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GAS CHROMATOGRAPHIC ANALYSIS OF TRACE METALS ISOLATED FROM AQUEOUS SOLUTIONS AS DIETHYLDITHIOCARBAMATES*

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SUMMARY

While the determination of trace levels of metal ions in sea waters and other marine samples can be accomplished by spectroscopic means (atomic absorption or inductively coupled plasma) recent publications describing the determination of metal ions as diethyldithiocarbamate derivatives has raised the possibility of using gas chromatographic techniques. A study was undertaken to establish optimum procedures both for the isolation of trace metals as diethyldithiocarbamates from aqueous media and for their quantitation by gas chromatography. The diethyldithiocarbamate standards required for this study [*i.e.* those of Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II) and Co(III)] were prepared and characterized. A gas chromatographic method was developed, involving the use of the mixed stationary phases QF-1 and OV-101 at low concentrations, which gave a highly efficient separation of mixtures of up to five of the metals studied. Contrary to other reports in the literature dealing with the gas chromatography of some metal diethyldithiocarbamate or other, the use of glass tubing to pack columns was found to be critical for obtaining successful separations, and elimination of possible degradation of the metal diethyldithiocarbamates on the columns. Linear responses were the rule in the nanogram concentration range investigated for each metal. Accuracy of analyses of ppm concentrations of the metals was in the order of ± 5% or better, with relative standard deviations of 5% or less. Low ppb (ng/ml) detection was feasible starting with metals dissolved in either distilled water, or in synthetic sea water.

Theoretical principles have been proposed to account both for the nature of the gas chromatographic separation observed and for the degradation problems encountered and overcome.

INTRODUCTION

The determination of traces of metals in marine specimens and in sea water is commonly carried out by spectroscopic methods which are not without their disadvantages. For example, atomic absorption is limited to analysis of a single metal at a time, while the very versatile inductively coupled plasma (ICP) technique is not universally available because of its high cost. There exists a need for a relatively versatile and inexpensive method. The possibility of using gas chromatography (GC) after conversion of the metals to suitable chelates (acetylacetonates, β-diketonates, β-thioketonates, etc.) has long appeared attractive, but has not been exploited because of volatility limitations and problems of thermal decomposition[1-9]. Some work has been focussed on metal diethyldithiocarbamate chelates because of the reported thermal stability of diethyldithiocarbamates of many but not all divalent metals[10-12]. Numerous publications have described the GC analysis of diethyldithiocarbamates of a particular metal or mixture of metals with varying degrees of success and employing a variety of chromatographic columns[13-22].

Given the contradictory nature of these reports considerable doubt exists as to the feasibility of GC for analysis of real samples for trace metal content. Optimum column conditions, attainable limits of detection, and possible degree of resolution are factors which remain to be defined. We report here on a study undertaken to resolve these questions. Experiments were carried out with diethyldithiocarbamates of Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) and Co(III). A column system was developed which gave excellent resolution and quantitation of mixtures of up to five of these metals present in low ppm amounts.

EXPERIMENTAL

Preparation of metal diethyldithiocarbamates: standards and stock solutions

The procedures used to prepare and characterize the required metal diethyldithiocarbamate standards will be the subject of a separate report by Carvajal and Zienius. The standards were used to make solutions for the GC tests which followed. Chloroform (ACS reagent grade, Anachemia Chemicals, Montreal, Canada) was used to dissolve accurately weighed portions of the diethyldithiocarbamates. Typically, stock solutions in the concentration range of 0.01 to 1.00 mg/ml were prepared and used for preliminary testing of columns.

Recovery of trace metals from aqueous solutions by extraction as diethyldithiocarbamates

Aqueous stock solutions of each metal tested, at 100 ppm concentration, were prepared by dissolution of the required amount of the carefully weighed out metal salt (*e.g.* CuSO$_4$ · 5H$_2$O, etc.) in deionized water or synthetic sea water depending on the experiment. These stock solutions were diluted to 1.00- to 10.0-ppm levels as required and hence referred to as "test solutions".

The metal ions in the test solutions were recovered as diethyldithiocarbamates via the following procedure. A measured volume of test solution, 50.0 to 100.0 ml, was placed in a 125-ml separatory funnel and 50 mg of citric acid was added to prevent any possible metal hydroxide formation[23,24]. The pH was maintained be-

tween 2.6 and 5.0. A 2.0% (w/w) diethyldithiocarbamate solution (5–10 ml) was added, and the funnel was shaken for about 1 min.

The cloudy mixture formed was extracted with three to four 3- to 5-ml portions of chloroform. The extracts were collected and diluted to volume in either 25.00- or 10.00-ml volumetric flasks. These solutions were then analyzed by GC.

GC procedures

A Shimadzu gas chromatograph Model GC-6AM equipped with a differential flame ionization detector (Model FID-6) and an electron-capture detector (Model ECD-6) was used. The injector/detector temperature was maintained at a constant value in the 260 to 300°C range as required. Gas flows for tests using the flame ionization detector were: 60 ml/min nitrogen carrier gas (purified by passage through moisture, hydrocarbon and oxygen traps); 46.7 ml/min hydrogen; and 0.90 l/min air. The same carrier gas conditions applied to tests with the electron-capture detector. All cylinder gases were products of Union Carbide.

The columns investigated were prepared using supports, stationary phases, and tubing purchased from Chromatographic Specialties (Brockville, Canada). A batch coating (evaporation) method as described by Supina[25] and Leibrand and Dunham[26] was used to prepare column packings. In the preparation of mixed stationary phase packings the two phases in question were simultaneously applied onto the supports from the same solution. After packing into suitable tubing, columns were preconditioned at 250°C with nitrogen flowing through at a rate of 15 ml/min for 12h. All glass tubing used was silylated using Sylon CT (Supelco Canada, Oakville, Canada) before being loaded with packing.

Sample solution injection into the gas chromatograph was with a 10-μl Hamilton microsyringe, Model 701 N.

RESULTS AND DISCUSSION

Testing of GC columns

The first tests were undertaken using columns containing stationary liquid phases and supports most commonly reported in the literature for some metal diethyldithiocarbamate analysis or other[7,13,14,19,20,22,27], and combinations of these stationary phases. Stainless-steel tubing was used in keeping with literature reports that results equivalent to those with glass columns would be obtained[14]. Problems such as decomposition, peak tailing and poor resolution were observed with most of the columns. Our best resolution of mixtures of diethyldithiocarbamates of Ni(II), Cu(II) or Hg(II), Zn(II) and Co(III) was obtained on 60 cm × 1/8 in. O.D. 5% OV-101 + 5% QF-1 on 80–100 mesh Gas Chrom Q. Total analysis time was 20 min.

The resolution was better than that reported previously on a similar, but 150 cm long, column[22] because our packing was prepared by equilibration of the support with a chloroform solution containing both OV-101 and QF-1, in amount sufficient to give a 5% coating of each stationary phase.

On the assumption that the stainless-steel tubing was at least partly responsible for the decomposition effects observed, subsequent columns were prepared in glass tubing. The relative merits of Type 304 stainless-steel and glass tubing were directly compared using columns A, B and C listed in Table I. On both columns B and C

TABLE I

GLASS TUBING PACKED COLUMNS

Column	Dimensions	Stationary phase	Support, 80–100 mesh
A	30 cm × 1/8 in. O.D.*	2% SE-30 + 2% QF-1	Gas Chrom Q
B	60 cm × 2.0 mm I.D.	2% SE-30 + 2% QF-1	Gas Chrom Q
C	60 cm × 5.0 mm I.D.	2% SE-30 + 2% QF-1	Gas Chrom Q
D	30 cm × 1/8 in. O.D.*	5% OV-101 + 5% QF-1	Chromosorb W HP
E	60 cm × 2.0 mm I.D.	5% OV-101 + 5% QF-1	Chromosorb W HP
F	60 cm × 2.0 mm I.D.	2.5% OV-101 + 2.5% QF-1	Gas Chrom Q
G	60 cm × 2.0 mm I.D.	1.5% OV-101 + 1.5% QF-1	Gas Chrom Q
H	60 cm × 2.0 mm I.D.	1.0% OV-101 + 1.0% QF-1	Gas Chrom Q

* Type 304 stainless-steel tubing.

moderately better resolution was obtained than that on column A at a column temperature of 205°C for a mixture of Zn(II), Cu(II), and Ni(II) diethyldithiocarbamates. This improvement in resolution was not due only to the additional length of the glass columns since previous attempts to use longer 60 cm, stainless-steel tubing packed columns gave unacceptably long retention times at 205°C. Furthermore, on columns B and C, single and almost symmetrical peaks were the norm for Pb(II), Cd(II) and Hg(II), with no signs of degradation.

Our next comparison of the relative merits of glass and stainless-steel tubing was using columns D and E. Advantageous behaviour of glass tubing was observed for a mixture of Zn(II), Cu(II) and Ni(II) diethyldithiocarbamates (Table II). Notice that resolution (R_s) values of 1.8 and 2.7 on column E were especially significant since for two gaussian peaks of the same width, a value of $R_s = 1.5$ represents 99.98% effective peak separation[28]. In addition, Ettre[29] has reported that for R_s greater than 2.0, an additional $(R_s - 1)$ peaks should be resolvable between the two peaks in question. Tests with up to five component metal diethyldithiocarbamate mixtures were therefore attempted and good results were obtained. For example, a mixture of Zn(II), Cd(II), Cu(II), Ni(II) and Co(III) diethyldithiocarbamates was easily resolved (Fig. 1). While these results were excellent, the total time per analysis, 19 min, was rather long. To attempt reduction of retention times without undue decrease in resolution, tests were carried out with columns F, G and H. An excellent separation of Zn(II), Cd(II), Cu(II), Ni(II) and Co(III) diethyldithiocarbamates was achieved on column F within 15 min (Fig. 2). Almost as good separations were obtained on

TABLE II

RETENTION TIMES AND RESOLUTION OF METAL DIETHYLDITHIOCARBAMATES

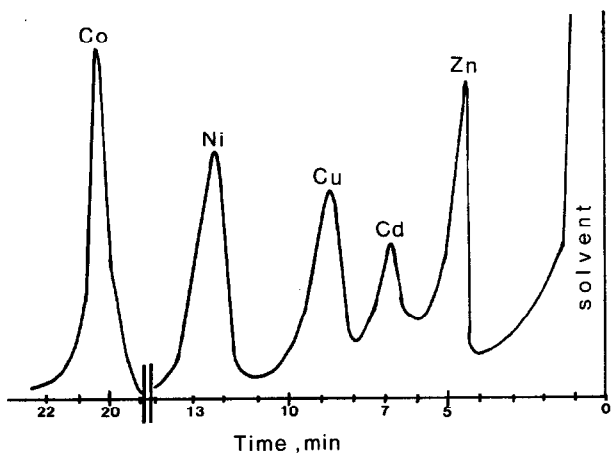| Metal	Column E		Column D	
	Retention time (min)	Resolution	Retention time (min)	Resolution
Ni(II)	8.8		5.9	
		1.8		1.4
Cu(II)	6.1		4.1	
		2.7		1.6
Zn(II)	3.4		2.6	

Fig. 1. Resolution of Zn(II), Cd(II), Cu(II), Ni(II) and Co(III) on column E at 210°C for 10 min followed by temperature programming at 10°C/min.

columns G and H with similar retention times but somewhat increased peak widths. On further testing it was found possible to resolve effectively a mixture of Zn(II), Cd(II), Pb(II), Hg(II) and Co(III) diethylthiocarbamates. When present in the sample mixture, however, peaks for Cu(II) and Pb(II), and for Hg(II) and Ni(II) interfered with one another. Calibration curves on these columns were linear as is illustrated for column G in Fig. 3.

Accuracy and precision

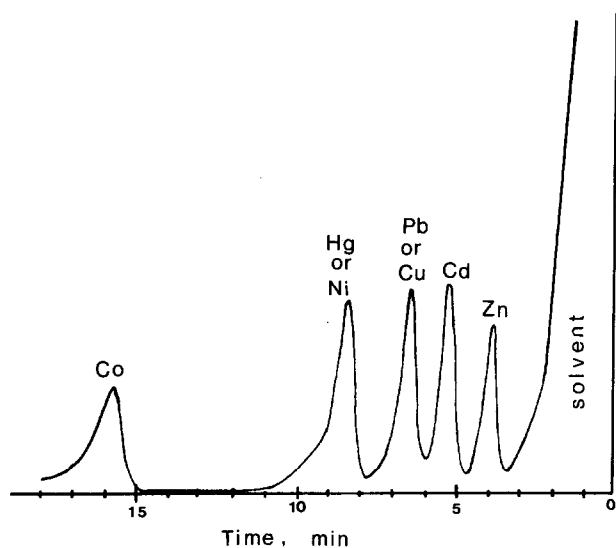It was necessary to establish the efficiency of extraction of ppm amounts of

Fig. 2. Resolution of Zn(II), Ni(II) or Hg(II), Cu(II) or Pb(II), Cd(II) and Co(III) on column F at 200°C for 10 min followed by temperature programming at 20°C/min to 245°C.
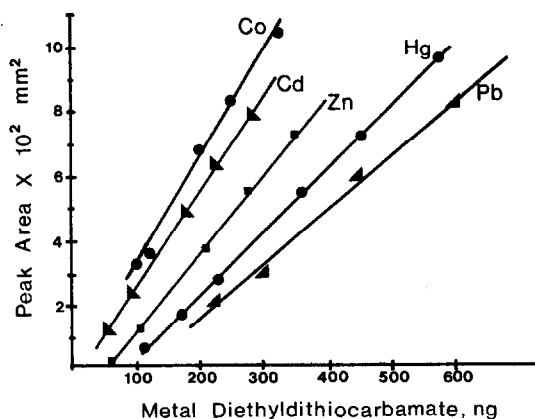
Fig. 3. Calibration curves for Co(III), Cd(II), Zn(II), Hg(II) and Pb(II) on column G at 205°C for 8 min followed by temperature programming at 20°C/min to 245°C.

trace metals from water as their diethyldithiocarbamates in chloroform, together with the accuracy and precision of GC analyses of the extracts. Three solutions were prepared, containing Zn(II), Cd(II), Cu(II), Pb(II), Ni(II), Hg(II) and Co(III) in various ppm amounts, the metals were extracted as diethyldithiocarbamates, and the extracts analyzed by GC using columns E, G or H. The metal concentrations investigated were in the range of what would be most commonly encountered in real sea waters. Results obtained are compiled in Table III. In all cases, acceptable accuracy and precision was obtained with relative standard deviations (R.S.D.) equal to or less than 5% 12 times out of 16, and equal to or less than 8.3% the other 4 times. Recovery of the metals ranged from 95 to 105% 13 times out of 16. In the remaining three instances recoveries were between 90 and 100%.

The question of whether recoveries of trace metals as diethyldithiocarbamates from sea water could be as efficiently accomplished as from distilled water was resolved in a separate study. Ni(II) and Zn(II) diethyldithiocarbamates were recovered from synthetic sea water containing a total of ten metals. The recoveries (average of three experiments), 101% for Ni(II) and 95% for Zn(II), were comparable to those from distilled water.

Detection limits

Tests were carried out with columns A and G to establish the lower detection limits for the metal diethyldithiocarbamates. The results obtained are summarized in Table IV. Lower detection limits by factors of up to 2 on column G indicated losses of the metal diethyldithiocarbamates by adsorption and/or degradation on the stainless-steel tubing used in making column A. Detection limits depended on the percent by weight metal content of each chelate. For example, smaller amounts of Co(III) and Ni(II) could be detected than of Pb(II) or Hg(II), a reflection of the behaviour of the flame ionization detector.

Calculation of the minimum metal concentration detectable reported in ppb in Table IV was done assuming an initial aqueous sample volume of 50.0 ml being extracted with 1.0 ml chloroform, and 4 μl of the latter being used for GC analysis.

TABLE III

RECOVERY OF TRACE METALS AS DIETHYLDITHIOCARBAMATES AND ACCURACY OF THEIR DETERMINATION BY GC

Metal	Concentration (ppm)			R.S.D. (%)	Average metal recovered (%)
	Theoretical	Range of 5 exp. determinations	Average		
Zn(II)***	5.1	4.6–4.9	4.7	2.1	92
Zn(II)*	3.1	3.1–3.4	3.2	4.4	103
Zn(II)**	2.0	1.8–2.0	1.9	5.3	95
Cd(II)*	5.1	4.5–5.0	4.9	4.5	96
Cd(II)***	3.1	2.9–3.1	3.0	2.7	97
Cd(II)**	2.0	1.6–1.9	1.8	8.3	90
Cu(II)*	2.1	2.1–2.4	2.2	5.0	105
Cu(II)***	2.1	2.1–2.2	2.1	2.4	100
Pb(II)**	8.1	7.7–8.3	8.0	3.8	99
Ni(II)*	2.1	1.8–2.0	2.0	4.5	95
Ni(II)***	2.1	2.1–2.3	2.2	4.1	105
Hg(II)**	5.1	4.8–5.3	5.1	3.9	100
Co(III)*	2.0	2.0–2.4	2.2	7.0	110
Co(III)***	2.0	1.9–2.1	2.0	4.5	100
Co(III)**	1.0	1.0–1.1	1.0	5.0	100

   * Column E: 210°C for 9 min, then programmed at 20°C/min to 250°C.
  ** Column G: 205°C for 8 min, then programmed at 20°C/min to 235°C.
*** Column H: 190°C for 7 min, then programmed at 20°C/min to 250°C.

TABLE IV

DETECTION LIMITS FOR METAL DIETHYLDITHIOCARBAMATES USING GC WITH FLAME IONIZATION DETECTION

Column G: 190°C, except 250°C for Co(III); column A: 210°C, except 250°C for Co(III).

Metal	Metal diethyldithiocarbamate (ng) required to give signal-to-noise ratio of 3		Equivalent amount of metal (ng)		Column G minimum amount of metal detectable (ppb)
	Column G glass tubing	Column A stainless steel	Column G glass tubing	Column A stainless steel	
Ni(II)	20	30	3.3	5.0	17
Cu(II)	40	70	7.1	12.4	35
Zn(II)	70	100	12.6	18.1	63
Cd(II)	56	110	15.4	30.2	77
Hg(II)	100	150	40.4	60.5	202
Pb(II)	150	220	61.7	90.5	310
Co(III)	30	30	3.5	3.5	18

Attempts to use injections larger than 4.0 μl for GC analysis resulted in a solvent peak large enough to interfere with the metal diethyldithiocarbamate peak.

In a separate study it was found that down to 0.2 ng of Ni(II) diethyldithiocarbamate could be detected using an electron-capture detector. This was equivalent to a minimum detectable limit of less than 0.2 ppb in an aqueous sample, a value close to that reported previously by Tavlaridis and Neeb[17].

Theoretical considerations

The order of elution of the components of a mixture in GC analysis depends upon the volatility of the components, and/or their affinity for the stationary phase. Based on our results that elution order was the same on both very non-polar, SE-30, and relatively polar, QF-1, stationary phases the dominant effect for metal diethyldithiocarbamates appears to be volatility. This being the case a consideration of factors determining the volatility of metal diethyldithiocarbamates is required to attempt to explain the elution order observed and to facilitate prediction of elution times for metal diethyldithiocarbamates not yet investigated.

Generally, highly polar or charged species like metal ions, in which intermolecular forces are high, are non-volatile. However, intermolecular forces are greatly reduced when such species are attached to and surrounded by ligand molecules[24]. This is the case for metal diethyldithiocarbamates. It is predictable that the ligand group will shield more effectively smaller metal ions than larger ones. Hence, in comparing the diethyldithiocarbamates of Zn(II), Cd(II) and Hg(II), that of Zn(II) would be predicted to elute first and that of Hg(II) last, since there is an increase in atomic radii from 74 pm to 110 pm going from Zn(II) to Hg(II) and a corresponding decrease in shielding of the metal. This prediction is confirmed by experiment. We cannot, however, use this hypothesis alone to explain relative volatilities in all cases. It does not explain why the retention time of the diethyldithiocarbamate of Co(III) is much longer than that of Zn(II) even though the atomic radii of these two elements are similar. To do so, the above argument must be expanded to include consideration of the hard/soft acid theory. For example, comparing the metal ions Zn(II), Cd(II) and Hg(II), Zn(II) is the hardest acid (least polarizable) and Hg(II) the softest. The same order of polarizability applies to the diethyldithiocarbamates of these metals[30]. Thus the diethyldithiocarbamate of Zn(II) will be the most volatile and that of Hg(II) the least. In applying this line of reasoning to explain the behaviour of Co(III) relative to Zn(II) diethyldithiocarbamate, since Co(III) is a harder acid than Zn(II) because of its greater charge/size ratio it would be expected to elute first. However, another factor to consider here is that Co(III) diethyldithiocarbamate has three ligand groups surrounding Co(III). This gives a molecule that is highly polarizable, more so than Zn(II) diethyldithiocarbamate. Hence its lower volatility. Similarly, consideration of degrees of polarizability explains why Cu(II) elutes after Cd(II) and Zn(II) even though its ionic radius is the least of the three, and why Hg(II) has a similar retention time to Ni(II) in spite of its larger ionic radius. From our experimental results, it would appear that although electronic effects due to bonding and to changes in polarizability are critical factors that need to be considered to predict elution order of metal diethyldithiocarbamates, other considerations exist which must be considered. Our conclusion is reinforced by results reported by Cardwell and Desarro[14] in their study of Ni(II), Pb(II) and Pt(II) diethyldithiocarbamates.

The diethyldithiocarbamates of Pb(II), Cd(II) and Hg(II) generally underwent some decomposition when chromatographed on stationary phase-coated supports packed in stainless-steel tubing. Our hypothesis is that these metal ions, relatively soft acids in their own right, become even softer upon reaction with the soft base diethyldithiocarbamate ion[31,32]. Both soft acids and soft bases, particularly in the gaseous state, are known to interact with metal surfaces (zero valence state of the metal) and undergo adsorption[33]. The soft acid behaviour of metal diethyldithiocarbamates is also the factor most likely responsible for their inferior resolution upon columns packed in stainless-steel tubing rather than in glass tubing. The evidence for this is that the only metals whose diethyldithiocarbamates could be adequately separated on stainless-steel tubing packed columns were those of Co(III), Ni(II), Cu(II) and Zn(II). These metal ions rank as borderline or hard metal acids.

Another possible reason for the observed instability of Pb(II), Cd(II), and Hg(II) diethyldithiocarbamates is that sulfur, being a strong nucleophile, may be able to initiate pyrolytic decomposition of the soft acid diethyldithiocarbamate ligand. In addition, sulfur can react with soft acid metals to form very stable sulfides[32]. These reactions might occur when metal diethyldithiocarbamates are heated to high column temperatures used in GC analyses.

CONCLUSIONS

A GC procedure has been developed, based on the use of mixed-stationary-phase-coated supports packed in glass tubing, for the separation of aqueous mixtures of up to five metals present in ppm amounts. Our separations of the diethyldithiocarbamates of Ni(II), Cu(II), Co(III), Cd(II) an Zn(II), and of Zn(II), Cd(II), Pb(II), Hg(II) and Co(III) were accomplished with better resolution than has been reported previously and are likely as good as is possible without resort to capillary columns. Linear responses were observed for all metal diethyldithiocarbamates in the nanogram concentration range with columns containing 1.0, 1.5, 2.5 or 5.0% each of OV-101 and QF-1 as stationary phase. Accuracy and precision of measuring ppm amounts of the metals in distilled water were excellent. Accuracy within 5% of the expected value was generally the norm, with relative standard deviations equal to or less than 5%. Detection limits were in the order of 17 to 300 ppb using flame ionization detection and as low as 0.2 ppb with electron-capture detection depending on the particular metal diethyldithiocarbamate studied. These limits are in the concentration range within which the investigated metals are commonly found in sea water.

Theoretical arguments have been presented to explain the order of GC elution of metal diethyldithiocarbamates. To do so, consideration must be given to both relative metal ion sizes, and degrees of polarizability of the metal diethyldithiocarbamates. The hard/soft acid/base theory also accounts for degradation observed of metal diethyldithiocarbamates such as Hg(II) when stainless-steel tubing packed columns are used.

The GC method described here should be applicable to the routine determination of selected metals in marine systems in many instances, with the advantage over atomic absorption spectrophotometry of making possible simultaneous multimetal analyses.

REFERENCES

1 M. Lederer, *Nature (London)*, 176 (1955) 462.
2 P. Jacquelot and G. Thomas, *Bull. Soc. Chim. Fr.*, (1971) 702.
3 R. Belcher, W. I. Stephen, I. J. Thomson and P. C. Uden, *J. Inorg. Nucl. Chem.*, 33 (1971) 1851.
4 R. S. Barratt, R. Belcher, W. I. Stephen and P. C. Uden, *Anal. Chim. Acta.*, 59 (1972) 59.
5 R. Belcher, R. J. Martin, W. I. Stephen, D. E. Henderson, A. Kamalized and P. C. Uden, *Anal. Chem.*, 45 (1973) 1197.
6 P. C. Uden, D. E. Henderson and A. Kamalized, *J. Chromatogr. Sci.*, 12 (1974) 591.
7 T. J. Cardwell, P. J. Marriott and P. S. McDonough, *J. Chromatogr.*, 193 (1980) 53.
8 R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, London, 1965.
9 P. Mushak, in K. Blau and G. S. King (Editors), *Handbook of Derivatives for Chromatography*, Heyden, London, 1977, p. 433.
10 G. D'Ascenzo and W. W. Wendlandt, *J. Therm. Anal.*, 1 (1969) 423.
11 G. D'Ascenzo and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 2431.
12 Y. I. Usatenko and N. P. Fedash, *Tr. Kom. Anal. Khim., Akad. Nauk, SSSR*, 14 (1963) 183.
13 J. Masaryk, J. Krupčik, J. Garaj and M. Košik, *J. Chromatogr.*, 115 (1975) 256.
14 T. J. Cardwell and D. J. Desarro, *Anal. Chim. Acta.*, 85 (1976) 415.
15 A. Tavlaridis and R. Neeb, *Frezenius' Z. Anal. Chem.*, 292 (1978) 199.
16 A. Tavlaridis and R. Neeb, *Frezenius' Z. Anal. Chem.*, 282 (1976) 17.
17 A. Tavlaridis and R. Neeb, *Frezenius' Z. Anal. Chem.*, 293 (1978) 211.
18 A. Tavlaridis and R. Neeb, *Frezenius' Z. Anal. Chem.*, 293 (1978) 290.
19 J. Krupčik, P. A. Leclercq, J. Garaj and J. Masaryk, *J. Chromatogr.*, 171 (1979) 285.
20 M. Ahmad and A. Aziz, *J. Chromatogr.*, 152 (1978) 542.
21 A. Radecki, J. Halkiewicz, J. Grzybowski and H. Lamparczyk, *J. Chromatogr.*, 151 (1978) 259.
22 A. Radecki and J. Halkiewicz, *J. Chromatogr.*,., 187 (1980) 363.
23 R. A. Chalmer and D. M. Dick, *Anal. Chim. Acta.*, 31 (1964) 520.
24 R. E. Sievers and J. E. Sadlowski, *Science (Washington, D.C.)*, 201 (1978) 217.
25 W. R. Supina, *The Packed Column in Gas Chromatography*, Supelco Inc., Bellefonte, PA, 1974, p. 21.
26 R. J. Leibrand and L. L. Dunham, *Res. Dev.*, September (1973) 32.
27 J. Krupčik, J. Garaj, Š. Holotík, D. Oktavec and M. Košik, *J. Chromatogr.*, 112 (1975) 189.
28 H. W. Moody, *J. Chem. Educ.*, 59 (1982) 291.
29 L. S. Ettre, *Chromatographia*, 8 (1975) 291.
30 E. Patsalides, B. J. Stevenson and S. Dilli, *J. Chromatogr.*, 173 (1979) 321.
31 J. E. Huheey, *Inorganic Chemistry Principles of Structure and Reactivity*, Harper and Row, New York, 1978, p. 276.
32 R. G. Pearson, *Science (Washington, D.C.)*, 151 (1966) 172.
33 D. J. Barclay, *J. Electroanal. Chem.*, 19 (1968) 318.