

CHROM. 18 008

Note

Gas chromatographic and mass spectrometric identification of sulphur gases in kraft digestion plants

JUHANI KANGAS

Kuopio Regional Institute of Occupational Health, Box 93, 70701 Kuopio (Finland)

(First received May 20th, 1985; revised manuscript received June 21st, 1985)

Little information has recently been published on gaseous emissions from the kraft digestion process in work areas. The sulphur gases from kraft digestion plants most often determined are hydrogen sulphide, methanethiol, dimethyl sulphide and dimethyl disulphide^{1,2}. Small amounts of 1-methylethanethiol and thiophene have also been analyzed in condensates³. The formation of 1-methylethanethiol and isopropyl sulphide occurs when eucalyptus chips are been used as a raw material in kraft digestion⁴. The main source of the sulphur gas emissions in digester plants are leaks in condensers, pumps and pipe seals¹.

In previous studies, identification of the sulphur compounds was by use of gas chromatography (GC)^{1,2}. The purpose of this study was to identify non-condensable sulphur compounds emitted in kraft digestion by use of gas chromatography–mass spectrometry (GC–MS).

MATERIALS AND METHODS

Samples were collected at a kraft pulp mill which used pine chips as raw material and a continuous digestion method. Non-condensable gases from the digester were collected after the turpentine condenser. Gases were allowed to pass from the gas line into a 10-l plastic bag. The direct analysis of samples with a mass spectrometer was not successful because nitrogen and oxygen interfered the mass spectrum of hydrogen sulphide and the concentrations of the sulphur gases were too low.

Sample gases were therefore concentrated using a cryogenic enrichment. The cold-traps were immersed in liquid nitrogen and the non-condensable gases collected were evacuated from the primary sampler bag through the trap using MSA pumps at a speed of 0.1 l/min. Sulphur gases condensed in the cold-trap and oxygen and nitrogen were thus excluded. After immersion of the cold-trap into a warm (30°C) water-bath, the expanded sulphur gases were collected in a 1-l plastic bag. High boiling sulphur compounds were extracted from the remainder in the cold-trap with 30 ml diethyl ether.

The samples were analyzed using a Hewlett-Packard 5790A gas chromatograph connected to a Jeol JM5D-300 mass spectrometer. A 25-m silica capillary column containing OV-101 was used. The gas samples were injected with a 0.5-ml gas-tight syringe. The injection-port temperature was 40°C and the oven temperature

was 0°C. Helium was used as a carrier gas at a flow-rate of 1 ml/min. For the analysis of liquid samples the injection-port temperature was 80°C, the oven temperature 60°C and the injection volume was 2 μ l. The mass spectrometer was used to detect the total ion current for the effluents from the column.

RESULTS

Chromatography of the sample evaporated from the cold-trap into the plastic bags yielded three main compounds, and of the sample extracted from the cold-trap

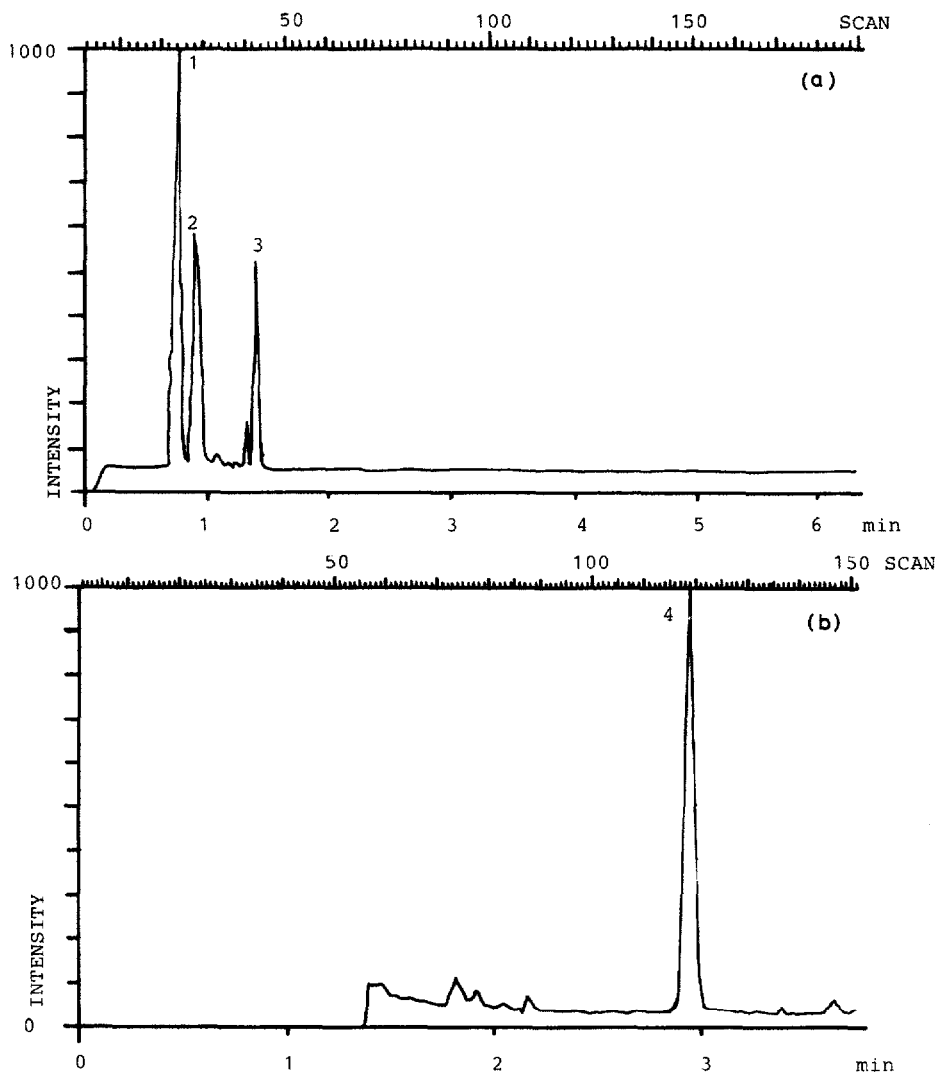


Fig. 1. Gas chromatogram of compounds evaporated from the cold-trap (a) and extracted with diethyl ether (b), recorded as the total ion current. Peaks: 1 = hydrogen sulphide; 2 = methanethiol; 3 = dimethyl sulphide; 4 = dimethyl disulphide.

with diethyl ether, one major compound. The gas chromatograms of both fractions recorded as the total ion current are presented in Fig. 1a and b.

Each compound eluted from the gas chromatograph was fed into the mass spectrometer. From the mass spectrum, hydrogen sulphide, methanethiol, dimethyl sulphide and dimethyl disulphide were identified by comparison with the prominent ions in the mass spectra of standard gases.

DISCUSSION

The sulphur gases emitted upon continuous sulphate cooking of pulp comprise: hydrogen sulphide, methanethiol, dimethyl sulphide and dimethyl disulphide. In this study the raw material used for digestion was pine chips. Under these conditions no other sulphur compounds were found among the non-condensable gases after the turpentine condenser. During the monitoring of industrial hygiene in a kraft pulp mill employing a continuous cooking system, only these four sulphur gases need be analyzed and among them hydrogen sulphide and methanethiol are of chief interest.

For successful mass spectrometric analysis of light sulphur compounds, the removal of oxygen and nitrogen is essential, because they may mask hydrogen sulphide.

REFERENCES

- 1 J. Kangas, P. Jäppinen and H. Savolainen, *Am. Ind. Hyg. Assoc. J.*, 45 (1984) 787.
- 2 J. M. Leach and L. T. K. Chung, *Tappi*, 65 (1982) 95.
- 3 B. R. Blackwell, W. B. MacKay, F. E. Murray and W. K. Oldham, *Tappi*, 62 (1979) 33.
- 4 P. O. Bothge and L. Ehrenborg, *Sven. Papperstid.*, 70 (1967) 347.
- 5 S. O. Farwell, S. J. Gluck, W. L. Barnesberger, T. M. Schulte and D. F. Adams, *Anal. Chem.*, 51 (1979) 609.