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

II. APPARATUS

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SUMMARY

The principle of direct measurement of retention volume, described earlier, has been realized in a computer-linked gas chromatograph. The pneumatic and electronic designs are described, as well as procedures for the calibration of the different sensors.

INTRODUCTION

A novel approach to the precise measurement of retention volume in gas chromatography was presented in an earlier paper[1], together with a brief outline of an apparatus designed for these measurements. This paper contains a more detailed description of the instrumental layout and of the built-in procedures for calibration of the instrument.

For the evaluation of retention volume, it is common practice to keep the carrier-gas flow-rate constant by means of careful regulation, to measure the retention time and to calculate the retention volume. A more direct method would be to measure continuously the gas flow-rate and to obtain the volume by integration of the flow-rate. This can be accomplished with a gas chromatograph equipped with an on-line computer. In the apparatus described here, a laboratory-built gas chromatograph is linked on-line with a small computer. At small time intervals, the computer reads sensors for the appropriate parameters (flow, pressure and temperature) and computes at each point the corrected gas volume that has passed through the column since the start of the run.

The computer also reads the detector signal at pre-determined time intervals (normally the same interval as for the other readings) and correlates the detector readings with the calculated volumes. The time intervals can easily be made small enough to approximately represent continuous measurement. Thus, a correlation

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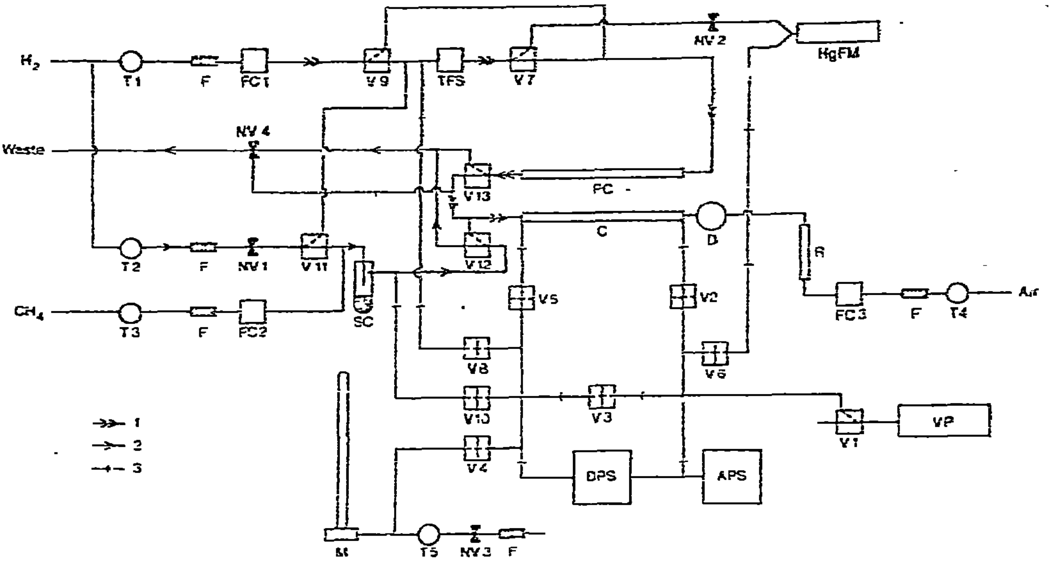

Fig. 1. Pneumatic system: 1 = flow of carrier gas; 2 = flow of sample gas; 3 = pressure-sensing lines. V1–V11, Solenoid valves [Bürkert, mod. 311 (3-way) and 211 (2-way), respectively]: V12, V13, solenoid valves (Hoke-Tomco, mod. 95HV): T, toggle valves (Hoke, mod. 1521); FC1–FC3, flow controllers (Brooks, mod. 8743); R, rotameter (Brooks, mod. 1355); NV1–NV3, needle valves (Brooks, mod. 8503); NV4, see text and ref. 2; TFS, thermal-flow sensor (Brooks, mod. 5810); DPS, differential-pressure sensor (Rosemount mod. 831A-18); APS, absolute-pressure sensor (Rosemount, mod. 830A-7): F, filters (Brooks, mod. 1390); PC, pre-column and C, column [both in an oil thermostat (Hallikainen, mod. 1120)]; M, manometer (Negretti and Zambra, mod. M2691); VP, vacuum pump; SC. sample chamber (see text and ref. 2); D, detector (Varian, mod. 02-000 968): HgFM, mercury flow-meter (ref. 3).

between volume and detector signal is obtained, and from this, by means of suitable soft-ware procedures, the retention volume and other properties of the gas chromatographic peaks can be evaluated.

FLOW SYSTEM

The flow system is shown in Fig. 1. The carrier-gas flow is regulated with the flow regulator (FC1) and measured with the thermal-flow sensor (TFS), from which the gas is fed to the injection system (V12 and V13) and further through the column (C) to a flame ionization detector (D). A pre-column (PC) can be included if desired. A hydrogen-feed line to the detector must be included when hydrogen is not used as carrier gas.

Through the valves V2 and V5, which are normally open, a sensor for absolute pressure (APS) is connected to the column outlet, and a sensor for differential pressure (DPS) is connected between the column ends.

Sample injection can be made either into a conventional injection port, with syringe injection through a rubber membrane, or with a more elaborate valve system[2] integrated with the rest of the flow system and operated by the computer. Sample gas is continuously fed to injection valves (V12 and V13) by means of a separate stream of hydrogen regulated with a needle valve (NV1). The gas flows through a thermostatically controlled glass flask (SC) containing the sample in liquid form. The vapour pressure of the sample can be adjusted by dilution with a non-volatile solvent and by variation of the temperature of the flask. The injection valves switch the sample gas instead of the normal carrier gas onto the column during a short time interval. A stream of methane, regulated by a separate flow controller (FC 2), is optionally added to the sample gas to provide for an "air peak".

The flow-rate of the sample gas can be checked by energizing the solenoid valves V9, V11 and V7; when this is done, the carrier gas by-passes the thermal-flow sensor and the sample gas is fed through the sensor.

In order to avoid pressure surges at injection, it is important that the pressure on the sample side of the injection valves equals the column head pressure. This is ensured by means of a special valve (NV4; see ref. 2). The sample-stream pressure can be measured by energizing valves V10 and V5, the differential-pressure sensor then being connected to the sample-gas stream.

CALIBRATION OF THE SENSORS

The sensors for flow and pressure must be calibrated frequently to avoid long-term drift; therefore, facilities for calibration are integrated with the rest of the system. All calibrations are governed by the computer, which is programmed to handle most of the procedures automatically and to indicate to the operator when to press a button or take a monometer reading. The computer also calculates and stores the calibration result in a form convenient for application to the gas chromatographic measurements.

Absolute-pressure sensor (APS)

Valves V1, V3 and V4 are opened, V2 and V5 are closed and a vacuum pump is started to decrease the pressure in the system; valve V1 is then closed, cutting off the vacuum line. By opening toggle valve T5, air can be admitted to adjust the pressure of the APS to 700 mm Hg; a needle valve (NV3) is used to slow down this procedure. A reading is taken from the manometer and the output from the APS is measured by the signal-acquisition system. The pressure is then somewhat increased (by means of T5), and another pair of readings is made. After eight readings, when the pressure has reached its ambient value, the regression line is calculated. The entire procedure is repeated in the pressure range 470 to 530 mm Hg needed for calibration of the differential-pressure sensor.

Differential-pressure sensor (DPS)

The pressure of the system is adjusted to 500 mm Hg as described above, then valve V4 is closed, separating the two sides of the DPS from each other. More air is admitted through T5 to adjust the pressure difference over the DPS to the first value chosen (normally 80 mm Hg), and readings of the manometer, the APS and the DPS are taken. The pressure difference over the DPS is the difference between the corrected manometer reaaing and the APS reading, with the calibration constants determined as described above. Another portion of air is then admitted, and the readings are repeated until a regression line can be computed.

Thermal-flow sensor (TFS)

The instrument for calibration of the flow sensor has been described[3]; it is connected by energizing valves V2, V5, V6, V7, V8, V9 and V11. The sample-gas stream is used for this calibration in order to adjust the flow with a needle valve and not with a flow controller. The APS is used to measure the pressure in the mercury flow-meter, and a needle valve (NV2) is used to adjust the pressure in the TFS to approximately the same value as during normal operation. A suitable flow is measured with both the mercury flow-meter and the TFS. The flow is then changed, and the process is repeated until a regression line can be calculated.

ACCURACY OF CALIBRATIONS

The mercury manometer (Negretti and Zambra M2691), readable to 0.05 mm Hg, is accurate to within 0.1 mm Hg (ref. 4). The uncertainty of the regression line is about 0.12 mm Hg (this figure includes the drift during one month).

The foregoing is valid only if the calibration is restricted to a relatively small part of the range, as the calibration graph is not straight, but has a well-defined curvature[5]. Thus, the calibration error for the APS is about 0.15 mm Hg ($\sqrt{0.12^2+0.1^2}$). For the DPS, it is 0.22 mm Hg ($\sqrt{0.15^2+0.1^2+0.12^2}$) as the calibration of the latter depends on the calibration of the former.

The accuracy of the flow sensor at 50 ml/min (760 mm Hg and 0°) is estimated to 0.05 ml/min ($\sqrt{0.035^2+0.035^2}$). The accuracy of the mercury flow-meter is about 0.07% (0.035 ml/min) (ref. 3), and the uncertainty of the calibration line is of the same magnitude.

The column-bath thermometer was calibrated by the Thermochemistry Laboratory, Lund; the total error in temperature measurement was less than 0.05 °K.

ELECTRICAL SYSTEM

Signal-acquisition system

In this system (shown in Fig. 2), the analogue signals from the different sensors (see Table I) are fed to an eight-channel multiplexer, which comprises two MOS analogue switches AM 3705CD, National Semiconductor) (M1 and M2). The "channel select" signals come from the control unit (see below). The multiplier has differential inputs, making it unnecessary to tie all signal returns in the system together and so eliminating some earthing problems.

From the outputs of the multiplexers, the signals pass two FET amplifiers (A1 and A2) (LH0042CD, National Semiconductor) connected as voltage followers in order to increase the input impedance of the system. After a μA725C amplifier (A3; Fairchild), the signal is referred to earth potential.

The "sample and hold" amplifier (SH) is built around an operational amplifier (LH 0023GC, National Semiconductor), the output from which goes to the 14-bit analogue-to-digital converter (AD) (MP2814, Analogics). The 14-bit digital-data lines from this are fed to an interface (16-bit digital I/O) connected to the computer (ALPHA LSI-2, Computer Automation).

The "start sampling" signal, developed from the control unit (see below), triggers a monostable multivibrator (SN74121, Texas Instruments). The pulse length

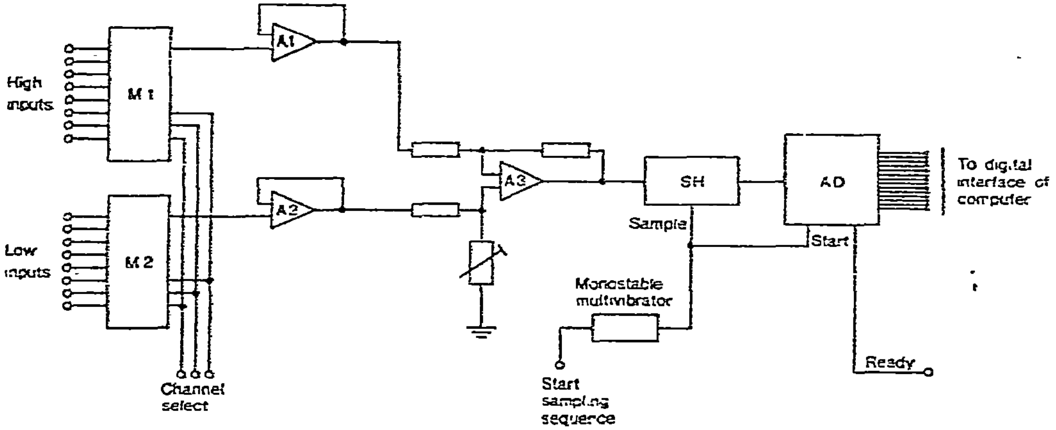

Fig. 2. Signal-acquisition system.

determines the sampling time of the "sample and hold" amplifier. The trailing edge starts the AD-conversion. The sampling time must be longer than the setting time of the multiplexers, buffer amplifier and "sample and hold" amplifier; 500 μsec has been found satisfactory. After the conversion (which takes approximately 80 μsec), the AD-converter issues the signal EOC (End of Conversion) to the interface, generating an interrupt to the computer and thereby signalling that signal measurement is ended and valid data are available.

Control unit

This unit is shown in Fig. 3. The 8 least-significant bits (numbered B0 to B7) of the output buffer of the interface are used to develop various control signals. Bits B4 to B7 are fed to a decoder (SN 74154, Texas Instruments). A clock pulse from the interface is distributed to one of the 16 outputs (C0 to C15) of the decoder, depending on the state of the inputs (B4 to B7). The remaining bits (B0 to B3) are connected to several 4-bit "latches" (D-type flip-flops, SN7475, Texas Instruments), connected in parallel, which are clocked by the signals C0 to C15. In ths way, it is possible to develop 16 independent sets of each 16 control signals for various uses.

At present, only 3 latch units (L0 to L2) are in operation (as shown in Fig. 3). The set of signals from L0 is used for the multiplexer control (signal C0 also starts the sampling sequence); the set from L1 is used for the thermometer select (see below);

TABLE I

ANALOGUE INPUTS

Channel No.	*Usage*
0	Mercury flow-meter
1	Temperature-measuring system
2	Flow sensor (TFS)
3	Pressure sensor (APS)
4	Differential-pressure sensor (DPS)
5	Electrometer (Keithley 417K) connected to the detector

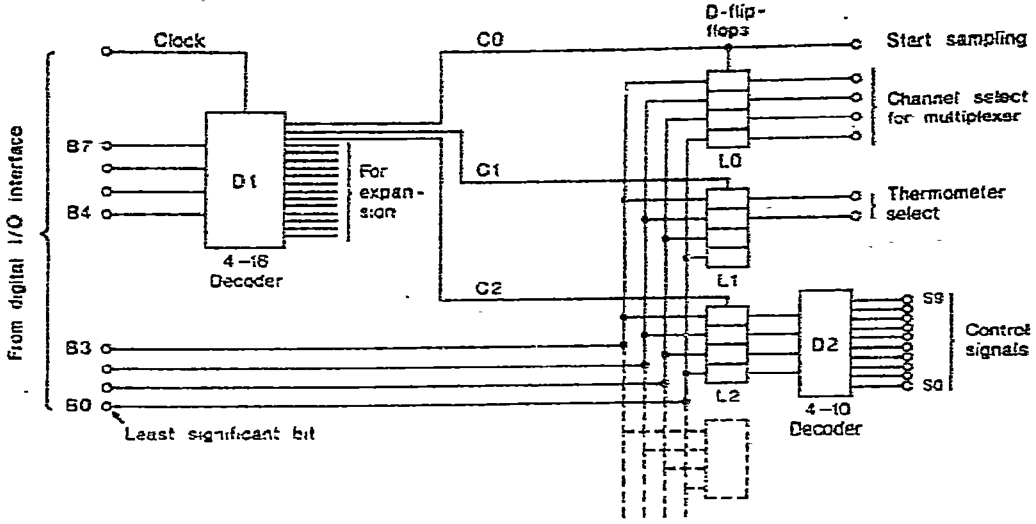

Fig. 3. Control unit.

and the set from L2, which is further decoded (SN7442, Texas Instruments), is used for other control functions, such as controlling the injection valves[2], controlling the mercury flow-meter[3] and placing marks on the recorder (see below). As an example, if the bit pattern 0010 0101 (hexadecimal 25) is placed on the output buffer, the clock pulse would cause latch L2 to be set to 0101, thus lowering the output S5, which would, in our system, reset the injection valves after an injection.

Temperature-measuring system

In this system, shown in Fig. 4, the temperatures of the column thermostat and the mercury flow-meter are measured by two platinum-resistance thermometers (E666 and E104, respectively; Rosemount Engineering Company), T_{COL} and T_{FM},

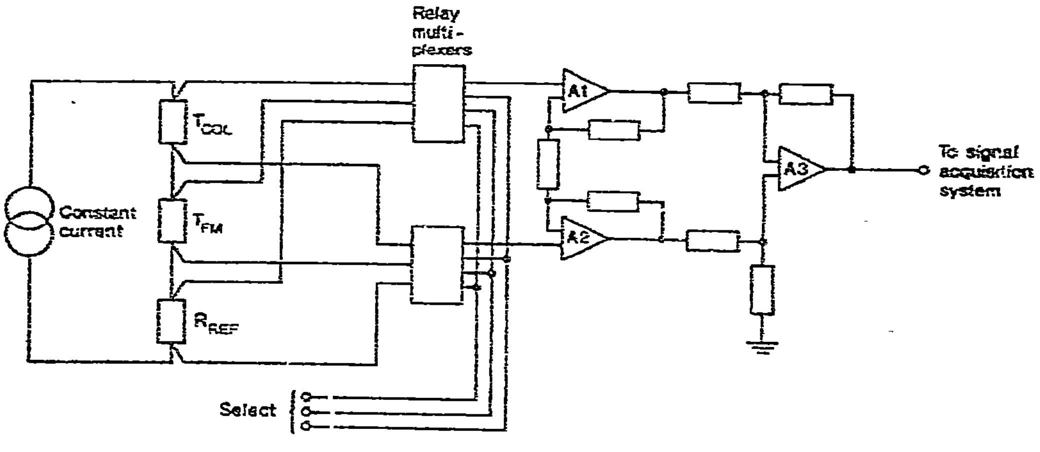

Fig. 4. Temperature-measuring system.

respectively; these thermometers are of the 4-lead type. One pair of leads is connected in series with a reference resistor (R_{REF}) of about 150 Ω (temperature coefficient 3 ppm/°C) and a constant current generator. By means of a relay multiplexer (controlled by signals from the control unit as described above), the voltage drop across each of the resistances T_{COL}, T_{FM} and R_{REF} can be measured. For this measurement, the second pair of leads is used.

An arrangement of three amplifiers [A1, A2 (LH0042CD National Semiconductor); A3 (μA725C, Fairchild)] provides high impedance and signal-level adjustment, and refers the output voltage to earth. The output is connected to input No. 1 of the signal-acquisition system.

The measurement of thermometer resistance consists of the following steps (handled by the computer):

(1) Connect R_{REF}
(2) Measure voltage
(3) Connect T_{COL} (or T_{FM})
(4) Measure voltage
(5) Divide readings, multiply by value of R_{REF}.

The computer then calculates the temperature with use of Callender's formula[6].

Peak marker

The detector signal (output from a 417K Chromatographic Electrometer, Keithley) is fed to channel No. 5 of the signal-acquisition system; it is also connected to a recorder via a circuit designed to apply marks to the recorder on order from the computer. This circuit (see Fig. 5) consists of a flip-flop built of two NAND-gates (SN7400, Texas Instruments). The outputs of this flip-flop trigger a monostable multivibrator (MV, SN74121, Texas Instruments). The outputs from the latter (one positive and one negative) are NANDed with the signals from the flip-flop. The

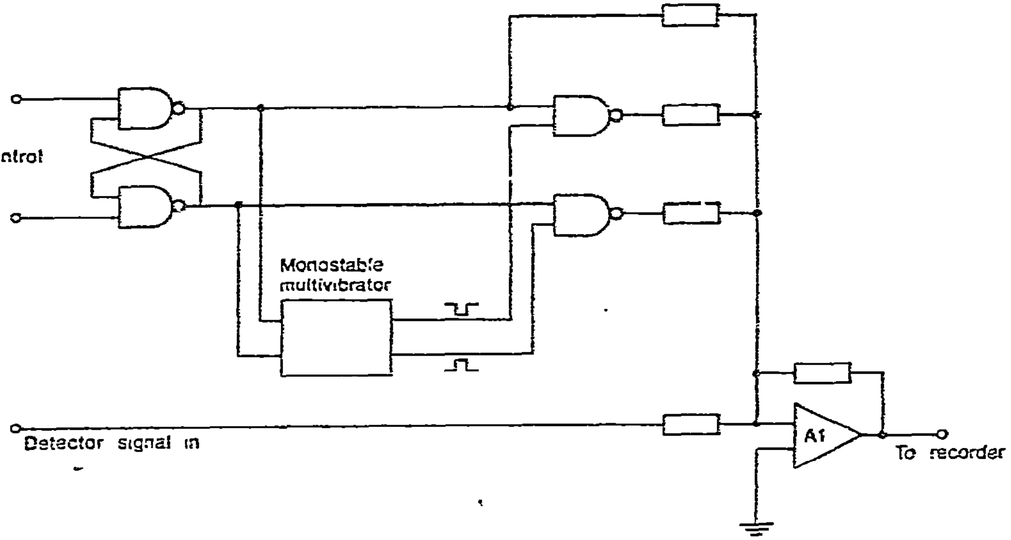

Fig. 5. Peak marker.

signals are applied via resistors to an operational amplifier (μA741, Fairchild), through which the signal from the detector passes. Thus, either a positive or a negative pulse is added to the detector signal when a transition appears on one of the inputs of the flip-flop. The length of this pulse is determined by the timing components of the multivibrator; 200 msec has been shown to be suitable. The height of the marks on the record can be adjusted by means of the resistors. The circuit can also amplify the total detector signal to suit a particular recorder.

This circuit is used to place a mark when the computer defines the beginning or end of a chromatographic peak, thereby enabling visual control of the performance of the peak-finding computer programs.

CONCLUSION

The principle of direct measurement of retention volume, realized in the apparatus described, can give considerable improvement in the accuracy and precision of retention-volume measurements[1]. This approach seems to have several advantages, especially for studies of the effects involved in gas chromatographic separation; it is also useful in analytical gas chromatography when accurate retention data are required.

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