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Automation of a Residual Gas Analyzer on a Time-shared Computer

Abstract: The automation of a quadrupole mass spectrometer - residual gas analyzer (RGA) on a time-shared IBM 1800 Data Acquisition and Control Computer is described. The RGA, which is used to determine the partial pressures of various gases in a vacuum system, may be operated up to a maximum data rate of about 20,000 points/sec (pps) in an interleaved manner with multiple slow-scanning (≤ 20 pps) instruments. We review in detail the hardware and software considerations regarding the design and subsequent interfacing of the instrument to the computer. Methods for initiating data collection, entering experimental parameters, and analyzing the experimental data, such as spectrum plotting, smoothing, peak location, mass identification, and calculation of the partial pressures by using a least-squares approximation to fit mass peaks, are discussed with examples.

Introduction

Residual gas analysis is a form of mass spectrometry directed toward determining partial pressures of gaseous species contained in a given ambient atmosphere. Because of evolution of gases from materials heated in a closed system, and also because of gettering action, spectral peaks are frequently transient in nature and require a means for rapid data collection. In addition, determining the partial pressures from the mass spectrum is ordinarily tedious and time consuming. Modern high-speed data acquisition and analysis tools have an obvious utility for processing such laboratory data. This paper discusses automation of a Residual Gas Analyzer (RGA) utilizing an IBM 1800 computer operating in a time-shared environment. Although other automated mass spectrometric systems are described in the literature[1-4], we believe our effort to be one of the few (if any) extant applications to residual gas analysis.

The time-sharing system concepts described by Gladney[5] are utilized in the present laboratory automation monitor[6], permitting the data from a high-scan-rate experiment (such as the one reported here) to be interleaved with data from slow-scanning experiments.

We describe in the next section some hardware and software details pertinent to our automation scheme. The subsequent section outlines the data acquisition and

data reduction phases of our experiment. Details of the implementation and operation of the system are discussed as they pertain to specific problems inherent in residual gas analysis. In our concluding remarks we discuss the advantages and the limitations of the current automated RGA system.

Automated residual gas analyzer

• *Time-shared system*

The IBM 1800 computer used in this work has a 32K core storage with an access time of $2 \mu\text{sec}$ per word and standard process input/output equipment. The software was developed under the Time-Shared Executive (TSX) operating system. For details of the software and hardware configurations, see Ref. 5. The 1800 is currently supporting a variety of laboratory automation applications and, to a lesser extent, process control studies. Fifteen laboratory instruments are currently automated on the 1800. The instruments may be classified into two main groups. The first group consists of slow-data-rate instruments, e.g., scanning spectrometers and chromatographs, etc., requiring an average data rate of about 5 points/sec. These instruments are routinely time-shared on the 1800 using a single, millisecond-interval timer.

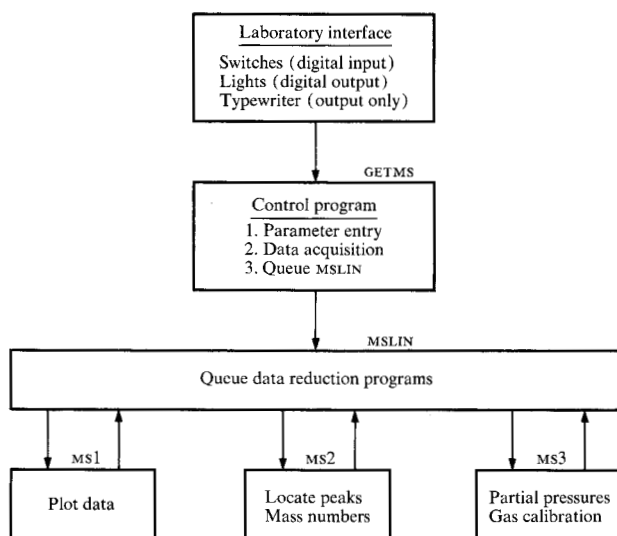


Figure 1 Block diagram of key features of the automation of the residual gas analyzer.

The second group comprises fast-scanning instruments and includes the residual gas analyzer. In this group average data rates are of the order of 5000 points/second and require dedication of the computer's analog-to-digital converter (ADC) for their duration. Since time requirements for these instruments are generally short, the system provides time blocks so that uncontrolled slow-scan instruments lose no more than four data points. Blocks of 2-15 sec are routinely available to the residual gas analyzer or to other fast-scanning instruments. The fast-scanning and slow-scanning instruments are thus interleaved in a way that minimizes their interaction but also provides maximum availability to all users. Data reduction, plotting and program development work are time-shared with the higher priority functions of data acquisition and control. Details of this technique are described by Grant[6].

• Software overview

The over-all structure for the operation of the RGA is quite simple. Figure 1 depicts in block form various key features of this system; a detailed flow chart for a similar operation is included in Ref. 7. The program GETMS provides over-all control for the various steps required to operate the RGA and implement final reduction of the experimental data. Depending on the switch setting, various steps of the process may be actuated, such as parameter entry, acquisition of the mass spectrum, or queuing of a second control program MSLIN which sets up the sequence of data reduction programs. These include plotting of the raw data by MS1, the location of

peaks and identification of mass numbers by MS2, and finally the partial-pressure calculation by MS3. Each data reduction program returns through the control program MSLIN to allow entry of programs into the "queue" by other users. This technique prevents long delays in response to other 1800 users. Details of each part of the system follow in the subsequent discussion.

• Laboratory interface

The laboratory interface consists primarily of a set of 16 digital contact input switches, a set of 16 lights driven by the 1800 digital output feature, a contact interrupt switch, and an IBM 1053 printer. Only four types of signals are sent to the computer, i.e. a 0 to 5 V sweep voltage, a 0 to 5 V output signal, a contact interrupt switch signal that initiates data logging or analysis, and 16 switches that are read by the computer to obtain coded information about important parameters or to indicate desired analysis. General information on the use of the data and interrupt switches has been described elsewhere[8]. The use of these switches in RGA automation is described in the next section. The 0 to 5 V sweep voltage is the standard sweep output on the RGA.

A logarithmic amplifier is used to measure the mass spectrometer response signal. This method allows both large and small currents to be measured quickly and without the complicated range switching required for a linear amplifier. It should be noted that small peaks often provide significant information about partial pressures; hence, a logarithmic amplifier with a dynamic range of at least 10^6 is needed. The output of the log amplifier is fed directly to the computer, where the signal may be exponentiated to yield the output current. The mass number range from 0 to 50 can be swept in about 4 sec. The limiting factor on the sweep is the slow response time of the log amplifier at low currents. For example, at 10^{-9} A the time constant is approximately 10 msec.

Communications from the computer are provided both by a set of 16 lights driven by a digital contact output group of the 1800 and an IBM 1053 character printer. Certain codes will appear in the lights, indicating the computer status at various stages of the process. Hard copy output is presented on the 1053 for the several data acquisition and reduction programs. This printer is fairly slow (15 characters/sec) and when larger quantities of output are required, the 1800-1443 printer is utilized.

• Parameters

In our system, ten parameters may be entered through the switches in the laboratory. They define run conditions and provide control of the various steps of the automated residual gas analysis. A simple editing pro-

cedure allows the routine changing of parameters, which may vary for successive runs. This flexibility proves to be an important feature of the system. These parameters are shown in Table 1 and will be described in detail as each phase of the operation of the automated RGA is described.

Experimental procedure

• Data acquisition

A signal from the computer starts the mass scan by closing a relay in the laboratory. A typical mass spectrum for an atmosphere containing CH₄, N₂, CO, Ar, and some H₂ and CO₂ is shown in Fig. 2. Note the logarithmic relationship between y-voltage and current. Parameter 1 determines the time interval between relay closure and the start of computer scanning, thus eliminating the storing of unwanted data at the beginning of the mass scan. Parameter 2 determines the maximum number of points allowed to be taken as the mass range is scanned, usually about 10,000 points, and parameter 3 determines the scan time. Typically the mass range 0 to 50 is scanned in 3 to 5 sec.

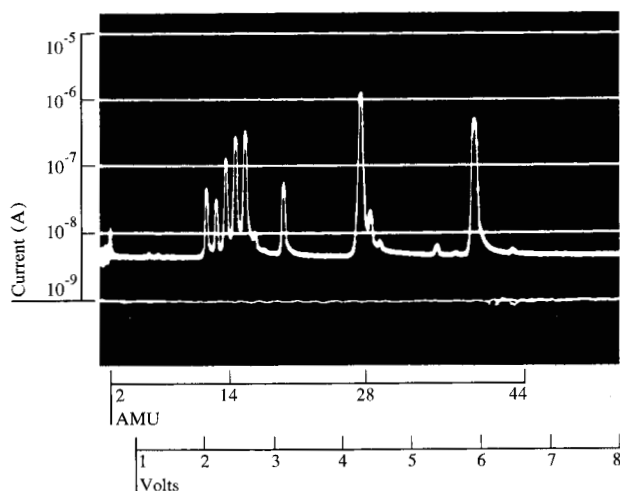
Figure 2 shows that there are often large portions of the mass range that do not contain significant data, e.g., between mass 8 and mass 10. Therefore, parameter 4 is used to indicate a threshold current below which points will not be stored by the computer. Usually out of the 10,000 points sampled, less than 1,700 are retained. The background current must be subtracted from the total current in order to obtain the signal due to the ambient atmosphere. This background can vary greatly, depending on the past history of the electron multiplier. The background is therefore measured during each scan and the result used in ms3 to make the appropriate correction. The number stored in parameter 5 designates the voltage at which the background is to be measured. In our experiments, this voltage usually corresponds approximately to mass 9.

When all parameters are initialized, data acquisition may be initiated under the control of GETMS. A block diagram of the data acquisition portion of this program is shown in Fig. 3. First, parameter validity is checked. If all parameters are reasonable, the system checks available scanning time against the request and an error message is printed if the time interval is not sufficient. At this time, the relay which triggers the mass scan is closed, followed by the preset delay time specified in parameter 1. When this time has elapsed, analog scanning begins. Each point is checked against the threshold before retention. If it is below threshold, the program checks to see if the data are in a region where background is to be determined. If it is, the point is added to the background. When data acquisition is complete, the average background current is computed, a message indicating status

Table 1 Parameters used in the automated residual gas analyzer.

| Number | Parameter function | Type |
|--------|------------------------------|------------------------|
| 1 | Relay closure delay | Run control |
| 2 | Total points to scan | Run control |
| 3 | Total scan time | Run control |
| 4 | Threshold current | Run control |
| 5 | Region to measure background | Run control |
| 6 | RGA sensitivity | Data reduction |
| 7-8 | Mass calibration | Data reduction |
| 9-10 | Task sequence and options | Data reduction control |

Figure 2 Mass spectrum for a mixture of Ar, CH₄, CO and N₂.



of the run is printed in the laboratory, the data is written to a disk file and the program exits.

• Data reduction

Mass identification and peak height determination

Coded entries are stored in parameters 9 and 10, which indicate the type and sequence of analysis programs to be used. For example, MS1, MS2 and MS3 provide plotting, peak and mass identification, and partial-pressure calculation, respectively. These programs can be used independently or in any sequence, depending upon the circumstances (Fig. 1).

The relationship between mass number and sweep voltage is linear for our quadrupole, i.e.,

$$N = a + b V(N), \quad (1)$$

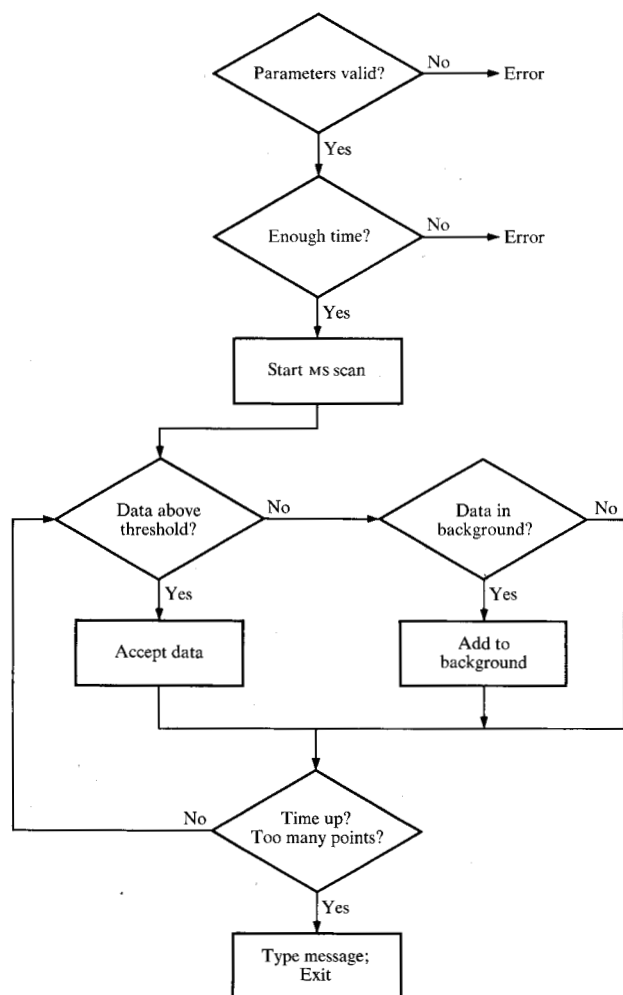


Figure 3 Flow chart of data acquisition portion of the control program, GETMS.

where N is the mass number, V is the sweep voltage, and a and b are constants stored at parameters 7 and 8, respectively. Electronic instabilities necessitate periodic changes in these parameters. Equation (1) is used in MS2 to assign a mass number to a given peak.

After a mass scan is completed under the control of GETMS, information equivalent to that shown in Fig. 2 is stored on disk. The procedure used by MS2 for determining the mass numbers follows. Raw data and parameters are read from the disk data files and the spectra scanned to locate "interesting regions", i.e., regions where there are points above threshold. For example, in Fig. 2 the distance between the initial rise at mass 12 and the final decay at mass 17 would be considered an "interesting region." Data above threshold but not providing sufficient points in a given region to locate peaks are discard-

ed. The data are interpolated to provide equal spacing along the mass scale, then smoothed and differentiated. Peaks are located by zero crossings in the derivative. Peak heights are computed simply by averaging the five largest points at the top of each peak. The smoothing has eliminated most of the noise so the peak height could be obtained almost as accurately by using only the largest point. The mass numbers are then computed by matching the located peak positions against the mass calibration determined by Eq. (1). The peak heights and mass numbers are printed in the laboratory and then stored on disk in a third data file for subsequent usage by MS3.

Calculation of partial pressures

Residual gas analysis is greatly simplified by the fact that there are usually only a limited number of low molecular weight gases present. One typically observes H_2 , He, CH_4 , H_2O , CO, N_2 , O_2 , Ar, CO_2 , and to a lesser extent organic gases such as C_2H_4 and C_2H_6 . The presence of only a small number of gases results in relatively simple spectra. Nevertheless, obtaining partial pressures from mass spectra is often quite complicated since several gases produce peaks at the same mass numbers. For example, CO, N_2 , C_2H_4 and CO_2 produce spectra at mass 28 while CO_2 , O_2 , CO, CH_4 and H_2O appear at mass 16.

The relationship between mass spectra and partial pressures is given by a set of linear equations which are expressed in matrix form and shown in Eq. (2);

$$I = AP$$

$$\begin{bmatrix} i_1 \\ i_2 \\ \vdots \\ i_m \end{bmatrix} = \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ a_{21} & \cdots & a_{2n} \\ \vdots & & \vdots \\ a_{m1} & \cdots & a_{mn} \end{bmatrix} \begin{bmatrix} p_1 \\ \vdots \\ p_n \end{bmatrix}, \quad (2)$$

where matrix I is a column vector whose elements are the mass spectrometer output currents, matrix P is a column vector whose elements are the desired partial pressures, and A is the cracking pattern matrix. In complicated, many-component systems, the elements of A would be difficult to obtain. However, for residual gas analysis A is relatively small ($\approx 10 \times 50$) and its elements can be determined in a routine manner by introducing known gases into the vacuum system.

In general, $m > n$, hence the system of equations is overspecified. However, one can choose to minimize some function of the difference between calculated and observed values of I . We choose the least squares criterion[9].

There are several variables, such as resolution and electron emission current, that change RGA sensitivity (i.e., current/pressure). Changes in sensitivity can be

accounted for in Eq. (2) by changing appropriate elements in **A**. In particular, if the sensitivity for all gases is changed by a constant ratio (e.g., by changing the electron emission), then each element of **A** is simply multiplied by a constant. This constant is entered through the switches and stored at parameter 6. When ms3 is subsequently called the elements of **A** are multiplied by parameter 6. This flexibility is particularly helpful in correcting for changes in multiplier sensitivity. In some cases, the analysis performed in ms2 is all that is required. On the other hand, if partial pressures or concentrations are needed, then ms3 is called. This program exponentiates the peak heights that were the output of ms2, thus yielding the currents. The background current is then subtracted from each peak, resulting in a set of current values which are the elements of matrix **I**[Eq. (2)]. The known values of **I** and **A** are introduced into a standard subroutine which uses a least-squares analysis to compute **P**. The computed values for the elements of **P** are then printed in the laboratory.

Table 2 compares known and computed partial pressures for a mixture of CO, N₂, Ar and CH₄ described in Fig. 2. The calculated values are the same as actual pressures within experimental error.

Determination of cracking patterns

The partial-pressure calculations described in the previous section depend quite critically on the accuracy of **A**. Hence, it is important to be able to routinely change the elements of **A**.

For an atmosphere containing only one gas, the matrix **P** has only one element, i.e., the known pressure (p_n) of the one gas that is present. Now if both sides of Eq. (1) are divided by p_n and if the two matrices on the right are multiplied, one obtains:

$$[i_1/p_n, i_2/p_n \cdots i_m/p_n]^T = [a_{1n}, a_{2n} \cdots a_{mn}]^T, \quad (3)$$

where **T** indicates the matrix transpose. Hence, the a values pertinent to the one gas that is present are known from the ratios of the i 's to p_n . The entire matrix **A** is easily determined by introducing series of known gases or mixtures into the vacuum system and doing the appropriate analysis.

Each analysis program can have up to 16 options. If ms3 is called with options 0 to 2, the partial-pressure analysis described in the previous section is completed. On the other hand, if options 8, 9, 10 or 11 are called, elements of **A** pertinent to N₂, CO, CH₄ or Ar, respectively, are calculated and stored. The appropriate option is entered through switches from the laboratory.

Concluding remarks

This paper describes the use of an IBM 1800 computer in the automation of a residual gas analyzer. The experi-

Table 2 Comparison of known and computed partial pressure for the mixture characterized in Fig. 2.

| Actual pressure ($\times 10^6$) | Measured pressure ^a ($\times 10^6$) in mixture of CO, AR, CH ₄ , N ₂ |
|-----------------------------------|--|
| $P_{AR} = 1.43 \pm 0.05$ | $P_{AR} = 1.39 \pm 0.04$ |
| $P_{N_2} = 1.98 \pm 0.05$ | $P_{N_2} = 2.00 \pm 0.06$ |
| $P_{CO} = 2.05 \pm 0.15^b$ | $P_{CO} = 2.00 \pm 0.15$ |
| $P_{CH_4} = 1.85 \pm 0.25^c$ | $P_{CH_4} = 1.63 \pm 0.04$ |

^aMeasured pressure is average of four runs

^bReversible adsorption causes uncertainty in the CO measurement

^cIon gauge pumping causes uncertainty in the CH₄ measurement

ments are characterized by submillisecond data rates and by the accumulation of bursts of data in short periods of time. Furthermore the data require a large amount of arithmetic manipulation before useful results are obtained. This has led to an automation scheme whereby data from the fast experiments is obtained during a brief period in which slower experiments are masked. A more detailed partial pressure analysis than could be obtained manually in a reasonable time is performed on-line within minutes. The speed of the operations allows the experimenter to interact closely with the data and to plan experimental modifications for succeeding measurements. The essential feature of the automation which makes the whole procedure easily possible is the direct digitization and input of data into core so that there is no unnecessary physical handling and conversion of other data media. A significant result is the ease with which corrections for sensitivity changes, cracking pattern changes, etc. can be introduced into the analysis.

It would be advantageous for observing transient pressures if repetitive scans of the mass spectrum could be taken at a rate 10 to 100 times faster than the present capability allows. The quadrupole RGA can perform at scan rates of 500 μ sec/AMU, while we are limited by the present automation scheme to about 50 msec/AMU, because of the time constant of the log amplifier.

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