by selecting the

310

neighboring intervals.) In addition, overlapping windows can increase the analysis time considerably.

One general caveat to IPLS variable selection should be carefully considered. It is possible that, given *n* different intervals, the best "single interval" model would be obtained by selecting a given interval (interval 10, for example). The best "two interval" model, however, might actually be obtained by selecting two different intervals (5 and 6, for example). Because of the step-wise approach to this IPLS algorithm, once the single-best interval is selected, it is required to be included in all additional models. As a result, the two-interval model might include intervals 5 and 10 (because 10 was selected first), even though 5 and 6 would provide a better RMSECV. This type of situation is most likely to arise when data are complex and require a significant number of factors for modeling. In these situations, using larger interval "windows" and requiring the addition of additional intervals (cycles) should be used. Additionally, the GA method of variable selection may provide superior results.

Using the IPLS Function

The PLS_Toolbox `ipls` function takes as input the X- and Y-block data to be analyzed, the size of the interval windows (1 = one variable per interval), the maximum number of latent variables to use in any model, and an options structure. The options structure allows selection of additional features including:

- `mode` : defines forward or reverse analysis mode.

- `numintervals` : defines the total number of intervals which should be selected. A value of `inf` tells IPLS to continue selecting until the RMSECV does not improve.

- `stepsize` : defines the number of variables between the center of each window. By default, this is empty, specifying that windows should abut each other but not overlap (*i.e.*, `stepsize` is equal to the window size).

- `mustuse` : indices of variables which must be used in all models, whether or not they are included in the "selected" intervals.

- `preprocessing` : defines the preprocessing to be performed on each data subset (for more information, see the `preprocess` function).

- `cvi` : cross-validation settings to use (for more information, see the `cvi` input to the `crossval` function).

Demonstration of the `ipls` function can be done through the analysis of the slurry-fed ceramic melter (SFCM) thermocouple data previously discussed in Chapter 5. Briefly, these data consist of measurements from twenty thermocouples at various depths in a tank of melted ceramic material. As the level of the material rises and falls, the different

thermocouples experience different temperatures. One can use IPLS to consider which thermocouple or thermocouples are the most useful in determining the level of material.

To do this, `ipls` is called with the SFCM data and inputs to set the maximum number of latent variables, interval width, and preprocessing options (autoscaling, in this case):

```
» load pls_data
» options = ipls('options');
» options.preprocessing = {'autoscale' 'autoscale'};
» int_width = 1;  %one variable per interval
» maxlv = 5;       %up to 5 latent variables allowed
» sel   = ipls(xblock1,yblock1,int_width,maxlv,options);
```

The result is the plot shown in Figure 11-8.
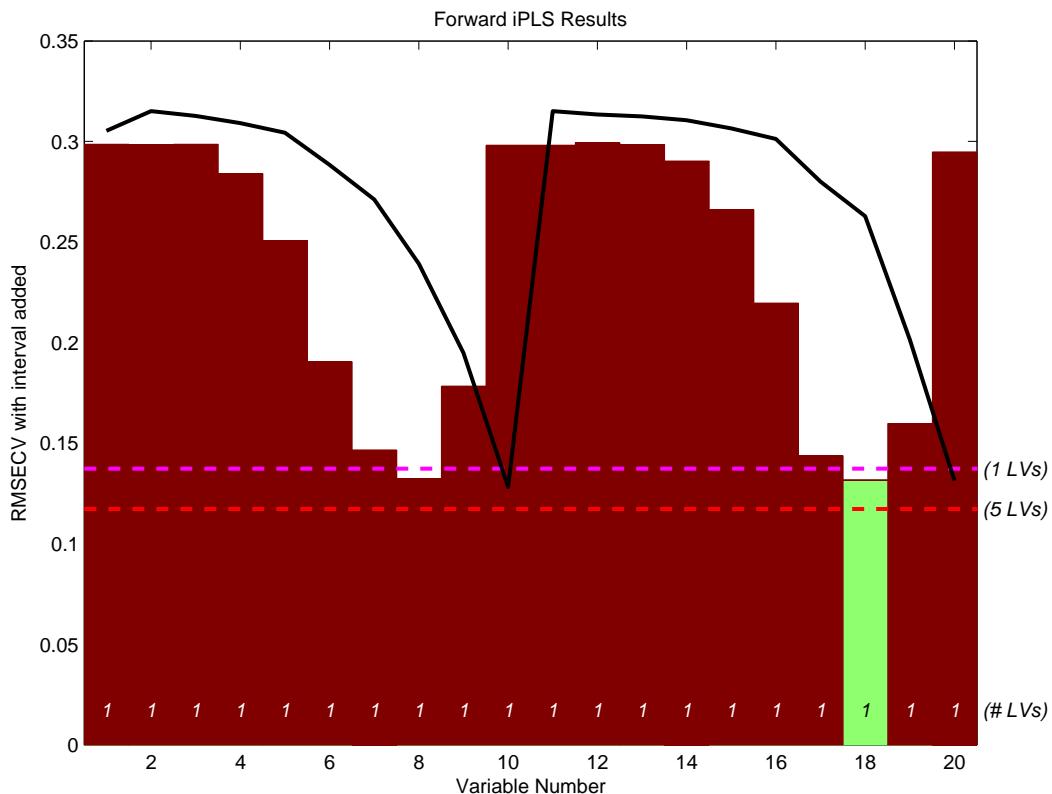
Figure 11-8. First selected interval for SFCM data.

The figure shows the RMSECV obtained for each interval (with the average sample superimposed as a black line). The numerical values inside the axes along the bottom (just above the variable number) indicate the number of latent variables (LVs) used to obtain the given RMSECV. Because each interval contains only a single variable, only 1 LV can be calculated in all cases. The green interval (variable 18) is the selected interval. The horizontal dashed lines indicate the RMSECV obtained when using all variables and

312

1 or 5 LVs. Note that interval 18 on its own gave a slightly better one-LV model than did the model using all twenty variables. However, a five-LV model using all variables still did better than any individual interval.

The commands below repeat this analysis but request that two intervals be selected instead of one. The plot shown in Figure 11-9 is the result.

```
» options.numintervals = 2;
» sel = ipls(xblock1,yblock1,int_width,maxlv,options);
```
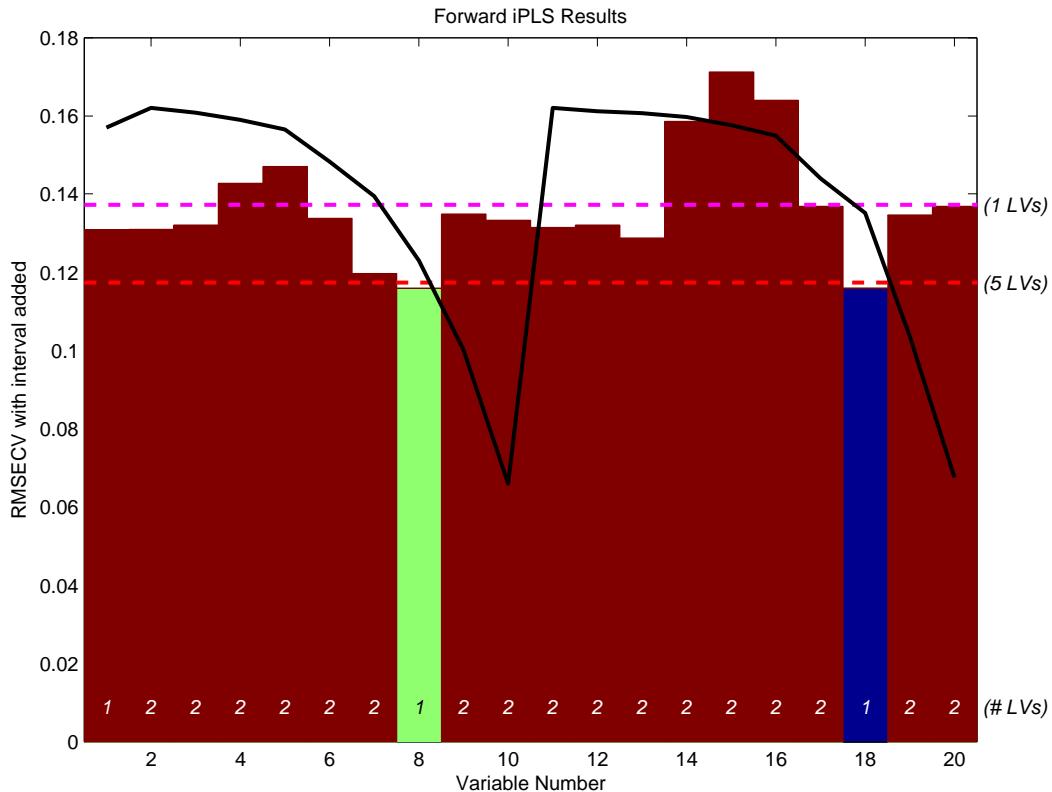

Figure 11-9. First two selected intervals for SFCM data.

The figure shows the results at the end of all interval selections. The final selected n^{th} interval is shown in green. Intervals selected in the first n-1 steps of the algorithm are shown in blue. Because this analysis included only two intervals being selected, there is only one interval shown in blue (the first selected interval) and the second selected interval is shown in green. The height shown for the selected intervals (blue and green) is equal to the RMSECV for the final model. In this case, the final model with two selected intervals used only one latent variable (as indicated at the bottom of the bars) and gave an RMSECV which was slightly better than the RMSECV obtained using five latent variables and all intervals (dashed red line). Interestingly, the variables selected (numbers 8 and 18) are duplicate measurements at the same depth in the tank. This is a good

indication that the given depth is a good place to measure, should only a single thermocouple be used.

The final example for IPLS shows the reverse analysis of the gasoline samples discussed in Chapter 6. In this case, the Y-block being predicted is the concentration of one of five components in these simulated gasoline mixtures and the X-block is the near-IR spectra measured for each sample. The reverse IPLS analysis indicates the effect on the RMSECV when each interval is discarded, and therefore the best interval(s) to discard. In this case, IPLS will be run with the maxintervals option set to infinity to trigger the "automatic" mode. The ipls function will continue to remove intervals until removing an interval would cause the RMSECV to increase. The MATLAB commands are shown below; the resulting plot is shown in Figure 11-10.

```
» load nir_data
» options = ipls('options');
» options.preprocessing = {'autoscale' 'autoscale'};
» options.numintervals = inf;
» ipls(spec1,conc(:,1),25,5,options);
```
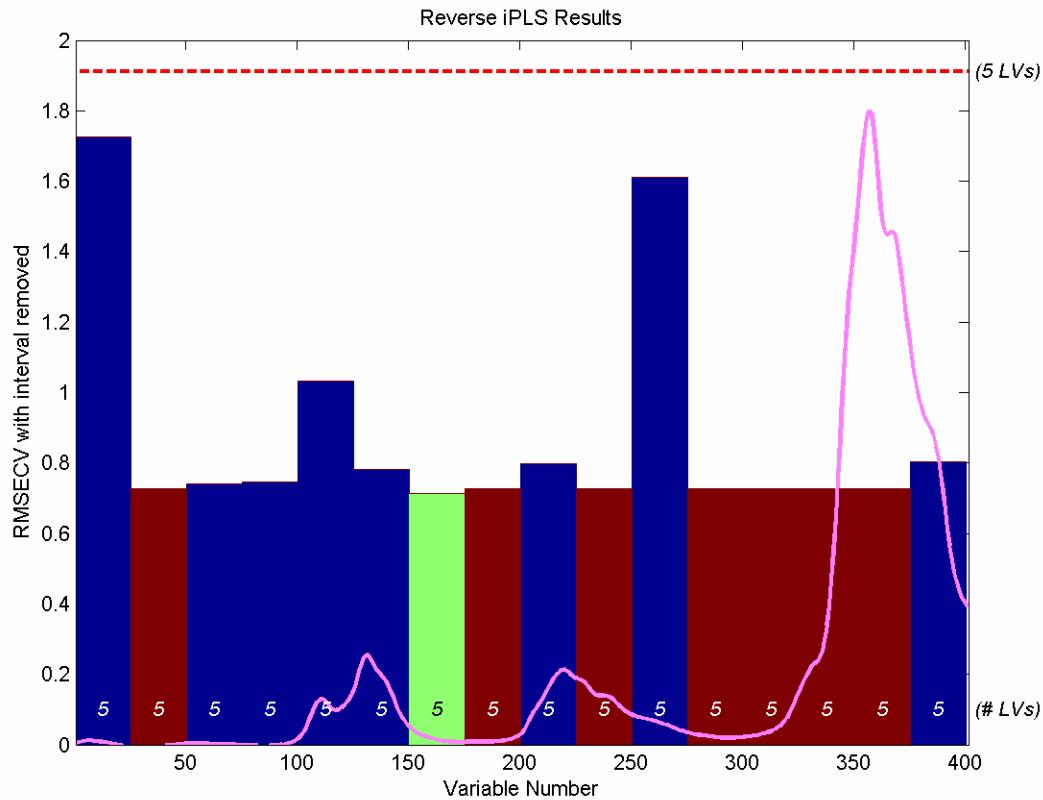

Figure 11-10. Reverse IPLS analysis for simulated gasoline samples.

A total of eight intervals were discarded before it was determined that removing any additional intervals would cause an increase in RMSECV. Intervals marked in red on the reverse IPLS results plot are those that were discarded in the first seven cycles. The

314

interval marked in green was the last discarded interval. The blue intervals are those that were retained. Each bar indicates the RMSECV which would have resulted, had the given interval been discarded. It can be seen that the intervals centered at 38, 113, and 263 are all critical for a good model (discarding these intervals would result in a significant increase in RMSECV.) It can also be seen that intervals at 63 and 88 were likely candidates for exclusion in the last cycle as the RMSECV change would have been nearly negligible.

It is interesting to compare the IPLS results on the gasoline simulant shown in Figure 11-10 to those from the GA run on the same data, shown in Figure 11-7. Note that, with a few exceptions, the same regions are discarded in each case. The biggest discrepancy is the inclusion of the interval centered at variable 113. This interval was under-represented in the GA models, but appears to be highly important to the model formed with IPLS-based selection. The difference is likely due to IPLS having excluded some region in an earlier cycle which left the 113-centered interval as the only source of some information. In contrast, the GA models discovered that a different combination of intervals could achieve a better RMSECV by discarding interval 113 and retaining a different interval. Note, incidentally, that the final model created by IPLS selection returns an RMSECV of around 0.71. This is in contrast with the GA result of 0.27 for the same data.

Conclusions

In general it should be remembered that, although variable selection may improve the error of prediction of a model, it can also inadvertently throw away useful redundancy in a model. Using a fewer number of variables to make a prediction means that each variable has a larger influence on the final prediction. If any of those variables becomes corrupt, there are fewer other variables to use in its place. Likewise, it is harder to detect a failure. If you keep only as many measured variables as you have latent variables in a model, you cannot calculate Q residuals, and the ability to detect outliers is virtually eliminated (except by considering T^2 values). As such, the needs of the final model should always be carefully considered when doing variable selection.

12. Instrument Standardization

Once a calibration for a process analytical instrument has been developed, it would be convenient if it could be transferred to other similar instruments. This would eliminate the need to run a large number of calibration samples and to develop a completely new calibration model. Direct transfer of calibrations is not usually satisfactory, however, because instruments are never identical. It also happens that instruments tend to drift, which changes their characteristics after some time. Instrument standardization methods were developed in order to deal with these similar problems.

This problem has been addressed in several different ways by various researchers, but the methods generally fall into two classes: 1) techniques that attempt to predict the response of the standard instrument based on the response of the subject instrument, *i.e.*, map the response of one instrument into another, and 2) techniques that eliminate the differences between instruments, leaving only the parts they have in common. In the first case, there is usually a single calibration model, developed on the standard instrument, through which data from both instruments are processed. In the second case, a model is generally developed using transformed data from both instruments.
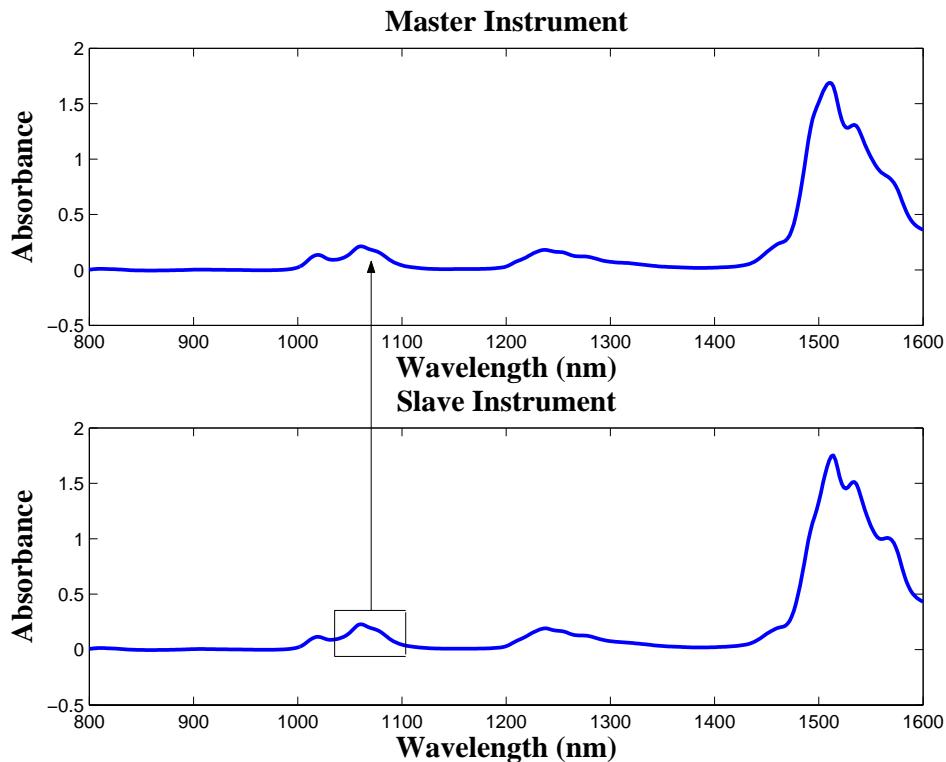
Figure 12-1. Relationship between spectra on different instruments in PDS.

The Piece-wise Direct Standardization (PDS) method (Wang *et al.,* 1991, 1992, 1994) is of the first type, and is perhaps the most successful calibration transfer technique. It works by forming "local" linear models that relate the response of the instrument to be standardized over a range of frequencies to the response of the standard instrument at a single frequency. This is shown schematically in Figure 12-1. This is in contrast to Direct

Standardization, (DS), which uses the entire spectrum. Additional techniques of the second type include Orthogonal Signal Correction (OSC) and Generalized Least Squares Weighting (GLSW).

Usually, standardization transforms are developed using a small number of samples that are run on both instruments (or a single instrument at two different times). These samples are then used to develop either a transform that maps the response of one instrument into another, or a model that eliminates differences.

Sample Subset Selection

The first step in developing a standardization transform is to select samples that will be measured on both machines. These can be samples used to form a calibration model or other samples designed to exercise the instrument in the spectral region of interest. A convenient method for choosing samples is based upon their multivariate leverage, which is a measure of their uniqueness in the calibration set. This is a simple procedure which starts by selecting the sample with the greatest deviation from the multivariate mean of the calibration samples. All other samples are then orthogonalized with respect to the first sample and the procedure is repeated. Given a calibration set from Instrument 1, $\overline{\mathbf{R}}_1$ (n samples by m wavelengths), that has been mean-centered, calculate the leverage matrix $\mathbf{H}$ as:

$$\mathbf{H} = \overline{\mathbf{R}}_1 \overline{\mathbf{R}}_1^T \tag{12-1}$$

Note that $\mathbf{H}$ is n by n. The diagonal elements of $\mathbf{H}$ are the leverages of the samples, *i.e.*, h_{ii} is the leverage of the ith sample. Select the sample with the highest leverage, $\mathbf{r}_{max}$. Set the elements of this spectrum equal to zero, then orthogonalize each remaining spectrum $\mathbf{r}_i$ in the data set by performing

$$\mathbf{r}_{io} = \mathbf{r}_i - \mathbf{r}_{max} ((\mathbf{r}_{max} \mathbf{r}_i^T)/(\mathbf{r}_{max} \mathbf{r}_{max}^T)) \tag{12-2}$$

for each spectrum where $\mathbf{r}_{io}$ is the orthogonalized $\mathbf{r}_i$. Note that this procedure subtracts from $\mathbf{r}_i$ the portion of $\mathbf{r}_{max}$ that projects onto it. This procedure is then repeated as in Equation 12-2, using the orthogonalized spectra in place of $\overline{\mathbf{R}}_1$. It is often better to select samples for calibration transfer utilizing the calibration model inverse $\overline{\mathbf{R}}_1^+$, *i.e.*, the PLS or PCR approximation to the inverse (see Equations 6-7 and 6-20), in the formation of the $\mathbf{H}$ matrix:

$$\mathbf{H} = \overline{\mathbf{R}}_1 \overline{\mathbf{R}}_1^+ \tag{12-3}$$

The diagonal elements of $\mathbf{H}$ are then the leverages of the samples with respect to their influence on the calibration model. The orthogonalization procedure above is then used to select the samples. This procedure emphasizes samples with a large influence on the calibration model, as opposed to the procedure above, which emphasizes samples that are far from the multivariate mean without regard to their direct influence on the model. As a

result, the procedure based on the model inverse tends to select samples that exercise the portions of the spectrum upon which the model most depends.

In some applications as few as three spectra are sufficient for building a transfer function between instruments; however, additional samples can be beneficial. Once the transfer samples are identified based on the leverage of their spectra, the samples must be measured on both spectrometers and the calculation of the standardization can commence.

The NIR spectra of the simulated gasoline samples contained in `nir_data.mat` can be used to demonstrate the development of a standardization transform. The file contains NIR spectra of the same thirty samples measured on two different instruments. We can now select five samples from the spectra based on leverage as follows:

```
» load nir_data
» [specsub,specnos] = stdsslct(spec1.data,5);
```

The following samples are selected in order: 22, 15, 26, 25, and 1. These are the samples that are unique. Hopefully, they will also be useful for describing the difference between the two instruments. Alternatively, a PLS model could be developed for the first analyte from the NIR data, then a subset could be selected with respect to this model inverse as shown below. First a default preprocessing structure would be generated and inserted into a `pls` options structure. The model could be then be generated, the inverse formed, and the spectra selected as follows:

```
» s = preprocess('default','mean center');
» opts = pls('options');
» opts.preprocessing = {s,s};
» mod = pls(spec1.data,conc(:,1),5,opts);
» rinv = rinverse(mod);
» [specsub,specnos] = stdsslct(spec1.data,5,rinv);
```

This procedure selects the samples 1, 20, 7, 21 and 27. Note, however, that the model inverse calculated above was based on only the first analyte out of the five analytes in the data set.

Development of the Standardization Transform

It is assumed that the calibration model is formulated as

$$\mathbf{y} = \mathbf{R}_1\boldsymbol{\beta} + \mathbf{1}b_1 \qquad (12\text{-}4)$$

where $\mathbf{y}$ is the concentration vector of the analyte of interest, $\mathbf{R}_1$ is the response matrix, $\boldsymbol{\beta}$ is the regression vector, $\mathbf{b}_1$ is the constant offset of the model and $\mathbf{1}$ is an m by 1 vector of ones, where m is the number of samples. After mean-centering:

$$\overline{\mathbf{y}} = \overline{\mathbf{R}}_1\boldsymbol{\beta} \qquad (12\text{-}5)$$

where $\overline{\mathbf{y}}$ and $\overline{\mathbf{R}}_1$ are the mean-centered $\mathbf{y}$ and $\mathbf{R}_1$, respectively. The relationship between the instruments is then modeled as:

$$\mathbf{S}_1 = \mathbf{S}_2\mathbf{F}_b + \mathbf{1}\mathbf{b}_s{}^T \tag{12-6}$$

where $\mathbf{S}_1$ is the response of Instrument 1 to the p transfer samples, $\mathbf{S}_2$ is the response of Instrument 2 (or Instrument 1 at a later time), $\mathbf{F}_b$ is the transformation matrix, $\mathbf{b}_s$ is the background correction which accommodates the additive background difference between the instruments, and $\mathbf{1}$ is a p by 1 vector of ones, where p is the number of transfer samples (rows) in $\mathbf{S}_1$ and $\mathbf{S}_2$. Note that it is assumed at this point that $\mathbf{S}_1$ and $\mathbf{S}_2$ are *not* mean-centered.

The transfer function matrix, $\mathbf{F}_b$, is then calculated to satisfy:

$$\overline{\mathbf{S}}_1 = \overline{\mathbf{S}}_2\mathbf{F}_b \tag{12-7}$$

where $\overline{\mathbf{S}}_1$ and $\overline{\mathbf{S}}_2$ are the mean-centered $\mathbf{S}_1$ and $\mathbf{S}_2$. As noted previously, $\mathbf{F}_b$ can be calculated several ways, one of which is the PDS method as described above. In PDS, $\mathbf{F}_b$ has the diagonal structure shown in Figure 12-2, where each local model (generally determined from PLS or PCR) relates the response of a number of channels of Instrument 2 to a single channel on Instrument 1. One such model is shown in bold in the figure.
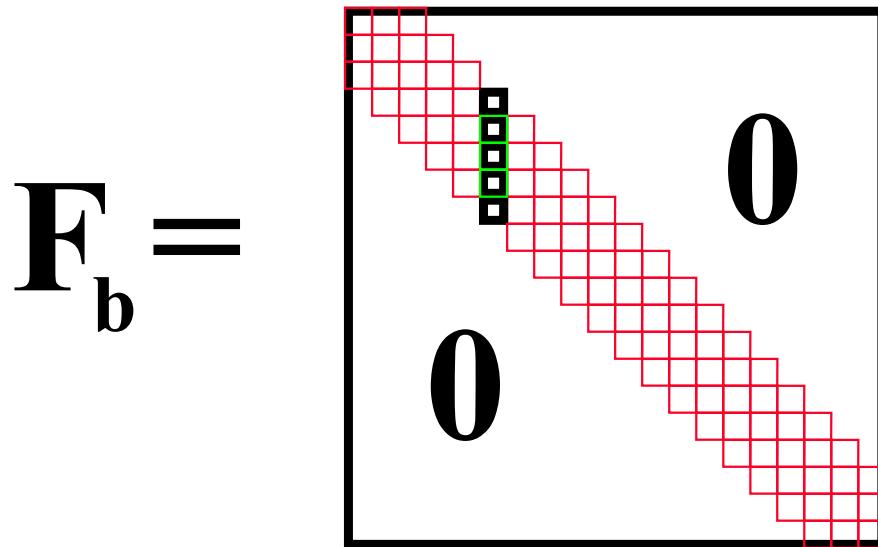
Figure 12-2. Structure of the PDS transformation matrix $\mathbf{F}_b$.

The PDS standardization matrix and additive background correction can be calculated with the PLS_Toolbox function 'stdgen'. Here we will use the subset selected by 'stdsslect' above to form the transform and use a window that is five channels wide:

```
»[stdmp,stdvp] = stdgen(spec1.data(specnos,:),spec2.data(specnos,:),5);
```

Another method, Direct Standardization (Wang *et al.,* 1994), uses

$$\mathbf{F}_b = \overline{\mathbf{S}}_2^+ \overline{\mathbf{S}}_1 \qquad (12\text{-}8)$$

where $\overline{\mathbf{S}}_2^+$ is the pseudoinverse of $\overline{\mathbf{S}}_2$. This is formed through use of the SVD as follows. Take

$$\overline{\mathbf{S}}_2 = \mathbf{U}\,\mathbf{S}\,\mathbf{V}^T \qquad (12\text{-}9)$$

then

$$\overline{\mathbf{S}}_2^+ = \mathbf{U}\,\mathbf{S}^{-1}\,\mathbf{V}^T \qquad (12\text{-}10)$$

where $\mathbf{S}^{-1}$ is $\mathbf{S}$ with all of the non-zero singular values replaced by their reciprocals.

The additive background term, $\mathbf{b}_s$, is calculated as

$$\mathbf{b}_s = \mathbf{s}_{1m} - \mathbf{F}_b^T \mathbf{s}_{2m} \qquad (12\text{-}11)$$

where $\mathbf{s}_{1m}$ and $\mathbf{s}_{2m}$ are the are the mean vectors of $\mathbf{S}_1$ and $\mathbf{S}_2$ respectively.

The DS standardization matrix and additive background correction are calculated with the same function, 'stdgen', by simply changing the argument of the window width to 0:

```
»[stdmd,stdvd] = stdgen(spec1.data(specnos,:),spec2.data(specnos,:),0);
```

Prediction using Standardized Spectra

After calibration and formation of the standardization transform, the concentration estimate for any spectrum, $\mathbf{r}_{2un}$, measured on Instrument 2 can be obtained using the calibration model developed on Instrument 1 as

$$\mathbf{y}_{2un} = (\mathbf{r}_{2un}\,\mathbf{F}_b + \mathbf{b}_s^T)\beta + b_1 \qquad (12\text{-}12)$$

where b_1 is defined from Equation 12-4. In MATLAB, the spectra from Instrument 2 can be standardized for both of the standardization models as follows:

```
» cspec2p = stdize(spec2.data,stdmp,stdvp);
» cspec2d = stdize(spec2.data,stdmd,stdvd);
```

The spectra are now ready for use with the models developed on the spectra from the first instrument.

Figure 12-3 shows the improvement in the root-mean-square difference between the instruments before and after the standardization. As you can see, there is a considerable

improvement in the difference of the responses. Although there appears to be little difference between the direct and piece-wise direct standardized spectra, in practice the PDS method produces somewhat better results when the spectra are used for prediction, because the PDS method does not "overfit" the spectra as much as the direct method.

A full demonstration of instrument standardization methods is contained in the demo `stddemo`. This demo uses the NIR data to develop standardization and calibration models and compare the methods.
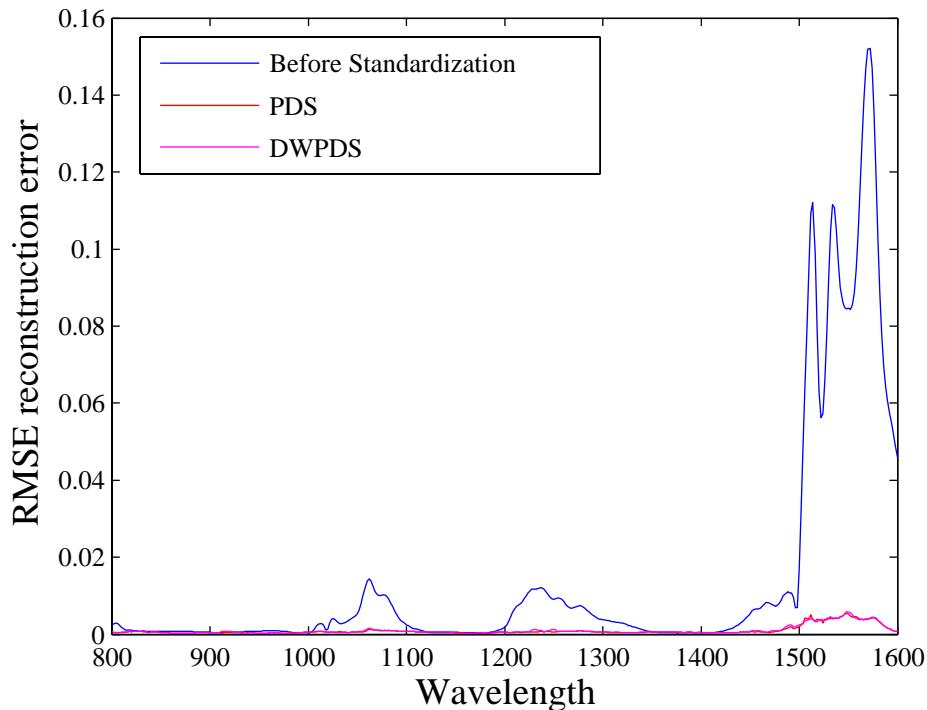
Figure 12-3. Mean difference between NIR spectra before and after standardization.

Non-Square Systems

In the example above, both of the instruments considered were very similar; they both measured the spectra of the samples at 401 points between 800 and 1600 nanometers. What if the instruments had a different number of channels in that range? The function `stdgen` will generate standardization transforms for non-square systems, and was developed for just such a case. The form of the model is very similar to that of PDS except the **F** matrix is not square; rather, it is the number of channels on the instrument to be standardized by the number of channels on the standard instrument.

Double Window PDS

Another potential issue in standardization involves the use of high resolution spectra such as FTIR spectra of gas phase samples. In these cases, the spectral features are very narrow with regions of only baseline noise in between. Models developed with PDS in

322

such a case are fine where there are features in the transfer spectra but not very good in between. Double window PDS addresses this problem by forming models based on data on both sides of the current window to be standardized. The second window defines the range of data outside the original window to be used. The form of the model is identical to that of PDS; only the way in which the model is identified is different. For instance, let the transfer spectra from the standard instrument be $\mathbf{R}_1$, and the spectra from the instrument to be standardized be $\mathbf{R}_2$. In PDS with a window width (model length) of $2j+1$, the model for the ith channel $\mathbf{b}_i$ is identified by

$$\mathbf{b}_i = \mathbf{R}_2(:,i\text{-}j:i+j)^+\mathbf{R}_1(:,i) \qquad (12\text{-}13)$$

where we have used MATLAB notation to indicate which columns of $\mathbf{R}_1$ and $\mathbf{R}_2$ are used in the formation of the model $\mathbf{b}_i$. The superscript $^+$ indicates a pseudoinverse. In double window PDS, with a first window width (model length) of $2j+1$ and a second window width (identification width) of $2k+1$, the model for the ith channel $\mathbf{b}_i$ is

$$\mathbf{b}_i = \mathbf{R}_{2DW}{}^+ \mathbf{R}_{1DW} \qquad (12\text{-}14)$$

where

$$\mathbf{R}_{2DW} = \begin{bmatrix} \mathbf{R}_2(:,i\text{-}j\text{-}k:i+j\text{-}k) \\ \mathbf{R}_2(:,i\text{-}j\text{-}k+1:i+j\text{-}k+1) \\ \mathbf{R}_2(:,i\text{-}j\text{-}k+2:i+j\text{-}k+2) \\ \\ ... \\ \\ \mathbf{R}_2(:,i\text{-}j:i+j) \\ \\ ... \\ \\ \mathbf{R}_2(:,i\text{-}j+k:i+j+k) \end{bmatrix}$$

and

$$\mathbf{R}_{1DW} = \begin{bmatrix} \mathbf{R}_1(:,i\text{-}k) \\ \mathbf{R}_1(:,i\text{-}k+1) \\ \mathbf{R}_1(:,i\text{-}k+2) \\ \\ ... \\ \\ \mathbf{R}_1(:,i) \\ \\ ... \\ \\ \mathbf{R}_2(:,i+k) \end{bmatrix}$$

Using this scheme, the model for the ith channel is based on a wider range of data. In order for this scheme to be useful, the instrument transfer function must not be a strong function of wavelength. The function `stdgen` implements DWPDS. Our experience using

DWPDS in FTIR shows that it may be optimal to have a narrow first window, on the order of the resolution of the instrument, and very wide second window. DWPDS is compared with PDS in `stddemo` using the NIR data, where one would not expect DWPDS to be particularly advantageous. Still, on the data considered, it is possible to derive a PDS model with a window width of 3 with the same performance as a model identified with DWPDS with a window width of 5. This suggests that it is possible to get a model with additional coefficients, provided that more data are used in the construction of each of the models. It may be that the DWPDS-derived models are more robust in practice, but this remains to be investigated.

Standardization with FIR Filters

The `stdfir` function can be thought of as a moving window MSC and is analogous to using a finite impulse response modeling methodology. The function, based on the work by Blank *et al.* (1996), uses a windowed MSC to correct the spectra to a reference spectrum with only the center channel of each window being corrected. This technique has the advantage of using MSC, *i.e.,* only one spectrum on the standard instrument is required to transfer spectra from a second instrument. Also, if the scattering effect is a function of wavelength, the windowing may avoid some of the limitations imposed by using a single multiplicative factor in MSC.

Note that it is advisable to cross-validate over the window width to find the best window for standardization. Also, it has been found that if the reference spectrum has regions about the size of the window width which are flat, estimates of the inverse of $\mathbf{r}'^{\mathrm{T}}\mathbf{r}'$ in that window can be poor, resulting in artifacts (*e.g.,* spikes) in the corrected spectra. If the flat region is not in an area with zero absorbance, the function results might improve if mean-centering is not used. Another way to stabilize the estimates is to add a constant slope to the spectra prior to using `stdfir` and then to take the derivative after standardization. Also, when using the FIR filter approach Sum and Brown (1997) have reported that "despite very good precision, a comparatively large bias is manifested in prediction in some systems." They also report a methodology for correcting the bias.

Orthogonal Signal Correction

Orthogonal Signal Correction (OSC) is a data preprocessing method that can be used prior to PLS modeling. In situations where the a PLS model captures a very large amount of predictor block (X) variance in the first factor but gets very little of the predicted variable (y or Y), this method can be very helpful. In these cases, it is useful to remove extraneous variance from X that is unrelated to y. OSC does this by finding directions in X that describe large amounts of variance while being orthogonal to y. PLS models are built on OSC-corrected data, then the OSC correction is applied to new data before the models are applied to that data. OSC can also be used for standardization purposes to remove variation between instruments that is not related to the variables to be predicted. An example of this is shown here using the `osccalc` and `oscapp` functions with the NIR data from the previous example.

```
» load nir_data
```

```
» [specsub,specnos] = stdsslct(spec1.data,5);
» x1 = spec1.data(specnos,:); x2 = spec2.data(specnos,:);
» y1 = conc.data(specnos,:);
» x = [x1; x2]; y = [y1; y1];
» [nx,nw,np,nt] = osccalc(x,y,2);
» newx1 = oscapp(spec1.data,nw,np);
» newx2 = oscapp(spec2.data,nw,np);
```

The difference before and after standardization over all thirty samples is shown in Figure 12-4 below. The RMS errors (not shown) are comparable to those shown in Figure 12-3.
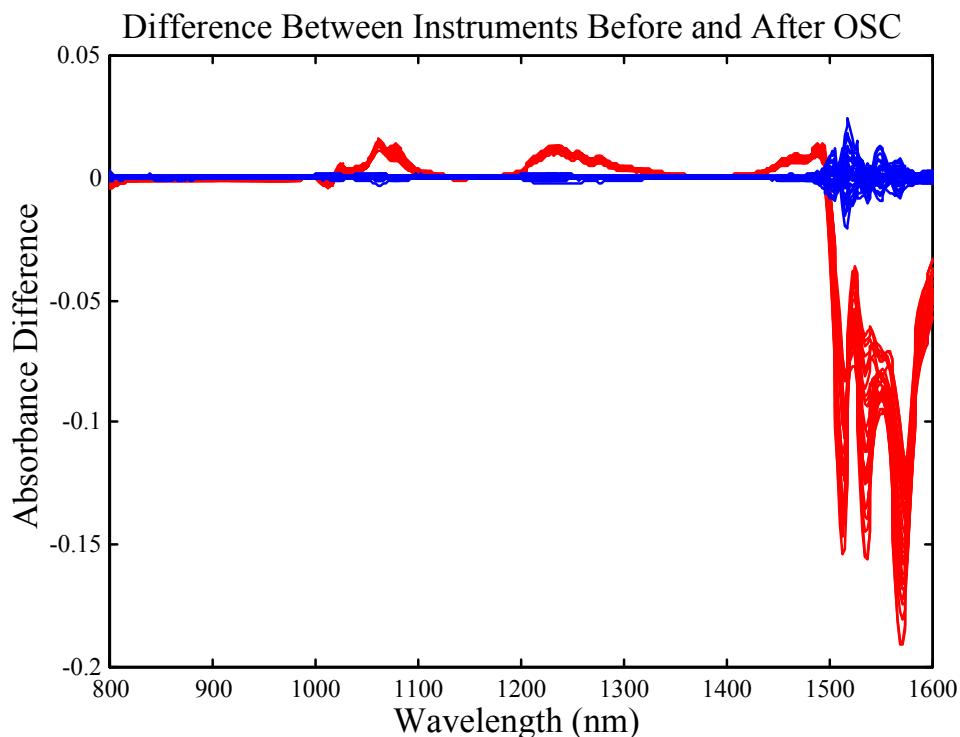
Figure 12-4. Difference between instruments before (red) and after (blue) application of OSC.

Standardization via Generalized Least Squares Weighting

Like OSC, Generalized Least Squares Weighting (GLSW) is a data preprocessing method that can be used prior to PLS modeling to remove extraneous variance. When used for standardizations, the objective is to remove variation that the instruments do not have in common. PLS models are built on GLSW-corrected data, then the GLSW correction is performed on new data before the models are applied to that data. An example of this is shown here using the glsw function and the NIR data from the previous example.

```
» load nir_data
» [specsub,specnos] = stdsslct(spec1.data,5);
» x1 = spec1.data(specnos,:); x2 = spec2.data(specnos,:);
```

```
» modl = glsw(x1,x2);
» newx1 = glsw(spec1.data,modl);
» newx2 = glsw(spec2.data,modl);
```

The difference before and after standardization over all thirty samples is very similar to the differences shown in Figure 12-4 for OSC. Likewise, the RMS errors (not shown) are comparable to those shown in Figure 12-3.

13. Robust Statistical Methods

Preface

PLS_Toolbox 4.0 includes robust statistical methods for Principal Components Analysis and Regression. The robust functionality has been incorporated by including a version of *LIBRA, a MATLAB Library for Robust Analysis*. LIBRA was developed by the research groups on robust statistics at Katholieke Universiteit Leuven and the University of Antwerp. More details concerning LIBRA can be found in Verboven and Hubert, (2005) and at http://wis.kuleuven.be/stat/robust/LIBRA.html. Eigenvector Research has licensed LIBRA, and with the help of Drs. Sabine Verboven and Mia Hubert, modified it to make it work with PLS_Toolbox. This chapter introducing robust statistics was developed primarily by Verboven and Hubert.

Introduction

Robust methods are developed because atypical observations in a data set heavily affect the classical estimates of data mean and variance/covariance. Consider the estimation of the center of the following set of numbers: [10 10.1 10.1 10.1 10.2 10.2 10.3 10.3]. For these data, the mean is 10.16, whereas the median equals 10.15. These two statistics do not differ much as there are no outliers. However, if the last measurement was wrongly recorded as 103 instead of 10.3, the mean would be 21.75, whereas the median still would equal 10.15. This exemplifies the robust nature of the median versus the non-robust (classical) nature of the mean. Outliers can occur by mistake (as in this example by misplacement of a decimal point), or other random error, for example, through an instrument malfunction or a measurement error. These are typically the samples that should be discovered and corrected or else removed from the data.

Another type of atypical observation is a systematic error where some measurements belong to a population other than the one under study (caused, for example, by a change in the experimental conditions). Often atypical observations reveal unique properties. Consequently, finding this kind of outlier can lead to new discoveries. Outliers are thus not always wrong or bad, although they are often referred to negatively. They are, however, different than the bulk of the data under consideration.
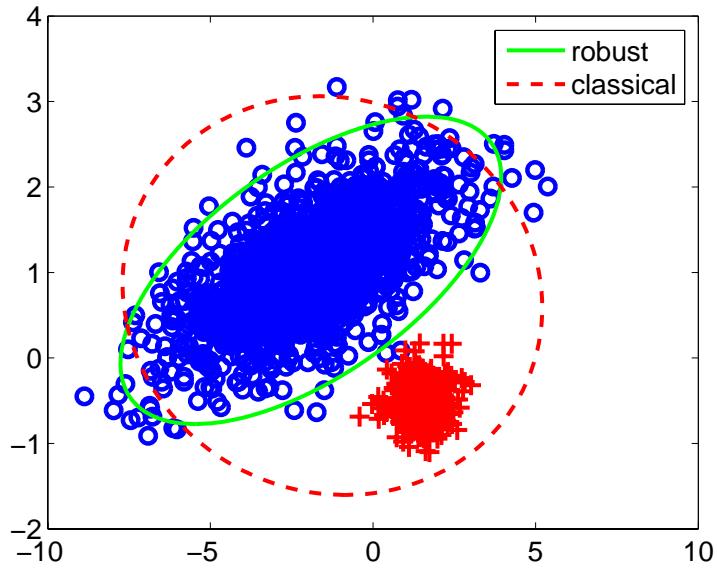
Figure 13-1. Simulated data set with outliers.

Outliers are the rule rather than the exception in real-world applications. This is especially true in the area of on-line process analysis, where outliers are always present because process sensors rarely operate within specifications 100% of the time. In general, the analyst has limited control over the process that generates the calibration data. Moreover, detecting multivariate outliers is very difficult, as illustrated in Figure 13-1. The outlying observations (indicated by '+') do not have abnormal values in either of the two variables, and hence will not be spotted by looking at the individual variables. The outliers can only be found by taking into account the covariance structure (the green ellipse) of the regular data (indicated by 'o'). The tolerance ellipse based on the classical covariance estimate (red dashed circle) is enlarged due to the presence of the outliers. In contrast, the robust Minimum Covariance Determinant (MCD) estimator (Rousseeuw, 1984) is an alternative method of calculating the covariance and clearly encloses only the regular data points (green ellipse). The need for and effectiveness of *robust statistical methods* has also been described in many papers and books; see Hampel (1986), Huber (1981), Rousseeuw and Leroy (1987).

Robust estimation of the covariance matrix

One of the keystones of the robust methods included in PLS_Toolbox through the LIBRA toolbox is the Minimum Covariance Determinant (MCD) estimator (Rousseeuw, 1984), a multivariate estimator of location (mean) and scale (variance/covariance). The main function of the MCD-estimator is to examine the data set X of size m by n for the h-subset containing the most concentrated data points, or, more formally, to search for the subset containing $h > m/2$ observations whose covariance matrix has the lowest determinant. (Note that the determinant of a covariance matrix is proportional to the volume enclosed by the corresponding data.) The raw MCD estimate of location is then the average of these h points, whereas the raw MCD estimate of scatter is their

328

covariance matrix (multiplied by a consistency factor which is discussed later). Based on these raw MCD estimates, a reweighting step can be added which considerably increases the finite-sample efficiency (a measure of the desirability of an estimator equal to the minimum variance in an estimated parameter divided by its actual variance) (Rousseeuw and Van Driessen, 2000).

The number h is also related to the fraction of outliers (1- α) by the equation

$$h = (\alpha m)_{int} \tag{13-1}$$

where m indicates the total number of observations in the data set, and $(...)_{int}$ indicates the integer part of αm. The MCD estimator can resist *(m-h+1)/m* outlying observations, hence h determines the robustness of the estimator. More formally, it is said that the MCD estimator has a breakdown value of *(m-h+1)/m*. The breakdown value of an estimator is the proportion of arbitrarily large incorrect observations an estimator can handle before giving an arbitrarily large result. The highest possible breakdown value of the MCD estimator is attained when $h = [(m+n+1)/2]$.

When a large proportion of contamination by outliers is presumed, h should be chosen close to $0.5m$ or α should be set equal to 50%. In other cases, an intermediate value for h, such as $0.75m$ or $\alpha = 75\%$, is recommended to obtain a higher finite-sample efficiency. In the algorithms, the default value $\alpha = 0.75$ is used, unless you have *a priori* information about the data set that can be translated into a smaller or larger value for α.

The `mcdcov` function is an implementation of the FAST-MCD algorithm of Rousseeuw and Van Driessen (1999). Note that the MCD can only be computed if $n < h$, otherwise the covariance matrix of any h-subset has zero determinant. Because $m/2 < h$, the number of variables n must be less than $m/2$. However, detecting several outliers becomes intrinsically delicate when m/n is small, as some data points may become coplanar by chance. This is an instance of the "curse of dimensionality". It is therefore recommended that $m/n > 5$ when $\alpha = 0.5$ is used. For small m/n it is preferable to use the MCD algorithm with $\alpha = 0.75$.

The MCD location and scatter estimates are affine equivariant, which means that they behave properly under affine transformations of the data. That is, for a data set **X** in **IR**^{mxn} the MCD estimates $\left(\hat{\mu}, \hat{\Sigma} \right)$ satisfy

$$\hat{\mu}(\mathbf{XA} + 1_m v^T) = \hat{\mu}(\mathbf{X})\mathbf{A} + v$$
$$\hat{\Sigma}(\mathbf{XA} + 1_m v^T) = \mathbf{A}^T \hat{\Sigma}(\mathbf{X})\mathbf{A} \tag{13-2,3}$$

for all non-singular n by n matrices **A** and vectors $v \in \mathbf{IR^n}$. The vector $\mathbf{1_m}$ equals the column vector $(1,1,\ldots,1)^T$ of length m.

Using LIBRA in MATLAB, the reweighted MCD estimator of a data matrix **X** is computed by typing:

```
>>out = mcdcov(X)
```

at the command line. The algorithm then runs using all the default settings including $\alpha =$ 0.75, `'plots'=1`, `'cor'=0`, `'ntrial'=500`. Running the algorithm in this manner means that diagnostic plots will be drawn, a correlation matrix will not be computed, and the algorithm will use 500 random initial $n+1$ subsets.

To change one or more of the default settings, the input arguments and their new values have to be specified. Assume, for example, that we have no idea about the amount of contamination (incorrect observations), and we prefer to apply a highly robust method and set $\alpha = 0.50$. If we are interested in the corresponding MCD correlation matrix, we set new parameters by typing:

```
>> out = mcdcov(X,'alpha',0.50,'cor',1)
```

The optional arguments can be omitted (meaning that the defaults are used) or they can be called in an arbitrary order. For example,

```
>>out = mcdcov(X,'cor',1,'alpha',0.50)
```

and

```
>>out=mcdcov(X,'alpha',0.50,'cor',1,'plots',1)
```

would produce the same result.

Note that the method of setting options for LIBRA functions is different than for PLS_Toolbox functions. In PLS_Toolbox functions, a single options structure can be obtained from the function and modified as desired, and then input to the function. In LIBRA functions, options are specified with option name/options value pairs, much like MATLAB handle graphics. To see all of the optional inputs, use the command line help for the function: `help mcdcov`.

Example of MCD Method with Body and Brain Weight Data Set

To illustrate the MCD method, we analyze the brain and body weight data discussed in Rousseeuw and Leroy, (1987). This bivariate data set ($n = 2$) consists of the body and brain weights of $m = 28$ animals, including 3 (extinct) dinosaurs. The data can be loaded into MATLAB and plotted with PLOTGUI by typing:

```
>> load brain_weight
>> plotgui(brains)
```

In the plot controls window, select Body Mass (kg) in the x-axis menu, Brain Mass (g) in the y-axis menu. Set axes to logarithmic by selecting View/Log Scales/All and add labels by selecting View/Labels/Set 1. This produces the plot shown in Figure 13-2 (the labels have been moved on some points for clarity).

330
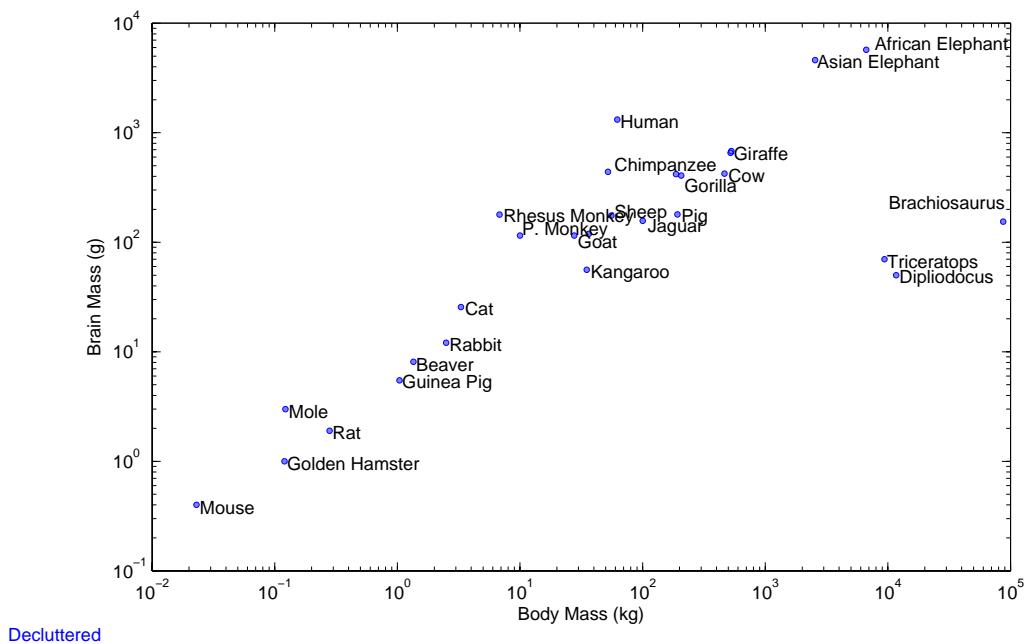
Figure 13-2. Plot of the Brain Weight data set with logarithmic scales.

The MCDCOV function can now be used to determine the subset of samples with minimum determinant. Because of the very wide range in the data, it will be pre-processed by taking a base 10 logarithmic transformation of both variables, as follows:

```
>>out = mcdcov(log10(brains.data))
```

The function will produce the MENU window shown in Figure 13-3 which allows the user to make a variety of plots. For now, select Exit and the following output structure is obtained:
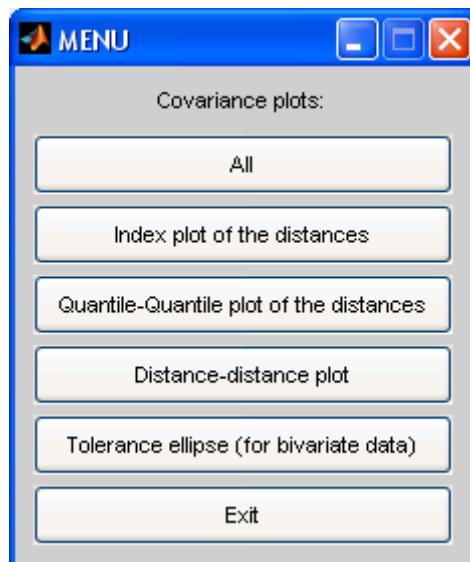
Figure 13-3. MENU window from MCDCOV function.

```
out =

     center: [1.3154 1.8569]
        cov: [2x2 double]
        cor: []
          h: 21
   Hsubsets: [1x1 struct]
      alpha: 0.7500
         rd: [1x28 double]
       flag: [1 1 1 1 1 0 1 1 1 1 1 1 1 1 0 1 0 0 1 1 1 1 1 1 1 0 1 1 1]
         md: [1x28 double]
     cutoff: [1x1 struct]
      plane: []
     method: [1x42 char]
      class: 'MCDCOV'
    classic: 0
          X: [28x2 double]
```

The output consists of several fields that contain the location estimate ('out.center'), the estimated covariance matrix ('out.cov'), and the correlation matrix ('out.cor'). Other fields such as 'out.h' and 'out.alpha' contain information about the MCD method, while some of the components (e.g., 'out.rd', 'out.flag', 'out.md' and 'out.cutoff') can be used for outlier detection and to construct some graphics. The 'out.class' field is used to detect which figures should be created for this analysis. Detailed information about this output structure (and that of the raw estimates) can be found in the help file of the mcdcov function.

The robust distance of an observation i is used to detect whether it is an outlier or not. It is defined as

$$\text{RD}_i = \sqrt{(x_i - \hat{\mu}_{MCD})^T \hat{\Sigma}_{MCD}^{-1} (x_i - \hat{\mu}_{MCD})} \qquad (13\text{-}4)$$

with $\ddot{\mu}_{MCD}$ and $\ddot{\Sigma}_{MCD}$ defined as the estimates of MCD location and scatter. This robust distance is the straightforward robustification of the Mahalanobis distance

$$\text{MD}_i = \sqrt{(x_i - \bar{x})^T \mathbf{S}^{-1} (x_i - \bar{x})} \qquad (13\text{-}5)$$

which uses the classical mean $\bar{x}$ and empirical covariance matrix $\mathbf{S}^{-1}$ as estimates of location and scatter. Under the normal assumption, the outliers are those observations having a robust distance larger than the cut-off-value $\sqrt{\chi^2_{n,0.975}}$, and they receive a flag equal to zero. The regular observations whose robust distance does not exceed $\sqrt{\chi^2_{n,0.975}}$ have a flag equal to one.

The algorithm provides several graphical displays based on the robust distances and the Mahalanobis distances to help visualize any outliers and to compare the robust and the classical results. One of these graphics is the distance-distance plot (Rousseeuw and Van Driessen, 1999) which displays for each observation its robust distance RD_i versus its Mahalanobis distance MD_i. A horizontal and a vertical line are drawn at the cutoff value $\sqrt{\chi^2_{n,0.975}}$. Figure 13-4 shows the distance-distance plot for the body and brain weight data, with lines drawn at the cutoff value of 2.72. A similar figure can be obtained by clicking the Distance-distance plot button in the **MCDCOV Menu**. Five outlying observations can be clearly seen in Figure 13-4: human, rhesus monkey, triceratops, brachiosaurus and diplodocus. However, the classical method only identifies the brachiosaurus measurement as an outlier, as its marker appears beyond the vertical cutoff line indicating the Mahalanobis distance. The other four outlying observations (human, rhesus monkey, triceratops and diplodocus) have a large robust distance but a small Mahalanobis distance. They are not recognized as outliers when using the classical approach.
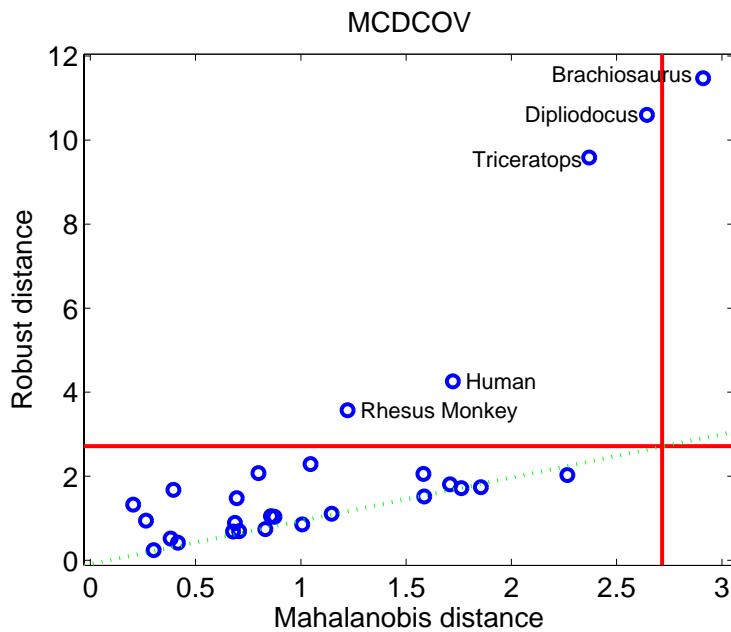
Figure 13-4. Brains data set: distance-distance plot.

As this data set is bivariate, we can understand its structure much better by making a scatter plot (Figure 13-5). Superimposed on the scatter plot is the 97.5% robust confidence ellipse, which encloses the set of points whose robust distance is equal to $\sqrt{\chi^2_{n,0.975}}$, as well as the 97.5% classical confidence ellipse, which encloses the set of points whose Mahalanobis distance is equal to $\sqrt{\chi^2_{n,0.975}}$. Observations outside these tolerance ellipses are classified as outliers. We again notice the five outliers found with the MCD method, while the classical tolerance ellipse again encloses all outliers except one, the brachiosaurus measurement, which is shown as a borderline case.
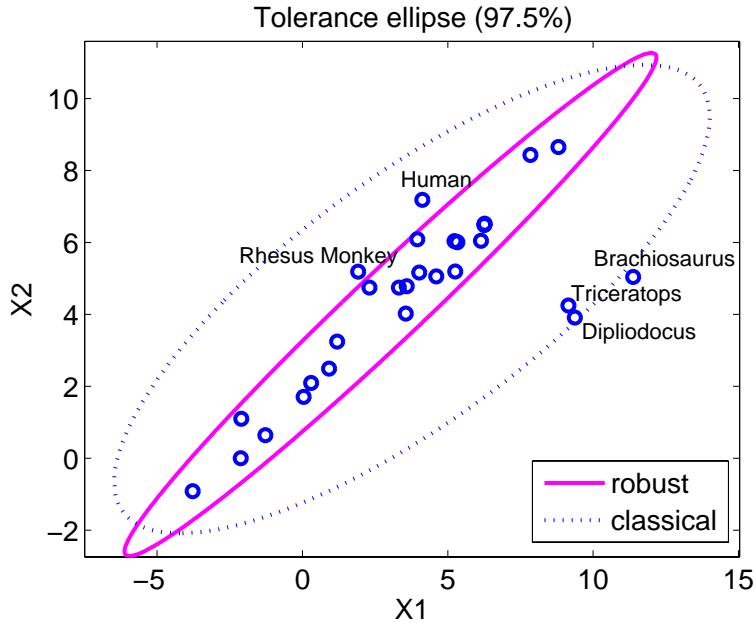
Figure 13-5. Brains data set: Tolerance ellipses.

Robust linear regression

The multiple linear regression model assumes that, in addition to the *n* regressors or *x*-variables, a response variable *y* is measured, which can be explained as an affine combination of the predictors. More precisely, the model says that for all observations (x_i, y_i) with i = 1,…, m it holds that

$$y_i = \beta_0 + \beta_1 x_{i1} + \mathsf{L} + \beta_n x_{in} + \varepsilon_i = \beta_0 + \beta^T \mathbf{x}_i + \varepsilon_i \qquad (13\text{-}6)$$

where the errors ε_i are assumed to be independent and identically-distributed with zero mean and constant variance σ^2. Applying a regression estimator to the data yields *n*+1 regression coefficients $\hat{\theta} = (\hat{\beta}_0,…,\hat{\beta}_n)^T$. The residual r_i of case *i* is defined as

$$y_i - \hat{y}_i = y_i - \hat{\theta}^T \begin{bmatrix} 1 \\ x_i \end{bmatrix}.$$

The ordinary least squares (OLS) estimator minimizes the sum of the squared residuals, but is very sensitive to outliers. LIBRA PLS_Toolbox also contains the Least Trimmed Squares (LTS) estimator (Rousseeuw, 1984) which minimizes the sum of the *h* smallest squared residuals, or

$$\hat{\theta}_{LTS} = \min_{\theta} \sum_{i=1}^{h} (r^2)_{i:m} \qquad (13\text{-}7)$$

Note that the residuals are first squared, and then ordered

$$(r^2)_{i:1} \le (r^2)_{i:2} \le \ldots \le (r^2)_{m:m} \qquad (13\text{-}8)$$

The interpretation of the h value in this method is the same as for the MCD estimator, and thus h should be chosen between $m/2$ and m. Setting $h = m$ yields the OLS estimator. For $h \approx m/2$ we find a breakdown value of 50%, whereas for larger h we obtain a breakdown value of $(m\text{-}h\text{+}1)/m$. The function **ltsregres** contains an implementation of the FAST-LTS algorithm (Rousseeuw and Van Driessen, 2000) which is similar to the FAST-MCD method.

The LTS estimator is regression, scale and affine equivariant. That is, for any $\mathbf{X} = (\mathbf{x_1}, \ldots, \mathbf{x_m})^T$ and $\mathbf{y} = (y_1, \ldots, y_m)^T$ it holds that

$$\hat{\theta}(X, y + Xv + 1_m c) = \hat{\theta}(X, y) + (v^T, c)^T$$

$$\hat{\theta}(X, cy) = c\hat{\theta}(X, y) \qquad (13\text{-}9,10,11)$$

$$\hat{\theta}(XA^T + 1_m v^T, y) = (\hat{\beta}^T(X, y)A^{-1}, \beta_0(X, y) - \hat{\beta}^T(X, y)A^{-1}v)^T$$

for any vector $v \in \mathbf{IR}^n$, any constant c and any nonsingular n by n matrix A. Again $\mathbf{1_m} = (1, 1, ..., 1)^T \in \mathbf{IR}^m$. This implies that the estimate transforms correctly under affine transformations of both the x and y variables.

Example of Robust Regression with Stars data set

We will now consider an example of robust regression with the stars data set (Rousseeuw and Leroy, 1987). This bivariate data set ($n = 2$) contains the surface temperature and the light intensity of $m = 47$ stars in the direction of Cygnus. The data were preprocessed by taking a logarithmic transformation of both variables. The linear model we will fit onto these data is

$$y_i = \beta_0 + \beta_1 x + \varepsilon \qquad (13\text{-}12)$$

The regression coefficients β_0 and β_1 will be estimated with the OLS estimator as well as the LTS estimator.
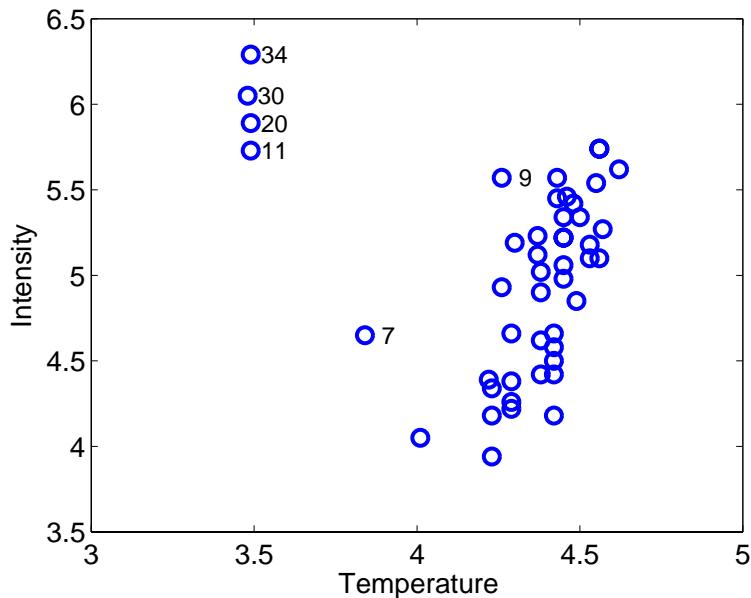
Figure 13-6. Stars data: scatter plot.

The data for this example can be viewed by performing the following commands:

```
>> load stars
>> plotgui(stars)
```

and selecting Temperature in the x menu and Intensity in the y menu of the Plot Controls window. Sample numbers can be added by selecting View/Numbers. From the resulting scatter plot, shown in Figure 13-6, we see that the majority of the data follow a linear trend but four outlying stars are apparent in the upper left. In astronomy this is a well-known phenomenon: the 43 stars in the data cloud belong to the main sequence (common hydrogen fusing stars), whereas the four remaining stars are giant stars with low surface temperature but high luminosity due to their great size. The data points representing the four giant stars are not incorrect observations, but simply come from another population than the regular data.

A LTS regression can be performed using the command:

```
>> out=ltsregres(stars.data(:,1),stars.data(:,2),'intercept',1,...
'h',floor(0.75*47),'classic',0,'plots',1)
```

which generates the interface, which allows access to several diagnostic plots, shown in Figure 13-7. When the Exit button is pressed, the following output results:

336
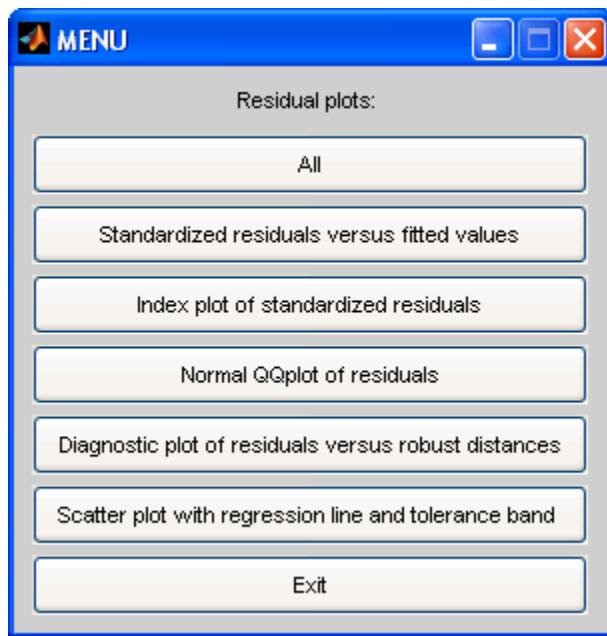
Figure 13-7. MENU window from LTSREGRES function.

```
out =

slope: 3.0462
int: -8.5001
fitted: [47x1 double]
res: [47x1 double]
scale: 0.3365
rsquared: 0.5544
h: 35
Hsubsets: [1x1 struct]
alpha: 0.7447
rd: [1x47 double]
resd: [47x1 double]
cutoff: [1x1 struct]
flag: [47x1 logical]
method: 'Least Trimmed Squares Regression.'
class: 'LTS'
classic: [1x1 struct]
X: [47x1 double]
y: [47x1 double]
```

in which the field 'classic' stores the OLS computations:

```
slope: -0.4133
int: 6.7935
fitted: [47x1 double]
res: [47x1 double]
```

```
scale: 0.5646
rsquared: 0.0443
md: [47x1 double]
resd: [47x1 double]
cutoff: [1x1 struct]
flag: [47x1 logical]
class: 'LS'
X: [47x1 double]
y: [47x1 double]
```

The OLS-fit for the stars data is thus:

$$- 0.4133 \, x_i + 6.7935$$

while the LTS-fit is

$$3.0462 \, x_i - 8.5001$$

Note that the slope term changes sign in this example. In the OLS model the slope is negative, suggesting that intensity goes down with increased temperature. Drawing the regression lines onto a scatterplot shows that the OLS fit was highly influenced by the four giant stars whereas the LTS fit nicely describes the linear trend in the majority of the data (Figure 13-8).
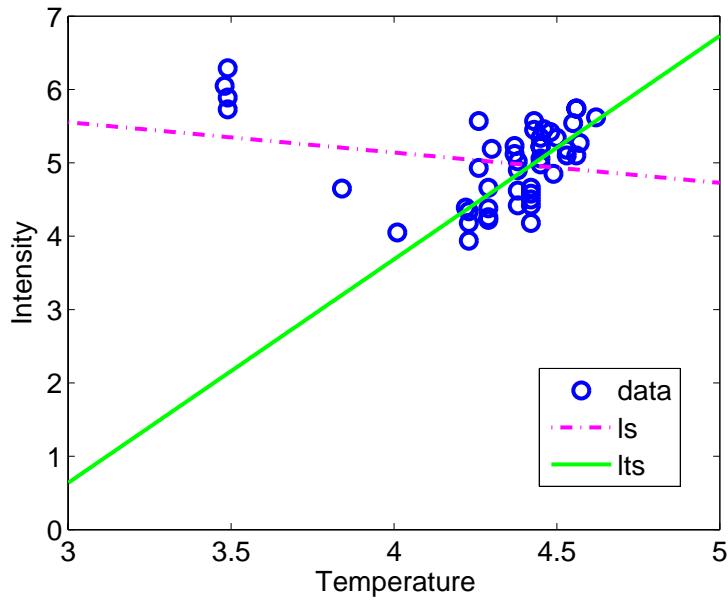
Figure 13-8. Stars data: OLS and LTS fit.

With the output of the `ltsregres` function, one can produce many plots as graphical tools for model checking and outlier detection, such as a normal quantile plot of the residuals, and a residual outlier map. The latter, shown in Figure 13-9 for the stars data, displays the standardized LTS residuals (the residuals divided by a robust estimate of their scale) versus the robust distances obtained by applying the MCD estimator on the x variables. The residual outlier maps are divided by cutoff lines into six different areas by which we can classify the outliers into four different groups: regular observations, good leverage points, bad leverage points, and vertical outliers.
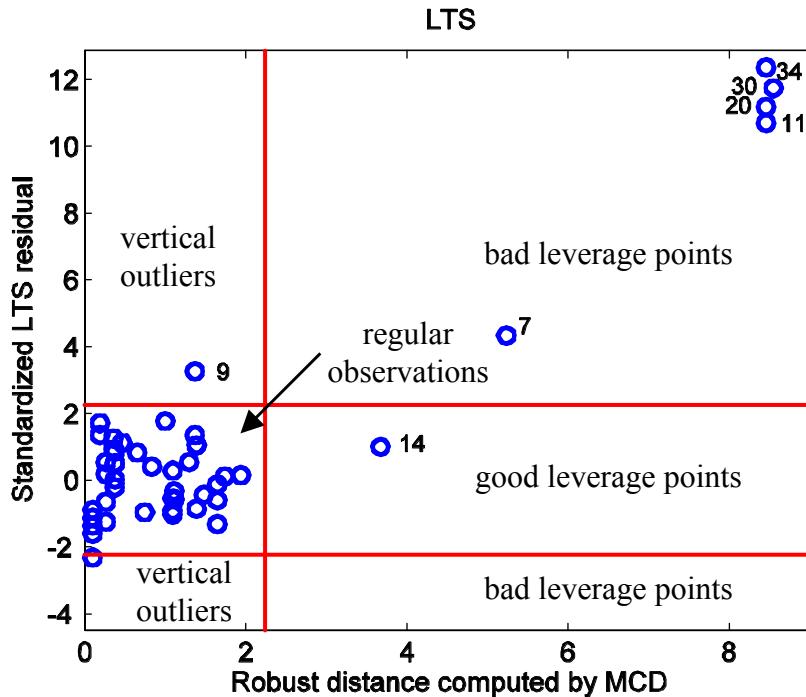
Figure 13-9. Stars data: Standardized LTS residuals versus robust distances with different types of outliers indicated.

In Figure 13-9 the regular observations do not exceed any of the cutoffs. The good leverage points are these observations having a small standardized residual but large robust (or Mahalanobis) distance. These data points confirm the linear relationship at larger x values. The observations which need to be examined more closely are the vertical outliers and the bad leverage points. The vertical outliers are the data points with regular x values but with y-values deviating from the majority of the y values; hence, they have a large standardized residual. The observations having aberrant x- and y-values are called the bad leverage points. Both vertical outliers and bad leverage points tend to pull the regression line towards them and thus greatly affect the regression line.

The outlier map generated from the classical OLS regression estimates for the Stars data is shown in Figure 13-10. Compared with the robust residual outlier map, the classical OLS map would lead to considerably different conclusions. Looking at the robust residual outlier map in Figure 13-9, five bad leverage points (cases 7, 11, 20, 30, and 34)

can be observed. However, the classical residual outlier map in Figure 13-10 describes cases 11, 20, 30, and 34 as good leverage points. The robust LTS method thus pinpoints the giant stars as bad leverage points, whereas the OLS method classifies them as good leverage points. Clearly, the giant stars attracted the OLS fit towards them; this phenomenon could already be observed in Figure 13-8 where the regression lines were fitted onto the data.
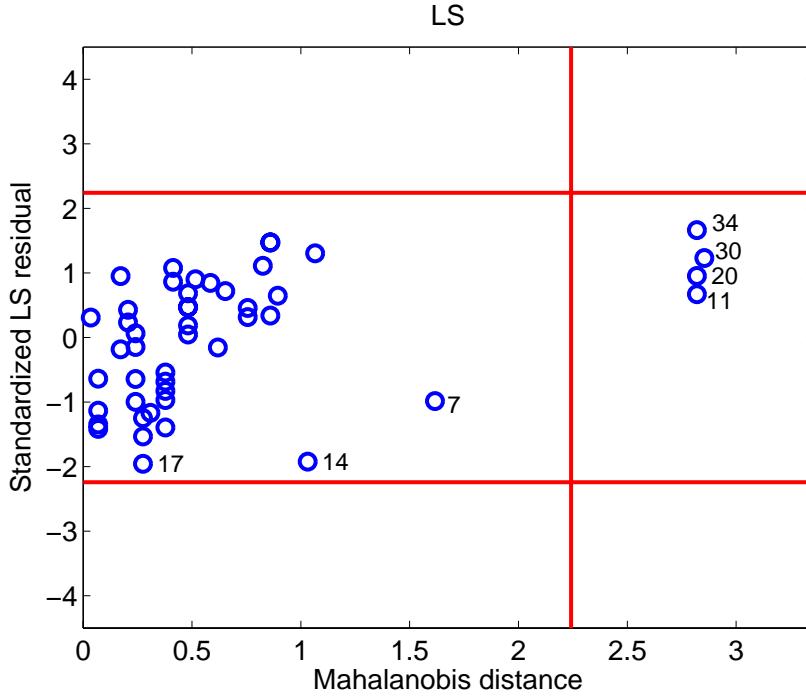
Figure 13-10. Stars data: Standardized LS residuals versus Mahalanobis distances.

When using LTS regression, the scale of the errors σ can be estimated by

$$\hat{\sigma}_{LTS} = c_{h,m}\sqrt{\frac{1}{h}\sum_{i=1}^{h}(r^2)_{i:m}} \qquad (13\text{-}13)$$

where r_i are the residuals from the LTS fit, and $c_{h,m}$ makes $\hat{\sigma}$ consistent and unbiased at Gaussian error distributions. The regression outliers are then identified by their standardized LTS residuals $r_i/\hat{\sigma}_{LTS}$.

It should be stressed that LTS regression does not throw away a certain percentage of the data. Instead, it finds a majority fit, which can then be used to detect the actual outliers. The purpose is not to delete and forget the points outside the tolerance band, but to study the residual plot in order to find out more about the data. For instance, we notice star 7 intermediate between the main sequence and the giants, which might indicate that this star is evolving to its final stage.

In regression analysis, inference is very important. The LTS by itself is not suited for inference because of its relatively low finite-sample efficiency. This issue can be resolved by carrying out a reweighed least squares step. To each observation i, one assigns a weight w_i based on its standardized LTS residual, by setting $w_i := w(|\frac{r_i}{\hat{\sigma}_{LTS}}|)$ where w is a decreasing continuous function. A simpler way, but still effective, is to put

$$w_i = \begin{cases} 1 & \text{if } |r_i / \hat{\sigma}_{LTS}| \leq 2.5 \\ 0 & \text{otherwise} \end{cases} \tag{13-14}$$

Either way, the reweighed LTS fit is then defined by

$$\text{minimize } \sum_{i=1}^{m} w_i r_i^2 \tag{13-15}$$

which can be computed quickly. The result inherits the breakdown value of the LTS regression, but is more efficient and yields all the usual inferential output such as t-statistics, F-statistics, an R^2 statistic, and the corresponding p-values.

Now, if we also want a reliable prediction of $q > 1$ properties at once, based on a set of n explanatory variables, the use of a multivariate regression method is appropriate. The linear regression model is then formulated as

$$y_i = \beta_0 + \beta^T x_i + \epsilon_i \quad i = 1,\dots,m \tag{13-16}$$

with y_i and ϵ_i being q-dimensional vectors that respectively contain the response values and the error terms of the ith observation with covariance matrix Σ_ϵ.

To cope with such data, we can use the MCD-regression method (Rousseeuw et al., 2004). It is based on the MCD estimates of the joint (x,y) variables and thereby yields a highly robust method. Within the toolbox, this method can be called with the `mcdregres` function.

Robust Principal Component Analysis

PCA captures the largest amount of variance of the data possible with the first and each subsequent component. These components are linear combinations of the original variables. Looking at them can lead to a better understanding of the different sources of variation in the data. As a data reduction technique, PCA is frequently the first step in the analysis of a high-dimensional data set, followed by classification, clustering or other multivariate techniques. The goal of a *robust* PCA method is to obtain principal components that are not influenced much by outliers.

A first group of robust PCA methods is obtained by replacing the classical covariance matrix by a robust covariance estimator, such as the reweighed MCD estimator (Croux and Haesbrouck, 2000). Unfortunately, the use of these affine equivariant covariance

estimators is limited to small to moderate dimensions. To see why, let us again consider the MCD estimator. As already explained, the MCD estimator can only be computed if the number of variables n is smaller than the parameter h. Since h also needs to be smaller than the number of observations m, consequently n must be smaller than m which is not the case for high-dimensional data sets.

A second problem is the computation of these robust estimators in high dimensions. Today's fastest algorithms can handle up to about 100 dimensions, whereas there are applications, *e.g.*, spectroscopy, with dimensions in the thousands. Moreover, the accuracy of the algorithms decreases with the dimension n, so it is recommended for small data sets not to use the MCD in (say) more than 10 dimensions.

Another approach to robust PCA has been proposed in Hubert *et al.* (2005) and is called ROBPCA. This method combines ideas of both projection pursuit and robust covariance estimation. The projection pursuit part is used for the initial dimension reduction. Some ideas based on the MCD estimator are then applied to this lower-dimensional data space. Simulations have shown that this combined approach yields more accurate estimates than the raw projection pursuit algorithm, called RAPCA (Hubert and Verboven, 2001). The entire description of the ROBPCA method can be found in Hubert et al. (2005).

Since the ROBPCA algorithm is rather complicated, we only describe its main stages.

First, the data are preprocessed by reducing their data space to the affine subspace spanned by the m observations. As a result, the data are represented using at most $m - 1 = \text{rank}(\boldsymbol{X_C})$ variables without loss of information.

In the second step, a measure of outlyingness is computed for each data point (Stahel 1981, Donoho 1982). This measure is obtained by projecting the high-dimensional data points on many univariate directions d through two data points. On every direction the univariate MCD estimator of location $\hat{\boldsymbol{\mu}}_{MCD}$ and scale $\hat{\Sigma}_{MCD}$ is computed on the projected points $x_j^T d$ (j = 1… m), and for every data point its standardized distance to that center is measured. Finally, for each data point its largest distance over all the directions is considered. This yields the outlyingness:

$$
\text{outl}(x_i) = \max_d \frac{\left| x_i^T d - \hat{\mu}_{MCD}(x_j^T d) \right|}{\hat{\sigma}_{MCD}(x_j^T d)}
\tag{13-17}
$$

Next, the covariance matrix $\hat{\Sigma}_h$ of the h data points with the smallest outlyingness values is computed.

The last stage of ROBPCA consists of projecting all the data points onto the k-dimensional subspace spanned by the k largest eigenvectors of $\hat{\Sigma}_h$ and of computing their center and shape by means of the reweighed MCD estimator. The eigenvectors of this scatter matrix then determine the robust principal components which can be collected in a

loading matrix $\boldsymbol{P}$ with orthogonal columns. The MCD location estimate $\hat{\boldsymbol{\mu}}_x$ serves as a robust center.

Note that classical PCA is not affine equivariant because it is sensitive to a rescaling of the variables, though it is still orthogonally equivariant, which means that the center and the principal components transform appropriately under rotations, reflections and translations of the data. More formally, classical PCA allows transformations $\boldsymbol{XQ}$ for any orthogonal matrix $\boldsymbol{Q}$ (that satisfies $\boldsymbol{Q}^{-1} = \boldsymbol{Q}^{\mathrm{T}}$). Any robust PCA method thus only has to be orthogonally equivariant.

Example of Robust PCA with Octane data (Esbensen, 2001)

We will illustrate ROPBCA and its diagnostic tools on the Octane data set from Esbensen (2001), which consists of $m = 39$ NIR-spectra of gasoline at $n = 226$ wavelengths from 1100 to 1550 nm. The data can be viewed by executing the following MATLAB commands:

```
>> load octane
>> plotgui(spec)
```

In the **Plot Controls** window, select **Plot/Data Summary**, then select **Data** in the y menu. The result is shown in Figure 13-11. It is known that six of the samples, numbers 25, 26 and 36-38, are anomalous because alcohol was added. Let us see how the classical and the robust PCA methods cope with this. We will first use the LIBRA command robpca, then do the analysis in the **Analysis** interface.
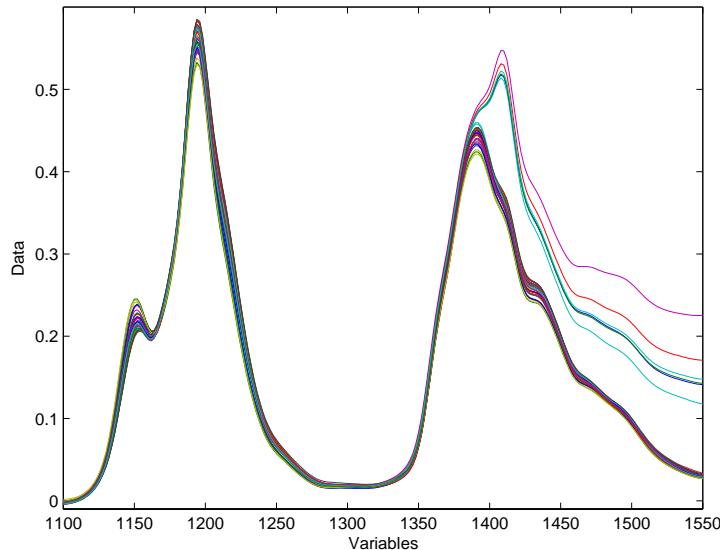
Figure 13-11. Octane data.

If we knew the optimal number of components k, we could call the robpca method with k specified, *e.g.*,

```
>> out=robpca(spec.data,'k',3)
```

Otherwise, we need to select the number of principal components k. The function call becomes

```
>> out=robpca(spec.data)
```

which generates a scree plot of the eigenvalues, as shown in Figure 13-12, and a cross validated Robust Predicted Error Sum of Squares (R-PRESS) plot, as in Figure 13-13. The scree plot is a graph of the monotonically decreasing eigenvalues. The optimal number k is then often selected as the one where the kink in the curve appears. From the scree plot of the Octane data in Figure 13-12, we decide to retain $k = 3$ components for further analysis.

In the output structure from the function robpca we find

```
P: [226x3 double]
L: [0.0114 0.0017 1.7362e-004]
M: [1x226 double]
T: [39x3 double]
k: 3
h: 32
Hsubsets: [1x1 struct]
sd: [39x1 double]
od: [39x1 double]
cutoff: [1x1 struct]
flag: [1x39 logical]
class: 'ROBPCA'
classic: [1x1 struct]
```

where the columns of P contain the robust eigenvectors, L is the vector with the corresponding robust eigenvalues, M is the robust centering vector and the columns of T contain the robust principal components. Other output variables hold information about the method and some of them will be used later on to draw outlier maps.
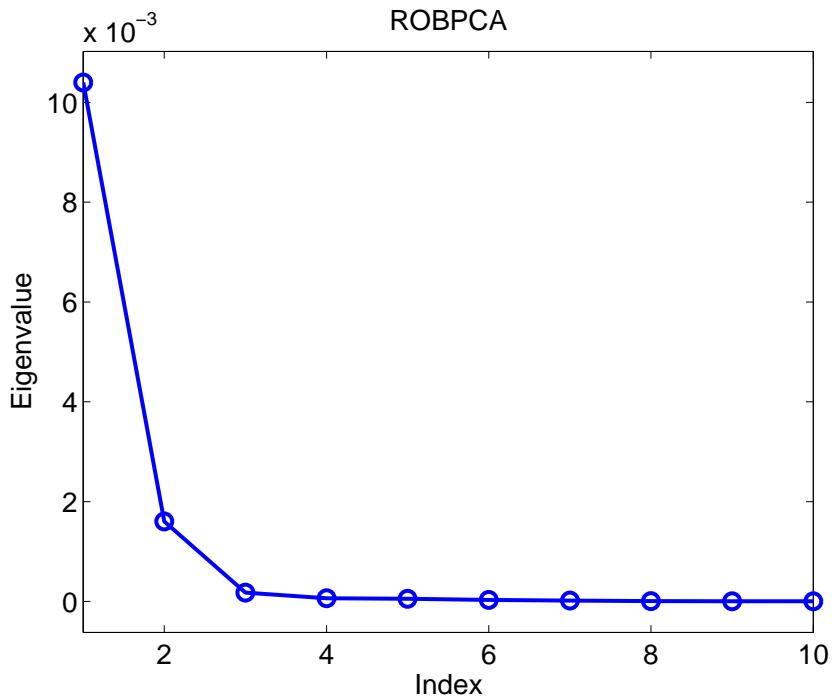
Figure 13-12. Octane data: Eigenvalue scree plot.
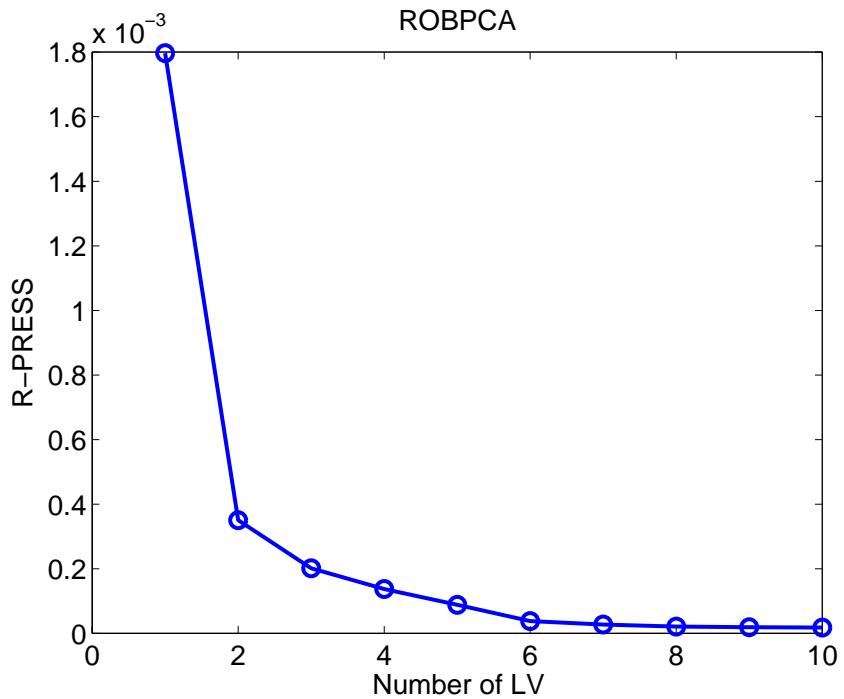
Figure 13-13. Octane data: Robust PRESS curve.

However, if we are more interested in the performance of our PCA model for prediction, a look at the robust PRESS-curve (Figure 13-13) will be more suitable. The robust PRESS statistic is defined as follows:

$$R\text{-PRESS}_k = \frac{1}{\sum_{i=1}^{m} w_i} \sum_{i=1}^{m} w_i \left\| x_i - \hat{x}_{-i,k} \right\|^2 \tag{13-18}$$

with $\hat{x}_{-i,k}$ the estimated x_i value based on a PCA model with k components and observation i omitted. The weight w_i is zero in case observation i was considered to be an outlier during the modeling process. When modeling contaminated data, we do not want to introduce the prediction errors of the outliers, so adjusting the classical PRESS statistic with these weights gives us a statistic which is more resistant to outlying observations. To look for the optimal k-value in the R-PRESS curve, we must look for the point where the curve reaches its minimum and flattens out. For the Octane data $k = 3$ components may be a good choice. One could argue that k = 6 has a smaller R-PRESS value but this is a relatively small improvement.

To visualize and classify the outliers, we can make score outlier maps, as shown in Figure 13-14 for the robust model and Figure 13-15 for the classical model. For each observation, the x-axis displays the score distance SD_i, (also known as Hotelling's T^2), within the PCA subspace

$$SD_i = \sqrt{t_i^T \Lambda^{-1} t_i} \text{ with } \Lambda = \begin{bmatrix} \lambda_1 & L & 0 \\ M & O & M \\ 0 & L & \lambda_k \end{bmatrix} \tag{13-19}$$

and on the y-axis the orthogonal distance OD_i (the square root of Q) to the PCA subspace

$$OD_i = \left\| x_i - \hat{\mu}_x - P t_i \right\| \tag{13-20}$$

where $\hat{\mu}_x$ is the (robust) center of X. For the score distances, we use the property that normally distributed data have normally distributed scores, and consequently their squared Mahalanobis distances have a χ_k^2 distribution. Hence, we use as cut-off value $\sqrt{\chi_{k,0.975}^2}$. For the orthogonal distances the approach of Box (1954) is followed. The squared orthogonal distances can be approximated by a scaled χ^2 distribution which in its turn can be approximated by a normal distribution using the Wilson-Hilferty transformation. The mean and variance of this normal distribution are then estimated by applying the univariate MCD to the $OD_i^{2/3}$.

Based on their cut-offs (c_{SD} and c_{OD}), these distances yield a classification of the observations (summarized in Table 1):

346

- the *regular data* are those observations whose SD and OD are both small, meaning SD $< c_{SD}$ and OD $< c_{OD}$
- the *good PCA-leverages points* have a large SD and a small OD, so SD $> c_{SD}$ and OD $< c_{OD}$
- the *orthogonal outliers* have a small SD and a large OD, yielding SD $< c_{SD}$ and OD $> c_{OD}$
- the *bad PCA-leverage points* having large SD and large OD which results in SD $> c_{SD}$ and OD $> c_{OD}$.

The latter two types of observations are highly influential for the classical PCA as this method tries to make all orthogonal distances as small as possible. For more information on this outlier map and the horizontal and vertical cut-off values, we refer to Hubert et al. (2005).

Table 1. Overview of the different types of observations based on their SD and OD

Distances	small SD	large SD
large OD	*orthogonal outlier*	*bad PCA-leverage point*
small OD	*regular observation*	*good PCA-leverage point*

On the robust outlier map of the Octane data, Figure 13-14, we immediately spot spectra numbers 25, 26, and 36-39 as bad PCA-leverage points. However, in Figure 13-15, the outlier map of the classical PCA, only spectrum 26 is indicated as a bad PCA-leverage point and spectrum 25 is indicated as an orthogonal outlier. This shows that the classical PCA was indeed influenced by the bad PCA-leverage points. They tilted the PCA-subspace towards them and hence masked the others for being recognized as bad PCA-leverage points in the classical analysis.
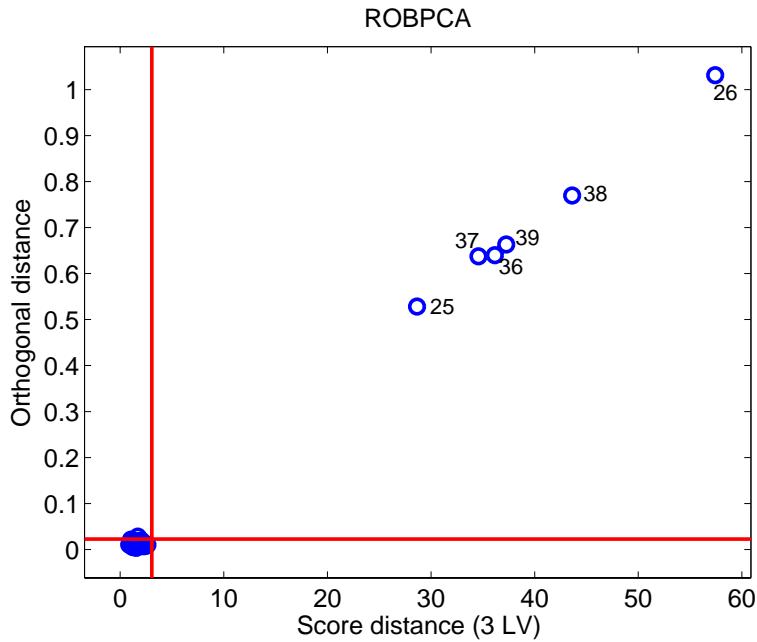
Figure 13-14. Octane data: robust score outlier map.
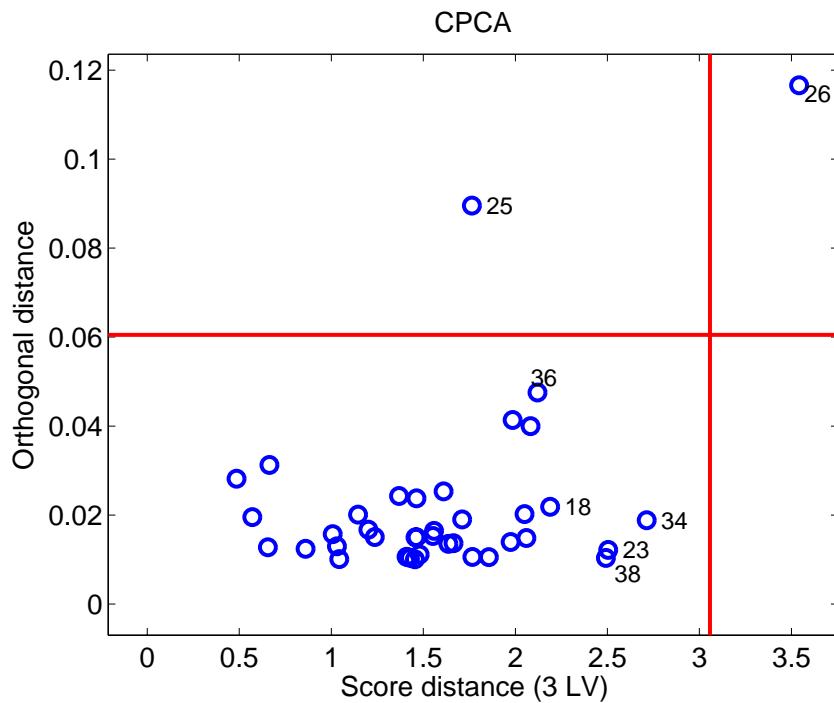
Figure 13-15 Octane data: classical score outlier map.

The same analysis can also be performed in the **Analysis** tool. Start the tool by typing *pca* at the MATLAB prompt. Load the variable *spec* into the tool by choosing **File/Load Data/Xblock** and selecting *spec* in the dialog box. Set the tool to perform robust PCA by selecting **Edit/Options/PCA Method Options**. A dialog box as shown in Figure 13-16

will appear. Set the menu to the right of 'algorithm' to 'robust pca', then click OK to close the window.
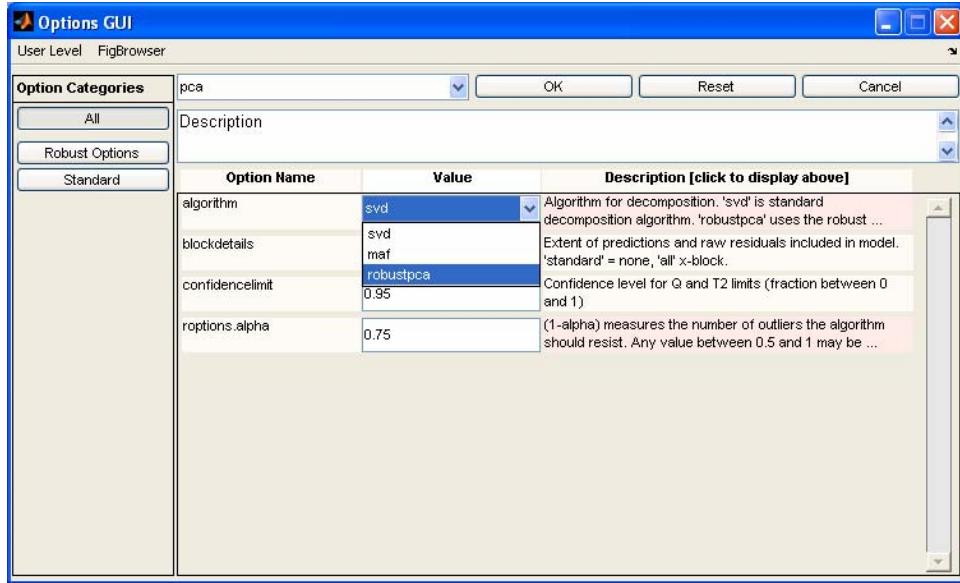
Figure 13-16. Options GUI from Analysis tool.

An analysis can now be done with robust PCA in the same manner as when one works with the interface with classical PCA. There are several important differences, however. Because the cutoff points are determined after the number of PCs has been specified, the robust PCA model is not nested; that is, the data the model is based on may change as the number of PCs is changed, and thus the early factors in the model may also be influenced. Thus, when the model is first calculated, the variance captured table only goes out to a one-PC model and subsequent PCs are not calculated. To see models with more PCs, click on the line of the table corresponding to the number of PCs desired and click **Calculate**.

Another important point is that robust PCA will set outlier data points to be excluded. To see these points, in the **Plot Controls** window choose **View/Excluded data**. The points will then show up as slightly grayed out.

Robust Regression for high-dimensional data

In case the number of variables n is larger than the number of observations m, there is no unique OLS solution, and neither can the LTS estimator be computed. Moreover, in any data set with highly correlated variables (multicollinearity), both OLS and LTS have a high variance. Two very popular solutions to this problem are offered by Principal Component Regression (PCR) and Partial Least Squares Regression (PLSR). Both methods first project the x-data onto a lower dimensional space, either based on maximizing variance described in the x-data (PCR) or based on maximizing the covariance between the x-data and y-data (PLS). The general idea is to compress the data

without losing important information. Next, a multiple (multivariate) regression analysis is performed in this lower dimensional design space.

More precisely, both PCR and PLSR assume the following bilinear model which expresses the connection between the response variable(s) and the explanatory variables as:

$$x_i = \mu_x + P \cdot t_i + f_i$$
$$y_i = \mu_y + \Theta^T \cdot t_i + g_i$$

(13-21)

with t_i the k-dimensional scores, Θ the k by q sized slope matrix in the regression of y_i on t_i, $k \ll p$ and $q \leq 1$. In terms of the original predictors this bilinear model can be rewritten as

$$y_i = \beta_0 + B^T x_i + e_i$$

(13-22)

The regression coefficients are then calculated as

$$B = P \, \Theta$$

(13-23)

$$\beta_0 = \mu_y - B^T \mu_x$$

(13-24)

To construct the scores t_i, PCR applies PCA to the x-variables, whereas in PLSR they are constructed by maximizing the covariance between linear combinations of the x and y-variables. As we are concerned with contaminated data, it is highly advisable to use robust alternatives. In analogy with classical PCR and PLSR, the robust versions apply ROBPCA on the x-variables, and on the joint (x,y)-variables, respectively. Next, a robust regression of the responses y_i on the robust scores t_i is applied. For PCR we can use the LTS or the MCD regression method, whereas for PLSR a regression based on the ROBPCA results is performed.

Robust Principal Component Regression

Example: The Octane data set (continued)

Let us return to the Octane data from the previous section. Besides the 39 NIR-spectra this data set also contains a univariate ($q = 1$) response variable which consists of the octane number for every sample. We know from previous analysis that the samples 25, 26, 36-39 were contained alcohol. We cannot use a classical least squares regression since the data clearly suffers from multicollinearity, so we apply a robust PCR analysis (Hubert and Verboven, 2003).

First we have to select the optimal number of components k_{opt}. Whenever we invoke the function rpcr with its default values, we can choose k_{opt} by looking at the plots of the robust R^2-values and the robust RSS-values.

```
>>load octane
```

```
>>rpcr(spec.data,octane.data)
```

In the univariate case (q = 1) the R^2-plot shows us the values

$$R_k^2 = 1 - \frac{\sum_{i=1}^{m} w_i r_{i,k}^2}{\sum_{i=1}^{m} w_i (y_i - \bar{y}_w)^2} \qquad (13\text{-}25)$$

with $\bar{y}_w = \sum_i w_i y_i / \sum_i w_i$ and k = 1,...,k_{max}. The R^2-value says in a robust sense that more than 95% of the y-variability can be described by the fitted model. The curve will become flat when adding a component does not reduce the residual variance significantly. We can choose the optimal k such that the R^2-curve attains a certain value, e.g. 80%, or until it becomes nearly flat. For the Octane data this means that $k = 3$ is a good choice, the curve becomes flat and the R^2-value already reaches more than 95%.

A second option is to look at the robust square root of the Residual Sum of Squares (RSS) also called the mean squared error (MSE)

$$\text{RSS}_k = \text{RMSE}_k = \sqrt{\frac{1}{\sum_{i=1}^{m} w_i} \sum_{i=1}^{m} w_i r_{i,k}^2} \qquad (13\text{-}26)$$

where $r_{i,k} = y_i - \hat{y}_{i,k}$ is the residual of the i-th observation of the calibration set in a k component model. From Figure 13-17, we see that for the Octane data a first minimum is reached at $k = 3$ and a second one in $k = 6$. The ultimate goal is to have a RMSE as small as possible but we also have to keep in mind that we are looking for a dimension reduction in order to have a manageable and interpretable model.
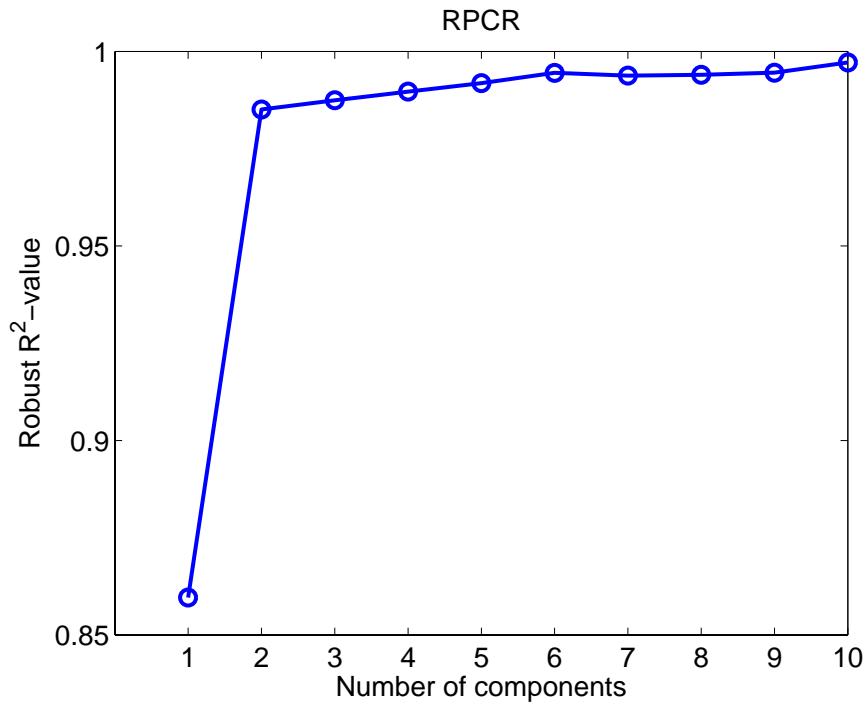
Figure 13-17. Octane data: the R^2-plot.
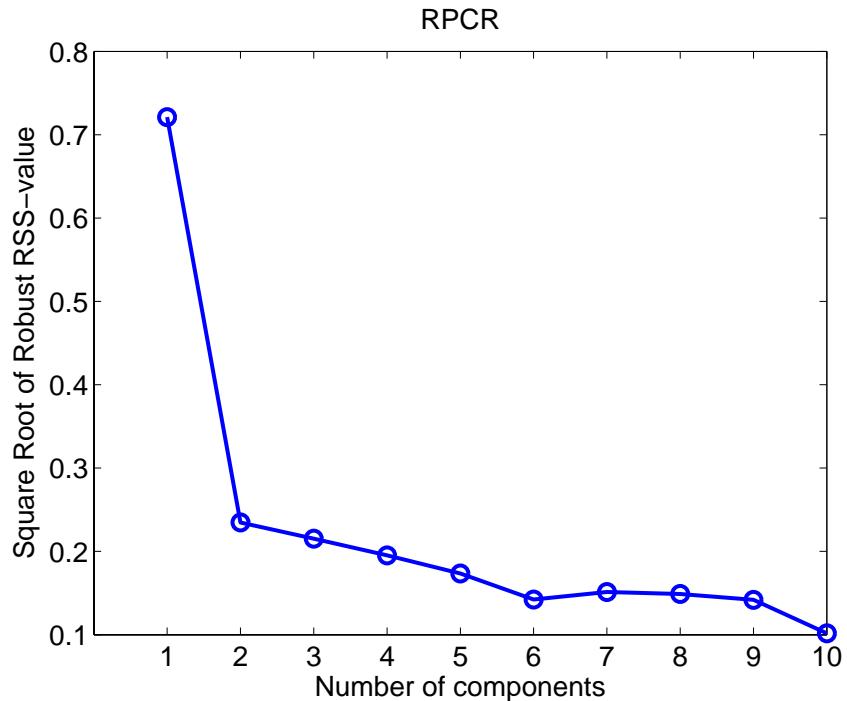
Figure 13-18. Octane data: RSS plot.

Comparing the $\text{RMSE}_6 = 0.0202$ against the $\text{RMSE}_3 = 0.0464$ gives us a 2% decrease in the error. Moreover, by looking at the R^2 we already know that we have a good prediction

model at $k = 3$. Taking all facts into account we decide to take 3 as the optimal number of components for this model.

Thus far, the decision about k_{opt} was based on the calibration data. It is also possible to perform a cross-validated version of the RMSE. The RMSECV can be defined in a robust way by taking into account weights w_i

$$\text{R-RMSECV}_k = \sqrt{\frac{1}{\frac{1}{m}\sum\limits_{i=1}^{m} w_i} \sum\limits_{i=1}^{m} w_i \left(y_i - \hat{y}_{-i,k} \right)^2} \qquad (13\text{-}27)$$

for univariate response variables y_i. Now, if we choose k_{opt} too small, much of the information in the data will be lost. Moreover, the regression model will not fit the data very well. On the other hand, if k_{opt} is too large, overfitting will cause a loss of prediction power because the regression model was fit to the noise in the data. So instead of making a decision about the optimal number based on a statistic explaining the predictive ability (e.g. the RMSECV) or the goodness-of-fit (e.g. RMSE) alone, let us look at a combination of these measurements.

$$\text{RCS}_k = \sqrt{\gamma\ \text{R-RMSECV}_k^2 + (1-\gamma)\ \text{R-RMSE}_k^2}\ ,\ 0 \le \gamma \le 1. \qquad (13\text{-}28)$$

The Robust Component Selection statistic (RCS) as proposed by Engelen and Hubert (2005) allows us to choose whether we like to emphasize on the prediction ($\gamma = 1$) or on the goodness of fit ($\gamma = 0$) aspects of our regression model.
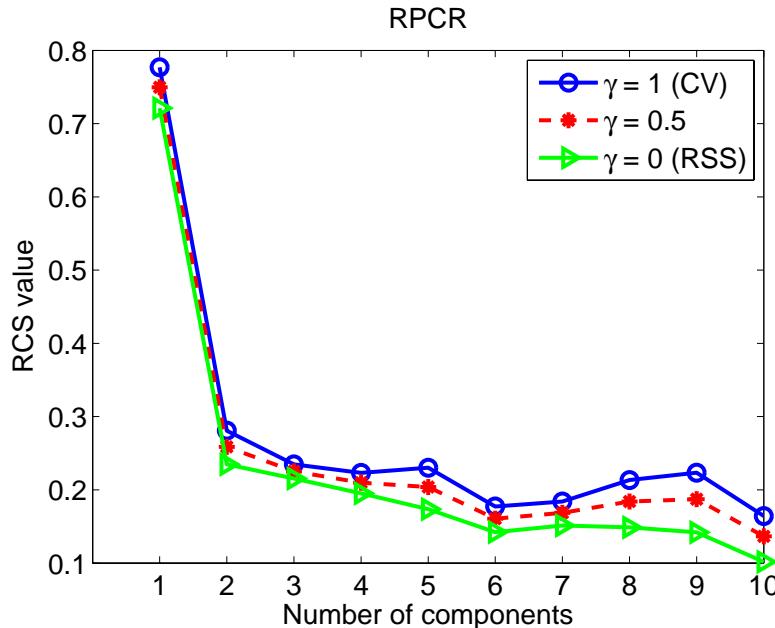
Figure 13-19. Octane data: Robust Component Selection plot.

Based on the curves in Figure 13-19, we decide to take $k = 3$ as our optimal choice for the Octane data. To produce this plot we have to call the rpcr function with the optional input variable 'rmsecv' set to one.

```
>> out = rpcr(X, y, 'rmsecv',1)
```

The output of the `rpcr` function also includes the score and orthogonal distances from the robust PCA analysis. By default, the PCA-score outlier map will again be plotted (Figures 13-14). In addition, both classical and robust residual outlier maps (Figures 20-21) are generated. The function displays the standardized LTS residuals versus the score distances, and can be used to classify the observations according to the regression model. As can be seen from Table 2, we distinguish *regular data* (small SD and small absolute residual), *good leverage points* (large SD but small absolute residual), *vertical outliers* small SD and large absolute residual), and *bad leverage points* (large SD and large absolute residuals). Large absolute residuals are those that exceed $\sqrt{\chi^2_{1,0.975}} = 2.24$. Under normally distributed errors, this happens with probability 2.5%. The vertical outliers and bad leverage points are the most harmful for classical calibration methods as they disturb the linear relationship.

Table 2. Overview of the different types of observations based on their SD and ResD distances

Distances	small SD	Large SD
large ResD	*vertical outlier*	*bad leverage point*
small ResD	*regular observation*	*good leverage point*

In Figure 13-20 we observe the six outlying spectra as good leverage points in the robust PCR regression model. Four other spectra are detected as vertical outliers (spectra 7, 9, 13, and 32) and should be investigated in more detail. The classical PCR, on the other hand, does not discover the vertical outliers (Figure 13-21). Only spectrum 26 is highlighted as a good leverage point. The presence of contamination in the data clearly affected the classical analysis.

354
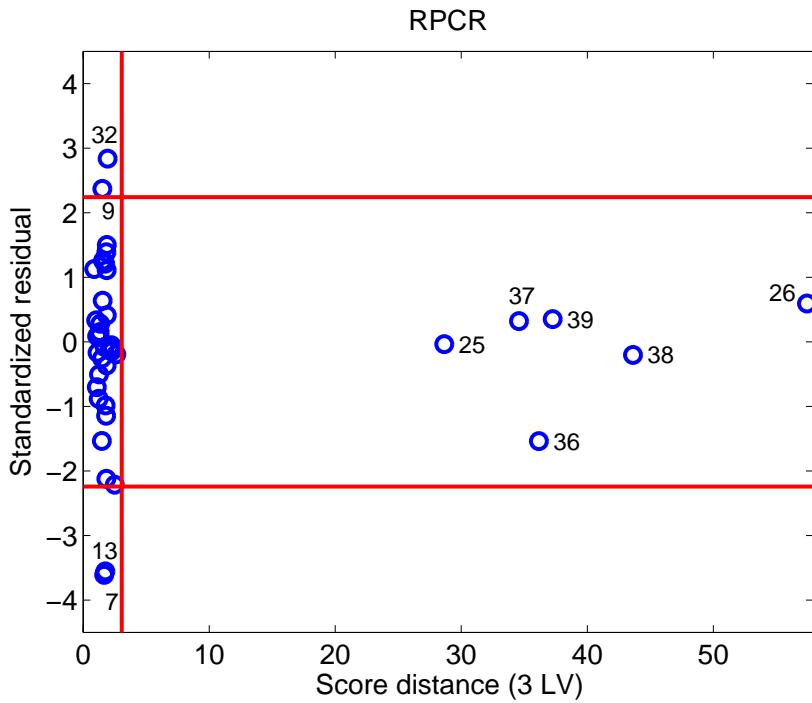
Figure 13-20. Octane data: robust regression outlier map.
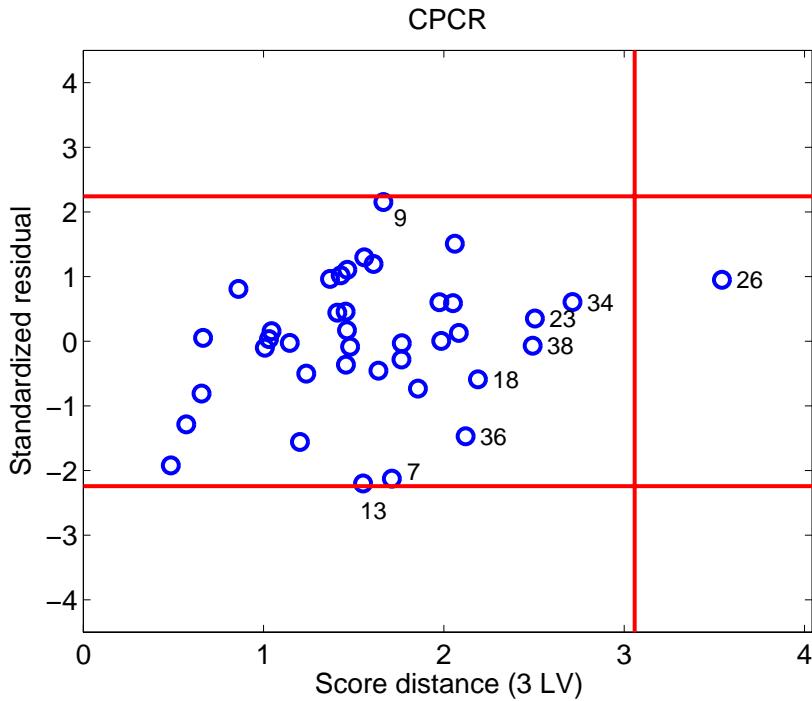
Figure 13-21. Octane data: classical regression outlier map.

Robust PCR can be performed in the **Analysis** GUI. Start the **Analysis** GUI by typing `pcr` at the command lin, or by starting the interface any other way and selecting

Analysis/PCR. Choose **File/Load Data/Both** from the menu and select spec for the x-data and octane for the y-data. Choose **Edit/Options/Method Options (PCR)**, which will bring up the window shown in Figure 13-22. Next to the algorithm label, select robustpcr from the menu, then click OK. Select **Preprocess/X-block/mean center**. A model can now be calculated by clicking the **Calculate** button. Note, however, that the variance captured table does not go beyond the first PC. To calculate a three-PC model, select the third line of the variance captured table and click **Calculate** again. The interface will now appear as shown in Figure 13-23. The PCR model can now be explored in the usual way. When viewing scores plots, choose **View/Excluded Data** to view the scores of the data points considered outliers and not used in the final model calculation.
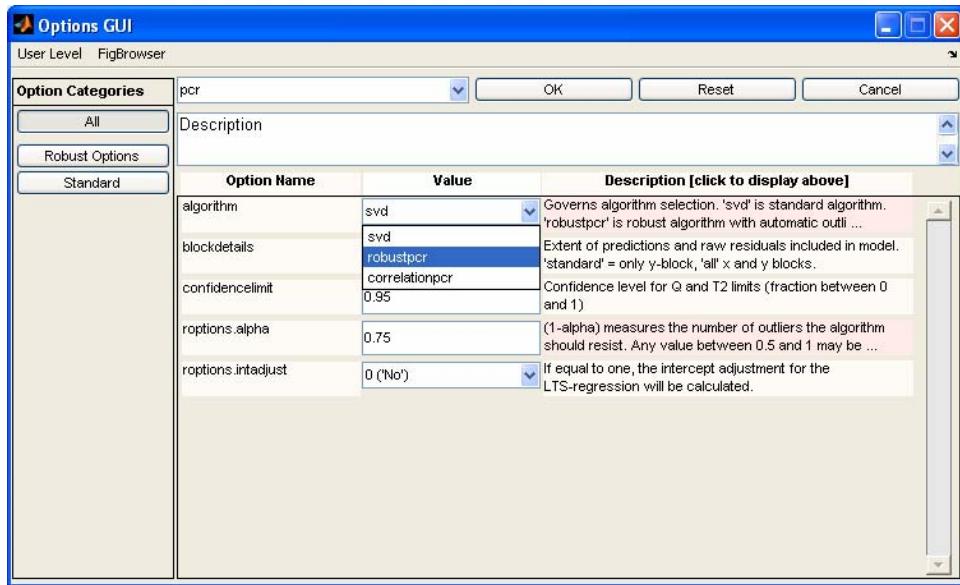
Figure 13-22 Options interface for PCR.
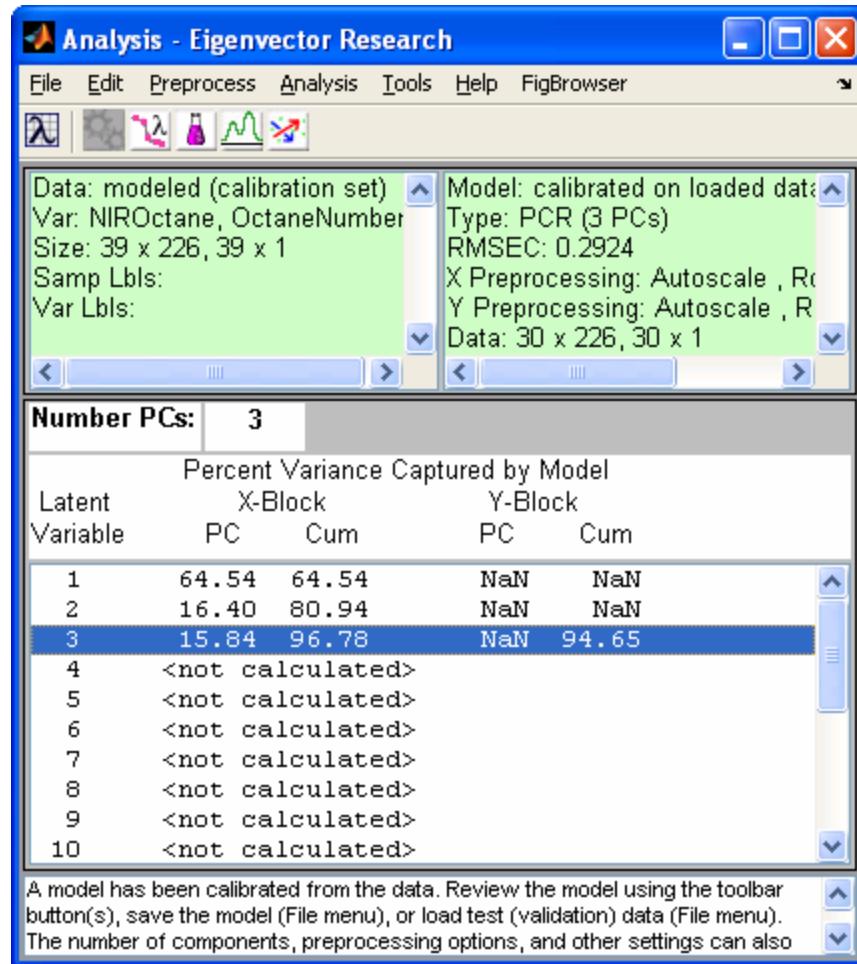
Figure 13-23 Analysis interface with robust PCR model variance captured table.

Robust Partial Least Squares Regression

Hubert and Vanden Branden (2003) developed a robust version of PLS known as RSIMPLS. The method starts by applying ROBPCA on the joint x- and y-variables in order to replace the empirical cross-covariance between X and Y and the empirical covariance matrix of X, by robust estimates, and then proceeds analogously to the SIMPLS algorithm. At the end, instead of the multivariate linear regression (MLR), a robust regression method will be performed.

The proposed robust PLS algorithm has several equivariance properties. The ROBPCA method is orthogonally equivariant, which means that orthogonal transformations of the data (rotations, reflections) transform the loadings appropriately and leave the scores unchanged. Consequently, it can easily be derived that RSIMPLS is equivariant for translations and orthogonal transformations in x and y. More precisely, let $\boldsymbol{u} \in \mathrm{IR}^n$, $\boldsymbol{v} \in \mathrm{IR}^q$, $\boldsymbol{C}$ any n-dimensional orthogonal matrix and $\boldsymbol{D}$ any q-dimensional orthogonal matrix. If $\left(\hat{\beta}_0, \hat{\mathrm{B}}\right)$ denotes the estimates by running RSIMPLS on the original data $(\boldsymbol{x}_i, \boldsymbol{y}_i)$, it holds that:

357

$$\hat{B}(Cx_i + u, Dy_i + v) = C\hat{B}D^T$$

$$\hat{\beta}_0(Cx_i + u, Dy_i + v) = D\hat{\beta}_0 + v - D\hat{B}^T C^T u$$

(13-29,30)
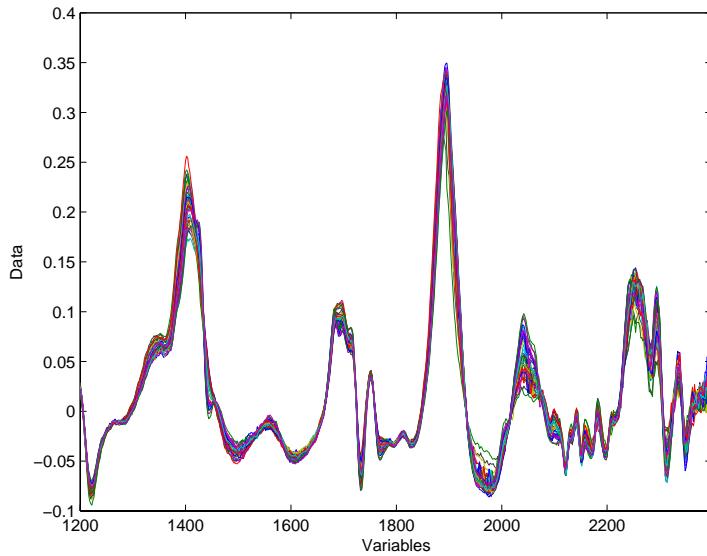
Figure 13-24. Biscuit data : raw spectra.

<u>Example</u>: Biscuit Dough data (Osborne *et al.*, 1984)

This data set consists of 40 NIR reflectance spectra of biscuit dough with measurements every two nanometers, from 1200nm up to 2400nm. The responses are the percentages of four constituents in the biscuit dough: y_1 = fat, y_2 = flour, y_3 = sucrose and y_4 = water.

The data can be viewed by executing the following MATLAB commands:

```
>> load biscuit
>> plotgui(spec)
```

From the **Plot Controls Window**, select **Plot/Data Summary**, then select **Data** from the menu for Y data. The plot shown in Figure 13-24 is the result.

Because there is a significant correlation among the regressors, it is appropriate to perform a multivariate regression. This can be done from the MATLAB command line with the rsimpls function as follows:

```
>> out = rsimpls(spec.data,recipe.data)
```
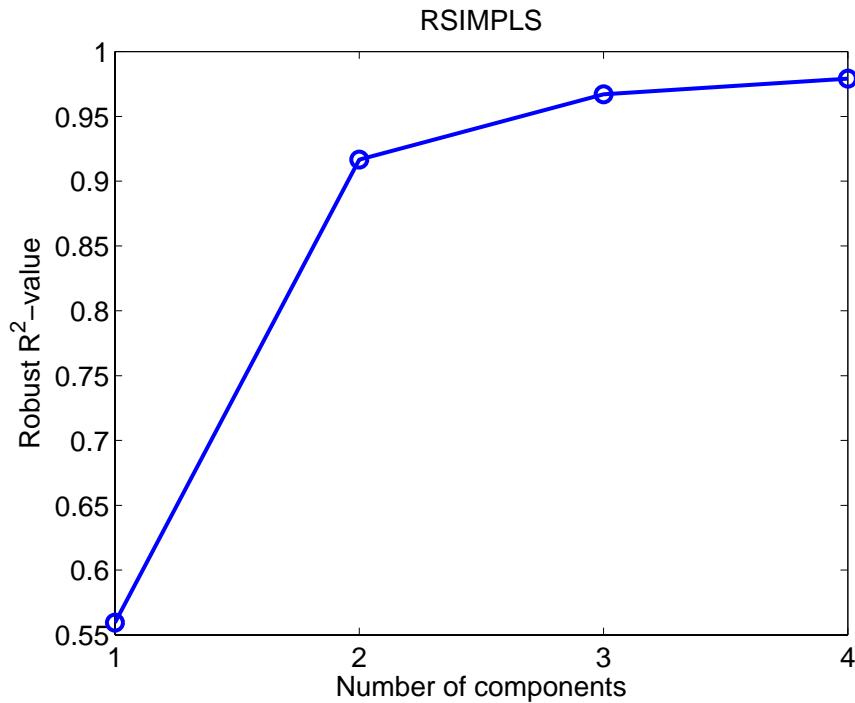
Figure 13-25. Biscuit data : Robust R^2-plot.
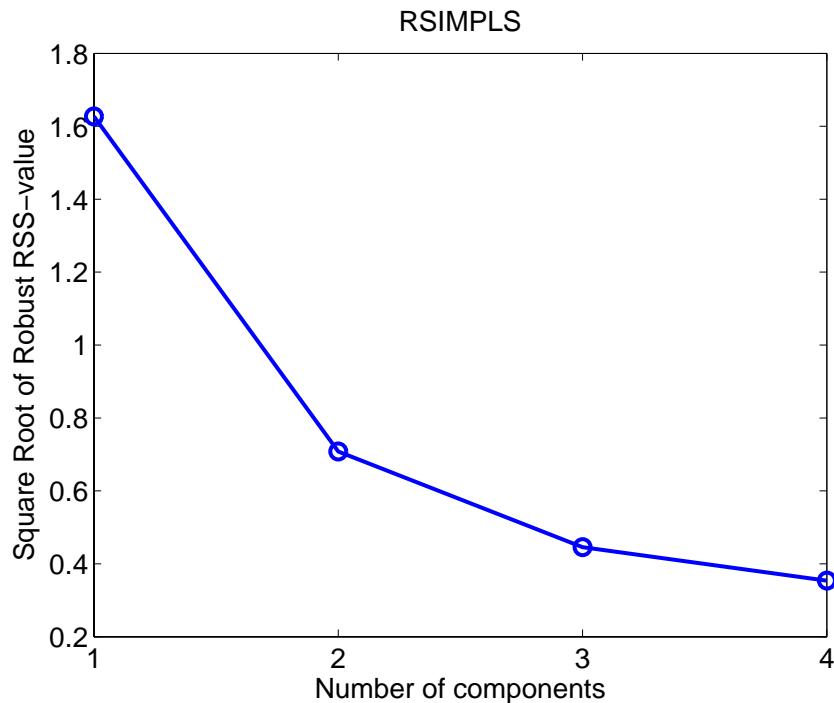
Figure 13-26. Biscuit data: Robust RSS plot.

In this example the number of components k is limited to 4 by the algorithm to avoid overfitting. Similar to the RPCR analysis, we draw plots (Figures 13-25 and 13-26) to

select the optimal number of components. Retaining three components gives us a R^2 of 96.7% and a RMSE of 0.4456.
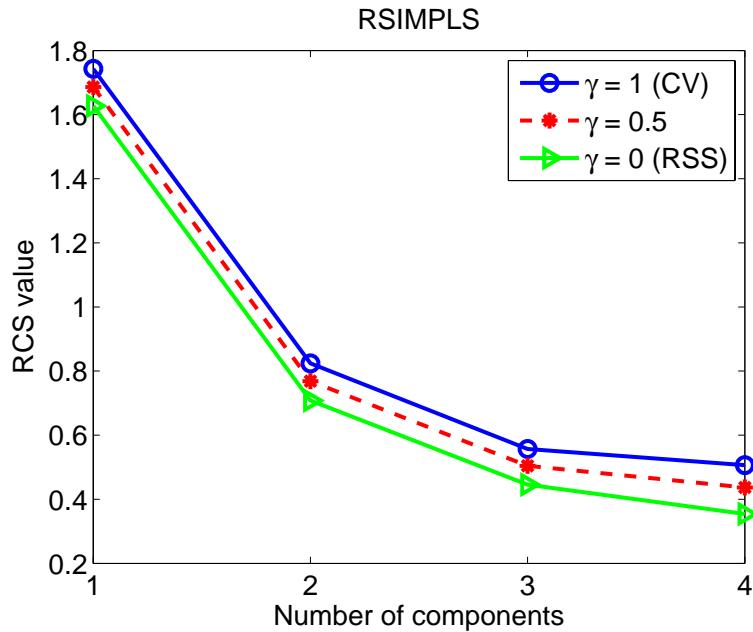
Figure 13-27. Biscuit data : Robust Component selection plot.

Calculating a leave-one-out cross validated RMSE (Figure 13-27) also leads to the conclusion that $k_{opt} = 3$.

The robust score outlier map shows four bad PCA-leverage points: spectra 20, 21, 23, and 24. Observation 7 is an orthogonal outlier. The classical score outlier map, howeve, only reveals observation 23 and observation 15 as outliers. Moreover, spectrum 23 is considered to be a good PCA-leverage point. This shows again that the bad PCA-leverages have such a large impact on the classical PCA-step of the algorithm that the 3-dimensional PCA-subspace also tries to enclose them and consequently camouflages these outliers.
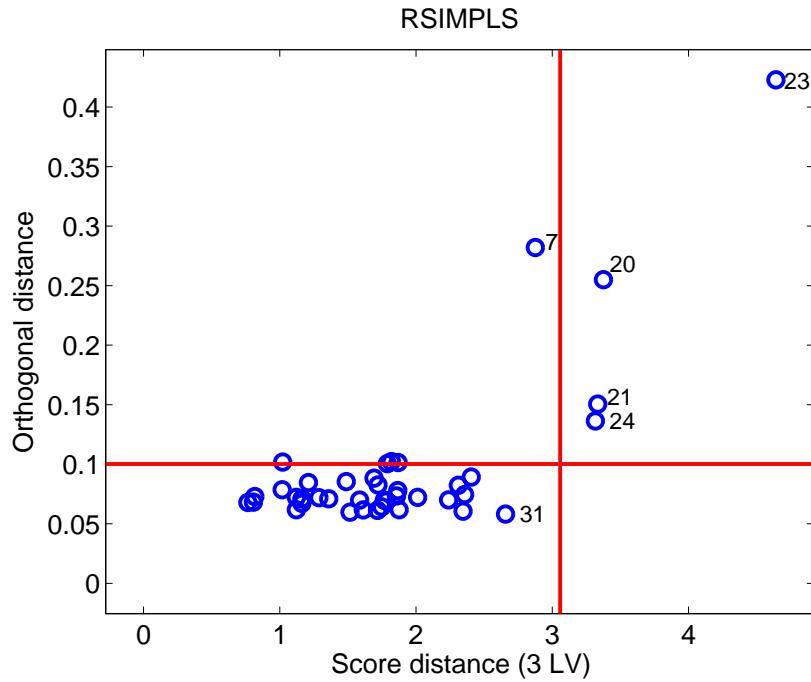
Figure 13-28. Biscuit data: Robust score outlier map.
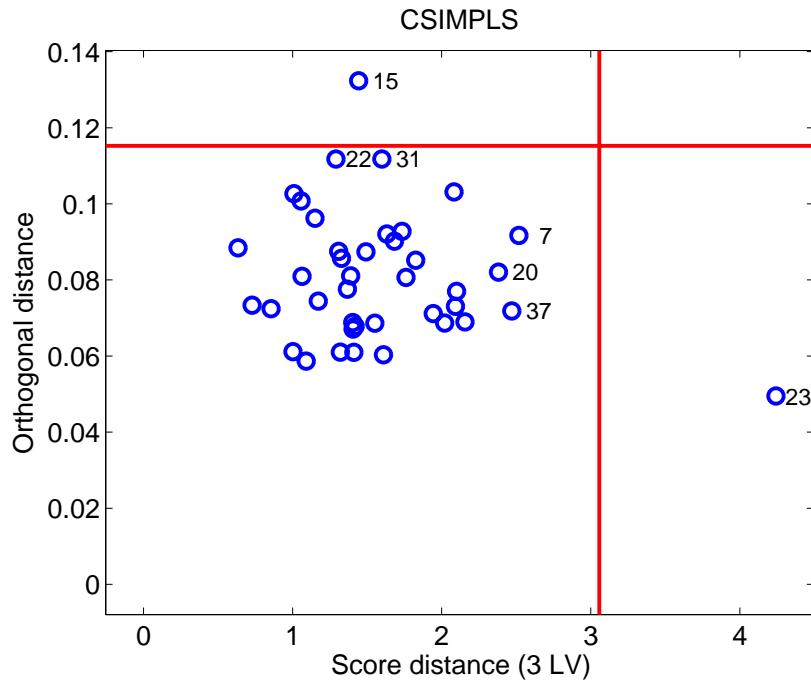
Figure 13-29. Biscuit data: Classical score outlier map.

For the Biscuit Dough data set, we obtain regression outlier maps for the robust (Figure 13-28) and the classical SIMPLS (Figure 13-29) which are slightly different from the regression outlier maps we found for the Octane data. In multivariate calibration ($q > 1$),

the residuals are also q-dimensional with estimated covariance matrix $\hat{\Sigma}_\varepsilon$. On the vertical axis the outlier map then displays the residual distances, defined as

$$\text{ResD}_i = \sqrt{\mathbf{r}_i^T \hat{\Sigma}_\varepsilon^{-1} \mathbf{r}_i} \tag{13-31}$$

with cut-off value $\sqrt{\chi^2_{q,0.975}}$.

RSIMPLS shows that observation 21 has an extremely high residual distance. Other vertical outliers are 7, and 22, whereas there are a few boundary cases. The bad leverage points spotted in Figure 13-30 are the spectra 20, 23, and 24. The classical SIMPLS on the other hand tries to make all the residuals as small as possible, resulting in exposing one clear vertical outlier 21. As in Figure 13-31, observation 23 is also distinguished, but due to its large score distance rather than to its residual distance, so it seems to fit the regression model rather well.

Robust PLS can be performed in the analysis interface by selecting Analysis/PLS from the menu, then selecting Edit/Options/Method Options (PLS). In the interface select robust PLS from the menu next to algorithm. The analysis then proceeds as usual. To view outlier data points, select View/Excluded Data from the plot controls window when viewing scores plots.
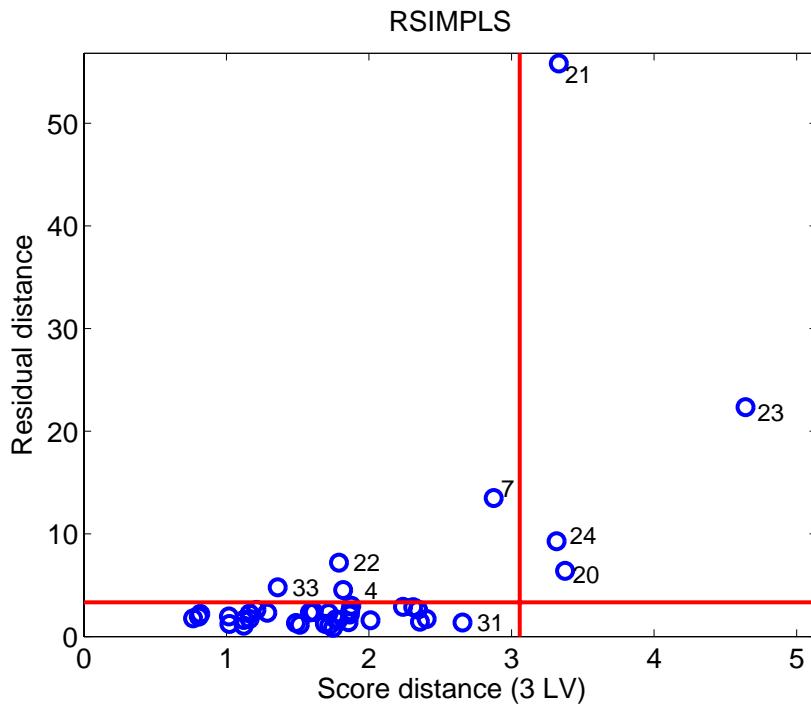
Figure 13-30. Biscuit data : robust regression outlier map.
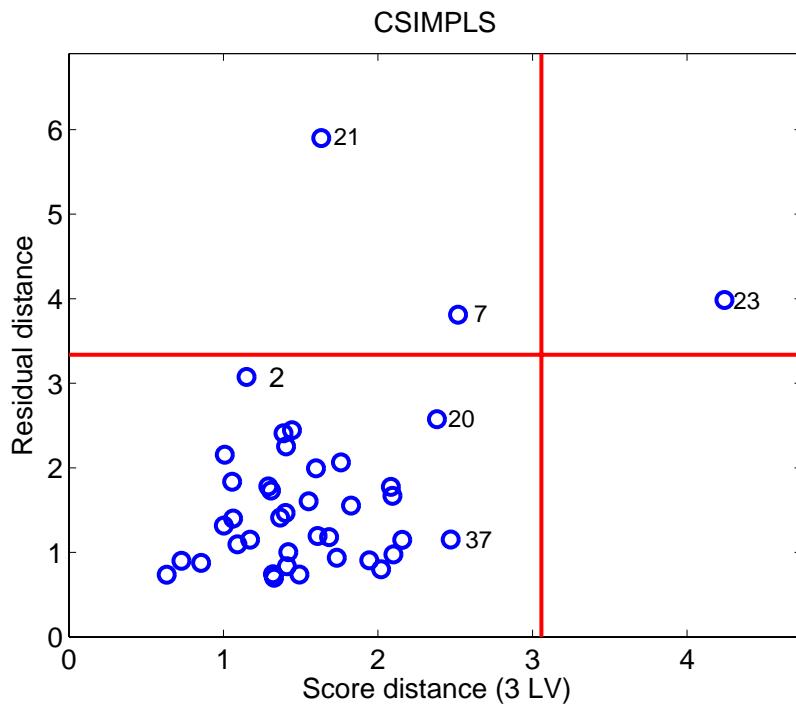
Figure 13-31. Biscuit data: classical regression outlier map.

14. Distribution Fitting Tools

NOTE: Throughout this section, we assume that you will want to investigate the distributional properties of a vector of data. The data should be stored as a column vector in MATLAB. Our examples in this section use random data generated by specifying

```
>> x = normdf('random',[100 1])
```

The Distribution Fitting Tool Set supplies capabilities for investigating the distribution of a sample of data. This includes functions for graphically assessing the fit of a sample to a distribution, as well as formal statistical tests. In addition, these tests and plots may be incorporated in your own analytical tools.

Probability Distributions

The Distribution Fitting Tool Set supports sixteen distributions. For each distribution, there is a function input describing the method being called. These methods include:
- Probability density function (`'density'`, `'d'`)
- Cumulative probability (distribution) function (`'cumulative'`, `'c'`)
- Quantile (inverse probability) function (`'quantile'`, `'q'`)
- Random number generator (`'random'`, `'r'`)

Table 14.1 lists the available distributions and their associated function names.

Table 14.1. Distributions and their function names.

Distribution	Function Name
Beta	`betadf`
Cauchy	`cauchydf`
Chi-squared	`chidf`
Exponential	`expdf`
Gamma	`gammadf`
Gumbel	`gumbeldf`
Laplace	`laplacedf`
Logistic	`logisdf`
Lognormal	`lognormdf`
Normal	`normdf`
Pareto	`paretodf`
Rayleigh	`raydf`
Student's t	`tdf`
Triangle	`triangledf`
Uniform	`unifdf`
Weibull	`weibulldf`

So, to find the quantile of the normal distribution for a value of 0.975 (for a two-sided test of the mean at, for instance, significance level 0.05), we can type:

```
>> normdf('q',0.975,0,1)
ans =
1.9600
```

All the above commands can be used either in an interactive way or in your own functions and scripts. In addition, the sixteen distributions are also supported in the goodness-of-fit tests and statistical plots. Commands that support the distributions expect you to provide the name of the distribution as one of the input arguments. Below is a table of names along with minimal acceptable abbreviations. Note that you do not have to abbreviate the distribution name if you choose not to.

Distribution	Abbreviation	Distribution	Abbreviation
Beta	bet	Lognormal	logn
Cauchy	cau	Normal	nor
Chi-squared	chi	Pareto	par
Exponential	exp	Rayleigh	ray
Gamma	gam	Student's t	stu
Gumbel	gum	Triangle	tri
Laplace	lap	Uniform	uni
Logistic	logi	Weibull	wei

These names are used for commands such as
```
plotqq(x,'distribution')
plotcqq(x,'distribution')
parammle(x,'distribution')
```

where `distribution` is the name (which may be abbreviated as indicated in the table) of the candidate distribution to consider in the command. For example, we can test the consistency of the random number generator and estimator at the same time (for the exponential distribution in this case) by typing:

```
>> parammle(rexp(100000,3.5),'exp')
ans =
a: 3.5031
b: 0
```

Parameter Estimation

You can obtain best-fit parameter estimates for the supported distributions with the `parammle` command. Note that the command returns a structure with up to three parameter estimates. See the Reference Manual entries for details on individual distributions.

```
>> n = normdf('r',[1000 1],3,2) ;
```

Now, using this randomly generated data (from known distributions), let's see how the command can be used to find the maximum likelihood estimates of the candidate distributions.

```
>> parammle(n,'normal')
ans =
a: 2.9097
b: 1.9691
```

Note that some distributions (beta, Cauchy, gamma, Gumbel, and Weibull) will take longer to find the maximum likelihood estimates, as the estimators are not analytically known. Instead, they are solved for by optimizing the likelihood. The next step in estimating parameters is to decide if the distribution with the maximum likelihood estimates for the associated parameters fits the data (the sample). Assessing the fit is the subject of the next two sections.

Hypothesis Tests

The Distribution Fitting Tool Set includes tests to formally assess the fit of data to distributions. In the previous section, we generated 1000 random numbers from a normal distribution. What if we had asked for the maximum likelihood estimates for the exponential distribution? We would have seen

```
>> parammle(n,'exponential')
ans =
a:0.3136
```

While we have obtained estimates for the distribution parameters, we have not obtained any information about how well that distribution fits the data in our sample. To do that, we use the testing commands. Below, we illustrate their use.

```
>> chitest(n,'normal')
ans =
chi2: 14.1162
pval: 0.7215
df: 18
classes: 19
parameters: [1x1 struct]
E: [1x19 double]
O:[1 10 13 21 47 57 97 108 126 139 115 108 59 50 27 10 6 4 2]
```

Using the defaults for the $B(v,w) = \int_0^1 u^{v-1}(1-u)^{w-1}\,du$ test (chi-squared test), we see that the first member of the returned structure is the test statistic and the second member is the

associated *p*-value. The null hypothesis of the test is that the candidate distribution is the parent distribution of the sample and the result of our test is not significant; there is not enough evidence to reject the hypothesis that the data come from a normal distribution. This is good as we actually synthesized the data from a normal distribution. Let's see what the test has to say for the logistic distribution.

```
>> chitest(n,'logistic')
ans =
chi2: 25.3681
pval: 0.1151
df: 18
classes: 19
parameters: [1x1 struct]
E: [1x19 double]
O:[1 10 13 21 47 57 97 108 126 139 115 108 59 50 27 10 6 4 2]
```

Again we fail to reject the hypothesis. This time the hypothesis was that the parent distribution was the logistic distribution. If we were faced with these results in practice, we would conclude that the normal distribution was a more likely candidate, as the *p*-value for that test was less significant; there was even less evidence to reject the normal distribution as the parent distribution. In practice, you will see that it is common to have a situation where more than one distribution can be used to characterize the sample. How about if we look at a more asymmetric distribution like the beta distribution?

```
>> chitest(n,'beta')
ans =
chi2: 57.1553
pval: 5.8475e-006
df: 18
classes: 19
parameters: [1x1 struct]
E: [1x19 double]
O:[1 10 13 21 47 57 97 108 126 139 115 108 59 50 27 10 6 4 2]
```

The results here show significant evidence (at 0.0000058 level) that the parent distribution is not the beta distribution. Did you notice that the result of the test is a structure? The `parameters` field of the returned structure contains the maximum likelihood estimates for the candidate distribution. Using the test is another way (different from using the `parammle` command) to obtain these estimates.

Another test is the Kolmogorov-Smirnov test. This test is less powerful than the chi-squared test as it does not provide a p-value. However, since the probability value (were it included) is a monotonic function of the returned statistic (Dn), we can base our conclusions on the statistic itself. The smaller the value of the returned statistic, the less evidence exists to reject that candidate distribution. So, if we were looking for the best candidate, we would choose the one with the smallest value of the Kolmogorov-Smirnov statistic.

```
>> kstest(n,'normal')
ans =
ks: 0.4894
Dn: 0.0155
parameters: [1x1 struct]
>> kstest(n,'logistic')
ans =
ks: 0.8606
Dn: 0.0272
parameters: [1x1 struct]
>> kstest(n,'exponential')
ans =
ks: 9.9796
Dn: 0.3156
parameters: [1x1 struct]
```

Again, we would conclude (based on these three comparisons) that the normal distribution best fits the data because the value of Dn is smallest for the most likely parent distribution. Instead of using these commands, however, we can use the `distfit` command to report the fit statistics for all of the distributions.

The command `distfit(n)` reports the results from most-likely to least-likely parent distribution using the chi-squared test.

```
            p-value   Distribution
            0.7215    Normal
            0.1151    Logistic
            0.0017    Weibull
            0.0000    Beta
            0.0000    Laplace
            0.0000    Uniform
            0.0000    Triangle
            0.0000    Rayleigh
            0.0000    Pareto
            0.0000    Lognormal
            0.0000    Gumbel
            0.0000    Gamma
            0.0000    Exponential
            0.0000    Chi squared
            0.0000    Cauchy

  Ordered from most likely to least likely parent distribution.
      P-values are for rejecting the associated distribution
```

It has been said that a picture is worth a thousand words, so the next section presents those commands that allow you to illustrate the fit of a distribution to the sample. You can do either before or after you have looked at the formal statistical test results.

Using these tests is backwards from most statistical analyses. Usually one wishes to reject the null hypothesis in some specific case, such that one may conclude the alternative hypothesis. In this case, however, we wish to reject all but one of the tests, such that we then conclude that there is evidence to exclude all but one possible parent distribution for the data. In many cases, we will fail to reject more than one test and must then choose one of the candidate distributions. We can do that by choosing the one with the smallest test statistic and therefore the least amount of evidence for rejection.

Statistical Plots

There are many plots available from the Distribution Fitting Tool Set; examples of each are included here. The data were generated as random Gaussian variates with mean zero and variance one, using the normdf command included in the Tool Set. On the left in Figure 14-1 is a symmetry plot. This plot illustrates the symmetric properties of a dataset. The plot on the right is a percentile plot.

a)   b)
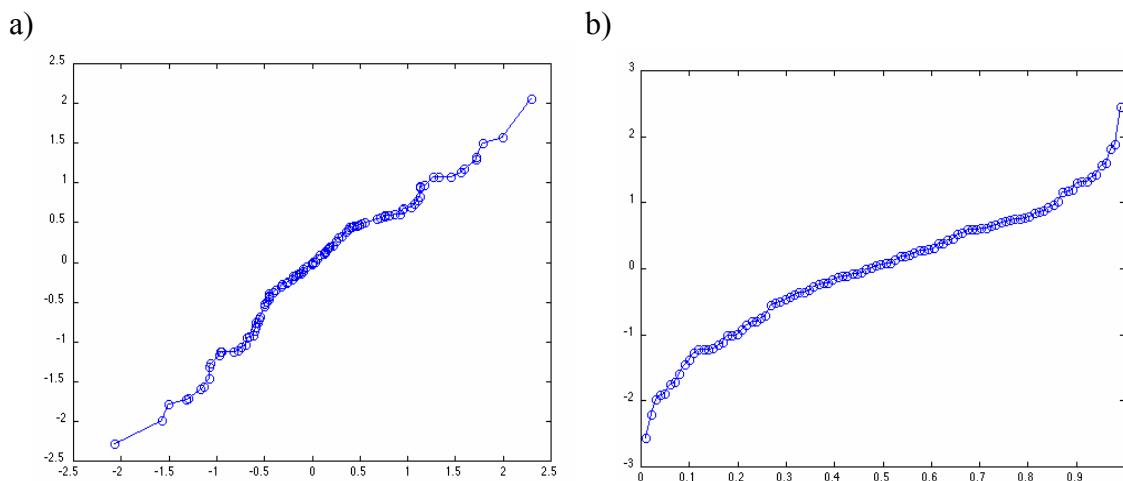
Figure 14-1. a) Symmetry plot (PLOTSYM)of 100 random normals, b) Percentile plot (PLOTPCT) of 100 random normals.

In addition to these exploratory data plots, the Tool Set includes commands for graphically investigating the distributional properties of a sample. One can produce empirical distribution plots, quantile plots (comparing to each of the supported distributions), conditional quantile plots (comparing to each of the supported distributions), and kernel density plots (comparing to each of the supported distributions).

The empirical distribution plot is a plot of the estimated cumulative distribution. All cumulative distributions, F(x), have the following properties:
1. $F(x_1) \geq F(x_2)$ if $x_1 \geq x_2$
2. $F(-\infty) = 0$
3. $F(\infty) = 1$.

For our sample of random normals (created using the command x=normdf('r',[100 1])), the empirical distribution plot obtained from plotedf(x) is shown in Figure 14-2.

370
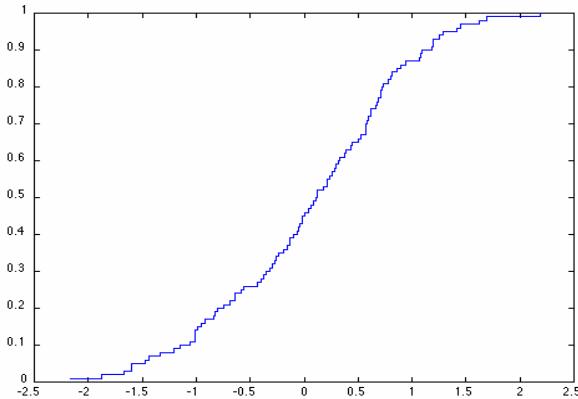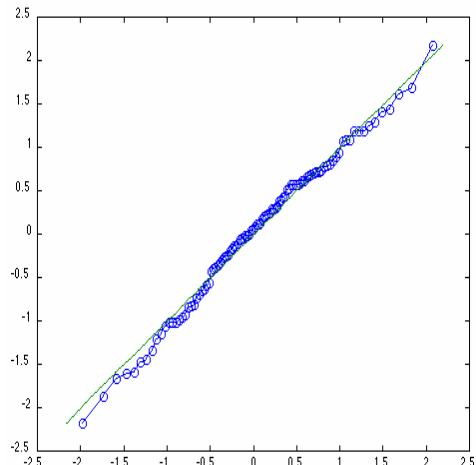
Figure 14-2. Empirical distribution plot.

The quantile plot is used to graphically assess the fit of a sample to a candidate distribution. More accurately, this is called a quantile-quantile plot, because it depicts a graph of the sample quantiles versus the quantiles of the candidate distribution. Figure 14-3 illustrates the quantile plot of our sample with the normal (correct) distribution (left) and the best-fit exponential distribution (right). The fit of the candidate distribution is assessed graphically by noting that using the correct distribution results in a diagonal line in the quantile plot. The plot on the left was obtained by specifying `plotqq(x,'normal')` and the plot on the right was obtained by specifying `plotqq(x,'exp')`.

a)   b)
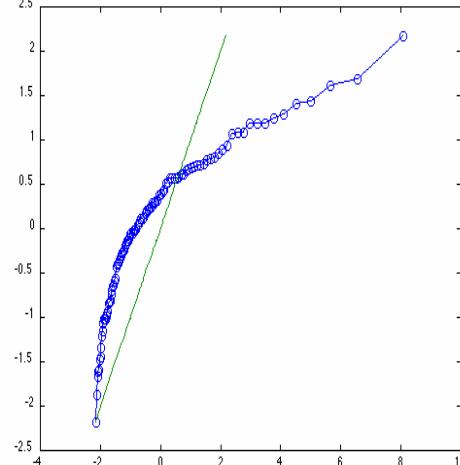
Figure 14-3. a) Quantile plot for normal distribution, b)Quantile plot for exponential distribution.

Note how the quantiles for the best-fit normal distribution fall along the solid diagonal line in the graph on the left, but the quantiles of the best fit exponential distribution do not coincide with a diagonal line.

In the Distribution Fitting Tool Set, the best-fit distributions include offsets such that the entire distribution is shifted to accommodate the range of the sample data. In addition to

371

plotting the quantile plots using the `plotqq` command, we could also use the `qtool` interactive tool to choose candidate distributions for comparisons. This tool is illustrated in Figure 14-4.
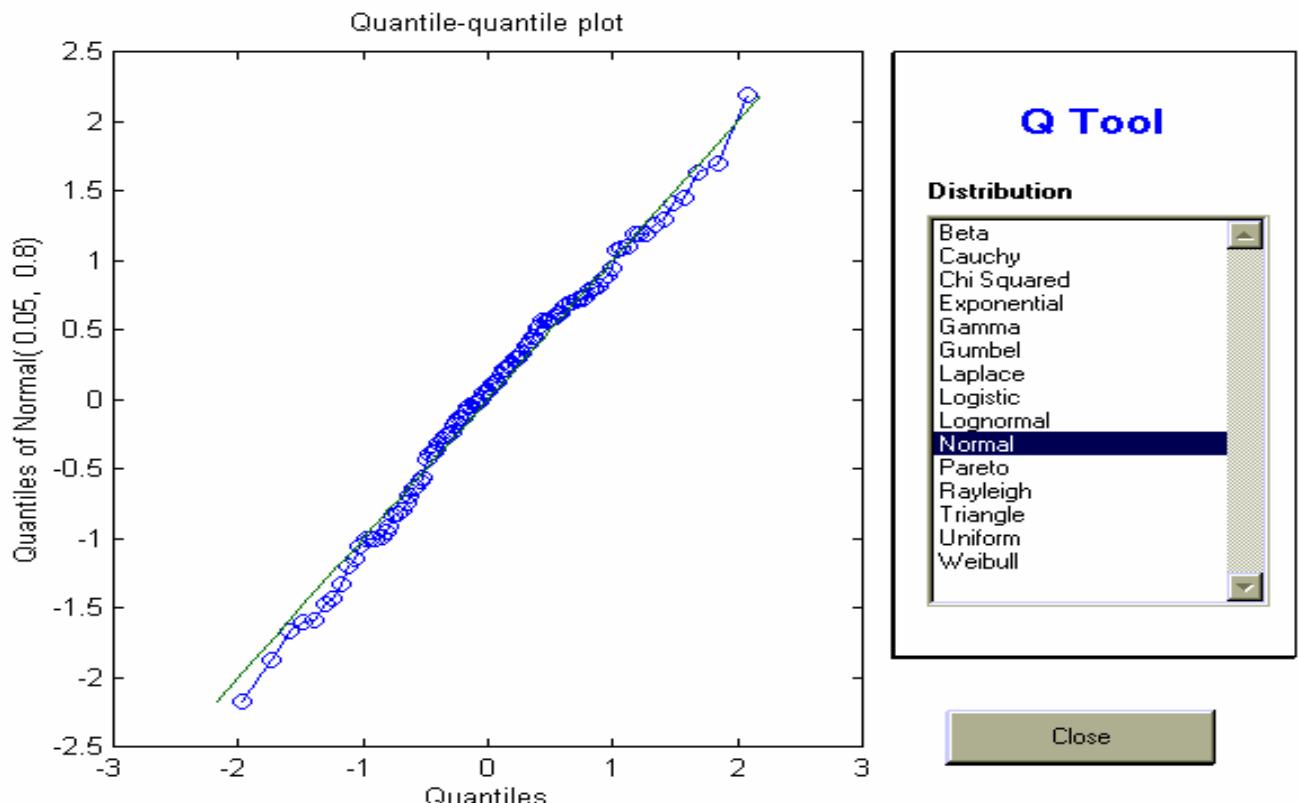
Figure 14-4. PLOTQQ GUI interface.

Conditional quantile plots as described in by Kafadar and Spiegelman (1986) are also available in this Tool Set.

Another method for investigating the density of a sample is to plot a density estimate. Density estimates are available from the toolbox where the density is calculated using a kernel density estimate. The user may use the interactive commands to investigate various kernel density estimates or may use the `ktool` graphical tool.

Figure 14-5 shows two density estimates. On the left is a density estimate using the Epanechnikov kernel with an overlaid best-fit normal density, and on the right is a density estimate using the Parzen kernel with an overlaid best-fit exponential density.
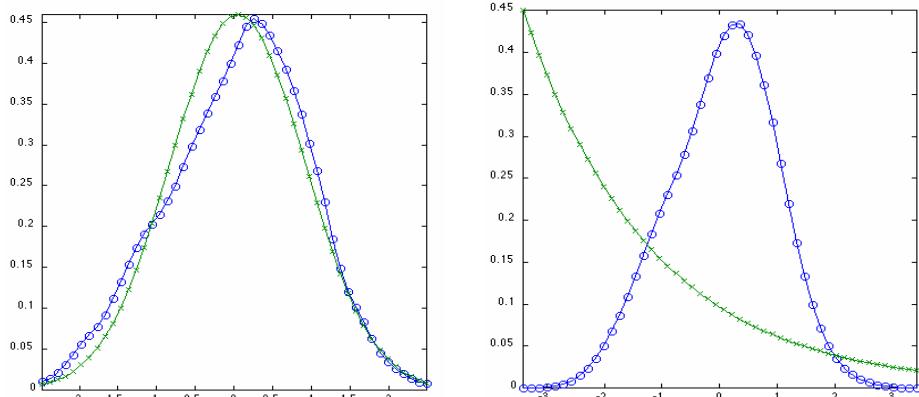
Figure 14-5. Density estimate plots.

Using the interactive tool (Figure 14-6) makes it easy to overlay different candidate distributions, select kernels, and alter the bandwidth selection for the kernel estimator.
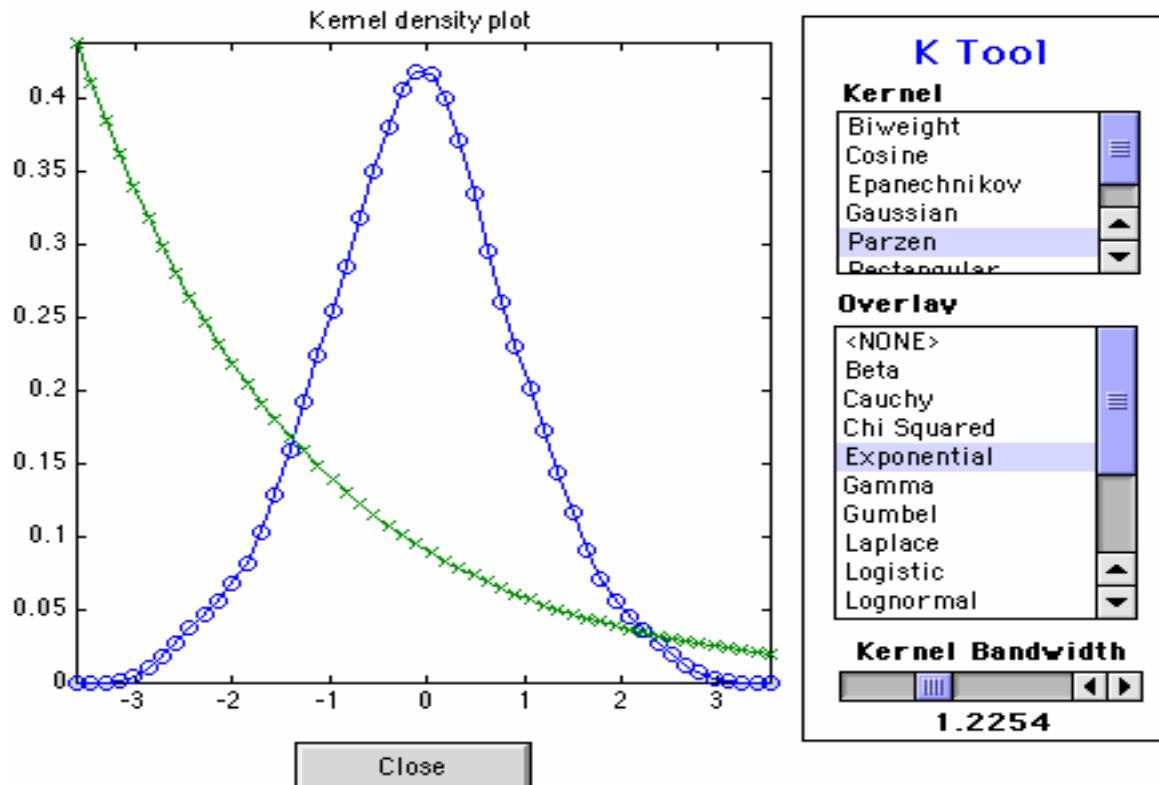
Figure 14-6. KTOOL GUI interface.

Other Commands

In addition to the focus on distribution fitting, the Tool Set also includes commands to assist investigations of usual hypothesis testing. There are commands for summarizing data, testing means, and testing variances. For exploratory data analysis, one typically wants to look at various summary measures. The summary command creates a structure

373

with these values. Additionally, the `means` command provides various measures of central tendency and the `pctile1` command provides percentiles. Using random data, we can see the usefulness of these commands:

```
>> summary(n)
ans =
ks: 31.3267
mean: 1.8708
std: 2.8305
n: 1000
min: -5.9327
max: 10.1949
p10: -1.7725
p25: -0.0858
p50: 1.9606
p75: 3.8402
p90: 5.5716
skew: -0.0307
kurt: 2.8300
```

15. Returning Users – New Features and Release Notes for PLS_Toolbox 4.0

Version 4.0 of PLS_Toolbox includes new functions, improvements in our existing functions, new "tool sets" of associated functions, and expansion of our Graphical User Interfaces. A list of all of these changes would be dry reading, so this chapter will highlight some of the most significant changes. There are, however, many underlying changes which are not reported in this document.

Tool Sets

This release of PLS_Toolbox includes several new "tool sets" which we have sub-divided into their own folders within PLS_Toolbox. These tool sets include:

1. **Distribution Fitting Tools** – This tool set provides a large set of distribution fitting tools including fifteen different distributions. The tools create random distributions for any of these fifteen common distributions, and also calculate the quantile, probability density function, and cumulative density function for each distribution. There are also a variety of GUI and Plotting tools for analyzing and generating data. This tool set is comparable to the contents of The Mathworks' statistics toolbox. For more information on this tool set type:

   ```
   helpwin pls_toolbox/dft
   ```

2. **Peak Fitting Tools** – This tool set includes command-line tools for rapid locating and fitting of standard peak shapes. This initial release includes fitting of any number of Gaussian, Lorentzian, and/or mixed peaks. For more information on this tool set, type:

   ```
   helpwin pls_toolbox/peakfit
   ```

   and see the new functions `peakfind`, `peakstruct`, and `fitpeaks`.

3. **Optimization Tools** – This tool set features a fast Levenberg-Marquardt nonlinear-optimization tool. It is included for use with peakfit tools or for custom user applications. For more information on this tool set type:

   ```
   helpwin pls_toolbox/optimize
   ```

4. **Robust Tools** – These robust analysis tools are a subset of the well-known LIBRA Toolbox, developed by Mia Hubert's research group at the Katholieke Universiteit Leuven (www.kuleuven.be). These tools are used to extend PCA, PCR, and PLS functionality to include robust analysis options. See the algorithm options on these functions for more information. Also, the individual LIBRA functions can be used directly. For more information on the robust functions, type:

   ```
   helpwin robust\LIBRA_PLStoolb
   ```

Graphical User Interface

Version 4.0 introduces some major changes to the Browse, Analysis, and DataSet Editor GUIs. These three GUIs now form the primary environment to analyze and manipulate data and models in PLS_Toolbox. PlotGUI has also been significantly enhanced to allow more plot manipulation, data selection, and data and plot exporting options. In addition, we are introducing two new GUI tools, FigBrowser and TrendTool.

1. **Browse** - The PLS_Toolbox Workspace browser has become a full-featured GUI to allow users to import, modify, and analyze data. The standard DataSet Editor import functions are available in this GUI's menus. In addition, double-clicking data items allows editing of those items. Some other highlights of this new interface include:

   - "Drag and drop" of data. Data can be operated on by dragging them to a variety of other objects including:
     - ➢ Other data, to augment two or more DataSet Objects
     - ➢ Models, to apply model to data
     - ➢ An Analysis Shortcut in the browser window, to start the specific analysis method and pre-load the data for analysis
     - ➢ Other PLS_Toolbox windows, to load the data into the specified Analysis, PlotGUI, or DataSet Editor window (if permitted).
   - "Drag and drop" of models. Models can be dragged into Analysis windows to load them into the Analysis GUI.
   - Right-click functionality. All workspace objects (data, models) can also be modified or operated on by right-clicking the object's icon.
   - New menu options to automatically load selected data or models into analysis for a specific analysis method.

2. **Analysis** – The primary GUI for multivariate data analysis in PLS_Toolbox now includes:

   - Color-coded status-boxes (top two boxes in window) indicating current status of the **Analysis** interface. The status boxes also have "right-click" functionality for the most commonly needed operations.
   - A new Help Window at bottom of main window offering guidance in working with the interface.
   - A shortcut to the PLS_Toolbox Workspace browser by clicking on the EVRI Logo button (see Browse for more information).
   - A new OptionsGUI for modifying options for almost all Analysis methods. This allows access to a variety of powerful options including:
     - ➢ Robust option selection of PCA, PCR, and PLS.
     - ➢ MCR options.
   - New Methods added to the Analysis menu:
     - ➢ MPCA – Multiway Principal Components Analysis.
     - ➢ MLR – Multiple Linear Regression.
   - Preprocess/Custom options (for both X and Y blocks) allowing the side-by-side viewing of the effect of selected methods on the data.
   - Better linking of selections in the data, preprocessed data, scores, and loadings plot windows. Selections in scores or loadings plots are reflected in original data

plots (however, the reverse is not true). Selections in data and preprocessed data plots are reflected between each.

- Improvements in delimited text file importer. The standard text-file importer (xclreadr from the command line) now attempts an intelligent parsing of generic text files to try to locate labels and extra data, and places these items into a DataSet Object for your use.

- Improved model status content. The model status window now reflects RMSEC, RMSECV, and RMSEP information, when available.

- A new demo for the Analysis GUI. A step-by-step demonstration of how to use the Analysis interface for PCA analysis is accessible by typing `analysis_pcademo`.

- Drill-down functionality in Q and T Contribution plots. Most standard analysis methods allow tracking from Q and T contribution plots back to the original data by clicking on a given variable. MPCA allows drill-down from "summary" contribution plots to the full (variable vs. time) contribution data.

- The ability of the Analysis GUI to recognize when you have re-loaded the data used to calibrate a model, allowing you to modify the model (when the model type and settings permit - some model types do not permit this feature).

3. **DataSet Editor** – The editor used to import, create, modify and edit DataSet Objects now includes:

- Exporting to CSV. DataSet Objects can now be exported to a standard Comma Separated Values format which is readable by Microsoft Excel and other programs.

- Direct editing of Label fields. Labels, classes, axis scales, and the "include" field can all be quickly edited by selecting the appropriate "mode" (rows, columns, etc.), clicking on the given label header button, and then selecting the **Edit/Edit field** menu (or by right-clicking the label heading and selecting **Edit field**).

- Quick bulk exclusion or inclusion of a range of samples or variables using the **Bulk Include Change** menu option.

- Improved copy and paste functionality for label fields. Copying and pasting between the different label fields (Label, Axis Scale, Class) is greatly enhanced. Pasting labels into the Class field, for example, now automatically translates text labels into the numerical codes required by the Class field, and the Label field accepts several standard text formats copied from other programs.

4. **PlotGUI** – The general interface used by most of the GUI functions in PLS_Toolbox for plotting of data and results now includes:

- Menu Additions:
  - ➢ **File**
    - **Export figure to MS PowerPoint** and **Export Figure to MS Word**. Provides an easy way to export a plot; similar to the MATLAB figure export function.

➢ **Edit**
  • **Copy Figure** and **Copy Plotted Data**. Sends image of figure (Copy Figure) or numeric data plotted in figure (Copy Plotted Data) to your system clipboard.
  • **Select Class.** All samples or variables of a given class (or classes) can be easily selected from a list of classes.
➢ **View**
  • **Labels**. Individual labels can now be dragged and dropped to adjust position.
  • **Classes/Outline Class Groups** Draws smallest-region borders around each group of samples in a class.
  • **Classes/Labels** now allows access to multiple class sets.
  • **Declutter Labels**. Additional levels of decluttering are now available along with improved logic. "Decluttered" notice now appears on figure when decluttering is in use (Right-click this notice to hide or change options).
  • **Subplots**. Multiple axes (subplots) are now supported. The contents of each subplot can be individually selected by clicking on the subplot, then selecting the desired data from the plot controls. Note that some settings are used for *all* subplots.
• Appearance: Improved support for date stamp labels. Date stamp axis scales are automatically recognized and plotted with best-fit labels. Click "Plot" after zooming to readjust labels.
• Keyboard shortcuts for **View** menu items.
• Better support for Data Set Objects with label problems (none or duplicates).
• Command-line support for color-coding scatter plots using either external data or a given column/row of the plotted data.

5. **Trendtool** – A new graphical analysis tool which permits the user to use right-click to mark a variable of interest and view how that variable changes in the "other" dimension of a Data Set Object. Subtraction of reference points or linear baselines, as well as integration of multiple adjacent variables, are also supported by right-clicking a previously-set marker. This tool can be accessed from the command line by typing: `trendtool(data)` where `data` is the DataSet Object to analyze.

6. **FigBrowser** - This new GUI is initially available on Analysis and PLS_Workspace browser windows but, when selected, is automatically available on all figures. It allows quick navigation between figures, either from thumbnail images of the figures or from a pull-down list in the **FigBrowser** menu.

7. **Genalg** – The genetic algorithm variable selection tool GUI. Improved preprocessing support includes viewing of preprocessed data and "pre-application" of preprocessing (allows faster analysis).

378

Complete List of New Functions

This release of PLS_Toolbox also includes the following new command-line functions:

1. **New importers, exporters, and data viewing tools**

```
encodexml     - Converts standard data types into XML-encoded text.
idateticks    - Converts axis labels into intelligent date ticks.
mtfreadr      - Reader for AdventaCT Multi-Trace Format files.
parsemixed    - Parses numerical and text data into a DataSet Object.
querydb       - Uses ODBC/ADO or JDBC to execute SQL queries.
trendtool     - Univariate trend analysis tool.
writecsv      - Exports a DataSet object to a comma-separated values
                 (CSV) file.
```

2. **New analysis functions and associated tools**

```
ipls          - Interval PLS variable selection.
matchvars     - Aligns variables of a dataset to allow prediction with
                 a model.
mlr           - Multiple Linear Regression for multivariate Y.
mlrengine     - Multiple Linear Regression computational engine.
modelselector - Creates or applies a model selector model.
```

3. **New calculation tools**

```
lsq2topb      - Fits a polynomial to the top/(bottom) of data.
med2top       - Fits a constant to top/(bottom) of data.
varcapy       - Calculate percent y-block variance captured by a PLS
                 regression model.
vip           - Calculate Variable Importance in Projection from
                 regression model.
```

4. **Figure and Workspace Management Aids**

```
clean         - Clears and closes everything in the workspace.
exportfigure  - Automatically exports figures to an external program.
figbrowser    - Browser with icons of all Matlab figures.
keep          - Clears all except named variables in workspace.
```

5. **User Customization**

```
browse_shortcuts - Defines shortcuts available on the EVRI Workspace
                    Browser.
editds_importmethods - List of user-defined import methods for DataSet
                    Editor.
editds_userimport - Example user-defined importer for editds.
optionsgui       - Creates options gui for specified function.
```

16. Advanced Software Information

MATLAB provides several different data types for managing and working with data. Along with all of the typical numeric and character data types, MATLAB also supports two higher order data types: structures and cell arrays. MATLAB also allows, through the use of classes, the creation of custom data types. In this chapter, you will see how PLS_Toolbox implements these data types to more effectively manage data.

The DataSet Object

A typical data set contains more than just a simple matrix or n-way array; the data set may also include labels for samples and variables, axes to plot the samples and variables against, and a host of other information such as class membership, authorship information, etc. When this information is entered in MATLAB, it often becomes a set of individual variables of different classes, such as a double array for the main data, character arrays or cell arrays containing character strings for the labels, and/or Boolean logicals to indicate which samples or variables are to be included in the analysis. The MATLAB workspace can quickly become cluttered with many different variables associated with the full data set.

A cluttered workspace can be an inconvenience, but real problems often occur when parts of the data set are deleted, or when parts are edited in a way that makes them inconsistent with other parts. An example would be if samples were deleted from a data matrix without deleting their corresponding sample labels. This can lead to problems further down the data analysis chain.

Overview of the DataSet Object

The DataSet Object (DSO) was created to address the problem of managing data in MATLAB. When added to a MATLAB installation, the DSO creates a new class of objects called `dataset`. DSOs are used to "glue" the individual parts of a data set together. This allows complete data sets to be described by single variables in the MATLAB workspace. But perhaps more importantly, DSOs have a number of features that assure that data are consistent and traceable. These features include:

- **Data consistency:** Fields in DSOs are not allowed to be inconsistent. For example, it is not possible to create a DSO where the number of labels for samples does not match the number of samples, or where the axis scale for variables does not match the number of variables.

- **Soft deletes:** The DSO contains information (in the `include` field) that can be used to exclude data from an analysis without deleting the excluded data.

Thus, a soft delete can be performed that excludes data from a particular analysis while still retaining the entire original data record.

- **Data history:** All additions and modifications to the DSO are stored in the `.history` field. This field provides a traceable record that can be used to reconstruct a DSO from the original data sources.

- **Data description:** Text describing the data set is stored in the `.description` field, and is easily viewed.

- **Userdata:** The `userdata` field of the DSO can be used to store any user-supplied meta-data associated with the DSO. This data can be extracted by user-defined routines. This feature makes the DSO easily extensible.

- **Date stamps, authorship:** The DSO includes creation (`date`) and modification (`moddate`) dates, author information (`author`), and the name of the data set (`name`).

- **Overloading:** Because a DSO is its own class of variable in the MATLAB workspace, existing functions can be *overloaded* with new functions which work on DSOs in a sensible way. For instance, the `size` function is overloaded for a DSO to give the size of the data matrix contained in the DSO.

All of these features make managing data in MATLAB easier than ever before.

DataSet Object Tour

Perhaps the best way to understand how DSOs work is to examine a couple of them. Several data sets are included with PLS_Toolbox, and all of them are in the form of DSOs. We will start with the smallest one, the Wine data set. Clear the MATLAB workspace (save anything important first!) and at the command line type:

```
» load wine
» whos
  Name        Size                 Bytes  Class

  wine       10x5                    6050  dataset object

Grand total is 920 elements using 6050 bytes
```

We have now loaded the Wine data set. When the 'whos' command is used, we see that there is a single variable in the workspace, `wine`, of Class `dataset object`, with a data field that is 10 by 5. We can look at the contents of `wine` by typing:

```
» wine

wine =
        name: Wine
        type: data
      author: B.M. Wise
        date: 14-May-2001 13:47:54
     moddate: 06-Jun-2001 10:27:24
        data: 10x5 [double]
       label: {2x1} [array (char)]
                 Mode 1  [Country: 10x6]
                 Mode 2  [Variable: 5x6]
   axisscale: {2x1} [vector (real)]
                 Mode 1  [: ]
                 Mode 2  [: ]
       title: {2x1} [vector (char)]
                 Mode 1  [: 'Country']
                 Mode 2  [: 'Variable']
class: {2x1} [vector (integer)]
                 Mode 1  [: ]
                 Mode 2  [: ]
     include: {2x1} [vector (integer)]
                 Mode 1  [: 1x10]
                 Mode 2  [: 1x5]
description: Wine, beer, and liquor consumption (gal/yr), life
             life expectancy (years), and heart disease rate
             (cases/100,000/yr) for 10 countries.
     history: {1x1 cell} [array (char)]
    userdata:
```

From this we see that the name of the data is Wine and that the type is "data." Other types are also possible, such as "image" and "batch." The author is listed, followed by the creation date and last-modified date. The next field, `data`, contains the actual data table. These data, or the data from any DSO field, can be extracted from the DSO just as they would be from a conventional structure array (type `help struct` or refer to the Examining a Structure Array section of Chapter 2 for help) using `DSOname.fieldname` syntax. For instance:

```
» wine.data

ans =

    2.5000   63.5000    40.1000    78.0000    61.1000
    0.9000   58.0000    25.1000    78.0000    94.1000
    1.7000   46.0000    65.0000    78.0000   106.4000
    1.2000   15.7000   102.1000    78.0000   173.0000
    1.5000   12.2000   100.0000    77.0000   199.7000
    2.0000    8.9000    87.8000    76.0000   176.0000
    3.8000    2.7000    17.1000    69.0000   373.6000
    1.0000    1.7000   140.0000    73.0000   283.7000
    2.1000    1.0000    55.0000    79.0000    34.7000
    0.8000    0.2000    50.4000    73.0000    36.4000
```

The labels can be extracted in a similar manner:

```
» wine.label

ans =

  [10x6] char
  [ 5x6] char
```

Note that ans is a cell array, i.e., the labels for each mode of the array are stored in a cell that is indexed to that mode. Thus, the labels for mode 1, the data set rows, can be extracted with:

```
» wine.label{1}

ans =

France
Italy
Switz
Austra
Brit
U.S.A.
Russia
Czech
Japan
Mexico
```

Note that curly brackets, {}, are used to index into cell arrays (type help cell for more information on cell arrays). In a similar way the labels for mode 2, the data set columns, can be extracted by executing:

384

```
» wine.label{2}

ans =

Liquor
Wine
Beer
LifeEx
HeartD
```

Other fields in the DSO include .axisscale (*e.g.*, time or wavelength scale), .title (titles for the axes), and .class (*e.g.*, class variables for samples). Note that a typical data set will not have all of the available fields filled. The Wine data set does not have axis scales, for instance, nor class variables.

DSOs also allow for multiple sets of many of these fields; for instance, you may store more than one set of labels for a particular mode. Most GUI tools including Analysis, PlotGUI and the DataSet Editor support multiple sets but there are some rare situations where their use has not yet been fully implemented. GUIs allow limited support of multiple sets; axis scales and titles are not yet completely supported in the main Analysis GUI.

The user is encouraged to explore more of the DSOs included with PLS_Toolbox. For an example with axis scales, please see spec1 in the nir_data.mat file. For an example with class variables, please see arch in the arch.mat file.

Creating DataSet Objects

There are several ways to create a DSO. The most basic way assumes that you are starting with many of the pieces already in your MATLAB workspace. As an example, let's create a small data set entirely from scratch, consisting of a small data table and the labels for samples and variables:

```
» data = [41 73 205
38 71 188
25 74 175
48 70 212
56 69 145]

data =

    41    73   205
    38    71   188
    25    74   175
    48    70   212
    56    69   145
```

```
» vars = {'Age','Height','Weight'}

vars =

    'Age'     'Height'     'Weight'

» names = {'Jim','Biff','Bob','Al','Scooter'}

names =

    'Jim'    'Biff'    'Bob'    'Al'     'Scooter'
```

Note that the easy way to create labels is to put them in cell arrays by using the curly brackets, {}. (This is easier than creating character arrays where all the rows have to be the same length.) We can form a DSO we'll call guydata using the dataset command and the variable data as follows:

```
» guydata = dataset(data)

guydata =
        name: data
        type: data
      author:
        date: 05-Nov-2002 10:57:47
     moddate: 05-Nov-2002 10:57:47
        data: 5x3 [double]
       label: {2x1} [array (char)]
              Mode 1  [: ]
              Mode 2  [: ]
   axisscale: {2x1} [vector (real)]
              Mode 1  [: ]
              Mode 2  [: ]
       title: {2x1} [vector (char)]
              Mode 1  [: ]
              Mode 2  [: ]
       class: {2x1} [vector (integer)]
              Mode 1  [: ]
              Mode 2  [: ]
     include: {2x1} [vector (integer)]
              Mode 1  [: 1x5]
              Mode 2  [: 1x3]
 description:
     history: {1x1 cell} [array (char)]
    userdata:
```

The DSO guydata now contains the 5x3 data table in the guydata.data field. The labels can be added into the structure as follows:

```
» guydata.label{1} = names;
» guydata.label{2} = vars;
```

What if we inadvertently tried to put the sample labels, which belong in mode 1 (data set rows), into the mode 2 (data set columns) .label field?

```
» guydata.label{2} = names
??? Error using ==> dataset/subsasgn
  Number  of  rows  (or  cell  elements)  in  input  'label'  must
=size(x.data,vdim) = 3.
```

This illustrates an important aspect of the DSO, which is that it will not let you make nonsensical assignments. It forces the data and their associated elements to be consistent.

Further assignments can be made into the DSO, with the following results:

```
» guydata.author = 'My name here';
» guydata.name = 'Guys in the Office';
» guydata.description = {'Some data describing the age, height,';
'and weight of some guys in the office.'};
```

```
We can now inspect the contents of guydata as follows:
```

```
» guydata
```

```
guydata =
        name: Guys in the Office
        type: data
      author: My name here
        date: 05-Nov-2002 10:57:47
     moddate: 05-Nov-2002 11:00:00
        data: 5x3 [double]
       label: {2x1} [array (char)]
                Mode 1   [: 5x7]
                Mode 2   [: 3x6]
   axisscale: {2x1} [vector (real)]
                Mode 1   [: ]
                Mode 2   [: ]
       title: {2x1} [vector (char)]
                Mode 1   [: ]
                Mode 2   [: ]
       class: {2x1} [vector (integer)]
                Mode 1   [: ]
                Mode 2   [: ]
     include: {2x1} [vector (integer)]
                Mode 1   [: 1x5]
                Mode 2   [: 1x3]
```

```
description: Some data describing the age, height,
             and weight of some guys in the office.
    history: {1x1 cell} [array (char)]
   userdata:
```

DSOs can also be created using the DataSet Editor GUI, which may be started by typing `editds` at the command prompt. The individual parts of the data may be loaded into the GUI, then saved as a DSO in the workspace by selecting **Save** from the **File** menu. Finally, there are some functions written into PLS_Toolbox to load data from files directly into DSOs. One example is `xclreadr`, which loads data from Excel spreadsheets that have been saved as delimited text. To try this, type:

```
» xcldata = xclreadr('xclreadrdata.txt')

xcldata =
        name: xclreadrdata.txt
        type: data
      author: Created by XCLREADR
        date: 05-Nov-2002 11:01:04
     moddate: 05-Nov-2002 11:01:04
        data: 3x3 [double]
       label: {2x1} [array (char)]
              Mode 1   [: 3x9]
              Mode 2   [: 3x11]
   axisscale: {2x1} [vector (real)]
              Mode 1   [: ]
              Mode 2   [: ]
       title: {2x1} [vector (char)]
              Mode 1   [: ]
              Mode 2   [: ]
       class: {2x1} [vector (integer)]
              Mode 1   [: ]
              Mode 2   [: ]
     include: {2x1} [vector (integer)]
              Mode 1   [: 1x3]
              Mode 2   [: 1x3]
 description: Test file for XCLREADR
     history: {1x1 cell} [array (char)]
    userdata:
```

Here the labels have been stripped off the original file and placed in the proper fields of the DSO, along with the data table.

Summary

The DataSet Object is a handy way to keep all the pieces of a data set organized. It is convenient to move new data into a DSO as soon as it is imported into MATLAB. Pieces, such as class identifiers, can then be added to it as the analysis proceeds. Because the

DSO keeps track of its own history, the entire story of its construction is contained within it. PLS_Toolbox contains several tools for editing and viewing DSOs. See Chapter 2 for more information on the DataSet Editor and PlotGUI. For more technical information on the structure of DSOs, please see the DataSet Object specification documentation (DataObject401.pdf).

Standard Model Structure

Introduction

Many higher-level PLS_Toolbox functions such as PCA and PLS output the results of analyses in a standard model format. This format, the Standard Model Structure, contains the key results of an analysis, as well as information needed to reproduce those results. The Standard Model Structure is typically used by PLS_Toolbox functions to review the model calibration or apply it to new data (for example, predicting on unknown data). However, the experienced user can access much of the information in the model from the command line to perform various tasks. This section describes the standard model structure in general and also shows some of these advanced applications.

Using Structures

As the name implies, Standard Model Structures are created with a MATLAB variable type called a "structure." In a MATLAB structure, a single variable contains one or more named "fields" (consider it like a variable containing other variables). These fields are accessed by giving the base variable name (here called "model") followed by a period and the name of the field. For example:

```
model.date
```

returns the contents of the `date` field from the model.

In the case of Standard Model Structures, the fields which show up are standardized to help the user identify useful parts of any model. Some of the fields of the Standard Model Structure have self-explanatory contents, such as description strings; other fields contain data matrices with varying contents. Additionally, some Standard Model Structure fields contain MATLAB cell arrays. A cell array is a container for matrices or strings that can be indexed into. When cell arrays are used, they are denoted either by the word "cell" or by surrounding the size or content with curly brackets, { }. For more information about indexing into cell arrays, see the MATLAB documentation on cells; in general, they are indexed using curly brackets giving the indices of the cell to extract, e.g., `mycell{2,3}`

One special field in all Standard Model Structures is the `detail` field. This field contains a separate structure with lower-level details about the model. The contents of this field vary between different model types and typically contains important details about the model. The contents are accessed by simply addressing first the top-level variable (e.g. "model"), then the detail field, then finally the sub-field to extract. For instance, to access

the sum squared captured information (ssq table) for a pca model you would use the following:

```
model.detail.ssq
```

Although the exact fields present in any model vary depending on the model type, the following example, a PCA model, shows many of the general model characteristics.

PCA Example

```
model =
        modeltype: 'PCA'
       datasource: {[1x1 struct]}
             date: '29-Mar-2004'
             time: [2004 3 29 8 57 37.4400]
             info: 'Scores are in cell 1 of the loads field.'
            loads: {2x1 cell}
             pred: {[]}
             tsqs: {2x1 cell}
     ssqresiduals: {2x1 cell}
      description: {3x1 cell}
           detail: [1x1 struct]

model.datasource{1}=
         name: 'Wine'
       author: 'B.M. Wise'
         date: [2001 5 14 13 47 53.9500]
      moddate: [2001 6 6 10 27 23.5100]
         size: [10 5]

model.detail=
             data: {[]}
              res: {[]}
              ssq: [5x4 double]
            rmsec: []
           rmsecv: []
            means: {[]}
             stds: {[]}
           reslim: {[3.1403]}
           tsqlim: {[10.0327]}
           reseig: [3x1 double]
               cv: ''
            split: []
             iter: []
           includ: {2x1 cell}
            label: {2x1 cell}
        labelname: {2x1 cell}
```

```
     axisscale: {2x1 cell}
 axisscalename: {2x1 cell}
         title: {2x1 cell}
     titlename: {2x1 cell}
         class: {2x1 cell}
     classname: {2x1 cell}
 preprocessing: {[1x1 struct]}
       options: [1x1 struct]
```

Description

model

> `modeltype:` Contains a keyword defining the type of model.
>
> `datasource:` Contains information about the data used for the model, but does not contain original data. `datasource` basically contains a subset of the fields of the original DataSet Object. If more than one block of data is used for a model (e.g., PLS models require two blocks), `datasource` will be size 1xj, where j is the number of blocks used for the model (1x2 in the case of PLS).
>
> `date:` Contains a string description of the date on which the model was calculated.
>
> `time:` Contains a time-stamp vector including, in order, the year, month, day, hour, minute, and second at which the model was created. Useful for distinguishing between different models, as no two models can be created with the same time-stamp.
>
> `loads:` Contains factors recovered for the data. In the case of PCA or PLS models, the rows are the "scores" and "loadings" of the data. For PARAFAC, it is the loadings of each mode. The size of the loads field will be dxj, where d is the number of modes (dimensions) and j is the number of blocks of data used by the model (Table 1). PCA models will be 2x1 (two modes, one block), PLS models will usually be 2x2 (two modes, two blocks), PARAFAC will often be dx1 where d is at least 3. Other model types follow this same pattern.

Table 16-1. Loads field contents.

Model Type	Field `loads` contains:	
PCA, MCR	{ X-block Scores	
	X-block Loadings }	
PLS, PCR	{ X-block Scores	Y-block Scores
	X-block Loadings	Y-block Loadings }
PARAFAC	{ X-block Loadings (mode 1)	
	X-block Loadings (mode 2)	
	X-block Loadings (mode 3)	
	…	}

The contents of each cell will generally be an `mxk` array in which `m` is the size of the given block for the given mode (e.g., for `loads{1,1}`, `m` would be equal to the size of the first mode of the X-block) and k is the number of components or factors included in the model. This format may be different for different model types.

Examples of indexing into the `loads` field:

For a PCA model, a plot of the scores for all principal components can be made using:

```
plot(model.loads{1});
```

To plot the scores for only the first principal component, type:

```
plot(model.loads{1}(:,1));
```

Similarly, a plot of the loadings for the first principal component can be made using:

```
 plot(model.loads{2}(:,1);
```

You can also use the model to export data so that they can be used in other programs. The following could be used to export an XY text-formatted file of the loadings of the first principal component:

```
xy=[ [1:size(model.loads{2},1)]'  model.loads{2}(:,1) ];
save xy.prn xy –ascii
```

If the `axisscale` field for this data contains a useful axis to plot against, the XY data can be created using

```
xy=[model.detail.axisscale{2}(model.detail.includ{2})'  ...
model.loads{2}(:,1)];
```

Similarly, the axisscale could be used in the plot commands given above.
 The goal of PCA is to recreate a data set from its loadings and scores. When the proper number of principal components is used one can reproduce the original data set within the noise level. The reconstructed data is calculated as follows:

```
data_reconstructed = model.loads{1}*model.loads{2}';
```

It is also possible to reconstruct the data with fewer factors. The general command for `n` principal components is:

```
model.loads{1}(:,1:n) * model.loads{2}(:,1:n)';
```

tsqs: Contains Hotelling's T^2 values. The T^2 values are a distance measure of the scores or loadings with respect to their respective origins. The tsqs field is a cell equal in size and similar in definition to the loads field. The field will be size dxj, where d is the number of modes (dimensions) and j is the number of blocks of data used by the model. Row 1 contains the mode 1 T^2 values (samples), row 2 contains the T^2 values for mode 2 (variables), etc., while column 1 contains T^2 values for the X-block and column 2 contains T^2 values for the Y-block (if any was used for the given model type).

A relatively large value in tsqs{1,1} indicates a sample that has relatively large influence and loading on the PCA model. Similarly, large values in tsqs{2,1} indicate variables with significant influence and loading on the model. These are often used with statistical limits given in the details field and discussed below.

When a model is applied to new data, the output prediction structure will contain the T^2 values for the predictions rather than the calibration data.

ssqresiduals: Contains the sum-of-squares (SSQ) differences between the original data and the reconstructed data. The field will be size dxj, where d is the number of modes (dimensions) and j is the number of blocks of data used by the model. The first row of the cell contains sum-of-squares differences for each sample (indicating samples which have large out-of-model residuals), while the second row contains sum-of-squares differences for each variable (indicating variables which have large out-of-model residuals). Again, each block is represented by a column, so the X-block sample sum-of-squares residuals can be extracted using:

    model.ssqresiduals{1,1}

When a model is applied to new data, the output prediction structure will contain the SSQ residuals for the predictions rather than the calibration data.

model.detail

data: Contains the data used to calculate the model. In order to save memory, many methods do not save the primary (X) block in the first cell. See the options for a given analysis method to learn more about storing the X-block data in the model (see, for example, the blockdetails option for PCA and PLS). Y-block data (i.e., model.detail.data{2}) is usually stored, when available.

res: Contains the residuals calculated as the difference between the reconstructed data and the original data. As with the detail.data field, the X-block residuals are not usually stored, due to excessive size. As such, this field may be empty. If using a two-block method such as PLS, the second cell of model.detail.res will usually contain the prediction residuals.

`rmsec` and `rmsecv`: Contain any root-mean-square error of calibration and cross-validation (respectively) that was calculated for the model. These are vectors equal in length to the maximum number of factors requested for a given cross-validation calculation. A value of `NaN` will be used for any value which was not calculated.

`ssq`: Contains the eigenvalues or other variance-captured information for a model. For PCA models–, the first column is the PC number, the second column contains the eigenvectors, the third column contains the eigenvalues scaled to a sum of 100, and the last column contains the cumulative eigenvalues. As such, the eigenvalues can be extracted using:

```
model.detail.ssq(:,3)
```

For PLS models, the first column is the Latent Variable number, followed by the variance captured for the X-block, the cumulative variance captured for the X-block, the variance captured for the Y-block, and the cumulative variance captured for the Y-block.

Users should be advised that other model types use this field in different ways. For more information contact Eigenvector Research at helpdesk@eigenvector.com.

`reslim`: Contains the 95% confidence limit for the block 1 sample Q residuals; i.e., for the values in `model.ssqresiduals{1}`. For PCA, this value is calculated using :

```
residuallimit(model,.95)
```

For some multiway model types this field may contain a structure with additional information. For help on this topic, contact Eigenvector Research at helpdesk@eigenvector.com.

`tsqlim`: A cell containing the 95% confidence limit for the block 1 sample T^2 values in `model.tsqs`. For PCA, this value is calculated using

```
[n_samples,n_pcs]=size(model.loads{1});
tsqlim(n_samples,n_pcs,.95);
```

For some multiway model types, this field may contain a structure with additional information. For help on this topic, contact Eigenvector Research at helpdesk@eigenvector.com.

`reseig`: Contains the residual eigenvalues for PCA models only.

`cv, split, iter`: Contain information about the settings used when cross-validating the model, including:

cv: the encoded cross-validation method

split: the total number of splits (test groups)

iter: the number of iterations (for random mode only)

`includ`, `label`, `labelname`, `axisscale`, `axisscalename`, `title`, `titlename`, `class`, `classname`: Contain information from DataSet Object fields. If the original data used to calculate the model were stored in a DataSet Object, certain fields from the DataSet Object are extracted and stored in the model. Each of these fields is extracted for each mode and each block such that `model.detail.label{1,2}` returns the mode 1 labels for block 2 (Y-block), and `model.detail.class{2,1}` returns the mode 2 classes for block 1 (X-block). For more information on these fields, see the DataSet Object section at the beginning of this chapter.

Note that although DataSet Objects use the second index of many of these fields to store multiple "sets," the model structures indicate the block number with the second index, and the set number with the third index.

`preprocessing`: Contains a cell of preprocessing structures. The preprocessing structures are used with the function `preprocess` to process the data for the model. There is one structure in the cell for each block required by the model and each structure may have zero, one or multiple records, with each record representing one preprocessing method applied to the data. Thus, the X-block preprocessing is stored in `model.detail.preprocessing{1}`.

`options`: Contains the options given as input to the modeling function.

Summary

Similar to a DataSet Object, the Standard Model Structure organizes results of an analysis into a logical hierarchy. From this structure, a user can both explore results and generate predictions. As you become more familiar with its organization, you will see how convenient it is to access and manipulate model information using the Standard Model Structure.

User-Defined Preprocessing

Each preprocessing method available in the `preprocess` function is defined using a preprocessing structure. The standard methods are defined in the `preprocatalog` file, and additional user-defined methods can be defined in the `preprouser` file. The methods defined in these two files are available to all functions making use of the `preprocess` function. See the `preprouser` file for examples of defining and adding methods to the available methods catalog. The fields in a preprocessing structure include:

`description`   - textual description of the particular method.

`calibrate`   - cell containing the line(s) to execute during a calibration operation.

`apply`	- cell containing the line(s) to execute during an apply operation.
`undo`	- cell containing the line(s) to execute during an undo operation.
`out`	- cell used to hold calibration-phase results for use in apply or undo.
`settingsgui`	- function name to execute when the "Settings" button is pressed in the GUI.
`settingsonadd`	- Boolean: 1 = automatically bring up settings GUI when method is "added".
`usesdataset`	- Boolean: indicates if this method should be passed a DataSet Object (1) or a raw matrix (0)
`caloutputs`	- integer: number of expected items in field `out` after calibration has been performed.
`keyword`	- text string which users can pass to preprocess to obtain this structure.
`userdata`	- user-defined variable often used to store method options.

Detailed Field Descriptions

description: Contains a short (1-2 word) description of the method. The value will be displayed in the GUI and can also be used as a string keyword (see also keyword) to refer to this method. For example:

```
pp.description = 'Mean Center';
```

calibrate, apply, undo: Contain a single cell of one or more command strings to be executed by preprocess when performing calibration, apply or undo operations. Calibrate actions are done on original calibration data, whereas apply is done on new data. The undo action is used to remove preprocessing from previously preprocessed data, although it may be undefined for certain methods. If this is the case, the undo string should be an empty cell.

The command strings should be valid MATLAB commands. Each command will be executed inside the preprocess environment in which the following variables are available:

data: The actual data on which to operate and in which to return modified results. If the field usesdataset is 1 (one) then data will be a DataSet Object. Otherwise, data will be a standard MATLAB variable which has been extracted from the DataSet Object. In the latter case, the extracted data will not contain any excluded columns from the original DataSet Object. In addition, in calibrate mode rows excluded in the original DataSet Object will not be passed. All rows, excluded or not, are passed in apply and undo modes.

If writing a DataSet Object-enabled preprocessing function, it is expected that the function will calibrate using only included rows but apply and undo the preprocessing to all rows.

out: Contents of the preprocessing structure field out. Any changes will be stored in the preprocessing structure for use in subsequent apply and undo commands.

userdata: Contents of the preprocessing structure field userdata. Any changes will be stored in the preprocessing structure for later retrieval.

Read-only variables: Do not change the value of these variables.

include: Contents of the original DataSet Object's include field.

otherdata: Cell array of additional inputs to preprocess which follow the data. For example, these inputs are used by PLS_Toolbox regression functions to pass the y-block for use in methods which require that information.

originaldata: Original DataSet Object unmodified by any preprocessing steps. For example, originaldata can be used to retrieve axis scale or class information even when usesdataset is 0 (zero) and, thus, data is the extracted data.

In order to assure that all samples (rows) in the data have been appropriately preprocessed, an apply command is automatically performed following a calibrate call. Note that excluded variables are replaced with NaN.

Examples:
The following calibrate field performs mean-centering on data, returning both the mean-centered data as well as the mean values which are stored in out{1}:

```
pp.calibrate   = { '[data,out{1}] = mncn(data);' };
```

The following apply and undo fields use the scale and rescale functions to apply and undo the previously determined mean values (stored by the calibrate operation in out{1}) with new data:

```
pp.apply       = { 'data = scale(data,out{1});' };
pp.undo        = { 'data = rescale(data,out{1});' };
```

out: Contains non-data outputs from calibrations. This output is usually information derived from the calibration data which is required to apply the preprocessing to new data. This field will be updated following a calibrate call, and the entire preprocessing structure will be output. For example, when autoscaling, the mean and standard deviation of all columns are stored as two entries in out{1} and out{2}. See the related field caloutputs. Usually, this field is empty in the default, uncalibrated structure.

<u>settingsgui</u>: Contains the name of a graphical user interface (GUI) function which allows the user to set options for this method. The function is expected to take as its only input a standard preprocessing structure, from which it should take the current settings and output the same preprocessing structure modified to meet the user's specifications. Typically, these changes are made to the `userdata` field, then the commands in the `calibrate`, `apply` and `undo` fields will use those settings.

The design of GUIs for selection of options is beyond the scope of this document and the user is directed to `autoset.m` and `savgolset.m`, both of which use GUIs to modify the `userdata` field of a preprocessing structure. Example:

```
          pp.settingsgui   = 'autoset';
```

<u>settingsonadd</u>: Contains a Boolean (1=true, 0=false) value indicating if, when the user selects and adds the method in the GUI, the method's `settingsgui` should be automatically invoked. If a method usually requires the user to make some selection of options, `settingsonadd=1` will guarantee that the user has had an opportunity to modify the options or at least choose the default settings.

    Example:
```
          pp.settingsonadd   = 1;
```

<u>usesdataset</u>: Contains a Boolean (1=true, 0=false) value indicating if the method is capable of handling DataSet Objects or can only handle standard MATLAB data types (double, uint8, etc).

   1 = function can handle DataSet Objects; preprocess will pass entire DataSet Object. It is the responsibility of the function(s) called by the method to appropriately handle the `include` field.

   0 = function needs standard MATLAB data type; `preprocess` will extract data from the DataSet Object prior to calling this method and reinsert preprocessed data after the method. Although excluded columns are never extracted and excluded rows are not extracted when performing `calibration` operations, excluded rows are passed when performing `apply` and `undo` operations.

    Example:
```
          pp.usesdataset   = 0;
```

<u>caloutputs</u>: Contains the number of values expected in field `out` if a calibrate operation has been performed, for functions which require a `calibrate` operation prior to an `apply` or `undo`. For example, in the case of mean centering, the mean values stored in the field `out` are required to apply or undo the operation. Initially, `out` is an empty cell (`{}`) but following the calibration, it becomes a single-item cell (length of one). By examining this length, `preprocess` can determine if a

preprocessing structure contains calibration information. The `caloutputs` field, when greater than zero, indicates to `preprocess` that it should test the `out` field prior to attempting an apply or undo.

> Example:
>> In the case of mean-centering, the length of `out` should be 1 (one) after calibration:

>> `pp.caloutputs    = 1;`

<u>keyword</u>: Contains a string which can be used to retrieve the default preprocessing structure for this method. When retrieving a structure by keyword, preprocess ignores any spaces and is case-insensitive. The keyword (or even the description string) can be used in place of any preprocessing structure in `calibrate` and `default` calls to preprocess:

> `pp = preprocess('default','meancenter');`

> Example:
>> `pp.keyword       = 'Mean Center';`

<u>userdata</u>: A user-defined field. This field is often used to hold options for the particular method. This field can also be updated following a `calibrate` operation.

> Example:
>> In `savgol` several variables are defined with various method options, then they are assembled into `userdata`:

>> `pp.userdata    = [windowsize order derivative];`

Examples

The preprocessing structure used for sample normalization is shown below. The `calibrate` and `apply` commands are identical and there is no information that is stored during the calibration phase; thus, `caloutputs` is 0. The order of the normalization is set in `userdata` and is used in both `calibrate` and `apply` steps.

```
pp.description = 'Normalize';
pp.calibrate   = {'data = normaliz(data,0,userdata(1));'};
pp.apply       = {'data = normaliz(data,0,userdata(1));'};
pp.undo        = {};
pp.out         = {};
pp.settingsgui   = 'normset';
pp.settingsonadd = 0;
pp.usesdataset   = 0;
pp.caloutputs    = 0;
pp.keyword       = 'Normalize';
pp.userdata      = 2;
```

The preprocessing structure used for Savitsky-Golay smoothing and derivatives is shown below. In many ways, this structure is similar to the sample normalization structure, except that `savgol` takes a DataSet Object as input and, thus, `usesdataset` is set to 1. Also note that because of the various settings required by `savgol`, this method makes use of the `settingsonadd` feature to bring up the settings GUI as soon as the method is added.

```
pp.description       = 'SG Smooth/Derivative';
pp.calibrate         =
      {'data=savgol(data,userdata(1),userdata(2),userdata(3));'};

pp.apply             =
      {'data=savgol(data,userdata(1),userdata(2),userdata(3));'};
pp.undo              = {};
pp.out               = {};
pp.settingsgui       = 'savgolset';
pp.settingsonadd     = 1;
pp.usesdataset       = 1;
pp.caloutputs        = 0;
pp.keyword           = 'sg';
pp.userdata          = [ 15 2 0 ];
```

The following example invokes multiplicative scatter correction (MSC) using the mean of the calibration data as the target spectrum. The `calibrate` cell here contains two separate operations; the first calculates the mean spectrum and the second performs the MSC. The third input to the MSC function is a flag indicating whether an offset should also be removed. This flag is stored in the `userdata` field so that the `settingsgui` (`mscorrset`) can change the value easily. Note that there is no undo defined for this function.

```
pp.description           = 'MSC (mean)';
pp.calibrate             = { 'out{1}=mean(data);
   data=mscorr(data,out{1},userdata);' };
pp.apply                 = { 'data = mscorr(data,out{1});' };
pp.undo                  = {};
pp.out                   = {};
```

```
pp.settingsgui          = 'mscorrset';
pp.settingsonadd        = 0;
pp.usesdataset          = 0;
pp.caloutputs           = 1;
pp.keyword              = 'MSC (mean)';
pp.userdata             = 1;
```

Summary

The Preprocessing Structure provides a generic framework within which a user can organize and automate preprocessing with PLS_Toolbox. Both MATLAB structure and cell data types are used extensively in the Preprocessing Structure. Any custom preprocessing you define yourself can be combined with the numerous methods provided by PLS_Toolbox in order to meet your analysis needs.

17. Bibliography

Anderson, T.W., *An Introduction to Multivariate Statistical Analysis*, Wiley, New York, New York, 1984.

Åstrom K.J. and B. Wittenmark, *Computer Controlled Systems*, Prentice-Hall, Englewood Cliffs, NJ, 1984.

Barker, M., W. Rayens, "Partial Least Squares for Discrimination", *J. Chemometrics*, **17**(3), 166-173, 2003.

Barnes, R.J., Dhanoa, M.S. and Lister, S.J. "Standard normal variate transformation and detrending of NIR spectra" *Appl. Spectrosc.* **43**, 772-777, 1989.

Beebe, K.R. and B.R. Kowalski, "An Introduction to Multivariate Calibration and Analysis", *Anal. Chem.*, **59**, 1007A, 1987.

Beebe, K.R., R.J. Pell and M.B. Seasholtz, *Chemometrics: A Practical Guide,* John Wiley & Sons, New York, 1998.

Berman, M., A. Phatak, and R. Lagerstrom, "ICE: A Statistical Approach to Identifying Constituents of Biomedical Hyperspectral Images," *IEEE Transactions on Geoscience and Remote Sensing*, **42**(10), 2085-2095, 2004.

Blank, T.B., S.T. Sum, S.D. Brown, and S.L. Monfre, "Transfer of Near-Infrared Multivariate Calibrations without Standards", *Anal. Chem.*, **68**(17), 2987–2995, 1996.

Booksh, K.S. and B.R. Kowalski, "Error Analysis of the Generalized Rank Annihilation Method", *J. Chemometrics*, **8**, 45-63, 1994.

Booksh, K.S., and B.R. Kowalski, "Theory of Analytical Chemistry," *Anal. Chem.*, **66**, 782A-791A, 1994.

Booksh, K.S., Z. Lin, Z. Wang and B.R. Kowalski, "Extension of Trilinear Decomposition Method with an Application to the Flow Probe Sensor", *Anal. Chem.*, **66**, 2561-2569, 1994.

Box, G.E.P., W.G. Hunter, and J.S. Hunter, *Statistics for Experimenters*, John Wiley and Sons, New York, NY, 1978.

Box, G.E.P., "Some theorems on quadratic forms applied in the study of analysis of variance problems: Effect of inequality of variance in one-way classification," *Annals of Mathematical Statistics* **25**, 33-51, 1954.

Bro, R., "Multiway calibration. Multilinear PLS," *J. Chemometrics*, **10**(1), 47-61, 1996.

Bro, R. and S. de Jong, "A Fast Non-Negatively Constrained Least Squares Algorithm", *J. Chemometrics*, **11**(5), 393-401, 1997.

Bro, R., A. K. Smilde, and S. de Jong, "On the difference between low-rank and subspace approximation: improved model for multi-linear PLS regression," *Chemom. Intell. Lab. Syst.*, **58**(1), 3-13, 2001.

Bro, R., Smilde, A.K., "Centering and Scaling in Component Analysis", *J. Chemometrics*, **17**, 16-33, 2003.

Brown, P.J., C.H. Spiegelman, and M.C. Denham, "Chemometrics and Spectral Frequency Selection", *Phil. Trans. R. Soc. Lond. A*, **337**, 311-322, 1991.

Cleveland, W.S., "Robust Locally Weighted Regression and Smoothing Scatterplots," *J. American Stat. Assoc.*, **74**(368), 1979.

Croux, C. and Haesbroeck, G., "Principal components analysis based on robust estimators of the covariance or correlation matrix: influence functions and efficiencies." *Biometrika* **87**, 603-618, 2000.

de Jong, S., "SIMPLS: an alternative approach to partial least squares regression", *Chemom. Intell. Lab. Syst.*, **18**, 251-263, 1993.

de Jong, S., B. M. Wise and N. L. Ricker, "Canonical Partial Least Squares and Continuum Power Regression," *J. Chemometrics*, Vol. 15, 85-100, 2001.

de Jong, S., "Regression coefficients in multilinear PLS," *J. Chemometrics*, **12**, 77-81, 1998.

de Juan, A., Rutan, S.C., Tauler, R., and Massart, D.L., "Comparison between the direct tri-linear decomposition and the multivariate curve resolution-alternating least squares methods for the resolution of three-way data sets," *Chemom. Intell. Lab. Syst.*, **40**, 19–32, 1998.

de Juan, A., M. Maeder, M. Martínez, R. Tauler, "Combining hard- and soft-modelling to solve kinetic problems," *Chemom. Intell. Lab. Syst.*, **54**, 123-141, 2000.

de Juan, A. and R. Tauler, "Comparison of three-way resolution methods for non-trilinear chemical data sets," *J. Chemometrics*, **15**(10), 749-771, 2001.

Donoho, D.L., "Breakdown properties of multivariate location estimators." *Qualifying paper*, Harvard University, Boston, 1982.

Draper, H.R. and H. Smith, *Applied Regression Analysis*, Second Edition, John Wiley and Sons, New York, NY, 1981.

Engelen, S. and Hubert, M., "Fast model selection for robust calibration methods," *Analytica Chimica Acta* **544**, 219-228, 2005.

404

Erickson, C.L., M.J. Lysaght, and J.B. Callis, "Relationship between Digital Filtering and Multivariate Regression in Quantitative Analysis," *Anal. Chem.*, **64**(24), 1155A–1163A, 1992.

Esbensen, K.H., "Multivariate Data Analysis in Practice," *Camo Process AS* (5th edition), 2001.

Faber, K., A. Lorber, and B.R. Kowalski, "Analytical Figures of Merit for Tensorial Calibration", *J. Chemometrics*, **11**(5), 419-461, 1997.

Freund, J.E., *Statistics A First Course*, 3rd Edition, Prentice Hall, NJ, 1981, p. 236.

Gallagher, N.B., B.M. Wise, and C. W. Stewart, "Application of Multi-way Principal Components Analysis to Nuclear Waste Storage Tank Monitoring," *Computers in Chem. Engng.*, **20**, suppl., s739-s744, 1996.

Gallagher, N.B., B.M. Wise, S.W. Butler, D.D. White, Jr., and G.G. Barna (1997). "Development and Benchmarking of Multivariate Statistical Process Control Tools for a Semiconductor Etch Process: Improving Robustness Through Model Updating," *Proc. IFAC ADCHEM 1997*, Banff, Canada, 1997.

Gallagher, N.B., J.M. Shaver, E.B. Martin, J. Morris, B.M. Wise, and W. Windig, "Curve resolution for images with applications to TOF-SIMS and Raman", *Chemo. and Intell. Lab. Sys.*, **73**(1), 105–117, 2003.

Gallagher, N.B., D.M. Sheen, J.M. Shaver, B.M. Wise, and J.F. Shultz, "Estimation of trace vapor concentration-pathlength in plumes for remote sensing applications from hyperspectral images", *SPIE Proceedings*, **5093**, 184–194, 2003.

Geladi, P., "Analysis of multi-way (multi-mode) data," *Chemo. and Intell. Lab. Sys.*, **7**, 11-30, 1989.

Geladi, P. and B.R. Kowalski, "PLS Tutorial" *Anal. Chim. Acta.*, **185**(1), 1986.

Geladi, P. and H. Grahn, *Multivariate Image Analysis*, Wiley, Chichester, 1996.

Geladi, P., "Sampling and local models for multivariate image analysis", *Microchimica Acta*, **120**, pps. 211-230, 1995.

Gemperline, P.J., "Computation of the Range of Feasible Solutions in Self-Modeling Curve Resolution Algorithms," *Anal. Chem.*, **71**, 5398-5404, 1999.

Gemperline, P.J., and E. Cash, "Advantages of Soft versus Hard Constraints in Self-Modeling Curve Resolution Problems. Alternating Least Squares with Penalty Functions", *Anal. Chem.*, **75**(16), 4236-4243, 2003.

Gurden, S.P., J.A. Westerhuis, S. Bijlsma, and A.K. Smilde, "Modelling of Spectroscopic Batch Process Data Using Grey Models to Incorporate External Information", *Journal of Chemometrics*, **15**, 101-121, 2001.

Hamilton, J.C., and P.J. Gemperline, *J. Chemometrics*, **4**, 1-13, 1990.

Hampel, F.R., Ronchetti, E.M., Rousseeuw, P.J., Stahel, W.A. *Robust Statistics: The Approach Based on Influence Functions*, Wiley: New York, 1986.

Harshman, R.A., *UCLA Working Papers in Phonetics*, **16**(1), 1970.

Harshman, R.A., "PARAFAC2: Mathematical and technical notes," *UCLA working papers in phonetics*, **22**, pps. 30-47, 1972.

Harshman, R.A., and M. E. Lundy, "Uniqueness proof for a family of models sharing features of Tucker's three-mode factor analysis and PARAFAC/CANDECOMP," *Psychometrika*, **61**, pps. 133-154, 1996.

Henshaw, J.M., L.W. Burgess, K.S. Booksh and B.R. Kowalski, "Multicomponent Determination of Chlorinated Hydrocarbons using a Reaction-Based Chemical Sensor. 1.", *Anal. Chem.*, **66**, 3328-3336, 1994.

Hirschfeld, T. *Anal. Chem.*, **52**, 297A, 1980.

Hoerl, A.E., R.W. Kennard and K.F. Baldwin, "Ridge regression: some simulations," *Communications in Statistics*, **4**, 105-123, 1975.

Holland, J.H., "Genetic Algorithms," *Scientific American*, **267**(1), 66, 1992.

Höskuldsson, A., *Prediction Methods in Science and Technology*, Thor Publishing, Denmark, 1996.

Huber, P.J., *Robust Statistics*, Wiley: New York, 1981.

Hubert, M., Rousseeuw, P.J. and Verboven, S., "A Fast Method for Robust Principal Components with Applications to Chemometrics," *Chemometrics and Intelligent Laboratory Systems* **60**, 101-111, 2002.

Hubert, M. and Verboven, S., "A robust PCR method for high-dimensional regressors." *Journal of Chemometrics* **17**, 438-452, 2003.

Hubert, M. and Vanden Branden, K., "Robust methods for Partial Least Squares regression," *Journal of Chemometrics* **17**, 537-549, 2003.

Hubert, M., Rousseeuw, P.J., Vanden Branden, K. "ROBPCA: a new approach to robust principal component analysis." *Technometrics* **47**, 64-79, 2005.

Jackson, J.E. and G.S. Mudholkar, "Control Procedures for Residuals Associated With Principal Component Analysis", *Technometrics*, **21**(3), 1979.

Jackson, J.E., "Principal Components and Factor Analysis: Part 1-Principal Components," *J. Qual. Tech.*, **13**(1), 1981.

Jackson, J.E., *A User's Guide to Principal Components*, John Wiley & Sons, New York, NY, 1991.

Kafadar, K. and C.H. Spiegelman. "An Alternative to Ordinary Q-Q Plots: Conditional Q-Q Plots," *Comp. Stat. and Data Anal*. **4**(3), 167-184, 1986.

Kargacin, M.E., and B.R. Kowalski, *Anal. Chem.*, **58**, 2300-2306 (1986).

Keenan, M.R. and Kotula, P.G. "Optimal scaling of TOF-SIMS spectrum-images prior to multivariate statistical analysis", *Appl. Surf. Science*, **231-232**, 240-244, 2004.

Keller, H.R. and D.L. Massart, "Evolving Factor Analysis," *Chemom. Intell. Lab. Syst.*, **12**, 209-224, 1992.

Kelly, J.J., C.H. Barlow, T.M. Jinguji and J.B. Callis, *Anal. Chem.*, **61**, 313-20, 1989.

Kiang, J.-H. and Y. Ozaki, Self-modeling curve resolution (SMCR): Principles, techniques, and applications" *Appl. Spectr. Rev*, **37**, 321-345, 2002.

Kiers, H.A.L., J. M. F. ten Berge, and Rasmus Bro, "PARAFAC2 - Part I. A direct fitting algorithm for the PARAFAC2 model," *Journal of Chemometrics*, **13**, pps. 275-294, 1999.

Kosanovich, K.A., M.J. Piovoso, K.S. Dahl, J.F. MacGregor and P. Nomikos (1994). "Multi-Way PCA Applied to an Industrial Batch Process," *Proc. 1994 American Control Conference*, 1994.

Kresta, J.V., J.F. MacGregor, and T.E. Marlin, "Multivariate Statistical Monitoring of Process Operating Performance," *Can. J. of Chem. Eng., **69**, 35-47, 1991.

Kroonenberg, P.M., and J. de Leeuw, "Principal component analysis of three-mode data by means of alternating least squares algorithms," *Psychometrika*, **45**, 69-97, 1980.

Kwakernaak, H., and R. Sivan, *Linear Optimal Control Systems*, Wiley, New York, NY, 1972.

Leardi, R., "Genetic algorithms in chemometrics and chemistry: a review", *J. Chemometrics*, **15**, 559-569.

Lindgren, F., P. Geladi, A. Berglund, M. Sjöstrom, and S. Wold, "Interactive Variable Selection (IVS) for PLS. Part II: Chemical Applications", *J. Chemometrics*, **9**(5), 331-342, 1995.

Lindgren, F., P. Geladi, R. Stefan, M. Sjöstrom, and S. Wold, "Interactive Variable Selection (IVS) for PLS. Part I: Theory and Algorithms", *J. Chemometrics*, **8**(5), 349-363, 1994.

Ljung, L., *System Identification Toolbox User's Guide*, The MathWorks, Inc., Natick, MA 1991.

Ljung, L., *System Identification: Theory for the User*, Prentice-Hall, Inc., New Jersey, 1987.

Lorber, A., L. E. Wangen and B. R. Kowalski, "A Theoretical Foundation for the PLS Algorithm," *J. Chemometrics*, **1**(19), 1987.

Lorber, A., N.M. Faber and B.R. Kowalski, *Anal. Chem.* **69**, 1620, 1997.

Lucasius, C.B. and G. Kateman, "Understanding and using genetic algorithms Part 1. Concepts, properties and context," *Chemom. Intell. Lab. Syst.*, **19**, 1-33, 1993.

Lucasius, C.B. and G. Kateman, "Understanding and using genetic algorithms Part 2. Representation, configuration and hybridization" *Chemom. Intell. Lab. Syst.,* **25**, 99-145, 1994.

Malinowski, E.R., "Factor Analysis in Chemistry", Second Edition, John Wiley & Sons, New York, NY, 1991.

Manne, R., "On the Resolution Problem in Hyphenated Chromatography", *Chemo. Intll. Lab. Sys.*, **27**, 89–94, 1995.

Martens, H. and Næs, T., *Multivariate Calibration*, John Wiley & Sons, New York, NY, 1989.

Martens H, Nielsen J.P., Engelsen S.B., *Anal. Chem.* **75**, 394–404, 2003.

Massart, D.L., B.G.M. Vandeginste, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke, "Handbook of Chemometrics and Qualimetrics, Part B," Elsevier, New York, 243-306, 1998..

McShane, M.J., G. L. Coté, and C.H. Spiegelman, "Variable Selection in Multivariable Calibration of a Spectroscopic Glucose Sensor", *Appl. Spectrosc.,* **51**(10), 1559–1564, 1997.

Moler, C.B. and G.W. Stewart, *SIAM J. Numer Anal.*, **10**, 241, 1973.

Musumarra, G., V. Barresi, D. F. Condorelli, C. G. Fortuna, S. Scirè, "Potentialities of multivariate approaches in genome-based cancer research: identification of candidate genes for new diagnostics by PLS discriminant analysis", *J. Chemometrics*, **18**(3), 125-132, 2004.

Næs, T. and H. Martens, "Principal Component Regression in NIR Analysis: Viewpoints, Background Details and Selection of Components," *J. Chemometrics*, **2**, 1988.

Næs, T., T. Isaksson and B. Kowalski, "Locally Weighted Regression and Scatter Correction for Near-Infrared Reflectance Data," *Anal. Chem.*, **62**(7), 1990.

Nomikos, P. and J.F. MacGregor, "Monitoring Batch Processes Using Multiway Principal Component Analysis," *AIChE Journal*, **40**(8), 1361-1375, 1994.

Nomikos, P. and J.F. MacGregor, "Multivariate SPC charts for monitoring batch processes," *Technometrics*, **37**(1), 1995.

Nørgaard L, and C. Ridder, "Rank annihilation factor analysis applied to flow injection analysis with photodiode-array detection," *Chemom. Intell. Lab. Syst.*, **23**, pp.107, 1994.

Osborne B.G., Fearn T., Miller A.R., and Douglas S., "Application of near infrared reflectance spectroscopy to the compositional analysis of biscuits and biscuit dough," *Journal of Scientific Food Agriculture* **35**, 99-105, 1984.

Paatero, P., "Least Squares Formulation of Robust Non-Negative Factor Analysis", *Chemometrics and Intelligent Laboratory Systems*, **37**, 23-35, 1997.

Phelan, M.K., C.H. Barlow, J.J. Kelly, T.M. Jinguji and J.B. Callis, *Anal. Chem.*, **61**,1419-24, 1989.

Qin S. J. and T. J. McAvoy, "Nonlinear PLS Modeling Using Neural Networks", *Computer & Chemical Engineering*, **16**, 379-392, 1992

Ricker, N.L., "The Use of Biased Least-Squares Estimators for Parameters in Discrete-Time Pulse-Response Models," *Ind. Eng. Chem. Res.*, **27**(2), 343, 1988.

Rousseeuw, P.J. "Least Median of Squares Regression." *Journal of the American Statistical Association* **79**, 871-880, 1984.

Rousseeuw, P.J., Leroy, A. *Robust Regression and Outlier Detection*, John Wiley: New York, 1987.

Rousseeuw, P.J. and Van Driessen, K., "A Fast Algorithm for the Minimum Covariance Determinant Estimator," *Technometrics* **41**, 212-223, 1999.

Rousseeuw, P. J. and Van Driessen, K., "An Algorithm for Positive-Breakdown Regression Based on Concentration Steps." in *Data Analysis: Scientific Modeling and Practical Application* (edited by W. Gaul, O. Opitz and M. Schader), Berlin: Springer-Verlag, 335-346, 2000.

Rousseeuw, P.J., Van Aelst, S., Van Driessen, K., and Agulló, J., Robust Multivariate Regression, *Technometrics*, **46**, 293-305, 2004.

Sage, A.P. and C.C. Whitle III, *Optimum systems control*, Second edition, Prentice Hall, Inc. Englewood Cliffs, N.J. 1977.

Sanchez, E., and B.R. Kowalski, "Tensorial Calibration: I. First Order Calibration", *J. Chemometrics*, **2**, 247-263, 1988.

Sanchez E., and B.R. Kowalski, "Tensorial Calibration: II. Second Order Calibration", *J. Chemometrics*, **2**, 265-283, 1988.

Sanchez E., and B.R. Kowalski, "Tensorial Resolution: A Direct Trilinear Decomposition", *J. Chemometrics*, **4**, 29-46, 1990.

Sánchez, F.C., Vandeginste, B.G.M., Hancewicz, T.M., and Massart, D.L., "Resolution of Complex Liquid Chromatography-Fourier Transform Infrared Spectroscopy Data", *Anal. Chem.*, **69**, 1477-1484, 1997.

Savitzky, A., and M.J.E. Golay, "Smoothing and Differentiation of Data by Simplified Least Squares Procedures, *Anal. Chem.*, **36**, 1627, 1964.

Sharaf, M.A., D.L. Illman, and B.R. Kowalski, *Chemometrics*, John Wiley & Sons, New York, 1986.

Sjöblom, J., O. Svensson, M. Josefson, H. Kullberg and S. Wold, "An evaluation of orthogonal signal correction applied to calibration transfer of near infrared spectra," *Chemo. and Intell. Lab. Sys.*, **44**, 229-244, 1998.

Smilde, A.K. and D.A. Doornbos, "Three way methods for the calibration of chromatographic systems: comparing PARAFAC and Three-way PLS," *J. Chemometrics*, **5**, 345-360, 1991.

Smilde, A.K., R. Tauler, J.M. Henshaw, L.W. Burgess and B.R. Kowalski, "Multicomponent Determination of Chlorinated Hydrocarbons using a Reaction-Based Chemical Sensor. 3.", *Anal. Chem.*, **66**, 3345-3351, 1994.

Smilde, A.K., "Three-Way Analyses Problems and Prospects", *Chemom. and Intel. Lab. Syst.*, **15**, 143-157, 1992.

Smilde, A.K., Y. Wang and B.R. Kowalski, "Theory of Medium-Rank Second-Order Calibration with Restricted-Tucker Models," *J. Chemometrics*, **8**, 21-36, 1994.

Smilde, A.K.,. "Comments on multilinear PLS" *J. Chemometrics*, **11**(5), pps. 367-377, 1997.

Spiegelman, C.H., M.J. McShane, M.J. Goetz, M. Motamedi, Q.L. Yue, and G.L. Coté, "Theoretical Justification of Wavelength Selection in PLS Calibration: Development of a New Algorithm", *Anal. Chem.*, **70**(1), 35-44, 1998.

Stahel, W.A., "Robuste Schätzungen: infinitesimale Optimalität und Schätzungen von Kovarianzmatrizen." *PhD thesis*, ETH Zürich, 1981.

Steinier, J., Y. Termonia, and J. Deltour, "Comments on Smoothing and Differentiation of Data by Simplified Least Squares Procedure," *Anal. Chem.,* **44**, 1906, 1972.

Stephanopolous, G., *Chemical Process Control*, Prentice Hall, Englewood Cliffs, N.J. 1984.

Stone, M. and R.J. Brooks, "Continuum Regression: Cross-validated Sequentially-constructed Prediction embracing Ordinary Least Squares, Partial Least Squares, and Principal Components Regression", *J. R. Statist. Soc. B*, **52**, 337-369, 1990.

Sum, S.T. and S.D. Brown, "Standardization of Fiber Optic Probes for Near Infrared Multivariate Calibrations", submitted to *Applied Spectroscopy,* MS No. 97-01793, 1997.

Tauler, R. "Multivariate Curve Resolution Applied to Second Order Data," presented at the First International Chemometrics InterNet Conference, *Chemo. and Intell. Lab. Sys.*, **30**(1), 133-146, 1995.

Tauler, R. and B. Kowalski, *Anal. Chem.*, **65**, 2040-2047, 1993.

Tauler, R., A. Izquierdo-Ridorsa and E. Casassas, "Simultaneous Analysis of Several Spectroscopic Titrations with Self-Modelling Curve Resolution", *Chemo. and Intell. Lab. Sys.*, **18**, 293-300, 1993.

Tauler, R., A.K. Smilde, J.M. Henshaw, L.W. Burgess and B.R. Kowalski, "Multicomponent Determination of Chlorinated Hydrocarbons using a Reaction-Based Chemical Sensor. 2 Chemical Speciation Using Multivariate Curve Resolution", *Anal. Chem.*, **66**, 3337-3344, 1994.

Tauler, R., A. Smilde, and B.R. Kowalski, "Selectivity, Local Rank, Three-Way Data Analysis and Ambiguity in Multivariate Curve Resolution", *J. Chemometrics*, **9**, 31-58, 1995.

Tauler, R., I. Marqués, and E. Casassas, "Multivariate Curve Resolution Applied to Three-Way Trilinear Data: Study of a Spectrofluorimetric Acid-Base Titration of Salycylic Acid at Three Excitation Wavelengths," *J. Chemometrics,* **12**, 55-75, 1998.

Tauler, R., "Calculation of maximum and minimum band boundaries of feasible solutions for species profiles obtained by multivariate curve resolution", *J. Chemometrics*, **15**, 627–646, 2001.

ten Berge, J.M.F., J. de Leeuw, and P. M. Kroonenberg, "Some additional results on principal components analysis of three-mode data by means of alternating least squares algorithms," *Psychometrika*, **52**, pps.183-191, 1980.

ten Berge, J.M.F., and H. A. L. Kiers, "Some uniqueness results for PARAFAC2," *Psychometrika*, **61**, pps. 123-132, 1996.

Tomasi, G., and R. Bro, *Comp. Stat. Data Anal.*, **50**,1700-1734, 2006.

Tucker, L. R., in *Problems in Measuring Change*, p. 122, University of Wisconsin Press, Madison, WI, 1963.

Tucker, L.R., "The extension of factor analysis to three-dimensional matrices," In: *Contributions to Mathematical Psychology*, edited by N. Frederiksen and H. Gulliksen, New York, Holt, Rinehart & Winston, 1964, p. 110-182.

Verboven, S., and Hubert, M., "LIBRA: a MATLAB Library for Robust Analysis," *Chemometrics and Intelligent Laboratory Systems*, **75**, 127-136, 2005.

Wang, Y., D.J. Veltkamp and B.R. Kowalski, "Multivariate Instrument Standardization," *Anal. Chem.*, **63**(23), 2750-2756, 1991.

Wang, Y., M.J. Lysaght and B.R. Kowalski, "Improvement of Multivariate Calibration through Instrument Standardization," *Anal. Chem.*, **64**(5), 562-565, 1992.

Wang, Z., T. Dean and B.R. Kowalski, "Additive Background Correction in Multivariate Instrument Standardization," *Anal. Chem.*, **67**(14), 2379–2385, 1995.

Wang, Z., T. Isaksson and B.R. Kowalski, "New Approach for Distance Measurement in Locally Weighted Regression," *Anal. Chem.*, **66**, 249-260, 1994.

Ward, R.C. *SIAM J. Numer Anal.*, **12**, 835, 1975.

Wentzell, P.D., D.T. Andrews, D.C. Hamilton, K. Faber, and B.R. Kowalski, "Maximum likelihood principal component analysis", *J. Chemometrics*, **11**(3), 1997.

Wilson, B.E., E. Sanchez and B.R. Kowalski, *J. Chemometrics*, **3**, 493-498, 1989.

Windig, W., "Self-Modeling Mixture Analysis of Spectral Data with Continuous Concentration Profiles", *Chemo. and Intell. Lab. Sys.*, **16**, 1-23, 1992.

Windig, W., and D.A. Stephenson, "Self-Modeling Mixture Analysis of 2nd-Derivative Near Infrared Spectral Data using the SIMPLISMA Approach", *Anal. Chem.,* **64**, 2735-2742, 1992.

Windig, W., B. Antalek, J.L. Lippert, Y. Batonneau, C. Bremard, "Combined use of conventional and second-derivative data in the SIMPLISMA self-modeling mixture analysis approach," *Anal. Chem.*, **74**, 1371-1379, 2002

Windig, W., N.B. Gallagher, J.M. Shaver and B.M. Wise, "A new approach for interactive self-modeling mixture analysis," *Chemom. Intell. Lab. Syst.*, **77**, 85-96, 2005.

Wise, B.M and N. B. Gallagher, "The Process Chemometrics Approach to Chemical Process Fault Detection and Supervision," *J. Process Control*, **6**(6), 329-348, 1996.

Wise, B.M. and B.R. Kowalski, "Process Chemometrics" in *Process Analytical Chemistry*, 259-312, Blackie Acadamic & Professional, London, 1995

Wise, B.M. and Gallagher, N.B. "Multi-way Analysis in Process Monitoring and Modeling," *AIChE Symposium Series*, **93**(316) 271-274, 1997.

Wise, B.M. and N. L. Ricker, "Identification of Finite Impulse Response Models using Continuum Regression," *J. Chemometrics*, **7**(1), 1-14, 1993.

Wise, B.M. and N. L. Ricker, "Identification of Finite Impulse Response Models with Principal Components Regression: Frequency-Response Properties," *Process Control and Quality*, **4**, 77-86, 1992.

Wise, B.M. and N. L. Ricker, "Recent Advances in Multivariate Statistical Process Control: Improving Robustness and Sensitivity," *IFAC Symposium on Advanced Control of Chemical Processes*, Toulouse, France, October 1991.

Wise, B.M., "Adapting Multivariate Analysis for Monitoring and Modeling Dynamic Systems," Ph.D. Dissertation, University of Washington, Seattle, 1991.

Wise, B.M., B.R. Holt, N.B. Gallagher and S. Lee, "A Comparison of Neural Networks, Non-Linear Biased Regression and a Genetic Algorithm for Dynamic Model Identification" *Chemom. Intell. Lab. Syst*, **30**, 81-89, 1995.

Wise, B.M., D.J. Veltkamp, N.L. Ricker, B.R. Kowalski, S.M. Barnes and V. Arakali, "Application of Multivariate Statistical Process Control (MSPC) to the West Valley Slurry-Fed Ceramic Melter Process," *Waste Management '91 Proceedings*, Tucson AZ 1991.

Wise, B.M., N. L. Ricker and D. J. Veltkamp, "Upset and Sensor Failure Detection in Multivariate Processes," *AIChE 1989 Annual Meeting*, November 1989.

Wise, B.M., N.L. Ricker, D.J. Veltkamp and B.R. Kowalski, "A Theoretical Basis for the Use of Principal Components Models for Monitoring Multivariate Processes", *Process Control and Quality*, **1**(1), 41-51, 1990.

Wise, B.M., N.B. Gallagher, S.W. Butler, D. White and G.G. Barna, "A Comparison of Principal Components Analysis, Multi-way Principal Components Analysis, Tri-linear Decomposition and Parallel Factor Analysis for Fault Detection in a Semiconductor Etch Process," *Journal of Chemometrics*, Vol. 13, pps 379-396, 1999.

Wise, B.M., N.B. Gallagher and E.B. Martin, "Application of PARAFAC2 to Fault Detection and Diagnosis in Semiconductor Etch," *J. Chemometrics*, Vol. 15, pps. 285-298, 2001.

Wise, B.M. and P. Geladi, "A Brief Introduction to Multivariate Image Analysis," *North American/International Chemometrics Society Newsletter*, Vol. 21, November, 2000.

Wold, S., "Nonlinear PLS modelling II: Spline inner relation (SPL_PLS)", *Chemom. Intell. Lab. Syst.*, **14**, 1992.

Wold, S., "Pattern recognition by means of disjoint principal component models." *Patt. Recog.*, **8**, 127-139, 1976.

Wold, S., A. Ruhe, H. Wold, and W.J. Dunn III, "The Collinearity Problem in Linear Regression. The Partial Least Square Approach to Generalized Inverses", *SIAM J. Sci. Stat. Compute.*, **5**, 735-743, 1994.

Wold, S., K. Esbensen, and P. Geladi, "Principal Components Analysis," *Chemo. and Intell. Lab. Sys.*, **2**, 37-52, 1987.

Wold, S., N. Kettaneh-Wold and B. Skagerberg, "Nonlinear PLS modeling," *Chemom. Intell. Lab. Syst.*, **7**, 53-65, 1989.

Wold, S., P. Geladi, K. Esbensen, and J. Ohman,. "Multi-Way Principal Components and PLS-Analysis", *J. Chemometrics*, **1**, 41-56, 1987.

Wold, S., H. Antti, F. Lindgren and J. Öhman, "Orthogonal signal correction of near-infrared spectra," *Chemo. and Intell. Lab. Sys.*, **44**, 175-185, 1998.

Zhu, C., and G.M. Hieftje, Appl. Spectrosc., **46**, 69-72, 1992.