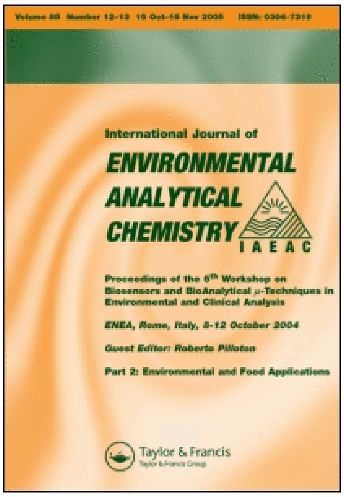

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L. Torres[a]; M. Frikha[a]; J. Mathieu[a]; M. L. Riba[a]; J. Namiesnik[b]
[a] Institut National Polytechnique, Ecole Nationale Supérieure de Chimie de Toulouse, Toulouse Cedex, France [b] Institute of Chemical Engineering, Technical University of Gdansk, Gdansk, Poland

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Preconcentration of Volatile Sulphur Compounds on Solid Sorbents†

L. TORRES, M. FRIKHA, J. MATHIEU and M. L. RIBA

Institut National Polytechnique, Ecole Nationale Supérieure de Chimie de Toulouse. 118, route de Narbonne, 31077 Toulouse Cedex (France).

and

J. NAMIESNIK

Institute of Chemical Engineering, Technical University of Gdansk. 11/12 Majakowski Street, 80–952 Gdansk (Poland).

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The development of industry and urbanisation is at the origin of ever-increasing levels of anthropogenic pollution. Emissions of sulphur-containing compounds are partly composed of volatile organic compounds which add to those generated through natural processes. For low concentrations, direct assaying is problematic and a preconcentration step is necessary at the time of sampling. In order to select efficient solid sorbents for use in preconcentration of volatile organic sulphur-containing compounds, the breakthrough volumes of a certain number of mercaptans and sulphides have been determined on 9 porous polymers (Chromosorb 101, 103, 107,—Porapak Q, T, N,—XAD-4, XAD-7 and Tenax G.C.) and on Carbosphere.

The breakthrough volumes were determined using a direct method with an apparatus based on diffusion tubes dynamically generating standard mixtures of carrier gas and sulphur-containing compounds.

KEY WORDS: pollution, solid sorbents, mercaptans, sulphides.

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INTRODUCTION

Gaseous organic sulphur derivatives (mercaptans and sulphides) represent a non-negligible fraction of both anthropogenic and natural atmospheric pollution. The main anthropogenic sources are primarily due to industry: petrochemistry, wood pulp treatment, pharmaceutics, and agrochemistry. The use of fossil fuels also generates sulphur pollution and, more rarely, spillage of oil on the seas constitutes an additional hazard. The natural sources are mainly of biological origin, dimethyl sulphide for example is produced in large quantities in the ocean zones by plankton and is more than likely one of the major sulphur-containing compounds released in coastal areas.[1,2] Indeed, certain species of algae are known to release large quantities of organic sulphides on dessication.[3,4] The influence of the ocean on the production of sulphur-containing compounds, although considerable is, as yet, poorly defined. Another important natural source of sulphur-containing organic molecules seems to be the interaction of H_2S oxidation products with the components usually occuring in the media presenting bacteriogenic H_2S production .[5]

Although most of the sulphur-containing products are noxious, very few toxicological studies have been carried out to date. Only methanethiol has been studied in mice, rats and monkeys[6,7] where it was observed that after 90 days exposure to an atmosphere containing 50 ppm, mortality was greater than 40%. The poisoning would seem to be due to the formation of sulphohaemoglobin. Death, by pulmonary embolus, of a man who had been subjected to high concentrations of methanethiol has been reported in a paper by Shults *et al.*[8]

Qualitative and quantitative analysis of gaseous sulphur-containing organic compounds is necessary if we are to determine their origin, the changes occurring in their physico-chemistry and their contribution to atmospheric pollution. Fuller understanding of the sulphur cycle also depends on this information.

However, direct analysis of these compounds is often difficult especially when their concentration in the atmosphere is between a few ppm and a few ppb. In order for assaying to become possible a preconcentration step at the time of sampling must be included in the analytical procedure. This operation can consist of condensation at low temperature, absorption in a solution which can be cooled or not, or by adsorption on a solid sorbent.

The chief difficulty involved is recuperating all the trapped compounds after sampling.

Among the main techniques used to concentrate sulphur-containing compounds we should mention trapping of mercaptans and sulphides in various organic solvents chilled to the temperature of dry ice.[9,10] Analysis is subsequently made by injection of the solvent into a gas-chromatograph. The compounds can also be concentrated on filters of several types impregnated with solutions of varying complexity (generally mercury salts) to fix the gases. Thiols are transformed into mercaptides then regenerated and extracted with a solvent.[10,11] The gas to be analysed can also be bubbled through a mercury salt solution at room temperature.[12] Here the sulphur-containing compound can be regenerated by acidification, trapped in a cooled organic solvent then analysed by gas chromatography. The transformation of mercaptans, trapped by bubbling, into reactants (which may be coloured or not) has also been carried out; the reactants are then assayed by colorimetry[13] or by coulometry.[14]

However, of all the available preconcentration techniques, the simplest and most efficient in trapping volatile organic compounds involves the use of solid sorbents like activated charcoal, silica-gel, aluminium oxide, graphitized carbon black or porous polymers. The latter group is the most widespread due to its ease of use. Generally the trapped substances are freed by heat desorption and injected into a gas chromatograph; sometimes, before this operation they are once more cold-trapped in a metal capillary which is then rapidly heated. The samples can also be recuperated using solvents but this technique has several disadvantages i.e. the trapped substance becomes diluted, automation is difficult and the procedure is time-consuming.

Although numerous studies have been made on various groups of organic compounds (amines, halogenated hydrocarbons, aromatic hydrocarbons etc.)[15] concentrated on to solid sorbents, only few investigations have been orientated towards organic sulphides and mercaptans. We should however mention trapping of aliphatic sulphides on Tenax G. C., at $-76°C$,[16] and of mercaptans and sulphides on glass beads at the temperature of liquid oxygen.[10] More numerous studies have been made of H_2S, SO_2 and CS_2 trapping on activated charcoal[17,18] and 5 Å molecular sieve,[19] desorption being carried out thermically or with solvents.

The present report describes an investigation aimed at defining the best solid sorbents of volatile organic sulphur-containing compounds. This study contributes to both the individual analysis of each compound and the global analysis of the element sulphur. The individual parameters of each compound (identity, concentration) or the overall parameters (total S) are essential to define the degree of pollution and to determine the nature of the pollutant.

We determined the breakthrough volumes of 8 mercaptans and 3 organic sulphides on 9 porous polymers and on Carbosphere.

EXPERIMENTAL

Reagents

The sorbents used in the preconcentration study were: Chromosorb 101, 103, 107 (Johns–Manville, Denver, Co. U.S.A.); Porpak N (Varian, Palo Alto, Ca, U.S.A.); Porapak Q and T (Waters Assoc., Milford, Ma, U.S.A.); XAD-4 and XAD-7 (Fluka AG., CH-9470, Buchs, Switzerland); Carbosphere and Tenax G. C. (Alltech Assoc. Deerfield, Il. U.S.A.).

The mercaptans and sulphides used to prepare the standard mixtures were of analytical reagent grade (Fluka).

Gas chromatography equipment

The chromatograph used was a Hewlett Packard 5750 fitted with a flame ionisation detector (FID) and linked up to an electronic integrator HP 3390. As the chromatographic circuit did not contain a packed column the gas mixtures were led directly to the detector. The generator-detector link was made with a nickel tube which is inert towards the studied reactants.

Apparatus

Breakthrough volume determination, according to our method, requires a constant supply of dynamically generated carrier gas-vapour mixture. Of the various dynamic methods for the preparation of gaseous mixtures we chose one based on the use of diffusion tubes as developed by the team of Kelvey and Hoelscher.[20]

The breakthrough volumes were determined using a direct method with the apparatus schematically presented in Figure 1—it was described in detail in a previous report.[15]

The apparatus is made of glass. It produces a constant flow of nitrogen with a very low but accurately known concentration of the sulphur-containing vapour. The only condition that the studied compound must fill is that its boiling point is well above room temperature. The apparatus consists of a generator of standard gas mixtures, working by diffusion, composed of a reservoir and a flask separated by a teflon tube of known bore and length; it is maintained at $20 \pm 0{\cdot}2°C$ in a thermostated bath. The liquid to be studied is placed in the reservoir and the vapour diffuses into the flask at a constant rate through the teflon tube and is then carried off by a flow of pure dry carrier gas ($50\,\mathrm{ml\,min^{-1}}$).

The obtained mixture then passes on to the flame ionization detector either directly or through the trap containing the sorbent to be studied.

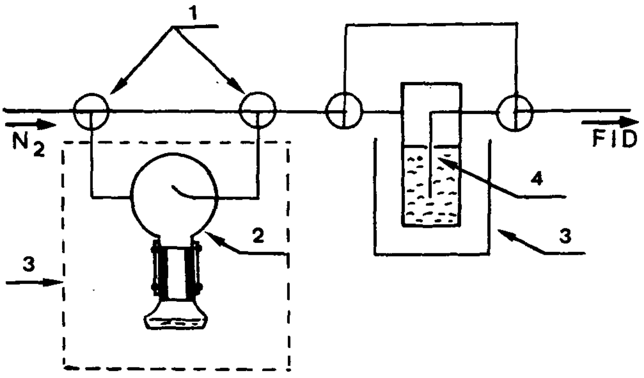

FIGURE 1 Schematic representation of the circuit used in determining the breakthrough volumes. 1 Three-way tap; 2 Generator of standard gas mixtures; 3 Thermostated bath; 4 Sorbent trap.

The concentration of the organic compound in the carrier gas can be calculated from the following relationship:[21]

$$C=\frac{R\cdot K}{F}=\frac{R}{F}\cdot\frac{22.4}{M}\cdot\frac{T}{273}\cdot\frac{760}{p}$$

where C is the concentration in ppm (v/v), R is the diffusion rate in ng. min^{-1}, K is the reciprocal vapour density in nl. ng^{-1}, F is the nitrogen flow rate in ml. min^{-1}, 22.4 is the molar volume of gas at S.T.P., M is the molecular weight of the compound, T is the temperature in °K and p the pressure in Torr.

The expression used to calculate the diffusion rate R is complex[21,22] and in practice it was preferred to determine its value by weighing the reservoir containing the liquid every 24 hours. In this way, diffusion rates of less than 1 μg. s^{-1} can be determined. By varying the temperature, the dimensions of the diffusion tube and the carrier gas flow rate this method allows a very wide range of diffusion rate values to be obtained.

The set-up developed in our laboratory also includes the trap containing the sorbent (the mass of which can be varied between 1 and 2 g). The sorbent is prepared for use by passing nitrogen through it for 24 hours at its maximum utilisation temperature.

Procedure

Breakthrough volume determination involves a certain number of steps each corresponding to a different path in the apparatus taken by the gas-vapour mixture (Figure 1). A schematic chromatogram representing the various stages is given in Figure 2.

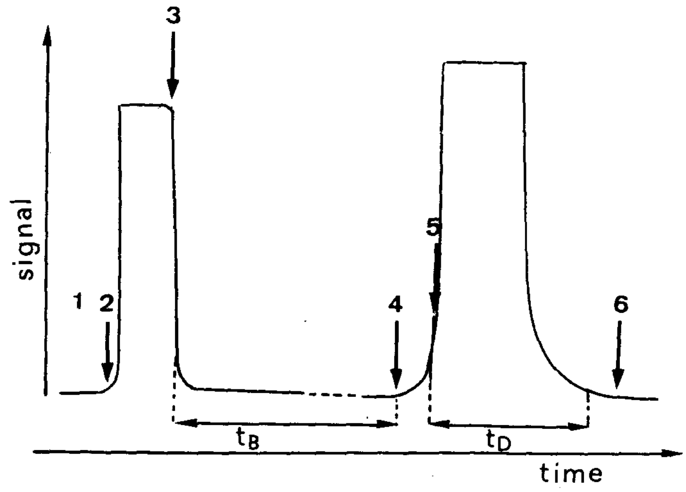

FIGURE 2 Schematic chromatogram allowing the breakthrough time (t_B) and the desorption time (t_D) to be determined.

The different stages observed are:

1→2 Arrival of the pure vector gas at the detector for zero setting.

2 Passage of pure carrier gas through the generator and arrival at the detector of the gas-vapour mixture.

3 Passage of the gaseous mixture through the sorbent trap.

3→4 Adsorption of the organic compound.

4 The compound starts to be no longer completely adsorbed.

5→6 Curve of thermal desorption of the trapped organic vapour by means of a heating jacket around the sorbent. During this operation the carrier gas by-passes the diffusion unit.

6 A new cycle can be started as soon as the original zero setting is reached and when the temperature of the sorbent is stabilized at 20°C.

RESULTS AND DISCUSSION

Knowing the breakthrough time t_B and the carrier gas flow rate, for a given organic vapour we can determine its breakthrough volume in the studied sorbent. This was done for 9 mercaptans and 3 volatile organic sulphides using the protocol described above; the results are presented in Table I (each result is the average of 3 consecutive determinations). Some of the studied compounds present very high breakthrough volumes which we do not need to know accurately; they are simply indicated in the table as being greater than 15 $1.g^{-1}$. In a breakthrough volume study, it is necessary to know the concentration of the vapour arriving in the sorbent. Indeed, certain studies[15,23] have shown that the breakthrough volumes drop sharply as the vapour concentration rises. Our determinations were carried out at between 239 and 1376 ppm (v/v). It was possible to vary the concentrations using different teflon diffusion tubes with internal diameters between 1 and 7 mm. Lower concentration ranges can be reached using permeation tubes.

Among the porous polymers studied, those with the highest adsorption capacities for volatile sulphur-containing organic compounds were found to be Porapak Q and Chromosorb 107 and the lowest capacities were seen in Tenax GC, Chromosorb 103 and Porapak T. Tenax GC however, does have the advantage of a much greater thermal stability than the other sorbents. The desorption times of the various vapours studied was between 5 and 65 min.

We also studied Carbosphere. It presents very high breakthrough volumes. Unfortunately, the thermal desorption times are also very high due to the very strong retention of sulphur-containing organic vapours.

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TABLE I

Breakthrough volumes of volatile organic sulphur compounds

Compound	Concentration p.p.m. (v/v)	Porapak Q		Porapak T		Porapak N		XAD-4		XAD-7	
		V_B(l/g)[a]	t_D(min)[a]	V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)
Ethanethiol Ethylmercaptan	668	4.99	35	2.84	20	3.54	12	2.32	11	1.90	10
2-Propene-1-thiol Allylmercaptan	473	>15	60	0.52	30	2.15	30	4.22	25	4.42	31
2-Propanethiol Isopropylmercaptan	1376	3.55	21	0.46	11	3.08	15	3.38	15	1.63	10
1-Propanethiol *n*-Propylmercaptan	688	4.73	58	0.61	12	3.08	30	0.70	15	3.54	31
1-Butanethiol *n*-Butylmercaptan	387	9	42	3.40	35	5.55	30	9.14	45	11.41	60
2-Butanethiol	631	11.63	40	10.45	48	9.52	40	13.53	30	6.52	41
2-Methyl-2-propanethiol tert-Butylmercaptan	1094	7.3	35	0.48	10	4.84	40	2.11	15	1.63	12
2-Methyl-1-propanethiol Isobutylmercaptan	576	>15	50	1.42	35	6.33	25	12.32	65	9.24	60
Dimethylsulfide	602	5.30	20	2.56	20	3.97	20	2.32	11	2.71	19
Diethylsulfide	598	>15	40	7.68	50	6.04	60	>15	65	8.15	51
Dimethyldisulfide	239	10	60	2	20	>15	60	0.28	10	1.08	12

Compound	Concentration p.p.m. (v/v)	Chromosorb 101		Chromosorb 103		Chromosorb 107		Tenax GC		Carbosphere	
		V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)	V_B(l/g)	t_D(min)
Ethanethiol Ethylmercaptan	668	1.89	15	1.66	16	4.24	17	0.59	5	2.75	60
2-Propene-1-thiol Allylmercaptan	473	2	25	1.37	20	6	40	1.57	20	>15	70
2-Propanethiol Isopropylmercaptan	1376	2.03	15	0.83	10	1.8	10	1.2	7	>15	65
1-Propanethiol *n*-Propylmercaptan	688	1.78	20	1.66	20	5.25	56	1.23	20	>15	85
1-Butanethiol *n*-Butylmercaptan	387	8.85	65	4.31	48	7.31	62	7.25	40	>15	80
2-Butanethiol	631	4.45	52	3.33	41	6.43	30	1.39	13	>15	120
2-Methyl-2-propanethiol ter-Butylmercaptan	1094	0.25	10	0.41	11	1.22	11	0.78	10	19.1	80
2-Methyl-1-propanethiol Isobutylmercaptan	576	4.45	40	3.25	39	12.5	65	3	25	>15	80
Dimethylsulfide	602	1.33	6	0.74	5	3.70	19	1.23	6	>15	55
Diethylsulfide	598	1.43	25	1.64	29	3.34	50	1.97	18	>15	65
Dimethyldisulfide	239	0.75	12	5	30	1.52	21	0.1	15	>15	65

*V_B = Breakthrough volume; t_D = *Desorption time.*

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