Journal of Chromatography, 319 (1985) 187–194
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,289

DETERMINATION OF TRACE LEVELS OF DIMETHYL POLYSULPHIDES BY CAPILLARY GAS CHROMATOGRAPHY

J. E. WAJON*, R. ALEXANDER and R. I. KAGI
School of Applied Chemistry, Western Australian Institute of Technology, Kent St., Bentley, Western Australia 6102 (Australia)
(Received September 13th, 1984)

SUMMARY

Dimethyl di-, tri-, tetra- and pentasulphides were determined quantitatively on a cross-linked methylsilicone fused-silica capillary column with cool on-column injection. Disproportionation and decomposition of dimethyl pentasulphide occurred during chromatography whenever the column temperature exceeded 115°C. Analytical conditions were determined under which decomposition of dimethyl pentasulphide was minimal, sensitivity was high, and analysis time was short. Similar results were obtained with inert vapourizing injectors, but decomposition and disproportionation reactions were observed with active injectors.

INTRODUCTION

In recent years, dimethyl polysulphides ($CH_3S_xCH_3$, x = 2–4) have been reported in such diverse media as food[1–4], beverages[5,6], air[7–13] and water[14–20]. Often their presence has been associated with an objectionable odour as these compounds have distinctive odours even at high dilution. Almost invariably, determination of these compounds has been carried out using gas chromatography (GC). Analysis of trace amounts of sulphur compounds by GC has often been difficult because many are thermally labile[21,22], light sensitive[23] or reactive towards metal, glass, the column phase or the support[5,24–29]. Current techniques of capillary GC with fused-silica columns avoid many of these problems because the analyte does not contact metal surfaces and because the capillary columns are extremely inert.

Concern has been expressed about the stability of dimethyl polysulphides during analysis using GC because of the high temperatures usually employed to vapourize the sample[30,31]. The dimethyl polysulphides containing three or more sulphur atoms are unstable at relatively low temperatures, the characteristic reaction being disproportionation to yield mixtures of polysulphides of varying sulphur chain length[1,21,30,32–35]. The ease with which this occurs increases with increasing sulphur chain length[21,33]. For example, dimethyl pentasulphide is so unstable that all reported attempts to purify it by distillation have resulted in the formation of dimethyl trisulphide[21]. Dimethyl tetrasulphide thermally disproportionates into dimethyl di-,

0021-9673/85/$03.30

tri-, penta- and hexasulphides with a half-life of 0.5 sec at 170°C and 5 h at 80°C[30,33,34]. Dimethyl trisulphide also disproportionates into dimethyl di-, tetra-, penta- and hexasulphides, though more slowly, with a half-life of more than 8 weeks at 80°C[33]. Dimethyl polysulphides undergo similar disproportionation reactions at room temperature under the influence of UV light or sunlight[23,36]. They are also unstable in the presence of bases and nucleophiles[23,30,31], suggesting that exposure to active sites with such properties in GC injectors or columns may promote decomposition.

Reports of analyses of dimethyl polysulphides by GC in which dimethyl penta-, tetra- or trisulphide have been measured[1,2,4,8–12,15,16,18–20,36–38] indicate that the lower homologues (*i.e.* dimethyl tri- and/or disulphide) are often also present[1,2,4,9–12,15,16,18,19,36,37]. In view of the reported thermal and chemical instability of the dimethyl polysulphides, it is conceivable that one or more of these compounds may be artefacts produced by disproportionation during analysis. Bartl *et al.*[9] and Hagenguth *et al.*[11] have reported that neither dimethyl trisulphide nor dimethyl tetrasulphide is formed in a hot injector by disproportionation of the lower dimethyl polysulphides, but they did not report whether the higher homologues could decompose or disproportionate into the lower homologues.

The decomposition of thermally labile compounds during injection can be avoided by the use of cool on-column injection[39]. In this paper, we report on the analysis of dimethyl polysulphides using capillary GC and on-column injection techniques. Analytical conditions have been established which result in no or minimal decomposition and which enable reliable analysis of dimethyl di-, tri-, tetra- and pentasulphides. The results obtained using this procedure were compared with those obtained using vapourizing injection techniques.

EXPERIMENTAL

Reagents

Dimethyl disulphide (more than 99%) was obtained from Merck (Darmstadt, F.R.G.) and used without further purification. Mixtures of dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS) and dimethyl tetrasulphide (DMTeS) were obtained by adding sodium polysulphide to a solution of methyl iodide and sodium thiosulphate at pH 8 in the presence of formaldehyde[33]. A typical mixture contained 5% dimethyl disulphide, 52% dimethyl trisulphide and 43% dimethyl tetrasulphide by weight, based on GC analysis (see below). After extraction into pentane, pure (more than 99.9%) dimethyl disulphide and dimethyl trisulphide were successfully obtained from these mixtures by fractional distillation at 0.5 mm pressure at temperatures below 100°C. It was not possible to obtain pure dimethyl tetrasulphide; pot temperatures in excess of 130°C were required, and the distillate contained 0.1% dimethyl disulphide, 4% dimethyl trisulphide and 29% dimethyl pentasulphide as well as 67% dimethyl tetrasulphide. The identities of these components were confirmed by GC–MS (see below).

Standard solutions containing 1–2500 ng/μl of the individual dimethyl polysulphides, or mixtures of them, were prepared in dichloromethane (Nanograde; Mallinckrodt, KY, U.S.A.). It should be noted that when these solutions were exposed

to light, the relative proportions of dimethyl penta- and tetrasulphides decreased, whereas that of dimethyl tri- and disulphides increased.

Gas chromatography

A Hewlett-Packard 5880 A gas chromatograph with a flame ionization detector and a Hewlett-Packard 5895 B gas chromatograph–mass spectrometer were used. GC was carried out on a 50 m × 0.22 mm I.D. WCOT BP-1 (cross-linked methylsilicone; SGE, Ringwood, Australia) fused-silica capillary column, and the gas chromatograph–mass spectrometer was fitted with a 50 m × 0.20 mm I.D. WCOT cross-linked methylsilicone (Hewlett-Packard) fused-silica capillary column. Hydrogen was used as the carrier gas at a flow-rate of 40 cm/sec. Nitrogen at 20 ml/min was used as a make-up gas for flame ionization detection (FID). Various temperature programmes were used, and are described in the text. On-column sample introduction (0.2 to 1.0 μl) was carried out at 30°C using an OCI-3 on-column injector (SGE) and samples (1 μl) were also introduced splitless using the standard HP vapourizing injector at temperatures between 140°C and 280°C. The silica liner in the vapourizing injector was deactivated by treatment with BSTFA (Supelco, Bellefonte, PA, U.S.A.) for 1 h at 120°C.

Column and overall system activity were evaluated with a seven-component mixture (Activity Mix A; SGE) containing octanone, octanol, 2,6-dimethyl phenol, 2,4-dimethyl aniline, naphthalene, *n*-C_{12} and *n*-C_{13}. Indications of activity were tailing peaks and/or unequal response from phenol and aniline.

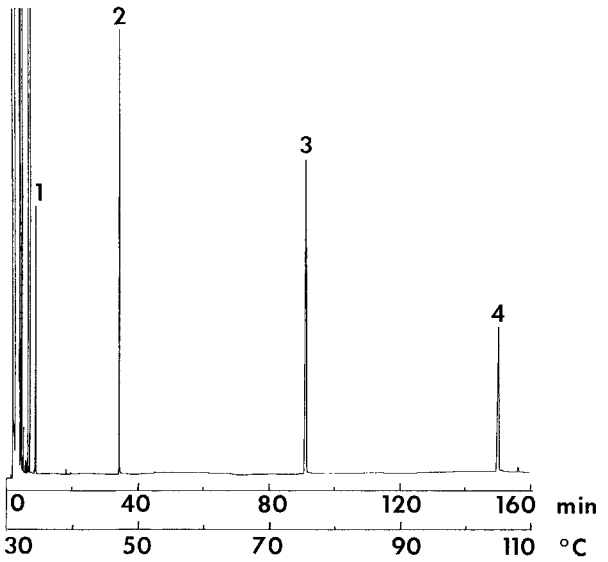

Fig. 1. Gas chromatogram of 1 μl of a mixture of dimethyl polysulphides in dichloromethane solution obtained using on-column injection. Initial temperature 30°C (1 min) followed by temperature programming at 0.5°C/min. Peaks: 1 = dimethyl disulphide; 2 = dimethyl trisulphide; 3 = dimethyl tetrasulphide; 4 = dimethyl pentasulphide.

RESULTS AND DISCUSSION

Chromatography of dimethyl polysulphides with on-column injection

The chromatogram shown in Fig. 1 was obtained from a solution containing dimethyl di-, tri-, tetra- and pentasulphides using a uniform temperature programme rate of 0.5°C/min from an initial value of 30°C. The smooth baseline and symmetrical peaks suggest that no significant disproportionation or decomposition has occurred during the chromatographic process, and that the column is inactive towards these compounds. The assignment of peaks 1–3 in Fig. 1 to dimethyl di-, tri- and tetrasulphide, respectively, was verified by GC–MS analysis. The mass spectra of these compounds have been reported previously[10] and are consistent with those obtained from the compounds represented by peaks 1–3. The mass spectrum shown in Fig. 2 was obtained from the compound represented by peak 4, which eluted after 150 min at a column temperature of 105°C. It is consistent with that expected from dimethyl pentasulphide in that it contains a molecular ion at *m/e* 190 and ions corresponding to loss of S_x and CH_3S_x (x = 1–4) from the molecular ion.

Quantitative analysis of dimethyl polysulphides without decomposition was carried out using the chromatographic conditions just described. However, the time required for analysis of all the dimethyl polysulphides up to dimethyl pentasulphide was extremely long (150 min) and the peaks obtained were so broad that the detection limits for dimethyl tetra- and pentasulphides were high. More rapid analysis obtained with faster temperature programming rates resulted in sharper peaks, but also in decomposition of dimethyl pentasulphide. An extreme example is presented in Fig. 3a which shows a chromatogram obtained from a solution containing dimethyl di-, tri-, tetra- and pentasulphides using a uniform program rate of 4°C/min. Dimethyl tetrasulphide eluted after 26 min at a temperature of 130°C, but a long sloping hump topped by a small peak at 34 min (column temperature 162°C) appeared near where dimethyl pentasulphide was expected to elute. Analysis of the sample by GC–MS showed that the peak at 34 min corresponded to dimethyl pentasulphide, and that the hump was due to varying proportions of dimethyl di-, tri- and tetrasulphide. A discrete peak corresponding to sulphur was also found by GC–MS.

The chromatogram shown in Figure 3b was obtained from a solution containing dimethyl polysulphides using a temperature programme in which a temperature of 90°C reached at 4°C/min was followed by a 1°C/min rise to 130°C. Dimethyl

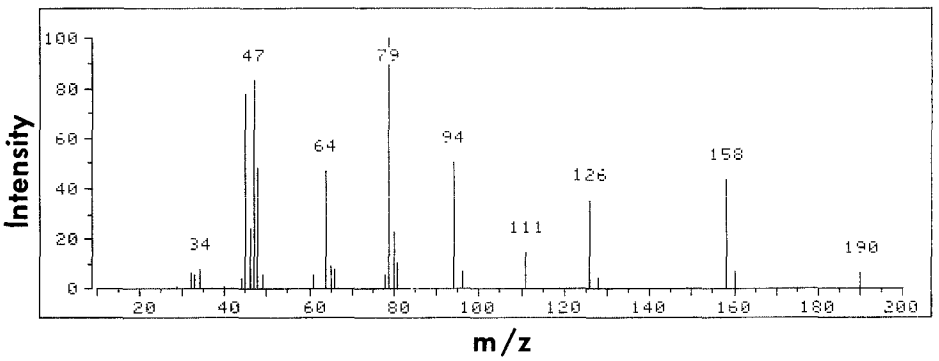

Fig. 2. Mass spectrum (70 eV electron impact) of dimethyl pentasulphide.

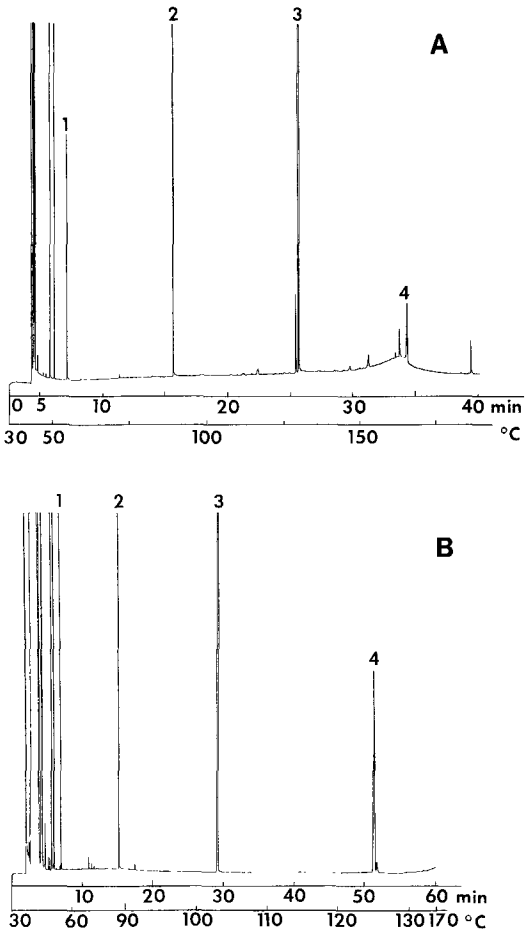

Fig. 3. Gas chromatogram of 1 μl of a mixture of dimethyl polysulphides in dichloromethane solution obtained using on-column injection. (a) Initial temperature 30°C (1 min) followed by temperature programming at 4°C/min. Peaks as in Fig. 1. (b) Initial temperature 30°C (1 min) followed by temperature programming to 90°C at 4°C/min, then to 130°C at 1°C/min and then to 280°C at 10°C/min. Peaks as in Fig. 1.

pentasulphide eluted after 53 min at a column temperature of 127°C, and by comparison with a chromatogram obtained using a uniform temperature programme rate of 0.5°C/min, it appeared that *ca.* 15% dimethyl pentasulphide had decomposed.

The detection limits for dimethyl di-, tri-, tetra- and pentasulphide under these conditions were 0.05, 0.15, 0.4 and 1.4 ng, respectively. These were the lowest detection limits obtained with any temperature programme, and were the result of a compromise between peak broadness and loss of dimethyl pentasulphide by decomposition at column temperatures above 115°C. Without pure standards of dimethyl tetra- and pentasulphide, quantitation of these compounds was based on the proportionality between FID response and carbon content. This relationship was shown to be valid for dimethyl di- and trisulphide.

Stability of dimethyl polysulphides in vapourizing injectors

It was found that, provided the injector was inactive (as indicated by equal response from 2,6-dimethylphenol and 2,4-dimethylaniline), dimethyl disulphide was not formed when solutions containing dimethyl tri-, tetra- or pentasulphide were introduced into the capillary column using a vapourizing injector at temperatures as high as 280°C. Similarly, dimethyl trisulphide was not formed when solutions containing dimethyl tetra- or pentasulphide were introduced into the column using an inactive injector. These observations complement the work of Bartl *et al.*[9] and Hagenguth *et al.*[11] who showed that neither dimethyl trisulphide nor dimethyl tetrasulphide were formed in the injector from dimethyl disulphide or dimethyl trisulphide, respectively, at temperatures as high as 280°C.

The situation was considerably different, however, when the vapourizing injector was active (as indicated by non-equal response from 2,6-dimethylphenol and 2,4-dimethylaniline). The results presented in Table I were obtained from analysis of solutions containing dimethyl polysulphides by GC using a vapourizing injector with various degrees of activity at a range of temperatures. A dilute solution of dimethyl trisulphide, shown by analysis with on-column injection to contain 1% dimethyl disulphide, apparently contained 2–11% dimethyl disulphide when analysed using an active vapourizing injector. The total mass of dimethyl polysulphides determined when using a vapourizing injector was only 50–80% that of the amount determined when using on-column injection.

The extent of disproportionation of dimethyl trisulphide to dimethyl disulphide and the extent of decomposition of dimethyl polysulphides increased with in-

TABLE I

EFFECTS OF INJECTOR ACTIVITY AND INJECTOR TEMPERATURE UPON ANALYSIS OF DIMETHYL POLYSULPHIDE SOLUTIONS

Injector temperature (°C)	*Activity index**	*Relative percent dimethyl polysulphide***				*Total mass of dimethyl polysulphides****
		DMDS	*DMTS*	*DMTeS*	*DMPeS*	
(a)§						
30§§	1.00	1	99	–	–	1.00
140	1.60	3	97	–	–	0.80
180	1.60	5	95	–	–	0.57
220	1.60	8	92	–	–	0.68
260	1.12	2	98	–	–	0.72
280	2.15	11	89	–	–	0.50
(b)§§§						
30	1.06	6	23	55	16	1.00
140	1.60	7	26	52	15	0.69
220	1.60	8	26	56	10	0.58

* Ratio of 2,6-dimethylphenol to 2,4-dimethylaniline in standard activity mix.

** DMDS = dimethyl disulphide; DMTS = dimethyl trisulphide; DMTeS = dimethyl tetrasulphide; DMPeS = dimethyl pentasulphide.

*** Relative to that obtained with on-column injection.

§ Chromatographic conditions as in Fig. 3a.

§§ On-column injection.

§§§ Chromatographic conditions as in Fig. 1.

creasing temperature and activity of the injector. With a slightly active injector (activity index 1.5–2) at 280°C, up to 10% of any dimethyl trisulphide present can disproportionate into dimethyl disulphide. Disproportionation and decomposition of more complex mixtures of dimethyl polysulphides in active vapourizing injectors tended to increase the proportion of dimethyl di- and trisulphide at the expense of dimethyl tetra- and pentasulphide. The extent of disproportionation and decomposition also increased as the temperature of the injector increased.

Disproportionation of dimethyl polysulphides

The rapid disproportionation of dimethyl pentasulphide to mixtures of dimethyl di-, tri-, and tetrasulphide and sulphur during GC analysis at temperatures greater than 127°C, and the formation of mixtures during attempts to distill dimethyl tetrasulphide, illustrate the relative instability of the dimethyl polysulphides. These processes result from a relatively weak sulphur–sulphur bond whose strength decreases as the sulphur chain length increases[30], so that homolysis of S–S bonds in $CH_3S_xCH_3$ (x = 2–5) through the action of heat or UV radiation occurs readily. The resulting CH_3S_{x-n} (n = 1–x) radicals[30,33,36] can recombine to form the complete array of dimethyl polysulphides, and can also eliminate sulphur, resulting in the formation of elemental sulphur. Apparently, however, the rate of disproportionation/decomposition of dimethyl polysulphides is sufficiently low in an inactive vapourizing injector at 280°C that no disproportionation occurs. Measurable disproportionation/decomposition only occurs when dimethyl polysulphides are exposed to high temperature for a longer time, such as in a distillation column[21], sealed vials[30,33,34], or a capillary column, or are exposed to a hot active surface, such as an active vapourizing injector.

CONCLUSIONS

Dimethyl di-, tri-, and tetrasulphide may be determined quantitatively by GC using cool on-column injection, or vapourizing injection with an inactive injector. Decomposition and disproportionation may occur in active vapourizing injectors. Quantitative determination of dimethyl pentasulphide on a cross-linked methyl silicone column additionally requires that the column temperature not exceed 115°C before dimethyl pentasulphide elutes.

ACKNOWLEDGEMENT

This work was supported by funds from the Metropolitan Water Authority, Perth, Western Australia, Australia.

REFERENCES

1 D. M. Oaks, H. Hartman and K. P. Dimick, *Anal. Chem.*, 36 (1964) 1560.
2 A. Miller, R. A. Scanlan, J. S. Lee and L. M. Libbey, *Appl. Microbiol.*, 26 (1973) 18.
3 L. Schutte, in T. E. Furia and N. Bellanca (Editors), *Fenaroli's Handbook of Flavour Ingredients*, CRC Press, Cleveland, OH, 2nd ed., 1975, p. 132.
4 F. B. Whitfield, D. J. Freeman and P. A. Bannister, *Chem. Ind.*, (1981) 692.
5 P. Ronkainen, J. Denslow and O. Leppanen, *J. Chromatogr. Sci.*, 11 (1973) 394.

6 O. A. Leppanen, J. Denslow and P. P. Ronkainen, *J. Agr. Food Chem.*, 28 (1980) 359.
7 A. G. Vitenberg, L. M. Kuznetsova, I. C. Butaeva and M. D. Inshakov, *Anal. Chem.*, 49 (1977) 128.
8 M. Hangartner, *Int. J. Environ. Anal. Chem.*, 6 (1979) 161.
9 P. Bartl, A. Schaaff and A. Zeman, *GWF-Wasser/Abwasser*, 120 (1979) 269.
10 W. A. Konig, K. Ludwig, S. Sievers, M. Rinken, K. H. Stolting and W. Gunther, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 415.
11 H. Hagenguth, H. Teichmann and A. Zeman, *GWF-Wasser/Abwasser*, 122 (1981) 263.
12 H. R. van Langenhove, F. A. van Wassenhove, J. K. Coppin, M. R. van Acker and N. M. Schamp, *Environ. Sci. Technol.*, 16 (1982) 883.
13 A. Zeman and K. Koch, *Int. J. Mass Spectrom. Ion Phys.*, 48 (1983) 291.
14 R. A. Rasmussen, *Tellus*, 26 (1974) 254.
15 K. Grob and G. Grob, *J. Chromatogr.*, 90 (1974) 303.
16 R. P. Schwarzenbach, R. M. Bromund, P. M. Gschwend and O. C. Zafiriou, *Org. Geochem.*, 1 (1978) 93.
17 D. F. Adams, S. O. Farwell, E. Robinson, M. R. Pack and W. L. Bamesberger, *Environ. Sci. Technol.*, 15 (1981) 1493.
18 P. M. Gschwend, O. C. Zafiriou, R. F. C. Mantoura, R. P. Schwarzenbach and R. B. Gagosian, *Environ. Sci. Technol.*, 16 (1982) 31.
19 R. F. C. Mantoura, P. M. Gschwend, O. C. Zafiriou and K. R. Clarke, *Environ. Sci. Technol.*, 16 (1982) 38.
20 J. E. Wajon, R. Alexander, R. I. Kagi and B. V. Kavanagh, *Chemosphere*, submitted for publication.
21 E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Co., New York, 1960, vol. 3.
22 R. W. Hiley and A. Cameron, *J. Chromatogr.*, 107 (1975) 393.
23 S. F. Birch, T. V. Cullum and R. A. Dean, *J. Inst. Petrol.*, 39 (1953) 206.
24 J. W. Gramshaw and A. Hussain, *J. Chromatogr.*, 157 (1978) 267.
25 M. Thompson and M. Stanisavljevic, *Talanta*, 27 (1980) 477.
26 T. L. C. de Souza, D. C. Land and S. P. B. Bhatia, *Anal. Chem.*, 47 (1975) 54.
27 V. B. Stein and R. S. Narang, *Anal. Chem.*, 54 (1982) 991.
28 J. K. Nelson, R. H. Getty and J. W. Birks, *Anal. Chem.*, 55 (1983) 1767.
29 M. O. Andreae and W. R. Barnard, *Anal. Chem.*, 55 (1983) 608.
30 I. Kende, T. L. Pickering and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 87 (1965) 5582.
31 L. McGrath and K. A. Prebble, *J. Appl. Chem. Biotechnol.*, 22 (1972) 811.
32 F. Feher, G. Krause and K. Vogelbruch, *Chem. Ber.*, 90 (1957) 1570.
33 T. L. Pickering, K. J. Saunders and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 89 (1967) 2364.
34 S. Chubachi, P. K. Chatterjee and A. V. Tobolsky, *J. Org. Chem.*, 32 (1967) 1511.
35 D. Grant and J. R. van Wazer, *J. Amer. Chem. Soc.*, 86 (1964) 3012.
36 B. Milligan, D. E. Rivett and W. E. Savige, *Aust. J. Chem.*, 16 (1963) 1020.
37 B. Milligan, B. Saville and J. M. Swan, *J. Chem. Soc.*, (1963) 3608.
38 L. W. Hillen and R. L. Werner, *J. Chromatogr.*, 79 (1973) 318.
39 K. Grob and K. Grob, Jr., *J. Chromatogr.*, 151 (1978) 311.