Journal of Chromatography, 245 (1982) 256–260
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,957

Note

Simple method for determination of breakthrough volumes for trace concentrations of volatile organic compounds in liquids

A. PRZYJAZNY*, W. JANICKI, W. CHRZANOWSKI and R. STASZEWSKI
Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, 11/12 Majakowski St., 80-952 Gdańsk (Poland)

(Received March 15th, 1982)

The determination of trace concentrations of organic compounds in liquids generally requires a pre-concentration step followed by liberation of the concentrated substances and the analysis proper. One of the most frequently employed methods of concentration of organic compounds is direct extraction with solid sorbents[1–3]. The most important parameters characterizing the usefulness of a given sorbent for pre-concentration purposes are adsorption capacity and breakthrough volume (BTV). The latter is defined as the volume of sample that can be passed through a sorbent bed before the investigated compound begins to be eluted from the container with the sorbent. Passage of larger volumes of sample results in a loss of compound and a decrease in recovery. The BTV for liquid samples 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.

So far, no direct method has been described for determining the BTV of sorbent beds at trace concentrations of organic compounds in liquids. The usual procedure was to study the overall recovery of compounds from model solutions and, if the recoveries were close to 100%, the conclusion was drawn that the BTV value has not been exceeded[4–8]. However, a more systematic approach would require a knowledge of BTV values, especially when optimizing an analytical procedure for the determination of trace amounts of organic compounds. It has been established[9] that the BTV increases with decrease in concentration of compounds. Thus, a knowledge of BTV values at low concentration levels is essential for the determination of maximum sample volume (the so-called "safe sampling volume") and the detection limit of the method. An attractive method for the direct determination of BTV would be connection of the outlet of a sorbent tube with a high-performance liquid chromatographic (HPLC) detector[10,11]. However, some of these detectors lack sufficient sensitivity (refractive index detectors) or are not universal enough (UV detectors) for this purpose.

A simple method has been developed that permits the determination of BTV values for volatile organic compounds (boiling points $\leqslant$ 180°C) in liquids, especially in aqueous solutions, at concentrations of the initial solution down to 50 ppb (w/w).

0021-9673/82/0000–0000/$02.75

The method employs a headspace (HS) technique for the stream of effluent from the sorbent bed.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The solution of organic compound is pumped from a 10-dm^3 glass bottle (5) through the sorbent bed (6) and the HS unit (7) under constant pressure of compressed gas. The system, consisting of a gas tank (1), reduction valve (2) and two needle valves (3 and 4) permits adjustment of the pressure so as to obtain the desired flow-rate. The latter can be measured at the outlet of the system by means of a graduated cylinder (9) and a stop-watch. Headspace samples are taken and injected on to the gas chromatographic (GC) column (10) by means of a gas syringe (8).

The design of the HS unit is shown in Fig. 2. The effluent from the bed is heated to an appropriate temperature so as to obtain a favourable value of the distribution coefficient, K_i, of the compound under study. This is carried out in a spiral heat exchanger (1) connected to a thermostat. Similarly, the cell (2) is equipped with a heating jacket (3). The volume of liquid momentarily present in the cell is *ca.* 10 cm^3 and that of the headspace is *ca.* 5 cm^3. A septum (4) permits sampling with a gas syringe. A baffle (5) intensifies circulation of the liquid in the cell. The outlet tube (6) is of a reverse U-shape to prevent the escape of the headspace to the atmosphere. A siphon tube (7) allows equalization of pressure in the cell after each sampling. The complete unit is made of borosilicate glass and has a dead volume of about 60 cm^3.

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: column, 2 m × 4 mm I.D. stainless steel; packing, 10% DC-200 on Chromosorb P DMCS (80–100 mesh); carrier gas, argon at 20 cm^3/min; injector temperature, 175°C; column temperature, depending on the compound (90°C for diisopropyl sulphide); detector temperature, 200°C; sample volume, 1 cm^3.

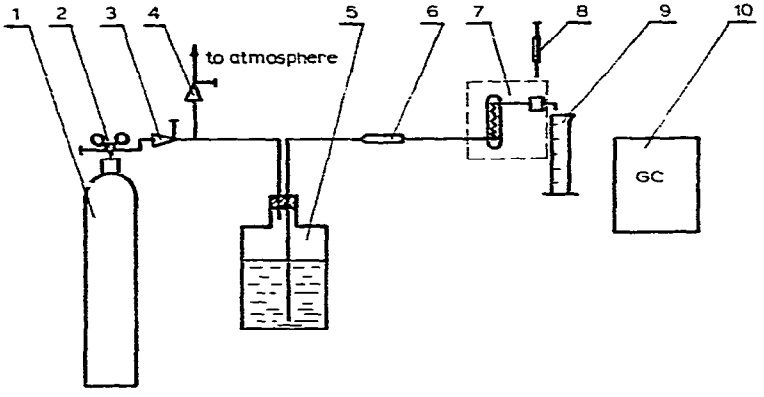

Fig. 1. Apparatus for the determination of breakthrough volumes. 1 = Gas tank; 2 = reduction valve; 3 and 4 = needle valves; 5 = 10-dm^3 glass bottle; 6 = sorbent bed; 7 = headspace unit; 8 = gas syringe; 9 = graduated cylinder; 10 = gas chromatograph.

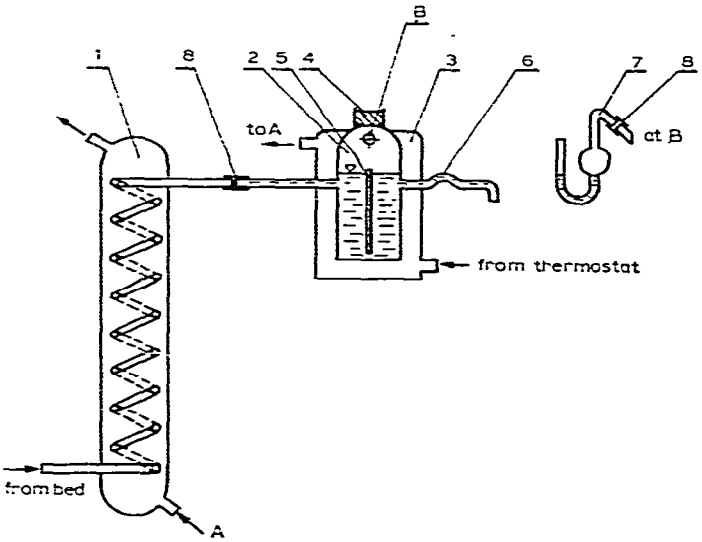

Fig. 2. Design of a headspace unit. 1 = Heat exchanger; 2 = cell; 3 = heating jacket; 4 = septum; 5 = baffle; 6 = outlet tube; 7 = siphon tube; 8 = silicone-rubber connections (the siphon tube is attached to the headspace cell at point B in the plane perpendicular to that of the drawing).

Materials

Model solutions of sulphur compounds in distilled and artificial sea water were prepared from a stock solution in methanol (*ca.* 3500 ppm). The concentration of the stock solution was checked daily. All reagents were of analytical-reagent grade. Sorbents were packed in 7.5 cm × 1.0 cm I.D. glass tubes. The bed contained 1.5–2 g of the sorbent.

Procedure

The temperature of the HS cell was 70°C, the flow-rate of the solution was varied from 10 to 50 cm^3, the concentrations studied ranged from 50 ppb to 5 ppm and gas samples were taken at 100-cm^3 intervals. Breakthrough curves were drawn on the basis of the peak heights of the investigated compounds.

RESULTS AND DISCUSSION

The apparatus has been employed for the determination of BTVs for the beds of porous polymers of Chromosorb Century Series, Porapak, Tenax GC and XAD. The sorption of sulphur compounds from distilled and artificial sea water solutions was studied at different concentration levels and flow-rates. The results of these studies will be published later.

As an example, a series of chromatograms for diisopropyl sulphide (boiling point 120°C) in distilled water (50 ppb, w/w) is shown in Fig. 3. Sorption was carried out at ambient temperature. The temperature of the HS cell was 70°C ($K_i \approx 1.1$). The sorbent was XAD-7 (20–60 mesh) (1.50 g). It can be seen that the BTV reached under these conditions is *ca.* 3 dm^3.

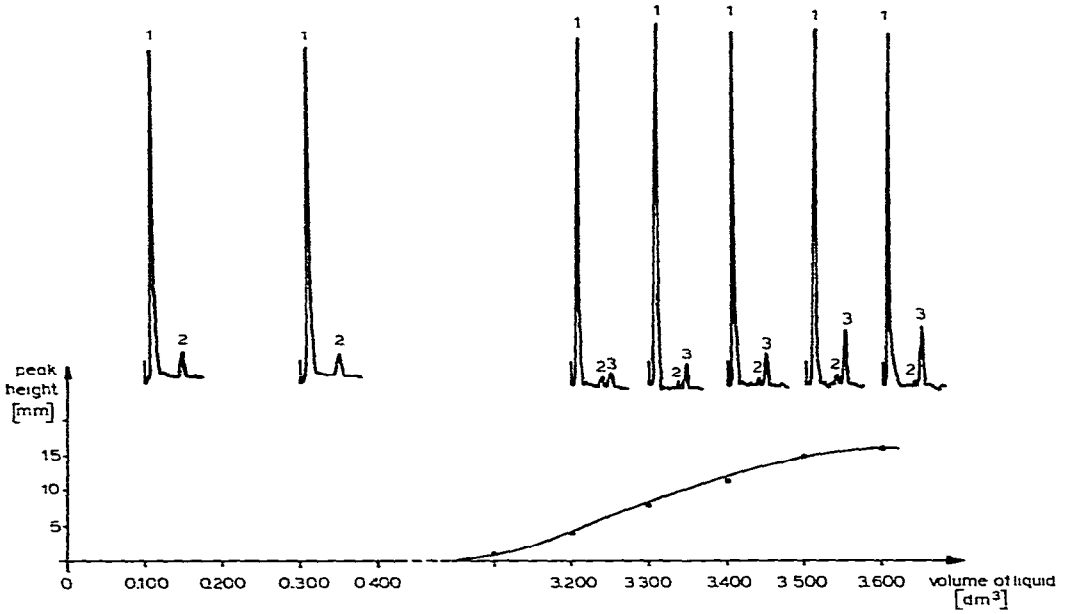

Fig. 3. Chromatograms for diisopropyl sulphide and the breakthrough curve determined on their basis. 1 = Methanol; 2 = unidentified impurity; 3 = diisopropyl sulphide.

The main advantages of the proposed method for the determination of BTVs from liquids are as follows:

(i) Applicability to very low concentrations of organic compounds in the initial solution. This depends on both the K_i value of the compound under study and the detection limit of the GC detector used. Even when K_i values are unknown, the applicability of the method to particular compounds can be roughly estimated on the basis of their boiling points.

(ii) Applicability when the initial solution represents a complex matrix, either organic or inorganic (*e.g.*, sea water), making inpossible direct analysis by GC.

(iii) The design of the apparatus and the practical application of the method are very simple and any gas chromatograph can be employed. The change of the sorbent tube and/or the solution is rapid and easy.

(iv) The method permits the investigation of the effect of the presence of organic compounds on BTV values of other compounds owing to the GC separation achieved.

ACKNOWLEDGEMENTS

This study was supported by grant MR.I-15 from the Institute of Oceanography (Sopot) of the Polish Academy of Sciences.

REFERENCES

1 A. A. Rosen and E. M. Middleton, *Anal. Chem.*, 31 (1959) 1729.
2 J. W. Eichelberger and J. J. Lichtenberg, *J. Amer. Water Works Ass.*, 63 (1971) 25.
3 M. Dressler, *J. Chromatogr.*, 165 (1979) 167.

4 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
5 A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec and R. Willis, *Anal. Chem.*, 44 (1972) 139.
6 A. Tateda and J. S. Fritz, *J. Chromatogr.*, 152 (1978) 329.
7 J. P. Mieure and M. W. Dietrich, *J. Chromatogr. Sci.*, 11 (1973) 559.
8 C. D. Chriswell, R. L. Ericson, G. A. Junk, K. W. Lee, J. S. Fritz and H. J. Svec, *J. Amer. Water Works Ass.*, 69 (1977) 669.
9 G. Bertoni, F. Bruner, A. Liberti and C. Perrino, *J. Chromatogr.*, 203 (1981) 263.
10 M. Krejči, M. Roudná and Z. Vavrouch, *J. Chromatogr.*, 91 (1974) 549.
11 D. Ishii, K. Hibi, K. Asai and M. Nagaya, *J. Chromatogr.*, 152 (1978) 341.