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Note

Determination of hydrogen sulphide by porous-layer open-tubular column gas chromatography–mass spectrometry

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Numerous papers[1–24] have been published on the determination of volatile sulphur compounds such as hydrogen sulphide in various matrices as mouth air, petroleum gases, atmosphere samples and aqueous samples. Generally, volatile sulphur compounds are determined by gas chromatography. Gas chromatographic analyses of, for example, hydrogen sulphide have mainly been carried out using packed columns. The separation of hydrogen sulphide is often performed on packing materials such as Porapak Q, N or QS[1–8]. However, several other packing materials and stationary phases have come into use, *e.g.*, Carbopack[2,9,10], Triton X-305[11,12], Chromosorb P and 102[13,14], Chromosil 330[15], Tenax GC[16], polyphenyl ether[12,17] and various methylsilicone phases[18–20]. The determination of hydrogen sulphide on capillary columns has been performed with non-polar or medium-polarity silicone phases[21–24]. For capillary columns to retain hydrogen sulphide sufficiently to provide separation from air components the columns have to be operated at sub-ambient temperatures. Commonly used detection techniques are flame photometric and thermal conductivity detection, although mass spectrometry has also been used in combination with capillary columns.

Recently, porous-layer open-tubular (PLOT) columns with PoraPLOT Q deposited on the column wall have become commercially available. In this paper we demonstrate the usefulness of such a column interfaced to a mass spectrometer for the headspace analysis of hydrogen sulphide in liquid and solid samples.

EXPERIMENTAL

Gas standards of 10 ppm (standard grade A) and 992 ± 50 ppm hydrogen sulphide were obtained from AGA (Lidingö, Sweden). Sampling and injections were carried out with gas-tight syringes.

A PLOT column 10 m × 0.32 mm I.D. with PoraPLOT Q deposited on the column wall (Chrompak, Middelburg, The Netherlands) was either kept at 40°C or temperature programmed, the linear flow velocity of the carrier gas (helium) being 40 cm/s at 40°C.

The gas chromatograph–mass spectrometer was a Shimadzu (Kyoto, Japan) QP-1000 in the selected ion monitoring (SIM) mode. The ion of m/z 34, corresponding to the molecular ion of H_2S, was monitored. The electron-impact energy was 70 eV and the ion source temperature was 250°C.

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To prevent particles from the column to entering and contaminating the ion source, the PLOT column was connected to the ion source via deactivated fused silica. A piece of deactivated quartz-wool was placed in the low-volume connector between the PLOT column and the fused silica.

For high hydrogen sulphide concentrations (amount of H_2S sampled > 2 ng), ordinary split injection could be used; however, for lower concentrations cryogenic focusing of the headspace sample was necessary. In this work the cryogenic focusing system (Fig. 1) was used throughout. A detailed description of a similar system has been published elsewhere[25]. Briefly, the hydrogen sulphide present in the headspace sample was injected into the dynamic headspace chamber and transferred to a cold trap by a flow of helium (20 ml/min). The cold trap was made of a deactivated fused silica (35 cm × 0.25 mm I.D.). This fused-silica tube was placed inside a U-shaped glass tube (1.6 mm O.D. × 0.7 mm I.D.), which was suspended in a Dewar flask containing liquid nitrogen. Around the glass tube a Kanthal A wire was coiled to achieve rapid heating on reinjection. With use of the cryogenic focusing technique relative large headspace volumes (1–10 ml) could be injected on to the capillary column without the need for splitting.

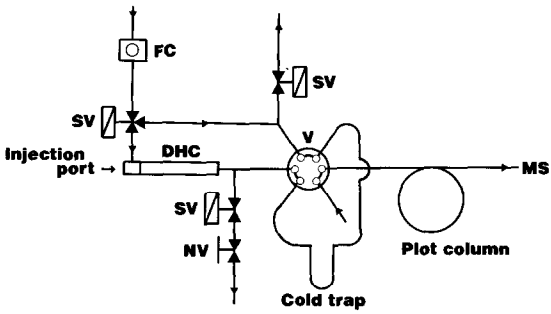

Fig. 1. Schematic diagram of the cold trap–reinjection interface. DHC = Dynamic headspace chamber used as an injector; FC = flow controller; MS = mass spectrometer; NV = needle valve; SV = solenoid valve; V = Valco six-port valve.

Liquid samples were analysed by use of the static headspace method. For quantitative determination, the standard additions technique was used. The sample was equilibrated in a glass vial (9 ml) with a aluminium-coated silicone septum. A known volume of the hydrogen sulphide gas standard was added to the liquid phase of the sample by means of a gas-tight syringe. The headspace of the equilibrated sample was examined by PLOT column gas chromatography–mass spectrometry. As the gaseous hydrogen sulphide was added to the liquid phase, the headspace concentration of hydrogen sulphide incrased with time and reached equilibrium within 60 min (Fig. 2). To simulate standard sample conditions, a liquid phase (N-acetyl-cysteine in water, 25 mg/ml) that had been heat treated at 120°C for 20 minutes prior to the equilibrium study was used.

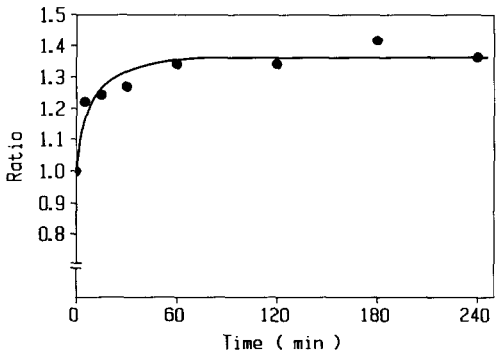

Fig. 2. Headspace concentration of hydrogen sulphide after addition of hydrogen sulphide gas (0.7 μg H_2S) to the aqueous phase (0.5 ml), containing N-acetylcysteine (25 mg/ml). The concentration is given as the ratio of the amount obtained after addition to that obtained prior to addition.

RESULTS AND DISCUSSION

The concept and preparation of PLOT columns are not new and date back to the early days of capillary gas chromatography[26,27]. Theoretically, PLOT columns should take advantage of the selectivity of the adsorbent–solid material deposited as a thin layer on the wall and on the large plate numbers that are generated by capillary columns. However, only recently have PLOT columns become commercially available from various suppliers.

The packing material is deposited on the wall as a layer with a film thickness of 10 μm. This solid layer may be assumed to redistribute on drastic pressure changes, and therefore care must be taken with installation and running the column. Further, in order to prevent particles from the column entering to the ion source, the precautions given under Experimental were employed. Under these conditions, the use of the PLOT column was found to be highly compatible with mass spectrometry. The PLOT column was connected to the mass spectrometer for more than 2 months without any serious contamination of the ion source, *i.e.*, the calibration set parametes for the ion source and the quadropole did not change over that period.

With the cryogenic focusing technique, linear calibration graphs for gas standards of hydrogen sulphide were obtained in the range 0.07–53 ng (Fig. 3). The best determination of hydrogen sulphide was obtained by use of peak height, as peak-area integration became restricted in the lower picogram range owing to less well defined hydrogen sulphide peaks (Fig. 4). Moreover, as can be seen in Fig. 4, the water present in the injection system also had a negative effect on the hydrogen sulphide peak. However, for higher amounts of hydrogen sulphide, the trace level of water present in the injection system did not constitute any problem with respect to peak shape (see Fig. 4C). Hydrogen sulphide is baseline separated from water under equimolar conditions, but a large excess of water distorts the SIM signal of hydrogen sulphide (*m/z* 34). The response of water at *m/z* 34 is attributed mainly to cluster formation. This cluster formation was not studied in any depth, but is probably related to the ion source temperature and pressure, *i.e.*, the amount of water injected. As an illustration, the headspace injection of 8 μg of water through the capillary column gave

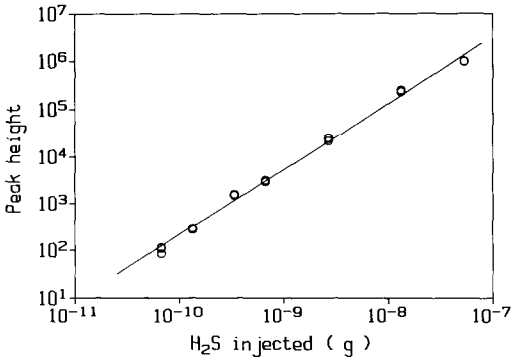

Fig. 3. Calibration graph for gas standards of hydrogen sulphide (r = 0.9994).

a response of the order of 0.01% at m/z 34 relative to that of m/z 18. The precision (relative standard deviation) of the cryogenic focusing method for gaseous standards of hydrogen sulphide was 1.13% at the 53-ng level ($n=5$) and 7.30% at the 0.67-ng level ($n=5$).

As hydrogen sulphide has a low boiling point (−60.7°C) the use of headspace analysis has been explored for the analysis of solid and liquid samples. The applicability of headspace analysis for the determination of hydrogen sulphide in various aqueous samples was studied. As the presence of water may have a negative effect on the SIM signal relating to hydrogen sulphide, the effect of water on the hydrogen sulphide peak was studied by co-injection of various amounts of water. Too large amounts of water (> 10 μg) can cause a decrease in the hydrogen sulphide peak. This restricts the headspace volume that could be sampled and analysed directly over an aqueous sample, *e.g.*, the largest headspace volume to be sampled over an aqueous

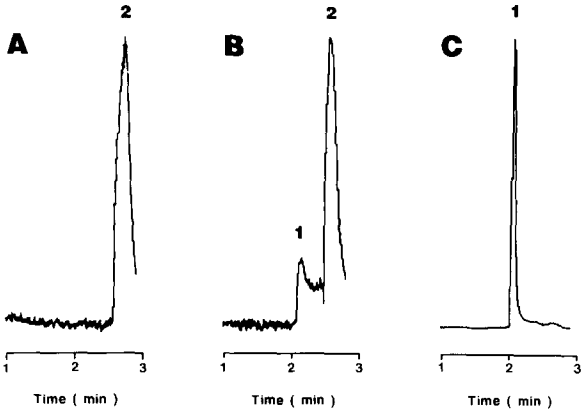

Fig. 4. (A) Blank chromatogram. (B) SIM chromatogram of 70 pg of hydrogen sulphide (peak 1). The peak at a retention time of 2.7 min (peak 2) was caused by water present in the carrier gas of the cryogenic focusing system (and is probably due to cluster formation of water). (C) SIM chromatogram of 3 ng of hydrogen sulphide.

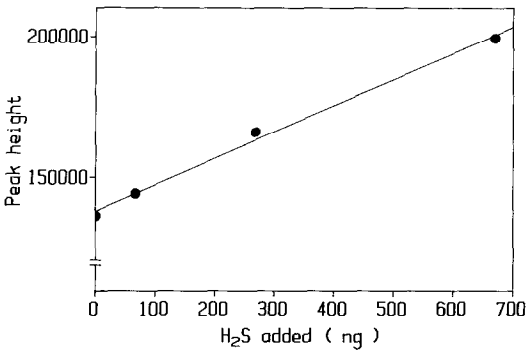

Fig. 5. Standard addition calibration graph. Addition of gaseous hydrogen sulphide to an aqueous sample (1.0 ml) at 25°C.

solution at 25°C and analysed as such is *ca.* 400 μl. Further, this also calls for identical procedures in calibration and analysis of the aqueous sample in order to generate reliable quantitative results. The standard additions method fulfils this criterion. By use of the standard additions method, hydrogen sulphide could be quantitatively determined (Fig. 5).

The precision (relative standard deviation) of the headspace analysis method was 4.4% at a hydrogen sulphide concentration of 1.4 μg/ml in an aqueous sample. The sample was repeatedly analysed five times. With the proposed method, concentrations of hydrogen sulphide in aqueous solutions in the low ng/ml range can be determined with a limit of detection of *ca.* 1 ng/ml (Fig. 6). If greater sensitivity is needed, however, an approach would be to use stripping analysis in combination with the cryogenic focusing device. A prerequisiste of such a method, however, is that water has to be removed prior to the trap, *e.g.*, by calcium chloride[14], in order to prevent plugging of the cold trap.

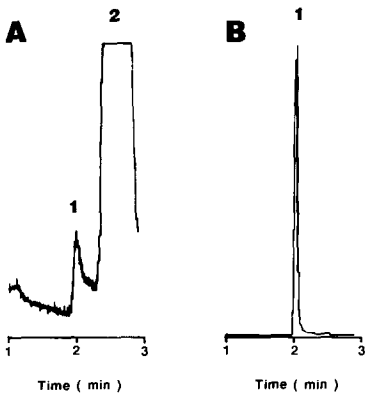

Fig. 6. (A) SIM chromatogram of 1.4 ng/ml of hydrogen sulphide (peak 1) in an aqueous sample (peak 2 = water). (B) SIM chromatogram of 1.6 μg/ml of hydrogen sulphide in an aqueous sample. The equilibrium temperature was 25°C and the headspace volume sampled was 100 μl.

A distinct advantage with the PLOT column is that the sub-ambient column temperatures that are generally needed for capillary column separations of many gaseous and highly volatile compounds can be circumvented. The combination of a PLOT column separation and mass spectrometric detection also provides a highly selective determination of hydrogen sulphide, with a sensitivity comparable to or better than that of flame photometric detection.

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