

Note

Analysis of sulphur compounds in environmental samples with specific detection and selective columns*

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In recent years, we have published several papers on the determination of gaseous sulphur compounds in air samples¹⁻³ and it was shown that very small amounts of H₂S, SO₂ and CH₃SH could be readily separated and determined by using liquid-modified adsorption columns. The compounds cited are the most common sulphur-containing substances in air samples, but in certain environments other compounds, such as COS, CS₂ and SF₆, can also be found. The last compound is important as it seems that the total amount produced remains in the atmosphere. Further, it is widely used as a tracer in diffusion studies.

Moreover, the detection of sulphur compounds in complex organic mixtures obtained from environmental materials such as water may be difficult because massive amounts of more abundant pollutants can obscure their FID signal.

In this paper, we report some improvements in column technology and the use of a double detection system. Graphitized carbon black (Carbopack B; Supelco, Bellefonte, Pa., U.S.A.) was coated with different amounts of ortho-phosphoric acid and XE-60 in order to improve the selectivity of the column previously described³.

The main use of H₃PO₄ is to deactivate the adsorbent in order to obtain linear elution of SO₂ and H₂S. XE-60 is a cyanosilicone that is a very polar liquid phase but does not form hydrogen bonds. The latter property is important because other polar phases such as polyethylene glycol and FFAP cause a much too high retention of SO₂ and CH₃SH, resulting in a lack of selectivity and tailing of the peaks. XE-60 acts as a deactivant of CH₃SH and SO₂, but retains SF₆ and COS better; in this way, the separation of H₂S and SF₆ is possible.

The relative amount of the two phases is critical, as shown in Fig. 1. Chromatogram (a) was obtained with the column previously used³, with an unsatisfactory separation of COS and SO₂. An increase in the amount of H₃PO₄ relative to XE-60 gives a much better separation of COS and SO₂, but CH₃SH gives a badly skewed peak, as shown in chromatogram (b). The best compromise is achieved by coating the adsorbent with 0.8% of H₃PO₄ and 1.2% of XE-60. In this way, the best separation of SF₆, H₂S, COS and SO₂ is produced. CS₂ is much more retained (about 12 min). A similar separation but with a much lower resolution was obtained by Brenner *et al.*⁴. An interesting feature of chromatogram (c) is that it was obtained at room

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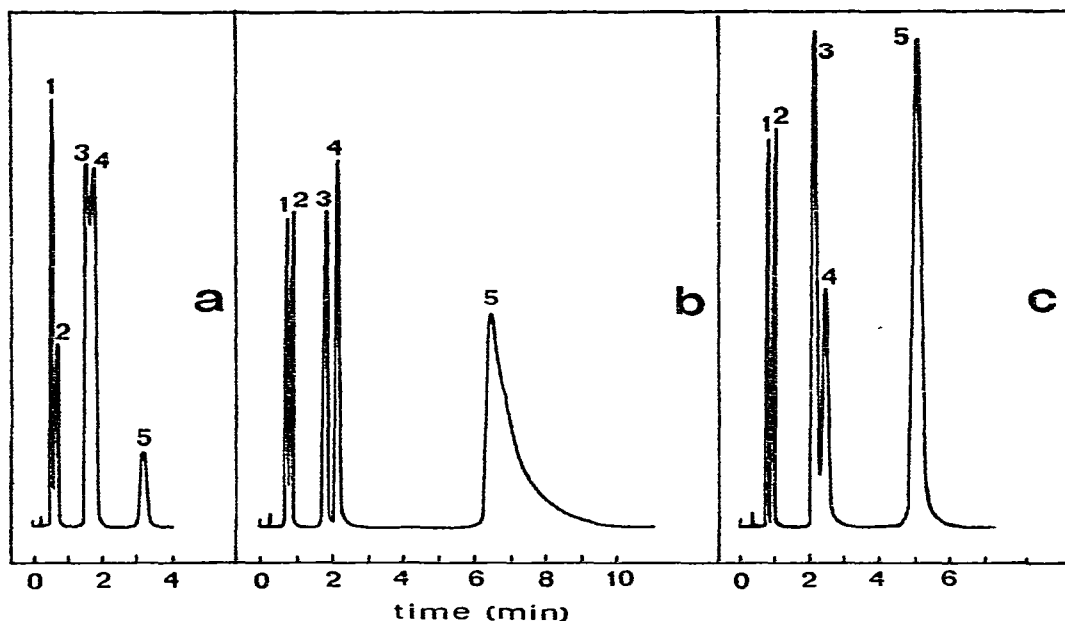


Fig. 1. Effect of relative amounts of the stationary phases on the separation. Glass column, 1.6 m \times 4 mm I.D., pressure, 1.5 kg/cm²; temperature 25°; flow-rate, 80 ml/min. Adsorbent: Carbopack B (60–80 mesh). Carrier gas: nitrogen. Amounts of H₃PO₄: (a) 0.8% (w/w); (b) 3.5% (w/w); (c) 0.8% (w/w). Amounts of XE-60: (a) 0.8% (w/w); (b) 1.2% (w/w); (c) 1.2% (w/w). Peaks: 1, H₂S; 2, SF₆; 3, COS; 4, SO₂; 5, CH₃SH.

temperature, so that the column can be used in a simple apparatus for field measurements. The column material is glass, previously heated at 200° in a stream of dry nitrogen for 2 h before filling it with the column packing. With this procedure, adsorption of sulphur gases, especially SO₂, on the glass walls does not occur, so that PTFE, which yields a poor column efficiency, can be avoided⁶.

The considerable improvement in the results, especially for the rapid identification of sulphur compounds in complex mixtures, is shown in Fig. 2, where a chromatogram of an organic extract from lowland river water is shown. The analysis was carried out using both an FID and an FPD (sulphur mode) for detection^{*}.

The column effluent is split into two streams through a three-way manifold and by means of tubing (0.5 mm I.D., 1.0 mm O.D.) connected to the two detectors. Both detectors are mounted on the top of the gas chromatograph (Carlo Erba, Model GI). The temperatures of the manifold and the tubing are kept slightly above the column temperature, being heated by the detector heating system. A Tracor (Austin, Texas, U.S.A.) FPD detector was mounted, using an electrometer and auxiliary equipment from the same company. Preliminary experiments showed that no loss of chromatographic resolution occurred compared with the single detector system.

The large peak due to the FID signal shown in Fig. 2 represents anthracene

* In this case Carbopack C + 1.2% FFAP was used; such a column is preferable when polar, high-boiling compounds have to be separated.

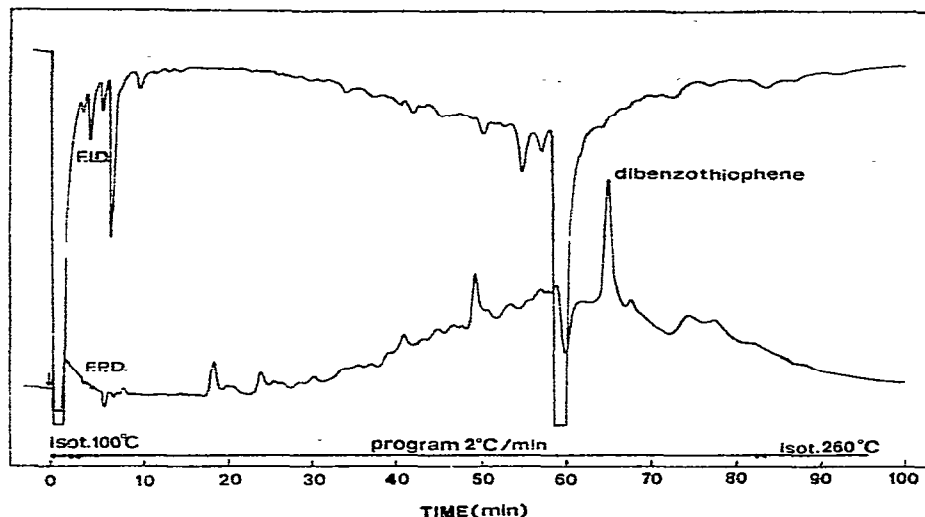


Fig. 2. Double-detection gas chromatogram of lowland river water. Column: 2 m \times 2 mm I.D. Adsorbent: Carbo-pack C (80-100 mesh) + 1.2% FFAP.

and phenanthrene, which give a negative peak in the FPD trace. This result, found also by other workers⁵, is a disadvantage of the specific detector, because a small peak due to a sulphur-containing compound emerging with a retention time the same as that of the larger hydrocarbon peak would not be detected.

However, the great advantage of specific detection is shown by the peak of dibenzothiophene. This compound, which is completely undetected in the FID signal, gives a pronounced peak in the FPD trace. Its structure could be definitely assigned by coupling the double detection system to a GC-MS system and observing the mass spectra in that zone. This could possibly be achieved only with the aid of an on-line computer system, which is presently not available in our laboratory.

In fact, the intensity of the spectrum is low, and only by knowing that in that particular zone of the chromatogram the spectrum of a sulphur compound should be present could it be possible to recognize it even though it is partially masked by more abundant compounds.

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