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Conference Papers on Mass Spectrometry Computer Control

COMPUTER CONTROL OF MASS ANALYZERS*

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ABSTRACT

Extending the use of digital computers from passive data collection to active control has increased the efficiency of computer-mass spectrometer systems. One such system devised, and described in this report, used a small digital computer and integer resolution (quadrupole and time-of-flight) mass spectrometers. The computer, by teletype, queries the user for operating parameters. The computer then translates these into detailed control functions that operate the instrument. Calibration is effected by the computer valving into the mass spectrometer a reference gas prior to introduction of the unknown sample. After calibration, the sample data acquired by the mass spectrometer is made available to the researcher in an on-line graphic system. Examples of processing GLC effluent are given. This work was sponsored in part by National Aeronautics and Space Administration Grant NsG 81 and Air Force Office of Scientific Research Grant AF 49(638)-1599.

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Some of the motivation for the work of this report has been the desire to utilize the decision making capabilities of a computer to direct the operations of certain instruments, primarily mass spectrometers. The system described uses a computer to perform a pre-calibration by the use of a reference gas and then to actively direct the mass spectrometer during data acquisition.

The computer used is a classic LINC, with 2K memory and a tape operating system. However we are shifting our computer interface to a time shared IBM 360/50 with a slave IBM 1800 to allow greater program flexibility. Also we are waiting until then to expand the present mass range of 1 to 256. Two sets of interfacing hardware have been built, and the system has been used on three integer-resolution mass spectrometers: a time-of-flight and two different quadrupole mass spectrometers.

Hence, this paper shall confine itself to describing the approach and system concept. The results from each of the mass spectrometers is actually shown.

It will be useful to establish a definition for a mass set voltage, Vc, the principal control voltage.

Most mass spectrometers that have an ion collector and electron multiplier to detect the ion signal, have some electronic control parameter, or have been adapted to have an electronic control parameter. I will call this parameter for setting the mass analyzer Vc. As indicated in Figure A-1, there is normally a provision to make Vc a linear or exponential function of time so that some interesting portions of the mass spectrum may be investigated. Often then the recorded output of the mass analyzer is interpreted by considering m/e to be a function of time. Such a recording is often referred to as a "scan". Actually m/e is a function of Vc and other parameters that have been kept constant.

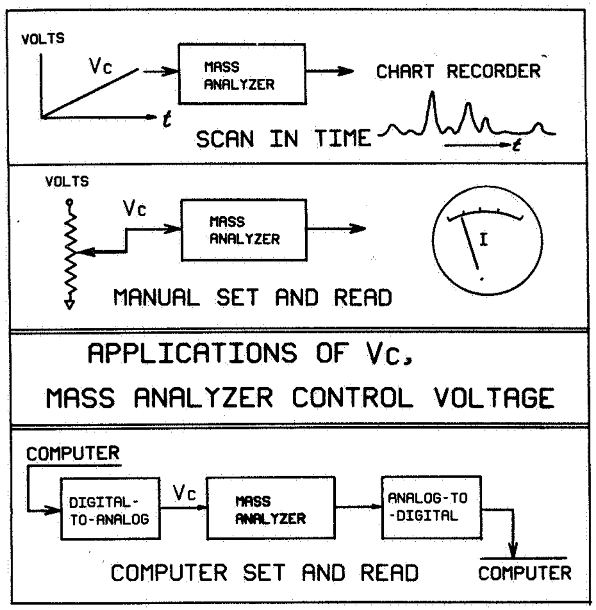


Figure A-1

Applications of Vc, a mass analyzer control voltage.

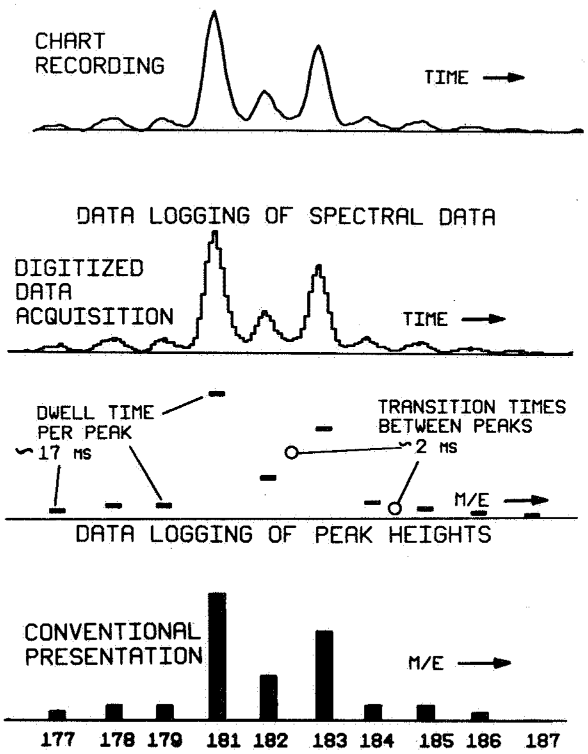


Figure A-2

Evolutionary stages of data acquisition and presentation.

If m/e = F(Vc) then the inverse function Vc = f(m/e) may be determined. To investigate the signal from m/e ions, a signal of Vc_i may be applied to the mass analyzer and the relative abundance read at the output of the electron multiplier. A manual method of applying this is diagrammed in the center portion of Figure A-1. This may seem a step backward in technology, but remember a computer is superb in doing routine repetitive operations.

So as shown in the lower portion of Figure A-1, the computer may supply the control voltage, Vc_i, and read the signal resulting from the m/e_i ions passed by the mass analyzer.

The rest of the report deals with the means and benefits of applying such signals Vc, to mass analyzer by computer logic. This is broad area and space will allow me to only hit the highlights of the systems concepts we have implemented or explored. Major points I will try to cover are:

1. The applicability of this manner of control to various mass spectrometers.
2. The concept of reading a m/e signal amplitude rather than scanning.
3. A hardware implementation.
4. A software implementation.
5. Some results.

1. Different types of mass spectrometers.

Types of mass spectrometers suitable may be evaluated in terms of the character of Vc, the speed of response to Vc, the stability of the function in time, and the basic nature, linear, parabolic, exponential, etc.

Magnet controls by current has been judged to be rather slow for our purpose, time constants running in the order of 2 to 10 seconds. Other controls that do not have to change magnetic fields seem more amenable and have time constants of 0.1 to 2 milliseconds are readily obtainable.

The accelerating voltage of magnetic sector instruments would have good time response. The function of Vc to m/e, being a reciprocal function, does pose some problems. The distribution of peak positions with the accelerating voltage is very non-linear. To insure proper ion transmittance very high precision digital-to-analog converters for accurate Vc are needed.

Monopoles and Quadrupoles have a dc control voltage that control the amplitude of the ac/dc voltage ratio on the rod or rods. This is a linear function of m/e and most suitable. The time-of-flight mass spectrometer has a dc control voltage that controls the time delay of a gating signal that effectively controls the passage of the signal from ions of a specific m/e. In the t-o-f the function is parabolic. We have implemented systems with both the quadrupole and time-of-flight type mass spectrometers.

The three dimensional mass spectrometer recently described by Dawson and Whetten should not be ignored. It has an interesting ion capture and holding property, and again a convenient dc control mode. And there are still other types that have some mode of Vc control.

Those that have dc voltage control are most easily amenable to computer control as high quality digital-to-analog converters are typically dc. And most such mass spectrometers have an easily identified connection point to apply the dc control voltage of proper polarity and range.

2. Some remarks about direct mass/charge (peak) measurements.

Typical conventional graphical recordings of mass spectrometer scans are similar to the portion shown at the top of Figure A-2. If the continuium is sampled by a digital to analog converter for computer storage, the scan may be represented as in the next section. This is commonly done today; some thousands of data points are fed into a computer. A computer program then reduces this to a few hundreds of numbers, the amplitude of the integer m/e positions. Often this calls for rather sophisticated and fast computers. It is necessary to store or process in real time the thousands of sample points and have a rather extensive computer program to extract the values of the integer m/e positions, the basic data expected of a low resolution mass spectrometer. It might be argued that there is a lot of data taken that has a very low information content.

Area is sometimes taken as the amplitude. However for most purposes the simple peak heights are sufficiently representative of peak amplitude. Again in Figure A-2, the digital measurement corresponding to the center of each peak is accentuated. This peak reading representation of amplitude is especially true if the peak shapes are uniform or known and/or the aperture (that affects mass spectrometer resolution) is broad enough.

Therefore, assuming that the integer m/e position can be forecast only the sample at that position need to be taken. This suggested by the next portion of Figure A-2. With computer control, just that can be done. The intervening measurements need not be taken and no time is wasted on data of such low information content.

Actually such prediction is possible. Typical control times that we have achieved runs about 2 milliseconds between any two samples and about 7 to 17 milliseconds upon a sample point. Each sampled point is at a specific m/e position and may be taken in any order the computer programmer desires.

We find best results if the aperture of the mass analyzer is broadened. This lowers the resolution. However, 10% valley criteria is meaningless as such. The only meaningful criteria is non-contribution to neighboring m/e positions.

Such single data point logging is most modes in requirement of storage area in the computer and of speed necessary for analog-to-digital conversion. The data may be presented to the researcher as in the bottom portion of Figure A-2, or in another manner, or just held in a computer file or tape for further logical analysis.

2.1 Signal to Noise Gain*

It may be shown that a method of control gives a manyfold increase in signal to noise available from a peak of given ion density. The values demonstrating this in Figure A-3 were obtained from a computer program written in PL-1 to simulate:

First: The results from a conventional scan.

Second: The result expected with a controlled sample system.

The simulation agreed well with our observations.

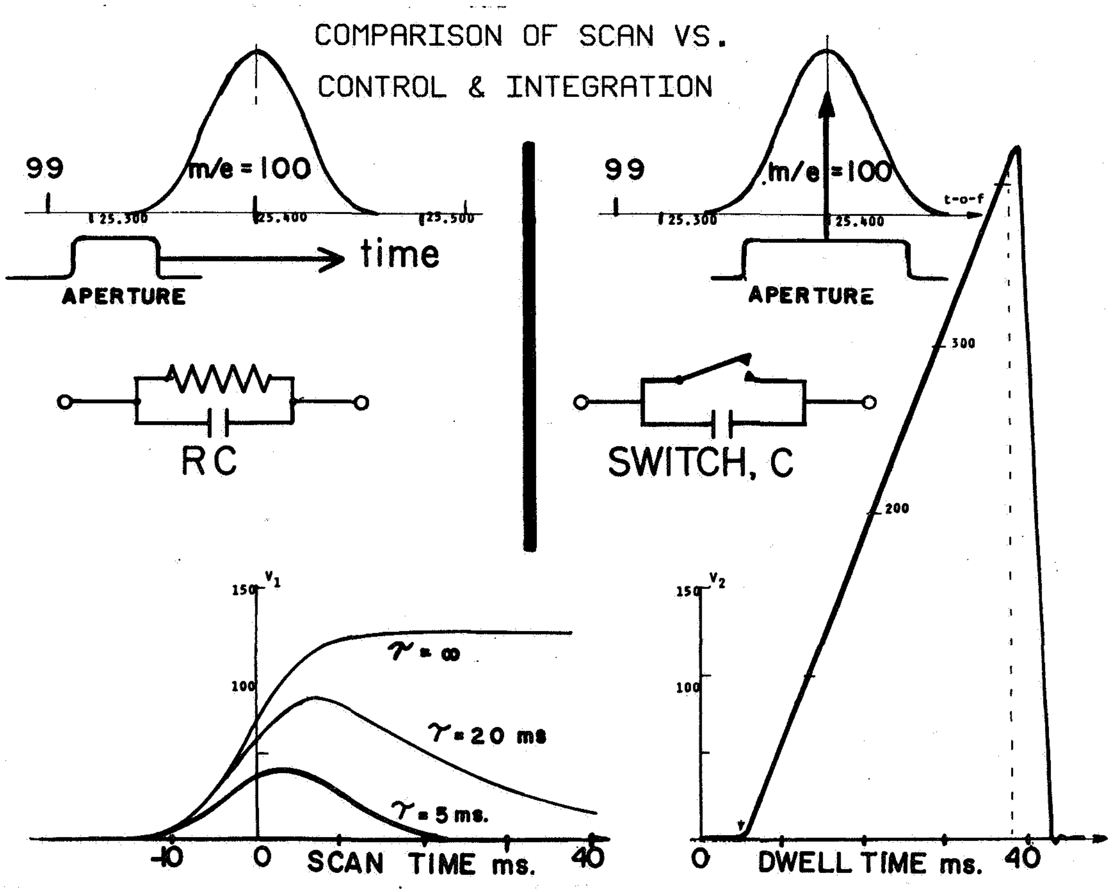


Figure A-3

Comparison of the signal obtained by conventional scans with RC (bandpass) amplifiers versus that obtained with no dissipation across the feedback condensor (full integration).

*This section was given only at the Pacific Conference on Chemistry and Spectroscopy at Anaheim, Calif. on Nov. 1, 1967.

The conditions of the comparison are:

1. A model of m/e - 100 in a t-o-f mass spectrometer is used.
2. The peak is gaussian and normalized.
3. In each case the scan rate or sample time would allow a complete spectra run is about 10 sec.
4. Gain of the multiplier and other similar functions are the same.
5. The peak is considered to be a current density function in time.

On the left is the conventional system. In any scanning system there is always some mass selector, aperture, such that only a small portion of the total spectral signal is allowed to pass at any one instant. Often this is much smaller than the peak width. This aperture is then moved as a function of time to effect a spectral scan.

In contrast it will be shown on the left that setting the aperture where you like and when you like can result in more signal passage. We have done just that. For now let us assume it is possible.

In either case, during some finite time, a given amount of the peak's signal is transmitted through the aperture to an electrometer amplifier. On the left, with $\tau = \infty$ is a curve showing just that, a time integral of the total signal psssed by the aperture.

However an RC amplifier has a finite band-width or time constant. Hence only a portion of that integrated total is available at the output of an RC amplifier at any one instant.

Below the $\tau = \infty$ curve is shown the relative response for 20 ms. and 5 ms. time constants.

As the name indicates, a finite band width RC amplifier has a condensor to integrate and conserve the signal and a resistor to dissipate it. If the dissipation is decreased, the time constant is long and skewed peaks and smeared resolution is the result. So some compromise is made. In this case a τ = 5ms. seems reasonable.

Now let us consider the right side. Here we have done away with the resistor - no signal dissipation. So the total signal is available at the output. This effects a gain of about 3.2. The integrator can be reset later with an electronic switch.

Also the aperture may be wider. There is no need to keep it any more narrow than to avoid adjacent peaks. And it is always centered. This allows the fast straight line rise in output signal shown. This is another factor of about 3 in gain of the signal passed by the aperture.

And finally it can be shown that the 3db point in frequency noise rejection has been improved. In this example it went from 32 Hz.to 18 Hz., for a gain of about 1.35.

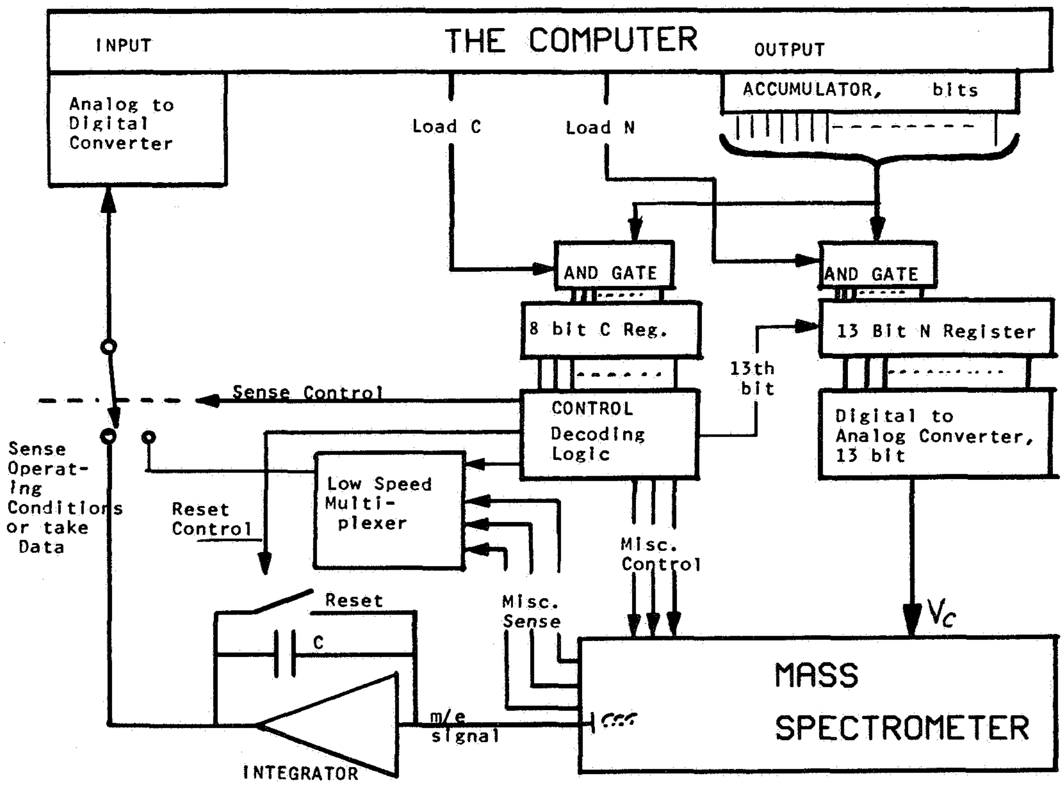
These all multiply to a total gain of 13 in signal to noise. At Stanford we have used this to greatly speed up the spectra acquisitions. And it is nice to know that the requirements on size and speed of a suitable control computer are not increased.

3. Hardware configuration

The system hardware requirements may be divided into two portions, the source inlets and the electronics interface.

First the source system. The only thing unusual here is that we have fitted the gas inlet system with electro-pneumatic valves to enable their operation by computer control. The valves are ones of our own design and allow bake out to 225°C. On each of the three mass spectrometers we have instrumented, we have installed a reference gas system using FC-43, a reference widely used in mass spectroscopy. The valving of this into the mass analyzer is, as we shall see, a function of a control register driven by the computer. The reference gas is normally valved in, a calibration to the known peaks is made, and the gas pumped out before the unknown sample is introduced. Interpolation is used to locate all other integer m/e positions.

On two of the systems we have installed GLC inlets. It was found desirable in this case to provide for computer operated valves to keep these systems closed off from the mass spectrometer while the solvent peak was coming through the GLC.



THE ELECTRONIC INTERFACE

Figure A-4

A block diagram of the interfacing electronics is shown in Figure A-4. It includes two registers, an N register and a C register to hold command words from the computer. These are loaded by putting the predetermined word (number) into the accumulator and executing a load command, a pulse out on the N or C line. This causes the word to be passed and held in the appropriate register.

The N register directly drives the D to A converter that generates the control voltage Vc. Hence the "N" number sets the mass analyzer to pass a desired specie of ions.

The C register is a general purpose control register. We are using 8 bits that can be decoded into 128 functions. Actually, to simplify logic, we have provided for the use of only about 32. These control the gas inlet to the mass analyzer and some spectral display modes. There are relays which may be used for other desired function. We do anticipate the use of stepping motors to control key potentiometers.

There is relay multiplexing of analog signals to enable sensing of general operating parameters of the mass spectrometer. All these and the reset to the integrator are controlled from the C register.

The input to the computer must respond to program control, internally or externally causing an analog to digital conversion to be made.

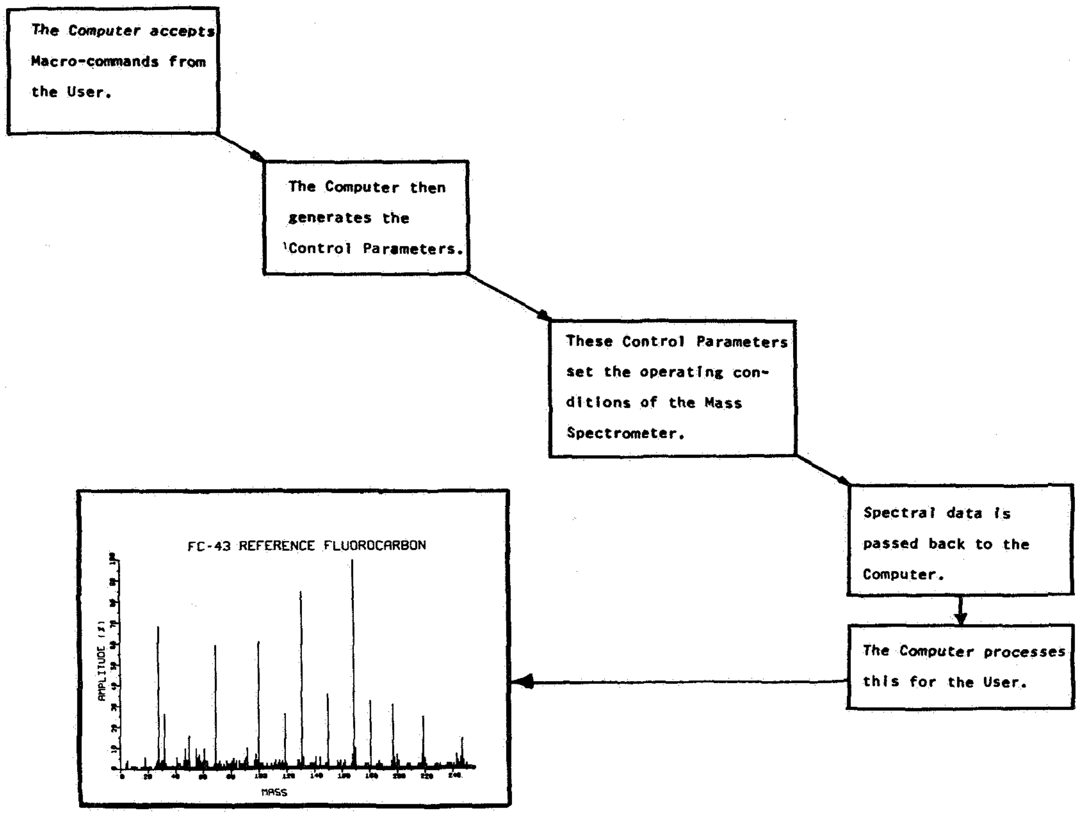
We intend to experiment with dynamic control of various operating parameters such as ion energy, trap current, sample temperature, and sensitivity resolution settings.

4. The Software

It is the computer programming that makes a system out of what we have discussed. There are enumerable computer logic approaches to intelligently use the mass analyzer and control options outlined.

A very fine exposure of one concept is made by R. J. Spinard in an October 1968 issue of _Science_ magazine.

COMPUTER-USER MASS SPECTROMETER CONCEPT



USER - COMPUTER CONVERSATION

```
SPECTRUM
GAS; *

REFERENCE GAS IS OFF
DO YOU WANT IT ON YES;
WAIT 15 SECS.


SPECTRUM
TAKE ONE;

TAKE ONE
T=31;
FILE NAME = MARS;
FILE # 3;
RETAKE? NO;
```

*Underlined items are User responses.
Everything else is Computer prompting.

```
SPECTRUM
PLOT;

NAME: REFERENCE GAS CHECK;
FILE #S: 3;
J TO K BY I.
J= 10;
K= 250;
I= 1;
X DIMEN.= 10;
Y DIMEN.= 5;
BAR GRAPH? YES;

SPECTRUM
GAS;

REFERENCE GAS IS ON
DO YOU WANT IT OFF YES;
WAIT 15 SECS.
```

Figure A-5

The logic concept of user-computer interaction and an example of user-computer dialogue.

The following are the elements of such an interaction.

a. The computer is to accept Macro Commands from the user.

b. The computer is to generate the necessary Control Parameters.

c. These Control Parameters set the operating conditions of the Mass Spectrometer.

d. Spectral data is passed back to the computer.

e. And the computer should process this and present back an intelligent digest of the data.

Figure A-5 diagrams the concept and gives an example of user-computer conversation in our system. Presumably the user wished to take a spectrum of the FC-43 reference gas to assure himself that everything was working. He has called and used three programs, one twice. There are about 15 such programs available, as I will show later.

The user-computer conversation is shown at the bottom of Figure A-5. The teletype and digital plotter are adjacent to the mass spectrometer. Hence this all transpired in the laboratory and took less than 10 minutes from valving in gas, giving parameters to the computer and receiving this plotted output.

The 15 odd programs in this realization are held in a monitor program called "SPECTRUM". Figure A-6 helps diagram their functions. They may be divided into 4 classes. The top are the Calibration group. Their general function is to allow the user to form and verify a correct "N" table. "GAS" controls the inlet valve for the reference gas. "LOCATE" is an initialization routine. "DISPLAY" and "MEASURE" will give detailed spectral information on a CRT or teletype, respectively. "TRACE" does a similar function on a digital plotter. "ALICE" is primarily to provide data dumps to a time shared 360/50. This has provided a data base for further program development.

"TWEAK" is a manual method of performing minor corrections to an "N" table from errors determined by reference gas measurements. "INCA"

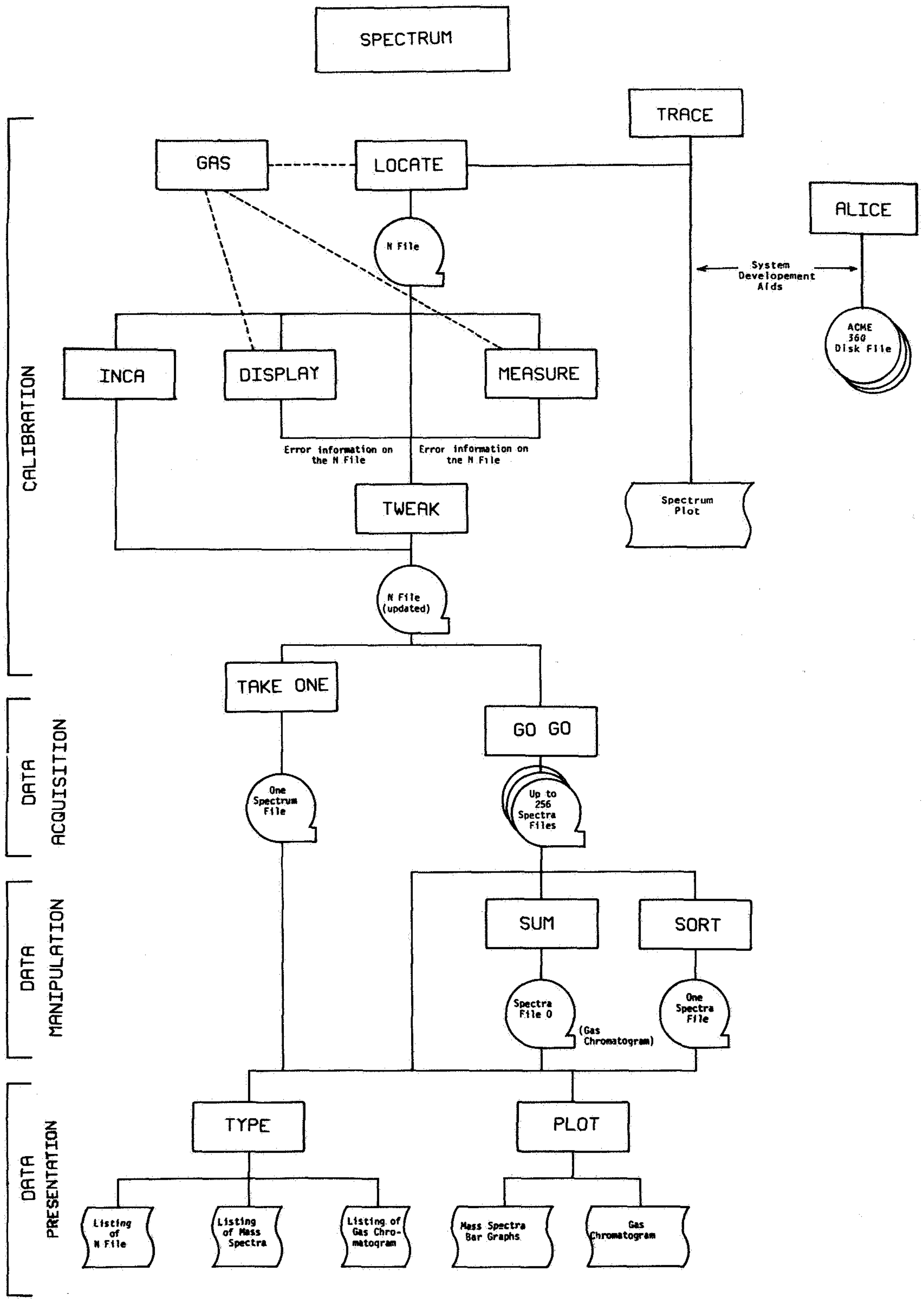
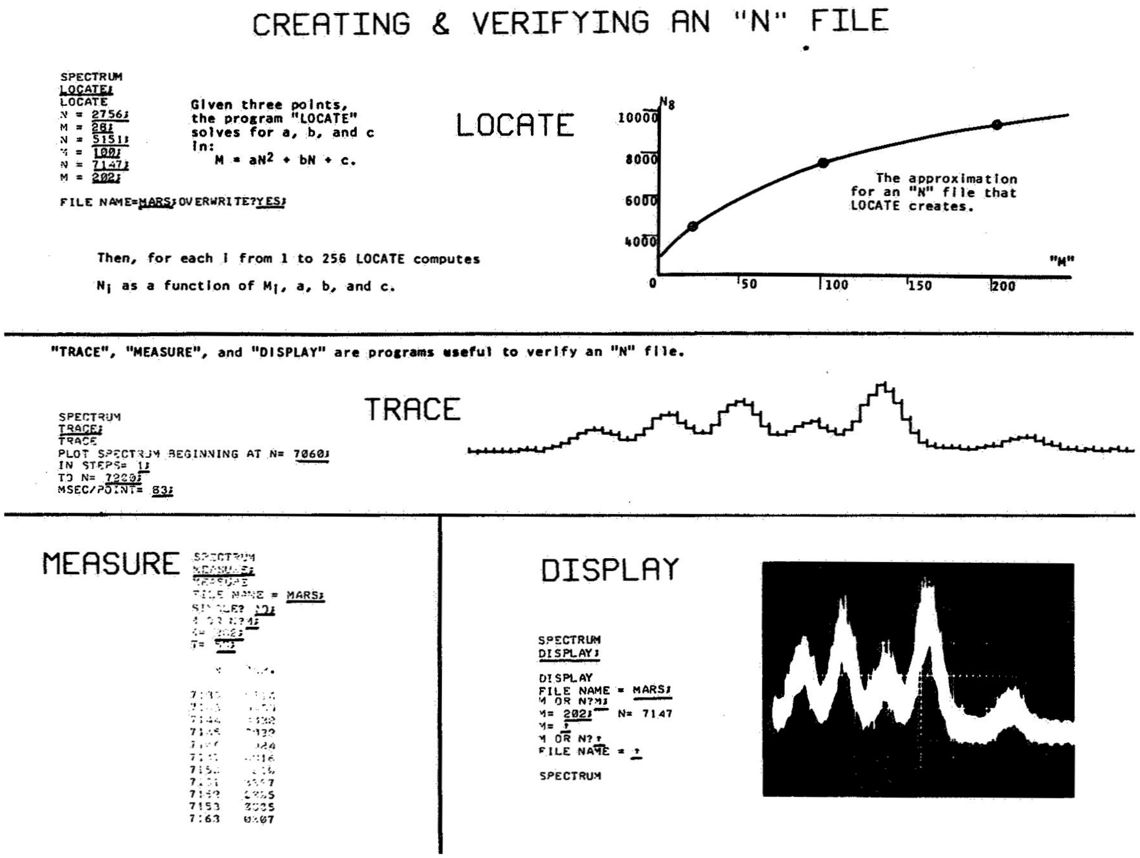


Figure A-6

The programs held in the "SPECTRUM" software system.

is our latest addition and provides nearly automatic recalibration. "INCA" searches for and locates Peaks in the reference gas, compares the found "N" position with that of a stored table, and makes such interpolation and corrections as necessary.



```
SPECTRUM
LOCATE;
LOCATE
N = 2756;
M = 28;
N = 5151;
M = 100;
N = 7147;
M = 202;

FILE NAME=MARS;OVERWRITE?YES;
```

Given three points, the program "LOCATE" solves for a, b, and c in:

$$M = aN^2 + bN + c.$$

Then, for each i from 1 to 256 LOCATE computes N_i as a function of M_i, a, b, and c.

The approximation for an "N" file that LOCATE creates.

"TRACE", "MEASURE", and "DISPLAY" are programs useful to verify an "N" file.

```
SPECTRUM
TRACE;
TRACE
PLOT SPECTRUM BEGINNING AT N= 7060;
IN STEPS= 1;
TO N= 7280;
MSEC/POINT= 83;
```

```
SPECTRUM
MEASURE;
MEASURE
FILE NAME = MARS;
SINGLE? NO;
[illegible]
[illegible]
T= [illegible]

[illegible]

7144     [illegible]
7145     [illegible]
7153     3025
7163     [illegible]
```

```
SPECTRUM
DISPLAY;

DISPLAY
FILE NAME = MARS;
M OR N?M;
M= 202;      N= 7147
M= ↑
M OR N? ↑
FILE NAME = ↑

SPECTRUM
```

Figure A-7
Examples of the calibration group.

Figure A-7 illustrates the type of work that can be done with four of these programs. These do not, repeat do not, result in stored spectral data as such.

Next, back in Figure A-6, are shown "TAKE ONE" and "GO GO". The first is for single spectra, such as may be obtained from solid samples: the later takes and stores a series (one about each 5 seconds) of spectra during a GLC run. These two programs, the ones that do useful work are perhaps the simplest.

Last, in Figure A-6, are shown the Data Manipulation and Data Presentation groups. Some examples of their use is shown beginning with Figure A-8.

We do get many questions from interested researchers that wish to know what these programs can do. But the important thing is to realize what programs can be included. There is capability to store literally hundreds of programs to exploit the inherent capability of the hardware. All that has to be done is to write that program in machine language and give it an unique name so that it may be called when desired. This may be something of a task, but is no severe limitation. "INCA", as pointed out is a late addition.

All results and usage are on-line, and at the site of the mass spectrometer. The computer is a few floors removed, but that is of little consequence. Figure A-8 shows the result of a spectral run on a solid sample.

The program for these plots asks and prompts the user to furnish the title and size. All other anotations and scalings are done by the program.

During a GLC run, "GO GO" took a series of spectra equally spaced in time. These individual spectra, about 217 in Figure A-9, may be individually summed for a representation of total ions vs time. Actually the axis is numbered in spectrum indices. Any individual spectrum is

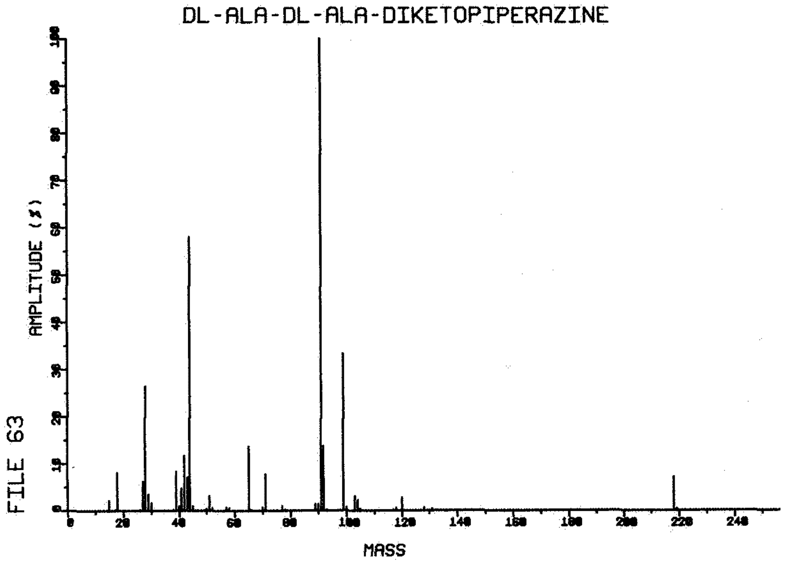


Figure A-8. A spectrum from a solid sample.

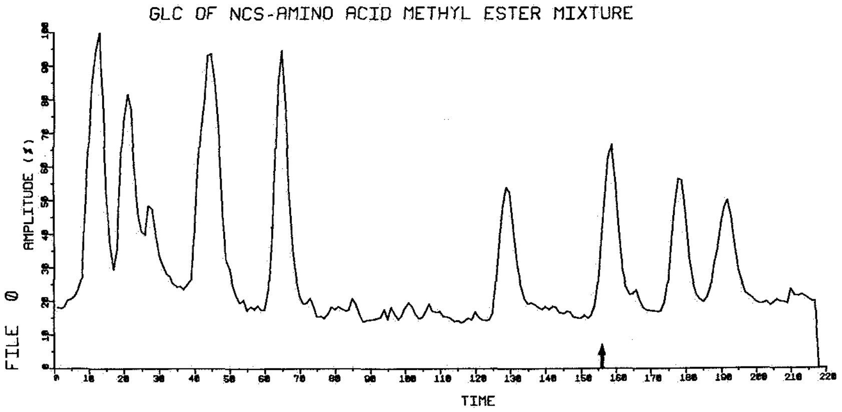


Figure A-9. A summed ion plot from a GLC run.

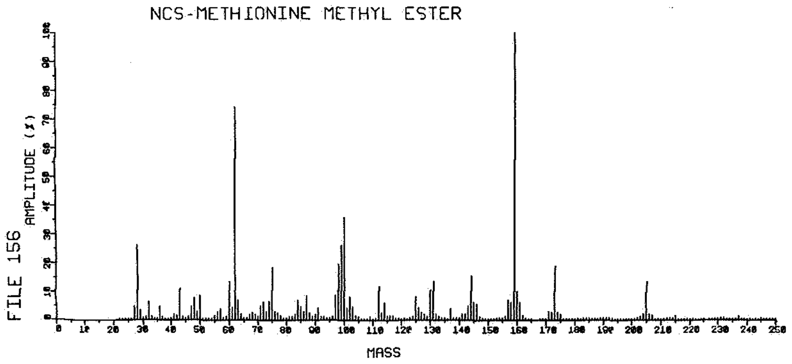


Figure A-10. The 156th spectrum indexed in Figure A-9.

available. In this case let us investigate the 6th major GLC peak at the 156th spectrum.

Figure A-10 is a spectrum taken at the time of that GLC peak, hence of that faction.

CONCLUSION

The system described does give a laboratory researcher a highly efficient data acquisition and presentation system that is both economical of the researcher's time and computer requirements.

It is also felt that the concept of this system, precalibration and computer control of the mass analyzer and other parameters offers a fruitful development area for mass spectrometer instrumentation. This may be particularly so in development of remote instruments where the user, because of convenience, hazardous conditions, or space explorations, cannot personally operate the knobs.