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DIRECT MEASUREMENT OF GAS CHROMATOGRAPHIC RETENTION VOLUME USING AN ON-LINE MINI-COMPUTER.

I. PRINCIPLES

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SUMMARY

A method is described for the direct measurement of retention volume in gas chromatography. With the aid of a computer, flow, pressures and temperature, as well as the detector signal, are continuously monitored during the chromatographic run. Thus, a point on a chromatogram is characterized by a corrected volume and concentration, and not by time and concentration. The retention volume is obtained as the first statistical moment. The direct registration of volume, instead of time, facilitates precise and accurate determinations without excessive control of flow and pressure. Retention volumes are obtained with a standard deviation of 0.02%.

INTRODUCTION

Physico-chemical studies in gas chromatography have long been undertaken¹⁻³, one interesting field being the study of complex-formation by gas chromatography⁴⁻⁹. The parameter of chief interest in many types of physico-chemical studies is the retention volume, and several instruments for its precise measurement have been described^{6, 10-14}. To obtain the necessary precision, a computer is a valuable aid for processing the detector signal, for controlling various parameters and for certain regulating processes.

For precise measurement of gas chromatographic retention volumes, it is common practice to determine the retention time of the solute (corrected for the air peak) and the flow of gas (corrected for the temperature dependence and compressibility); multiplication of these quantities yields the corrected retention volume. With this approach, however, great demands are placed upon the stability of the flow, the temperature, the pressure drop across the column and the ambient pressure.

An alternative method would be continuously to measure the required parameters during the chromatographic run and then to calculate the fully corrected volume of gas that has passed through the column from the moment of sample injection. In this way, it would be possible to substitute a volume scale for the time scale. Minor

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variations in flow and pressure would, in such circumstances, be of little importance, since they would be taken into consideration in the computing process and because the chromatographic process should not be highly dependent on flow or pressure. Thus, the measurement of retention volume would not rely on the stability of the flow and pressure controllers, but instead on the corresponding measuring instruments. Temperature variations could be treated in a similar fashion; however, as most partition constants are highly dependent on temperature (and this dependence is generally unknown), only very small variations in temperature could be tolerated. In an instrument working according to these principles, there would still be the need for effective thermostatic control.

THEORY

The fully corrected volume, V , of gas (assumed to be ideal) having passed through a column during time t is given by

$$V = t \cdot F \cdot R \cdot T \cdot J_3^2 \cdot \frac{1}{p_0} \quad (1)$$

where F is the mass-flow (in mole/sec), T is the absolute temperature, R is the gas constant, p_0 is the pressure at the outlet of the column and J_3^2 is given by the expression

$$J_3^2 = \frac{\left(\frac{p_i}{p_0}\right)^2 - 1}{\left(\frac{p_i}{p_0}\right)^3 - 1} \cdot \frac{3}{2} \quad (2)$$

where p_i is the pressure at the inlet of the column¹.

If Δp is the pressure drop across the column, $p_i = \Delta p + p_0$, and eqn. 2 can be algebraically transformed to

$$J_3^2 = \frac{3}{2} \cdot \frac{(2p_0 + \Delta p) \cdot p_0}{3p_0^2 + 3 \cdot \Delta p \cdot p_0 + \Delta p^2} \quad (3)$$

Eqn. 3 is used in this work, since measurement of the pressure drop was technically more convenient than measurement of the inlet pressure. Hereafter, the subscript in p_0 is dropped and the outlet pressure is designated p .

Eqn. 1 may be used for every value of t , provided that T , p , Δp and F are constant during this time; the error in V depends on the stability of these parameters during time t . When t is the corrected retention time, eqn. 1 describes the classical approach for calculation of retention volume V_R .

In order to obtain high precision in the measurement of V (and hence in V_R), either the stability of T , p , Δp and F must be improved, or these parameters must be measured at sufficiently short intervals of time. If the time interval is Δt , the small volume of gas, ΔV , that has passed through the column during time Δt is given by

$$\Delta V = \Delta t \cdot F \cdot R \cdot T \cdot J_3^2 \cdot \frac{1}{p} \quad (4)$$

and these small volumes are summed to give the volume of gas passing through the column for any arbitrary period.

For a computer-based system, it is convenient to measure F , p , Δp and T with the same time interval as the detector signal, D . This interval depends on the width of the chromatographic peaks and can range from about 0.05 sec to several seconds. In a gas chromatographic system, variations in flow and pressure are slow and there is generally no need to use a shorter time interval for measurement of these parameters. Thus, all parameters are sampled and a new value for ΔV is calculated and added to the accumulated volume for each point taken on the chromatogram. The necessary speed in computation and sampling is well within the ability of a mini-computer.

The points taken on the chromatogram are characterized by two co-ordinates, V_i and D_i ; V_i is the fully corrected volume and D_i is the detector response, which is proportional to the concentration. The retention volume of a peak is calculated as the first moment, m_1 (see ref. 15)

$$m_1 = \frac{\sum_i (V_i \cdot D_i)}{\sum_i D_i} \quad (5)$$

The area, A , of the peak is given by

$$A = k \cdot \Delta t \cdot \sum_i D_i \quad (6)$$

where k is an apparatus constant. The "air" peak can be treated like any other peak, and the corrected retention volume for a sample is thus given by a simple subtraction, *viz.*,

$$V_R = m_1 (\text{sample}) - m_1 (\text{air peak}) \quad (7)$$

APPARATUS

An instrument has been constructed according to the principles outlined above; its general features are shown in Fig. 1.

The carrier gas passes through a thermal mass flow meter (Brooks Instrument, Emerson Electric, Veenendaal, The Netherlands; Model 5910), which can, when desired, be calibrated against the mercury analog of a soap-film flow meter¹⁶. Injection is made by means of a valve system⁶.

The columns are V-shaped and are immersed in an oil-bath (Hallikainen Instruments, Lewisham, London, Great Britain; Model 1120) equipped with a thermostat to keep temperature variations below 0.01°. Temperature is measured by means of a calibrated platinum-resistance thermometer (Rosemount Engineering, Bognor Regis, Great Britain; Model E666). The detector is a flame ionization detector (Varian, Walnut Creek, Calif., U.S.A.; Model 02-000968), the signal from which is amplified by a 417-K Chromatograph Electrometer (Keithly Instruments, Cleveland, Ohio, U.S.A.).

The outlet pressure is measured with a Rosemount capacitive pressure sensor,

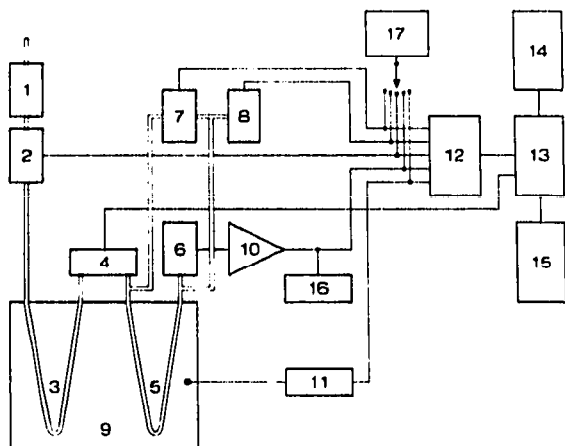


Fig. 1. Gas-chromatographic system. 1 = Flow regulator; 2 = thermal flow sensor; 3 = pre-column; 4 = sample-injection system; 5 = column; 6 = flame ionization detector; 7 = differential-pressure sensor; 8 = absolute-pressure sensor; 9 = thermostat; 10 = amplifier; 11 = platinum-resistance thermometer; 12 = multiplexer and analog-to-digital converter; 13 = computer with interfaces; 14 = digital cassette recorder; 15 = teletypewriter; 16 = strip-chart recorder; 17 = digital voltmeter for manual control of variables.

measuring absolute pressure (0–830 mmHg, 0–111 kPa) (Model 830A-7). The pressure drop is measured with a similar differential-pressure sensor (0–235 mmHg, 0–31 kPa) (Model 831A-18). The pressure sensors are calibrated against a mercury manometer, which can be read with a precision of 0.05 mmHg, (Negretti & Zambra, London, Great Britain; Model M2691). The signals from the thermometer, flow and pressure sensors, and from the electrometer, are fed to a multiplexer and then to a 14-bit analog-to-digital converter (Analogic Corp., Wakefield, Mass., U.S.A.; Model MP 2814) connected to the computer. The computer is an ALPHA LSI-2 (Computer Automation, Irvine, Calif., U.S.A.), and is equipped with a 16k memory of 16-bit words, a double cassette recorder and a console teletypewriter; it uses a modified BASIC language. The complete apparatus, and the programs, will be described in more detail later^{17,18}.

RESULTS

Several tests have been made to check the performance of the system. Table I shows the results of nine consecutive runs with *n*-heptane on a column with 20% of *n*-octadecane at 60.00°; V_R is the retention volume derived as described above, t_R is the retention time measured at the position of the first moment, f is the mean of the corrected flow before and after this series of runs (completed during 45 min). Thus, $t_R \cdot f$ is the retention volume, calculated as the product of time and flow-rate. It can be seen from Table I that the variance of V_R is significantly smaller than that of $t_R \cdot f$ and that the two respective means do not differ significantly; the greater variance of $t_R \cdot f$ is attributable to small variations in flow-rate. Thus, it can be seen that absolute stability of flow-rate is not mandatory for achieving only small variations in retention-

TABLE I
RETENTION VOLUMES (ml) MEASURED BY TWO DIFFERENT METHODS

| Run No. | V_R | $t_R \cdot f$ |
|-------------|---------------|---------------|
| 1 | 329.25 | 329.59 |
| 2 | 329.35 | 329.88 |
| 3 | 329.32 | 329.89 |
| 4 | 329.23 | 329.66 |
| 5 | 329.28 | 329.39 |
| 6 | 329.42 | 329.22 |
| 7 | 329.38 | 328.97 |
| 8 | 329.36 | 328.81 |
| 9 | 329.27 | 328.80 |
| Mean | 329.32 | 329.36 |
| Stand. dev. | 0.064 | 0.43 |
| Variance | 0.0041 | 0.185 |
| Width* | 0.05 (0.016%) | 0.33 (0.1%) |

* 95% confidence interval.

volume values measured by the method described above. These runs show a relative standard deviation of 0.02%, which is typical for this equipment.

In a second experiment, in which the temperature was 60.17° and all other conditions were as before, the value of V_R was 327.47 ml. From this, it can be seen that a difference in V_R of 0.02% corresponds to a temperature difference of about 0.006°, indicating that the deviation in V_R arises mainly from the temperature dependence of the partition constant.

The absolute accuracy of the system could be evaluated from the accuracies of the instruments monitoring the different parameters. With the sensors currently used, the absolute uncertainty does not exceed 0.1%.

CONCLUSIONS

In contrast to the conventional method of measuring flow and retention time, our method offers a direct measurement of retention volume; in our opinion, this procedure has several advantages. High precision and accuracy can be achieved by using conventional flow and pressure controllers. There is no need for special precautions concerning flow equilibration and pressure control, often the main problems in this type of measurements. Further, with our method, precise and accurate measurements can be made during flow- or temperature-programming. The measurement of retention volume relies on hundreds of individual measurements, giving, statistically, an advantage over the classical method.

Our results, to date, indicate that considerable improvement in the determination of the retention volume can be obtained, thereby extending the applicability of gas chromatography to physico-chemical measurements.

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