Journal of Chromatography, 219 (1981) 427–430
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,242

Note

System for injection of continuously variable amounts of sample vapours for physico-chemical measurements by gas chromatography

JAN ÅKE JÖNSSON* and LENNART MATHIASSON
Department of Analytical Chemistry, University of Lund, POB 740, S-220 07 Lund (Sweden)
(Received July 27th, 1981)

In previous publications[1–3], a computer-linked apparatus for precise measurements of gas chromatographic retention volume was described. With this equipment, the retention volume is directly measured by means of integration of the carrier gas flow-rate, without going through the concept of retention time. For such equipment, used exclusively for different types of physico-chemical measurement, special considerations must be given to the sample inlet system in comparison with a conventional analytical gas chromatograph. The sample must be injected without appreciably disturbing the carrier gas flow-rate and pressure, so that errors are not created in the retention volume measurements. The instant of injection, *i.e.* the starting point of the chromatogram, must be accurately known. Samples of widely differing sizes (down to the limit of detection) should be injected, without simultaneously introducing large volumes of solvent. It must be possible to automate the process of sample injection, to permit unattended operation and the collection of large amounts of data. It is also characteristic of the process that the samples studied are usually pure substances or simple mixtures of pure substances.

With the sample inlet system, originally designed for our apparatus[4], injection of vapours of the sample substances was performed. The amount of sample injected could be controlled by variation of the time interval during which the sample vapours were fed to the chromatographic column, and by variation of the concentration of the vapour by diluting the liquid to be vapourized with non-volatile solvents. The combination of these techniques permitted a variation of sample size over more than four decades, with some time-consuming manual operations. As it is of great interest to study the variation of the retention volume in this wide interval[5], and as the rest of the equipment is highly automatic, a pneumatic system was developed which can automatically provide the desired variation of vapour concentration, under computer control. The aim of this note is to present the technical solution of this problem.

APPARATUS

Fig. 1 shows a schematic diagram of the carrier gas system and the sample inlet system. The components for sample size variation are NV1, FR3, RV, and SC (see the legend to Fig. 1 for descriptions). The other components are present in approximately the same configuration as in previous descriptions of this apparatus (Fig. 1 in ref. 2;

0021-9673/81/0000–0000/$02.50

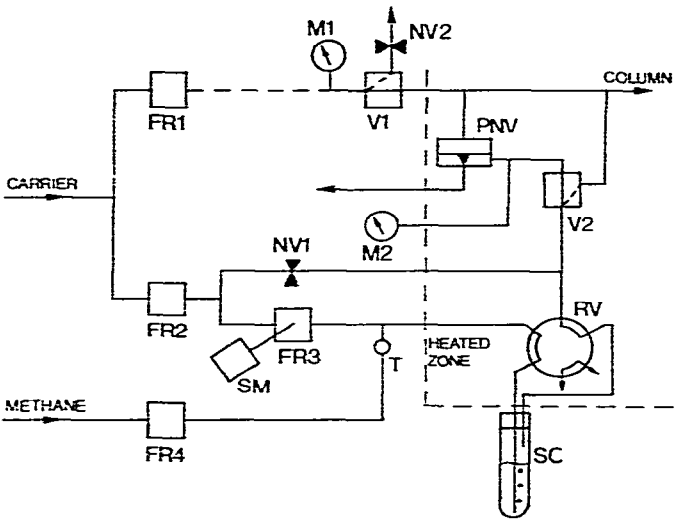

Fig. 1. Schematic diagram of the apparatus. FR1–FR4 = flow controllers (Brooks, Model 8743); M1 and M2 = manometers, 0.6 atm (Sv. Manometerfabriken, Stockholm, Sweden); NV1 and NV2 = needle valves (Brooks Model 8503); PNV = pressure-controlled needle valve (see text); RV = rotary valve (Valco, Model V-6-HPa); SC = sample chamber; SM = stepper motor (Philips, Model 9904 112 27001); T = toggle valve (Hoke, Model 1521); V1 and V2 = solenoid valves (Bürkert, Model 329, modified).

Fig. 1 in ref. 4) and are included here for completeness and ease of understanding.

In normal operation, the carrier gas passes via the flow regulator FR1 and the valve V1 to the column. Between FR1 and V1, the gas passes through various valves, a flow sensor and, optionally, a pre-column (see Fig. 1 in ref. 2). These components are irrelevant in this context. Another stream of the same gas is regulated by FR2 and afterwards split into two streams. One stream (the sample stream) is passed through a third flow regulator, FR3, a six-port valve, RV, a sample container, SC, (which is a test-tube with a ground-glass joint), to the solenoid valve V2. In front of the latter it is joined by the other stream (the diluting stream), which has passed through the needle valve NV1. The combined gas streams further pass through the pressure-controlled needle valve PNV, described below and in ref. 4.

The sample gas stream bubbles through the sample in SC and becomes approximately saturated with sample vapour. The sample concentration when the combined gas streams have reached V2 is obviously determined by the relation between the flow-rates in the diluting stream and the sample stream. This relation is adjusted by FR3 in co-operation with NV1, which is always kept in a fixed position, open about one turn. When FR3 is fully open, practically all the gas passes through the sample stream, giving maximum sample concentration. As FR3 is gradually closed, an increasing proportion of the total gas flow passes through NV1, diluting the sample. This can be continued until FR3 is completely closed. Essential for this simple arrangement to work is FR2, which ensures that the sum of the flows in the two gas streams is constant and independent of the variation in total flow resistance, which is created by FR3. By means of the valve RV, the sample container SC can be isolated from the system, permitting easy sample change, without appreciably disturbing the pressure and flow conditions in the system.

The gas stream containing the sample is directed to the column ("injected") by the simultaneous activation of V1 and V2. The carrier gas is vented to the atmosphere through the needle valve NV2. After a fixed time interval (typically 200 ms), V1 and V2 return to their original states. It is essential that the switching of the flows occurs without pressure and flow disturbances, otherwise the accuracy of the retention volume measurements is impaired. Within the present configuration the flows are easily balanced by the following procedure. With the valves V1 and V2 energized, the needle valve NV2 is adjusted until the manometer M1 shows the normal value. After this adjustment, which is not critical, the flow resistance of NV2 is approximately the same as that of the column. Secondly, still with V1 and V2 operationg, FR2 is adjusted so that the pressure drop over the column (measured by the computer system[2] is the same as normal, ensuring that the flow-rate through V2 is the same as that of the carrier gas. After these adjustments and after restoring normal gas paths, the PNV automatically adjusts its pneumatic resistance closely to that of the column, and the switching of flows can be performed with negligible disturbances.

Dead volumes usually are measured by injection of methane, introduced into the system as shown in Fig. 1. It is most convenient to measure the retention of methane separately, so RV should be turned to isolate SC from the rest of the system. All parts of the system that conduct sample vapour are heated to *ca.* 100 C to prevent condensation and adsorption. The tubings connecting SC and RV are made of glass, and those connecting RV and V2 are made of glass-lined stainless steel (SGE, Australia).

AUTOMATION

The valves V1 and V2 are controlled as described in ref. 2; they are directly connected to the computer interface and they are simultaneously energized or released by two separate computer commands, decoded in the control unit (Fig. 3 in ref. 2). The automatic variation of sample concentration is accomplished by a stepper motor, which by means of a simple gear operates the flow regulator FR3. One revolution of the system of FR3 corresponds to 96 steps by the stepper motor, so the total resolution over the fifteen possible turns is 1440 steps. The stepper motor is powered by a drive unit, built around the integrated circuit SAA 1027. The drive unit is connected to the control unit in the computer interface, and the computer can command the stepper motor to move one step in either direction. The counting of steps and the choice of direction is made by software.

RESULTS

Fig. 2 shows a typical dependence of peak area on the position of FR3. The shape of such curves are nearly independent of the nature of the sample. It is normally desired to inject samples, the sizes of which are approximately equally distributed over the available range, in such a way that the number of moles in successive injections forms a geometric series. As can be seen from Fig. 2, it is necessary to operate FR3 in a strongly non-linear way; between two of the smallest samples it should be turned only few steps, while for the largest samples several complete turns are necessary to produce the same relative change in concentration. Neither is the necessary

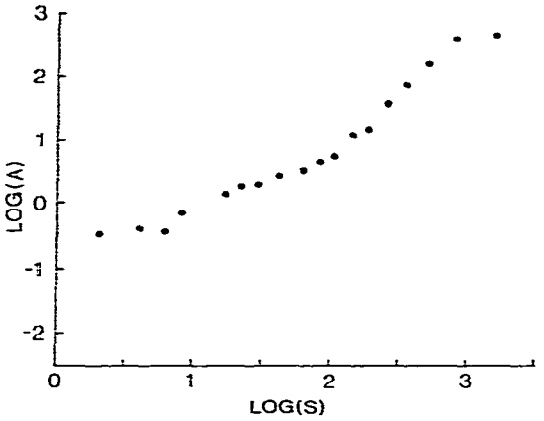

Fig. 2. The logarithm of peak area (A) as a function of the logarithm of the number of steps (S) of the stepper motor from the closed position of the flow regulator FR3. Solute: diisopropyl ether.

function linear when expressed logarithmically (as in Fig. 2). It would undoubtedly be possible to find a function that well enough approximates the curvature, but we found it more convenient to use 40 fixed positions (arranged in a table), dividing the range of possible concentrations into 40 approximately equal (in the geometrical sense) intervals. The "language" GASIC, described in ref. 3, has been extended with commands to control this process.

Usually, FR3 is initially nearly closed, giving the minimum concentration. Then for each injection (or, say, every second injection), it is successively opened to the next (or second next...) position, until the maximum concentration is reached, whereafter it is successively closed again in a similar manner. The flexibility of the software system permits many variations on this pattern. When the minimum concentration is reached, a turning (manual) of RV further decreases the concentrations to very low, soon undetectable values. During this time, further measurements can be made, if desired. After this, the system is clean and ready for a new sample.

This sample inlet system has been used in several investigations[6–8]. It makes possible the coverage of a wide range of solute concentrations, and thus the measurement of complete isotherms, with great convenience. This offers possibilities for detailed studies of adsorption phenomena in gas chromatography.

REFERENCES

1 J. Å. Jönsson and R. Jönsson, *J. Chromatogr.*, 111 (1975) 265.
2 J. Å. Jönsson, R. Jönsson and K. Malm, *J. Chromatogr.*, 115 (1975) 57.
3 J. Å. Jönsson, *J. Chromatogr.*, 139 (1977) 156.
4 R. Jönsson and J. Å. Jönsson, *J. Chromatogr.*, 120 (1975) 197.
5 J. Å. Jönsson and L. Mathiasson, *J. Chromatogr.*, 179 (1979) 1.
6 J. Å. Jönsson, L. Mathiasson and Z. Suprynowicz, *J. Chromatogr.*, 207 (1981) 69.
7 Z. Suprynowicz and J. Å. Jönsson, *Chromatographia*, 14 (1981) 455.
8 A. M. Olsson and J. Å. Jönsson, in A. Zlatkis (Editor), *Advances in Chromatography 1981*, Chromatography Symposium, Houston, TX, 1981, p. 149.