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MODIFICATION OF THE DETERMINATION OF ORGANIC COMPOUNDS BY HEADSPACE GAS CHROMATOGRAPHY AFTER SORPTION ON SOLID SORBENTS AND LIQUID DESORPTION

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SUMMARY

A method of determination of organic compounds by headspace gas chromatography after sorption on solid sorbents and liquid desorption has been developed. Water (50%) is added to dimethyl sulphoxide after completion of desorption, which results in an increase of up to two orders of magnitude in the concentration of compounds in the gaseous phase. Owing to its increased sensitivity, the method can be employed for the determination of compounds in the sub-ppb* range from small volumes of air or water. An apparatus enabling simultaneous analysis of several samples containing compounds with high and low boiling points without the loss of the latter, and multiple extraction of the sorbent bed, is described. Average recoveries of model compounds [$(CH_3)_2S$, $(CH_3)_2S_2$, $(C_2H_5)_2S_2$] are close to 100%, indicating the high accuracy of the method. The calibration curves were linear over the studied range of concentrations. The overall precision, expressed as the relative pooled standard deviation, varied from 2.4% [$(CH_3)_2S$] to 5.2% [$(C_2H_5)_2S_2$] for samples and from 2.5% [$(CH_3)_2S$] to 9.1% [$(C_2H_5)_2S_2$] for standards. The detection limit was estimated to be 0.17, 0.77 and 0.76 ppb for $(CH_3)_2S$, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$, respectively, assuming a 1-dm^3 liquid sample.

INTRODUCTION

The determination of organic pollutants in water and the atmosphere by gas chromatography (GC) frequently requires a preconcentration step, usually sorption on solid sorbents, due to their low concentration. This step is followed by desorption of the concentrated compounds, generally either by heating[1–3] or with a liquid[4–10]. Both methods have several disadvantages. Although thermal desorption ensures high sensitivity, it can sometimes lead to decomposition of the compounds to be analyzed and/or sorbent. Liquid desorption overcomes this problem but results in decreased

* Throughout this article, the American billion (10^9) is meant.

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sensitivity, since only a fraction of the extract can be injected onto a gas chromatograph.

An interesting method of solving the problems described above was proposed by Kolb and Pospišil[10]. In this procedure the concentrated compounds are desorbed with benzyl alcohol and then subject to headspace gas chromatography (HSGC). The advantages of the method compared with the procedures mentioned above include:

(1) improved sensitivity due to the possibility of injecting much larger samples (1 cm^3 of gas instead of 1–10 mm^3 of liquid)

(2) lack of a solvent peak in the chromatographic region of interest as a result of using a high boiling solvent

(3) possibility of automation of the chromatographic analysis, *e.g.*, by employing the Perkin-Elmer HS 6 headspace analyzer.

The drawback of this procedure lies in the fact that the solvent used should fulfil two contradictory conditions: first, if the desorption is to be quantitative the compounds to be determined should be soluble in the solvent; secondly, for headspace analysis of trace amounts of organic pollutants, their solubility in the eluent should be low. Thus, the solubility of compounds in the solvent should change significantly on passing from desorption to the analysis proper. This could be achieved by addition of a second solvent which decreases the solubility of the compounds, *e.g.*, water, after transfer of the eluate to an HS sample vial. The effect of an addition of water to an organic solvent (dimethylformamide) on the amount of compounds in the gaseous phase has been discussed by Hachenberg[11] in terms of the relative error of the determination.

The principle of the method described in the present paper is based upon the addition of a considerable amount of water (50%) to an organic solvent (dimethyl sulphoxide, DMSO) after completion of the desorption, resulting in a significant increase (up to two orders of magnitude) of the amount of compounds in the gas phase, followed by headspace analysis. Owing to the increased sensitivity, the method can be employed for the determination of compounds in the sub-ppb range from small volumes of air or water. The design of the apparatus permits simultaneous determination of compounds with high and low boiling points without the loss of the latter, several samples can be analyzed simultaneously and the desorption can be carried out with several small portions of the eluent, resulting in complete recovery of the compounds and use of a small total volume of the eluent.

XAD-2 and molecular sieve 13X were selected as sorbents since the former is commonly employed for sorption of organic compounds (especially those with high molecular weights) from water, whereas the latter is particularly suitable for preconcentration of volatile pollutants from gaseous samples.

EXPERIMENTAL

Apparatus

Gas syringes (capacity 2 cm^3) with the flanges cut off were used as adsorption tubes. They were half-filled with the sorbent which was kept in place by two quartz wool plugs. The average weight of the sorbent was *ca.* 0.35 g and *ca.* 1 g in the case of porous polymers and molecular sieve 13X, respectively. During desorption the

syringes were heated electrically in an aluminium heating block with ports for six syringes. The temperature was measured with a thermometer placed in the block.

Headspace sample vials were made of modified 20-cm^3 interchangeable syringes (Fig. 1). The gaseous phase is in contact only with PTFE and glass, preventing losses of compounds due to sorption. A gas sample was withdrawn by means of a 1-cm^3 gas syringe through an injection chamber, which replaces the needle of the HS syringe, by pushing the plunger of the HS syringe upwards. This ensures a constant pressure of the gas. A constant temperature (65°C) in the HS syringes was maintained by mounting them in a thermostatted chamber made of Plexiglas (see Fig. 1). The chamber contained six HS syringes, the inlet and outlet of the thermostating water, a thermometer and two brass rods, by means of which the entire device could be held vertically in two stands. This arrangement facilitated cleaning of the syringes after the experiments by turning the chamber upside down. It was established that the equilibrium temperature inside the HS syringes was reached after 30 min at the most and that the temperature difference between any two syringes did not exceed 0.2°C.

A Hewlett-Packard Model 5830 A gas chromatograph equipped with a flame ionization detector (FID) was employed for GC analysis. The chromatographic conditions were as follows: column, 2.4 m × 2 mm I.D., stainless steel; packing, 10% Dexsil 300 GC on Chromosorb W AW DMCS (80–100 mesh); carrier gas, argon at 17 cm^3/min; injector and detector temperatures, 130°C; column temperatures, 50°C for dimethyl sulphide and 105°C for dimethyl and diethyl disulphides; sample volume, 0.5 cm^3.

Materials

The solvents used in the experiments, dimethyl sulphoxide (DMSO) (Reachim, U.S.S.R.), dimethylformamide (DMF) (POCh, Poland) and benzyl alcohol (POCh), were purified by vacuum distillation. Dimethyl and diethyl disulphides (E. Merck, G.F.R.) were of analytical reagent grade. Dimethyl sulphide was synthesized from methyl iodide and sodium sulphide and purified by fractional distillation. The stock solutions of sulphur compounds, *ca.* 3000 ppm (w/w), were prepared in DMSO and their concentration was checked daily.

Molecular sieve 13X (60–80 mesh) (Serva, G.F.R.) was activated for 3 h at 350°C. Amberlite XAD-2 resin (20–50 mesh) (Rohm & Haas, U.S.A.) was cleaned by successive 8-h extractions with methanol, acetonitrile and diethyl ether in a Soxhlet extractor followed by heating for 2 h at 200°C in a stream of argon.

Procedure

Model aqueous solutions (0.14–3.5 ppm) of sulphur compounds (dimethyl and diethyl disulphide) for the investigation of sorption/desorption on XAD-2 were prepared from the stock solution in DMSO. A plunger and a needle were removed from the sorption syringe packed with XAD-2 and the sorption of compounds was carried out by passing a 100-cm^3 volume of the model solution from a separatory funnel connected to the syringe by means of a piece of silicone tubing. The sorption of dimethyl sulphide was performed by injecting an aliquot of the stock solution in DMSO directly onto the front of the bed of molecular sieve 13X and passing 2–3 dm^3 of air to distribute the compounds more uniformly throughout the sorbent. The

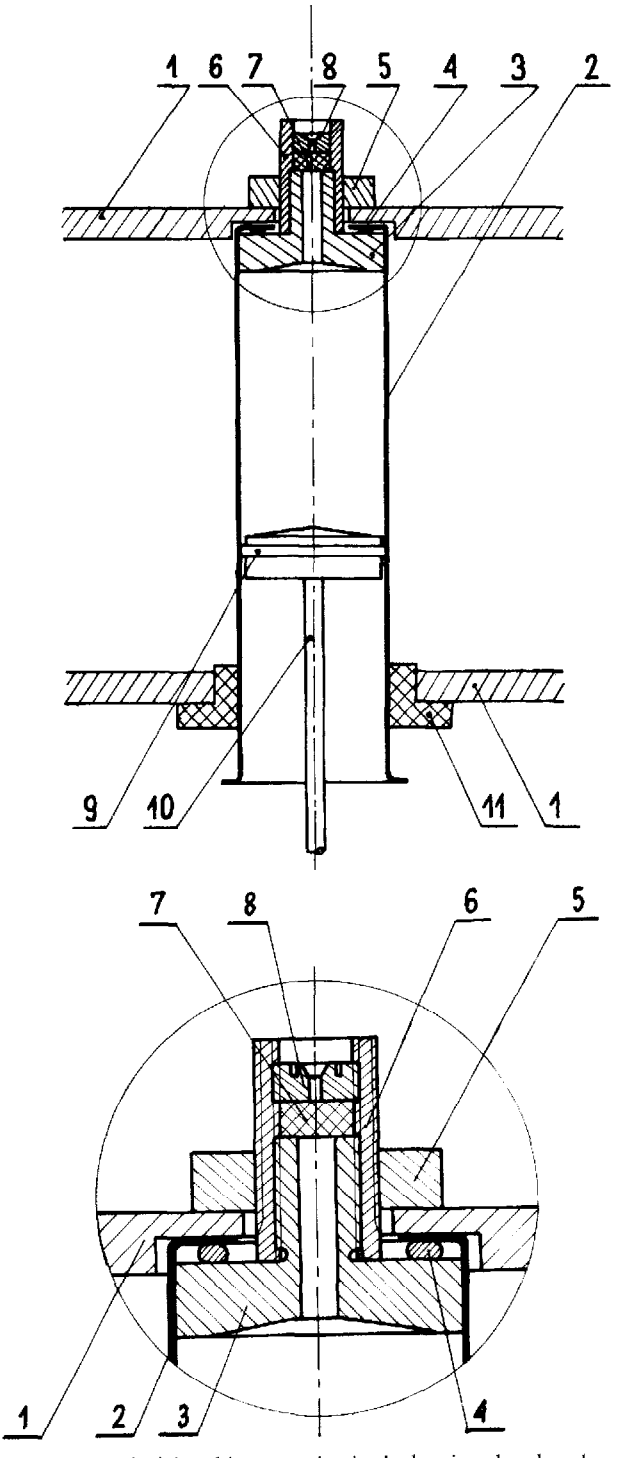

Fig. 1. The HS vial and its mounting in the heating chamber: 1 = wall of the Plexiglas heating chamber; 2 = glass body of the interchangeable syringe; 3 = PTFE insert; 4 = silicone rubber O-ring; 5 = main fixing nut; 6 = brass sleeve with female screw, additionally connected to the PTFE insert by means of anaerobic glue (Loctite Europe, Austria); 7 = septum with lower surface covered with PTFE foil; 8 = septum fixing screw; 9 = PTFE O-ring; 10 = plunger; 11 = rubber gasket.

excess of water from the XAD-2 bed was removed by drawing air through it for 30 sec by means of a water aspirator.

The desorption was carried out by replacing the plunger and the needle of the sorption syringe, drawing *ca.* 1 cm^3 of DMSO through the sorbent bed, sealing the needle with a piece of silicone rubber and heating the syringe to 100°C for 15 min in the heating block to facilitate extraction of the compounds by decreasing the viscosity of DMSO and increasing the diffusion. Subsequently, the eluate was transferred to the HS syringe through a septum in the injection chamber and the entire operation was repeated four more times, so that the total volume of DMSO amounted to *ca.* 5 cm^3. Next, 5 cm^3 of distilled water were added to the HS vial using a syringe and the volume of the gaseous phase was adjusted to 5 cm^3. The vials were kept at 65°C for 30 min to attain equilibrium and the chromatographic determination was performed by injecting 0.5 cm^3 of the gas over the solution. Hence, at least six analyses could be carried out from one sample.

After the desorption the XAD-2 beds were regenerated by drawing through them five 1-cm^3 portions of methanol followed by diethyl ether and drying under vacuum. Molecular sieve 13X was discarded and replaced with a fresh portion from a hermetically sealed dispenser.

The purity of the sorbents and DMSO was checked by running a blank in the manner described above for the desorption. No contaminants that would interfere in the determination were found.

The distribution coefficients of the solute between the liquid and gaseous phases, K_i, were determined by introducing known amounts of compounds to the HS vials and determining chromatographically the equilibrium concentration in the gaseous phase.

The linearity of the method was studied by constructing calibration curves, *i.e.*, of the relationship between the solute concentration in the liquid and gaseous phases, respectively (see Fig. 3).

The overall recovery of the method was investigated by following the procedure described above and, simultaneously, introducing the same amount of compound directly into the HS syringe containing identical volumes of DMSO, water and air, then analyzing the gaseous phase over both solutions. The ratio of the concentrations, measured as the chromatographic peak areas, of the studied and standard solutions yielded the recovery.

RESULTS AND DISCUSSION

The aim of the preliminary experiments was to investigate the effect of addition of water to various solvents on the distribution coefficients of the solutes between the liquid and gaseous phases in order to determine the analytical gain, *i.e.*, the enrichment of the gaseous phase in the compound of interest. The distribution coefficient was defined as

$$K_i = \frac{c_L}{c_G} = \frac{c_{L_0} - \dfrac{c_G V_G}{V_L}}{c_G} \qquad (1)$$

TABLE I

EFFECT OF ADDITION OF WATER TO DMSO ON THE DISTRIBUTION COEFFICIENTS OF SELECTED SULPHUR COMPOUNDS

$\bar{K}_i$ = Average distribution coefficient at 338°K; n = number of measurements; s_r = relative standard deviation = $\frac{s}{\bar{K}_i} \cdot 100\%$; $\bar{K}_i^*$ = distribution coefficient calculated by linear regression from the data in Fig. 3; G = analytical gain, *i.e.*, lowering of the detection limit due to enrichment of the gaseous phase in the solute, equal to the ratio of K_i for the systems DMSO–air and DMSO/water–air, respectively.

	$(CH_3)_2S$		$(CH_3)_2S_2$		$(C_2H_5)_2S_2$	
	DMSO–air	*DMSO/water air**	*DMSO air*	*DMSO/water–air*	*DMSO–air*	*DMSO/water–air*
$\bar{K}_i$	70.0	7.42	748	26.79	2756	39.20
n	2	4	5	7	4	7
s_r(%)	2.8	3.3	1.5	5.5	1.9	4.9
$\bar{K}_i^*$		7.38		25.71		38.03
G	–	9.4	–	27.9	–	70.3

* The DMSO–water ratio was 1:1 (v/v).

where c_L and c_G are the equilibrium concentrations of the solute i in the liquid and gaseous phases, respectively, V_L and V_G are the volumes of those phases and c_{L_0} is the initial concentration in the liquid phase, calculated from

$$c_{L_0} = c_S V_S / V_L \tag{2}$$

where c_S and V_S are the concentration and volume of the standard solution introduced into the HS vial. The concentration c_G was determined chromatographically

$$c_G = \cot \alpha \cdot \bar{A}_G \cdot \frac{1}{V_{iG}} \tag{3}$$

where $\bar{A}_G$ is the average peak area in the analysis of the gaseous phase of the standard solution, V_{iG} is the injected volume of this phase and cot α is the calibration coefficient equal to

$$\cot \alpha = c_S V_{iS} / \bar{A}_S \tag{4}$$

where $\bar{A}_S$ and V_{iS} are the average peak area and the volume of the liquid standard solution used in the calibration. The values of c_G were determined on the basis of a number of injections (3 30). The experimental uncertainty measured as the confidence interval for $\bar{A}_G$ and $\bar{A}_S$ did not exceed 10% and 4%, respectively, at a 95% confidence level.

The solvents studied included DMSO, DMF, benzyl alcohol as well as cyclohexane, isopropanol and *n*-butanol. In each case, the distribution coefficients were determined in the systems solvent–air and solvent/water–air. On the basis of the experimental results, DMSO was selected as desorbing agent for the following reasons:

(1) infinite miscibility with water

(2) dissolves the majority of organic compounds

(3) low volatility (the solvent peak is absent on a chromatogram of the headspace over the DMSO solution)

(4) large change in the distribution coefficients of the solutes upon addition of water (see Table I).

It follows from the data in Table I that the addition of an equal volume of water to DMSO results in a lowering of the detection limit of the headspace determination of organic compounds by one to two orders of magnitude compared to HS analysis over pure solvent. This effect is more pronounced for compounds with higher molecular weights and, hence, lower solubilities in polar solvents. On the other hand, the distribution coefficients for other solvents were less favourable than those for the system DMSO/water–air, *e.g.*, in a system DMF/water (1:1)–air, K_i was *ca.* 71 for $(CH_3)_2S_2$.

The method of selection of an optimum ratio of DMSO–water is presented in Fig. 2. Curve I shows the effect of addition of water to DMSO on the distribution coefficient, K_i, for $(CH_3)_2S$; curves II and III illustrate the dependence of the equilibrium concentration of $(CH_3)_2S$ in the gaseous phase upon the fraction of DMSO in

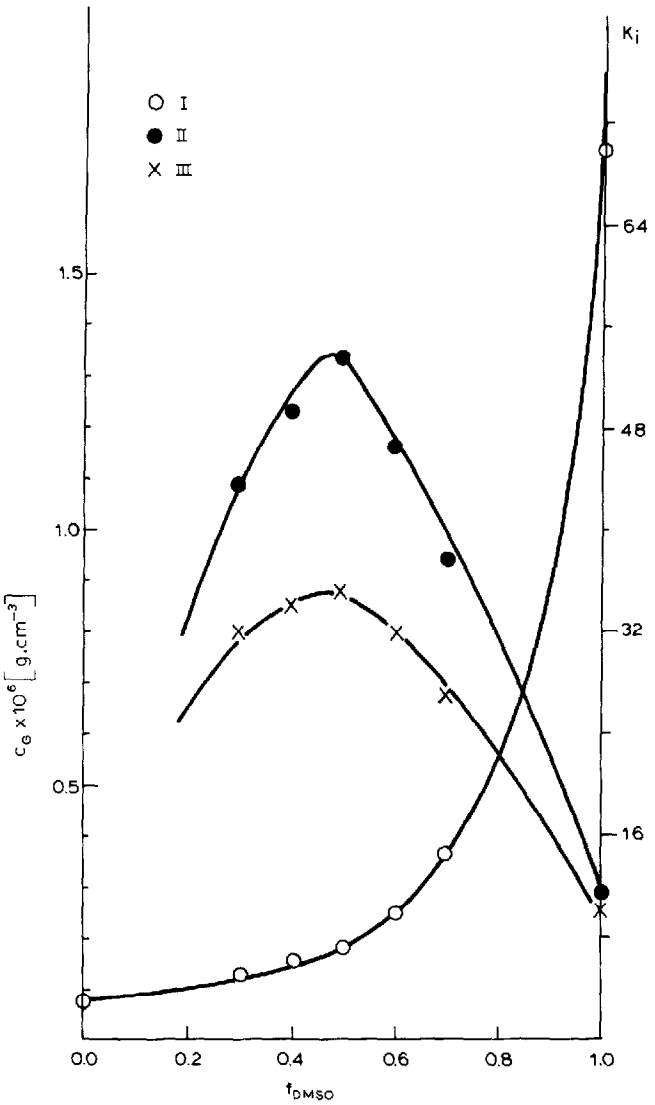

Fig. 2. The effect of the volume fraction of DMSO in the liquid phase on the distribution coefficient of $(CH_3)_2S$ (I) and the equilibrium concentrations of $(CH_3)_2S$ (II and III) in the gaseous phase. Curves II (V_G = 5 cm^3 = constant) and III ($V_T = V_G + V_L$ = 55 cm^3 = constant) were calculated from $c_G = m/(K_i V_L + V_G)$ where $V_{L(DMSO)}$ = 5 cm^3 = constant, $m_{(CH_3)_2S} = 1.03 \cdot 10^{-4}$ g = constant, K_i was taken from curve I and $V_L = V_{L(DMSO)} + V_{L(water)}$

the liquid phase. It is evident that the maximum amount of $(CH_3)_2S$ in the gaseous phase is obtained at a volumetric ratio of DMSO–water = 1:1. Therefore, this ratio was selected for further investigations.

The analytical characteristics of the method, that is its accuracy (in terms of recoveries), overall precision, linearity and estimated detection limit for $(CH_3)_2S$, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$, are listed in Table II. The overall recoveries were calculated

TABLE II

ANALYTICAL CHARACTERISTICS OF THE DESCRIBED METHOD

Characteristic			*Compound*		
			$(CH_3)_2S$	$(CH_3)_2S_2$	$(C_2H_5)_2S_2$
Precision for standards	$\sum_{j=1}^{j=g} n_j$		21	34	24
	g		6	11	8
	$s_{g,r}$(%)		2.5	7.2	9.1
Parameters of the curve $c_G = bc_L + a$ (Fig. 3)	a		$9.69 \cdot 10^{-9}$	$-3.54 \cdot 10^{-8}$	$-1.60 \cdot 10^{-8}$
	$b = (\bar{K}^*)^{-1}$		0.1355	0.0389	0.0263
	r^2		0.9991	0.9996	0.9996
Precision for extracted samples	$\sum_{j=1}^{j=g} n_j$		11	41	32
	g		4	14	12
	$s_{g,r}$(%)		2.4	4.5	5.2
Investigated range of masses	(g)	from	$1.7 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$
		to	$3.4 \cdot 10^{-6}$	$1.4 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
	(decades)		1.3	2	2
Average recovery (± confidence interval for $P = 95\%$)	R (%)		98.5	102.0	98.8
	$t\bar{s}$ (%)		2.18	3.21	3.89
Average FID sensitivity, 1/cot α	(area units per g)		$2.377 \cdot 10^{11}$	$1.705 \cdot 10^{11}$	$2.542 \cdot 10^{11}$
Estimated detection limit	(ppb)		0.17	0.77	0.76

on the basis of four [$(CH_3)_2S$] and ten [$(CH_3)_2S_2$, $(C_2H_5)_2S_2$] results. The average recoveries of 98.5, 102.0 and 98.8% for $(CH_3)_2S$, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$, respectively, are close to 100% indicating the high accuracy of the method and its lack of systematic error. Since the method involves many steps, such as sorption/desorption, partitioning and equilibrium in the vapour phase, it was extremely difficult to estimate the precision of successive operations. Therefore, the overall precision, expressed in terms of the relative pooled standard deviation, $s_{g,r}$, was calculated on the basis of peak areas for the entire number of measurements, $\sum_{j=1}^{g} n_j$, in all "g" series

$$s_{g,r} = \frac{s_g}{\bar{x}_w} \cdot 100\% \tag{5}$$

where s_g is the pooled standard deviation defined as

$$s_g = \sqrt{\sum_{j=1}^{j=g} \sum_{i=1}^{i=n} e_i^2 \Big/ \sum_{j=1}^{j=g} n_j - g} \tag{6}$$

where

$$e_i = x_i - \bar{x} \tag{7}$$

and $\bar{x}_w$ is the weighted average of areas:

$$\bar{x}_w = \sum_{j=1}^{j=g} \bar{x}_j \Big/ \sum_{j=1}^{j=g} n_j \tag{8}$$

Thus $s_{g,r}$ was found to range from 2.4% [$(CH_3)_2S$] to 5.2% [$(C_2H_5)_2S_2$] for the samples and from 2.5% [$(CH_3)_2S$] to 9.1% [$(C_2H_5)_2S_2$] for the standards. The linearity of the calibration curves (Fig. 3) is excellent in the studied range of concentrations, as evidenced by the coefficient of determination, r^2, which was greater than 0.999. Speaking strictly, Fig. 3 represents the relationship between the equilibrium concentrations in the gaseous and liquid phases; however, it can be used for the determination of c_{L_0} by means of eqns. 1 and 2. The detection limit, c_{DL}, was estimated from the relationship

$$c_{DL} = \frac{\bar{A}_{min} \cdot \cot \alpha \cdot V_L}{V_{sample} \cdot V_{iG}} \left(K_i + \frac{V_G}{V_L} \right) \tag{9}$$

assuming $V_{iG} = 1$ cm^3, the minimum peak area that can be correctly integrated, $\bar{A}_{min} = 500$ a.u. (arbitrary units) and the volume of the liquid sample, $V_{sample} = 1$

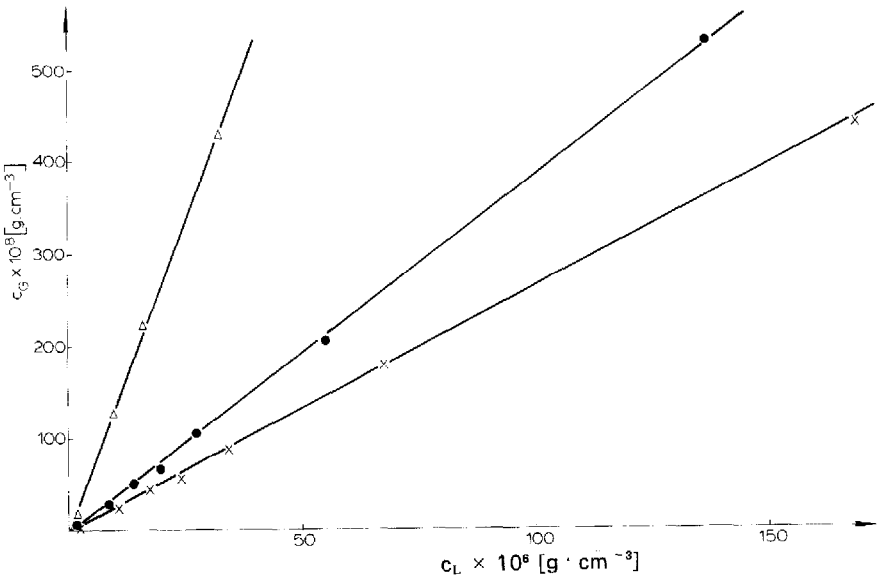

Fig. 3. The dependence of the equilibrium concentration in the gaseous phase on the equilibrium concentration in the liquid phase for selected sulphur compounds. Liquid phase: DMSO–water (1:1, v/v). Temperature: 338°K. △ = $(CH_3)_2S$; ● = $(CH_3)_2S_2$; × = $(C_2H_5)_2S_2$.

dm^3. It was found to be 0.17, 0.77 and 0.76 ppb for $(CH_3)_2S$, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$, respectively. This limit can be substantially lowered by using larger sample volumes providing the breakthrough volumes are not exceeded.

The advantages of the described method can be summarized as follows:

(1) high analytical gain (up to 100) and, hence, low detection limit (in the sub-ppb range)

(2) wide linear dynamic range

(3) recovery close to 100% owing to multiple extraction with small volumes of solvent

(4) possibility of simultaneous determination of compounds with low [$(CH_3)_2S$, b.p. = 37°C] and high [$(C_2H_5)_2S_2$, b.p. = 151°C] boiling points

(5) simple apparatus permitting multiple simultaneous injections of six samples

(6) rapid analysis due to the lack of a solvent peak on chromatograms

(7) DMSO is a good eluent for at least two types of sorbents differing in the type and strength of the interactions.

In its present form the method is limited to the determination of compounds soluble in DMSO, *i.e.*, polar and moderately polar compounds. However, any solvent miscible with water can be employed as the eluent.

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