

CHROM. 5222

METHODS FOR COATING THE STATIONARY LIQUID PHASE ON THE SOLID SUPPORT IN ANALYTICAL AND PHYSICO-CHEMICAL APPLICATIONS OF GAS-LIQUID CHROMATOGRAPHY

A CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF IMPURITIES

A. A. ZHUKHOVITSKII, M. L. SAZONOV, M. KH. LUNSKII AND V. YUSEFIN
Department of Gas Chromatography, VNIGNI, Moscow E-275 (U.S.S.R.)

SUMMARY

The method for coating the stationary phase on the solid support with the application of vacuum results in an improved spreading of the film, acceleration of internal diffusion, and hence a decrease in plate height.

Using as an example the measurement of retention volumes of some alcohols on squalane it has been shown that the addition of small amounts of a modifying agent insoluble in the stationary phase eliminates adsorption at the liquid-gas interface.

A method for multiple thermal enrichment of impurities has been developed which is based on an alternate action of the carrier gas stream and of the temperature field.

(I) COATING THE STATIONARY LIQUID PHASE ON THE SOLID SUPPORT

The selection of the method for coating the stationary liquid phase on the support and of the percentage loading of this phase g_u is of certain interest in connection with the analytical applications of gas-liquid chromatography (GLC) and of decisive importance in the determination of thermodynamic functions.

Of no lesser importance is a consideration of the methods for adding the liquid phase when thermodynamic studies are to be conducted. Investigations of this kind should furnish information as to the nature of the interaction between the stationary liquid and the solid support, and the sorbate-stationary phase.

Generally speaking, five possible types of sorption of the sorbate on sorbents in GLC may be distinguished, namely:

- (1) solution in the stationary phase;
- (2) adsorption at the solid support-gas phase interface;
- (3) adsorption at the stationary phase-gas interface;
- (4) adsorption at the stationary phase-solid support interface; and
- (5) solubility in thin films of the stationary phase.

The subject of the present study is the selection of conditions under which all processes except the first one are reduced to minimum.

It is known^{1,2}, that the role of process (2) is reduced with an increase in g_u , and at a g_u of 3 to 5% this factor may be practically neglected. The contribution of process (4) (ref. 3) must be essentially lower than that of process (3). Adsorption from solutions is significantly less than that from gases since it is accompanied by a displacement of the solvent molecules.

Moreover the stationary phase may be a good solvent for the sorbate. This last effect however is only observed in some special cases. Thus only two basic processes have to be considered, namely (3) and (5), which in the case of sufficiently thin films cannot generally be viewed separately.

To ascertain the role of these processes and methods for their elimination, the values of specific retention volume V_0^T , depending on g_u , were measured for the following systems: hexane-squalane; ethanol-squalane; propanol-squalane. The hexane-squalane system was selected as the basic one since sufficiently reliable static measurements of the activity coefficients of the system are available.

Columns, 10–15 cm long and 3.8–4 mm I.D. were used; they were connected in series to a thermal conductivity detector. Celite 545, 60–80 mesh, was used as the solid support. The weight of the stationary phase in the column was determined to within 0.0001 g. The temperature of the column was kept constant to within 0.2°.

The size of the sample was chosen so that upon its further reduction the retention volume of the component of interest should not vary and would be independent of concentration. The retention volumes considered as true ones were those that corresponded to the horizontal portion of the retention time against peak area plot (Fig. 1). The size of the injected liquid sample did not exceed 0.1 μ l, and that of the gas sample 0.05 cm³.

In the course of determining the retention times, t_R , the flow rate was periodically checked (after each measurement). The retention time was calculated as the average of 10 to 15 measurements.

The formation of a film, evident from hysteresis effects in capillary conden-

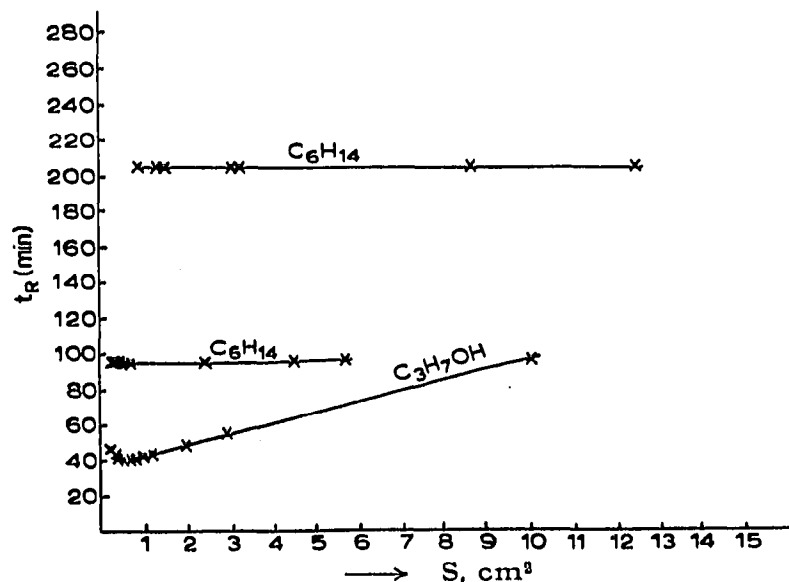


Fig. 1. Plot of retention time as a function of the peak area, S .

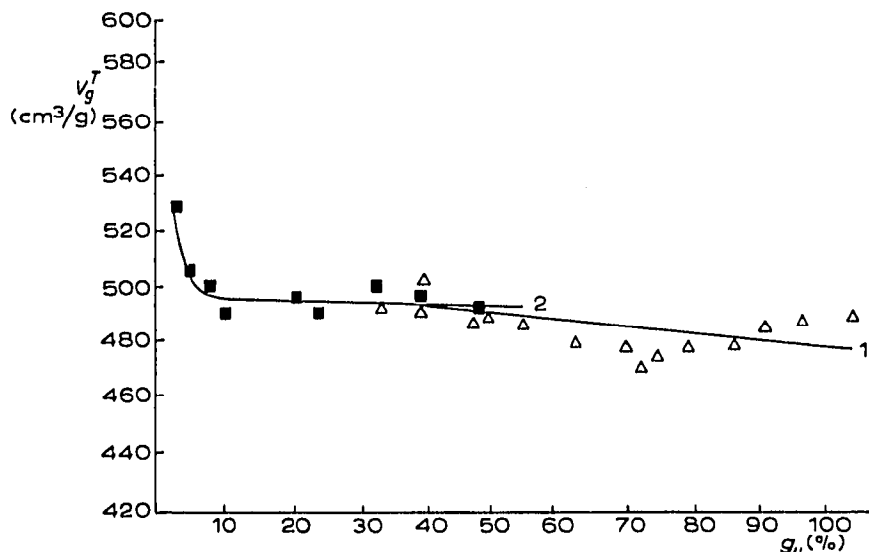


Fig. 2. Plot of specific retention volume of hexane on squalane as a function of percent liquid coating. Curve 1 = liquid phase coated under vacuum conditions; curve 2 = vacuum treatment of sorbents prepared by the usual procedure.

sation, can be prevented by the presence of air in the capillary pores, though the presence of air may hinder the complete filling of the support. It was therefore of interest to carry out the addition of the stationary phase under vacuum. To do this, a measured volume of the liquid was coated on a support previously subjected to vacuum ($p = 0.01$ mm) (Fig. 2, curve 1). The experiments showed that practically the same results could be achieved by subjecting the sorbent prepared by the usual method to vacuum (Fig. 2, curve 2). As will be seen from curves 1 and 2 of Fig. 2, a practically constant value of V_g^T is observed over a rather wide range of liquid phase load. It should be noted that when effecting the coating under vacuum higher values of g_u (up to 100%) can be achieved than by the usual procedure (up to 80%).

We have also measured V_g^T as a function of g_u (Fig. 3) for ethanol (curve 1) and propanol (curve 2) on squalane using the vacuum coating procedure.

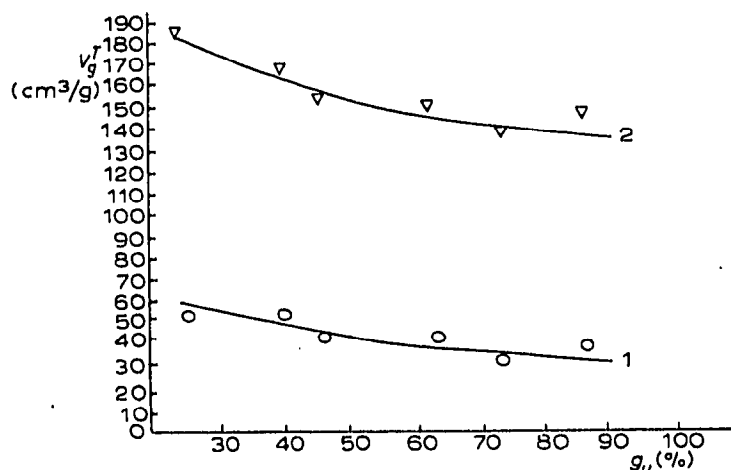


Fig. 3. Plot of specific retention volume of ethanol (curve 1) and propanol (curve 2) as a function of percent of squalane coating on Celite.

In order to characterise the difference in the state of the stationary phases when using the two different methods of coating considered here we made a study of the broadening of the hexane peak as a function of g_u and v_a (flow rate).

From the $\log(\mu v_a) - \log v_a$ relationship (μ is the half-width of the peak) the position of the external and internal diffusion regions may be determined. It has been found that in the case of the usual coating procedure the region of internal diffusion begins at 28% of liquid phase and when vacuum coating is used, external diffusion is the controlling process up to 46%, and only above 95% can internal diffusion be considered as the controlling factor.

Thus the use of the vacuum coating procedure results in a reduction of peak broadening due to a more uniform distribution of the liquid. This fact confirms the suggestion made above concerning the pattern of the liquid phase distribution and the nature of its interaction with the adsorbate. This more uniform distribution, however, has been the reason why we have not achieved any decisive progress in attempting to minimize the role of the additional effects. Therefore we have investigated the possibility of eliminating these effects by modifying the sorbent.

The addition of a very small amount of a polar substance, practically insoluble in a non-polar stationary phase, can eliminate adsorption of the sorbate at the surface of the stationary phase (if it occurs) as a result of adsorption of the modifier at the stationary phase-gas interface.

We have investigated the effect of modification with the following six systems: (1) liquid phase squalane, modifier polyethylene glycol 300, sorbate hexane; (2) squalane, polyethylene glycol 300, ethanol; (3) squalane, polyethylene glycol 300, propanol;

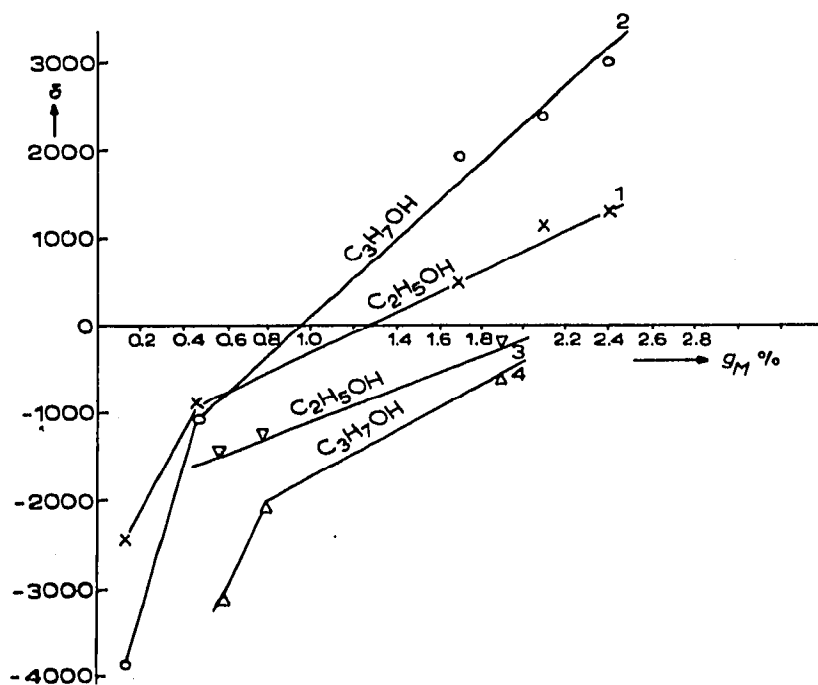


Fig. 4. The value of δ as a function of the amount of modifying agent added. δ is the difference between specific retention volumes of alcohol on squalane with and without modifying agent (PEG) addition (per unit weight of PEG).

(4) squalane, polyethylene glycol 1000, hexane; (5) squalane, polyethylene glycol 1000, ethanol; (6) squalane, polyethylene glycol 1000, propanol.

The experiments have revealed a significant decrease in V_g^T of the alcohols as a result of the modification. Fig. 4 shows a plot of the specific values of the change in V_g^T referred to 1 g of the modifier per 1 g of squalane ($\delta = \Delta V_g^T \cdot 100/g_M$) depending on the percentage of the modifier (the percentage of the modifier, g_M , is calculated depending on the weight of squalane).

It will be seen that in the case of the alcohols with low values of g_M a distinct decrease in V_g^T takes place, which because of the solubility of the alcohols in the modifier changes to an increase in V_g^T with high values of g_M (curves 1, 2). Experiments with a solid modifier (polyethylene glycol 100) showed a marked decrease in V_g^T with high values of g_M as well (curves 3, 4).

In the case of hexane no decrease in V_g^T is observed, while the increase, probably due to adsorption on the modifier, somewhat exceeds the experimental errors.

The difference observed in the behaviour of alcohols and hexane as far as modification is concerned suggests that in the case of hexane the increase in V_g^T is due to additional solution in thin films, and in the case of alcohols, to adsorption.

(2) CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF IMPURITIES

Despite the fact that a large number of thermal, adsorption, and chromatographic methods for concentrating and determining impurities are available the problem cannot be considered as solved. The availability of detecting devices with a fast response such as the flame ionisation detector enables one to envisage the possibility of increasing the sensitivity by repeatedly concentrating the impurity and transferring it to an extremely small volume. At the same time in the usual preliminary thermal concentration method only a concentration of I_0/I times is achieved in a single enrichment (I being the Henry coefficient in the zone of heating, and I_0 the Henry coefficient outside the zone of heating).

In the heat-dynamic and the chromatographic versions, concentration is limited by stationary band broadening. To reduce this broadening the use of large temperature gradients is necessary, which sharply deteriorates the resolution.

The broadening of the band hindering thermal enrichment can be diminished by discarding the stationary regime of the process and by decreasing the time spent for broadening.

In the method described here a number of acts of thermal enrichment are achieved on a single column. Broadening, particularly that in the last stages, is reduced by decreasing the time during which it can occur.

The test mixture is injected on to a column with an adsorbent and occupies a length of the bed approximating to the length of the furnace. The furnace which will heat to a certain constant temperature is subsequently made to move along the bed. Then either the carrier gas or the mixture to be analysed is swept through the bed. Upon leaving the heated portion the band width naturally decreases I_0/I times. This cycle of moving the furnace and sweeping with gas can be repeated.

If there were no broadening, enrichment (O) would be expressed by the formula

$$O = \left(\frac{I_0}{\bar{I}}\right)^n \quad (1)$$

(where n is the number of acts of enrichment).

Broadening, however, restricts the magnitude of O to a certain limit (O_T) beyond which no further increase in n is justified.

Let τ be the time of residence of the band in the furnace. Then the band width μ , regardless of the initial width (if it is small enough) will be

$$\mu = 4\Gamma \sqrt{\left(\frac{D}{\bar{I}}\right) \tau} \quad (2)$$

where D is the effective longitudinal diffusion coefficient. (D/\bar{I}) characterises a certain average value of this ratio at a time τ . If for the sake of simplicity it is assumed that the temperature rises in a linear fashion ($T = T_0 + \gamma t$) and the temperature dependence of D is neglected, then

$$\bar{I} = \frac{I}{t} \int_0^t I dt \quad (3)$$

Since

$$I = I_0 e^{-\sigma t}$$

where

$$\sigma = \frac{Q\gamma}{RT^2}$$

then

$$\bar{I} = \frac{I_0}{\sigma\tau} (1 - e^{-\sigma\tau})$$

and for sufficiently large values of τ ,

$$\bar{I} = \frac{I_0}{\sigma\tau}$$

$$\mu = 4\Gamma\tau \sqrt{\frac{D\sigma}{I_0}} \quad (4)$$

and $O_T = \mu_0/\mu$. Here $\mu_0 = LI_0$ is the volume of the mixture injected, referred to unit area. Then

$$O_T = \frac{LI_0^{\frac{3}{2}}}{4\Gamma\tau\sqrt{D\sigma}} \quad (5)$$

It may be seen then that the method can achieve comparatively high enrichment. The result of the enrichment, however, is still inferior to that achieved with two acts (10^6) by the usual method.

It might appear that the method proposed here is of no essential interest since it only corresponds to two stages of the usual thermal enrichment. Such a view, however, is not justified. If the I_0 to \bar{I} ratio is high enough then in the usual thermal

method of enrichment the same difficulties caused by broadening will arise and will not permit the second stage to be realised.

An experimental illustration of the method for two cases is now given. In the first case, the Henry coefficient is low, and it is therefore possible to realise a large number of enrichment stages. In the second case I' is large, and enrichment equivalent to a small number of stages is achieved.

Enrichment achieved in the two cases is shown in Table I.

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED ENRICHMENT VALUES

Number of stage	Chromosorb with PPMS concentration of propane 10^{-2} % (vol.)		SKT carbon concentration of propane $1.2 \cdot 10^{-6}$ % (vol.)	
	Experimental enrichment	Calculated enrichment	Experimental enrichment	Calculated enrichment
I	4	4	$4 \cdot 10^3$	$4 \cdot 10^3$
II	14	16	10^4	$1.6 \cdot 10^7$
III	40	64		

The first case consists in propane enrichment on Chromosorb with 20% (by weight) of polyphenyl methyl silicone oil (PPMS). It is seen that the results of enrichment at all of the three stages closely approximate those calculated by the formula $O = (I'_0/I)^n$.

The second case represents sorption of propane on SKT carbon. Here it can be seen that by the second stage poorer enrichment than that calculated is obtained, the same formula being used for calculation.

REFERENCES

- 1 G. F. FREEGUARD AND R. STOCK, in M. VAN SWAAY (Editor), *Gas Chromatography*, 1962, Butterworths, London, 1962, p. 115.
- 2 R. L. PECSCK, A. DE ILLANE AND A. ABDUL-KARIM, *Anal. Chem.*, 36 (1964), 452.
- 3 V. G. BEREZKIN, V. P. PAKHOMOV, B. S. TATARINSKI AND V. M. FATEEV, *Dokl. Akad. Nauk S.S.S.R.*, 180 (1968) 1135.