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## QUANTITATIVE ANALYSIS OF ZINC, COPPER AND NICKEL DIETHYL-DITHIOCARBAMATES BY GAS-LIQUID CHROMATOGRAPHY

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### SUMMARY

A column packed with a 1:1 mixture of 5% OV-101 and 5% QF-1 on Gas-Chrom Q was used for the gas-liquid chromatographic assay of zinc, copper and nickel diethyldithiocarbamates in artificial mixtures and in samples of natural origin. The quantitative determination of complexes in artificial mixtures may be performed at concentration ratios of metal to *n*-dotriacontan (internal standard) of 0.11-5.57. The precision obtained for the determination of zinc, copper and nickel was *ca.* 11% in sea sand and 10% in sea mud.

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### INTRODUCTION

In an earlier paper<sup>1</sup>, the possibility of the gas-liquid chromatographic (GLC) determination of zinc, copper and nickel in the form of their diethyldithiocarbamate (DEDTC) complexes in marine bottom sediments was demonstrated. The most suitable stationary phases were 5% OV-101 or 5% QF-1 on Gas-Chrom Q. As described in another paper<sup>2</sup>, a mixed column packing consisting of a 1:1 mixture of 5% OV-101 and 5% QF-1 on Gas-Chrom Q is particularly useful for the GLC assay of the complexes. This packing has now been used for assaying the complexes in standard solutions and in samples of natural origin.

### EXPERIMENTAL

#### *Preparation of metal chelates*

Pure DEDTC complexes of zinc, copper and nickel, synthesized by known procedures<sup>3,4</sup>, were used for preliminary investigations.

#### *Gas-liquid chromatography*

A Pye Unicam series 104 gas chromatograph with a flame-ionization detector (FID) was used. A glass column (1.5 m × 2 mm I.D.) was packed with a 1:1 (w/w) mixture of 5% OV-101 and 5% QF-1 coated on Gas-Chrom Q (100-120 mesh).

#### *Preparative GLC and identification of the DEDTC complexes of zinc, copper and nickel*

The DEDTC complexes of the metals were isolated from the column by using

a 1:25 splitting ratio. Solutions of pure zinc, copper or nickel complexes, solutions containing artificial mixtures of the complexes and solutions containing a mixture of the complexes obtained from the digestion of a sample of bottom sediment were applied on to the column.

The identities of the complexes in the eluate were determined by comparing their UV spectra with those of authentic samples.

*Sample preparation and procedure for assaying zinc, copper and nickel in marine bottom sediments*

A study of the effect of pH, addition of the carrier, extent of extraction at different pHs and the ratio of phases on the results of analyses by GLC<sup>5</sup> indicated that it was necessary to modify the original procedure slightly, as follows. A ground sample (0.3 g) was placed in a Perkin-Elmer Model 2 autoclave, wetted with doubly distilled water; 2 ml of concentrated nitric acid were added, followed by 10 ml of 40% hydrofluoric acid. The contents were mixed and autoclaved for 45 min at 150°. After cooling, the contents were transferred into a 100-ml PTFE dish, 10 ml of 40% hydrofluoric acid and 1 ml of concentrated nitric acid were added and the solution was evaporated to dryness on a sand-bath. After adding to the residue 1 ml of concentrated nitric acid and 10 ml of 40% hydrofluoric acid, the evaporation was repeated. Then the residue was dissolved in 10 ml of 8 M hydrochloric acid at elevated temperature. The solution was transferred quantitatively into a 25-ml volumetric flask and made up to the mark with doubly distilled water. This solution was used in the following analyses.

(i) Aliquots of 7 ml were withdrawn, placed in a 25-ml volumetric flask, treated with 0.5 ml of lanthanum(III) solution (1000  $\mu\text{g}/\text{ml}$ ) and made up to the mark with doubly distilled water. The contents of zinc, copper and nickel were determined by atomic-absorption spectrometry with an air-acetylene flame.

(ii) Aliquots of 7 ml were withdrawn, placed in a 250-ml beaker, treated with 5 ml of lanthanum(III) solution (1000  $\mu\text{g}/\text{ml}$ ) and diluted with doubly distilled water to *ca.* 100 ml. Then the beaker was placed on a boiling water-bath. After 2 min, 20 ml of 25% ammonia solution followed by 1 ml 30% hydrogen peroxide were added, mixed and heated for 10 min. The solution was filtered through a small-pore filter-paper and the precipitate was washed twice with 10-ml portions of warm ammonia solution. The filtrate was transferred into a 250-ml separating funnel and extracted with three 5-ml portions of methyl isobutyl ketone (MIBK). After extraction, 10 ml of 3% NaDEDTC solution, previously freed from metal impurities by extraction with MIBK, was added to the solution in the separating funnel. The complexes were extracted after 10 min with one 10-ml portion and two 5-ml portions of MIBK. The combined extracts were placed in a 25-ml volumetric flask and made up to the mark with MIBK. The contents of zinc, copper and nickel were determined by atomic-absorption spectrometry with an air-acetylene flame (lean fuel).

(iii) In the GLC assay, 10-ml aliquots were withdrawn and placed in a 250-ml beaker. The following analytical operations were the same as in (ii). However, for the extraction of the DEDTC complexes chloroform was used (three 5-ml volumes). The combined extracts were evaporated to dryness on a water-bath at 80°. To the dry residue a 717.6  $\mu\text{g}/\text{ml}$  solution of *n*-dotriacontan as internal standard was added.

*Preparation of standard solutions for assaying zinc, copper and nickel in marine bottom sediments*

The concentrations of the aqueous solutions of zinc, copper and nickel were 5, 10, 15, 20 and 50  $\mu\text{g}$  per 150 ml. After complexing the metals with ammoniacal NaDEDTC solution, the complexes were extracted with chloroform as described. After evaporation of chloroform from the combined extracts, a 717.6  $\mu\text{g}/\text{ml}$  solution of *n*-dotriacontan was added with a microsyringe to the residue and the mixture was diluted with chloroform to a pre-determined volume.

The same procedure was employed for the preparation of a solution of extracts from marine bottom sediments, using the same volume of the internal standard solution and the same final dilution as for the standard solutions.

## RESULTS AND DISCUSSION

The separation of metal complexes and internal standard is shown in Fig. 1.

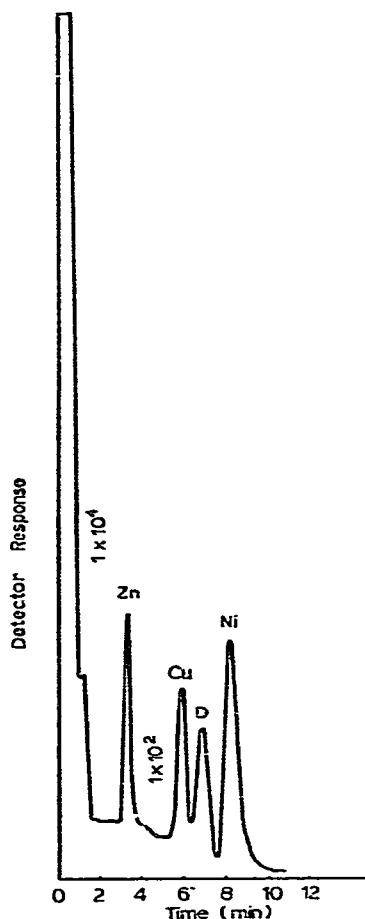


Fig. 1. GLC of  $\text{Zn}(\text{DEDTC})_2$ ,  $\text{Cu}(\text{DEDTC})_2$  and  $\text{Ni}(\text{DEDTC})_2$  and *n*-dotriacontane on a 1.5 m  $\times$  2 mm I.D. glass column packed with a 1:1 (w/w) mixture of 5% OV-101 and 5% QF-1 on Gas-Chrom Q. Column temperature, 240°; detector temperature, 250°; argon flow-rate, 17.6 ml/min. D = *n*-dotriacontan.

The peaks are symmetrical and well separated. To identify the DEDTC complex of metals, they are isolated by preparative GLC.

As can be seen in Fig. 2, the retention times of the metal complexes obtained from a sample of the sediment were identical with those of each standard used. This was also confirmed by the UV spectra shown in Fig. 3. The similarity of the spectra indicates that the complexes are eluted without decomposition.

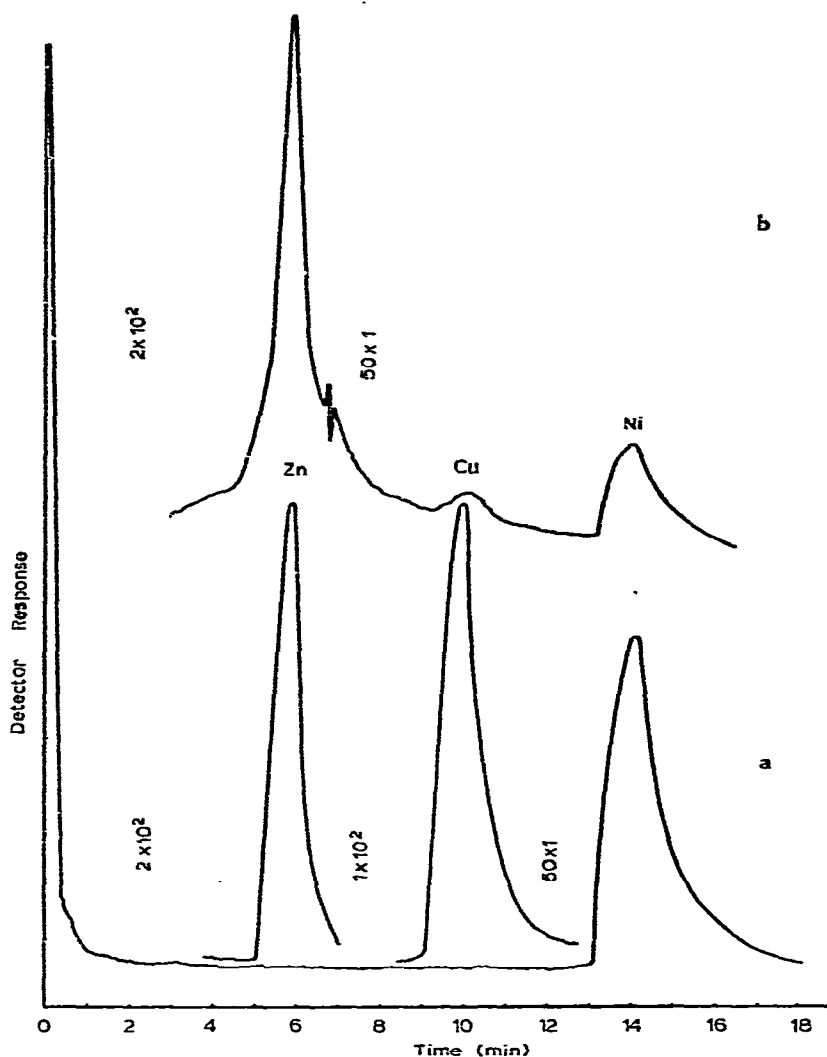


Fig. 2. Preparative GLC of  $\text{Zn}(\text{DEDTC})_2$ ,  $\text{Cu}(\text{DEDTC})_2$  and  $\text{Ni}(\text{DEDTC})_2$  on a  $1.5 \text{ m} \times 2 \text{ mm}$  I.D. glass column packed with a 1:1 (w/w) mixture of 5% QF-1 and 5% OV-101 on Gas-Chrom Q. Column temperature,  $240^\circ$ ; detector temperature,  $250^\circ$ ; splitting ratio, 1:25; argon flow-rate at outlet of the preparative section, 21.4 ml/min. (a) Separation of a simple complex; (b) separation of a mixture of complexes obtained from a marine bottom sediment.

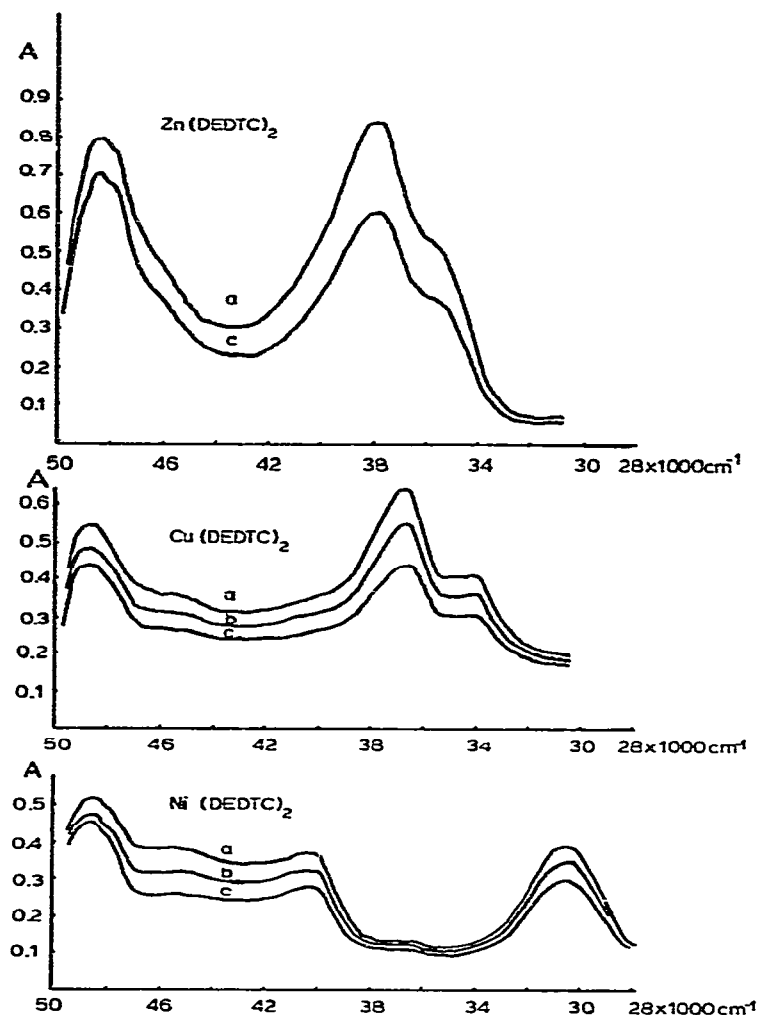


Fig. 3. UV spectra of  $\text{Zn}(\text{DEDTC})_2$ ,  $\text{Cu}(\text{DEDTC})_2$  and  $\text{Ni}(\text{DEDTC})_2$ . (a) Pure complex; (b) complex obtained from the preparative column; (c) complex obtained from a bottom sediment sample after GLC separation.

The analytical usefulness of the column packing employed was further demonstrated by the unaltered peak shapes obtained after repeated injections of a solution consisting of a mixture of the complexes and *n*-dotriacontan (*cf.*, Figs. 4–6). A suitable ratio of the concentration of the complexes (based on the metal content) to the concentration of *n*-dotriacontan is 1.55. The values of the ratio of the peak area of a given complex to that of *n*-dotriacontan (*D*) were as follows: for nickel,  $D = 5.40 \pm 0.22$  (coefficient of variation, C.V. = 6.5%); for copper,  $D = 2.38 \pm 0.13$  (C.V. = 9.2%); and for zinc,  $D = 7.16 \pm 0.63$  (C.V. = 13.1%).

For quantitation, calibration graphs were constructed (Fig. 7) for each complex based on the chromatogram of an appropriate standard mixture of known concentration of the complex and *n*-dotriacontan. The ratio of the peak area of a given

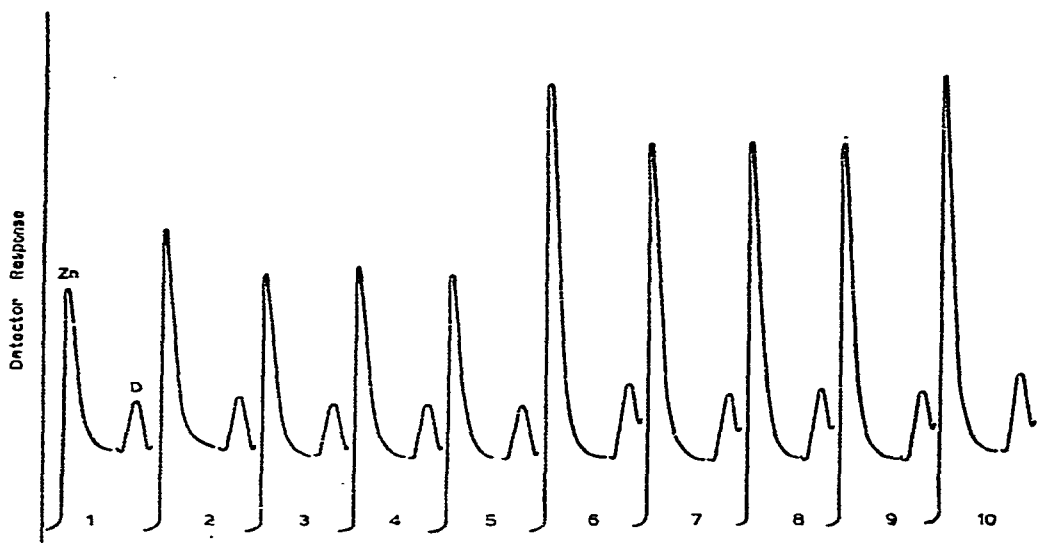


Fig. 4. Gas chromatogram of extracted mixture of  $Zn(DEDTC)_2$ , illustrating sample stability under chromatographic conditions. Glass column, 1.5 m  $\times$  2 mm I.D., packed with a 1:1 (w/v) mixture of 5% OV-101 and 5% QF-1 on Gas-Chrom Q. The column was operated isothermally at 210° for 3 min, then programmed at 15°/min and held at 240°; argon flow-rate, 35.7 ml/min. D = *n*-dotriacontan.

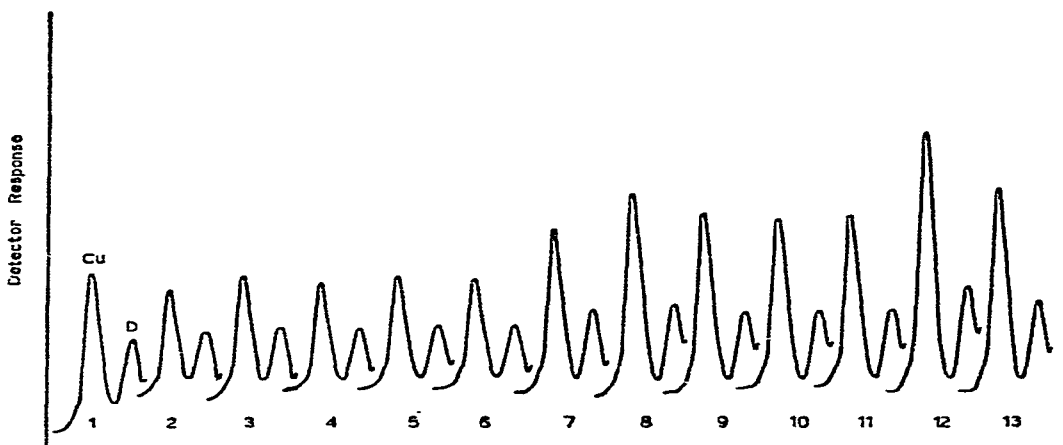


Fig. 5. As Fig. 4, for  $Cu(DEDTC)_2$ .

complex to that of *n*-dotriacontan was plotted against the ratio of the concentration of the complex (based on its metal content) to the concentration of *n*-dotriacontan. As the response of the detector to small amounts of complex is poor<sup>2</sup>, the calibration graphs do not pass through the origin. Corrections to the graphs were effected by the least-squares method. The concentration ranges studies for the zinc and nickel complexes and for *n*-dotriacontan were 44.4–114.3 and 76.4–416.0 ng/ $\mu$ l, respectively;

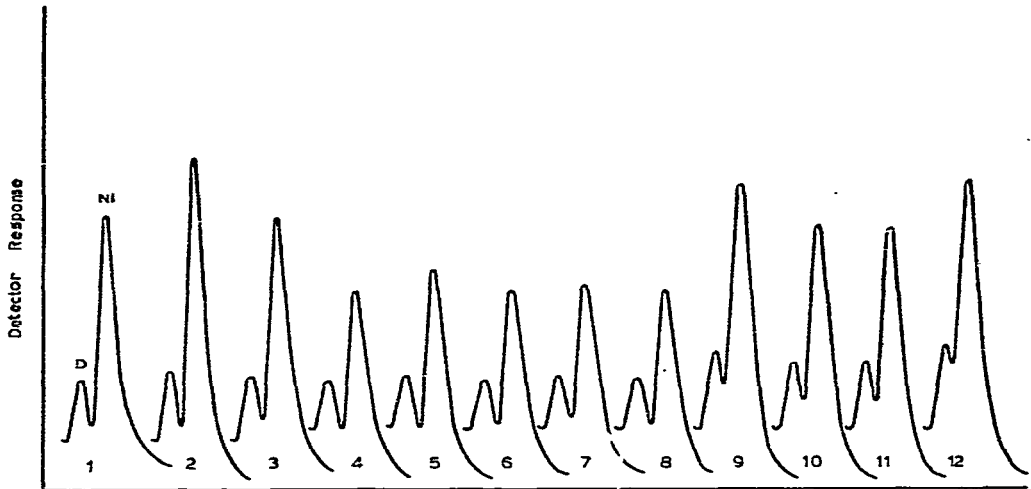


Fig. 6. As Fig. 4, for Ni(DEDTC)<sub>2</sub>.

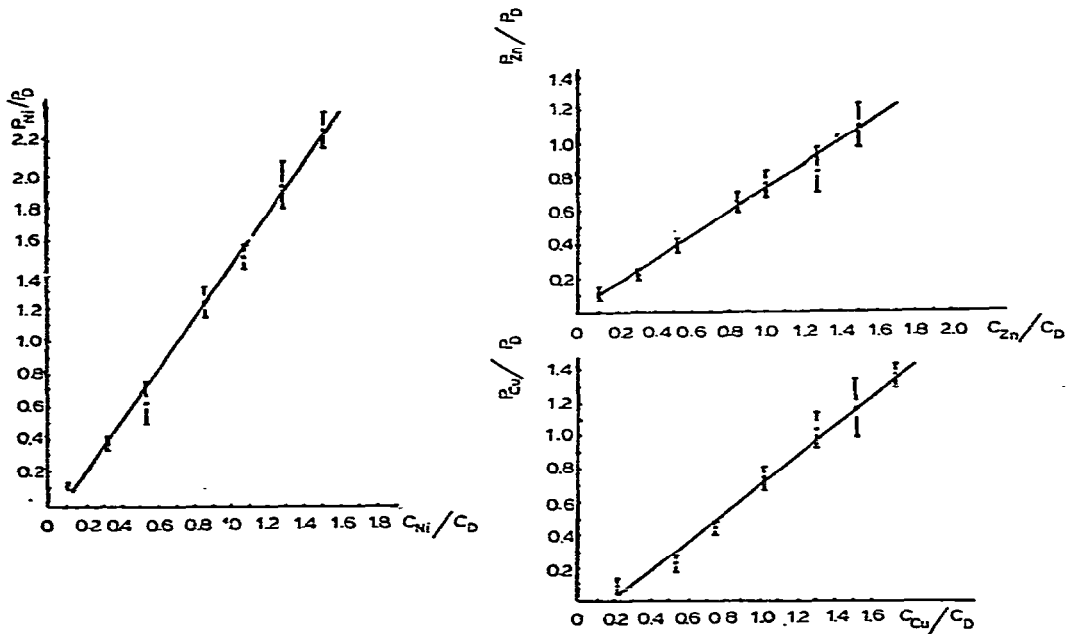


Fig. 7. Calibration graphs of peak area ratio ( $P_{complex}/P_D$ ) versus concentration ratio ( $C_{metal}/C_D$ ).

for copper the concentration range was 88.8–143.5 ng/ $\mu$ l and for *n*-dotriacontan 96.0–416 ng/ $\mu$ l.

Fig. 8 shows chromatograms in which the ratios of the concentrations of the complexed metal to that of *n*-dotriacontan and the peak areas differ widely.

Typical chromatograms obtained from a sample of sea sand and from a sample of sea mud are shown in Figs. 9 and 10, respectively. It is worth noting that larger

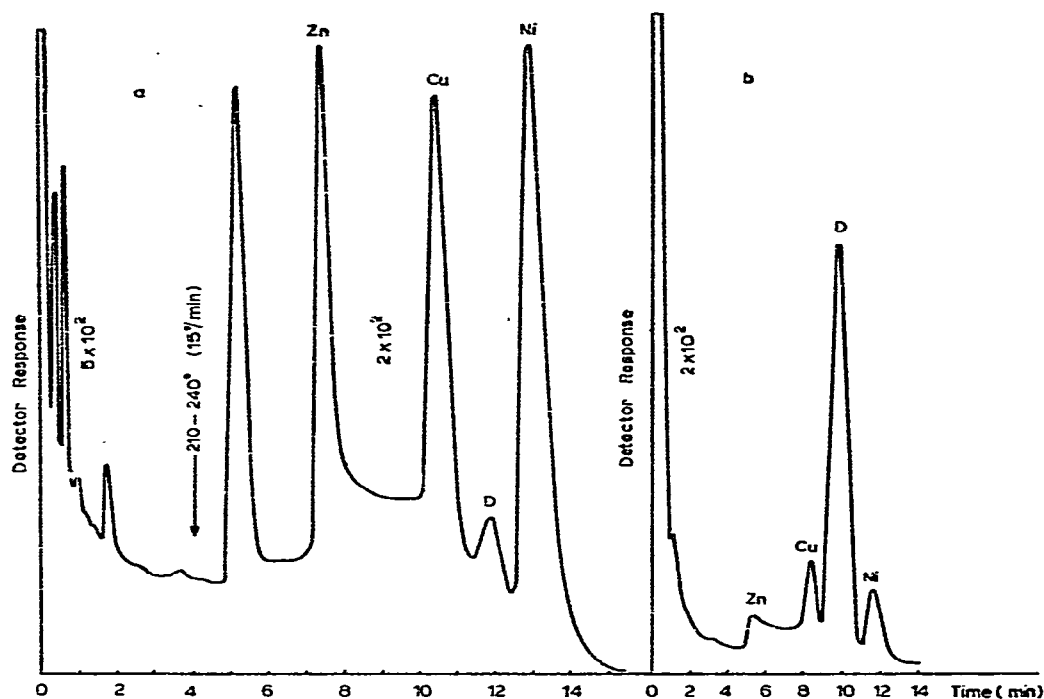


Fig. 8. (a) GLC of  $Zn(DEDTC)_2$ ,  $Cu(DEDTC)_2$  and  $Ni(DEDTC)_2$  with  $n$ -dotriacontan (D) at a  $C_{metal}/C_D$  ratio of 5.57. This corresponds to 200 ng of metal and 35.88 ng of  $n$ -dotriacontan. (b) GLC of DEDTC complexes of Zn, Cu and Ni with  $n$ -dotriacontan. Concentration ratio ( $C_{metal}/C_D$ ) for Zn and Ni is 0.11 and for Cu 0.21. This corresponds to 44.4 ng of Zn and Ni, 88.8 ng of Cu and 416.0 ng of  $n$ -dotriacontan.

TABLE I  
RESULTS OF ANALYSIS OF MARINE SEDIMENTS

Metal	Method*	No. of replicates	Sea sand		Sea mud	
			Found** ( $\mu\text{g/g}$ dry weight)	C.V.*** (%)	Found** ( $\mu\text{g/g}$ dry weight)	C.V.*** (%)
Zinc	(i)	6	$42.72 \pm 0.46$	1.01	$99.21 \pm 1.27$	1.78
	(ii)	6	$40.73 \pm 1.48$	4.9	$97.45 \pm 2.08$	2.8
	(iii)	10	$37.98 \pm 3.97$	9.87	$92.35 \pm 3.75$	5.70
Copper	(i)	6	$11.03 \pm 0.28$	2.44	$27.96 \pm 1.96$	5.94
	(ii)	6	$9.26 \pm 0.39$	4.1	$26.11 \pm 1.73$	9.26
	(iii)	10	$9.40 \pm 0.84$	8.5	$25.87 \pm 1.83$	9.86
Nickel	(i)	6	$12.93 \pm 0.22$	1.62	$30.40 \pm 0.96$	4.6
	(ii)	6	$11.46 \pm 0.52$	4.36	$27.14 \pm 1.37$	7.07
	(iii)	10	$10.01 \pm 1.19$	11.3	$27.05 \pm 1.44$	7.43

\* See text.

\*\* Found value = mean at 95% probability level.

\*\*\* C.V. = coefficient of variation

$$= \left( \frac{\text{standard deviation of single measurement}}{\text{mean value}} \right) \times 100\%$$



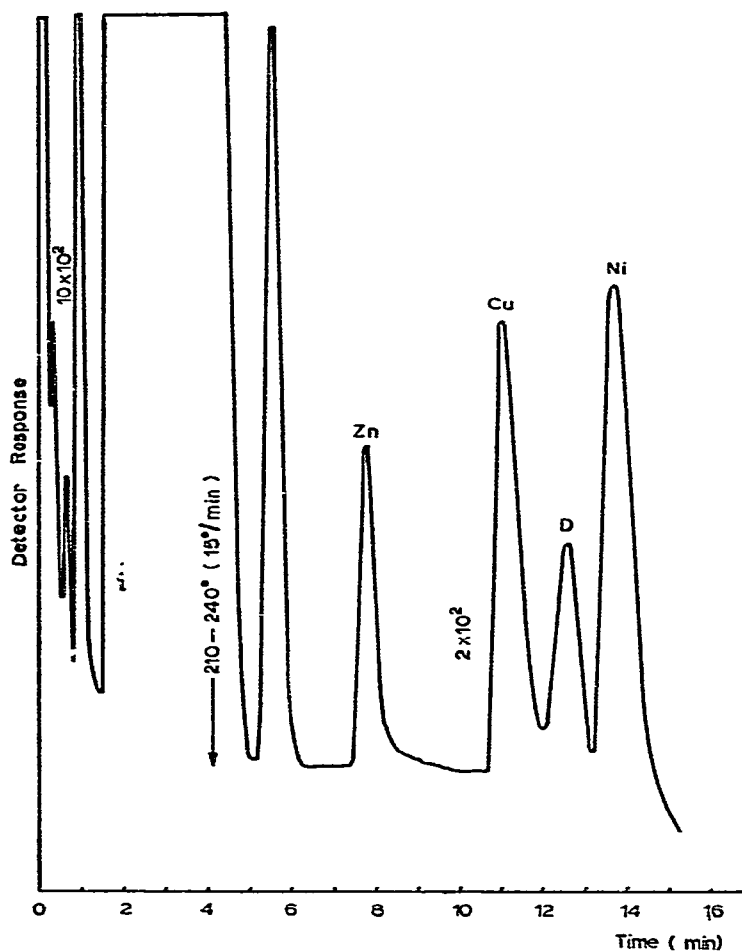


Fig. 9. Typical chromatogram obtained with the solution of extracted complexes from the sample of sea sand. The column was operated isothermally at 210° for 4 min, then programmed at 15°/min and held at 240°. Argon flow-rate, 19.74 ml/min; addition of 5  $\mu$ l of *n*-dotriacontan (D) solution (717.6  $\mu$ g/ml). Final volume, 100  $\mu$ l; injection volume, 0.8  $\mu$ l.

zinc levels than those of copper and nickel can be quantified by suitable attenuation of the signal if it falls within the range of the linear response of the detector.

The GLC measurements of zinc, copper and nickel in samples of sediments carried out according to method (iii) are shown in Table I together with the results obtained by methods (i) and (ii).

The zinc, copper and nickel contents calculated from chromatograms shown in Figs. 9 and 10 are averages of five runs. Each extract of the complexes was applied on to the column three times.

The results are encouraging for the use of an FID in the GLC assay of the DEDTC complexes of zinc, copper and nickel. Further, they show the usefulness of the procedure for processing marine bottom sediments for the simultaneous assay of

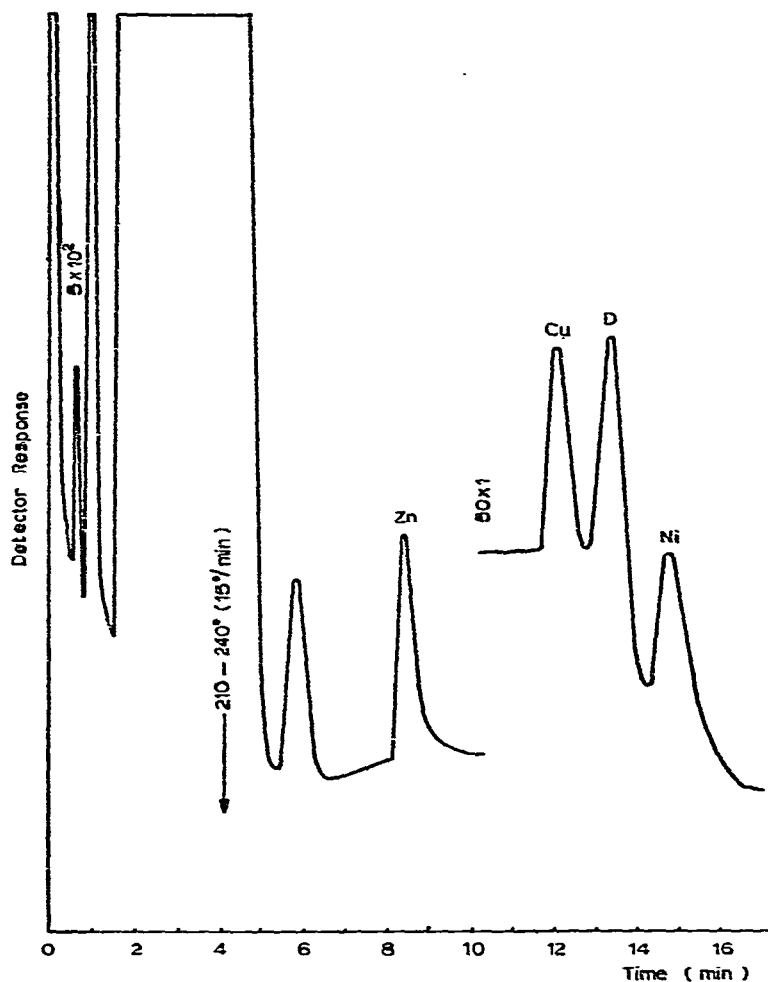


Fig. 10. Typical chromatogram obtained for a solution of a sample of mud. Column temperature, 240°; detector temperature, 250°; argon flow-rate, 18.75 ml/min. Addition of 10  $\mu$ l of *n*-dodecyl-acontan (D) solution (717.6  $\mu$ g/ml). Final volume, 100  $\mu$ l; injection volume, 0.8  $\mu$ l.

zinc, copper and nickel without the risk of thermal decomposition of the metal complexes in the column or interferences by other metals that form complexes with DEDTC.

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