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Note

Gas–liquid chromatographic determination of zinc, copper and nickel in marine bottom sediments

ALEKSANDER RADECKI, JAN HALKIEWICZ, JANUSZ GRZYBOWSKI and HENRYK LAMPARCZYK

Institute of Chemistry and Analytics, Medical Academy, 80-416 Gdańsk (Poland)

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The quantitative determination of metals in marine bottom sediments and minerals by means of atomic-absorption spectrophotometry (AAS) has been subject to some problems associated with the necessity for elimination of interferences due to components of the bed and accompanying elements and to the reagents employed. The application of gas–liquid chromatography (GLC) allows complications inherent in the AAS technique to be eliminated and permits the simultaneous assay of a few elements in one sample.

In order for organic metal complexes to be suitable for GLC assay, they should have a high volatility and a high thermal stability, and a variety of compounds that meet these requirements have been described[1,2]. However, only a few of them have been used in the GLC assay of metals. D'Ascenzo and Wendlandt[3] found that certain metal cations form volatile complexes with diethyldithiocarbamate (DEDTC). Masaryk *et al.*[4] separated zinc from nickel by GLC using this reagent and Krupčik *et al.*[5] used it for assaying nickel(II). Cardwell and Desarro[6] separated chromatographically by DEDTC complexes of nickel, palladium, platinum, zinc, cadmium, copper, lead and mercury. Tavlaridis and Neeb[7] carried out a comparative study on the GLC separation of the DEDTC and bis(trifluoroethyl)dithiocarbamates of zinc, nickel, cadmium, antimony and bismuth.

It should be emphasized that all of the studies mentioned were carried out on artificial mixtures of pure reagents and there are no reports of the application of DEDTC to the GLC assay of several elements in real samples except for the determination of arsenic in urine and water by Daughtrey *et al.*[8].

The object of this work was to determine zinc, copper and nickel in marine bottom sediments in the form of their DEDTC complexes.

EXPERIMENTAL

Analysis of standard solutions of the metals

The concentration range of the standard zinc, copper(II) and nickel chloride solutions was 1–1000 μg/cm^3 based on the cations. To remove organic contaminants from the standard solutions, an aliquot was extracted for 1 min with chloroform–acetone (5:2, v/v) in a 250-ml separating funnel and the organic phase was discarded.

To the remaining aqueous phase, 5 ml of 2% sodium diethyldithiocarbamate solution, previously freed from metal impurities by extraction with the chloroform–acetone mixture, were added. The DEDTC complexes of the metals were then extracted for 1 min once with 5 ml and three times with 2 ml of the chloroform–acetone mixture. The combined extracts were evaporated to dryness on a water-bath in a stream of oxygen-free nitrogen. To the dry residue, 100 µl of chloroform were added by means of a microsyringe and 2-µl aliquots were then withdrawn for the GLC assay.

Analysis of bottom sediments

A sample of bottom sediment (1.5 g) was dried for 2 h at 110°, powdered in a vibrational agate mortar, and a 1-g amount (weighed exactly) was treated in a microautoclave (Perkin-Elmer Model 3) with a few drops of redistilled water, 2 ml of concentrated nitric acid and 5 ml of 40% hydrofluoric acid for 30 min at 150°. The solution was cooled, treated with 5 ml of 60% perchloric acid and 5 ml of 40% hydrofluoric acid and then evaporated to white fumes (to remove silicon compounds). The residue was again treated with 40% hydrofluoric acid, evaporated and dried. The dry residue was dissolved in 10 cm^3 of 6 *N* hydrochloric acid. The solution was then transferred into a 250-ml beaker, treated with 2 ml of 30% hydrogen peroxide, heated to 50°, 25 ml of lanthanum(III) chloride solution were added [to co-precipitate iron and manganese; lanthanum(III) concentration 1000 µg/ml], the solution was heated to 60° and an excess of a 25% aquous ammonia solution was added under stirring. The temperature was then increased to 60–70° for 2–3 min and the precipitate was filtered through filter-paper and washed three times with hot ammonia solution. The pH of the filtrate was adjusted to 8 with 6 *N* hydrochloric acid and the solution was transferred into a 500-ml separating funnel. To the aqueous phase, 5 ml of 2% sodium

TABLE I

COLUMNS AND OPERATING CONDITIONS

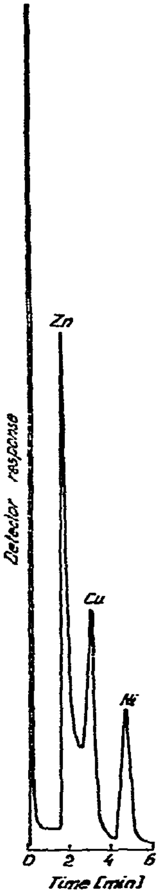
Column No.	*Dimensions (m × mm I.D.)*	*Stationary phase*	*Column temperature (°C)*	*Total plate number (N*)*	*Resolution (R_s*)*
1	1.5 × 4	3% SE-30	Programmed, 240–290° at 10°/min	584.2	0.39
2	1.5 × 2	3% OV-7	280	403.1	0.44
3	1.5 × 2	5% OV-101	Programmed, 200–290° at 10°/min	293.0	0.5
4	3.0 × 2	Tenax (60–80 mesh)	Programmed, 200–290° at 5°/min	238.5	No resolution
5	1.5 × 2	3% SE-30	Programmed, 240–290° at 10°/min	470.4	0.37
6	1.8 × 2	2.5% BBBT	250	234.3	No resolution
7	1.5 × 2	5% QF-1	235	558.5	0.80

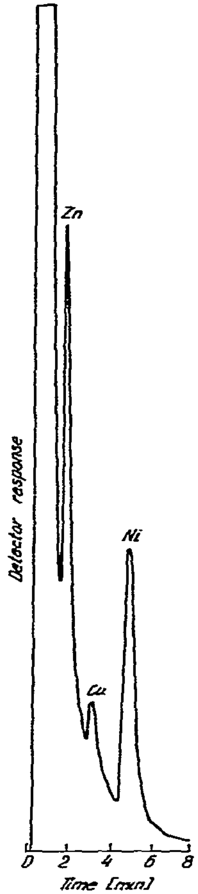
* The values of *N* and R_s were calculated according to Grushka[9].

diethyldithiocarbonate solution, previously freed from metal impurities by extraction with the chloroform–acetone mixture, was added and the solution was analysed as described in the previous section.

Gas–liquid chromatography

A Pye Unicam Series 104 gas chromatograph with a flame-ionization detector was used. In Table I, the column packings and operating conditions for the GLC of the DEDTC complexes of the three metals are given. Nitrogen was used as the carrier gas throughout.





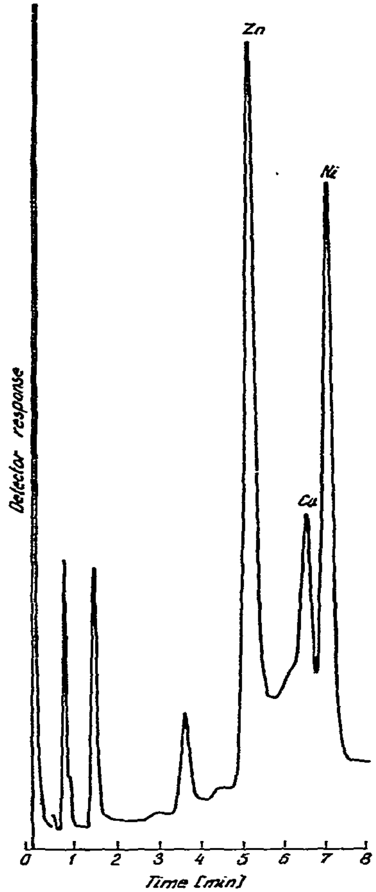


Fig. 1. GLC of bis(N,N-diethyldithiocarbonates) of Zn, Cu and Ni. Glass column No. 7 (Table I), on Chromosorb W-HP (80–100 mesh). Carrier gas, nitrogen, flow-rate 20 ml/min. Column temperature, 235°; detector (FID) temperature, 280°.

Fig. 2. Separation of a marine bottom sediment sample. Concentrations of $Zn(DEDTC)_2$, $Cu(DEDTC)_2$ and $Ni(DEDTC)_2$: 17.1, 1.6 and 4.9 ppm, respectively. Column and other chromatographic conditions as in Fig. 1.

Fig. 3. Chromatogram of a sample of the bottom sediment. Glass column No. 3 (Table I) on Chromosorb W-HP (80–100 mesh). Carrier gas, nitrogen, flow-rate 20 ml/min. Column temperature, programmed from 200° to 290° at 10°/min; detector temperature, 320°.

RESULTS AND DISCUSSION

A chromatogram of a mixture of standard solutions is shown in Fig. 1. The components of the mixture were separated on column No. 7 (Table I). Similar results were obtained with column No. 3, but the temperature had to be programmed over the range 200–290° at a rate of 10°/min. The remaining columns listed in Table I failed to give satisfactory separations of the metal peaks ($R_s < 0.5$).

The chromatogram shown in Fig. 2 was obtained by using column No. 7. It can be seen that the procedure ensures the removal of extraneous metals and allows the separation of the three complexes of zinc, copper and nickel. By comparison of these chromatograms with those of the standard solutions, the concentrations of zinc, copper and nickel in the sample were determined to be 17.1, 1.6 and 4.9 ppm, respectively.

The results of a similar analysis, obtained on column No. 3 packed with OV-101 temperature with programming, are shown in Fig. 3. There are three additional peaks that could not be identified.

Our current efforts are aimed at finding an appropriate internal standard that would permit a more accurate determination of the concentrations of the three metals. Of the compounds tested so far, coronene, anthanthrene and dotriacontane have given encouraging results, which will be published later.

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