

CHROM. 17 964

EVALUATION OF THE SUITABILITY OF SELECTED POROUS POLYMERS FOR PRECONCENTRATION OF ORGANOSULPHUR COMPOUNDS FROM WATER

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(Received June 11th, 1985)

SUMMARY

The breakthrough volumes (V_B) of a number of porous polymeric sorbents (Amberlite XAD-2, XAD-4, XAD-7; Chromosorb 102, 105, 106) have been determined for a variety of organosulphur compounds (thiols, sulphides, disulphides, thiophenes) in aqueous samples. The determination was based on a headspace gas chromatographic technique developed earlier. Among the investigated sorbents, Chromosorb 106 and Amberlite XAD-2 were found to be best suited for preconcentration of organic sulphur compounds from water. An attempt was undertaken to correlate the experimental V_B values with the aqueous solubility determined previously from the distribution constants in gas-liquid systems, in order to predict the capacity of sorbents for any organic solute using only the solubility of the analyte. The prediction is useful as a guide for estimating the appropriate ratio of sample to sorbent size in the preconcentration of organic solutes from water.

INTRODUCTION

Organosulphur compounds constitute a significant source of environmental pollution. They are frequently present in industrial wastes, particularly in the effluents from the paper industry. Because of the high toxicity of these pollutants, the corresponding tolerance limits are very low. For example, the maximum allowable concentrations in class I waters for the production of drinking water are 0.003 and 2 mg/l for dimethyl sulphide and thiophene, respectively¹. The odour of some sulphur-containing compounds can be detected at extremely low levels, e.g., 0.00025 mg/l for diethyl sulphide, 0.81 $\mu\text{g/l}$ for di-*n*-propyl sulphide and 0.075 $\mu\text{g/l}$ for *n*-propanethiol¹, thus reducing the suitability of water for drinking purposes.

On the other hand, biologically produced sulphur compounds are thought to account for one half of the total sulphur in the atmosphere. The identity of the sulphur carriers, which must be volatile, biogenically derived compounds transferring sulphur from the sea to the atmosphere, remains to be determined. Efforts to identify these compounds have resulted in the measurement of several sulphur-containing

compounds²⁻⁶. The discovery that living organisms produce volatile, methylated sulphur compounds⁷ has led to investigations of the importance of dimethyl sulphide in the transfer of sulphur from the sea to the atmosphere.

The solution of the analytical problems presented above requires extremely sensitive methods which should permit selective determination of sulphur compounds at the ppm level or below. Numerous papers have dealt with the determination of volatile organosulphur compounds in aqueous samples using headspace gas chromatography (HSGC)^{3,8-18}. Although this method has inherent advantages resulting from the elimination of errors due to the instability and ease of oxidation of the sulphur derivatives, the detection limit of static HSGC is of the order of ppb^{11,13,19}, which may be insufficient in some cases*. For this reason, a preconcentration step was included in procedures for determination of organosulphur solutes, particularly dimethyl sulphide (DMS). One preconcentration procedure involves extraction of DMS via carbon tetrachloride and mercury(II) chloride from large volumes (15 dm³) of sea-water^{2,20}. The determination of dipropyl disulphide and DMS through a purge-and-trap method has also been reported^{21,22}. A search of the recent analytical literature indicates, however, that the most frequently employed method of preconcentration of organic compounds from water involves sorption on solid sorbents, particularly on porous polymers²³. A fundamental parameter characterizing the usefulness of a given sorbent for preconcentration purposes is the breakthrough volume, V_B . For liquid samples, this is a function of a number of variables, the most important being the type of sorbent and geometry of the sorbent bed, the type of compounds and their concentration, the properties of the liquid and its flow-rate through the sorbent bed and the presence of other inorganic and organic compounds in the sample matrix. The determination of V_B values for organic solutes is an essential step in the optimization of analytical procedures for trace impurities, enabling calculations of the safe sampling volumes and the detection limit. Breakthrough volumes can be determined by connection of the outlet of a sorbent tube through which a sample is passed to a high-performance liquid chromatographic (HPLC) detector²⁴⁻²⁶. However, some of these detectors lack sufficient sensitivity (refractive index detectors) or are not universal enough (UV detectors) for this purpose.

This paper presents the results of a determination of the V_B values on a number of porous polymeric sorbents for ten organosulphur compounds (thiols, sulphides, disulphides, thiophenes) in artificial sea-water²⁷ samples using an HSGC technique developed earlier²⁸. The method permits the determination of V_B values for volatile organic compounds at concentrations down to 50 ppb in complex inorganic or organic matrices. The design of the apparatus and the practical application of the method²⁹ are very simple.

An attempt is made to correlate the experimental V_B values with the fundamental physicochemical parameter, aqueous solubility, as determined previously from distribution constants in gas-liquid systems¹⁹, in order to predict the capacity of sorbents for any organic solute using only the solubility of the analyte³⁰. The prediction is useful as a guide for estimating the appropriate ratio of sample to sorbent size in the preconcentration of organic solutes from water.

* Throughout this article, the American billion (10⁹) is meant.

EXPERIMENTAL

Apparatus

The design of the apparatus for the determination of breakthrough volumes by means of the HSGC technique has been described elsewhere²⁸. A Carlo Erba Fractovap Model 2200 gas chromatograph equipped with a flame ionization detector was employed for GC analysis. The chromatographic conditions were as follows: stainless-steel column, 2 m × 4 mm I.D.; packing, 10% DC-200 on Chromosorb P DMCS (80–100 mesh); carrier gas, argon at 40 cm³/min; injector temperature, 175°C; column temperature, dependent on the compound; detector temperature, 200°C; sample volume, 1 cm³.

Materials

Model solutions of sulphur compounds in artificial sea-water were prepared from stock solutions in methanol (*ca.* 3000 ppm). The concentration of the stock solution was determined daily. All reagents (E. Merck, F.R.G.) were of analytical-reagent grade.

Amberlite XAD-2, XAD-4, XAD-7 resins (20–50 mesh; Rohm & Haas, Philadelphia, PA, U.S.A.) and Chromosorb 102, 105 and 106 (60–80 mesh; Johns-Manville, Denver, CO, U.S.A.) were cleaned as described previously³¹. Sorbents were packed in glass tubes (4 cm × 8 mm I.D.). The bed contained *ca.* 0.6 g of the sorbent. Desorption of the retained solutes from the sorbent bed was carried out by washing the tubes with five 1-cm³ portions of methanol, followed by heating for 1 h at 150°C in a stream of argon.

Procedure

The temperature of the headspace cell was 70°C, the flow-rate of the solutions was 40 cm³/h (in some experiments it was varied from 40 to 400 cm³/h), the concentration of sulphur compounds was 1 ppm (w/w) and gas samples were taken at 10- or 100-cm³ intervals. Breakthrough curves were determined on the basis of the peak heights of the investigated compounds.

RESULTS AND DISCUSSION

The breakthrough volumes of the investigated organosulphur compounds on selected porous polymers are listed in Table I. It is seen that the V_B values range from *ca.* 0.2 to 38 dm³/g, the largest values corresponding to compounds with the highest molecular weights and hence boiling points. Among the investigated sorbents, Chromosorb 106 is best suited for preconcentration of thiols and thiophenes, Amberlite XAD-2 for disulphides, whereas either Chromosorb 106 or Amberlite XAD-2 can be used for preconcentration of sulphides (Table I).

The dependence of V_B on the flow-rate was studied for dimethyl disulphide on Amberlite XAD-2 in the range 40–400 cm³/h. It was established that V_B decreased steadily from 3.17 dm³/g at 40 cm³/h to 0.6 dm³/g at 400 cm³/h. This suggests that the adsorption at flow-rates exceeding 40 cm³/h (20 bed volumes) may be a non-equilibrium process. An identical amount of Amberlite XAD-2 was then packed into a glass tube (16 cm × 4 mm I.D.) and the V_B value of dimethyl disulphide was

TABLE I

BREAKTHROUGH VOLUMES (dm^3/g) ON VARIOUS SORBENTS FOR SELECTED ORGANOSULPHUR SOLUTES IN SEA-WATERTemperature: 20°C. Concentration: 1 ppm. Flow-rate: 40 cm^3/h .

Compound	Sorbent					
	Chromosorb 105	Chromosorb 106	Amberlite XAD-2	Amberlite XAD-4	Amberlite XAD-7	Chromosorb 102
Dimethyl sulphide	0.52	0.37	0.40	0.55	0.22	0.42
Diethyl sulphide	1.29	1.10	2.11	1.10	0.44	1.66
Di- <i>n</i> -propyl sulphide	12.1	38.0	34.0	12.0	1.78	28.3
Diisopropyl sulphide	8.8	13.5	6.1	8.7	0.67	13.3
Dimethyl disulphide	2.32	2.56	3.17	2.74	1.11	0.42
Diethyl disulphide	8.7	12.8	37.7	8.5	1.78	4.99
Thiophene	2.9	2.86	2.29	1.37	0.72	
2-Methylthiophene	7.5	11.7	2.56	1.51	0.91	
Ethanethiol	0.46	1.10	0.90	0.55	0.22	0.42
<i>n</i> -Propanethiol	0.82	1.83	1.51	1.51	0.56	0.62

determined at a flow-rate of 40 cm^3/h . The value obtained was 1.73 dm^3/g , which is consistent with the previous results, since the linear velocity of the sample in a tube of smaller diameter is four times higher than in the tube with 8 mm I.D. Consequently, a flow-rate of 20 bed volumes per hour (40 cm^3/h) was used in the investigations.

The molar aqueous solubilities, S_i , of the compounds studied were calculated from distribution coefficients in the air-water system and other relevant thermodynamic data¹⁹. These values are listed in Table II together with other physicochemical

TABLE II

ESTIMATED VALUES OF SOLUBILITY IN SEA-WATER FOR SELECTED ORGANOSULPHUR COMPOUNDS CALCULATED FROM THE DISTRIBUTION COEFFICIENTS AT 20°C AND OTHER RELEVANT THERMODYNAMIC DATA

 p_i^0 = Saturated vapour pressure.

Compound	Mol.wt. (g/mol)	B.p. (°C)	p_i at 20°C (atm)	K_i at 20°C*	S_i (mol/dm ³)
Dimethyl sulphide	62	37.3	0.523	13.81	0.301
Diethyl sulphide	90	92.1	0.060	12.80	0.032
Di- <i>n</i> -propyl sulphide	118	142.38	0.006	6.98	0.002
Diisopropyl sulphide	118	120.02	0.014	5.94	0.004
Dimethyl disulphide	94	109.7	0.029	19.73	0.024
Diethyl disulphide	122	154	0.004	13.09	0.002
Thiophene	84	84.16	0.082	11.10	0.038
2-Methylthiophene	98	112.56	0.027	9.96	0.011
Ethanethiol	62	35	0.572	6.73	0.160
<i>n</i> -Propanethiol	76	67.7	0.162	5.75	0.039

* $K_i = c_L/c_G$, where c_L and c_G are the equilibrium concentrations of the analyte in the liquid and gaseous phases, respectively.

TABLE III

PARAMETERS OF THE REGRESSION CURVE $\log V_B = a + b \cdot \log S_i$ FOR VARIOUS SORBENTS V_B is expressed in dm^3/g and S_i in mol/dm^3 .

Parameter	Sorbent					
	Chromosorb 105	Chromosorb 106	Amberlite XAD-2	Amberlite XAD-4	Amberlite XAD-7	Chromosorb 102
Number of compounds, n	10	10	10	10	10	8
Intercept, a	-0.75	-0.80	-0.67	-0.73	-0.84	-0.98
Slope, b	-0.68	-0.80	-0.72	-0.63	-0.39	-0.78
Correlation coefficient, r	0.938	0.946	0.926	0.951	0.896	0.928

constants. When the logarithms of S_i for the ten solutes were plotted vs. $\log V_B$, rather well defined linear relationships were found with a correlation coefficient greater than 0.9 (except for Amberlite XAD-7). Parameters of the regression curves $\log V_B = a + b \cdot \log S_i$ are presented in Table III. This relationship between V_B and S_i can be attributed to the hydrophobic effect as reported by Karger *et al.*³². Exemplary plots of the $\log V_B = f(\log S_i)$ dependence for Chromosorb 106 and Amberlite XAD-2 are shown in Figs. 1 and 2. It follows from the data in Table III and Figs. 1 and 2 that the aqueous solubilities can be used to predict V_B values for diverse organic solutes when preconcentrating them on non-ionic porous polymers of low or moderate polarity.

From a comparison of the solubility values in Table II with the V_B values in Table I it is seen that although the S_i values and hence the solute-solvent interactions determine the affinity of the solutes for the sorbents, two other factors associated

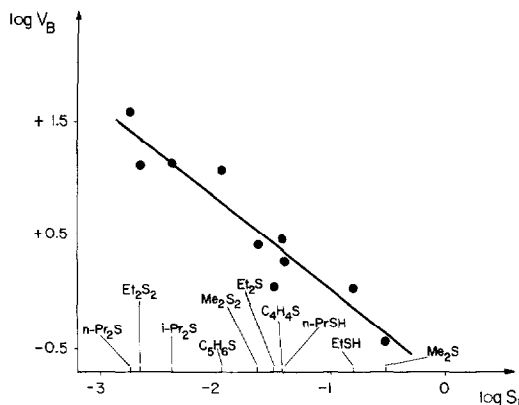


Fig. 1. The dependence of the breakthrough volume (dm^3/g) for organosulphur compounds on Chromosorb 106 on their molar solubility in artificial sea-water. Concentration: 1 ppm (w/w). Flow-rate: 40 cm^3/h . Temperature: 20°C. Compounds: $n\text{-Pr}_2\text{S}$ = di- n -propyl sulphide; Et_2S_2 = diethyl disulphide; $i\text{-Pr}_2\text{S}$ = diisopropyl sulphide; $\text{C}_6\text{H}_6\text{S}$ = 2-methylthiophene; Me_2S_2 = dimethyl disulphide; Et_2S = diethyl sulphide; $\text{C}_4\text{H}_4\text{S}$ = thiophene; $n\text{-PrSH}$ = n -propanethiol; EtSH = ethanethiol; Me_2S = dimethyl sulphide.

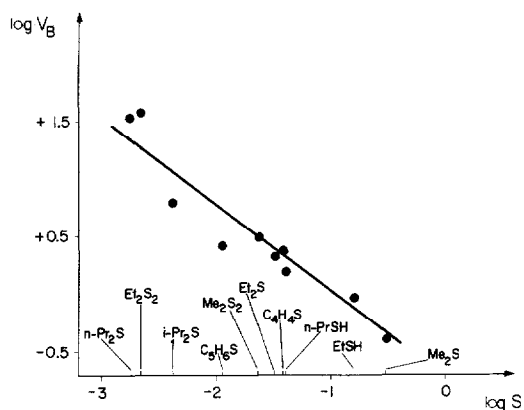


Fig. 2. The dependence of the breakthrough volume (dm^3/g) for organosulphur compounds on Amberlite XAD-2 on their molar solubility in artificial sea-water. Conditions and compounds as in Fig. 1.

with the solute-sorbent interactions should be considered. The first one is connected with the type of sorbent used for preconcentration, *i.e.*, with its monomer composition and surface area. As mentioned above, Chromosorb 106, which is a non-polar polystyrene copolymer with a specific surface area of $700\text{--}800\text{ m}^2/\text{g}$ ²³, is recommended for preconcentration of thiols and thiophenes, whereas Amberlite XAD-2 (styrene-divinylbenzene copolymer with average specific surface area $290\text{--}330\text{ m}^2/\text{g}$)²³ is best suited for extraction of disulphides from aqueous solutions. Although in the latter case Amberlite XAD-4 should apparently give larger V_B values, since it has the same monomer composition as XAD-2 but considerably higher specific surface area ($750\text{ m}^2/\text{g}$)²³, a decisive factor in this case might be the average pore diameter, which is equal to $8.5\text{--}9\text{ nm}$ and 5 nm for XAD-2 and XAD-4, respectively²³. The second factor concerns the type of solute retained on the sorbent. It can be seen from Table I that aromatic compounds are better retained than aliphatics of similar solubility (*cf.*, thiophene, $S_i = 0.038\text{ mol}/\text{dm}^3$ and propanethiol, $S_i = 0.039\text{ mol}/\text{dm}^3$). The same holds true for compounds of different polarity: less polar *n*-propyl sulphide ($S_i = 0.002\text{ mol}/\text{dm}^3$) is better sorbed than diethyl disulphide ($S_i = 0.002\text{ mol}/\text{dm}^3$). Hence, when selecting a sorbent for preconcentration of organic solutes from water, the solubilities of the solutes and the chemical composition as well as the type of sorbent should all be considered. Finally, it should be pointed out that when isolating compounds of low molecular weight, *e.g.*, dimethyl sulphide or ethanethiol, from aqueous solutions of typical volume 1 dm^3 , the sorbent bed should have a mass of several grams in order to avoid losses of the analyzed compounds.

On the basis of the above discussion the following conclusions can be drawn.

(1) The V_B values of the analytes studied range from *ca.* 0.2 to *ca.* $38\text{ dm}^3/\text{g}$, the largest values corresponding to compounds with the lowest aqueous solubility (Table I and II).

(2) Among the investigated sorbents, Chromosorb 106 is best suited for preconcentration of thiols and thiophenes, Amberlite XAD-2 for disulphides, whereas either Chromosorb 106 or Amberlite XAD-2 can be used for preconcentration of sulphides (Table I).

(3) Due to the dependence of V_B on the sample flow-rate, all determinations

should be carried out at a constant flow-rate not exceeding 20 bed volumes per hour.

(4) There is a rather well defined linear relationship between $\log S_i$ and $\log V_B$ (see Table III and Figs. 1 and 2). This dependence can be used to predict the capacity of any sorbent of low polarity for solutes, using only the solubility of the analyte.

ACKNOWLEDGEMENTS

This work was supported by grant MR. I-15 from the Institute of Oceanology (Sopot) of the Polish Academy of Sciences. The author also thanks Mrs. L. Zaslawska for her help in carrying out the experiments.

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