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Note

Gas chromatographic method for the determination of elemental sulphur in sediments

CSABA HEIM and ISTVÁN DÉVAI

Waterworks of Hajdu-Bihar County, Hétvezér street 21, H-4034 Debrecen (Hungary)

and

JÁNOS HARANGI*

Institute of Biochemistry, L. Kossuth University, P.O. Box 55, H-4010 Debrecen (Hungary)

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The chlorinated hydrocarbon content of sediments of Lake Balaton, the river Zala (Hungary) and some open-air waste water cleaning equipment (so-called BMKO systems^{1,2}) was measured by gas chromatography for environmental protection purposes. In these examinations a large, broad peak with a retention time similar to that of aldrin occurred on the chromatogram of the hexane eluate from the column chromatographic cleaning method³ of the extracts of sediments. In agreement with earlier gas chromatographic results⁴ this peak was assigned to elemental sulphur by mass spectrometry⁵.

The geochemical and hyrobiological importance of the occurrence of elemental sulphur in high concentrations (sometimes higher than 10 g/kg dry sediment) in sediments of lakes, rivers and open-air waste water cleaning systems has been previously reported. Attention was drawn to the possibility of a more significant sulphur circulation which may be the cause of the high sulphur concentrations of sediments. This possibility can vary the importance of sulphur as compared to that of the other elements of sediments⁵.

The above considerations prompted us to examine the sulphur circulation, the qualitative and quantitative determination of sulphur compounds arising from various types of sediments and also the bacterial background of the transformations. In the first phase of this work a method was required for determining small amounts of sulphur in the presence of large amounts of other sulphur compounds (sulphides, sulphites, and sulphates). These requirements excluded the application of classic analytical methods⁶ for the measurement of the sulphur content of sediments, so it was necessary to search for an alternative sensitive and selective method.

Several papers on the chromatographic determination of sulphur-containing compounds, based on various principles, have appeared in recent years. Hydrogen sulphide, carbonyl sulphide, methanethiol and thiophene can be measured by gas chromatography on a packed non-polar column with flame photometric detection⁷⁻⁹. The Hall detector has been suggested for the detection of sulphur-containing compounds, as it has a larger linear range and higher sensitivity than the flame photometric detector¹⁰.

For determining of the total sulphur content the sulphur derivatives are converted into sulphur dioxide, which is measured⁹, or, for organic sulphur compounds, the mixture is catalytically hydrogenated and the sulphur content is calculated from the ratio of the methane and hydrogen sulphide formed¹¹. There are only a few papers on the gas chromatography of elemental sulphur, possibly because below 800°C sulphur forms several different molecules. At about 150°C the ring-type sulphur molecules, with eight sulphur atoms, open and form chain-like molecules of various lengths, the longest one existing at 187°C¹². The sulphur does not appear in a chromatographically homogeneous form, as was shown by Chen *et al.*¹³ by extracting sulphur from marine sediments with various solvents and measuring elemental sulphur by gas chromatography. Several peaks were observed that could be ascribed to the molecular forms S₂-S₈.

In our study of sulphur circulation, and primarily the examination of elemental sulphur, the first difficulty was the lack of a reproducible and sensitive quantitative method applicable for serial determinations. Gas chromatographic measurements of elemental sulphur with electron-capture detection were also unsuccessful. The peaks assignable to the different forms of elemental sulphur were not separable on any stationary phase at any temperature. Methylation and ethylation reactions of elemental sulphur were unsuccessful as the reaction was not reproducible and the alkylation yield was very low.

After these unsuccessful experiments we developed a rapid, reproducible gas chromatographic method for the determination of the elemental sulphur content of sediments.

EXPERIMENTAL

Materials

Anhydrous sodium sulphate, Kieselgel 60 (0.2-0.5 mm) activated at 200°C for 12 h, precipitated sulphur (Reanal, Budapest, Hungary), *n*-hexane (Merck, Darmstadt, F.R.G.) and Porapak Q (80-100 mesh) (Waters Assoc., Milford, MA, U.S.A.) were used. All reagents were of analytical-reagent grade.

Apparatus

A Hewlett-Packard 5840A gas chromatograph, equipped with a 1.8 m × 2 mm I.D. stainless-steel column packed with Porapak Q (80-100 mesh) and a thermal conductivity detector, was used. The carrier gas (hydrogen) flow-rate was 5 ml min⁻¹, the injector temperature was 400°C, the oven temperature was held at 60°C for 4 min then increased to 200°C at 20°C min⁻¹ and the detector temperature was 100°C.

Preparation of sample

For the extraction of sulphur from sediments various solvents were used, but *n*-hexane proved to be the best and is also convenient in the subsequent clean-up procedure. The extraction has to be made from a fresh, original and not dried sediment sample, because during drying the sulphur could be oxidized in air. For extraction a 5-25-g sediment sample (the amount depends on the sulphur content) was homogenized with anhydrous sodium sulphate to give a sand consistency. The sample was extracted with four 40-ml volumes of *n*-hexane on a shaking machine for 45-45

min. To obtain a higher extraction yield the third extraction step was prolonged overnight. The yield of this extraction of elemental sulphur was 98–99%, which was checked by repeated extraction. After the second extraction we could measure only 1–2% of the sulphur concentration measured after the first extraction.

The solvent was decanted and evaporated to about 1 ml with a vacuum evaporator. As this procedure removes some other components (non-polar organic compounds), it is necessary to clean the extract. This clean-up was carried out on a silica gel column (5 × 4 cm I.D.). The extract was washed into the column and eluted with 150 ml of *n*-hexane. The chlorinated hydrocarbon components, adsorbed on the silica gel, could be eluted with benzene and used in pesticide analysis. The *n*-hexane eluate was evaporated and the final volume was adjusted to 1–5 ml, depending on the amount of sulphur. The concentration of sulphur should be in a range corresponding to the linear range of the detector sensitivity. In the extraction procedure oxygen-free *n*-hexane was used, deoxygenation being effected by bubbling carbon dioxide, and the flasks were filled with carbon dioxide to prevent oxidation.

A flow diagram of the sample preparation is shown in Fig. 1.

RESULTS AND DISCUSSION

The gas chromatographic analysis of elemental sulphur is based on the formation of hydrogen sulphide from sulphur in a hydrogen atmosphere below 300°C.

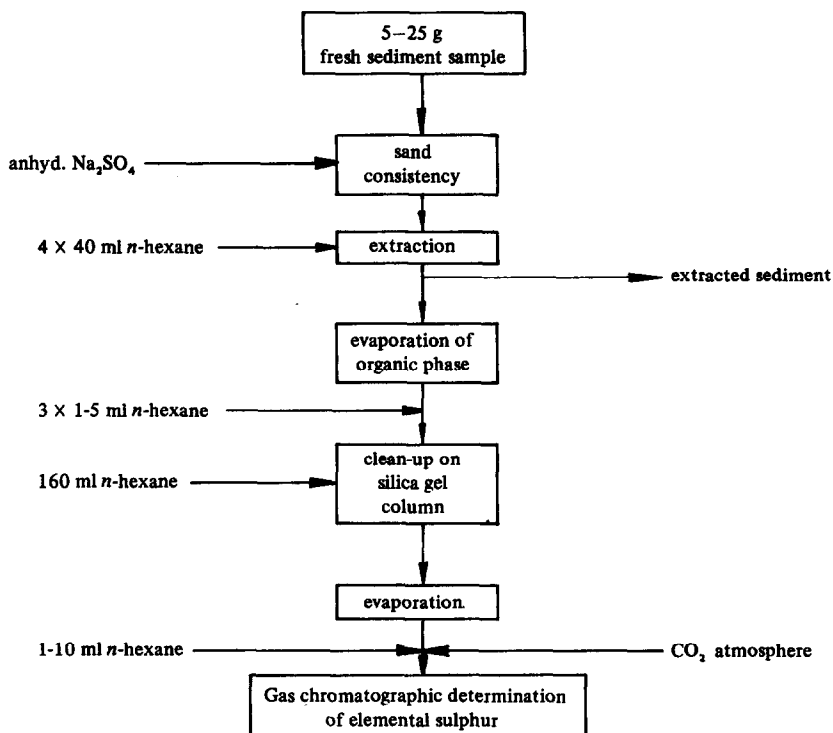
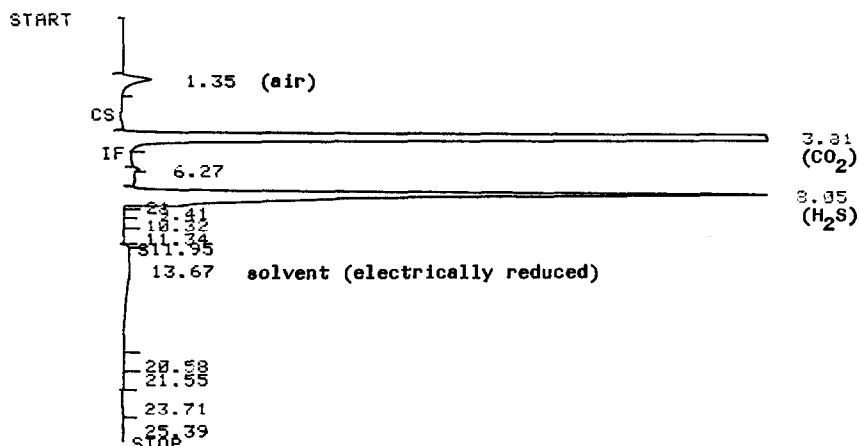


Fig. 1. Flow diagram of the procedure for the determination of the elemental sulphur content of sediments.



HP RUN # 76 SEP/13/83 TIME 13:47:32
 ESTD

RT	EXP RT	AREA	CAL #	AMT
8.05	8.05	404100	(R) 1	20.992

DIL FACTOR: 1.0000 E+ 0

Fig. 2. Gas chromatogram obtained after injection of 20 μg of sulphur.

In the proposed method, this reaction is accomplished in the injection port of the gas chromatograph at 400°C in hydrogen as the carrier gas. To achieve complete recovery, the injection port was filled with glass-wool (large reaction surface) and the carrier gas flow-rate was low (longer reaction time). The application of a carbon dioxide atmosphere in the extraction procedure prevents the oxidation of finely distributed sulphur, and the *n*-hexane used for extraction should be oxygen-free. Under these conditions 99% of the injected sulphur will be converted into hydrogen sulphide; this was checked by calibration of the detector response by the injection of hydrogen sulphide gas. According to our experiments, the linear range of the thermal conductivity detector is 5–30 μg of sulphur. The chromatogram of a 20 μg sulphur sample is shown in Fig. 2. The calibration was effected in the range 1–50 μg .

The elemental sulphur content of various samples can also be determined with this simple, rapid and reproducible method in the presence of other sulphur compounds. The different forms of the sulphur molecules do not affect the results. The method is suggested for use particularly in the determination of the elemental sulphur concentration of sediments and other multicomponent samples in environmental examinations.

Using this method, the elemental sulphur content of the sediment of Lake Balaton (Keszthely basin) was determined and the results of seven measurements on the same sample were as follows (all values in mg/kg dry sediment): minimal sulphur content, 170.80; maximal sulphur content, 186.20; average sulphur content, 179.74; and standard deviation, 5.00.

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