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A THEORETICAL FOUNDATION FOR THE PLS ALGORITHM

AVRAHAM LORBER*, LAWRENCE E. WANGEN†, AND BRUCE R. KOWALSKI

Center for Process Analytical Chemistry, and Laboratory for Chemometrics, Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195, U.S.A.

SUMMARY

Partial least squares (PLS) modeling is an algorithm for relating one or more dependent variables to two or more independent variables. As a regression procedure it apparently evolved from the method of principal components regression (PCR) using the NIPALS algorithm, which is similar to the power method for determining the eigenvectors and eigenvalues of a matrix. This paper presents a theoretical explanation of the PLS algorithm using singular value decomposition and the power method. The relation of PLS to PCR is demonstrated, and PLS is shown to be one of a continuum of possible solutions of a similar type. These other solutions may give better prediction than either PLS or PCR under appropriate conditions.

KEY WORDS Calibration Indirect calibration Multivariate Matrix decomposition PLS PCR

INTRODUCTION

As chemists are faced with difficult problems that demand accurate quantitative information on multicomponent samples, they are relying on advanced data reduction from statistics, applied mathematics, and chemometrics.[1] Foremost among these methods are the many variations on multiple linear regression analysis (MLR).[2] MLR methods are suitable for situations where the individual chemical component spectral or sensor-array patterns are not unique but, in fact, overlap extensively. This condition is referred to as the collinearity problem and can cause considerable error amplification when it is severe.[3] Nevertheless, it is remarkable that these methods, which are becoming standard software in commercial instruments, can accurately estimate the concentrations of many analytes in samples even when collinearity is severe, such as the use of near infra-red reflection spectra for analysis of agricultural products.[4]

One of the newest and most promising multivariate statistical methods to find application in chemistry is partial least squares (PLS) developed by Herman Wold.[5] A growing number of chemists have used PLS to build calibration models that seem to have superior prediction to other methods.[6,7] However, in spite of the many and varied applications of PLS and some useful papers describing the algorithm, theoretical understanding is far from complete. The paper by Naes and Martens[8] used statistical concepts that began to provide a theoretical basis for PLS.

* Nuclear Research Centre — Negev, P.O. Box 9001, Beer-Sheva 84190, Israel.
† Analytical Chemistry Group, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.

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In this paper a theoretical foundation for PLS is presented based on singular value decomposition (SVD), the power method for finding the eigenvalues and eigenvectors of a matrix, and principal components regression (PCR). This work forms the basis for an understanding of PLS and how it fits into the range of other regression methods. It also provides a framework for improved methods of building calibration models that will appear in the future.

MULTIVARIATE QUANTITATION USING FIRST-ORDER DATA

This paper is concerned with the problem of quantitation using the information contained in observations derived from measurements made on K analytes using J sensors where it is assumed that the sensors respond linearly to the quantity of each analyte. Examples of such systems in an analytical chemistry are absorbance of mixtures that satisfy Beer's model or, under appropriate conditions, the response of a photodiode array detector to emissions from an inductively coupled plasma source.

Estimating the concentration, $c_{\mathrm{un},k}$, of the kth chemical component ($k = 1, \ldots, K$) in an unknown sample requires measuring the vector, $\mathbf{r}_{\mathrm{un}}$, which consists of $j = 1, \ldots, J$ responses at the J sensors. The measured responses are assumed to be related to analyte concentrations by a linear additive model. Thus the response measured at each sensor may be described as

$$r_{\mathrm{un},j} = \sum_{k=1}^{K} c_{\mathrm{un},k} s_{j,k} + b_j + e_j \tag{1}$$

Here $s_{j,k}$ designates the sensitivity (slope of the analytical calibration function) of the jth sensor to the kth analyte, b_j is the background contribution, and e_j is the error. By including the background in a zero offset term or by mean centering, the response vector $\mathbf{r}_{\mathrm{un}}$, can be written in matrix notation as

$$\mathbf{r}_{\mathrm{un}}^{\mathrm{T}} = \mathbf{c}_{\mathrm{un}}^{\mathrm{T}}\mathbf{S} + \mathbf{e}^{\mathrm{T}} \tag{2}$$

where $\mathbf{r}_{\mathrm{un}}$ is the J by 1 response vector, $\mathbf{c}_{\mathrm{un}}$ is the K by 1 vector analyte concentrations in the sample, $\mathbf{S}$ is the K by J matrix of sensitivities, and $\mathbf{e}$ is a J by 1 vector representing errors in each response. The superscript T designates a matrix or vector transpose.

To use equation (2) for predicting analyte concentrations in an unknown sample, it is necessary to determine the the matrix of sensitivities $\mathbf{S}$. This is accomplished by calibration. For K analytes and J sensors this will require at least K linearly independent samples, assuming that J is greater than or equal to K. Thus the linear additive model estimate for the calibration set is written as

$$\mathbf{R}_0 = \mathbf{CS} + \mathbf{E} \tag{3}$$

where $\mathbf{R}_0$ is the matrix of measured responses during calibration for the J sensors to the K analytes and $\mathbf{E}$ is the error matrix. If I samples are used for calibration, $\mathbf{R}_0$ is an I by J matrix. $\mathbf{C}$ is the I by K matrix of known concentrations of *all* K constituents in the calibration set. By inverting the matrix $\mathbf{C}$, the matrix of sensitivities can be estimated by

$$\begin{aligned} \hat{\mathbf{S}} &= \mathbf{C}^{+}\mathbf{R}_0 \\ \hat{\mathbf{S}}^{+} &= (\mathbf{C}^{+}\mathbf{R}_0)^{+} \end{aligned} \tag{4}$$

The superscript + denotes the pseudoinverse or Moore–Penrose inverse matrix. The pseudoinverse is used rather than the inverse in anticipation of nonsquare and overdetermined matrices. When the columns of $\mathbf{C}$ are linearly independent $\mathbf{C}^{+} = (\mathbf{C}^{\mathrm{T}}\mathbf{C})^{-1}\mathbf{C}^{\mathrm{T}}$, that is the

ordinary least squares solution is obtained. Solving equation (2) for concentration and directly substituting equation (4) into the result gives

$$\hat{\mathbf{c}}_{un}^{T} = \mathbf{r}_{un}^{T}\mathbf{S}^{+} \tag{5}$$

As above, if **S** has linearly independent columns, $\mathbf{S}^{+} = (\mathbf{S}^{T}\mathbf{S})^{-1}\mathbf{S}^{T}$.

The case represented by equation (5), where the concentrations of all constituents in the calibration samples are known, is called the *direct* or *total calibration* model and is quite restrictive because knowledge of the concentrations of all chemical components giving a response is required. It is possible to perform quantitation for cases where the concentrations of all chemical components in the calibration set is not known. These cases are solved by use of the method of *indirect* or *partial calibration.* To solve equation (5) directly, sensitivities for all of the chemical components contributing to the measured responses must be known. However if *partial calibration* is used it is only necessary to known the concentrations of the analyte desired because **S** does not have to be determined. This is shown by the following arguments.

A solution of the form

$$\hat{\mathbf{c}}_{un} = \mathbf{r}_{un}^{T}\mathbf{R}^{+}\mathbf{c} \tag{6}$$

is desired where **c** is the concentration vector from calibration for the *desired analyte only* and $\hat{\mathbf{c}}_{un}$ (a scalar) is the estimated concentration of this analyte in the unknown sample. This solution is found as follows. Solving the calibration equation (3) for **C** gives

$$\mathbf{C} = \mathbf{R}_0\mathbf{S}^{+} \tag{7}$$

Multiplying both sides by $\mathbf{R}_0^{+}$ results in

$$\mathbf{R}_0^{+}\mathbf{C} = \mathbf{R}_0^{+}\mathbf{R}_0\mathbf{S}^{+} = \mathbf{S}^{+} \tag{8a}$$

Thus, $\mathbf{S}^{+} = \mathbf{R}_0^{+}\mathbf{C}$, which can be substituted into equation (5) to give

$$\hat{\mathbf{c}}_{un}^{T} = \mathbf{r}_{un}^{T}\mathbf{R}_0^{+}\mathbf{C} \tag{8b}$$

The rules of matrix multiplication can be used to show that the concentrations of any specific analyte in the determination of the response matrix, $\mathbf{R}_0$, may be expressed as in equation (6), and desired solution is obtained. Therefore, only the concentration of the desired analyte must be known in the calibration set, although $\mathbf{R}_0$ contains information about all components causing a response.

Having obtained the matrix of responses $\mathbf{R}_0$ in the calibration process, the problem of quantitation becomes one of estimating the pseudoinverse ($\mathbf{R}_0^{+}$). The pseudoinverse can be calculated by use of SVD. This is discussed in the appendix, which may be referred to for additional details supporting the following discussion. The matrix $\mathbf{R}_0$ is decomposed by SVD as

$$\mathbf{R}_0 = \mathbf{U}\boldsymbol{\Sigma}\mathbf{V}^{T} \tag{9}$$

from which the pseudoinverse is easily calculated as

$$\mathbf{R}_0^{+} = \mathbf{V}\boldsymbol{\Sigma}^{-1}\mathbf{U}^{T} \tag{10}$$

where **V**, $\boldsymbol{\Sigma}$, and **U** are as described in the appendix.

Usually, because of random errors, the rank of the response matrix $\mathbf{R}_0$ will be greater than the number of chemical components, K, in the calibration set. In fact, the rank of $\mathbf{R}_0$ will usually approach, or be the same as, the minimum of I and J. If the full mathematical rank of $\mathbf{R}_0$ is included in the estimation, $\mathbf{R}_0^{+}$, all of the random errors from the calibration procedure are automatically included, and the solution is equivalent to that obtained using MLR. If this

is done, the error in the prediction of analyte concentrations in unknown samples following calibration will not be optimal because of the unnecessary incorporation of random errors from the response matrix, $\mathbf{R}_0$, into the prediction model represented by $\mathbf{R}_0^+$.

It is the intention of this paper to discuss some approaches for obtaining approximations for the prediction matrix, $\mathbf{R}_0^+$, that are optimal according to some criterion, for predicting analyte concentrations in an unknown sample. These approximations will be designated as $\hat{\mathbf{R}}^+$ to signify (i) that they are approximations, and (ii) that they are not simply the inverse or pseudo-inverse of $\mathbf{R}_0$. A theoretical basis for the PLS algorithm is presented and it is shown how the PLS concept can be extended to improve its predictive performance. Although the discussion is presented for one dependent variable, the concept applies to situations of more than one dependent variable.

PRINCIPAL COMPONENTS REGRESSION (PCR)

In PCR, only the numbers of eigenvectors and singular values required to calculate $\hat{\mathbf{R}}_0$ in equation (9), within the known or estimated random errors in its individual entries, are retained and subsequently used to estimate $\hat{\mathbf{R}}_0^+$. Those singular values associated with the small singular vectors representing mostly random errors not correlated to analyte responses are not used in the calculation of $\hat{\mathbf{R}}^+$. Thus PCR uses a response matrix, $\hat{\mathbf{R}}_0$, of lower mathematical rank that contains less error while retaining most of the real information caused by non-random sources of variation. This is similar to a smoothing of the data such as is accomplished in simple linear regression by drawing a smooth curve through bivariate data points that contain random errors but which otherwise are known to follow a linear relationship. If all of the information in $\mathbf{R}_0$ not associated with random errors is necessary to predict the unknown concentrations, the PCR method should be quite satisfactory. (The use of singular value decomposition in MLR and PCR has been nicely discussed in a recent paper[9] by Mandel.)

THE PARTIAL LEAST SQUARES ALGORITHM FOR ONE DEPENDENT VARIABLE (PLS1)

The general PLS1 mode A algorithm is a method for decomposing $\mathbf{R}_0$, in order to calculate an estimate of the pseudoinverse $\hat{\mathbf{R}}^+$, that differs from that obtained by PCR. We will present here a PLS1 algorithm in a form that differs slightly from the original presentation;[5,8] nevertheless, it is the same in that the derived score and loading matrices span the same vector spaces.

Decomposition procedure

In PLS1 the decomposition step refers to the estimation of two matrices, $\mathbf{T}$ and $\mathbf{P}$, with orthonormal columns, that estimate the response matrix, $\mathbf{R}_0$, by a different linear combination of the singular vectors than does PCR. (The reader familiar with other PLS algorithms should not be confused by the matrix $\mathbf{T}$ here. In the usual formulation each $\mathbf{t}$ vector has a length different from unity, whereas in this formulation $\mathbf{t}$ is normalized to unit length.) By 'estimation of $\mathbf{R}_0$' is meant that the two matrices, $\mathbf{T}$ and $\mathbf{P}$, span subspaces of the column and row spaces, respectively, of the $\mathbf{R}_0$ matrix, such that $\hat{\mathbf{R}}$ estimated from $\mathbf{T}$ and $\mathbf{P}$ is a lower rank approximation to $\mathbf{R}_0$. The error in this approximation depends on the number of vectors composing the $\mathbf{T}$ and $\mathbf{P}$ matrices. One purpose of PLS is to approximate $\mathbf{R}_0$ by the minimum number of components required to optimally predict the concentration of the *desired analyte*. This differs from PCR, where $\mathbf{R}_0$ is decomposed and the singular vectors used to approximate it are based only on their

importance for reproducing $\mathbf{R}_0$ without regard for their relation to the desired analyte. The steps in the PLS1 algorithm are as follows.

Step 0

Normalize the data to zero mean and unit variance if desired (assumed here).
Designate the original response matrix by $\mathbf{R}_0$.
Initialize the PLS component index, h, to 0.

Step 1

Compute the two vectors, $\mathbf{p}_{h+1}$ and $\mathbf{t}_{h+1}$:

$$\mathbf{p}_{h+1} = \mathbf{R}_h{}^{\mathrm{T}}\mathbf{c} / \| \mathbf{R}_h{}^{\mathrm{T}}\mathbf{c} \| \tag{11}$$

$$\mathbf{t}_{h+1} = \mathbf{R}_h\mathbf{p}_{h+1} / \| \mathbf{R}_h\mathbf{p}_{h+1} \| = \mathbf{R}_h(\mathbf{R}_h{}^{\mathrm{T}}\mathbf{c}) / \| \mathbf{R}_h\mathbf{R}_h{}^{\mathrm{T}}\mathbf{c} \| \tag{12}$$

The right side of equation (12) shows that these two steps give a $\mathbf{t}_{h+1}$ that is a scaled average of the simple linear predictions of $\mathbf{c}$ by each of the J sensors. The estimation of each PLS1 component is *not* an iterative procedure.

Step 2

Construct the residual matrix, $\mathbf{R}_{h+1}$, orthogonal to the two vectors by the standard method (see the Appendix) as follows:

$$\mathbf{R}_{h+1} = (\mathbf{I}_I - \mathbf{t}_{h+1}\mathbf{t}_{h+1}{}^{\mathrm{T}})\mathbf{R}_h(\mathbf{I}_J - \mathbf{p}_{h+1}\mathbf{p}_{h+1}{}^{\mathrm{T}}) \tag{13}$$

(the subscripts for the identity matrices denote their dimensionality, and are chosen to be consistent with the dimensions of the corresponding outer product matrices).

Step 3

A procedure such as cross-validation is used to calculate a predicted residual error sum of squares (PRESS) for the concentrations, $\mathbf{c}$. This PRESS can be used to determine the number of components. If more components are desired, increment the component h by 1 and go to step 1, otherwise go to the prediction. It is important to recognize that $\mathbf{R}_{h+1}$ may contain information important for explaining the variance of the original response matrix ($\mathbf{R}_0$), but if it is orthogonal to $\mathbf{c}$, no more components, $\mathbf{t}_{h+1}$, can be derived because the calculation represented by equation (11) will give a null vector.

Prediction

As mentioned, the PLS1 algorithm gives two column orthonormal matrices, $\mathbf{T}$ and $\mathbf{P}$, that are used to obtain the PLS1 approximation:

$$\hat{\mathbf{R}} = \mathbf{T}\mathbf{Q}\mathbf{P}^{\mathrm{T}} \tag{14a}$$

Because $\mathbf{T}$ are $\mathbf{P}$ are both column orthonormal

$$\mathbf{Q} = \mathbf{T}^{\mathrm{T}}\hat{\mathbf{R}}\mathbf{P} \tag{14b}$$

If **T** and **P** were left and right singular vectors of $\mathbf{R}_0$, the corresponding singular values should equal **Q**, and thus its pseudoinverse could be easily obtained. Although this version of PLS1 gives **T** and **P** that are column orthonormal, they are not singular vectors of $\mathbf{R}_0$ but rather they are linear combintions of the singular vectors of $\mathbf{R}_0$. In order to obtain the PLS1 estimate of the pseudoinverse, $\hat{\mathbf{R}}^+$, needed for prediction, the following calculations are performed.

The SVD of **Q** is

$$\mathbf{Q} = \mathbf{U}_q\mathbf{\Sigma}_q\mathbf{V}_q^T \tag{15}$$

The subscripts (q) are used to indicate that the associated $\mathbf{U}_q$, $\mathbf{S}_q$ and $\mathbf{V}_q$ refer to the decomposition of **Q**.

Equating equations (14b) and (15) and solving for $\hat{\mathbf{R}}$, we obtain

$$\hat{\mathbf{R}} = \mathbf{T}\mathbf{U}_q\mathbf{\Sigma}_q\mathbf{V}_q^T\mathbf{P}^T \tag{16a}$$

as an approximation for $\mathbf{R}_0$ *based on the PLS1 algorithm.* It may be noted that because **T** and **P** are column orthonormal, $\mathbf{T}\mathbf{T}^T$ and $\mathbf{P}\mathbf{P}^T$ are projection matrices. Thus multiplication by any other matrix that is in the space spanned by them leaves it unchanged. Therefore, $\hat{\mathbf{R}} = \mathbf{T}\mathbf{T}^T\hat{\mathbf{R}}\mathbf{P}\mathbf{P}^T$. Solving for the pseudoinverse, the corresponding approximation is

$$\hat{\mathbf{R}}^+ = \mathbf{P}\mathbf{V}_q\mathbf{\Sigma}_q^{-1}(\mathbf{T}\mathbf{U}_q)^T \tag{16b}$$

Equation (16a) is the approximation for $\mathbf{R}_0$ that results from the PLS1 algorithm. For this approximation the singular value decomposition is $\mathbf{U} = \mathbf{T}\mathbf{U}_q$, $\mathbf{\Sigma} = \mathbf{\Sigma}_q$, and $\mathbf{V} = \mathbf{P}\mathbf{V}_q$. Calculating the SVD of the PLS method is also important for multivariate statistical characteristics of PLS as described by Mandel.[9] It should be noted that this approximation is not necessarily the same as that obtained by, for example, the PCR method, because it is based on a different subset of singular vectors. That is, the subspace of $\mathbf{R}_0$ found by the PLS1 algorithm for calculating $\hat{\mathbf{R}}^+$ is not generally the same as that found by the PCR method. This is explained in more detail in the following section. Thus the reader is cautioned not to be confused by the use of the same symbol ($\hat{\mathbf{R}}^+$) in these different sections; $\mathbf{R}^+$ is used here to indicate the model used *for the* prediction calculation expressed by equations (6) and (8b).

Finally, the PLS1 solution for prediction is obtained by substituting the above expression for $\mathbf{R}^+$ into equation (6). Note that as in PCR, **T** and **P** are a lower rank approximation of $\mathbf{R}_0$. Thus the PLS1 solution also has a noise-reducing potential similar to that of PCR.

AN EXPLANATION OF THE DIFFERENCE BETWEEN PLS1 AND PCR

In order to understand the PLS method the following two properties of the SVD are used:

$$\mathbf{R}_0\mathbf{R}_0^T = \mathbf{U}\mathbf{\Sigma}^2\mathbf{U}^T \tag{17a}$$

$$\mathbf{U}^T\mathbf{U} = \mathbf{I} \tag{17b}$$

By construction, **U** is an orthonormal basis set of vectors that spans the sample space (column space of $\mathbf{R}_0$). Furthermore, since equation (7) assumes that **c** is contained in the column space as $\mathbf{R}_0$, it follows that **c** can be expressed as a linear combination of **U**. The specific linear combination of **U** which gives **c** is

$$\hat{\mathbf{c}} = \mathbf{U}\mathbf{a} \tag{18}$$

Into equation (12), substitute $\mathbf{U}\mathbf{\Sigma}^2\mathbf{U}^T$ from equation (17a) die $\mathbf{R}_0\mathbf{R}_0^T$ and **Ua** from equation (18) for **c**, and the expression $\mathbf{t}_1$ becomes

$$\mathbf{t}_1 \,\|\, \mathbf{R}\mathbf{R}^T\mathbf{c} \,\| \;= \mathbf{R}\mathbf{R}^T\mathbf{c} = (\mathbf{U}\mathbf{\Sigma}^2\mathbf{U}^T)\mathbf{U}\mathbf{a} = \mathbf{U}\mathbf{\Sigma}^2\mathbf{a} \tag{19}$$

The subscripts h used in equation (12) have been dropped from equation (19) for convenience. Equation (19) shows that $\mathbf{t}_1$, the first component found by the PLS1 algorithm, is a linear combination of the set of orthonormal singular vectors that are computed from the SVD of the response matrix. It also demonstrates that the importance of each singular vector, $\mathbf{u}_k$, in determining $\mathbf{t}_1$ is given by the product $\sigma_k{}^2 a_k$, where the σ_k and a_k are elements of $\mathbf{\Sigma}^2$ and $\mathbf{a}$, respectively. This is in contrast to PCR where only the first singular vector is involved in the estimation of the concentration vector in a one-component model. The belief is that the PLS1 linear combination is more relevant for describing the concentration vector than is the first principal component (i.e. the first singular vector). This should be true unless $\sigma_1{}^2 a_1$ is much greater than $\sigma_k{}^2 a_k$, $k \neq 1$. This characteristic helps to explain why prediction by PLS1 is often superior to that of PCR. Additionally, because the error is distributed over all components, if PLS1 succeeds at describing concentration using fewer components than PCR, the predicted concentrations will contain less error. In PCR the order of selection of singular vectors to be used in the development of the model describing concentration does not have any relation to their significance for describing concentration. They only describe, in order of decreasing variance, the variance structure of $\mathbf{R}_0$. Therefore, for estimating the concentration of a specific analyte, the PCR uses all the singular vectors needed to describe the variation in the matrix of responses regardless of whether or not they contain any information relevant to the desired analyte. In PLS1 the singular vectors are weighted by the a_k term in equation (19), and if a vector is not needed to describe an analyte (a_k will be zero) the vector $\mathbf{u}_k$ will not be used in the estimation of analyte concentration. Therefore, by using PLS1, it is possible to describe analyte concentration using fewer components than, or the same number of components as, required by PCR.

According to equation (19) the contribution of each singular vector to $\mathbf{t}_1$ is determined by the product $\sigma^2{}_k a_k$. Recalling that the singular values, σ_k, are determined only by the $\mathbf{R}_0$ matrix, it is apparent that they are not necessarily related to the true significance of their associated vectors in describing that vector's contribution to spanning the subspace of $\mathbf{R}_0$ which contains the information relating to concentrations of any specific analyte. This vector weighting can be even more limiting because of the fact tht the singular values are ordered in decreasing magnitude and their weights are squared in equation (19). In practice, situations that may be the most difficult to solve are likely to be those in whch the singular vectors most significant for describing an analyte concentration variance are associated with the smaller singular values.

PLS1–PCR COMPARISONS

The improvement in prediction expected from PLS1 compared to PCR is illustrated in Tables 1 and 2. The response and concentration data are from a calibration experiment reported by Fearn[10] and were derived from near infra-red reflectance measurements of 50 ground wheat samples. The independent variables, the $\mathbf{R}_0$ data, consist of the logarithm of reflected intensity at six selected wavelengths, and the dependent variable, $\mathbf{c}$, is protein content. Fearn originally used the data to illustrate the misuse of ridge regression for calibration when the largest eigenvector is not very important for describing variation of the desired analyte. These same data were also used by Naes and Martens in their fundamental paper on PLS.[8] In Table 1 the first 24 samples were used as calibration set and the remaining 26 for prediction. In Table 2 only the first 12 samples were used for calibration, and the same 26 samples were used for prediction. In both cases, the square of the first singular value is about 20 times that of the second. In Table 1, a_1 is relatively large ($a_1 = 0{\cdot}464$). Therefore the product $\sigma_1{}^2 a_1$ is dominant and the PRESS values after the first component are essentially the same for both PLS1 and

Table 1. Data for 24 calibration samples

k	σ_k	a_k	$a_k\sigma_k^2$	(PRESS)$^{1/2}$ PCR	PLS
1	2·422	0·464	2·721	1·907	1·909
2	0·317	−0·409	−0·041	1·793	1·344
3	0·137	−0·764	−0·014	0·489	0·334
4	0·111	−0·116	−0·001	0·359	0·356
5	0·015	0·035	0·000	0·314	0·233
6	0·012	−0·045	0·000	0·238	0·238

Table 2. Data for 12 calibration samples

k	σ_k	a_k	$a_k\sigma_k^2$	(PRESS)$^{1/2}$ PCR	PLS
1	2·355	0·004	0·020	1·634	0·924
2	0·522	0·433	0·118	1·662	1·129
3	0·368	0·871	0·118	1·028	0·611
4	0·217	0·163	0·008	0·284	0·279
5	0·031	−0·087	0·000	0·448	0·713
6	0·020	0·087	0·000	0·833	0·833

PCR. In contrast, for Table 2 the first vector has virtually no importance for describing concentration ($a_1 = 0{\cdot}004$), and in this data set the PRESS after the first factor for the PLS1 is less than for PCR. For both data sets the PRESS values for six components are the same for PLS1 and PCR. Since $\mathbf{R}_0$ is composed of six variables, these six component PRESS values are also equivalent to the MLR PRESS values.

When 24 calibration samples were used, PLS1 best described the data (lowest PRESS) using five components, whereas PCR required six. However, when only 12 calibration samples were used, both methods best described the data using four factors, although PLS1 had a lower PRESS. It is also observed that decreasing the number of calibration samples from 24 to 12 increases the MLR PRESS from 0·238 to 0·833. A value of 0·232 (see Table 4) was the smallest PRESS found by any method for this data set using the 24 calibration samples. The MLR PRESS value in Table 1 approaches this 'best' value and indeed does almost as well as the PLS1 model. In contrast, the MLR PRESS for the prediction equation developed using 12 calibration samples of 0·833 is not nearly as close to the corresponding PCR and PLS1 values of 0·284 and 0·279, respectively, both for four-component models. Furthermore these PCR and PLS1 PRESS results for a 12 sample calibration set are much closer to the 'best' value of 0·232 obtained using 24 calibration samples tabulated in Table 4.

EFFECT OF VARIOUS POWERS OF THE SINGULAR VALUES

Recall that the PLS1 solution for $\mathbf{t}_i$ as represented by either equation (12) or equation (19) is obtained after only one iteration through the algorithm, and that the algorithm is a decomposition of the response matrix, $\mathbf{R}_0$. If the algorithm were repeated n times with the most recent iterate's estimate of $\mathbf{t}$ used in place of $\mathbf{c}$ after the first iteration until it converged, that is until

the most recent iterate of $\mathbf{t}_1$ was the same as the previous one, the eigenvalues and eigenvectors of the matrix $\mathbf{R}_0\mathbf{R}_0^T$ would result. At convergence the result would be

$$\sigma_1^2\mathbf{t}_1^{(n)} = (\mathbf{R}_0\mathbf{R}_0^T)\mathbf{t}_1^{n-1} \tag{20}$$

This is in fact the power method[11] for estimating eigenvalues and eigenvectors of a matrix. Thus the $\mathbf{t}_1$ and σ_1^2 estimated by repeating the PLS1 algorithm n times are the true first row eigenvector and associated eigenvalue of $\mathbf{R}_0\mathbf{R}_0^T$ (the eigenvalues are the square of the singular values). This is the PCR solution. Recalling that the PLS1 algorithm uses only one iteration, it is observed that the difference between $\mathbf{t}_1$ as estimated by PLS1 as compared to the $\mathbf{t}_1$ as estimated by PCR is in the power to which the matrix $\mathbf{R}_0\mathbf{R}_0^T$ must be raised to obtain the solution. The implications of this can be seen using the SVD of $(\mathbf{R}_0\mathbf{R}_0^T)^n$ to derive its eigenvectors and eigenvalues as follows:

$$(\mathbf{R}_0\mathbf{R}_0^T)^n = \mathbf{U}\boldsymbol{\Sigma}^{2n}\mathbf{U}^T \tag{21}$$

Inspection of equation (21) shows that when n becomes large, as in the power method, the largest eigenvalue will dominate the decomposition of $(\mathbf{R}_0\mathbf{R}_0^T)^n$.

In the limiting case at the opposite extreme to that of large n, that is when $n = 0$, all values of $\boldsymbol{\Sigma}^{2n}$ in equation (21) will be $1 \cdot 0$. This means that $\boldsymbol{\Sigma}^{2n} = \boldsymbol{\Sigma}^0 = \mathbf{I}$. Thus, as seen by equation (19), for $n = 0$, $\mathbf{t}_1$ is a scalar multiple of $\mathbf{Ua}$. Substitution of this result into equation (18) shows that $\mathbf{t}_1 = \mathbf{c}/\|\mathbf{c}\|$. Now if $\mathbf{t}_1$ is a multiple of $\mathbf{c}$ it follows by substitution of this $\mathbf{t}_1$ into equation (13) that $\mathbf{R}_1^T\mathbf{c}$ in equation (11) is equal to zero because $\mathbf{R}_1$ was constructed orthogonal to $\mathbf{R}_0$ equation (13). This means that no additional components can be calculated by the algorithm for estimation of $\mathbf{R}_0$. Therefore a rank-one solution for the matrix $\hat{\mathbf{R}}^+$ results. This solution is the epitome of overfitting. It is exact for describing the desired analyte's concentration vector $\mathbf{c}$ used in the calibration but may be quite useless for predicting the concentration of future 'unknown' samples. This is so because the information in the calibration response matrix that describes the variation of the other chemical components not correlated to $\mathbf{c}$ has not been retained in the estimate, $\hat{\mathbf{R}}^+$.

From this discussion it is seen that by changing the power, n, of the singular values it may be possible to describe the concentration vector, $\mathbf{c}$, with fewer components. However, fewer components will not necessarily result in better prediction. The optimal weighting must lie in the range

$$0 < n < \infty$$

For $n = 1$ the PLS1 solution is obtained.

These observations suggest that different selection criteria can be applied to the estimation of $\mathbf{t}_1$ by choice of n. Indeed, fractional powers of n would give the largest eigenvalues even less weight than occurs for PLS1. When n approaches infinity, a principal components analysis is obtained and the $\mathbf{t}_h$ are calculated in order of decreasing variance components of the $\mathbf{R}_0$ matrix. Vectors for reproducing $\mathbf{R}_0$ selected in this way may or may not have any relevance to the concentration vector $\mathbf{c}$. In contrast, if $n = 0$, analyte concentration is described by the least number of components, but the predicted results may be poor. A value of n somewhere between these extremes should give the best prediction.

This presentation demonstrates that the common PLS1 method constitutes one choice among many possible values of the power n. To compensate for over-fitting, Martens and Jensen[12] suggested different weighting schemes equivalent to values of n greater than one. In that case the computed $\mathbf{t}_h$ will lie between PLS1 and PCR solutions. Here we suggest use of values of n that are less than one. As indicated in the above discussions, this suggestion is motivated by

the possibility that eigenvectors of $\mathbf{R_0}^T$ associated with the largest singular values may not have much importance in explaining the variance for the analyte for which quantitation is desired. Therefore, powers of n less than one will give higher weights to lower eigenvalues than does PLS. This has the effect of weighting the variance represented by the eigenvectors. The concept of raising $(\mathbf{R_0R_0}^T)^n$ was discussed at the 1984 MULDAST meeting.[13]

Our proposed version of PLS1 is accomplished by changing step 1 in the PLS algorithm. Recall that $\mathbf{R_0} = \mathbf{U\Sigma V}^T$ is the SVD of the response matrix $\mathbf{R_0}$.

Step 1 (revised)

Increment the component index h by 1.
Compute the SVD of the matrix $\mathbf{R}_h = \mathbf{U}_h\mathbf{\Sigma}_h\mathbf{V}_h^T$.
Compute the two vectors

$$\mathbf{p}_{h+1} = \mathbf{V}_h\mathbf{\Sigma}_h{}^n\mathbf{a} / \| \mathbf{V}_h\mathbf{\Sigma}_h{}^n\mathbf{a} \| \quad (22a)$$

$$\mathbf{t}_{h+1} = \mathbf{U}_h\mathbf{\Sigma}_h{}^{2n}\mathbf{a} / \| \mathbf{U}_h\mathbf{\Sigma}_h{}^{2n}\mathbf{a} \| \quad (22b)$$

This algorithm was used to calculate $\hat{\mathbf{R}}^+$ as a function of various values of n using the same data sets for calibration as was used for the results presented in Tables 1 and 2. Values of n from very large (PCR), to $n = 1{\cdot}0$ (PLS1) to $n = 1/4$ were used to estimate different $\hat{\mathbf{R}}^+$s based on 12 calibration samples and 24 calibration samples. The PRESS results of using these $\hat{\mathbf{R}}^+$s to predict the concentrations of the 26 samples in the prediction set as a function of one to six components are presented in Tables 3 and 4. For the case of 12 calibration samples, Table 3 shows the best prediction at four components for all values of n. The best overall result of 0·267 is obtained at $n = 0{\cdot}6$. For the case of 24 calibration samples, results in Table 4 show

Table 3. Square root of PRESS value as a function of the power of the matrix for the 12 calibration samples

k	PCR	4	2	1(PLS)	0.6	1/2	1/3	1/4
1	1·634	1·634	1·251	0·924	0·858	0·834	0·790	0·766
2	1·662	1·475	1·284	1·129	1·111	1·002	0·718	0·596
3	1·028	0·953	0·816	0·611	0·484	0·444	0·344	0·542
4	0·284	0·284	0·284	0·279	0·267	0·275	0·271	0·373
5	0·448	0·501	0·605	0·713	0·777	0·796	0·682	0·754
6	0·833	0·833	0·833	0·833	0·833	0·833	0·988	0·848

Table 4. Square root of PRESS value as a function of the power of the matrix for the 24 calibration samples

k	PCR	4	2	1(PLS)	2/3	1/2	1/3	1/4
1	1·907	1·907	1·906	1·909	1·942	2·004	2·162	2·313
2	1·793	1·767	1·640	1·344	1·104	0·907	0·691	0·596
3	0·489	0·382	0·346	0·334	0·332	0·332	0·332	0·332
4	0·359	0·359	0·358	0·356	0·360	0·371	0·373	0·332
5	0·314	0·260	0·238	0·233	0·232	0·233	0·234	0·245
6	0·238	0·238	0·238	0·238	0·238	0·238	0·258	0·742

an optimal prediction at five components for $n = 2/3$, but the difference from PLS1 ($n = 1$) is trivial.

CONCLUSION

It has been shown that PLS can be understood using the framework provided by SVD and the power method. PLS is one of a continuum of variations similar to PCR making specific implicit assumptions about the importance of each principal component or eigenvector for describing the dependent variable, in this case concentration. It is inherently no better than those methods formed by selecting individual eigenvectors (principal components, latent roots) or independent variables (stepwide or ridge regression). Many different solutions can be obtained by varying the value of n. An iterative scheme could be used for any specific dependent variable to determine an optimal value of n.

The results presented in this paper generalize beyond the calibration problem discussed here which is of particular interest to chemists. Indeed, they affect any modeling problem involving independent and dependent variables.

Finally, the results in this paper provide a framework for further understanding and improved algorithms for calibration and other forms of modeling.

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APPENDIX

Singular value decomposition

Any real matrix $\mathbf{X}$ with I rows ($i = 1, \ldots, I$) and J columns ($j = 1, \ldots, J$) can be decomposed into three matrices $\mathbf{U}$, $\mathbf{\Sigma}$ and $\mathbf{V}$ as follows:

$$\mathbf{X} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^{\mathrm{T}} \tag{23}$$

The matrices $\mathbf{U}$ and $\mathbf{V}$ are orthonormal (i.e. $\mathbf{U}^{\mathrm{T}}\mathbf{U} = \mathbf{I}$, $\mathbf{V}^{\mathrm{T}}\mathbf{V} = \mathbf{I}$ where $\mathbf{I}$ is the identity matrix) and the matrix $\mathbf{\Sigma}$ is a diagonal matrix whose diagonal elements σ_k ($k = 1, \ldots, K$) are the singular values, and equal to the square roots of the eigenvalues of the matrices $\mathbf{X}^{\mathrm{T}}\mathbf{X}$ and $\mathbf{X}\mathbf{X}^{\mathrm{T}}$. The columns of $\mathbf{U}$ span the column space and the columns of $\mathbf{V}$ span the row space of $\mathbf{X}$. By using the orthonormal properties of $\mathbf{U}$ and $\mathbf{V}$ it is easy to verify the following properties which are important for an understanding of the PLS algorithm:

$$\mathbf{X}^{\mathrm{T}}\mathbf{X} = \mathbf{V}\mathbf{\Sigma}^2\mathbf{V}^{\mathrm{T}} \tag{24a}$$

$$\mathbf{X}\mathbf{X}^{\mathrm{T}} = \mathbf{U}\mathbf{\Sigma}^2\mathbf{U}^{\mathrm{T}} \tag{24b}$$

$$\mathbf{X}^{\mathrm{T}}\mathbf{u}_k = \sigma_k\mathbf{v}_k \tag{24c}$$

$$\mathbf{X}\mathbf{v}_k = \sigma_k\mathbf{u}_k \tag{24d}$$

$$\mathbf{X}^{+} = \mathbf{V}\boldsymbol{\Sigma}^{-1}\mathbf{U}^{\mathrm{T}} \tag{24e}$$

$$(\mathbf{X}^{\mathrm{T}})^{+} = \mathbf{U}\boldsymbol{\Sigma}^{-1}\mathbf{V}^{\mathrm{T}}$$

$$= \mathbf{X}(\mathbf{X}^{\mathrm{T}}\mathbf{X})^{-1} \text{ iff columns of } \mathbf{X} \text{ are linearly independent} \tag{24f}$$

When $\mathbf{X}$ is derived from real data its mathematical rank is almost always the lesser of I and J. However the true rank from the point of view of the number of physically and/or chemically meaningful components is usually less than the mathematical rank. It is common in such cases for some of the singular values estimated by the SVD to be small and/or to represent only random error. In such cases, the data matrix $\mathbf{X}$ can be reconstructed within the limits of error using fewer than the minimum of either I or J vectors. Reconstruction of $\mathbf{X}$ using only the physically meaningful singular vectors as suggested can actually reduce the random errors.

The matrices $\mathbf{X}^{+}\mathbf{X} = \mathbf{V}\mathbf{V}^{\mathrm{T}}$ and $\mathbf{X}\mathbf{X}^{+} = \mathbf{U}\mathbf{U}^{\mathrm{T}}$ are projection matrices. If they are multiplied by any vector $\mathbf{x}$, that part of $\mathbf{x}$ that belongs to the space spanned by $\mathbf{X}^{\mathrm{T}}\mathbf{X}$ or $\mathbf{X}\mathbf{X}^{\mathrm{T}}$, depending on the dimensionality of $\mathbf{x}$, will remain and the part of $\mathbf{x}$ not contained in this space will be zero. In contrast the matrices defined by $\mathbf{I}_J - \mathbf{X}^{+}\mathbf{X} = \mathbf{I}_J - \mathbf{V}\mathbf{V}^{\mathrm{T}}$ and $\mathbf{I}_I - \mathbf{X}\mathbf{X}^{+} = \mathbf{I}_I - \mathbf{U}\mathbf{U}^{\mathrm{T}}$ are also projection matrices but they span the spaces orthogonal to that spanned by $\mathbf{X}^{\mathrm{T}}\mathbf{X}$ and $\mathbf{X}\mathbf{X}^{\mathrm{T}}$. Therefore, multiplication of a J or I element vector by one of these matrices will result in a new vector that is orthogonal to the space spanned by $\mathbf{X}^{\mathrm{T}}\mathbf{X}$ and $\mathbf{X}\mathbf{X}^{\mathrm{T}}$. These operations have the effect of separating an arbitrary vector into its orthogonal components that are contained in the spaces spanned by a projection matrix and its orthogonal complement.

The equivalence of the NIPALS algorithm and the power method

The PLS algorithm was originally based on the NIPAS algorithm;[13] however in this paper it is represented differently. This presentation is made possible by recognition that NIPALS is essentially the power method. This is shown in the following.

The idea behind the NIPALS algorithm is to use equations (24c) and (24d) to obtain successive approximations to $\mathbf{u}_k$ and $\mathbf{v}_k$. Having an initial estimate of $\mathbf{u}_k^{(0)}$, which may be any row of the matrix $\mathbf{X}$, the first estimate to $\mathbf{v}_k^{(1)}$ is according to equation (24c)

$$\mathbf{v}_k^{(1)} = \mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(0)} / \| \mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(0)} \| \tag{25}$$

Comparison of equation (25) to equation (24c) immediately reveals that the norm $\| \mathbf{X}^{\mathrm{T}}\mathbf{u}_k \|$ is an approximation of the singular value σ_k. According to equation (24d), the calculated $\mathbf{v}_k^{(1)}$ may be used to give a refined estimate for $\mathbf{u}_k$ as

$$\mathbf{u}_k^{(1)} = \mathbf{X}\mathbf{v}_k^{(1)} / \| \mathbf{X}\mathbf{v}_k^{(1)} \| \tag{26}$$

and now $\| \mathbf{X}\mathbf{v}_k^{(1)} \|$ is an improved approximation of $\sigma_k^{(1)}$. At this point the latest estimate of the singular value is compared to the previous one or alternatively the elements of the eigenvectors may be compared to test for convergence. If there is no convergence, the algorithm continues to the $(h+1)$th iteration:

$$\mathbf{v}_k^{(h+1)} = \mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(h)} / \| \mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(h)} \| \tag{27a}$$

$$\mathbf{u}_k^{(h+1)} = \mathbf{X}\mathbf{v}_k^{(h+1)} / \| \mathbf{X}\mathbf{v}_k^{(h+1)} \| \tag{27b}$$

At convergence, the information or variance represented by that eigenvector is removed from

the data matrix, **X**, by the following procedure:

$$\begin{aligned} \mathbf{E}_1 &= \mathbf{X} - \sigma_1 \mathbf{u}_1 \mathbf{v}_1^{\mathrm{T}} \\ \mathbf{E}_2 &= \mathbf{E}_1 - \sigma_2 \mathbf{u}_2 \mathbf{v}_2^{\mathrm{T}} \\ &\vdots \quad \vdots \quad \vdots \\ \mathbf{E}_k &= \mathbf{E}_{k-1} - \sigma_k \mathbf{u}_k \mathbf{v}_k^{\mathrm{T}} \end{aligned} \tag{28}$$

The iterations continue until all significant factors are found. These steps are equivalent to the NIPALS algorithm as presented.

The two steps (equations (27a) and (27b)) may be combined to give for the hth iteration step

$$\mathbf{u}_k^{(h+1)} = \mathbf{X}\mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(h)} / \| \mathbf{X}\mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(h)} \| \tag{29}$$

and there is no need to calculate $\mathbf{v}_k^{(h+1)}$ at each iteration step. It is calculated after convergence using equation (27a). The singular value is equal to the square root of the norm $\| \mathbf{X}\mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(h)} \|$ or to $\| \mathbf{X}^{\mathrm{T}}\mathbf{u}_k^{(h+1)} \|$.

Using arguments analogous to the above, an iteration scheme may be derived for estimating $\mathbf{v}_k^{(h+1)}$ by

$$\mathbf{v}_k^{(h+1)} = \mathbf{X}^{\mathrm{T}}\mathbf{X}\mathbf{v}_k^{(h)} / \| \mathbf{X}^{\mathrm{T}}\mathbf{X}\mathbf{v}_k^{(h)} \| \tag{30}$$

The approximation schemes proposed by equations (29) and (30) are the same as those used by the power method.[11] The only difference is that in the power method the approximation is calculated for the matrix **X** or $\mathbf{X}^{\mathrm{T}}$, whereas here it is calculated for the matrices $\mathbf{X}\mathbf{X}^{\mathrm{T}}$ and $\mathbf{X}^{\mathrm{T}}\mathbf{X}$. Multiplication of the matrix by its transpose gives a square matrix for which the power method is applicable. The criterion for convergence for the power method is that the singular values should decrease in magnitude (i.e. $\sigma_1 > \sigma_2 > , \ldots, > \sigma_k$). The rate of convergence speed is linearly dependent on the ratio of the kth to the first singular value.

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