

CHROM. 17 776

IN SITU GENERATION OF ALKYL SULPHIDES AND ALKYL DISULPHIDES FOR GAS CHROMATOGRAPHIC IDENTIFICATION

TOSHIYUKI HOB0*, KOUICHI ISHIKAWA and SHIGETAKA SUZUKI

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, 2-1-1 Fuka-sawa, Setagaya-ku, Tokyo 158 (Japan)

and

KATSUNORI WATABE

Department of Organic Chemistry, The Weizmann Institute of Science, 76100 Rehovot (Israel)

(Received March 12th, 1985)

SUMMARY

New methods for the generation of alkyl sulphides and alkyl disulphides were developed. Alkyl sulphides were generated by the coinjection of S-alkylisothiurea salts and alkyl sulphates or halogenated alkanes into a precolumn containing sodium hydroxide-impregnated Gas-Chrom R. Alkyl disulphides were generated by a mild oxidation of alkanethiols which were generated by hydrolysis of S-alkylisothiurea salts in the same precolumn. The gas chromatograms of the sulphides generated have proven to be useful aids for their identification.

INTRODUCTION

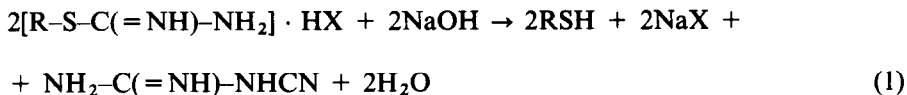
Low-molecular-weight alkyl mono- and disulphides have similar importance to alkanethiols in terms of their abundance and properties. These compounds have an unpleasant odour even at ppm or lower levels. As in the case of alkanethiols, they are produced and introduced into our environment through biological reactions^{1–3}, petroleum refining⁴, oil-shale retorting⁵, pulp milling^{6,7} and other processes^{8,9}. Consequently, there is an increasing need for standards of these compounds in order to accomplish a reliable identification and determination.

Generally, the measurement of these compounds is done by gas chromatography (GC) with flame photometric detection (FPD)^{2,5,8–11}. It is sufficient for quantitative purposes to have at least one standard sulphur compound because the calibration curve constructed by using the standard compound can be applied to other sulphur-containing compounds. On the other hand, for identification it is desirable to have as many standard as possible, even when a gas chromatograph–mass spectrometer is available.

In previous paper¹² we reported a method for the generation of standard alkanethiol gases which could be used for both identification and quantification purposes. It was based on the hydrolysis of S-alkylisothiurea salts by sodium hydroxide.

S-Alkylisothiurea salts are easy to prepare and are stable and odourless. Methane-, ethane- and butanethiols would be quantitatively generated in the range of 10^{-11} to 10^{-9} mol.

The purpose of this study was to extend the alkanethiol method to the generation of alkyl sulphides and alkyl disulphides by slightly changing the procedure. Alkyl disulphides were generated using S-alkylisothiurea salts by successive hydrolysis by sodium hydroxide,



and mild oxidation by coexisting trace oxygen:



Alkyl sulphides were generated by the hydrolysis of S-alkylisothiurea salts, eqn. 1, followed by alkylation using alkyl sulphate or halogenated alkane:



The sulphides could be generated whenever required.

EXPERIMENTAL

Apparatus

The GC system used is shown in Fig. 1. A Shimadzu Model GC-5A gas chromatograph equipped with a flame photometric detector was employed after modification of its carrier gas line. Pure nitrogen gas was used as the carrier gas. Its flow-rate in the valve line was 40 ml min^{-1} and that in the direct line was 30 ml min^{-1} , consequently the flow-rate in the separation column was 70 ml min^{-1} . The conditions

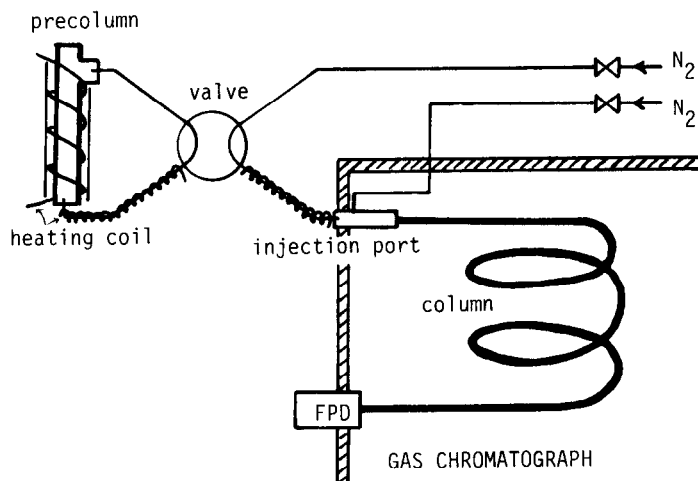


Fig. 1. Schematic flow diagram of the system.

employed for the GC measurement of sulphides were as follows: separation column, glass (1.5 m × 3 mm I.D.) packed with 25% 1,2,3-tris(2-cyanoethoxy)propane-impregnated Chromosorb W AW DMCS (80–100 mesh); column temperature, 65–120°C; flow-rates of hydrogen and air, 45 and 40 ml min⁻¹, respectively.

The reaction precolumn was a Pyrex glass column (10 cm × 6 mm I.D.) packed with sodium hydroxide-impregnated Gas-Chrom R (60–80 mesh) in the first 2 cm. Behind this reaction zone, Gas-Chrom R was packed. The precolumn could be isolated from the carrier gas stream for a certain period so that the reaction time could be controlled.

Reagents and chemicals

S-Methylisothiurea sulphate, S-ethylisothiurea sulphate and S-butylisothiurea hydrogen bromide were prepared as described previously¹². Solutions of these salts in distilled, deionized water were injected into the precolumn.

Dimethyl sulphate (EP grade), diethyl sulphate (EP grade) and 1-bromobutane (GR grade) were purchased from Tokyo Kasei Co. (Tokyo, Japan) and used without further purification. The compounds were dissolved in methanol, and volumes of 1 μl were used in the reaction.

Procedure

In the case of disulphide generation, an aqueous solution of an S-alkylisothiurea salt was injected into the reaction precolumn which was isolated from the carrier gas stream. After a while, the carrier gas was introduced and the products were swept into the separation column.

Alkyl sulphides were generated by coinjecting an aqueous solution of S-alkylisothiurea salts and a methanolic solution of an alkyl sulphate or halogenated alkane into the precolumn which was also isolated from the carrier gas stream. One or two minutes later, the products were transferred into the separation column.

Usually, the injection volume of each solution was 1 μl.

RESULTS AND DISCUSSION

Alkyl disulphide

In the method developed previously for alkanethiol generation it was observed that when the reaction precolumn was isolated from the carrier gas line, even only for several seconds, quantitative generation of thiols did not result. This was thought to be due to the oxidation of the product alkanethiols, *i.e.*, to the formation of disulphides. Fig. 2 illustrates that, for methanethiol, prolonged reaction led to the generation of dimethyl disulphide. When the reaction time was 2 min at 180°C, about 25% of methanethiol was transformed into dimethyl disulphide. It was, however, not possible to generate dimethyl disulphide or other disulphides quantitatively, even using longer reaction times and/or higher reaction temperatures. Therefore, as mentioned above, the following experiments were carried out to generate sulphides only for identification purposes.

Alkyl disulphide mixture

As shown in eqn. 2, one molecule of disulphide was produced from two mole-

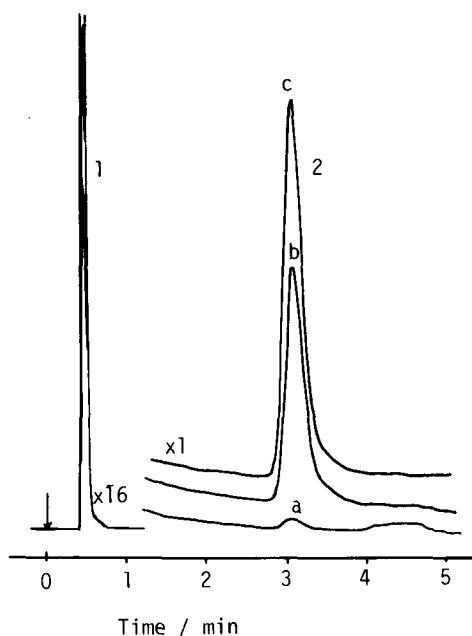


Fig. 2. Effect of reaction time on the generation of dimethyl disulphide. Amount of S-methylisothiouraea sulphate: $2.15 \cdot 10^{-10}$ mol ($1 \mu\text{l}$). Reaction time: a, 0; b, 1; c, 2 min. Reaction temperature: 180°C . Carrier gas flow-rate in separation column: 70 ml min^{-1} . Separation temperature: 80°C . Peaks: 1 = methanethiol; 2 = dimethyl disulphide.

cules of thiol. Therefore, it was thought possible to generate disulphides having different kinds of alkyl groups by mixing two kinds of S-alkylisothiouraea salt. Further, if more than two S-alkylisothiouraea salts were coinjected, disulphides having every possible combination of alkyl groups might be formed. Fig. 3 demonstrates that this was realized in practice.

Alkyl sulphide and alkyl disulphide mixture

As was suggested by eqns. 1–3, a mixture of mono- and disulphides could be generated by coinjecting an S-alkylisothiouraea and an alkyl sulphide or halogenated alkane into the precolumn. As is seen in Fig. 4, when S-methylisothiouraea sulphate was coinjected with dimethyl sulphate, methanethiol, dimethyl sulphide and dimethyl disulphide were the products. The reaction temperature was 200°C , and the reaction time was 1 min.

Reaction conditions

In order to obtain information on the reaction conditions, three factors which were thought to be important were examined by using dimethyl sulphide as a example.

First, the effect of reaction time on the yield was examined. The results obtained at a reaction temperature of 200°C are presented in Fig. 5. It is seen that the reaction proceeds very quickly, and hence reaction times of more than 30 sec do not yield different results. In this case, the ordinate of the figures, corrected peak height,

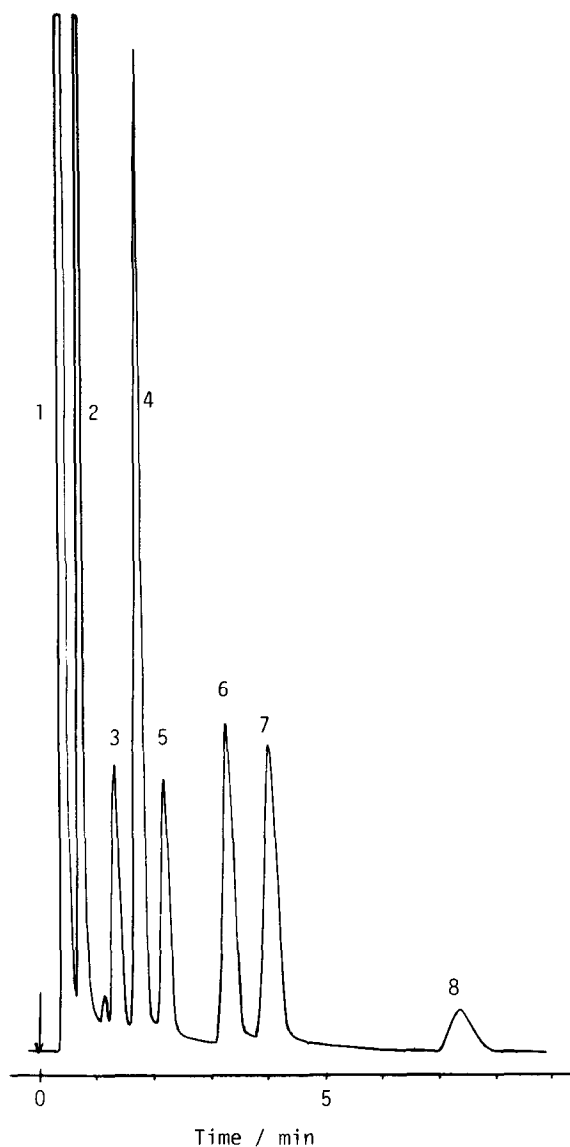


Fig. 3. Gas chromatogram of disulphides generated from a mixture of S-methylisothiurea sulphate, S-ethylisothiurea sulphate and S-butylisothiurea hydrogen bromide (each $1 \cdot 10^{-9}$ mol). Reaction time: 30 sec. Reaction temperature: 210°C . Column temperature: 120°C . Peaks: 1 = methanethiol + ethanethiol; 2 = butanethiol; 3 = dimethyl disulphide; 4 = methyl ethyl disulphide; 5 = diethyl disulphide; 6 = methyl butyl disulphide; 7 = ethyl butyl disulphide; 8 = dibutyl disulphide.

indicates the n th root of the peak height, where n is the slope of the logarithmic plot of the calibration curve.

As for the reaction temperature, an almost constant yield was obtained at temperatures between 180 and 220°C .

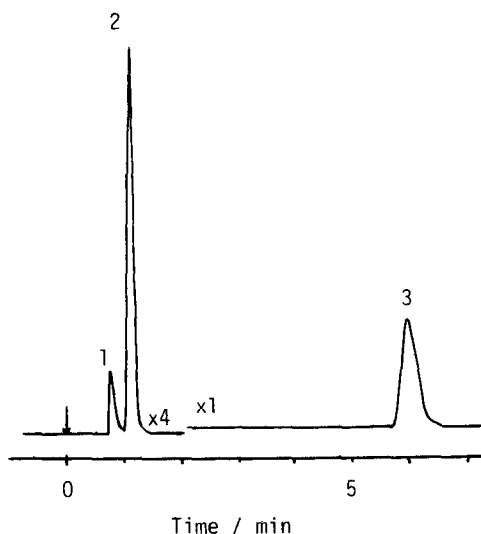


Fig. 4. Typical gas chromatogram of dimethyl sulphide. Amount of S-methylisothiouria sulphate: $5 \cdot 10^{-10}$ mol. Amount of dimethyl sulphate: $1 \cdot 10^{-8}$ mol. Reaction temperature: 200°C . Reaction time: 1 min. Column temperature: 65°C . Peaks: 1 = methanethiol; 2 = dimethyl sulphide; 3 = dimethyl disulphide.

The effect of the amount of dimethyl sulphate on the peak height of dimethyl sulphide was also investigated. Fig. 6 shows that the minimum amount of dimethyl sulphate needed was about ten times that of S-methylisothiouria sulphate. The maximum yield was obtained when ≥ 100 times more dimethyl sulphate than S-methylisothiouria sulphate was injected.

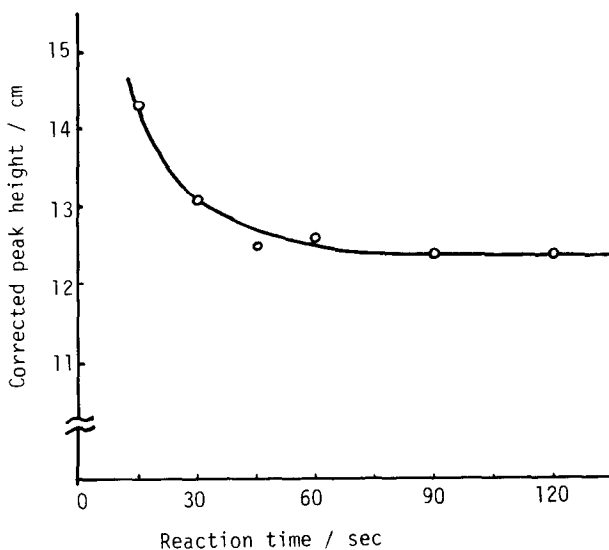


Fig. 5. Effect of reaction time on the amount of dimethyl sulphide produced. Amount of S-methylisothiouria sulphate: $5 \cdot 10^{-10}$ mol. Amount of dimethyl sulphate: $1 \cdot 10^{-8}$ mol. Reaction temperature: 200°C .

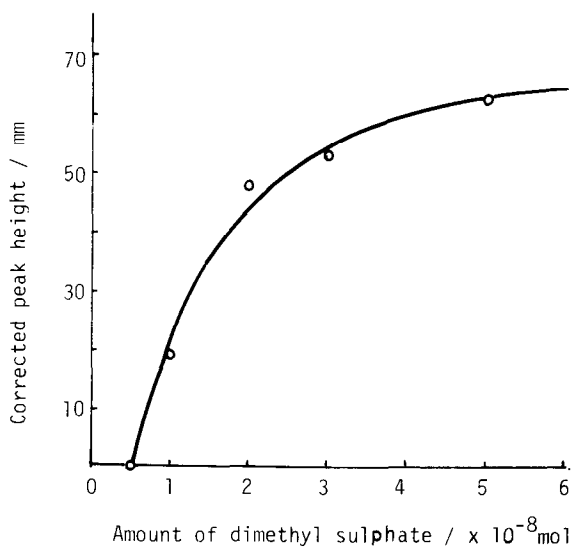


Fig. 6. Effect of dimethyl sulphate amount on the amount of dimethyl sulphide produced. Amount of S-methylisothiurea sulphate: $5 \cdot 10^{-10}$ mol. Reaction temperature: 200°C. Reaction time: 30 sec.

Figs. 7–10 show typical chromatograms of alkyl sulphides and alkyl disulphides generated under the conditions thought to be favourable. The products in Fig. 7 were obtained from a mixture of alkylating agents, dimethyl sulphate and diethyl sulphate. As shown by eqn. 3, combination of methyl groups, one from S-methyl-

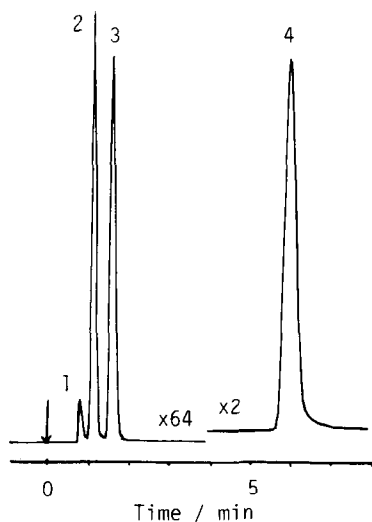


Fig. 7. Products from S-methylisothiurea sulphate ($5 \cdot 10^{-10}$ mol), dimethyl sulphate ($2 \cdot 10^{-8}$ mol) and diethyl sulphate ($5 \cdot 10^{-7}$ mol). Reaction temperature: 200°C. Reaction time: 1 min. Column temperature: 65°C. Peaks: 1 = methanethiol; 2 = dimethyl sulphide; 3 = methyl ethyl sulphide; 4 = dimethyl disulphide.

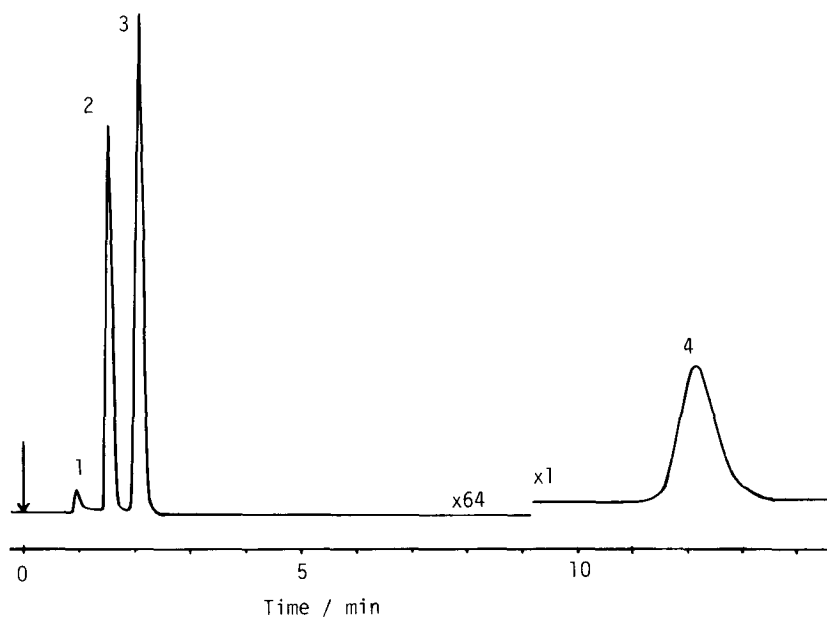


Fig. 8. Products from S-ethylisothiurea sulphate ($5 \cdot 10^{-10}$ mol), dimethyl sulphate ($2 \cdot 10^{-8}$ mol) and diethyl sulphate ($5 \cdot 10^{-7}$ mol). Conditions as in Fig. 7. Peaks: 1 = ethanethiol; 2 = methyl ethyl sulphide; 3 = diethyl sulphide; 4 = diethyl disulphide.

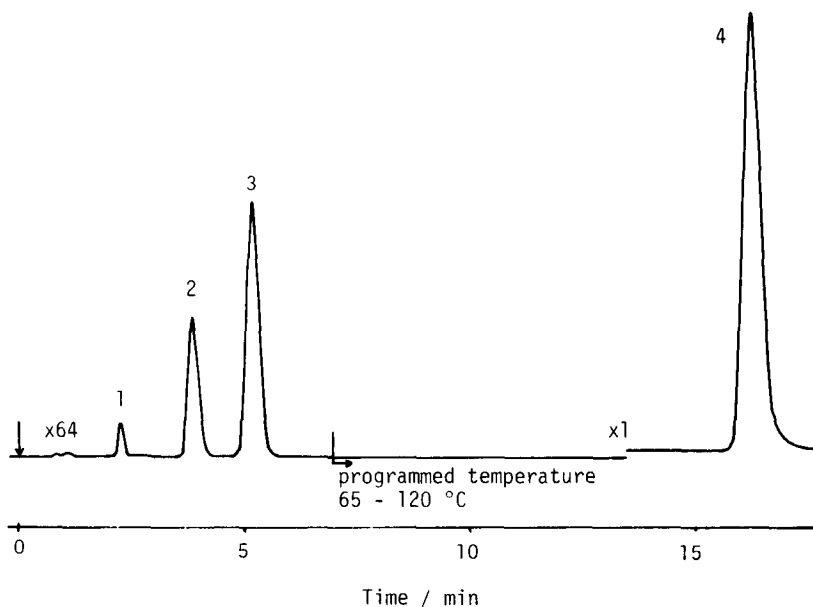


Fig. 9. Products from S-butyliothiurea hydrogen bromide ($1 \cdot 10^{-9}$ mol), dimethyl sulphate ($2 \cdot 10^{-8}$ mol) and diethyl sulphate ($5 \cdot 10^{-7}$ mol). Reaction temperature: 210°C . Reaction time: 1 min. Peaks: 1 = butanethiol; 2 = methyl butyl sulphide; 3 = ethyl butyl sulphide; 4 = dibutyl disulphide.

isothioureia sulphate and one from dimethyl sulphate, gives dimethyl sulphide, and combination of a methyl group from S-methylisothioureia sulphate and an ethyl group from diethyl sulphate gives methyl ethyl sulphide.

Similarly, a mixture of ethyl methyl and diethyl sulphides was obtained (Fig. 8) by coinjecting S-ethylisothioureia sulphate, dimethyl sulphate and diethyl sulphate. It is important to note that the formation of diethyl sulphide and diethyl disulphide in the former case (Fig. 7) and dimethyl sulphide and dimethyl disulphide in the latter case (Fig. 8) did not take place. Exactly the same explanation could be applied to the results shown in Figs. 9 and 10.

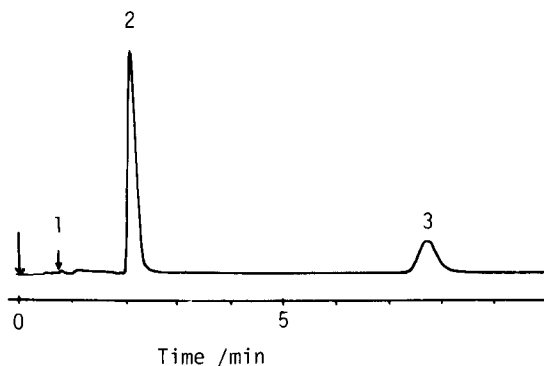


Fig. 10. Products from S-butylisothioureia hydrogen bromide ($1 \cdot 10^{-10}$ mol) and butyl bromide ($1 \cdot 10^{-6}$ mol). Reaction temperature: 210°C . Reaction time: 1 min. Column temperature: 120°C . Peaks: 1 = butanethiol; 2 = dibutyl sulphide; 3 = dibutyl disulphide.

CONCLUSION

It is possible to generate minute but sufficient amounts of alkyl sulphides and alkyl disulphides whenever required, although their yields are not quantitative. One of the advantages of the method is that it utilizes the same parent compounds and reaction system as those used for the generation of alkanethiols. Therefore, when standard sulphur compounds are required for GC analysis with flame photometric detection, the alkanethiols provided by the previously reported method could be utilized for both identification and determination purposes, while the sulphides generated as described above could be used for reliable identification.

REFERENCES

- 1 P. J. Maroulis and A. R. Bandy, *Science (Washington, D.C.)*, 196 (1977) 647.
- 2 D. F. Adams, S. O. Farwell, E. Robinson, M. R. Pack and W. L. Bamesberger, *Environ. Sci. Technol.*, 15 (1981) 1493.
- 3 N. O. Andreae and H. Raemdonck, *Science (Washington, D.C.)*, 221 (1983) 744.
- 4 M. A. Poirier and G. T. Smiley, *J. Chromatogr. Sci.*, 22 (1984) 304.
- 5 N. E. Hester, Z. C. Mester and Y. G. Wang, *Environ. Sci. Technol.*, 17 (1983) 714.
- 6 D. F. Adams, R. K. Koppe and W. N. Tuttle, *J. Air Pollut. Control Assoc.*, 15 (1965) 31.
- 7 H. W. Bialkowsky and G. G. DeHaas, *Pulp Paper Mag. Canada*, 53 (1952) 99.

- 8 M. S. Smith, A. J. Francis and J. M. Duxbury, *Environ. Sci. Technol.*, 11 (1977) 51.
- 9 P. A. Steudler and W. Kijowski, *Anal. Chem.*, 56 (1984) 1432.
- 10 R. K. Stevens, J. D. Mulik, A. E. O'Keeffe and K. J. Krost, *Anal. Chem.*, 43 (1971) 827.
- 11 S. O. Farwell, S. J. Gluck, W. L. Bamesberger, T. M. Schutte and D. F. Adams, *Anal. Chem.*, 51 (1979) 609.
- 12 K. Ishikawa, T. Hobo, S. Suzuki and K. Watabe, *J. Chromatogr.*, 295 (1984) 445.