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Instrument Database System and Application to Mass Spectrometry/Mass Spectrometry

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An instrument database system first used for mass spectrometry/mass spectrometry but applicable to other instruments is described. This software system allows real-time storage and rapid retrieval of all fixed instrument parameters, any variables chosen to be stored by the user, and X-Y data of any type from a computer-interfaced source. Timing data from three different minicomputer and disk systems are provided to show speeds for typical data extraction. This instrument database system allows the storage and ready retrieval of data from many dimensions. All possible data surfaces available from a particular database can be reconstructed. Plotting and tabulating routines are also discussed. It is written primarily in FORTRAN IV and is designed to operate efficiently on a minicomputer. This software has been submitted to DECUS for general availability.

Many modern analytical instrumentation systems are capable of creating vast amounts of data in a very short period of time. The advent of computer-controlled instruments allows the routine variation of a number of measurement parameters, each of which can provide another dimension of information. In addition, multiple instruments can be coupled to simultaneously probe multiple characteristics of a sample. Among the first of such instruments was GC/MS (gas chromatography/mass spectrometry).

Many other examples have appeared in recent years, including GC/FTIR (gas chromatography/Fourier transform infrared spectrometry) and GC/MS/FTIR. The advent of MS/MS (mass spectrometry/mass spectrometry) created multidimensional data on an even larger scale. Each of these instrument systems is capable of creating hundreds of data points per second for hours. Without computer storage and retrieval of data, these techniques would not be practical.

The ability of these instruments to record rapidly and store efficiently has modified to some degree the classical approach to experimental design, especially in nonacademic laboratories. It is no longer cost-efficient to carry out a large number of exploratory experiments to get only the data necessary for the analysis. It is far more efficient to use a small amount of additional time recording unused data than to have to repeat an analysis because of missing data. Naturally, some care must be exercised in selecting reasonable parameters for storage.

The evolution of GC/MS brought with it the development of computer data systems designed to handle the dimension of time in addition to mass and intensity. However, even three dimensions are inadequate to cope with the measurement capabilities of MS/MS instruments and many other modern computer-controlled systems. In the case of a totally computer-controlled MS/MS, a large number of variables can be scanned, either singly or jointly. Each such scan will produce

one plane of information in the multidimensional database. As an example, the ion axial energy can be scanned at a fixed mass or the mass can be scanned with incremental changes in axial energy. Other variables (dimensions) include direct inlet probe temperature, collision gas pressure, ionization voltage, chemical ionization gas pressure, lens voltages (both in the source and between quadrupoles), and collision gas type. Since recording unneeded data requires time, the user needs the ability to choose the most appropriate selection of data to be stored for any given run. To do this, a new, more versatile instrument database system is required.

Fortunately, the storage of all these data has become affordable with the use of computers with high speed, large capacity disks and magnetic tapes. Now the analyst can store on disk all selected data as it is acquired for later manipulation and display, and subsequently put it on magnetic tape for archival storage. The general problem is one of rapidly and flexibly accessing the stored data. An additional problem in multidimensional instrumentation is the need to extract any available plane of information in the database, even if that plane does not correspond to the types of scans that produced the data.

The chemical literature contains many examples of systems for creating and searching libraries (1-11). There are also suggestions for using pattern recognition (12-20) and artificial intelligence or heuristic (21-25) means of interpreting data. Little is said though about initial storage of raw data in real time. We have developed a software system that provides rapid, versatile, and efficient storage of data and includes algorithms for rapidly accessing and extracting it.

A large body of literature has developed, primarily in the business world, dealing with databases (26-29). Airline reservation systems, banking transactions, and police work are examples of common applications for database management systems. These systems must provide rapid, versatile access to large amounts of data. In addition, the ability to modify, insert, and delete records is important to these users. Fortunately, instrument database systems are somewhat simpler since modification, deletion, or addition of data is rarely carried out on the raw data. Therefore, using many of the same techniques used for database management systems, we have developed an instrument database system that provides the rapid storage and access time characteristic of these database systems, using a dense index (pointer file) with counters at the head of each variable length record.

At the same time, we have included in our system several areas that either have been overlooked or have not been necessary in past scientific instrumentation database implementations: (1) the ability to store all initial instrument parameters; (2) the ability to select from an unlimited set of instrument variables the particular changing parameters that will be stored; (3) the ability to store selected *X-Y* data pairs (such as mass-intensity); and (4) the ability to add comments before, during, or after the experiment. We believe that this software system could be the basis for a standard to be used by many laboratories and that such widespread use would allow easy exchange of data and reduce duplication of program development. Our two laboratories (Lawrence Livermore National Laboratory and Michigan State University) have found it extremely beneficial.

The development of our own computer-automated triple quadrupole mass spectrometer (TQMS) instruments (30, 31) provided impetus for our initial implementation since their inherent multidimensional nature requires a much more versatile software system than the simple *X-Y-time* data storage programs commonly available for GC/MS systems. Though MS/MS provides the examples and illustrations used in this paper, this database system could readily be applied

to other computer-interfaced instrument types, using standard computer programming techniques.

The interface of this database system to an existing instrument control and data acquisition computer consists of a series of six Fortran subroutines, three to write data and three to read it. Thus, any instrument with a computer control program in Fortran could use this system. In the simplest form, only eight lines of code would need to be added to store data; one to get the file name, three to open the files, one to initialize the counters, one to store initial instrument parameters, one to store comments, and a final one contained in a loop to store real-time data contained in standard Fortran arrays. A similar sequence would be needed to read the data.

Because the subroutines are short and data storage is efficient, this system could be added to many existing dedicated instrument control computers. It could also be put on a separate, time-shared computer system, with a high-speed data link. As an example, one of the MS/MS implementations for this database system uses two DEC LSI-11 microprocessors linked with a 2 megabyte per second interprocessor linker (31).

The function of an effective database structure is to allow fast and flexible storage and retrieval of data. In addition, data must be stored more or less permanently (easily archivable) and at reasonable cost. Nearly all computer-based systems use disks as the storage media for data. Computer memory would be faster but is more expensive, and many small computer systems are limited in the amount of memory they can address. Magnetic tape is inexpensive and can be written very rapidly, but access time is very long. Disks combine reasonable cost, very high capacity, and rapid access.

In its simplest form, a disk file is a sequentially ordered collection of information, placed in the file as received and packed in an unstructured way. If the data are written in such a way that they can be printed or displayed directly without any processing, it is called a Formatted ASCII file. This type of file is almost never used for large amounts of data, as it requires a great deal of space on the disk and is cumbersome to access.

A second file type is again sequential, but the data are written in internal (unformatted) mode. This is the most compact form of storing data. It has been used in some instrument data systems but has several drawbacks, the most severe being access speed. The only way to find any particular piece of data is to start at the beginning of the file and read all entries until the particular datum is encountered, a very slow process.

A third type of file is the direct access file. The file is broken into fixed length records, and any one of these records may be accessed almost immediately. An elementary direct access file, consisting of one record per scan could be used by an instrument that always puts out a fixed amount of data. For mass spectrometry, this format would waste a great deal of space, as the record length would have to be fixed long enough to hold the maximum number of mass/intensity pairs that might be recorded in any one scan.

In our system we have combined elements of several file types to create a fast, efficient system (see Figure 1). An unformatted, sequential file, the header file, is used to store a variety of information that describes the instrument, the experimental conditions, and the variables selected to be recorded. A second file, the pointer file, is written with short, direct access records. The major function of this file is to record the starting record number for the variables and data pairs located in the third file. The third file, the data file, is also direct access and one or more records contain the values of the selected variable parameters and the *X-Y* data pairs acquired for each scan. The fourth file, the dictionary file, is also direct access and each record contains a definition of

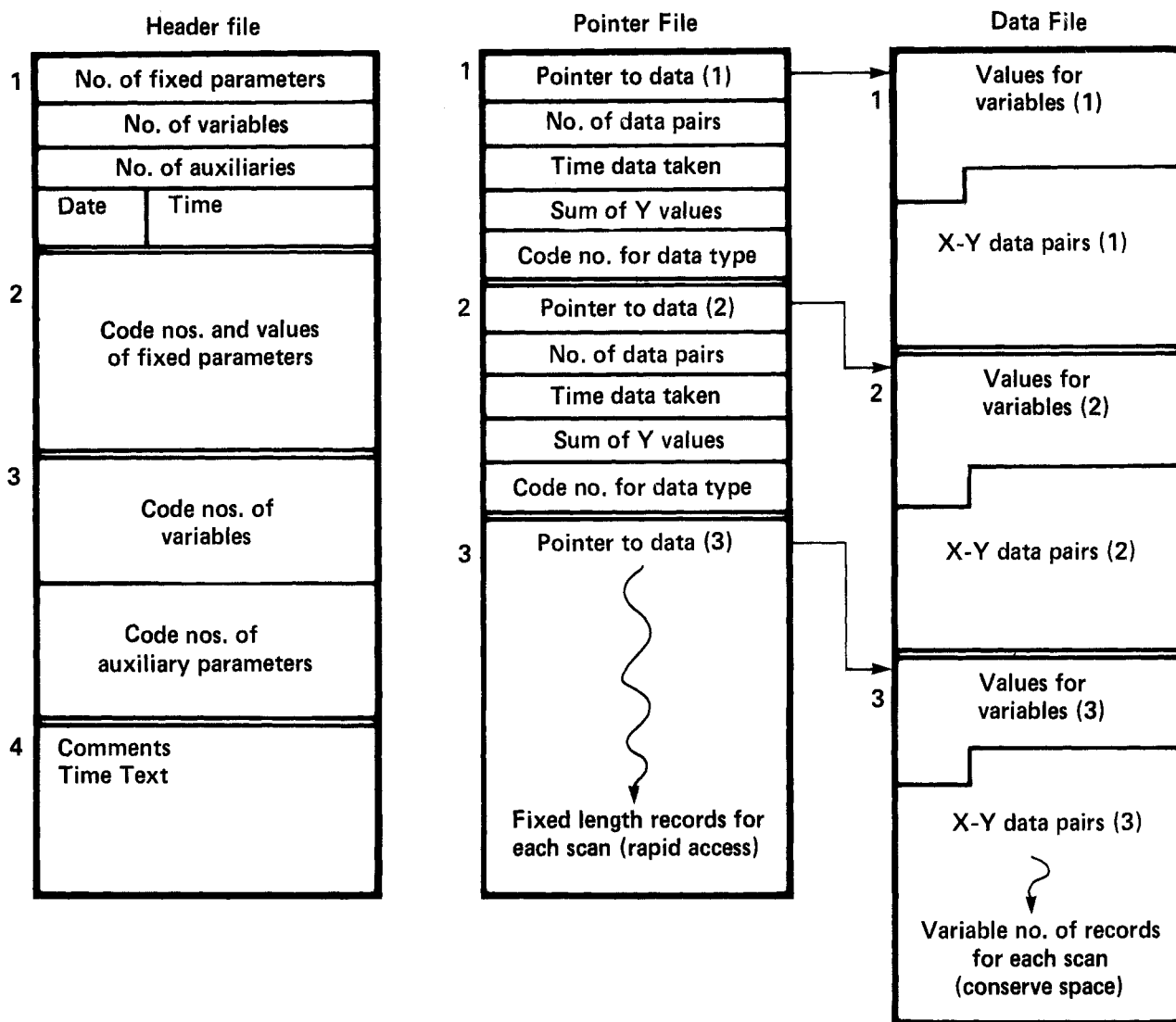


Figure 1. Block diagram of files used in instrument database system.

a variable or parameter. Each file is described in more detail below.

Header File. The contents and order of data in the header file are shown in the left side of Figure 1. This file contains (1) the number of fixed parameters (all computer readable instrument settings that are useful to store), (2) the number of variables (computer readable or controllable instrument settings) which the operator has selected as likely to be changed during the analysis, (3) the number of auxiliary variables, (4) date, (5) time, (6) the code numbers and values of fixed parameters, (7) the code numbers of variables, (8) the code numbers of auxiliary parameters, and (9) comments as needed, with time of comment entry in front of each.

The header file serves primarily as a notebook, storing a variety of numerical and textual descriptions of the analysis. In addition, the number of variables and their code numbers are necessary to interpret the data files. The code numbers refer to definitions in a dictionary file. The file is constructed so the comments are stored at the end. This allows comments to be entered before, during, and after a run, thus providing exceptional archival value. The computer clock time is prefixed to each comment so that the coincidence of comments and particular sections of the collected data can be established during postcollection analysis.

Pointer File. The contents and order of data in the pointer file are shown in the center of Figure 1. Each scan produces one record in the pointer file. Each record contains the following: (1) the record number (pointer) in the data file

where the data for each scan begins; (2) the number of data pairs in the scan; (3) elapsed time (in seconds) from experiment start to scan start; (4) the sum of the Y values (for MS, the total ion current) for the scan; (5) a code number for the independent variable; and (6) three code number/value pairs for up to three selected parameters.

In each record the first entry, i.e., the record number, allows one to rapidly access any data in an experiment and still provide flexible, compact storage. Entries two through four in the record increase the speed of graphing and sorting. The fifth entry, the code number for the data type, is especially important for multidimensional work. This code, with a look up into the dictionary (detailed below), describes the independent variable of the data pair. The last entries in the pointer file are three code number and value pairs, known as fast access variables. These may be any of the variable parameters but are usually chosen such that data extraction time is minimized. For example, in MS/MS, in a daughter scan the independent variable (the X of the X-Y data pairs stored) would be defined as quadrupole three mass, and one of the fast access code/value pairs would be the mass on quadrupole one (parent ion mass). In an aging study with multiple thermocouples, the independent variable would be defined as thermocouple number, and a fast access data pair might be pressure.

Data File. The data file contains one or more records per scan. The contents and order of data in this file are shown in the right side of Figure 1. Each record or records associated

Table I. Time in Seconds Required to Extract Data from Typical Databases

| | Extract Speed | | | | | | | | |
|-------------------------------------|---------------------------------|-------|-------|-----------------------------|-------|-------|----------------|-------|-------|
| | high speed disk | | | medium speed disk | | | low speed disk | | |
| | | slow | fast | | slow | fast | | slow | fast |
| memory speed | 11/23 | 11/45 | 11/45 | 11/23 | 11/45 | 11/45 | 11/23 | 11/45 | 11/45 |
| computer type | | | | | | | | | |
| normal MS-500 records | | | | | | | | | |
| selected ion | 21.7 | 14.1 | 9.5 | 24.5 | 16.7 | 12.6 | 59.5 | 55.5 | 52.0 |
| total ion | 2.1 | 1.2 | 0.8 | 2.1 | 1.4 | 0.8 | 3.7 | 3.2 | 3.2 |
| daughter MS-400 records, 14 parents | | | | | | | | | |
| select daughter | 3.9 | 2.4 | 1.8 | 5.1 | 3.6 | 3.0 | 12.9 | 9.7 | 8.8 |
| CAD press. vs. scan | 3.1 | 1.7 | 1.2 | 3.4 | 2.6 | 1.6 | 6.7 | 6.2 | 6.1 |
| Disk Speeds | | | | | | | | | |
| | av access time, ms | | | data transfer rate, Mbits/s | | | | | |
| high speed (Ampex/Calcomp) | 36.4 | | | 9.68 | | | | | |
| medium speed (Diablo/RK05) | 70 | | | 1.44 | | | | | |
| low speed (floppy) | 386 | | | 0.5 | | | | | |
| Computer Speeds | | | | | | | | | |
| | average execution time, μ s | | | | | | | | |
| | MOV | | | MULF | | | | | |
| | (move data within computer) | | | (decimal multiply) | | | | | |
| 11/23 | 4.6 | | | 80 | | | | | |
| 11/45 core mem. (980 ns) | 3.1 | | | 11.7 | | | | | |
| 11/45 bipolar (300 ns) | 1.2 | | | 10.2 | | | | | |

with a particular scan contains the following: (1) the values of operator selected variable parameters, such as probe temperature, lens voltage, etc.; and (2) the *X-Y* data pairs (intensity vs. independent variable).

Dictionary File. To reduce computer storage, all variables and parameters are assigned a code number. The dictionary file is a direct access file containing the descriptions of each code number and is the only instrument specific part of the database system. Two descriptions are stored for each code number, short (less than 20 characters) and long (up to 60 characters). The short descriptions are used for speed when the operator is entering them, and the long descriptions are more suitable for tables and graphs.

RESULTS

One of the most critical aspects of an instrument database system is its speed. When operated interactively, computer-aided interpretation routines generally occupy a considerable amount of operator time while waiting for plots to appear. Our system was designed to minimize this wasted time. A series of timing tests were run on three different data sets extracting four different kinds of data. These tests were run on two computers, one containing two memory types. Each computer had three disk systems associated with it. Table I gives a summary of the results of these tests. There are approximately 17 000 data pairs in the normal mass spectrum set used for the first two extractions (selected ion and total ion), 8000 data pairs in the third (selected daughter ion), and 2000 data pairs in the last (scan number vs. collision gas pressure). For those not familiar with computer terms, disk access time is the average time required for the disk to precisely locate the data on the disk surface. Disk transfer rate is given in the number of data bits that can be transferred from the disk surface to the computer per unit time, expressed in millions of bits per second (32 bits are required for a decimal number). Computer speeds are measured in units of microseconds for two operations. The first is simply moving one piece of data from one point in the computer to another point in the computer. The second is multiplying one decimal number times another. The two memory types for the 11/45 computer have different speeds for performing a basic cycle,

one is over three times faster than the other.

As can be seen in Table I, the data extraction speed is affected primarily by the type of extraction being performed. Other factors include the number of scans involved, the amount of data in each scan, the speed of disk access, and the basic speed of the computer. The very fastest operation (less than half a second) is recovery of *X-Y* data as it was recorded. The longest extraction times involve looking for select data from each scan contained in the database. The most common example of this is creating a simulated single ion monitor curve by extracting intensity at one mass from each scan of all masses, vs. scan number or time. As can be seen in the first entry in Table I, it can take a minute or longer to extract these kinds of data from a very large data set (many scans, each containing many peaks). If all information to create a plot is contained in the pointer file, these data can be extracted in 4 s or less. An example of this is the total ion plot, or the sum of *Y* values in a scan vs. the scan number. Because the pointer file can identify additional information, such as the mass of the parent in the case of daughter spectra, one can rapidly look for data from only one parent among many parents. In the third example in Table I, a single daughter from one parent among 14 parents is selected and extracted vs. scan number. The final example in Table I shows that any recorded variable can be extracted vs. any other meaningful parameter.

Disk reading is a time-consuming step in this process. At present, we are using only standard FORTRAN reads, making the programs portable. We will be modifying the programs to make use of powerful system calls that allow large blocks of data to be read from the disk rapidly. In addition, we may use assembly language calls to speed the search process. These types of calls are available on most operating systems, and the knowledgeable programmer can easily incorporate them into our codes.

The system uses several approaches to extracting data in usable form. One method is menu driven in which a variety of options are displayed and the user selects from them using cursor controls. The other system uses a series of questions with the most common responses as defaults. It is up to the user to select from a printed guide the options to enter. This

Table II. Dialog Used to Extract Data^a

```

>EXT
Data set name: N00432
STOP? [NO] :
PLOTING FILE NAME [N00432] :
X AXIS [SCAN] :
Y AXIS [INTENSITY] : (FIG. 3)
MASS [ ] : 44
ENTER PARENT MASS [0] : 222
LABEL IS:
MASS=46 PARENT=222 HMX A-336XL, 100 TO 300 RAMP WITH SOURCE
ENTER OWN LABEL ? [NO] :
STOP? [NO] : Y
Wrote 1 sets of data

>EXT
Data set name: N00444
STOP? [NO] :
PLOTING FILE NAME [N00444] :
X AXIS [SCAN] :
Y AXIS [INTENSITY] : CAD PRESS. MTORR
LABEL IS:
CO2 STD. DAUGHTERS 44,28, VARY CAD GAS PRESSURE
ENTER OWN LABEL ? [NO] :
STOP? [NO] : Y
Wrote 1 sets of data

```

^a Underlined material is operator response, material in brackets is the default value. The first part of this dialog was used to create Figure 3.

| Scan number | Experiment type | 1 | 2 |
|----------------------|-----------------|---------------------------------|---------------------------------|
| Variable parameters: | | 1 | 2 |
| | | 5.000 | 4.000 |
| | | QUAD 2 POLE OFFSET (FIELD AXIS) | QUAD 3 POLE OFFSET (FIELD AXIS) |
| X | intensity | X | intensity |
| 35.0 | 75. | 69.0 | 206. |
| 45.0 | 157. | 72.0 | 37. |
| 56.0 | 82. | 83.0 | 46. |
| 58.0 | 1988. | 84.0 | 41449. |

| Scan number | Experiment type | 2 | |
|----------------------|-----------------|---------------------------------|-----------|
| Variable parameters: | | 1 | |
| | | 5.000 | |
| | | QUAD 2 POLE OFFSET (FIELD AXIS) | |
| X | intensity | X | intensity |
| 25.0 | 80. | 58.0 | 9329. |
| 32.0 | 57. | 69.0 | 262. |
| 38.0 | 33. | 83.0 | 210. |
| 40.0 | 50. | 84.0 | 65349. |
| 45.0 | 472. | | |

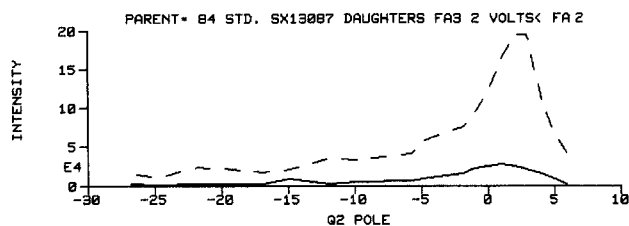


Figure 2. Example of extracting a plane of data from the database that was not specifically scanned. The upper portion shows the first two scans of digital data from which the curves below were extracted. Underlined data were used in the graph. The dashed curve is mass 84, the solid is 58.

latter dialog system is used in the examples. An example of the dialog used to do the extractions for Table I is shown in Table II. The operator enters the underlined material. Default values are in brackets. Since all parameters are linked to the dictionary file by code number, we can use the dictionary name to describe a variable. Since daughters from more than one parent can be stored, the program prompts for the mass of the parent if the run was of daughters, or the mass of the daughter if the scans are of parents.

One of the most important characteristics of our system is the versatility that allows us to extract planes of data that were not specifically scanned. As an example, one of the more important parameters in TQMS is the ion axial energy in the collision chamber (quadrupole 2). While it would be possible to scan ion axial energy vs. intensity at a fixed mass, it is more common to scan mass vs. intensity. A variety of axial energies could be selected and the power of the database system would be used to extract intensity vs. ion axial energy for any

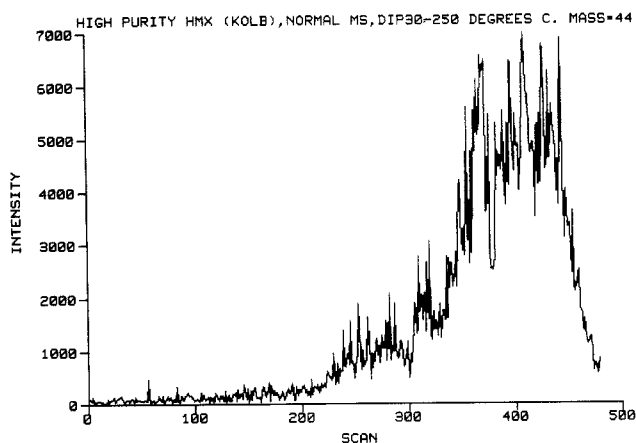


Figure 3. Example of PLOTMS output (Table II shows how these data were extracted).

JET A Aircraft fuel

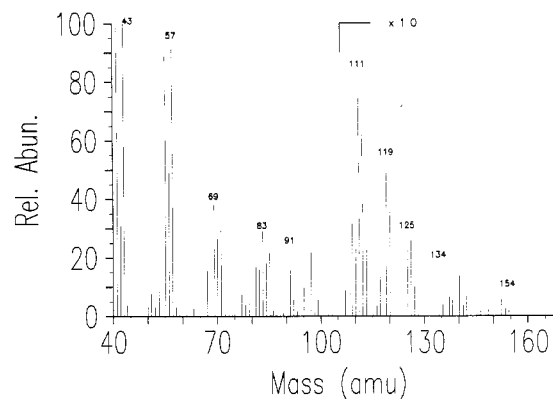


Figure 4. Example of MULPLT output.

daughter ion. This type of data is shown in Figure 2. At the top of the figure is the data from several scans of mass vs. intensity at different ion axial energies (field axis voltage). In this particular experiment the field axes of quadrupole two and three were varied at the same time, with the field axis voltage on quadrupole three always 2 V less than that on quadrupole two. This illustrates the ability to perform and store data for experiments with one independent variable and one virtual variable, allowing the study of variable interdependence. At the bottom is the graph of field axis voltage for quadrupole two vs. intensity at a fixed mass. A similar graph would be obtained with the field axis voltage for quadrupole three as the independent variable, with the X axis offset 2 V. This illustrates that any plane of data can be extracted by using this system.

This instrument database system can be readily applied to other instruments or experiments that are already interfaced to computers. Since there is no mass spectrometric specific code in the database system, the definition of a dictionary transforms this general package into an instrument-specific database.

Our system can be used with a variety of graphical output programs and devices. PLOTMS (32) is typical of the types of programs available. The extract routine automatically creates axis and main labels based on the extraction command line and the title entered when the sample was run. As an example, the operator enters the title HMX A-336XL, 100 TO 300 RAMP WITH SOURCE when data are collected from a sample, and [SCAN VS] [INTENSITY] [MASS] 46 [PARENT] 222 (material in brackets is default or prompt) at the time of extraction. Without additional operator entries, the

Table III. Example of Tabular Output Showing Contents of Header File and Both Averaged and Normalized Data for the Daughters of One Parent (mass 62)

File created 23-FEB-83 13:29:32 for dataset W00570

1 variable parameter:

1 COLLISION GAS PRESSURE, MTORR

1 auxiliary parameter:

1 DAUGHTER ION SCAN

46 machine parameters:

| | | |
|----|---------|-------------------------------------|
| 1 | 70.00 | ELECTRON ENERGY |
| 2 | 300.0 | EMISSION CURRENT |
| 3 | 8.100 | REPELLER |
| 4 | 270.0 | DRAWOUT |
| 5 | 166.0 | FOCUS |
| 6 | 200.0 | SOURCE TEMPERATURE |
| 7 | 33.00 | DIRECT INLET PROBE TEMPERATURE |
| 8 | 1.000 | POSITIVE OR NEGATIVE IONS |
| 9 | -15.80 | QUAD 1 LENS A |
| 10 | -139.8 | QUAD 1 LENS B |
| 11 | -9.900 | QUAD 1 LENS C |
| 12 | -0.6000 | QUAD 1 POLE OFFSET (FIELD AXIS) |
| | | |
| 44 | 97.00 | 8TH PARENT |
| 45 | 1000. | NUMBER OF READINGS AVERAGED PER AMU |
| 46 | 0.8000 | COLLISION GAS PRESSURE, MTORR |

Comments:

13:29:54 DAUGHTS OF MB6-5 "MASTER BATCH"
 13:30:05 SOURCE AT 6*10-6 TORR
 13:41:09 NSCANS= 800

| | | |
|--------------------------|-----------|------|
| No. of scans averaged | 100 | |
| 1st, last scan no. | 4 | 800 |
| Start, end time(seconds) | 1.00 | 554. |
| Total ave. ion current | 0.599E+05 | |
| Experiment type | 3062 | |

Ave. variable parameters:

1 0.8196 COLLISION GAS PRESSURE, MTORR

| X | Average intensity | Percent | X | Average intensity | Percent |
|------|----------------------|---------|------|----------------------|---------|
| 26.0 | 26. | 0.06 | 46.0 | 282. | 0.66 |
| 27.0 | 48. | 0.11 | 47.0 | 701. | 1.65 |
| 28.0 | 40. | 0.09 | 60.0 | 296. | 0.70 |
| 29.0 | 263. | 0.62 | 61.0 | 15462. | 36.35 |
| 34.0 | 30. | 0.07 | 62.0 | 42534. | 100.00 |
| 45.0 | 34. | 0.08 | | | |

Y axis is labeled INTENSITY, the X axis SCAN, and the title becomes HMX A-336XL, 100 TO 300 RAMP WITH SOURCE MASS=46 PARENT=222 (see Figure 3) when the data are plotted. Both axes are automatically scaled to the nearest suitable number and plotted. Figure 3 is an example of this output using the data files described in Table I. Figure 4 is an example of document quality graphics created by MULPLT (33). Other graphic packages are available to provide a variety of output including overlays and full color features.

Three types of hardcopy output are provided. The first can print just header file information (all computer readable/controllable data), selected data (selection based on scan number and/or index code), or all data in tabular form. The second output also prints header file information and an average of any selected set of scans (selection based on scan number and/or index code) showing both raw and normalized

data. An example of this output is shown in Table III. The third can perform a variety of normalizations and print all or part of the data.

This system of programs has met our goals of speed, flexibility, and ease of use. In addition, these programs are transportable and have been submitted to DECUS (Digital Equipment Corporation Users group, Marlboro, MA) for general availability. The programs should operate without change on DEC PDP-11 series computers using either RT-11 or RSX-11M operating systems. They should readily adapt to other computer systems.

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Lead-Selective Neutral Carrier Based Liquid Membrane Electrode

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Certain synthetic, lipophilic oxa- and dioxadicarboxylic amides act as lead-selective neutral carriers in liquid-membrane electrodes. Lead is detected as monovalent permeating species of the type PbX^+ ($X: OH^-, Cl^-, NO_3^-, CH_3COO^-$). Membranes based on *N,N*-dioctadecyl-*N',N'*-dipropyl-3,6-dioxaoctanediamide reject alkali metal ions by a factor of at least 10^3 and alkaline-earth metal ions by at least 10^4 .

Several electrically neutral crown ethers (1-4) and a large number of nonmacrocyclic ionophores based on dioxo diamides and related compounds have found diverse applications in ion-selective electrodes especially for group 1A and 2A cations (5). Analytically relevant selectivity for UO_2^{2+} has been found for membranes based on selected dioxo diamides (6, 7). As expected, a replacement of coordinating oxygen atoms by sulfur atoms leads to selectivity of certain ligands for transition or B metal ions such as Cd^{2+} (8). Although dicyclohexyl-18-crown-6 complexes Pb^{2+} clearly stronger than group 1A and 2A cations (9), there is no report on an ana-

lytically relevant lead sensor based on the incorporation of this ligand into membranes. Here we describe a liquid-membrane electrode with relevant selectivity for lead which is based on a nonmacrocyclic ion carrier.

EXPERIMENTAL SECTION

Reagents. Double quartz distilled water and chemicals of the highest purity available were used throughout.

Synthesis. The structures of ligands 1 to 6 are given in Figure 1. The synthesis of ligands 2 (10), 3 (11), 4 (10), and 5 (12) has been described earlier.

Ligand 1 was prepared according to the procedure in ref 11. The 1H NMR, ^{13}C NMR, IR, and mass spectra of the product are in accordance with its structure. Anal. Calcd for $C_{22}H_{44}N_2O_4$ (400.60): C, 65.94; H, 11.07; N, 6.99. Found: C, 65.52; H, 11.04; N, 6.92.

Ligand 6 was prepared according to the procedure in ref 13. The 1H NMR, ^{13}C NMR, IR, and mass spectra of the product are in accordance with its structure. Anal. Calcd for $C_{51}H_{102}N_2O_4$ (807.39): C, 75.87; H, 12.72; N, 3.47. Found: C, 75.62; H, 12.29; N, 3.33.

Membranes. The matrix of the membranes was PVC, S 704, high molecular (Lonza AG, Basel, Switzerland), with bis(1-bu-