

# A REMOTE ON-LINE ANALOG DATA ACQUISITION-DIGITAL PROCESSING SYSTEM FOR A LOW RESOLUTION COMBINATION MASS SPECTROMETER-GAS CHROMATOGRAPH

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To obtain the maximum use of the mass spectrometer-gas chromatograph appropriate high speed data acquisition and analysis equipment must be used. The high volume and high rate of its signal output poses formidable problems of data acquisition and ones of lesser magnitude for data reduction and data analysing. The primary functions required include data gathering, data analysis, data filing, and bar graph plotting of mass spectra. The objective of this research was to develop a low cost analog data transmission system so that the large central university computer could process the data

rapidly. The complete objective, however, has not been realized at this time.

## METHODS

The LKB-9000 Prototype mass spectrometer-gas chromatograph (1) was linked with the IBM 360/50 computer by means of two analog lines from the LKB-9000 to the IBM 360/50 for the transmission of the two channels of mass spectral signal output to the computer. An example of the mass spectral analog signal output, which is ordinarily recorded on photographic paper by a galvanometer, is shown in Figure 1 using a standard reference compound, perfluoro kerosene.

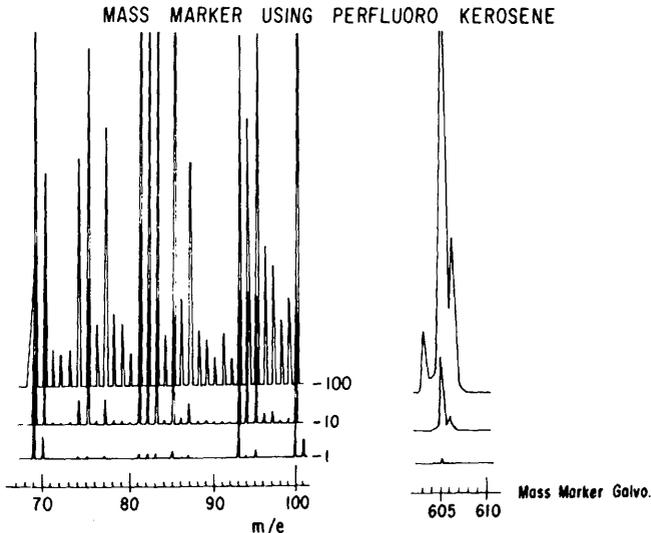


FIGURE 1. Typical mass spectrometer output using perfluoro kerosene. The mass marker galvanometer tracing (horizontal bottom) contains an identifying mass mark for each  $m/e$  value, a slightly higher mark for each tenth  $m/e$  and a still higher mark for each hundredth  $m/e$ . The top three tracings are of ion intensities representing the three sensitivities.

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Upon command from the mass spectrometer operator at the beginning of taking a mass spectrum, the computer converts 15,000 points of the spectrum signal to digital form and 15,000 points of the mass marker (Hall generator) signal to digital form and stores these data in core. Before taking the next spectrum the program searches out and records the spectrum intensities at integral mass values and stores the resulting number of spectrum points ( $m/e$  1-1,500) in the disk. When a number of spectra has been taken, the mass spectrometer operator designates to the computer those spectra that are to be plotted as graphs and those spectra that are to be used as background. This is accomplished by means of an IBM 2741 remote typewriter terminal located next to the mass spectrometer. Backgrounds are subtracted. The resulting spectra are then normalized and drawn by a CalComp 565 digital incremental plotter located near the mass spectrometer.

#### Hardware description

The hardware configuration is shown in Figure 2. Since the computer is located

approximately 1800 feet from the mass spectrometer and the conversion of the analog spectrum signal to digital form is done at the computer end, maximum care was taken in transmitting the spectrum signal to the computer to avoid noise pick-up and signal distortion. The analog lines used were of Belden 8760 cable which consisted of a twisted pair of insulated 18 gauge stranded copper wires shielded by an aluminized Mylar wrapping. They were installed in a  $\frac{3}{4}$  inch thin-walled conduit along their whole length, both for mechanical protection and for further electrical shielding. Near the computer the cables were routed away from pulse-carrying computer cables. Two Hewlett Packard 8875A-04 differential amplifiers were used at the mass spectrometer ends of the lines to isolate the mass spectrometer from noise occurring on the lines. Two similar amplifiers, H-P 8875A-02-04, equipped with high frequency filtering, were used at the receiving ends of the lines at the computer in order to reject any noise common to both wires in a line and to provide any filtering of the signal at the computer if it was necessary. The signal transmission and

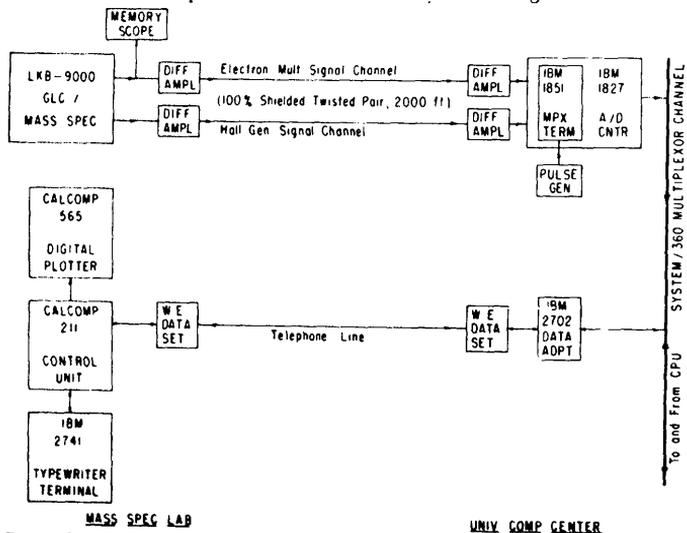


FIGURE 2. Hardware configuration.

ground circuitry are shown in Figure 3.

The IBM 1827 analog to digital converter (ADC) required the user to supply a pulse

interface control unit which controls the signal flow to either the plotter or the typewriter terminal (see Figure 2).

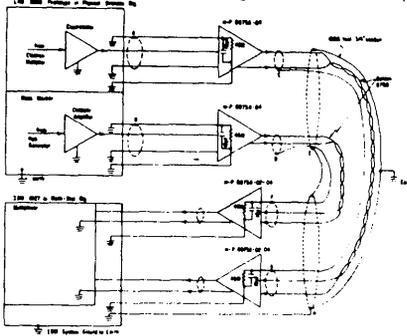


FIGURE 3. Analog signal transmission and ground circuitry for LKB-9000 MS-GC.

when it was desired that data should be converted to digital form. Since in this application the digitization process occurs at a constant rate, a Hewlett Packard 222AC general purpose pulse generator was mounted in the enclosure housing the IBM 1827 (Figure 2).

Since the 1827 ADC available had only one-half the maximum number of multiplexor terminals, a special time sequence for sampling the analog input was required. The system adopted is shown in Figure 4.

A MODEM line (from Southwestern Bell Telephone Co.) was provided to handle the two way digital communication

### RESULTS AND DISCUSSION

#### Analog signal transmission

The two signals being transmitted to the computer are a voltage representing the spectrum intensity and referred to as "data signal" and a voltage whose square is proportional to the mass of the simultaneous data signal and called "mass marker signal." The data signal is the same signal ordinarily used by the mass spectrometer itself for producing a mass spectrum, i.e., it is taken directly from the output of the electron multiplier electrometer. Mass number is determined in the mass marker, a com-

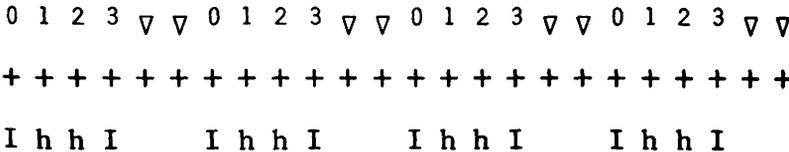


FIGURE 4. Time sequence for sampling analog input.

between the CPU and the IBM-2741 and the one way plotting signal transmission from the IBM 360/50 to the plotter. The digital signals from the IBM 360/50 reached the mass spectrometry laboratory via an IBM-2702 data adapter, two Western Electric 103F data sets, and a CalComp 211 data

ponent of the mass spectrometer, by precisely monitoring the magnetic field in the magnetic sector of the mass spectrometer by means of the output from an electronic squarer driven by a chopper amplifier whose input is from a Hall generator in the magnetic field. The mass marker signal is the

chopper amplifier output. The data signal is 0 to +10 volts. Measurement of this voltage by the computer must be within 2% for levels above 1 volt; however, the noise in the system must be below 10 millivolts to permit detection of the smaller peaks which are almost always present in a mass spectrum. In other words, the data channel measurement must be of ordinary precision but have wide dynamic range, i.e., 60 db. Measurement of the mass marker signal presents a more serious problem since this signal must be measured quite precisely at all voltages in its 0 to 10 volt range. For example, at mass 100, the signal level is -3.16 volts and 14 millivolts (0.44%) represents a change of one mass unit, while at mass 500, the signal level is -7.07 volts and 6 millivolts (0.09%) represents a change of 1 mass unit. Thus for accurately assigning mass numbers to peaks up to mass 500 the mass marker signal must be measured to within 2 millivolts, a .03% measurement accuracy.

The entire signal transmission scheme as diagrammed in Figure 4 was set up and tested. The noise levels were randomly occurring 10 mv bursts of noise and 80 mv spikes separated by several seconds. The diagram shows the best setup found. Noise was indifferent to grounding at points A, B and E, but grounding as shown at H was necessary. Grounding the cable shields at the sending ends, points C and D, was worse than grounding them at the receiving ends, points F and G, or not at all. Grounding points F and G gave a slight improvement. With the entire IBM 360/50 system turned off there was 2 mv peak-to-peak of random noise and 0.3 mv peak-to-peak of power line frequency.

The line noise was such that it was not possible to assign correct mass numbers to mass spectrum peaks above mass 200 (mass marker signal). Useful information could be obtained from the "data signal" transmission, but it too was noisier than desired.

#### FM analog data transmission

In an attempt to improve the analog transmission, an FM modulation-demodulation system was set up. Typical results are shown in Figure 5. In this experiment, the mass marker output was transmitted at 14.5

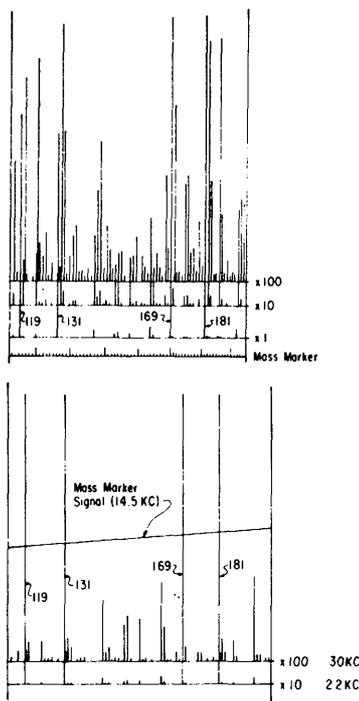


FIGURE 5. Results from FM analog data transmission using perfluoro kerosene. Top, Galvanometer output of MS-GC at MS lab. Bottom, Galvanometer output of demodulated FM signal at the computer center (the X 1 signal was not transmitted). Note, scales are different due to the recorder speeds.

kilocycles frequency, the mass spectrum signal on the X 100 scale was transmitted at 30 kilocycles frequency, and the signal on the X 10 scale was transmitted at 22 kilocycles frequency. The demodulated mass marker scale is shown as a continuing increase in voltage and is the top line which increases proportionally to the magnet field strength increase. It can be observed that there was a significant reduction in intensity of the demodulated mass spectral signal but this signal was essentially noise-free. This was a highly successful experi-

ment in analog "data signal" transmission, but we were faced with a problem of the unavailability of FM equipment accurate enough to permit the sampling of the "mass marker signal." An accuracy of about 70 db. would be required for the accuracy needed (.03%), whereas equipment of only 55 db. is currently available (2).

#### Computer programming (data processing)

A program was written with the multipurpose functions of fast data acquisition, fast data reduction, secondary data filing, bar graph plotting and tabular print-out of intensities. The detailed programs are available from the authors upon request.

The nature of the on-line data acquisition of a mass spectrometer-GLC system requires that the computer respond immediately when instructed by the mass spectrometer operator to acquire data, process it and set it aside into secondary storage as quickly as possible, and then make the core storage available for the next data to be collected. Since the next mass spectrum to be sampled may appear within 30 seconds to 30 minutes, the program instructs the computer to give up control and go to a WAIT state. Plotting, tabulation, and other processing of data were done after the mass spectrometer-GLC system was shut down,

because such tasks performed by the computer keep the IBM-2741 terminal busy and, therefore, accessibility of the CPU would be temporarily lost. The program waiting time was arbitrarily set at 18 min. If, during this 18 min, the computer had not received any command from the mass spectrometry laboratory, the program would cut itself out.

The data analysis method used was based on integrating the area under the curve, as well as finding the point of maximum intensity by measuring the smallest incremental difference in voltage for a given peak. The digital signals from the IBM 1827 ADC unit were arranged in a 30,000 half-word storage array so that, after rearranging, odd numbered locations contain the mass marker values and even numbered locations contain the m/e intensity values. The gross storage layout provided for a total of 130 K-bytes of devoted core of the IBM 360/50. Only "data signal" peaks at integral mass numbers were of interest; the program called for a check of each of the 1000 mass marker values to determine how many locations were entered for the same mass value (3). This gave an interval that told how often to check for "data signal" peaks. At every interval the program located the highest point of the "data signal" and, after it was found, the ascending points preceding it and the descending points following it were used to calculate the area under that curve, which was stored in the disc as the intensity value at the calculated m/e value. The relationship between the data collected and the desired output forms are shown in Figure 6. Digitized and reduced intensity-mass value pairs (up to 1,500 mass

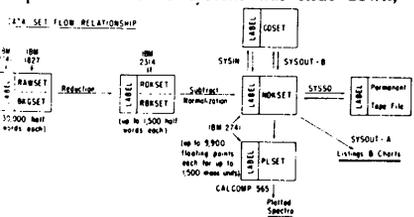


FIGURE 6. Data set flow relationship.

<b>Legend:</b>	<b>RAWSET</b> - digitized M S & Hall Generator Input.	<b>PLSET</b> - Data to be used for plotting (always in core, not in disc) mass spectrum (CalComp Plotter).
	<b>BKGSET</b> - digitized M S & Hall Generator Input.	<b>SYSIN</b> - system input from off-line source.
<b>Recognition Features: Spectra No. (10 Charac.)</b>	<b>RDKSET</b> - digitized and calibrated reduced MS data stored in disk.	<b>SYSOUT - B:</b> card puncher for providing off-line source.
	<b>RDKSET</b> - Digitized, calibrated and reduced MS data recognized as background which is stored in disk.	<b>SYSOUT - A:</b> Printer
<b>Bkg. No. (10 Charac.)</b>	<b>NDKSET</b> - normalized MS data (background subtraction); based on 10,000 units representing the base peak for computing accuracy of 0.01%.	<b>SYSBQ</b> - sequential data storage on permanent tape file.
	<b>CDSET</b> - card punch-out for off-line use.	<b>DISK</b> = used either sequentially or directly (requires a key for latter).

<sup>1</sup>Separated by a comma which automatically assumes second one will be a background. Will not plot a negative value.

values) along with spectra labels were stored in the disk. The processed data (i.e., background subtracted and normalized) could be listed on the printer, punched on cards, stored on magnetic tape or plotted as a bar graph on a CalComp 565 digital incremental plotter upon request by the mass spectrometer operator.

After 30,000 points of data were digitized, a check was made on the validity of data. The following two examples will suffice. A check was made when the mass marker signal did not increase, which implied something was out of order. A similar situation could happen when the spectrum was very short, and occupied only a small space of the raw data storage. One would therefore be unwilling to reduce all 30,000 points and waste the computer time. Therefore, the mass marker signal was checked at a few points, e.g., at points separated from each other by 1,000 digitized points. For 15,000 mass marker points, only 16 points were checked. If it was found that the value of these points increased steadily up to a certain point, e.g., the sixth, and decreased from then on, it could be concluded that the scanning ended between the 6,000th and 7,000th points of mass marker signal. Further reduction beyond 7,000 was, therefore, not advisable. Thus, a substantial amount of computer time was saved for both economy and assistance in collecting the high volume output of the MS-GC system. Mass marker signal also was checked when the maximum intensity digitized from the data channel was less than 2,000. Here, the accuracy of the data would become questionable, and a warning should be issued. Unless the sample was so precious that something is better than nothing, such data would be rejected.

The "mass marker signal" was then smoothed up to the point where scanning ended. Although we have argued that to achieve mass separation by the use of mass marker signals only, at least 70 db. down noise figure is required (3), while the best remotely transmitted data can achieve only 55 db., the average process will, in fact, filter the noise by quite a number of dbs because the noise has a mean value of zero.

It has been reported (4) that 40 to 68 db. filtering can be achieved.

Even if the "mass marker signal" were so inaccurate that  $\Delta m = 1$  could not be resolved, the time sequence of digitizing would not be reversed; therefore, the time sequence could be used as a guide in locating new peaks. Hites and Biemann (5) succeeded in using time sequence only to resolve peaks. It should be pointed out that to average more points in the vicinity it is not necessary to do more addition, but merely to drop two preceding points and add two succeeding points. The average was taken according to the following procedure. An odd number of cycles of digitization (see Figure 4 where each cycle represents the execution of one channel command word) was taken. This average value is the "mass marker signal" at the center point of the period averaged. Taking two such consecutive average values, one can easily evaluate the "mass marker signal" at the points when the intensity values were taken.

Smoothed "mass marker signals" were then used to calculate the  $m/e$ . A few low mass value peaks were first located and their separation recorded. The average separation was then used to search new locations of integral  $m/e$  values without a point by point check. When a new peak was found, its separation from a previous  $m/e$  was used to revise the separation table. Rather complicated logic was employed to safeguard the data reduction. An example of the data obtained is presented in Computer Print-Out 1 (Figure 7).

On the other sections of the program, provision was made to check the raw data either on the terminal console in the mass spectrometry laboratory or on the computer center printer. These were used to evaluate the proportionality constant  $k$  manually or for trouble shooting.

A permanent disk file of the reduced data is used for later processing and plotting. The plotting program has been previously described (6). The CalComp 211 interface software are six basic FORTRAN callable subroutines provided by CalComp and we provided the routine to make it compatible with the IBM software.

**FORMAT OF A TYPICAL SAMPLE RUN**

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*****NASC SPEC PROGRAM NOW RUNNING!*****
69/155      16.00.54      PLEASE ENTER YOUR (NEXT) REQUEST WITHIN 18 MINUTES *****
ENTER SPEC #, AND LABEL INFORMATION UP TO 60 CHAR.
0001-07-01-RICININE TEST RUN
THE COEFFICIENTS FOUND IN DISK ARE AS FOLLOWING.  REPLY 'OK' OR OVERRIDING VALUES IN %10.6 FORMAT.
-0.5741644E-04      -0.5058596E-04      0.1205700E 03
C.C0000000.00050000.00000000
THE COEFFICIENTS FOUND IN DISK ARE AS FOLLOWING.  REPLY 'OK' OR OVERRIDING VALUES IN %10.6 FORMAT.
0.0      0.05049999E-03      0.0
C.C0000000.00050000.00000000
THE COEFFICIENTS FOUND IN DISK ARE AS FOLLOWING.  REPLY 'OK' OR OVERRIDING VALUES IN %10.6 FORMAT.
0.0      0.5039999E-03      0.0
CA
READY 0001-07-01

AOC ERROR. TRY AGAIN

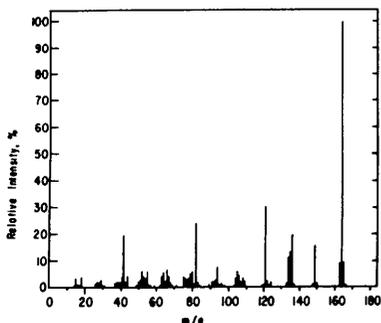
SCANNING NOT FOUND
PLEASE MAKE NECESSARY ADJUSTMENT(S).
READY 0001-07-01

PRINTING COMPLETED.
**WARNING** PR MAX FOUND AT END OF INTERVAL EXAMD BY 'FITPR'.
**WARNING** PF MAX FOUND AT END OF INTERVAL EXAMD BY 'FITPR'.
REDUCTION COMPLETED
  70      54      58      58      60      58      126      62      64      70      78      67      56      58      72
  84      58      62      56      60      66      58      72      58      54      78      68      66      68      56      118
  98      65      64      68      86      77      77      58      54      78      68      66      68      68      68      60
  112      60      100      67      77      54      74      72      46      58      56      68      62      67      60
  126      72      67      77      57      90      67      62      64      62      70      74      117      60      62
  140      64      100      58      68      70      58      78      70      64      182      58      76      62      80
  154      76      138      87      68      60      60      80      56      58      132      717      117      77      87
  168      90      80      170      70      108      76      56      67      212      77      67      58      88      70
  182      70      205      127      170      76      56      67      66      66      62      62      60      60      60
  196      68      62
READY 0001-07-02

HALL GEN BELOW 2000 ADCH
PLEASE MAKE NECESSARY ADJUSTMENT(S).
READY 0001-07-02

```

FIGURE 7. Format of a typical sample run (Computer Print-Out 1). It is not corrected for background noise.



**Spectra plotting and print-out in  
M. S. Lab (data display)**

The format of a typical sample (ricinine) run is shown by Computer Print-Out 1 (Figure 7). A ricinine plot compared with an authentic (hand measured and drawn) plot of ricinine is shown in Figure 8. It can be readily observed that a number of additional peaks is present in the spectrum resulting from the automatic data acquisition system which renders this spectrum unusable.

On the positive side, however, are the very good results obtained from 1) hand measuring the original mass spectrum, 2) punching the mass marker intensity —  $m/e$  values on cards and introducing these to the IBM 360/50. Typical results are shown in Figure 9. It is observed that these data are quite accurate and reproducible.

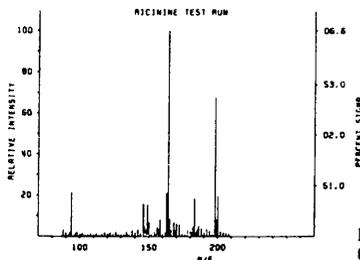


FIGURE 8. Comparison of ricinine plots. Top: Ricinine, hand counted, measured and drawn. Bottom: Ricinine via automatic data acquisition system.

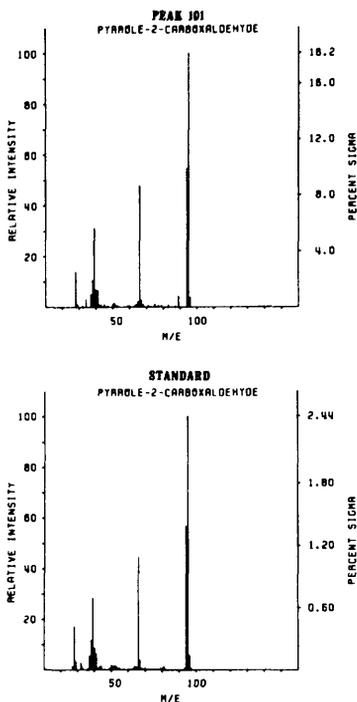


FIGURE 9. Results from a capillary column run. Peak 101 was a compound eluted in an unknown mixture which had a retention time of about 90 minutes and represented about 0.2 micrograms of the sample.

Consequently we must conclude that the existing state of knowledge concerning the rapid transmission of precise analog signals is inadequate for handling the data output of a low resolution combination mass spectrometer-gas chromatograph.

#### ACKNOWLEDGEMENTS

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#### REFERENCES AND NOTES

1. G. R. WALLER, Proc. Okla. Acad. Sci. 47: 271-292 (1968). Since the last report describing this instrument, there have been added an automatic mass marker (discussed briefly in this paper under Results and Discussion) and an alternating voltage accelerator (C. S. Sweeley, W. H. Elliott, I. Fries, and R. Ryhage, Anal. Chem. 38: 1549-1553, 1966).
2. It would appear that when FM equipment of 70 db. accuracy becomes commercially available, a successful analog transmission system can be obtained.
3. The equation  $(m/e)^{1/2} = kh$ , where  $h$  is the output in relative units of the Hall element in the mass marker, arises from the fact that  $m/e$  is proportional to the square of the magnetic field strength which is, in turn, proportional to the Hall element output. However, the equation  $(m/e)^{1/2} = k_0 + k_1 h^2 + k_2 h^4 + \dots$  is used to correct for deviations from ideality.  $k_0$  is the offset term,  $k_1$  is the  $k$  above and  $k_2$  etc. are higher order correction terms.
4. T. W. LEE, Statistical Theory of Communication, John Wiley and Sons, New York, 1960.
5. R. T. HITES and K. BIEMANN, Anal. Chem. 39: 965-970 (1967).
6. H-Y. LI, G. R. WALLER, D. ETTER, and J. WALDEN, Proc. Okla. Acad. Sci. 48: 250-257 (1969).