Journal of Chromatography, 111 (1975) 409–412

CHROM. 8330

Note

Investigation of pre-column sample dilution in chromatographic systems with packed capillary columns

A. F. ANISIMOV, V. G. BEREZKIN, M. A. ZHURAVLEVA, V. N. LIPAVSKY, V. F. MARKELOV and L. A. SHKOLINA

Institute of Petrochemical Synthesis, Academy of Sciences of the U.S.S.R., Leninsky pr. 29, Moscow 117071 (U.S.S.R.)

(First received September 6th, 1974; revised manuscript received December 2nd, 1974)

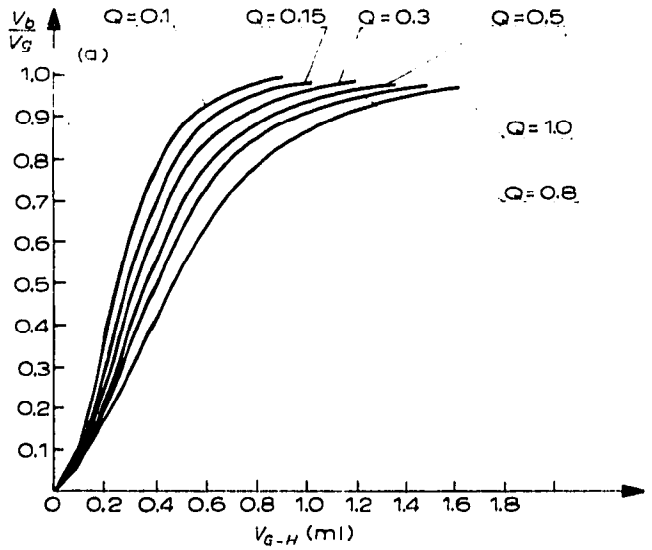
Sorbent-packed capillary columns (0.5–1.0 mm I.D.) combine the advantages of hollow capillary and conventional packed columns. The sorbent accounts for their high selectivity and capacity, makes the sensitivity requirements of the detector less stringent and permits sample introduction without splitting the flow. The columns are highly efficient with stationary liquid phases and adsorbents.

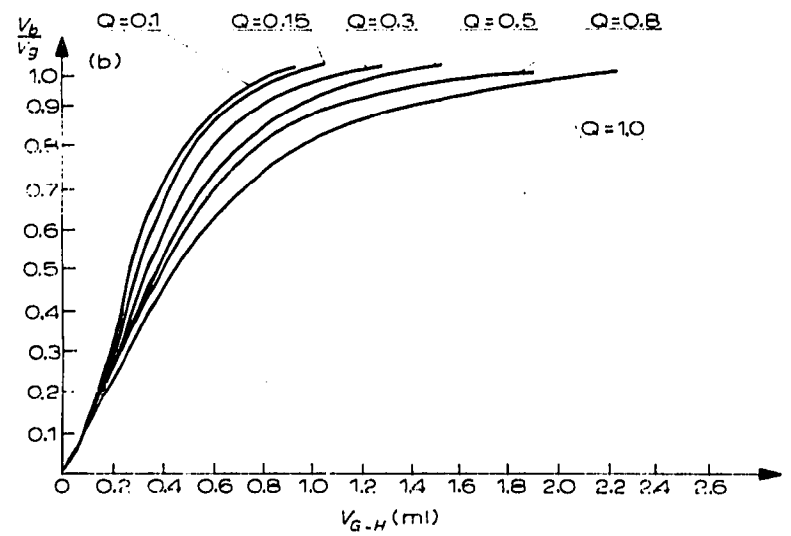
The advantages of this type of column compared with conventional packed columns are due to the small diameter of the former. Such columns are characterized by high efficiency, the possibility of using expensive and scarce sorbents and carrier gases (the consumption of the carrier gas even at high linear speeds is approximately one order of magnitude lower than in conventional columns), higher stability in temperature programming as a result of the thermal inertia of the columns and the possibility of using miniaturized apparatus with a compact thermostat, thus permitting rapid heating and cooling of the column.

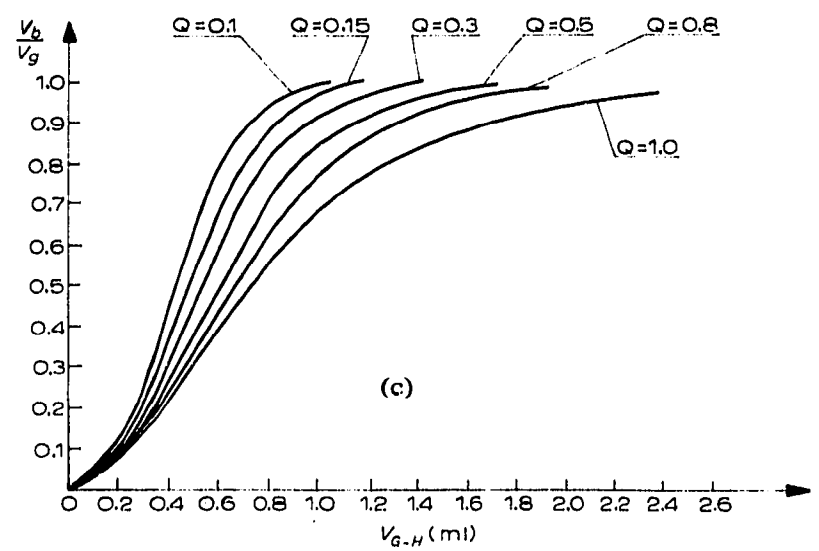
Long packed capillary columns ensure the reliable separation of complex multicomponent mixtures, while short columns should preferably be used for rapid analyses.

The above advantages make sorbent-packed capillary columns highly promising for use in gas chromatography and their application will probably increase in the future.

Most chromatographic analyses with packed capillary columns are carried out on apparatus fitted with specially designed units or units that are not normally used in chromatography; for example, galvanometers and oscillographs are used as recorders and microkatharometers as detectors. Samples are often introduced, as for capillary columns, by splitting the flow. These changes have been introduced as it is feared that the apparatus designed for conventional packed columns may cause substantial distortions of chromatographic peaks, adversely affecting the efficiency of the column and the separation being carried out. Therefore, the development of criteria for estimating the suitability of apparatus for use with packed capillary columns is of great interest. Below we consider the problems relating to gas and vapour sampling systems operating with packed capillary columns. Because, however, the conditions of analysis with conventional and packed capillary columns (as far as the


$\frac{V_b}{V_G}$
(a)
Q=0.1
Q=0.15
Q=0.3
Q=0.5
Q=1.0
Q=0.8
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8
V_{G-H} (ml)


$\frac{V_b}{V_g}$
(b)
Q=0.1
Q=0.15
Q=0.3
Q=0.5
Q=0.8
Q=1.0
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6
V_{G-H} (ml)


$\frac{V_b}{V_g}$
Q=0.1
Q=0.15
Q=0.3
Q=0.5
Q=0.8
Q=1.0
(c)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6
V_{G-H} (ml)

(Fig. 1).

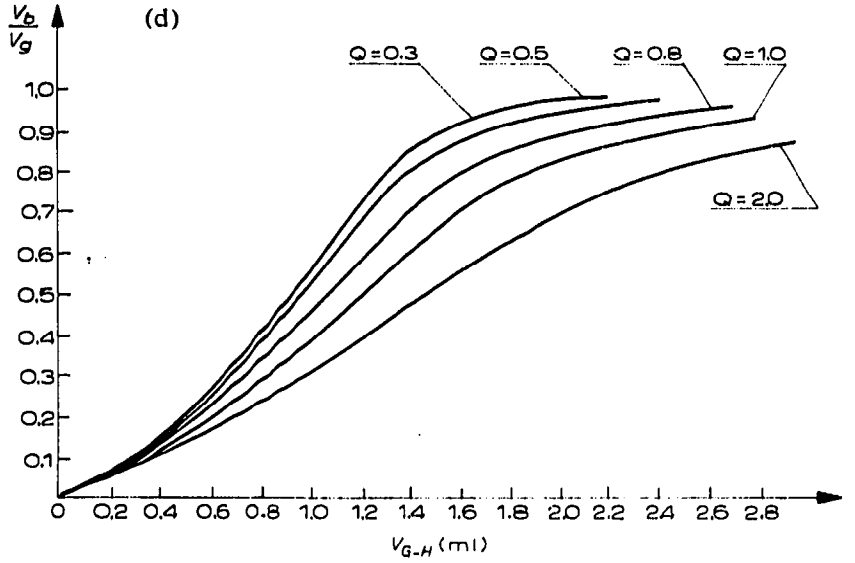


Fig. 1. Relationship between the volume of sample at the column inlet and the amount of carrier gas flowing through. V_{G-H}, volume (ml) of carrier gas passed through the column; V_n, initial sample volume; V_b, amount (ml) of the substance introduced into the column; Q, flow-rate of carrier gas (l/h). V_n: a, 0.1 ml; b, 0.15 ml; c, 0.5 ml; d, 1.0 ml.

requirements for the apparatus are concerned) differ only quantitatively, the relationships given below and the conclusions drawn from them are also valid in assessing the usefulness of apparatus for use with conventional packed columns.

Gas and vapour sampling is usually carried out with the aid of a sampling loop coupled to a switching device. When the switch is set to one position the sampling loop is filled with the product being analyzed, and in the other position of the switch the loop receives the carrier gas flow that carries the sample into the column. The amount of the substance being analyzed trapped in the sampling loop is referred to below as the initial sample. During the transfer of the sample, the substance being analyzed is diluted with the carrier gas and the volume of the initial sample increases. As a result, the efficiency of separation is decreased. A number of methods have been proposed for estimating the maximum volume of the sample. For example, Klinkenberg[1] proposed that the permissible volume of a sample for packed columns can be found from the following equation:

$$V_n \leqslant \frac{0.5 V_R}{\sqrt{N}} \qquad (1)$$

where V_n is the sample volume at the column inlet, V_R is the component retention volume and N is the number of theoretical plates. If eqn. 1 is obeyed, the dispersion of the chromatographic peak increases by more than 2%.

The volume of the sample at the column inlet can be determined only when the increase in the volume of the initial sample during transfer of the sample is known. We have determined the volume experimentally and also the profile of the sample at the column inlet for a sampling system comprising a sampling loop and a pneumatically controlled diaphragm switch with practically no dead volumes.

Tests were carried out on a conventional laboratory chromatograph whose

TABLE I

PARAMETERS OF SAMPLING SYSTEM WITH SWITCHING VALVES WITHOUT DEAD VOLUMES

Parameter	*Carrier gas flow-rate (l/h)*	*Initial sample volume, V_0, (ml)*			
		0.1	*0.15*	*0.5*	*1.0*
Sample volume at column inlet*	0.1	0.55	0.6	0.75	—
	0.15	0.62	0.7	0.85	—
	0.3	0.72	0.8	1.0	1.5
	0.5	0.82	1.0	1.2	1.7
	0.8	0.92	1.15	1.4	2.0
	1.0	1.1	1.4	1.8	2.45
Ratio between sample and initial sample volumes**	0.1	5.5	4.0	1.5	—
	0.15	6.2	4.7	1.7	—
	0.3	7.2	5.3	2.0	1.5
	0.5	8.2	6.7	2.4	1.7
	0.8	9.2	7.7	2.8	2.0
	1.0	11.0	9.3	3.6	2.45
Ratio between concentrations in maximum sample and initial sample	0.1	0.6	0.7	1.0	--
	0.15	0.55	0.65	1.0	—
	0.3	0.5	0.6	1.0	1.0
	0.5	0.42	0.45	0.9	0.95
	0.8	0.36	0.4	0.8	0.85
	1.0	0.32	0.35	0.7	0.8

* Taken as the sample volume at the column inlet the volume of the carrier gas in which 90% of the initial sample substance is distributed.

** The initial sample volume is equal to the volume of the sampling loop.

standard sample injector had been replaced with the one described above, and a low-inertia thermal conductivity cell was installed in front of the column and recorded the instantaneous values of the concentration of the substance in the initial sample in the carrier gas flow. The time constant of the thermal conductivity cell did not exceed 0.5 sec at pre-set carrier gas flow-rates. Nitrogen was used as the carrier gas and the test sample being analyzed consisted of 4% of propane in nitrogen.

The results were used to plot integral curves of the amount of substance introduced into the column *versus* the volume of the carrier gas that had passed through the column (Fig. 1, a–d). These graphs enable the loss of initial sample during transfer to be evaluated.

Table I gives the volumes of a sample containing 90% of the initial sample substance, the degree of dilution of the sample and the ratio between the concentrations in the maximum sample and the initial sample.

By using eqn. 1, the integral curves and the results in Table I, one can calculate the permissible volume of the initial sample. For example, if, according to eqn. 1, the permissible sample volume, under definite conditions, is 0.8 ml and the carrier gas flow-rate is 0.5 l/h, the initial sample volume should, in accordance with Table I, be not more than 0.1 ml.

REFERENCE

1 A. Klinkenberg, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, pp. 182–183.