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A DISC SPLITTER FOR CAPILLARY COLUMNS

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SUMMARY

A disc-type splitter used for sample injection into the chromatographic column is described. The sample is introduced into the centre between two discs. At one or more points of the disc margin, a given amount of sample is passed into one or more columns. The splitter was tested up to the separation ratio of $1:10^3$. The reproducibility of the separation ratio estimated along with the reproducibility of the sample injection is 1 %.

INTRODUCTION

A sampling device for capillary columns was needed which would separate a certain part of the sample, as a rule 1 %. This part of the sample will enter a capillary column as a narrow zone. Splitters are very simple sampling devices suitable for quantitative analyses. The original splitter had a T-form and was useless for quantitative analyses. The latest splitters have been constructed of two tubes, one inserted into the other (see Fig. 1). ETTRE AND AVERILL[1] bring the sample in by the larger tube (Fig. 1a), and the narrow tube, represented here by a capillary column, permits removal of the required part of the sample. The rest of the sample is exhausted at the bottom of the larger tube. Other constructions use the narrow tube for sample inlet and the larger one for sample outlet. The capillary column inlet is situated either at the bottom of the larger tube (HALASZ AND SCHNEIDER[2]) (Fig. 1b) or in the narrower tube (CLARKE[3]).

Some authors[4,5] reported poor reproducibility of the results when using a splitter in the case of samples consisting of components with boiling points over a wide temperature range. They assumed that the split part of the sample did not have the same composition as the original one. BRUDERRECK *et al.*[5] assumed that compounds of lower molecular weight would have lower kinetic energy and would be more easily diverted at the splitting point. This would give rise to a higher concentration of low molecular weight particles in the diverted gas stream. It is obvious that when 1 or 0.1 % of the sample enters the capillary column, a little non-homogeneity of the sample will have a strong effect on the quantitative analyses. A simple T-splitter usually gives poor results. It may be assumed that the sample composition varies in individual streamlines of the carrier gas. Taking into consideration the shape (let us say paraboloid with tailing) of the vapourised sample into the carrier gas, it is fully

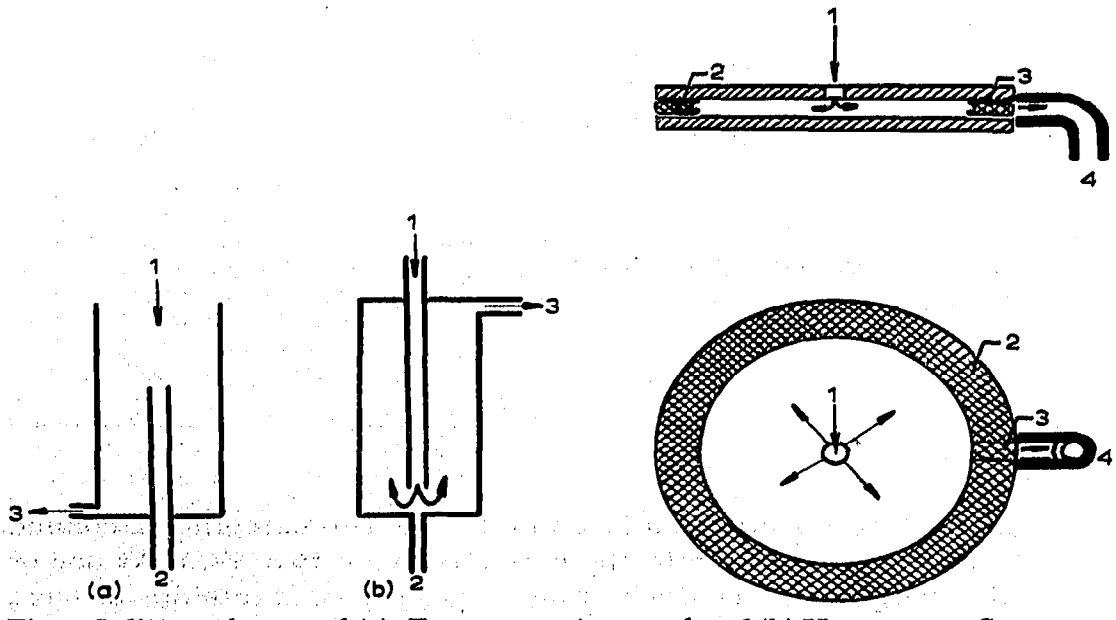

Fig. 1. Splitter schemes of (a). ETTRE AND AVERILL[1] and (b) HALASZ AND SCHNEIDER[2]. 1 = inlet of the carrier gas with the sample; 2 = capillary column inlet; 3 = outlet of the carrier gas with the sample.

Fig. 2. Functional scheme of the proposed splitter. 1 = carrier gas inlet; 2 = sample circular ring; 3 = part of the sample circular ring taken into the column; 4 = inlet part of the column.

understandable that splitter construction, arrangement and working conditions are very important and that they determine whether the splitter functions well.

The principle of the splitter proposed (Fig. 2) consists in bringing the mixture of a carrier gas with a sample into the centre of two circular discs. A rapid change of flow with the following evenly distributed dispersion into the gaseous mixture enables the sample, shaped as a circular ring, to move in the carrier gas media from the middle in the direction of the circular disc edge. In one or more places on the disc circumference there is an inlet of one or more capillary columns through which a certain circular ring can be brought into the column.

STUDY OF PARAMETERS

In spite of the fact that the principle of the design is such that an unequal dissipation of sample cannot be assumed, the slit height Z can be calculated from the shape of a cylinder with the radius L as if sample mixing occurs only in the space between the circular discs in the action known from mixing tubes of the splitter, the parameters of which were calculated, *e.g.* by GOLAY[6].

The time t needed for an efficient mixing of a sample with a carrier gas in the area S can be expressed by the formula

$$t = a\frac{S}{D} = \frac{V_0}{F} \qquad (1)$$

where a is the safety coefficient and D is the diffusion coefficient of the sample. If the volume of the mixing cylinder V_0 and the volume velocity F are known, the same time t can also be expressed by the ratio V_0/F.

From eqn. 1 the length of the slit radius L can also be calculated.

$$L \geq \frac{2aF}{D} \tag{2}$$

The radius length L can be calculated by estimating the diffusion coefficient and by determining the volume flow.

The sample dispersion in a very narrow slit can be expressed by means of the height equivalent to a theoretical plate H for a non-adsorbed substance, provided the speed of the carrier gas is high (right assumption since the flow is 100 times higher in the slit than in the capillary column), in the following way.

$$H_{cyl.} \cong \frac{2}{105} \cdot \frac{z^2F}{DS} d \tag{3}$$

The volumetric variance W can be expressed as

$$W = S^2\sigma_{cyl.} = S^2LH_{cyl.} \tag{4}$$

which can be transferred by using relations (2) and (3) into

$$W = S^2 \frac{2aF}{D} \cdot \frac{2}{105} \cdot \frac{z^2F}{DS} d = \frac{4ad}{105} \cdot \frac{Sz^2F^2}{D^2} \tag{5}$$

Volumetric variance w of the sample in the column inlet can be calculated as follows. The ratio of the carrier gas flow on the splitter outlet to the flow of the carrier gas entering the capillary column is designated α.

$$w = \frac{W}{\alpha^2} \tag{6}$$

From this the space variance σ_{tc}^2 caused by the sampling in the capillary column inlet is

$$\sigma_{tc}^2 = \frac{W}{\alpha^2 s^2} = \frac{4ad}{105} \cdot \frac{Sz^2F^2}{D^2} \cdot \frac{1}{\alpha^2 s^2} \leq \sigma_{oc}^2 = \frac{ns}{3\pi b} \tag{7}$$

where s represents the area of the capillary column cross section, n is the number of plates of the capillary column and b is the safety coefficient. This space variance σ_{tc}^2 must be lower than the space variance σ_{oc}^2 of the non-sorbed sample on the capillary column outlet.

Knowledge of the splitting ratio, of Taylor's formula for the speed of non-sorbed substance and of optimum sample speed in the capillary column, which is $1/c$ times lower than the speed of non-sorbed substance, enables one to express the sample flow through any mixing element in the following way.

$$F = \frac{\alpha D}{c} \cdot \sqrt{48\pi s} \tag{8}$$

Substituting expression 8 for 7 leads to

$$6da \cdot \frac{Sz^2}{sc^2} \leq \frac{ns}{3\pi b} \tag{9}$$

and by expressing $S = 2\pi Lz$,

$$z \leq \left(0.008 \cdot \frac{c^2}{abd} \cdot \frac{ns^2}{L}\right)^{1/3} \tag{10}$$

is obtained. If the value 2 is substituted for safety coefficients a and b, and for factor c, d expression 10 can be simplified into

$$z \leq 0.2 \cdot \left(\frac{ns^2}{L}\right)^{1/3} \tag{11}$$

which is the precondition for the height of mixing cylindric slit. Using expression 2 and eqn. 8 the following relation can be derived.

$$L \geq \frac{2a}{c} \cdot \alpha \sqrt{48\pi s} \tag{12}$$

If again $a = c = 2$, then it holds that

$$L \geq 24\alpha\sqrt{s} \tag{13}$$

The calculation shows that the most ideal cylindric slit would be very narrow and of corresponding radius. According to the author, it will not harm the splitter function if an actual radius is less than the calculated one. The design presented permits the sample to be placed on the disc after passing the capillary so that it is already partly homogenised. The reason for using the capillary is justified by the assumption that not all the splitter users employ a sampling syringe with the needle cut perpendicularly.

In the design presented, there are three factors enabling the homogenisation of the sample with the carrier gas, *viz.* the capillary pre-column, rapid change of the flow direction with a symmetric gas exhaust and capillary interspace between circular discs.

EXPERIMENTAL

The analyses were carried out on the Pye 104 flame ionisation chromatograph with new highly effective columns in common connection. The evaluation was carried out on a Kent Chromalog 2 integrator with a reproducibility of ± 0.1 %. Hamilton 1-μl syringes were used for sampling. The splitter ratio was 1:100. The samples analysed were three different mixtures containing pentane, benzene, toluene and xylene (ten analyses). The calculation of mixture composition was carried out in the way common for the flame ionisation detector. The results are shown in Table I. As the error for xylene was twice as high with mixtures I and III than with other samples, a Hamilton splitter for capillary columns was also tested. Under the same experimental conditions it was found that, although the reproducibility for its application was ± 0.6 %, the error for ten analyses for xylene in mixture I was ± 1.2 % and for xylene in mixture II was ± 1.8 %.

TABLE I

ANALYSIS OF THREE MIXTURES WITH THE NEW TYPE SPLITTER

Mixture	*Pentane* (%)	*Benzene* (%)	*Toluene* (%)	*Xylene* (%)
I	15.1 ± 0.5	28.0 ± 0.6	28.5 ± 0.3	28.5 ± 1.0
II	49.5 ± 0.5	17.3 ± 0.1	16.8 ± 0.3	16.45 ± 0.3
III	7.2 ± 0.5	13.7 ± 0.7	13.7 ± 0.4	65.4 ± 1.5

The experiments further showed that it is not advisable to lead the sample into the centre of the disc directly with the syringe having a common needle end. Entrance onto the disc is best when the sample is introduced into the splitter block by the capillary path in which the carrier gas changes rapidly the direction of its flow (see Fig. 3).

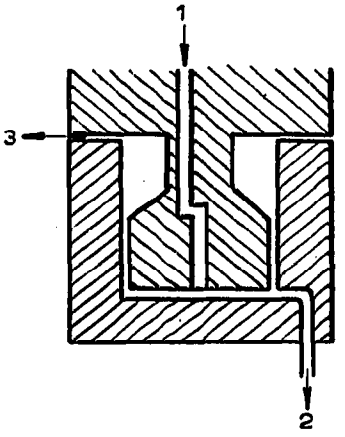

Fig. 3. Scheme of the splitter. 1 = carrier gas inlet; 2 = capillary column inlet; 3 = outlet of the carrier gas with the sample.

With a small modification (*e.g.* when introduction onto the disc is from below), a sample may be led first into a capillary tube in which premixing of the sample with the carrier gas occurs. Splitter prototype was in the shape of the cylinder with a radius of about 1 cm and a height of about 3 cm.

The splitter also proved to be suitable for high concentrations of sample when the flow ratio was 1:1,000. The error of analysis was $\pm$ 0.5 %.

DISCUSSION

The principle of sample splitting is new for this design which eliminates sample fractionation and is very simple. A sample is introduced into the centre of the two discs (see Fig. 2). When the carrier gas is introduced into the centre, the sample expands in all directions. The sample, shaped as a circular ring, moves from the centre and the circular ring grows. Undoubtedly, the sample composition is the same in any section of the circular ring.

Now let us assume that a sample fractionation exists which could explain poor results obtained with some splitters. An extreme example of our assumption for a new splitter is the following. The sample circular ring consists of two circular rings (one larger and the other smaller) with different types of molecules. The same molecules have the same velocity of movement from the centre to the edges and form a constant concentration circumference of the ring.

Let us say that the inlet part of the column is directed against the sample path, of which the open end is equal to an arc of 3.6° (which is 1 % of the inlet ring circumference). A section of both assumed circular rings will enter the chromatographic column. It is possible to say that a corresponding amount of all types of molecules of the sample comes into the column and represents the injected sample. The amount of sample from the circular ring entering the column will practically depend on the

carrier gas flow ratio which is given by the ratio of the amount of the carrier gas going through the column to the exhausted one.

Let us consider a constant position of the column inlet towards the centre of the disc. Further let us consider representative ratios of carrier gas flow (*i.e.* carrier gas flow exhausted to carrier gas flow in the column). The carrier gas flow ratio can be approximately equal to the ratio of the length of the auxiliary column (the same column as a chromatographic one but shorter) to the length of the chromatographic column. When the carrier gas flow ratio is 1:100, as in this example, 1% of the circular path (that is 1% of sample) enters the column without moving sample molecules from the environment from which the sample molecules are taken away (diffusion movement has no influence here). When the carrier gas flow ratio is higher than before (*e.g.* 2:200) as in this case, more carrier gas enters the chromatographic column. The sample ring is partly asymmetrical but asymmetry is small in accordance with sample splitter ratio. It is possible to say that the more carrier gas enters the column, the larger the amount of sample (in this case 2%) that also enters the column. And lastly, the carrier gas flow ratio is lower than in the first example. Then a small amount of carrier gas enters the chromatographic column. The sample circular ring never changes its shape, as in the first example.

From the above, the sample part entering the column represents the sample injected under any of the carrier gas flow conditions. The new splitter system (see Fig. 3) permits one to remove determined amounts of sample for more than one column on different circumferences or on the same one but in different places. The new splitter enables the use of larger samples than ever used before.

SYMBOLS

a,b,c,d = safety coefficients
D = diffusion constant of the sample in the carrier gas
F = volume flow in the cylindrical space
f = volume flow in the capillary column
L = radius of the cylinder
n = number of the theoretical plates in the capillary column
s = cross section area of the capillary column
S = cross section area of the cylinder
t = time needed for expansion of the sample into the cylinder
α = splitter ratio ($\alpha = F/f$)
W = volumetric variance in the cylinder
w = volumetric variance in the inlet part of the capillary column
σ_c^2 = space variance in the cylinder
σ_{ic}^2 = space variance in the inlet part of the capillary column
σ_{oc}^2 = space variance on the outlet of the capillary column
H = height equivalent to a theoretical plate
z = slit height

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