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## **GAS CHROMATOGRAPHIC DETERMINATION OF Zn, Cu AND Ni IN BOTTOM SEDIMENTS IN THE FORM OF DIETHYLDITHIOCARBAMATE COMPLEXES**

Contents: 1. Introduction, 2. Experimental, 3. Conclusions; Streszczenie; References.

### **1. INTRODUCTION**

Gas-liquid chromatography (GLC) provides a versatile technique for qualitative and quantitative analysis of mixtures. The technique is usually employed for analysis of organic compounds which meet the requirements posed by operative conditions of the chromatographic column, i.e. they exhibit proper volatility and thermal stability.

A particular section of GLC provides analysis of organic and inorganic compounds of metals. These compounds are usually nonvolatile at the temperature of the column due to their ionic nature exhibited in the solid state and in solution, moreover, they have an additional property — a high reactivity in respect to column packings and the columns themselves. Studies on the application of GLC in the analysis of metals and their compounds have been carried out in several directions. One of them involves the application of metal complexes with organic ligands in the chromatographic analysis.

The metal complexes used for chromatography should meet the following requirements:

- i) they should be neutral;
- (ii) they should exhibit proper thermal stability during elution from the column;
- (iii) they should not interact with the column packing;
- (iv) ligands should be slowly released from the complex;
- (v) there should be no exchange of the ligands between the complexes fed onto the column;

(vi) they should be solvolytically stable;  
 (vii) they should possess proper volatility under preservation of integrity of a molecule in the gas phase on a hot and active packing surface;

(viii) they should be available on the market.

The GLC method of determining metals has the following advantages over other analytical methods:

(i) high detection selectivity of complexes leaving the column, owing to the use of a proper detector (ECD, FID, etc.);

(ii) possibility of using a relatively inexpensive gas chromatograph;

(ii') possibility of assaying of trace and ultratrace amounts of metals;

(iv) possibility of simultaneous qualitative and quantitative determination of several metals in one sample;

(v) possibility of limitation of the sample (liquid or solid) taken for analysis;

(vi) possibility of multiple analysis of metal complexes in the sample;

(vii) possibility of assaying metal levels in samples containing an element at the detection limits, by other methods;

(viii) possibility of a several-hundred-fold concentration of metal complexes extracted from a sample;

(ix) application onto a column of small portions of the analyte (0.5—2.0  $\mu$ l).

Tabela 1. Comparison of the detection limits in the GLC and other methods for some elements

Tabela 1. Porównanie wartości granicy wykrywalności otrzymanych dla niektórych pierwiastków metodą GLC oraz innymi metodami

Metal to be assayed Oznaczany metal	GLC	AAS ASA	Neutron activation analysis Aktywacyjna analiza neutronowa	Emission spectrography Spektrografia emisyjna	Spark-source mass spectrography Iskrowa spektrografia mas
Be	$4 \times 10^{-13}$	$1 \times 10^{-8}$	—	$2 \times 10^{-10}$	$8 \times 10^{-12}$
Cr	$2 \times 10^{-14}$	$2 \times 10^{-9}$	$1 \times 10^{-6}$	$1 \times 10^{-9}$	$5 \times 10^{-11}$
Rh	$2 \times 10^{-13}$	$2 \times 10^{-8}$	$5 \times 10^{-11}$	$2 \times 10^{-8}$	$9 \times 10^{-11}$
Al	$7 \times 10^{-11}$	$1 \times 10^{-6}$	$1 \times 10^{-9}$	$3 \times 10^{-9}$	$2 \times 10^{-11}$
Co	$1 \times 10^{-11}$	$2 \times 10^{-9}$	$5 \times 10^{-10}$	$1 \times 10^{-6}$	$5 \times 10^{-11}$
Pd	$1 \times 10^{-10}$	$3 \times 10^{-8}$	$5 \times 10^{-11}$	$1 \times 10^{-6}$	$5 \times 10^{-10}$
Ni	$1 \times 10^{-11}$	$2 \times 10^{-9}$	$5 \times 10^{-9}$	$8 \times 10^{-8}$	$7 \times 10^{-11}$

Table 1 lists the absolute detection limits (in grams) obtained in the determination of metals by various analytical techniques [15]. High detection limits of GLC are associated with an important feature of the method, namely with the separation of impurities from a complex leaving the column and with the possibility of employing a detector of proper quality.

Of the ligands studied hitherto, dialkyldithiocarbamates, and particularly diethyldithiocarbamates of certain metals, constitute a little studied and prospective group. Before using them in GLC, their volatility was studied. Results of the investigations of diethyldithiocarbamates of Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Fe(III) and Ag (I), carried out by D'Ascenzo [3, 4] confirmed the possibility of using some of them in chromatographic studies. Despite sceptical views [6, 12, 17] on the usefulness of the complexes of this ligand in GLC, successful attempts [7, 8] have been reported on the separation of a mixture of some dithiocarbamates [2, 9, 18]. These papers, with the exception of [5], were confined to attempts to separate some complexes on randomly chosen packing only. There are no reports on optimization of either qualitative or quantitative elution of mixtures of metal complexes.

In this paper the parameters of qualitative and quantitative separation of zinc, copper and nickel complexes have been established and applied to assaying metals in marine bottom sediment.

## 2. EXPERIMENTAL

GLC separation was carried out on a Pye Unicam Model 104 gas chromatograph equipped with a flame ionization detector (FID). Argon was used as carrier gas.

Solutions of metal complexes were prepared immediately before GLC separation. The complexes were prepared by using procedures reported in [2, 3, 7]. Chloroformic solutions of the complexes contained 2000  $\mu\text{g}$  of each of the metals in 1  $\text{cm}^3$ . They were properly diluted, if needed, to concentrations of 400, 100 and 40  $\mu\text{g}/\text{cm}^3$ .

### 2.1. Chromatographic separation

Attempts to separate both individual metal complexes and their mixtures were made by using conditions and packings specified in Table 2. Results of preliminary tests revealed the possibility of separating the zinc, copper and nickel complexes on 3% SE-30 coated on Chromosorb W-HP (item 1, Table 2). The retention times conformed with those obtained for single complexes. These conditions did not, however, en-

Table 2. Column packings and conditions of GLC analyses in this paper  
 Tab. 2. Zestawienie użytych do badań warunków analizy chromatograficznej

No. Nr	Column packing Wypełnienie	Column di- mensions Wymiary kolumny	Fig. Rys.	Temp. of thermostat Temp. ter- mostatu (°C)	Temp. of detector Temp. detektora (°C)	Flow ra- te of carrier gas (cm <sup>3</sup> /min)	No. of the- oretical plates Liczba pótek teo- ret.	Diethylthiocarbamates									
								Retention times Czasy retencji (min)		Rel. retention times Wzgl. czasy retencji		Retention times Czasy retencji (min)		Rel. retention times Wzgl. czasy retencji			
								Zn	Cu	Ni	Ni	Zn	Cu	Zn	Ni		
1	3% SE-30 on (na) Chromosorb W-HP	1.5 m/2mm		240—290 10°/min	320	30	6018	4.6	6.0	6.6							
2	3% OV-7 on (na) Chromosorb W-HP	1.5 m/2mm	1	280	330	45	355	1.87	3.03	4.0							
3	Tenex GC	3.0 m/2mm						does not differentiate the complexes — nie różnicuje kompleksów									
4	2.5% BMBT	1.8 m/2mm						does not differentiate the complexes — nie różnicuje kompleksów									
5	5% OV-101 on (na) Gas Chrom Q	1.5 m/2mm	2	200—290 10°/min	320	20	554	5.2	6.57	7.3							
											a)						
	b)		3	240	250	20	299	2.96	5.39	7.57	0.46	0.83	1.17				
6	5% QF-1 on (na) Gas Chrom Q	1.5 m/2mm	4	240	250	20	702	3.05	5.8	9.12	2.93	5.58	8.77				
7	Mixed packing Wypełnienie mie- szane	1.5 m/2mm	5	240	250	17.6	866	3.2	5.68	8.0							

sure reproducible chromatograms of a mixture fed onto the column, similarly as with packing consisting of the OV-7 phase (3%) coated on Chromosorb W-HP (Figs. 1A and 1B, item 2, Table 2). By using the OV-101 (5%) phase on Gas Chrom Q, the separation of a mixture of

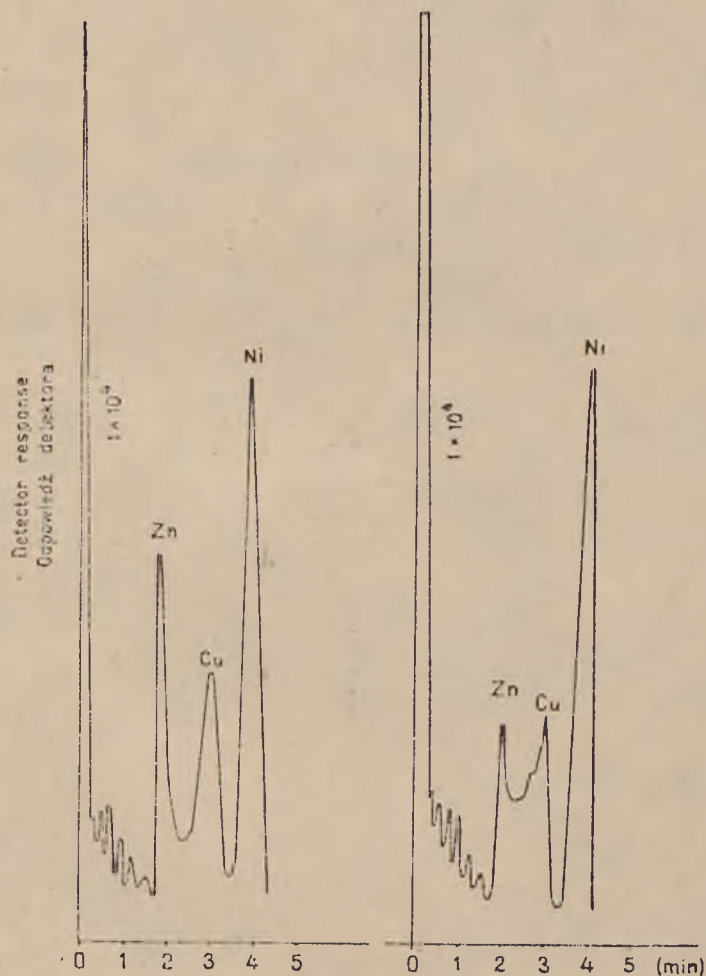


Fig. 1A and 1B. A chromatogram of a mixture of the Zn, Cu and Ni complexes obtained by using a column packed with 3% of OV-7 on Chromosorb W-HP during two successive injections.

Rys 1A i 1B. Chromatogram mieszaniny kompleksów Zn, Cu, Ni otrzymany na kolumnie wypełnionej 3% OV-7 na Chromosorbie W-HP w kolejnych dwóch nastrzykach.

zinc, copper and nickel complexes was markedly improved. At the same time the effect of the compactness of the packing on the quality of GLC separation of the complexes was investigated. This was accomplished by using two columns of equal dimensions filled with identical packing of different compactness. A mixture of diethyldithiocarbama-

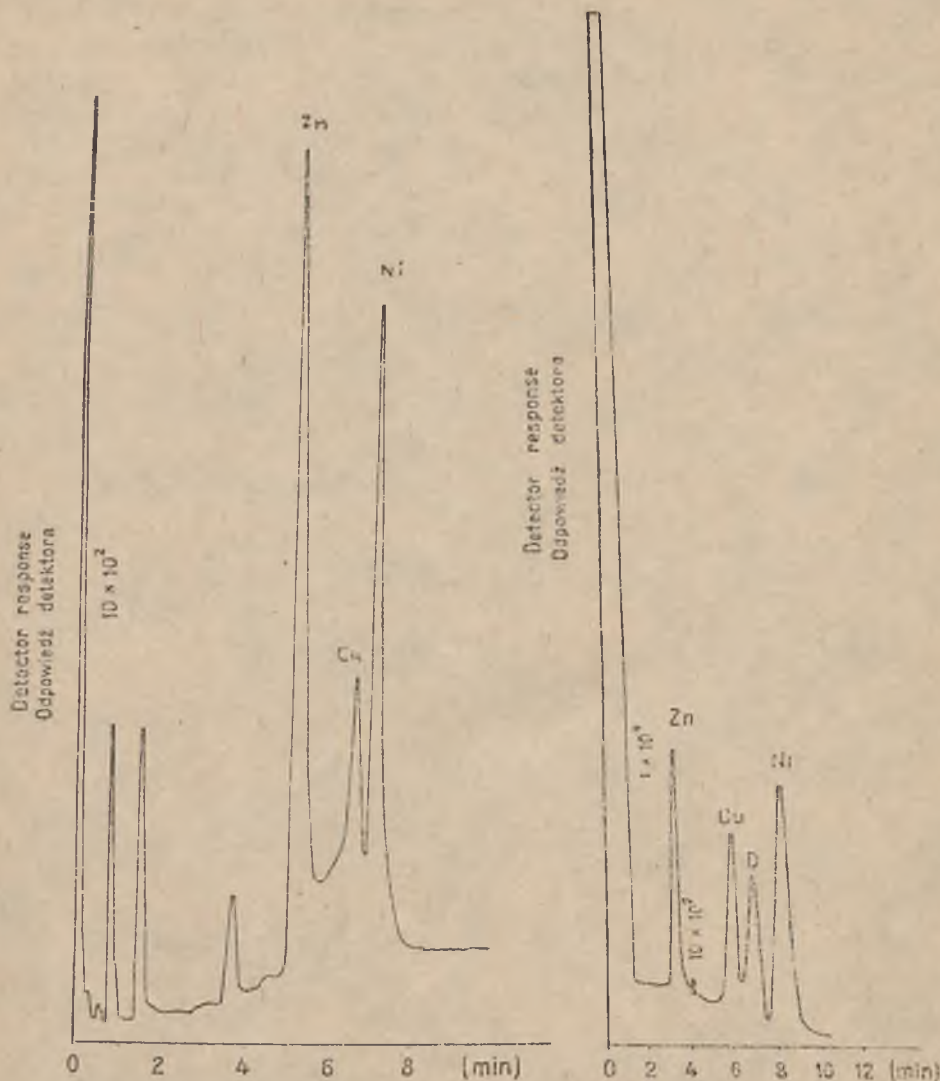


Fig. 2. The separation of the diethyldithiocarbamate complexes on a column loosely packed with 5% of OV-101 on Gas Chrom Q.

Rys. 2. Rozdział mieszaniny kompleksów z DEDTK uzyskany na wypełnieniu 5% OV-101 na Gas Chromie Q (wypełnienie luźno upakowane).

Fig. 3. A chromatogram of the zinc, copper and nickel complexes, together with an internal standart, obtained by using more compact packing (5% of OV-101)

Rys. 3. Chromatogram mieszaniny kompleksów cynku, miedzi i niklu wraz z wzorcem wewnętrznym otrzymany na wypełnieniu 5% OV-101 (wypełnienie bardziej upakowane).

tes of zinc, copper and nickel could not be resolved on a loosely packed column (the peaks of copper and nickel coalesced), although one-by-one injected complexes separated well. Adequate separation of the complexes was achieved by using programmable heating of the thermostat

(item 5a, Table 2, Fig. 2). With the more compact column, a good separation of individual diethyldithiocarbamates and of their mixture was attained (item 5b, Table II, Fig. 3). Under the specified conditions, the peaks of the zinc, copper and nickel complexes were symmetrical and well separated. Similar results to those achieved on the OV-101 packing were obtained with the QF-1 (5%) phase on Gas Chrom Q. The results confirm the usefulness of the packing for the separation of components of a mixture of zinc, copper and nickel complexes. The peaks are symmetrical, well-shaped and have precisely determined parameters (item 6, Table 2, Fig. 4).

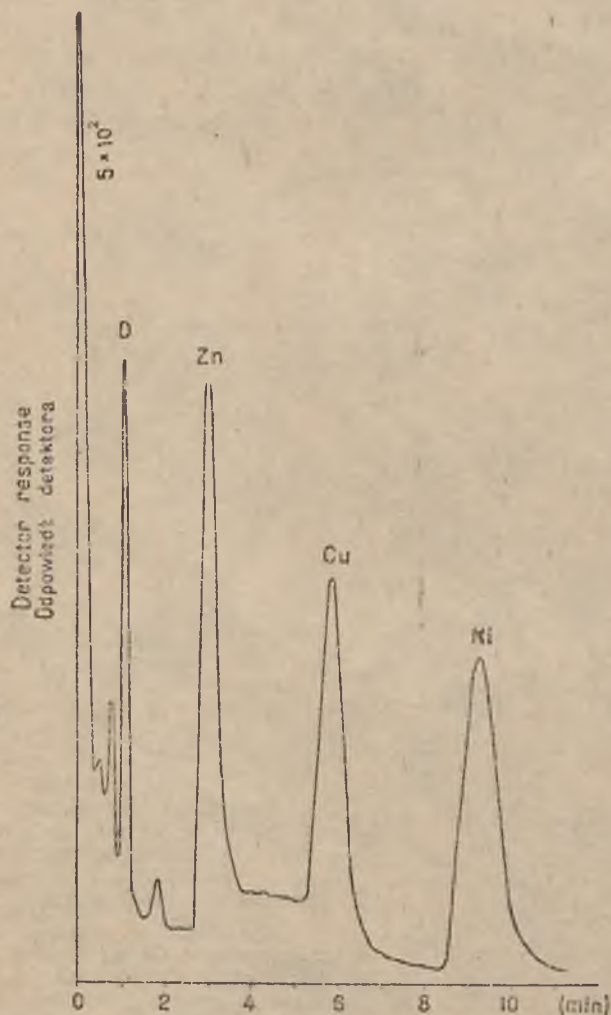


Fig. 4 A chromatogram of a mixture of the zinc, copper and nickel diethyldithiocarbamates, together with an internal standard, obtained on the OF-1 packing.

Rys. 4. Chromatogram mieszaniny kompleksów dwuetylodwutiokarbaminianowych cynku, miedzi i niklu wraz z wzorcem wewnętrznym otrzymany na wypełnieniu 5% OF-1.

In order to use the packings for quantitative analysis, the behaviour of certain organic compounds which could be used as internal standards in the presence of metal complexes was investigated. The organic

compounds used were, among others, dehydroepiandrosterone, n-dotriacontane and benzo[ghi]perylene. Of these compounds, n-dotriacontane was the most suitable for analytical purposes (Fig. 3).

To determine mutual positions of particular complexes in more detail, relative retentions were calculated for each of them in respect to n-dotriacontane (Table 2, items 5b and 6). Due to a high polarity of the QF-1 stationary phase, the peak of n-dotriacontane introduced together with the complexes was shifted. This disqualifies the compound as an internal standard. It leaves the column together with volatile impurities (Fig. 4). In view of the fact that the liquid phases possess different acceptor-donor properties, the packing was modified by mixing together in the 1:1 ratio by weight packings specified under 5 and 6. The values of retention fractions calculated for particular packings by

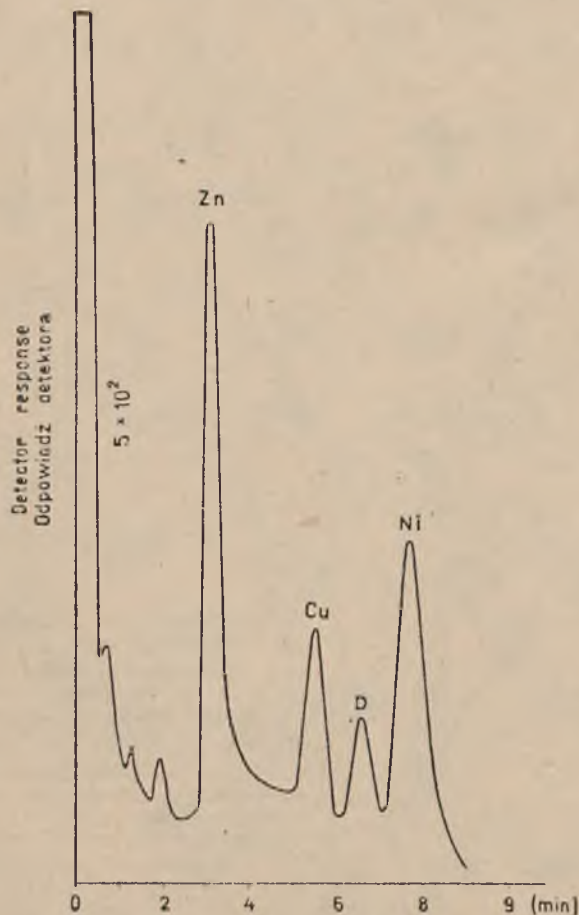


Fig. 5. A chromatogram of the zinc, copper and nickel diethyldithiocarbamates and of n-dotriacontane obtained on a mixed packing

Rys. 5. Chromatogram mieszaniny dwuetylodwutio-karbaminianów cynku, miedzi i niklu oraz n-dotriakontanu otrzymany na wypełnieniu mieszanym.

the Brown method [16] showed that the packing considered retained its nonpolarity similar to that of the OV-101 phase and its acceptor-donor properties were reduced as compared with those of the QF-1 phase,



thus contributing to separation of the complexes. By using this packing, attempts were made to separate the zinc, copper and nickel diethyldithiocarbamates from both a standard mixture and from a bottom sediment. The chromatogram in Fig. 5 illustrates excellent separation of the Zn(II), Cu(II) and Ni(II) complexes and of *n*-dotriacontane.

To assay zinc, copper and nickel, the response of the flame ionization detector was determined on progressively growing masses of the metal complexes applied onto the column. Chromatographic peaks due to particular masses of the complexes are shown in Figs. 6—8. A relationship between peak area and the mass of a complex (based on the metal) is shown in Fig. 9. These data reveal a linear relationship between the amount of a complex fed onto the column (based on the me-

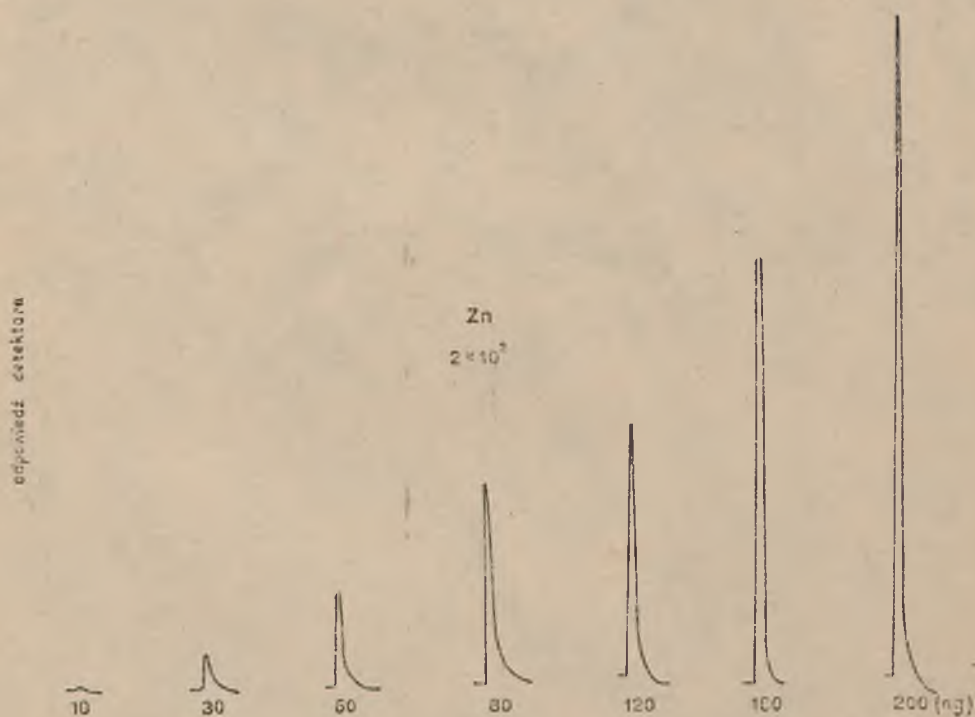


Fig. 6. A chromatogram showing the response of the flame ionization detector on a progressively increasing mass of the zinc complex.

Rys. 6. Chromatogram określający reakcję detektora płomieniowo-jonizacyjnego na wprowadzoną masę kompleksu cynku.

tal content) and peak areas for copper and nickel over the range 10—200 ng and for zinc over the range 30—160 ng. Application onto the column of smaller quantities of the metals than the lower ones indicated, brought about a nonproportional detector response, probably due to sorption of the complexes on the packing.

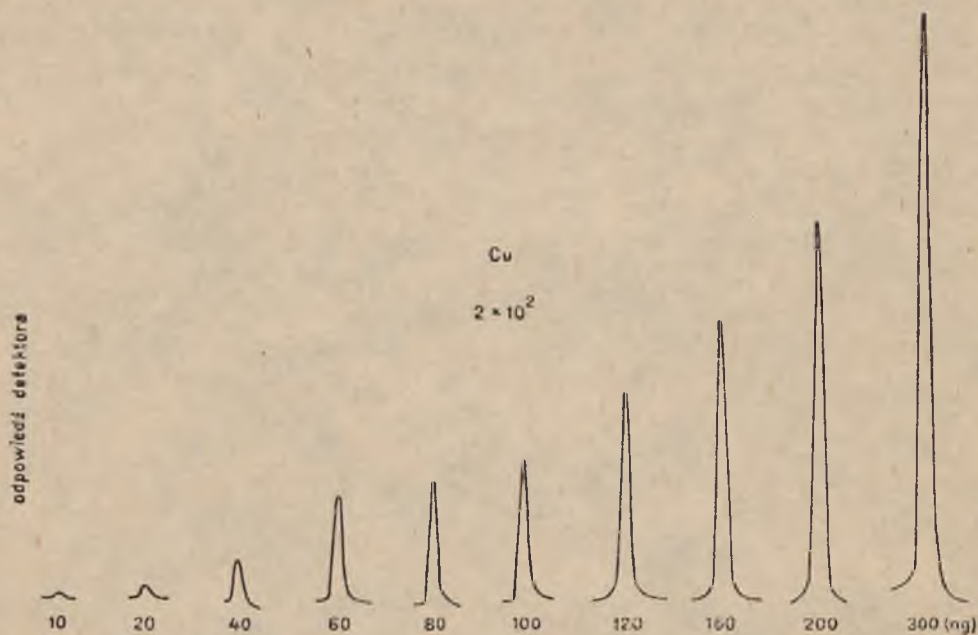


Fig 7. A chromatogram showing the response of the flame ionization detector on a progressively increasing mass of the copper complex.

Rys. 7. Chromatogram określający reakcję detektora płomieniowo-jonizacyjnego na wprowadzoną masę kompleksu miedzi.

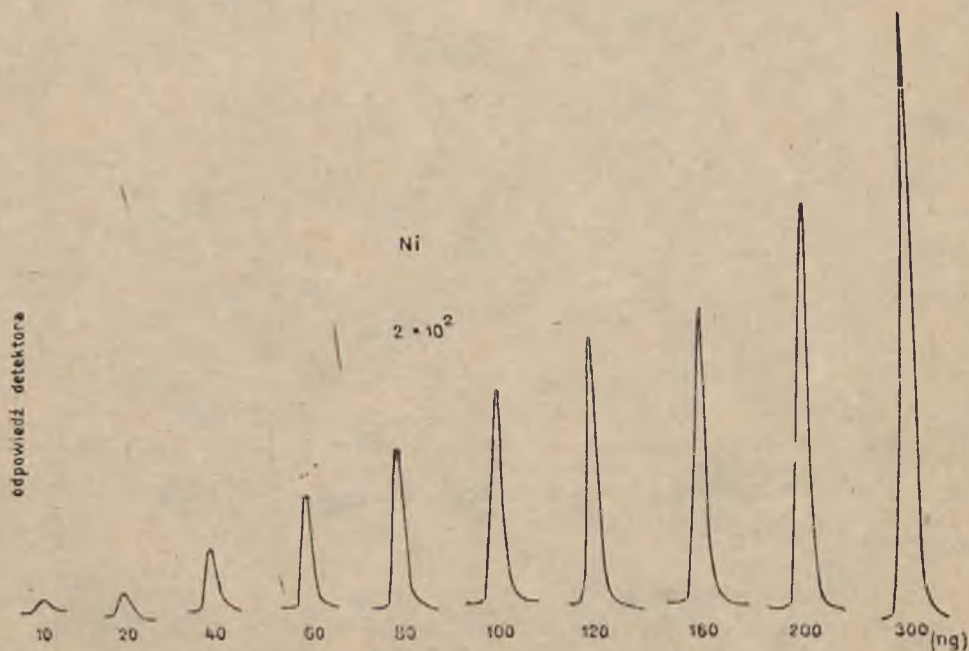


Fig. 8. A chromatogram showing the response of the flame ionization detector on a progressively increasing mass of the nickel complex.

Rys. 8. Chromatogram określający reakcję detektora płomieniowo-jonizacyjnego na wprowadzoną masę kompleksu niklu.

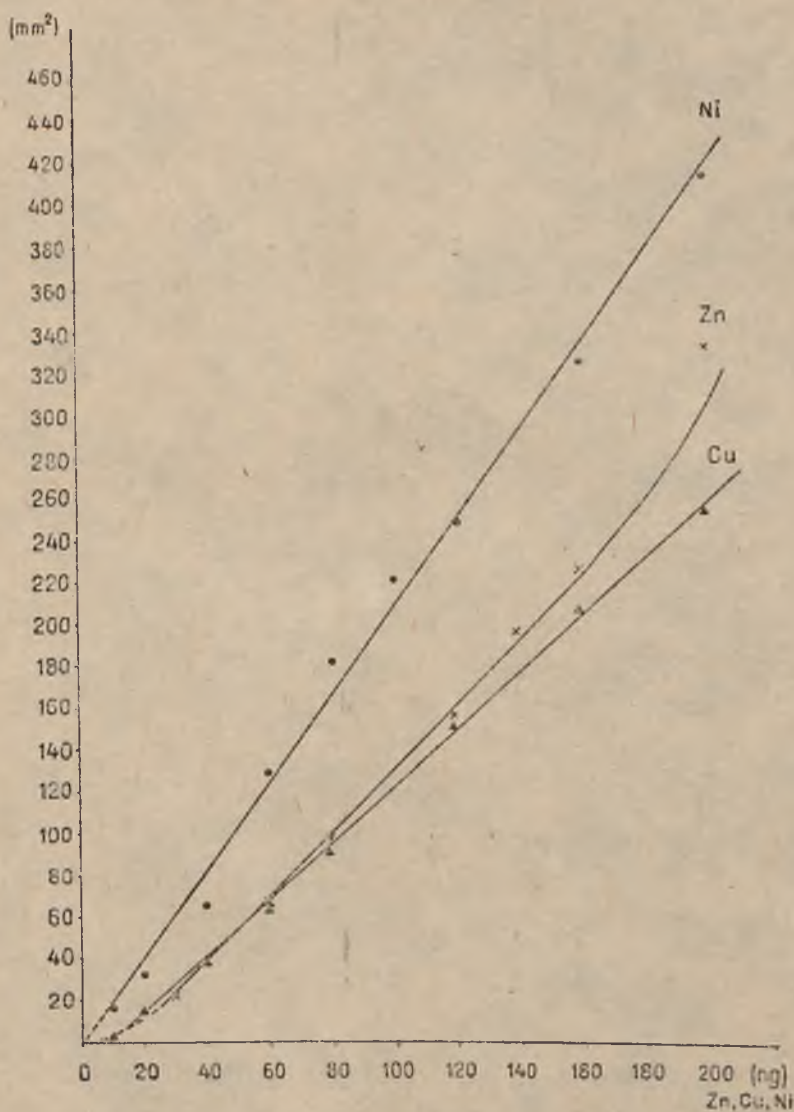


Fig. 9. Relationship between peak area and the mass of a complex (based on the metal content).

Rys 9. Krzywa zależności powierzchni piku od wprowadzonej masy danego kompleksu (w przeliczeniu na metal).

## 2.2. Qualitative and quantitative GLC assay of zinc, copper, and nickel in marine bottom sediments

Samples of the sediments (sands, loams) were supplied by the Institute of Marine Geology, Sopot.

The samples (ca 10 g) were dried at 110°C for 2 hrs., ground in a porcelain mortar and tempered in a muffle furnace at 500°C for 2

hrs. After cooling the sample, a 2-g portion was taken and milled in a vibrational agate mill for 30 min. The material was then wet digested by using the procedure described in [1, 10, 11, 13, 14].

A weighed sample (0.2—0.5 g) was placed in a Model 2 Perkin Elmer autoclave, moistened with 1 cm<sup>3</sup> of double-distilled water, followed by the addition of 2 cm<sup>3</sup> of concd. HNO<sub>3</sub> (sp. gr. 1.14) and 10 cm<sup>3</sup> of 40% H<sub>2</sub>F<sub>2</sub> solution. The content of a teflon insert was mixed and autoclaved at 150°C for 45 min. After cooling to room temperature, the

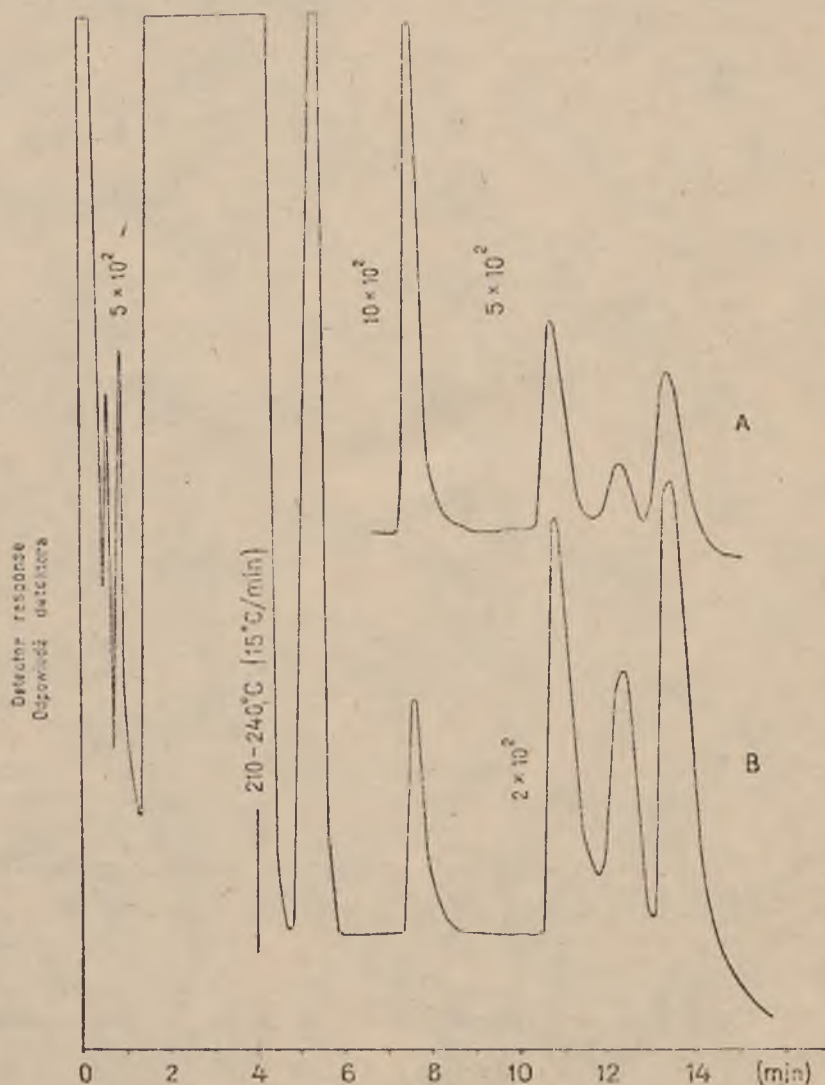


Fig. 10. Chromatograms of a mixture of the zinc, copper and nickel complexes obtained from marine sand and loam with the addition of *n*-dotriacontane (internal standard).

Rys. 10. Chromatogramy mieszaniny kompleksów cynku, miedzi i niklu otrzymanej z próby piasku morskiego oraz łu wraz z dodatkiem wzorca wewnętrznego — *n*-dotriakontanu.

content was transferred to a 100-cm<sup>3</sup> teflon dish and treated with 10 cm<sup>3</sup> of the 40% H<sub>2</sub>F<sub>2</sub> solution and 1 cm<sup>3</sup> of conc. HNO<sub>3</sub>. The solution was evaporated to dryness on a sand bath and the procedure was repeated. To the dry residue, 10 cm<sup>3</sup> of 8M HCl was added and the content was gently heated to dissolve the solids. The solution was transferred to a 250-cm<sup>3</sup> beaker, 0.5 cm<sup>3</sup> of a LaCl<sub>3</sub> solution (concentration 1000 μg cm<sup>-3</sup>) was added, the volume was made up to 100 cm<sup>3</sup> with double-distilled water, the solution was placed on a boiling water bath for approx.

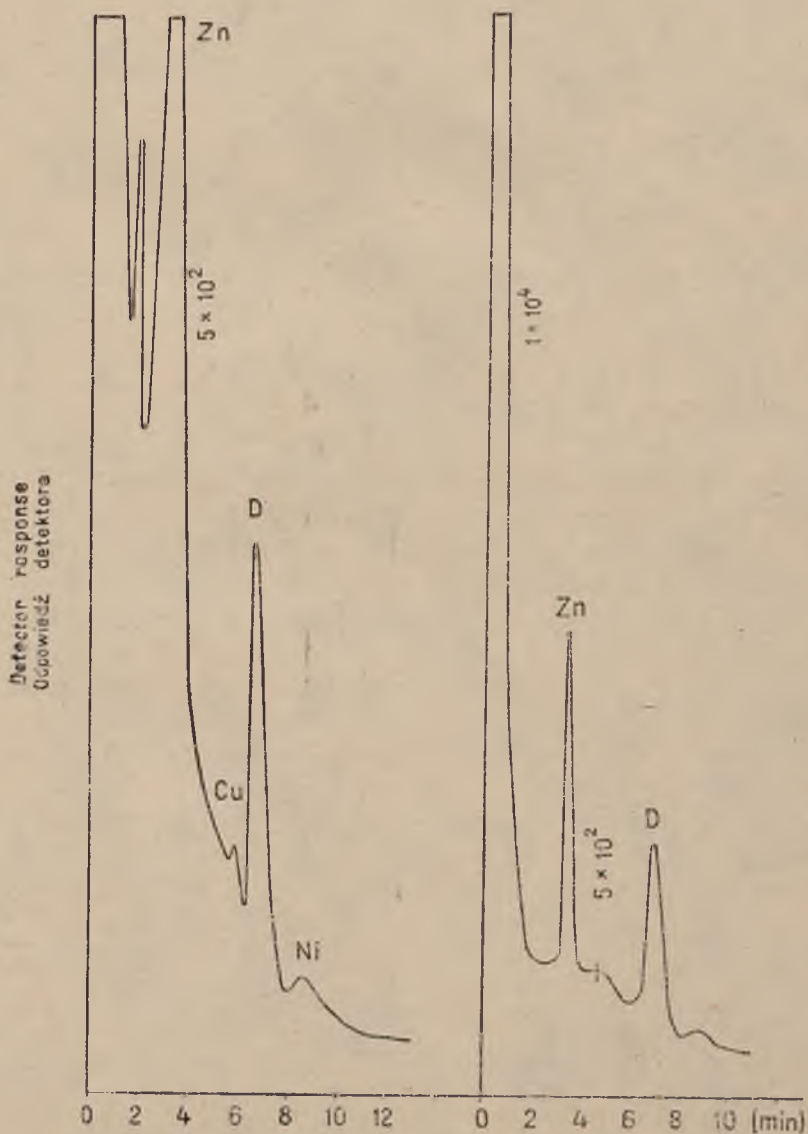


Fig 11. Chromatogram of a mixture of complexes from the blank.

Rys. 11. Chromatogram mieszaniny kompleksów uzyskanych z próby odnośnej.

5 min, then 20 cm<sup>3</sup> of concentrated ammonia solution and 1 cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> were added. Under continuous stirring the solution was heated for 5 min, filtered through a small-pore filter paper, the precipitate was washed twice with 10-cm<sup>3</sup> portions of concentrated ammonia solution, the filtrate was transferred to a 250-cm<sup>3</sup> separating funnel and 10 cm<sup>3</sup> of a 3% solution of sodium diethyldithiocarbamate (previously purified from metallic impurities by extraction with chloroform) was added. After 10 min the complexes were extracted with chloroform, successive extracts being collected in flasks with conical bottom. Chloroform was then completely removed on a water bath at 80°C. To the dry residue, a solution of n-dotriacontane was added and the solution was applied with a microsyringe (0.6—0.1- $\mu$ l portions) onto the column filled with the mixed packing (cf. item 7, Table 2). Illustrative chromatograms of the zinc, copper and nickel complexes isolated from a sample of sand and loam are shown in Figs. 10.

A blank was prepared, using pure reagents only, by the procedure just described. A chromatogram of the blank is shown in Fig. 11. The accuracy and precision of the method are now being determined.

### 3. CONCLUSIONS

(i) To obtain a good separation of the zinc, copper and nickel diethyldithiocarbamates, a packing containing 5% of OV-101 and 5% of QF-1 coated on Gas Chrom Q should be employed. For quantitative separation, a mixed packing can be recommended consisting of a 1:1 (w/w) mixture of 5% of OV-101 and 5% of QF-1 both coated on the Gas Chrom Q carrier.

(ii) The linear range of the relationship between the signal intensity of the flame ionization detector and the mass of a complex fed onto the column extends from 30 to 160 ng for zinc and from 10 to 200 ng for copper and nickel.

(iii) The procedure used to isolate zinc, copper and nickel from a sample in the form of their diethyldithiocarbamates affords well-developed chromatograms in the presence n-dotriacontane as an internal standard.

## OZNACZANIE KOMPLEKSÓW Zn, Cu i Ni Z DEDTK ZA POMOCĄ CHROMATOGRAFII GAZOWEJ W PRÓBACH OSADÓW DENNYCH

### Streszczenie

Zaletą stosowania chromatografii gazowej w analizie śladowej materii jest możliwość oznaczania jednoczesnego kilku metali w tej samej próbie.

W artykule opracowano warunki analizy chromatograficznej kompleksów Zn, Cu i Ni z dwuetyłodwutiokarbaminianem (DEDTK) dla mieszaniny wzorców i dla próby osadów morskich.

Do badań użyto chromatografu gazowego Pyc Unicam model 104, zaopatrzonego w detektor płomieniowo-jonizacyjny (FID). Użyto kolumn szklanych o przekrojach wewnętrznych: 2 i 4 mm i długości 1,5 m, 1,8 m, 3,0 m, stosując nośniki: Chromosorb W-HP oraz Gas Chrom Q, pokryte fazami stacjonarnymi: SF-30, OV-7, OV-101, QF-1, BBT i Tenex o różnych stopniach pokrycia.

Rozdziału mieszaniny wzorcowej zawierającej kompleksy dwuetyłodwutiokarbaminianowe Zn, Cu i Ni dokonano na 5% OV-101 i stosując wypełnienie mieszane o składzie 5% OV-101 i 5% QF-1 w stosunku wagowym 1:1. Wypełnienie mieszane zastosowano również do analizy ilościowej kompleksów. Zakres prostoliniowości dla zależności powierzchni pików od wprowadzonej masy kompleksu w przeliczeniu na metal mieścił się w zakresie dla Cu i Ni: 10—200 ng i dla Zn: 30—160 ng.

Analizy próbki dokonano pobierając 0,5 g porcję osadu suszonego a następnie wyprażonego w temperaturze 500°C. Rozdrobniony materiał poddano roztwarzaniu w autoklawie ciśnieniowym firmy Perkin Elmer w temperaturze 150°C przez 40 min., stosując mieszaninę roztwarzającą o składzie podanym w załączonej przez firmę instrukcji. Po roztworzeniu badanego materiału oraz po odpędzeniu krzemu w postaci SiF<sub>4</sub> suchą pozostałość rozpuszczono w 10% roztworze HCl. Po dodaniu do roztworu porcji 30% H<sub>2</sub>O<sub>2</sub> a następnie 5 000 µg La (III) współstrącano przeszkadzające w analizie chromatograficznej Fe i Mn. Współstrącanie przeprowadzono dodając do roztworu badanego 25% NH<sub>3</sub> · H<sub>2</sub>O. Po przesączeniu przez twardy sączek uzyskany osad przemyto roztworem NH<sub>3</sub> · H<sub>2</sub>O i wodą dojonizowaną. Do przesączu dodano 3% NaDEDTK (oczyszczonego wcześniej od zanieczyszczeń organicznych przez ekstrakcję CHCl<sub>3</sub>/CH<sub>3</sub>/CO w stosunku objętościowym 5 : 2). Powstałe kompleksy ekstrahowano tą samą mieszaniną co czysty odczynnik. Po odparowaniu rozpuszczalnika na łaźni wodnej w temp. 80° do suchej pozostałości dodawano CHCl<sub>3</sub> oraz roztworu wzorca wewnętrznego *n*-dotriakontanu i analizowano na chromatografii gazowej nastrzykując porcję 0,5—1,0 µl na kolumnę wypełnioną Gas Chrom Q z naniesioną mieszaniną faz QF-1 i OV-101.

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