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DETERMINATION OF VOLATILE SULPHUR COMPOUNDS IN AIR AT THE PARTS PER TRILLION LEVEL BY TENAX TRAPPING AND GAS CHROMATOGRAPHY

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SUMMARY

A gas chromatographic technique is described for measuring various volatile sulphur compounds (H_2S, COS, CS_2, thiols, sulphides, disulphides) in air at the parts per trillion level. The sulphur compounds are trapped and concentrated at −196°C in a small glass tube filled with the porous polymer Tenax GC. The excess of water in the air samples is pretrapped by calcium chloride, which drying agent does not adsorb any of the sulphur volatiles. The Tenax trap tube fits exactly in the injection port of the gas chromatograph, where the adsorbed sulphur compounds are liberated at 200°C directly into the carrier gas stream and are transferred to the gas chromatographic column. The sulphur compounds are then assayed by means of a flame photometric detector. The Tenax trap tubes can be stored at −196°C for more than 1 week without any loss of sulphur volatiles.

INTRODUCTION

Interest in the detection of volatile sulphur compounds stems from the fact that they have been suggested as one of the endogenous factors responsible for hepatic coma[1,2]. The so-called foetor hepaticus has been ascribed to the presence of sulphur volatiles in the breath[3–5]. The scope of breath analysis as a diagnostic potential was recently reviewed by Manolis[6]. Another important application of the measurement of sulphur volatiles is found in the field of atmospheric pollution control[7–10].

Sulphur volatiles are generally measured by gas chromatography (GC) using the specific flame photometric detector developed by Brody and Chaney[11]. Other detectors used are the electron-capture detector[12] and the photoionization detector[9].

Measurement of sulphur volatiles, especially that of thiols containing the reactive SH group, is often complicated by their reactivity towards among other things glass and metal. Moreover, their ambient air concentrations are usually too low for determination by direct injection of air samples. Stevens *et al.*[13], analysing 10-ml air samples by GC, reported detection limits down to 2–10 ppb. Since then many authors have used sample preconcentration to lower these detection limits[8,10]. The most popular technique involves the use of solid adsorbents such as activated charcoal, molecular sieve and Tenax GC. Other techniques used are concentration by means of wet chemical or impregnated filter techniques, chemisorption onto gold foil, trapping of thiols and sulphides by chemical reactions with mercury salts and the use of liquid argon, nitrogen and oxygen cryogenically to trap and concentrate a variety of sulphur gases. Most of these methods are complicated and not widely applicable for all kinds of sulphur gases.

This paper presents a simple and reliable method for the GC detection of different kinds of sulphur volatiles (H_2S, COS, CS_2, thiols, sulphides, disulphides) in air at the parts per trillion* (ppt) level. Preconcentration of the sulphur compounds was performed on the porous polymer Tenax GC at −196°C (liquid nitrogen). The water in the air samples was pretrapped by means of calcium chloride.

EXPERIMENTAL

Apparatus and reagents

The sulphur compounds were obtained from Merck (Darmstadt, F.R.G.) and Fluka (Buchs, Switzerland). The Tenax GC (80–100 mesh) and the column packing material, 20% SE-30 on Chromosorb P (60–80 mesh), were from Chrompack (Middelburg, The Netherlands).

A Packard gas chromatograph, Type 429 (Packard-Becker, Delft, The Netherlands), equipped with a flame photometric detector (Packard, Model 906) was used for analysis. The detector was supplied with a glass filter having a maximum transmission at 355 nm for the detection of sulphur compounds. The glass chromatographic column (2 m × 4 mm I.D.) was packed with 20% SE-30 on Chromosorb P (60–80 mesh). The injection port temperature and the detector temperature were 200 and 180°C, respectively. The injection port was supplied with a glass liner which could be replaced within seconds by the Tenax trap tube (Fig. 1). Typical gas flow-rates were: nitrogen (carrier gas), 30 ml/min; hydrogen, 140 ml/min; air 1, 80 ml/min; air 2, 110 ml/min. Column temperatures between 30 and 100°C were used (see Results). When using Tenax trapping at −196°C (see below), the column was heated at 120°C for a few minutes after each GC experiment, to remove traces of water and thus prevent interaction of water with thiols inside the column in a subsequent experiment. The glassware (column, trap tubes, vials) was coated with dichlorodi-

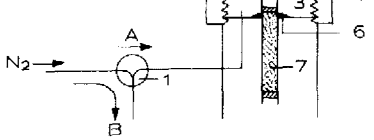

Fig. 1. GC inlet system. 1 = Three-way valve; 2 = injection port head retainer; 3 = injection port head; 4 = septum retaining cap; 5 = septum; 6 = O-ring; 7 = Tenax GC trap tube. A = Nitrogen flow through GC system; B = nitrogen flow switched off.

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* Throughout this article the American trillion (10^{12}) is meant.

methylsilane (5% in toluene) to prevent adsorption of sulphur volatiles. Contact of sulphur volatiles with metal surfaces was avoided. Under the conditions used in this work, the GC column is very stable and is still working perfectly after thousands of injections.

Tenax trapping

Preliminary reports on the technique of trapping and preconcentrating sulphur volatiles (methanethiol, dimethyl sulphide, dimethyl disulphide) from breath and serum have recently been published[5,14]. The adsorption tube consisted of a small glass tube (8 cm × 6 mm O.D. × 4 mm I.D.) filled with 200 mg of Tenax GC (Fig. 2A). The air sample in the large sampling syringe was passed through the trap tube with a flow-rate of about 500 ml/min. The glass liner in the injection port (Fig. 1) was replaced within seconds by the Tenax trap tube, having the same dimensions as the glass liner. The adsorbed sulphur compounds were thermally liberated directly into the carrier gas stream (injection port temperature: 200°C) and transferred to the GC column. When concentration onto Tenax was performed at −196°C, the trap tube was immersed in liquid nitrogen with the top of the tube just above the nitrogen surface (Fig. 2B). To prevent build-up of water in the Tenax trap tube at these low temperatures, the water was pretrapped by means of the drying agent calcium chloride ($CaCl_2 \cdot 2H_2O$, Merck). The powdery $CaCl_2$ (about 300 mg) was placed in a small glass tube, which was installed in the sampling line between the Tenax trap tube and the sampling device. Part of the drying tube, the connecting tubing and the upper part of the Tenax trap tube was wrapped with aluminium foil (Fig. 2B), in order to prevent cryogenic trapping of the sulphur volatiles by the cold nitrogen vapours in these regions. The Tenax trap tube was removed from the liquid nitrogen after trapping of the sulphur volatiles and kept at room temperature for about 20 s to allow the liquid nitrogen to evaporate out of the tube. The trap tube, still cold, was then immediately inserted into the injection port. This latter condition is es-

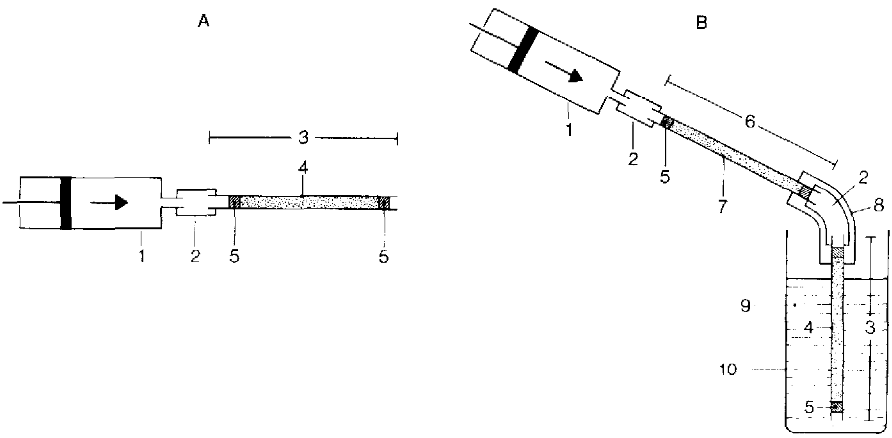


Fig. 2. Preconcentration of air samples onto Tenax GC at room temperature (A) and at −196°C (B). 1 = Polypropylene gas-tight syringe (capacity 100 ml); 2 = polypropylene connecting tubing; 3 = glass trap tube; 4 = Tenax GC; 5 = silane-treated glass wool; 6 = glass tube; 7 = $CaCl_2 \cdot 2H_2O$; 8 = aluminium foil; 9 = liquid nitrogen; 10 = Dewar.

pecially important when analysing H_2S or COS, because warming the trap tube to room temperatures resulted in considerable losses of these most volatile components.

The breakthrough volumes of the Tenax tubes were tested for some sulphur volatiles at room temperature and at −196°C, utilizing two Tenax GC trap tubes in series. The sulphur compounds were loaded onto the top of the first trap tube. Then air was passed through the trap tubes and breakthrough was measured by inspection of both trap tubes. At −196°C the trap tubes in series were both immersed in liquid nitrogen and compressed air was passed through the trap tubes with a flow-rate of 1 l/min, after loading.

Before use the Tenax trap tubes were conditioned for a few minutes at 200°C in the injection port under a flow of nitrogen, to remove contaminants. The trap tubes were reused more than 25 times without any loss in capacity. They can be stored for at least 1 week at −196°C in liquid nitrogen without any loss of sulphur volatiles. The calcium chloride tubes were closed with parafilm at both ends, before use. These drying tubes can be used until the inlet has become plugged through reaction of water with calcium chloride. When dealing with air samples having high humidity, it is recommended to use drying tubes with an inside diameter larger than 4 mm, to prevent plugging.

Calibration of sulphur volatiles

Standard gaseous samples were prepared by injection of known amounts of pure sulphur compounds (gas or liquid) into glass flasks of known volume through an inlet closed with a rubber septum. The flask was warmed with hot tap water to ensure complete evaporation of injected liquids. After further dilution, between 30 and 400 pmol of the sulphur volatiles were injected into the large sampling syringe containing 100 ml of air. These gas mixtures were concentrated onto Tenax and analysed as described. The lines produced by plotting the logarithm of the dose *versus* the logarithm of the peak height were used for calibration purposes.

During substitution of the glass liner by the Tenax trap tube, valve 1 (Fig. 1) was kept in position A. Heating of, *e.g.*, methanethiol inside the injector for 10 s (valve 1 in position B) gave rise to the appearance of the corresponding disulphide, due to oxidation by the oxygen in the air in the trap tube. A complete oxidation into dimethyl disulphide was observed after a heating period of 60 s. The calibration line for dimethyl disulphide, produced by the oxidation of methanethiol, was the same as that obtained by direct injection of dimethyl disulphide. This demonstrated a complete conversion of methanethiol into dimethyl disulphide without loss of any of the volatiles. Other thiols were also oxidized to their corresponding disulphides when heated inside the injection port in the presence of oxygen. No appreciable oxidation of thiols was observed when valve 1 was kept in position A during substitution of the glass liner by the Tenax trap tube. In this case the thiols were immediately transferred to the GC column after desorption in the injection port.

RESULTS AND DISCUSSION

GC separation

Fig. 3a demonstrates the GC separation of 15 volatile sulphur compounds at a column temperature of 50°C. Their retention times are listed in Table I. The sep-

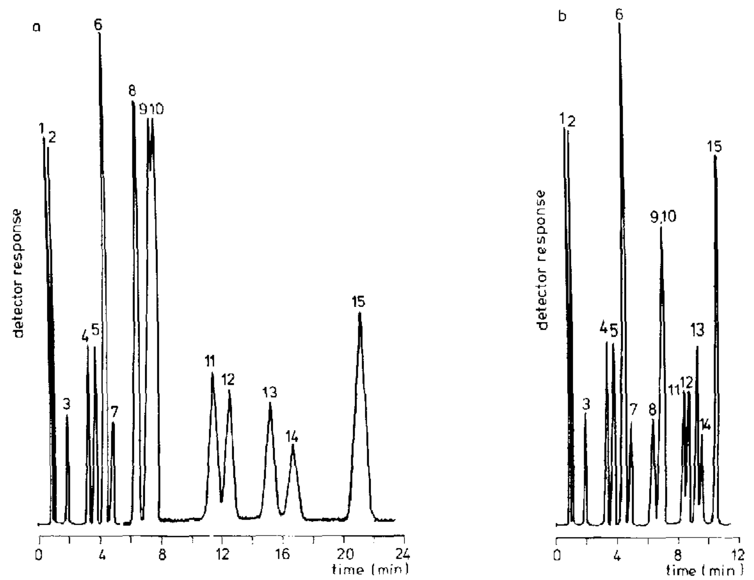


Fig. 3. Gas chromatogram of a standard gas mixture of volatile sulphur compounds. Amounts injected: 0.2 nmol of each for compounds 1–3 and 0.4 nmol of each for 4–15. (a) Isothermal experiment. Detector attenuation: 10 × 512 for compounds 1–7 and 10 × 64 for 8–15. (b) Temperature programmed experiment. Detector attenuation: 10 × 512.

aration between compounds 9 and 10 was improved at a column temperature of 30°C, resulting in retention times of 14.10 and 15.15 min, respectively. Thiophene (b.p. 84.2°C) had exactly the same retention time as 2-butanethiol (compound 11, b.p. 85°C). Fig. 3b shows a gas chromatogram of the same sulphur volatiles in a programmed experiment (initial temperature of 50°C for 5.5 min, then increased at a rate of 35°C/min to a final temperature of 100°C). The retention times of compounds 8–15 were considerably decreased while the separation was still good; only compounds 9 and 10 coeluted under these experimental conditions.

It is known[15] that a plot of the logarithm of the retention volume *versus* boiling point yields approximately straight lines with similar slopes for each homologous series, particularly on relatively non-polar stationary phases. Such a plot for the sulphur volatiles 4–15 (Fig. 4) resulted in a straight line, although not all the sulphur compounds belong to the same homologous series. The line for the sulphides 5, 10 and 13 deviates to a small extent from that of the other sulphur volatiles 4–15, but has a similar slope. The gases H_2S, COS and methanethiol lie on a line with a slope different from that of the other two lines; SO_2 falls outside this relationship. The method as described in this paper is not suitable for the detection of SO_2 (see below). The relationship shown in Fig. 4 may be of practical importance for the prediction of retention times of other sulphur volatiles not examined in this study.

The detector response to sulphur

Fig. 5 shows the relationship between the detector response (peak height) and the dose injected, using the experimental conditions given in Fig. 3b. The log–log plots are straight lines with a slope of 2 for all sulphur compounds studied. This

TABLE I

BOILING POINTS, RETENTION TIMES AND CORRECTED DETECTOR RESPONSES FOR VARIOUS SULPHUR COMPOUNDS

Name	*Formula*	*GC number*	*Boiling point [°C (1 atm)]*	*Retention time* (min)*	*Corrected response, $\sqrt{H} \cdot w$ (mm$^{3/2}$)***
Hydrogen sulphide	H_2S	1	−61	0.96	6.3
Carbonyl sulphide	COS	2	−50	1.10	6.2
Sulphur dioxide	SO_2		−10	1.30	
Methanethiol	CH_3SH	3	6.2	2.00	5.9
Ethanethiol	CH_3CH_2SH	4	35	3.40	6.0
Dimethyl sulphide	CH_3SCH_3	5	37.3	3.90	6.1
Carbon disulphide	CS_2	6	46.3	4.50	12.0
2-Propanethiol	$(CH_3)_2CHSH$	7	52.6	5.02	6.1
2-Methyl-2-propanethiol	$(CH_3)_3CSH$	8	64.2	6.70	6.3
1-Propanethiol	$CH_3CH_2CH_2SH$	9	67.5	7.65	6.2
Ethyl methyl sulphide	$CH_3CH_2SCH_3$	10	66.6	7.95	6.3
2-Butanethiol	$CH_3CH_2CHSHCH_3$	11	85	11.55	6.1
Thiopene	C_4H_4S		84.2	11.55	
2-Methyl-1-propanethiol	$(CH_3)_2CHCH_2SH$	12	88.7	12.65	6.3
Diethyl sulphide	$CH_3CH_2SCH_2CH_3$	13	92.1	15.30	6.6
1-Butanethiol	$CH_3CH_2CH_2CH_2SH$	14	98.5	16.85	5.5
Dimethyl disulphide	CH_3SSCH_3	15	109.7	21.30	11.7

* At a column temperature of 50°C.

** Calculated for 200 pmol of each compound at a detector attenuation of 10 × 64 and an initial column temperature of 50°C, increased at a rate of 35°C/min to 100°C after 8 min.

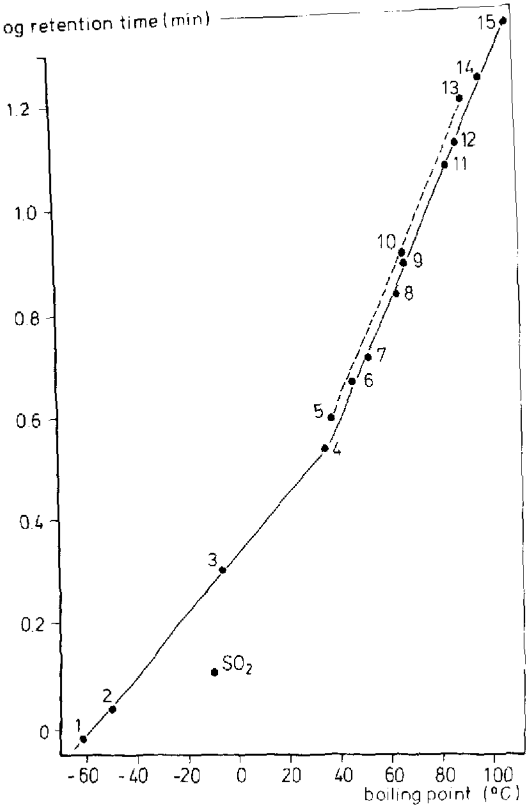


Fig. 4. A plot of the logarithm of the retention times of the sulphur volatiles at 50°C against their boiling points.

means that the response depends on the square of the dose injected, $H = bM^2$, where H = peak height response, b = a constant depending on the experimental conditions, M = amount (mol) of the component injected. Such a quadratic relationship was also found by Maruyama and Kakemoto[16]. Other authors[17–20] have reported values for the exponent, n, ranging between 1 and 2.2. These different findings might be due to differences in the experimental conditions.

Maruyama and Kakemoto[16] proposed the following equation

$$R'_A = \sqrt{H} \cdot w = cM$$

where R'_A = corrected detector response for peak area, H = peak height response, w = peak width at half peak height, c = a constant depending on the experimental conditions, M = amount (mol) of sulphur component injected. This expression gives a constant response for the same amount of a sulphur compound, independent of the retention time. The corrected detector responses for peak area for 200 pmol of sulphur compounds 1–15 are listed in Table I. The values for the sulphur compounds 1–5 and 7–14, containing one sulphur atom, were nearly constant: 6.15 ± 0.26 $mm^{3/2}$

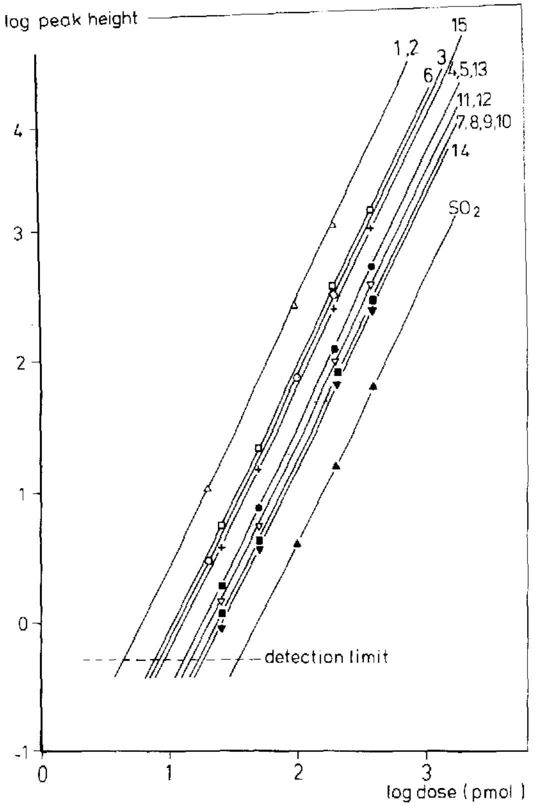


Fig. 5. Standard calibration graphs. Peak height is expressed in mm (10-mV recorder) for a detector attenuation of 10 × 64.

(mean ±S.D.), $n = 13$. The results also show that the corrected response depends only on the number of sulphur atoms in the molecule and not on its chemical structure. The corrected response for CS_2 and dimethyl disulphide, containing two sulphur atoms, was twice as high as those of the other compounds, containing one sulphur atom.

Tenax trapping

Direct injection of the sulphur volatiles into the gas chromatograph generally resulted in the same peak heights as obtained when injection of the same amounts was performed via concentration onto Tenax. This means that no loss occurs during substitution of the glass liner in the injection port by the Tenax trap tube. No differences in the GC outcome were observed when the tubes were installed in the injection port with the injection side up or down. Under certain experimental conditions, the three most volatile sulphur compounds, H_2S, COS and methanethiol, gave slightly lower and broader peaks when injected via the Tenax system compared with direct injection. However, in that case the corrected detector response for peak area ($\sqrt{H} \cdot w$), representing the true amount of sulphur compound, was the same for both injection procedures.

TABLE II

BREAKTHROUGH VOLUMES OF THE TENAX TRAP TUBES FOR SOME SULPHUR VOLATILES (l/200 mg TENAX)

Temperature	H_2S	CH_3SH	CH_3CH_2SH	CH_3SCH_3	$(CH_3)_2S_2$
Room temperature	0.004–0.015	0.10–0.21	0.45–1.1	0.55–1.3	>1
−196°C	>40	>40	>40	>40	>40

The breakthrough volumes of the Tenax trap tubes for some representative sulphur volatiles are compiled in Table II. It is evident that the capacity is increased enormously by keeping the trap tube at −196°C (liquid nitrogen) compared with the situation at room temperature. At −196°C, concentration of 40 l of air onto the Tenax trap tubes can easily be done without loss of any of the sulphur volatiles. This was confirmed by the quantitative recovery of all sample components in the upstream Tenax trap tube and by the absence of any sample components in the downstream collector in a series of experiments utilizing two Tenax trap tubes in series.

The use of Tenax GC has become very popular as a sorbent in trapping columns for air analysis[6,21–25]. Its thermal stability is very high and its breakthrough volumes at room temperatures are relatively low compared with other sorbents, allowing the adsorbed sample components to be desorbed more rapidly from Tenax than from other sorbents. However, this relatively low capacity of Tenax is a major drawback when analysing compounds of low and intermediate volatility, such as the volatile sulphur compounds. Other sorbents are often used for the concentration of these sulphur volatiles such as XAD-4[25] or molecular sieve 5A[8,10]. However, thermal desorption from, *e.g.*, molecular sieve is very difficult due to strong retention of sulphur compounds. The desorption recoveries were very low even at temperatures of 265°C, and desorption times of 6–15 min at 265°C have been mentioned[10]. In a few experiments I also used molecular sieve 5A instead of Tenax. At room temperature, molecular sieve 5A had a large capacity for H_2S, COS and methanethiol. However, with the method described in this paper, none of the adsorbed sulphur compounds could be detected. Desorption inside the injection port (200°C) was probably too slow.

Cryogenic trapping of sulphur volatiles onto Tenax trap tubes in combination with calcium chloride drying tubes (see below) appears to be a promising tool for measuring sulphur volatiles in air at the ppt level. It combines the advantage of a high capacity at −196°C with a low capacity at the desorption temperature, which latter condition results in a fast and almost quantitative desorption recovery.

Pretrapping of water

The water in the air samples was pretrapped by means of calcium chloride drying tubes (Fig. 2B). Omitting these drying tubes causes serious chromatographic problems, at least when preconcentration onto Tenax was performed at −196°C. For example, concentration of 60 ml of an air sample onto Tenax at −196°C and insertion of the Tenax tube into the injection port of the gas chromatograph resulted in a much lower detector response for thiol compounds between 2 and 4 min after insertion of the tube (column temperature 50°C). Concentration of 1 l of air gave a lower detector response for thiol compounds between 2 and 7 min after insertion of the Tenax tube. Between 4 and 7 min, only diffuse, very low, broadened peaks were observed. This disturbance was not seen for neutral sulphur volatiles, such as dimethyl sulphide and CS_2. Probably, the cotrapped water interacts with thiols containing the SH group through hydrogen bonding. The use of drying tubes has now solved these problems.

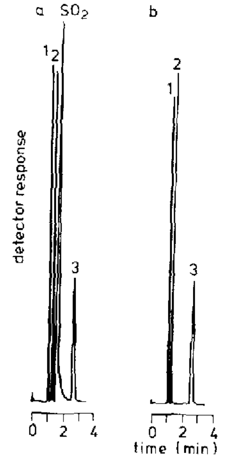
Calcium chloride seems to be the material of choice for pretrapping water without any adsorption of sulphur volatiles. Other drying agents investigated, *viz.*, $MgSO_4$, Na_2SO_4 and Na_2CO_3, showed part adsorption of, *e.g.*, H_2S, COS and methanethiol, which rendered these agents less suitable.

The response for SO_2

The detector response for SO_2 is much lower than that for other sulphur volatiles studied, when performing direct injection of these volatiles into the gas chromatograph (Figs. 5 and 6a). Preconcentration of SO_2 onto Tenax at −196°C and GC gave a complete loss of SO_2 while the response for H_2S, COS and methanethiol remained constant (Fig. 6b). Probably, in spite of the use of calcium chloride tubes, traces of water in the Tenax tube or in the GC column react with SO_2, thereby preventing its detection. Perhaps the use of other column materials such as used by Black *et al.*[8] for the detection of SO_2 might solve this problem.

Sensitivity, recovery and storage experiments

The absolute detection limit of the GC procedure, defined as a signal-to-noise



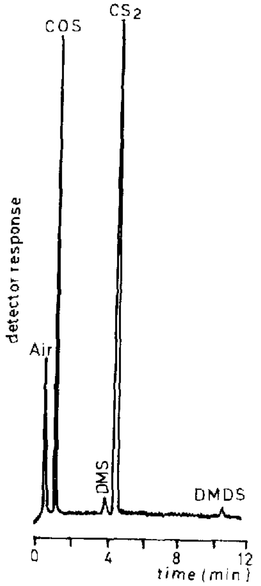


Fig. 6. Gas chromatograms of a standard mixture of H_2S(1), COS(2) and methanethiol(3), each 0.2 nmol and of SO_2 (1.2 nmol). Column temperature: 35°C. Detector attenuation: 10 × 256. (a) Direct injection; (b) injection via concentration on Tenax at −196°C.

Fig. 7. Gas chromatogram of an air sample. Detector attenuation: 1000 × 16 for COS and 1000 × 1 for dimethyl sulphide (DMS), CS_2 and dimethyl disulphide (DMDS).

TABLE III

PERCENTAGE RECOVERY OF SULPHUR VOLATILES AFTER STORAGE FOR 1 WEEK AT −196°C ON TENAX TRAP TUBES

Recovery values are the mean ± S.D. of six determinations.

Sulphur volatile	*Recovery (%)*
H_2S	92 ± 16
COS	91 ± 10
CH_3SH	93 ± 7
CH_3CH_2SH	98 ± 11
CH_3SCH_3	100 ± 8

ratio of 2, ranges from 5 pmol for H_2S and COS to 20 pmol for thiol 14, when using the experimental conditions given in Fig. 3b (see Fig. 5). Concentration of sulphur volatiles from 40 l of air onto Tenax at −196°C then results in detection limits in air ranging from 3 ppt for H_2S and COS to 12 ppt for thiol 14. Thse limits can be lowered by concentration of larger amounts of air (see Table II).

A chromatogram of an air sample is given in Fig. 7. Concentration from 40 l of air onto Tenax gave four sulphur compounds in the following concentrations: COS, 0.5 ppb; dimethyl sulphide, 70 ppt; CS_2, 0.3 ppb; dimethyl disulphide, 25 ppt. The air sample was obtained from compressed air normally used in this laboratory. The same four sulphur volatiles were seen in an open air sample. No H_2S was found in these air samples, in contrast with the findings of Black *et al.*[8] and Braman *et al.*[7]. However, Braman *et al.*, preconcentrating sulphur volatiles on gold-coated glass beads, could not distinguish between H_2S, COS and CS_2.

Storage experiments on Tenax trap tubes were performed for the most volatile sulphur compounds: H_2S, COS, methanethiol, ethanethiol and dimethyl sulphide. The volatiles (each 0.5 nmol) were concentrated at −196°C onto Tenax and the trap tubes were stored in liquid nitrogen. The results after storage for 1 week (Table III) show that almost quantitative recoveries were obtained for all the sulphur volatiles studied. These results are very important, *e.g.*, for field analysis where direct analysis is not possible and the trap tubes have to be stored for later analysis.

CONCLUSIONS

A method for the collection and analysis of H_2S, COS, CS_2, thiols, sulphides and disulphides at the ppt level has been developed. It is simple, rapid and free from interferences and gives high recoveries of all sulphur volatiles studied, except SO_2. Cryogenic trapping of air volatiles onto Tenax in combination with drying tubes has not been described before and may be a step forward in the analysis of volatiles, especially at very low levels (ppt).

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