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Note

Oxidation of thiols within gas chromatographic columns

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Detection difficulties and response abnormalities in the chromatography of sulphur compounds with flame photometric detection (FPD) do not always arise from the detectors themselves. The chromatographic system plays an important rôle. In most cases the troubles can be attributed to system adsorptivity and/or to impurities in gas streams which interfere with the equilibrium of the flame species H, OH, SH, SO, S₂, etc., resulting in alteration of the overall sensitivity^{1,2}. Sometimes other unexpected factors may also have serious consequences. In this paper the oxidation of thiols within chromatographic columns is reported.

EXPERIMENTAL

Apparatus

A Shanghai Model 102G gas chromatograph equipped with a laboratory-made flame photometric detector was used in all experiments. The carrier gas channel of the detector was provided with a quartz lining and PTFE tubings were used for all connections. The detector was operated in S-mode, and its temperature was 100°C. The sample volume was 5 ml. High-purity argon or nitrogen was used as the carrier gas. Chromatographic columns and operational parameters are given in the individual examples.

Materials

The liquid phases were of chromatographic grade. The solid support, Shimalite, was from Shimadzu (Japan). The carrier gas and fuel gas were commercial gases compressed in cylinders. Samples containing methanethiol were diluted in argon or clean air to appropriate concentrations. The diluent air was obtained from the instrument air pipeline and was purified by passing through an highly efficient desulphurizer cartridge.

RESULTS AND DISCUSSION

The problem arose from the determination of methanethiol and dimethyl sulphide in a natural gas sample. A 25% DNP/Shimalite stainless-steel column was operated at 60°C. The sample natural gas was diluted 50 times before injection. While

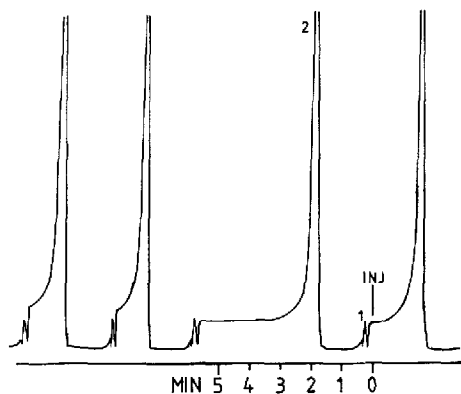


Fig. 1. Effect of sample oxygen on adsorbed methanethiol. Column: 2 m \times 3 mm I.D. stainless steel, 25% DNP on Shimalite, deteriorated owing to prolonged use, 60°C. Sample: methanethiol in clean air. Peaks: 1 = air; 2 = methanethiol.

the average peak height of dimethyl sulphide was unchanged as the diluting gas argon was replaced by clean air, the average peak height of methanethiol was much lower (8 mm against 60 mm for argon).

Another example of the unusual chromatographic behaviour of methanethiol is illustrated in Fig. 1. The sample was methanethiol in clean air. In this case the column had considerable adsorptivity, as shown by the serious tailing of the methanethiol peaks. The elevated baseline to the rear of the peak is obviously due to the gradual release of the adsorbed methanethiol. It is interesting that consecutive injections of air always bring the baseline back to its original position. These facts can be explained by the oxidation of methanethiol and the retardation of the oxidation products within the column.

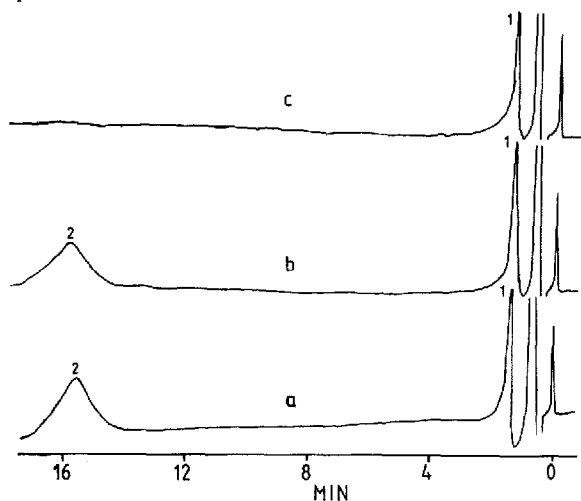


Fig. 2. The influence of solid supports and column materials. Column: 2 m \times 3 mm I.D., 60°C. Sample: methanethiol in clean air. Peaks: 1 = methanethiol; 2 = oxidation product. (a) Stainless steel, 25% TCP on Shimalite; (b) stainless steel, TCP on PTFE powder; (c) PTFE column, 25% TCP on Shimalite.

The oxidation may occur mainly on the surface of the heterogeneous solid support, but this seems to be inconsistent with the result of the present experiments. Fig. 2 gives three chromatograms of a methanethiol sample (in a clean air matrix) obtained on different columns. The sample has been shown to contain no measurable amount of sulphur compounds other than methanethiol. In chromatogram (a) an oxidation product is observed at about 15 min, which is very close to the retention time of dimethyl disulphide. In chromatogram (b) the oxidation product is again present even though the solid support in this case is PTFE powder instead of the heterogeneous Shimalite. When, on the other hand, the column material is changed from stainless steel to PTFE with the solid support unchanged, the oxidation product disappears (Fig. 2c). These results indicate that the oxidation takes place mainly on the metallic column walls.

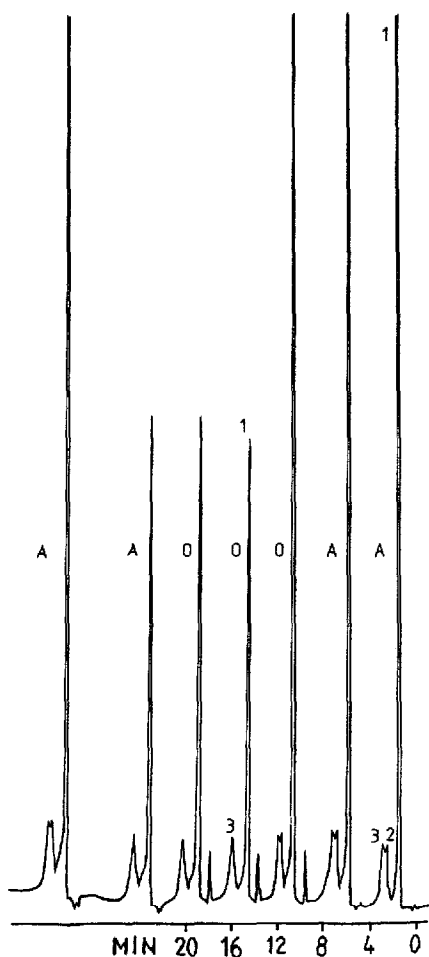


Fig. 3. The influence of diluting gases. Column: 2 m \times 3 mm I.D. stainless steel, 25% DNP on Shimalite, 60°C. Sample: natural gas diluted in argon (A) or air (O). Peaks: 1 = methanethiol; 2 = ethanethiol; 3 = dimethyl sulphide.

In oxidations on metal surfaces, the adsorbed oxygen molecules must first become activated³. The activation and the build-up of activated species on the surface requires a certain time. The injected oxygen, therefore, can not act on the oxidizable materials immediately. The present results show this. Fig. 3 shows seven successive injections of a natural gas sample. In the first two and the last two injections argon was used as the diluting gas, while in the middle three injections clean air was used. The peak height of methanethiol is much higher in the argon matrix, and the peak of ethanethiol can also be detected in this case. The most noteworthy feature of this figure occurs when the diluting gas is changed. Although oxygen was introduced into the column in the third injection and the oxygen would have adsorbed on the column walls before the thiol, there was no sign of thiol oxidation. A decrease in the methanethiol peak height and the disappearance of the ethanethiol peak can be discerned only after the fourth injection. This indicates that it takes time for the adsorbed oxygen molecule to be activated. By comparing the peak heights after the sixth and the seventh injections one can conclude that the active oxygen species exist for some time on the surface after the disappearance of the gas phase oxygen.

Thus, oxidation within chromatographic columns must be considered in the determination of trace amounts of thiols, and it would be of interest to ascertain whether this effect is important with other labile sulphur compounds, such as hydrogen sulphide.

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