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GAS–LIQUID CHROMATOGRAPHY OF *s*-TRIAZINES ON A SURFACE-BONDED SUPPORT IN SHORT COLUMNS

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SUMMARY

The use of surface-bonded PEG 20M Chromosorb P as the support, coated with Versamid 900 or PEG 20M stationary phases, in short columns allows the rapid isothermal gas–liquid chromatographic separation of *s*-triazine derivatives. The preparation of the support involved preliminary acid washing and subsequent polymer deactivation; a modified Soxhlet apparatus was used for acid washing, in which hot extraction acid vapours were used. The iron content of Chromosorb P (80–100 mesh) was reduced to 0.01–0.02% in 6 days.

Two columns were suggested: 3% Versamid 900 (0.45 m × 3 mm I.D.) for the separation of a mixture of methoxy-, chloro- and thiomethyl-*s*-triazines and 2% PEG 20M (0.35 m × 3 mm I.D.) for the separation of chloro-*s*-triazines alone. The analysis time on the former column was about 9 min and on the latter about 4 min.

INTRODUCTION

s-Triazine derivatives are widely used as herbicides, and in the last two decades a number of methods for their analysis have been developed[1–3], such as spectroscopy (UV–visible), gas–liquid chromatography (GLC) and paper and thin-layer chromatography. Although some of the first investigations were carried out by GLC[4–6] and the number of publications continued to grow up to 1970, by about 1976 the number of such papers had fallen to half that in 1970, probably owing to the time-consuming GLC analysis on conventional stationary phases in long columns[4]. The disadvantages of the other methods employed[3], *viz.*, insufficient separation possibilities of spectroscopy and the semi-quantitative results of paper and thin-layer chromatography, have directed the efforts of investigators during the last 2–3 years towards high-performance liquid chromatography (HPLC)[7] and back to GLC[8–14]. One of the main reasons is the suggested use of surface-bonded phases, allowing the solution of adsorption problems related to inefficient, poorly silanized commercially available supports[14–16].

In this paper we report the application on surface-bonded PEG 20M Chromosorb P as the support, coated with Versamid 900 or PEG 20M, for the separation of methoxy-, chloro- and thiomethyl-*s*-triazines using short columns and isothermal temperatures.

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EXPERIMENTAL

Preparation of surface-bonded packings

The surface-bonded support was prepared in accordance with the original idea suggested by Aue *et al.*[19,20] and the procedure described in a previous paper[17]. Acid washing of Chromosorb P (80–100 mesh) with 6 *N* hydrochloric acid was carried out in a modified Soxhlet apparatus of our own design (Fig. 1), in which hot extraction acid vapours were used; the acid-washing period was shortened to 6 days and the iron content was reduced to 0.01–0.02%. After coating the support with PEG 20M, heat conditioning to 280°C, removal of non-bonded PEG 20M by solvent extraction with methanol and drying, the surface-bonded support was ready. The support was divided into two parts: one was coated with Versamid 900 and the other with PEG 20M.

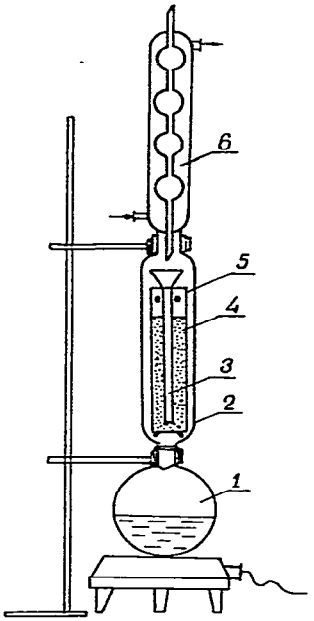


Fig. 1. Modified Soxhlet apparatus for acid washing of the support with the hot extraction acid vapours. 1, Flask (500 cm^3) with a ground-glass joint; 2, 340 mm × 450 mm I.D. tube with ground-glass joints at both ends; 3, 160 mm × 11 mm I.D. funnel with an elongated tube; 4, Chromosorb P (80–100 mesh); 5, 210 mm × 28 mm I.D. overflow cartridge with three openings for the extraction solution; 6, reflux condenser with ground-glass joint.

Gas–liquid chromatography

GLC measurements were carried out isothermally on a Carlo Erba Fractovap GI instrument equipped with a flame-ionization detector (FID) and an injector connected directly to the column (Rasoterm U-shaped 0.35 and 0.45 m glass columns of our design; the end fittings were straight without any additional glass or metal components for connection to the FID).

The glass columns were previously deactivated with dimethyldichlorosilane (DMCS) and then filled with the prepared packings. Versamid 900 was deposited on

the support from chloroform–*n*-butanol (1:1) and PEG 20M from dichloromethane. The working temperatures of the Versamid 900 and PEG 20M columns were 200 and 195°C, respectively. Oxygen-free argon was used as the carrier gas.

A Leeds and Northrup Spedomax W recorder was employed at a chart speed of 116 cm min^{-1}.

Chemicals

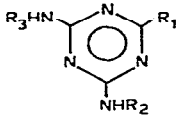
s-Triazines of analytical-reagent grade were employed. The Chromosorb P (80–100 mesh) support was supplied by Johns-Manville (Denver, CO, U.S.A.) and the Versamid 900 and PEG 20M liquid phases by Carlo Erba (Milan, Italy).

GLC measurements

The herbicides selected were polar, high-molecular-weight 1,3,5-triazines, substituted at the second, fourth and sixth positions (Table I). The methoxy-, chloro- and thiomethyl-*s*-triazine mixture (Fig. 2A) and the chloro-*s*-triazine mixture (Fig. 2B) were injected in the form of a dimethylformamide solution.

TABLE I

s-TRIAZINES USED



s-Triazine	*2-Substituent* (R_1)	*4-Substituent* (R_2)	*6-Substituent* (R_3)	*Molecular weight*
Prometone	OCH_3	iso-C_3H_7	iso-C_3H_7	225.3
Atratone	OCH_3	C_2H_5	iso-C_3H_7	211.0
Simetone	OCH_3	C_2H_5	C_2H_5	197.2
Propazine	Cl	iso-C_3H_7	iso-C_3H_7	229.7
Atrazine	Cl	C_2H_5	iso-C_3H_7	215.7
Simazine	Cl	C_2H_5	C_2H_5	201.5
Prometryne	SCH_3	iso-C_3H_7	iso-C_3H_7	241.3
Ametryne	SCH_3	C_2H_5	iso-C_3H_7	227.3
Simetryne	SCH_3	C_2H_5	C_2H_5	213.3

The retention times were measured by means of a stop watch and the peak widths by a micrometric magnifying glass (±0.1 mm) "Karl Zeiss"-Jena.

The reproducibility of GLC measurements such as resolution criterion ($R_{t,w}$), relative retention times (RRT) and asymmetry coefficient (K_a) was evaluated from the standard deviation (SD) and the relative standard deviation (RSD, %), obtained in 6 experiments with each mixture analyzed on the corresponding column (Table II).

RESULTS AND DISCUSSION

A large number of polar and non-polar stationary liquids have been suggested[4,8,11,13] for the GLC analysis of *s*-triazines, such as XE-60, Reoplex 400, PEG

TABLE II

STATISTICAL EVALUATION OF RELATIVE RETENTION TIME (*RRT*), $R_{t,w}$ AND K_a DATA

SD = standard deviation; RSD = relative standard deviation.

Column	*s-Triazine*	*RRT*	*SD*	*RSD*	$R_{t,w}$	*SD*	*RSD*	K_a		*RSD*
Versamid 900	Prometone	1.0	–	–	–	–	–	1.4	0.03	2.1
	Atratone	1.2	0.04	3.3	1.2	0.01	0.8	1.1	0.02	1.8
	Simetone	1.3	0.03	2.3	1.2	0.02	1.7	1.2	0.04	3.3
	Atrazine	1.6	0.05	3.1	2.8	0.12	4.2	1.3	0.02	1.5
	Prometryne	1.8	0.06	3.3	1.4	0.05	3.2	1.4	0.05	3.6
	Ametryne	2.1	0.07	3.5	1.5	0.02	1.6	1.3	0.04	3.1
	Simetryne	2.5	0.08	3.2	1.4	0.05	3.3	1.5	0.05	3.4
PEG 20M	Propazine	1.0	–	–	–	–	–	1.4	0.02	1.4
	Atrazine	1.3	0.03	2.3	1.6	0.05	3.1	1.2	0.04	3.3
	Simazine	1.7	0.02	1.2	1.7	0.03	1.8	1.3	0.04	3.0

20M, PEG A, OV-210, Versamid 900 and SE-30 with liquid loadings mainly below 5% (w/w), and also a combination of polar and non-polar liquids (SE-30 and Reoplex 400)[13]. Diatomaceous supports of the Chromosorb W type[4,11,13] treated or untreated with silanes have been employed. However, in most instances peak tailing and/or broadening was observed and there was a lack of reproducibility between different laboratories. A possible explanation is that separations on packed columns with liquid loadings below 5% depend on the support employed[21] because the separations are effected by a complex mechanism of retention. Recently these problems and those related to the use of poorly silanized supports in the analysis of polar compounds were overcome by the use of surface-bonded supports[8,20,21], which allowed an efficient low liquid loading of 1–3% (w/w)[17]. Some disadvantages associated with the use of Chromosorb P for the analysis of polar compounds[18], including pesticides[8], have been mentioned[8,18] in comparison with other diatomaceous supports such as Chromosorb W and G and Gas-Chrom P and Q. Nevertheless, in our investigation we used Chromosorb P.

Before we discuss the reliable results achieved by applying surface-bonded Chromosorb P as the support for the analysis of polar *s*-triazines, the reasons why this type of support was selected will be given.

First, as was mentioned above, the preparation of a surface-bonded support is time consuming (minimum 15 days). Therefore, it is better to use Chromosorb P, which has a higher mechanical resistance and is less fragile than Chromosorb W, with which the removal of fines at all stages is required.

Second, for additional deactivation of the support to achieve a fairly inactive clean surface, it is important to remove iron and other mineral impurities. As mentioned above, during acid washing (Fig. 1) the iron content is reduced to 0.01–0.02%. Moreover, Chromosorb P does not contain Fe_2O_3 as a complex as does Chromosorb W, and the iron is more readily extracted from the Chromosorb P surface.

Third, Chromosorb P is more suitable than Chromosorb W and G for modification and additional coating with polar liquids such as PEG 20M and Versamid 900. Moreover, according to Ottenstein[22], Chromosorb W supports have a larger pore size (about 9 μm), compared with about 2 μm for Chromosorb P. This difference could explain the variation in the column behaviour of the two types of supports: the former retains the liquid stationary phase in broad pools, whereas the latter does it in smaller pools, leading to less tailing with Chromosorb P.

As can be seen from Table II and Fig. 2, the surface-bonded Chromosorb P support employed in short columns provides good reproducibility of the relative retention times (relative standard deviation not over 3.5%), with good resolution. The resolution criterion ($R_{t,w}$) values for both columns are higher than 1.2 and the reproducibility of $R_{t,w}$ measured as the relative standard deviation is 0.8–4.2%. The values of the asymmetry coefficient (K_a) are close to unity with good reproducibility (relative standard deviation not over 3.6%).

When the relative standard deviation of the relative retention time was higher (*e.g.*, the relative standard deviation for atrazine was 4.2%), a check with the t_α criterion was made. The tabulated values of the t_α criterion (for a significance level of $\alpha = 0.05$ and five degrees of freedom) were higher than those of the calculated t_α criterion. Therefore, there was no systematic error in the relative retention data obtained.

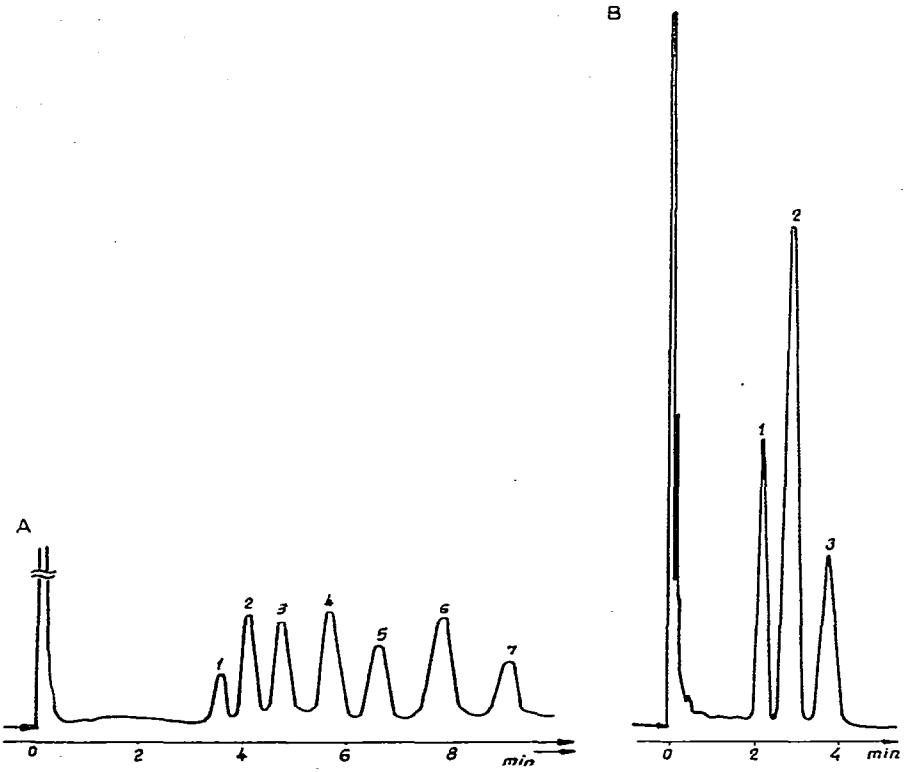


Fig. 2. Gas chromatograms of *s*-triazine mixtures. (A) Mixture of methoxy-, chloro- and thiomethyl-*s*-triazines: 1 = prometone; 2 = atratone; 3 = simetone; 4 = atrazine; 5 = prometryne; 6 = ametryne; 7 = simetryne. Operating conditions: column, 0.45 m × 3 mm I.D., packed with 3% Versamid 900 on Chromosorb P AW (80–100 mesh) (0.01% Fe), deactivated with a non-extractable layer of PEG 20M; argon flow-rate, 35 ml min^{-1}; column temperature, 200°C. (B) Mixture of chloro-*s*-triazines: 1 = propazine; 2 = atrazine; 3 = simazine. Operating conditions: column, 0.35 m × 3 mm I.D., packed with 2% PEG 20M on the support as in (A); argon flow-rate, 45 ml min^{-1}; column temperature, 195°C. Injection volume, 0.8 μl; attenuation, 16 × 10^2.

The time of analysis for the mixture of methoxy-, chloro- and thiomethyl-*s*-triazines on the Versamid column (Fig. 2A) is about 9 min. For the separation of the chloro-*s*-triazine series alone the most polar column PEG 20M (Fig. 2B) was found to be more suitable, with a shorter analysis time of about 4 min.

CONCLUSION

Surface-bonded supports in short columns have proved suitable for the GLC analysis of *s*-triazines, with an efficiency approaching that of HPLC[7,23,24].

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