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DETERMINATION OF THE AMOUNT OF STATIONARY PHASE IN PACKINGS FOR GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

A method is described for the determination of the content of the liquid phase in packings for gas-liquid chromatography. It is shown that the extraction method is subject to an error due to the solubility of some inorganic compounds of the support.

A more satisfactory method involves the evaporation of the stationary phase and an accuracy of 0.05–0.10% is obtained. It is necessary, however, to apply a correction for the weight loss of the pure support at the same temperature.

INTRODUCTION

The amount of stationary phase present is an important characteristic of the column packings used in gas-liquid chromatography. The amount of stationary phase is usually calculated from the data available from the preparation of the packing. This method, however, includes errors due to the loss of some stationary liquid on the walls of the vessel and is also inapplicable to packings in which the amount of stationary phase changes after coating.

A more suitable method seems to be the extraction method, in which a known weight of the packing is extracted with a solvent¹⁻³, but unfortunately there are no data on the conditions necessary for the practical realization of the method to give the maximal accuracy, and the precision of the method is also not known.

A relatively new method for the analysis of column packings involves a technique similar to those used in organic elemental analysis⁴. A sample of the packing is treated at a high temperature in a flow of oxygen and the stationary phase burns quantitatively. It is evident that this method will not be applicable to packings in which the stationary phase could produce ash, for instance metal stearates, other salts and silicones. It is not known whether silanized supports would be stable under these conditions.

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The present work was an attempt to find a convenient, simple and, if possible, universal method for determination of the amount of stationary phase present in packings for gas-liquid chromatography, and to show the limits of its applicability. Such a method is particularly necessary when the packing contains a low percentage of the stationary phase (high-temperature gas chromatography, investigations in connection with surface adsorption, etc.).

EXPERIMENTAL

Packings with known percentages of the stationary phase were prepared by drying the support for 1 h at 110° and then leaving it in a desiccator for a further 1 h. The support and the stationary phase, weighed with an accuracy of $\pm 2 \cdot 10^{-4}$ g, were mixed with the solvent, which was evaporated off by heating. In order to avoid errors as a result of losses on the walls of the flask, in most instances the coating of the stationary liquid on the support was carried out in the same crucible in which the determination was later carried out. After the removal of the solvent, the packing was dried at 110° for 1 h and kept in a desiccator.

Two methods for the determination of the amounts of the stationary liquid in the packing were examined, *viz.*, extraction and evaporation.

In the extraction method, the amount of the packing (about 1 g) was extracted with the solvent used for the coating. For this purpose, 5 ml of solvent were added to the sample and after 5 min the solvent was removed with a thin syringe needle and a water pump. This procedure was repeated several times. The washed support was dried at 110° for 1 h, then cooled for 1 h in a desiccator and weighed. The amount of the stationary phase was calculated from the difference between the weights of the packing and the washed support.

In the evaporation method, a weighed sample of the packing (about 1 g) was heated in a pot furnace at 300° for 2 h. The crucible with the remaining support was kept for 1 h in a desiccator and then weighed.

The supports used were Sterchamol (Schuchardt, München, G.F.R.), 30-60 mesh, Chromosorb P (Carlo Erba, Milan, Italy), 30-60 mesh, and Chromosorb W (Carlo Erba) acid washed, 80-100 mesh. The Sterchamol support has a relatively high specific surface area with adsorption properties and it was expected that it would give the least satisfactory results, which was the reason why it was used in the investigation of the influence of different factors on the accuracy. On Chromosorb P and W, which are often used in practice, only the general applicability of the results was shown.

The stationary liquids were chosen so as to give a range of polarities: squalane (non-polar), dinonyl phthalate (medium polarity) and 1,2,3-tris-(2-cyanoethoxy)propane (high polarity). These stationary phases are used in the medium temperature (100-200°) region; the investigation of high-temperature stationary liquids was not an object of the present work.

RESULTS AND DISCUSSION

Determination of the amount of stationary phase in the packing by the extraction method

In some instances there was a considerable difference between the results of

the determination and the figures obtained from the preparation of the packing. In these instances, the amount of the liquid phase determined analytically was always about 2% absolute greater than the actual amount present. Fig. 1 shows the relationship between the number of extractions and the percentage of stationary liquid washed from a packing that actually contained 11.01% of 1,2,3-tris-(2-cyanoethoxy)-propane on Sterchamol (curve 2).

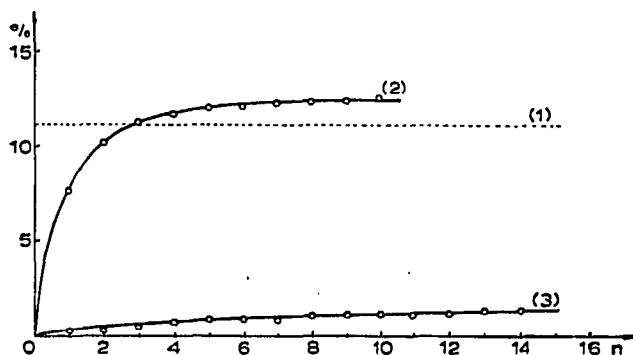


Fig. 1. Percentage loss in the weight of the packing *versus* the number of extractions. (1) Actual percentage of stationary phase present in the packing; (2) results for the extraction of this packing; (3) results for the extraction of a support containing no stationary phase.

The fact that the error was always positive and that it was greater when a more polar solvent was used led us to the assumption that some soluble components in the support were extracted. Their removal with ethanol was considerably more than with diethyl ether.

Curve 3 in Fig. 1 shows the results of the extraction of Sterchamol containing no stationary phase, which illustrates the loss in the weight of the support due to the dissolution of the soluble components.

In further work, a portion of the support was boiled for 2 h each in water, 95% ethanol and diethyl ether in order to dissolve any soluble components present. After ten extractions with ethanol, a 0.14% loss in weight was found while the usual sample represented in Fig. 1 (curve 3) gave a weight loss about ten times greater.

It can therefore be seen that the extraction method will always give higher results, regardless of whether the calculations are made on the basis of the weight of the support after extraction of the packing, or on the basis of the weight of the extract after evaporation of the solvent.

Determination of the amount of stationary liquid in the packing by the evaporation method

The method of heating a sample of the packing at a temperature at which the stationary liquid evaporates quantitatively, but does not burn, was found to be more satisfactory than the extraction method. In this instance also there was a weight loss of the support, but in contrast to the extraction losses, however, they were constant and could be determined in advance so that, when calculating the analytical results, a correction could be used.

Weight correction for the support. The loss in weight of the support at high temperature is due to moisture, which is strongly adsorbed and is not removed on drying the sample at 110°. Up to this temperature, the support loses only 0.11% of its air-dry weight.

Heating of a sample, dried at 110°, for 2 h at 300° leads to an additional 0.28% loss in weight. The weight of a dried sample, kept in desiccator, does not show any change after 1–2 days. The same sample heated for a further 2 h at 300° does not lose moisture and retains a constant weight.

When a column packing is to be analyzed, there are two possible procedures. Firstly, the support can be treated in advance at the corresponding temperature and then coated with the stationary liquid. In this instance, a correction for the moisture of the support is not necessary, but the determination has to be done at the same temperature as the pre-treatment, and during the coating moisture must be excluded from the support. In the second possible procedure, which we consider to be preferable, the correction is found using a separate sample of the support.

Table I shows the change in the correction for Sterchamol at different temperatures. The results in this table and in all subsequent cases refer to a support dried at 110°.

TABLE I
TEMPERATURE DEPENDENCE OF THE WEIGHT CORRECTION FOR STERCHAMOL

Temperature (°C)	Percentage of the support weight
200	0.24
300	0.28
400	0.41

Table II gives the results for the corrections for the supports used in this investigation. Each value is the arithmetic mean of ten measurements.

Precision of the method. The precision was found using a packing of dinonyl phthalate on Sterchamol. For this purpose, nine samples of about 1 g were analyzed for the content of the stationary liquid by the procedure mentioned above. The results obtained are given in Table III. The arithmetic mean of the nine results was $\bar{X}=4.73\%$. The standard deviation for a single measurement was $S=\pm 0.03\%$, which, when multiplied by Student's coefficient for 95% confidence limits, gave a probable error of $\pm 0.07\%$.

TABLE II
VALUES OF THE SUPPORT CORRECTIONS AT 300°

Support	Correction (%)	Standard deviation (%)
Sterchamol	0.28	± 0.01
Chromosorb P	0.16	± 0.01
Chromosorb W	0.20	± 0.01

TABLE III
PRECISION OF THE DETERMINATIONS

No. of the sample	Amount of stationary phase found (%)	$\Delta X = X_i - \bar{X}^*$	$(\Delta X/X_i) \cdot 100$
1	4.77	0.04	0.84
2	4.70	-0.03	-0.64
3	4.75	0.02	0.42
4	4.69	-0.04	-0.84
5	4.71	-0.02	-0.42
6	4.77	0.04	0.84
7	4.71	-0.02	-0.42
8	4.75	0.02	0.42
9	4.69	-0.04	-0.84

* \bar{X} = The arithmetic mean of the series; X_i = the value found for sample i .

The results in Table III were obtained with a packing containing about 5% stationary liquid, and it would be expected that the error would depend on the amount of the stationary phase in the packing. In order to test this postulate, determinations were carried out with packings containing approximately 10, 5 and 2% dinonyl phthalate on Sterchamol, and the results are given in Table IV.

TABLE IV
ACCURACY OF THE DETERMINATIONS FOR DIFFERENT PERCENTAGES OF THE STATIONARY PHASE

Amount of stationary phase (%)		$\Delta X = X_i - \bar{X}$	$(\Delta X/X_i) \cdot 100$
Actual	Found		
1.89	1.86	-0.03	1.59
4.69	4.71	0.02	0.43
8.88	8.83	-0.05	0.56

It can be seen that in all instances the error does not exceed the error found above. The relative error, however, as expected, is higher for the packing with the lower percentage of stationary phase.

Influence of the polarity of the stationary liquid on the results. Another factor which could influence the normal evaporation of the liquid phase from the support surface is its polarity and it would be expected that the support surface will hold more strongly the more polar stationary liquids. Comparative experiments were therefore carried out with packings containing 5% squalane, dinonyl phthalate and 1,2,3-tris-(2-cyanoethoxy)propane on Sterchamol. The results are given in Table V.

The results show that in all instances the error is in the usual range and it does not depend on the polarity of the stationary liquid.

Influence of the type of support. The supports differ in their porosity, specific surface and adsorption properties, and in some instances, therefore, difficulties in

TABLE V
ACCURACY OF THE DETERMINATIONS WITH DIFFERENT SUPPORTS AND STATIONARY LIQUIDS

Support	Stationary liquid	Amount of stationary liquid (%)		$\Delta X = X_i - \bar{X}$	$(\Delta X/X_i) \cdot 100$
		Actual	Found		
Sterchamol	Squalane	4.24	4.21	-0.03	0.71
	Dinonyl phthalate	4.69	4.71	0.02	0.43
	1,2,3-Tris(2-cyanoethoxy)propane	4.64	4.60	-0.04	0.86
Chromosorb P	Squalane	5.42	5.38	-0.04	0.74
	Dinonylphthalate	4.85	4.81	-0.04	0.82
	1,2,3-Tris(2-cyanoethoxy)propane	6.01	5.96	-0.05	0.83
Chromosorb W	Squalane	5.28	5.24	-0.04	0.76
	Dinonylphthalate	5.08	5.07	-0.01	0.20
	1,2,3-Tris(2-cyanoethoxy)propane	4.83	4.84	0.01	0.21

the evaporation of the liquid phase might arise so that a low accuracy would be obtained in the analysis.

Table V gives the results for the determination of the stationary liquid contents of packings with different supports, *viz.*, Sterchamol, Chromosorb P and Chromosorb W, and the stationary phases squalane, dinonyl phthalate and 1,2,3-tris-(2-cyanoethoxy)propane comprising about 5% of the weight of the packing.

It is evident that the type of support does not influence the accuracy of the analysis and the error is in the usual range.

CONCLUSIONS

The following conclusions can be drawn from the present results.

(1) It is more satisfactory to determine the content of the stationary phase in the packing by means of the evaporation method than by the extraction method.

(2) The suggested method of analysis can be used successfully in instances when an accuracy of 0.05–0.1% absolute is satisfactory.

(3) The accuracy of the determination does not depend on the polarity of the stationary liquid or on the type of the support (for diatomite supports). The temperature of the analysis must be above the maximal working temperature of the stationary phase, but not so high that its degradation will occur. The influence of temperature, however, was not an object of this investigation.

REFERENCES

- 1 P. Urone, Y. Takahashi and G. H. Kennedy, *J. Phys. Chem.*, 74 (1970) 2326.
- 2 D. F. Cadogan, J. R. Conder, D. C. Loche and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 708.
- 3 R. A. Keller and H. Freiser, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960.
- 4 D. E. Martire and P. Riede, *J. Phys. Chem.*, 72 (1968) 3478.