Journal of Chromatography, 299 (1984) 151–158
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,829

DETERMINATION OF THE LIQUID LOADING IN GAS CHROMATOGRAPHIC PACKINGS BY AN EXTRACTION METHOD

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(First received February 8th, 1984; revised manuscript received April 11th, 1984)

SUMMARY

An extraction method for the determination of liquid loadings in chromatographic packings is described in detail, and the various causes that could invalidate the results are pointed out. The extraction time and precision of the results were examined for both single and homogeneously mixed liquids on silanized and non-silanized supports. Errors below 2% were found. Extraction was complete in all instances except for dimethylsilicones on non-silanized Chromosorb W.

INTRODUCTION

The determination of the amount of stationary phase present in column packings is important in most physico-chemical measurements in gas–liquid chromatography (GLC). The amount of stationary phase is sometimes determined from weighings during the preparation of the column packing, but this method is subject to error owing to undefined changes in the proportions of the support and stationary liquid during the procedure. Another method involves combustion of the stationary phase, heating the packing under a flow of oxygen[1–6]. It is obvious, however, that this method will not be applicable to packings in which the stationary phase could produce ash, as would be the case for salts and silicones. Also, it is doubtful whether silanized supports would be stable under these conditions. Evaporation of the liquid at high temperatures has been claimed[2] to be a precise method for the determination of the amount of stationary phase in packings, but corrections must be made owing to weight loss of the support. Extraction seems to be a suitable method, in which a known weight of the packing is extracted with a solvent[7–10]. Matthiasson[11] described the direct determination of the liquid phase loading using a combination of Soxhlet extraction and GLC. Althought interesting, the method has been applied only to volatile stationary phases with defined molecular formulae. Petsev *et al.*[2] describe another extraction method, but they reported that it is subject to error due to the solubility of some inorganic compounds of the support.

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0021-9673/84/$03.00

We have found that undesirable weight losses during the extraction process may frequently be due to the presence of fine powder in the support. In this work, this fine powder was eliminated before the preparation of the packings. We have also tried to find conditions of general applicability for the extraction method, and we describe it in detail because normally only rough indications are offered in the literature.

DETERMINATION OF THE AMOUNT OF STATIONARY PHASE

The amount of stationary phase was determined by extracting the liquid from a sample of the packing and weighing the dry solid, as follows.

A sample of the packing (normally less than 0.5 g) was weighed in a small weighing bottle (30 mm diameter, 50 mm high). The cover was removed and it was introduced into a Soxhlet extractor, and placed on top of a piece of glass of convenient size (see Fig. 1 and list of precautions below). A glass funnel was placed with its tip above the surface of the packing, and the extraction was carried out. Subsequently, the weighing bottle containing the solid was placed inside a larger vessel (a 300-ml beaker), most of the liquid was pipetted out and the larger vessel was covered with a Petri dish. The whole was then placed in the furnace of a gas chromatograph, where the residue was dried under a flow of about 40 ml/min of nitrogen, which was introduced deep inside the larger vessel, but outside the small vessel containing the solid. After the drying process, the weighing bottle containing the residue was left to cool for 30 min inside a desiccator before being weighed. The extraction run was repeated as many times as necessary until the weight was constant.

Precautionary measures

Fine powder present in commercial supports may invalidate the results ob-

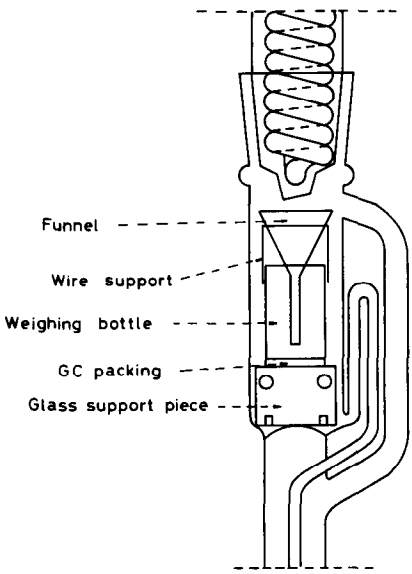

Fig. 1. Arrangement of components inside the Soxhlet extractor.

tained with some of the extraction methods proposed in the literature. With our method, slight turbidity was observed when the fine powder was removed from the packing by the solvent at the beginning of the extraction process. This would lead to too high a value for the liquid loading. Consequently, fine powder was previously removed from commercial supports as follows. Chromosorb W AW was treated with hydrochloric acid and subsequently washed with deionized water, which flowed continuously through the Chromosorb under the conditions of a fluidized bed in a special device[12]. Silanized Chromosorb could not be treated in the same way with water. Fine powder was removed by washing the support with acetone in a vertical glass tube (60 cm long) with a PTFE tap at the bottom. The support was dropped from the top five times, recovering each time at the bottom the coarser fraction of the packing. This method should be equally useful for non-silanized supports, substituting water for the acetone.

After the washing process, the support was treated at 50°C in a flow of nitrogen until it was apparently dry, then it was temperature programmed at a low rate up to 300°C and maintained at that temperature for 10 h. The presence of the silane covering after the heating process in the case of silanized supports was checked by preparing a column of squalane, observing the absence of large tails on peaks corresponding to polar compounds. In every instance, blank extraction runs proved that the fine powder had been eliminated from the support.

During the extraction, a small funnel collects the drops of solvent from the condenser, directing it to the surface of the packing being extracted. The tip of the funnel must be placed 5–10 mm above the sample by means of a supporting device made of stainless-steel wire (Fig. 1).

The top of the weighing bottle containing the sample must be sufficiently high that turbulence of the packing is not produced at the moment of discharge of the solvent. This is best achieved if the cone of the funnel is above the level of the liquid when the discharge begins.

Soon after the start of the extraction process, when the sample is covered by a layer of 2–3 mm of liquid, the heating is interrupted, the condenser and funnel are removed and the sample is stirred very gently with a thin glass rod to eliminate air bubbles. This is done otherwise the bubbles would rise to the top of the liquid later, producing turbulence that would eliminate a few particles of the packing, thus invalidating the results. The funnel and condenser are then replaced and heating is resumed.

The solvent flow-rate was kept at about 13 ml/min. The most convenient flow-rate will depend on the dimensions of the container of the solid sample. It is important to bear in mind that the flow-rate will also depend on the density of the solvent used, as denser solvents will tend to carry away solid particles more easily.

The drying of the residue must be performed carefully. It is necessary to avoid bursting of the wet residue due to sudden evaporation of the solvent. Hence the solvent was evaporated off at a temperature 15°C below its boiling point, and only when the sample was apparently dry was it further heated to 120°C and maintained at that temperature for 1 h.

The weighing bottle containing the packing must not be touched with the hands. Trying to handle it safely, we introduced it into a larger vessel. However, we had great difficulty with dry packings owing to strong electrostatic effects produced

by the contact of the finger tips with the outer vessel. We overcame this by cleaning the outer surface of the larger vessel with an antistatic spray and wrapping it with aluminium foil.

RESULTS AND DISCUSSION

Table I shows results for a number of packings prepared using commercial stationary phases. Table II gives the results obtained with packings of homogeneous mixed stationary phases. In all instances Chromosorb W AW (80–100 mesh) was used as the solid support, after elimination of "fines" as described. Preparation was carried out in a 0.5 l round-bottomed flask in amounts of 10–15 g.

Extraction time

Experiments carried out with different extraction times using seven stationary phases are shown in Fig. 2. Extraction for between 2 and 4 h is necessary with our experimental setup. The extraction time cannot be shortened because an increase in solvent flow-rate would bring about turbulence and, hence, the risk of some of the particles being carried away.

Number of extractions

Some of the samples were extracted more than once and the results showed that the actual number of extractions is immaterial, provided that the extraction is carried out for a sufficient length of time. In our routine work we extract only once for a minimum of 4 h.

Completeness of extraction

Experiments were carried out to check whether the extraction was complete. Packings were prepared with great care *in situ*, *i.e.*, using the same weighing bottle that was to be used in the extraction process. The preparation of the packings was as follows. The support and the stationary phase were weighed, solvent was added up to the level of the solid and the solvent was then left to evaporate at room temperature. Solvent was added again and left to dry, and the procedure was repeated at least ten times, in order to achieve a reasonably homogeneous distribution of the liquid phase on the support.

The results shown in Table III for various stationary phases and solvents indicate that the errors are below 2%, with the exception of QF-1, perhaps because the solvent was unsuitable. This means that extraction results should be considered to be correct within 2%, provided that the extraction is carried out for a sufficient length of time.

Precision

Tables I and II show average values from various determinations, and the individual errors expressed as a percentage error with respect to the mean value. The errors are generally well below 2%, except for OV-17, if a minimum of 4 h is considered. A higher phase loading might have brought the 2.13% error well within the 2% limit.

A general conclusion that can be drawn is that, as a rule, percentage phase

ABLE I

XTRACTION OF COMMERCIAL STATIONARY PHASES

)lvent: acetone.

'ationary phase	*Apparent load (%)**	*Sample weight (g)*	*No. of extractions***	*Extraction time (h)****	*Weight loss (%)§*	*Mean weight loss (%)*	*Error (%)§§*
V-3	16.75	0.34226	1	5.5	15.90	15.92	0.13
			2	9	15.86		0.38
		0.32148	1	5.5	15.93		0.06
			2	9	16.00		0.05
V-7	16.7	0.38455	1	5	15.8	15.73	0.45
			2	9	15.82		0.57
		0.29912	1	5	15.79		0.38
			2	9	15.76		0.19
		0.36229	1	2	15.59		0.89
		0.27455	1	2	15.62		0.70
		0.24752	1	2	15.71		0.13
V-11	17.5	0.30167	1	2.5	16.01	16.20	1.17
		0.24998	1	2.5	16.09		0.68
		0.30118	1	2.5	16.17		0.19
		0.29550	1	4	16.29		0.56
		0.32527	1	4	16.29		0.56
		0.28337	1	4	16.22		0.12
		0.31234	1	4	16.39		1.17
		0.33055	2	9	16.15		0.31
V-17	9.84	0.36645	1	2	9.79	9.86	0.71
		0.51270	1	2	9.62		2.43
		0.29285	2	4	9.99		1.32
		0.30132	2	4	9.95		0.91
		0.33354	2	4	9.65		2.13
		0.45925	1	2	10.10		2.43
		0.45437	1	2	9.92		0.61
V-22	16.6	0.43226	1	5	14.45	14.55	0.69
			2	9	14.59		0.27
		0.39089	1	5	14.50		0.34
			2	9	14.64		0.62
-2300	16.9	0.26798	1	1	15.34§§§		
		0.72936	1	2	16.65§§§		
			2	5	16.49	16.54	0.30
		0.53509	1	5	16.50		0.24
		0.64793	1	2	15.07§§§		
			2	6	16.62		0.48
			3	9	16.56		0.12
-2330	16.57	0.54736	1	5	15.73	15.83	0.63
			2	10	15.71		0.73
		0.35289	1	5	15.92		0.57
			2	10	15.92		0.57
		0.34057	1	5	15.87		0.25
			2	10	15.83		0.0

(*Continued on p. 156*)

TABLE I (*continued*)

Stationary phase	*Apparent load (%)**	*Sample weight (g)*	*No. of extractions***	*Extraction time (h)****	*Weight loss (%)§*	*Mean weight loss (%)*	*Error (%)§§*
OV-61	16.59	0.32805	1	5	16.18	16.15	0.19
		0.29763	1	4	16.13		0.12
Dinonylphthalate	10.27	0.49790	1	5	9.99	10.06	0.70
			2	8	10.04		0.20
		0.27677	1	5	10.14		0.80
			2	8	10.15		0.89
		0.41104	1	5	9.88		1.79
			2	8	10.18		1.19
Squalane	8.70	0.36130	1	4	8.77	8.70	0.80
			2	8	8.75		0.57
		0.28550	1	4	8.70		0.0
			2	8	8.66		0.46
		0.31309	1	4	8.65		0.57
			2	8	8.68		0.23
Polyphenyl ether OS-124	9.93	0.31841	1	1	9.72§§§		
			2	3	9.84	9.92	0.81
		0.30119	1	2	9.94		0.20
			2	4	9.97		0.50

* Percentage liquid loading, as calculated from the preparation weighings.
** Number of extractions for the same sample.
*** Total extraction time, including previous extractions where applicable.
§ Percentage weight loss of the sample after extraction.
§§ Individual error, referred to the mean value, and expressed as % absolute.
§§§ These values were not been used in the calculation of the mean value owing to the insufficient extraction time.

TABLE II

EXTRACTION OF HOMOGENEOUS MIXED PHASES

Composition of mixed phases: A1, 22% OV-101, 78% OV-25; A2, 35.3% OV-101, 64.7% OV-25; A3, 79.99% OV-101, 20.01% OV-25; B1, 10.05% OV-225, 89.95% SP-2340; B2, 1.96% OV-225, 98.04% SP-2340. For explanations of column headings, see footnotes to Table I.

Packing	*Load (%)*	*Sample weight (g)*	*Extraction time (h)*	*Weight loss (%)*	*Mean weight loss (%)*	*Error (%)*	*Solvent*
A1	16.6	0.43887	6	16.03	16.01	0.12	Acetone
		0.35563	6	16.08		0.43	
		0.39812	6	15.92		0.56	
A2	16.8	0.33101	4	16.67	–	–	Chloroform
A3	16.6	0.41233	4	17.04	16.74	1.79	Chloroform
		0.37133	4	16.77		0.18	
		0.33052	5	16.42		0.91	
B1	16.61	0.40120	4	16.17	16.22	0.31	Acetone
		0.29767	4	16.26		0.25	
		0.31448	4	16.23		0.006	
B2	16.76	0.23262	4	16.50	16.50	0.0	Acetone
		0.24966	4	16.47		0.18	
		0.25158	4	16.54		0.24	

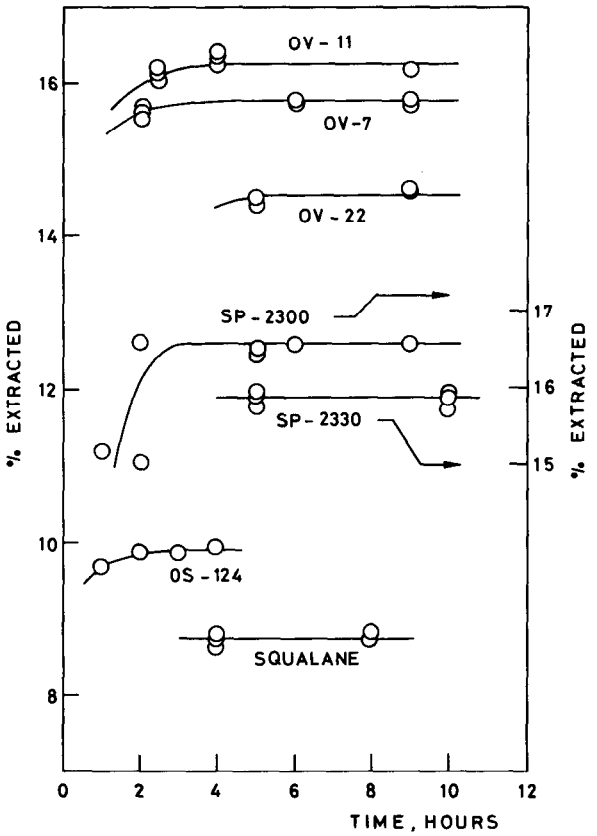

Fig. 2. Effect of the extraction time on percentage weight loss for various packings.

TABLE III

EXTRACTION OF PACKINGS PREPARED *IN SITU*

Stationary phase	*Sample weight (%)*	*Weight (%)*	*Extraction time (h)*	*Weight loss (%)*	*Error (%)*	*Solvent*
Squalane	0.29871	14.13	9	14.05	−0.56	Toluene
DEGS	0.37246	12.50	4	12.53	0.24	Acetone
DEGS	0.84995	15.26	8	15.29	0.2	Acetone
QF-1	0.38631	12.71	8	12.41	−2.4	Acetone
QF-1	0.41363	9.40	8	9.1	−3.2	Acetone
OV-225	0.28932	13.96	4	13.7	−1.9	Acetone
Apiezon M	0.40013	15.03	3	15.0	−0.2	Chloroform
Carbowax 20M	0.46659	9.46	4	9.3	−1.7	Chloroform
Carbowax 1540	0.30429	17.29	4	17.2	−0.52	Chloroform
Diglycerol	0.55818	16.82	8	16.97	0.89	Chloroform
Igepal CO 880	0.34377	13.19	2	13.17	0.15	Methanol

loadings as deduced from preparation weighings are usually incorrect, perhaps owing to adsorption on the flask walls or losses of light components during the conditioning stage.

A few exceptions

Two stationary phases, SE-30 and OV-101, present special problems in the application of the method, and we assume that the same problem will arise with any dimethylsilicone. These liquids could not be extracted (less than 1%) using chloroform, acetone, toluene or *n*-hexane.

However, if the stationary phase was coated on silanized Chromosorb G DMCS, or deposited directly on the weighing bottle (with no solid support), then the extraction was effective. It is curious that mixed stationary phases with a proportion of OV-101 even as high as 80% could be extracted without any difficulty when coated on Chromosorb W AW (see Table II).

FINAL REMARKS

Problems such as those found with the dimethylsilicones, could arise in other instances. Conditioning of packings prior to column filling can produce certain changes that would render the extraction process unreliable: bonded or cross-linked stationary phases will not give correct results when extracted. If any problem is known or suspected, evaporation or combustion methods, perhaps followed by elemental analysis, should be employed. This is the normal case with commercial packings, which as a rule will contain "fines". The results in this paper show that even in the most favourable instances certain precautions are necessary if reliable results are to be expected. This will best be accomplished if the packing is prepared with the purpose in mind. Normally, precise values of the percentage loading of stationary phase on the support are needed in special instances where specific retention volumes must be known. In these instances the packings is normally prepared in the laboratory and the conditioning stage can be carried out carefully.

ACKNOWLEDGEMENT

This work was carried out under Project 14.128 of the Comisión Asesora de Investigación Científica y Técnica.

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