Journal of Chromatography, 99 (1974) 309–318

CHROM. 7619

NON-FLUORINATED TETRADENTATE β-KETOAMINES AS DERIVATIZING LIGANDS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF Cu(II), Ni(II) AND Pd(II)

PETER C. UDEN and DAVID E. HENDERSON
Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002 (U.S.A.)

SUMMARY

The use of a gas chromatographic substrate consisting of Dexsil 300GC on Chromosorb 750 support permits the elution of non-fluorinated tetradentate β-ketoamine chelates of Cu(II), Ni(II) and Pd(II) to the nanogram level without degradation. The enhanced volatility of these chelates and the capability for copper and nickel resolution is demonstrated in determinations on noble metal "matte" samples.

INTRODUCTION

It has become evident in the field of metal complex gas chromatography (GC) that the nature of the chelating ligands has a fundamental effect on the viability of development of quantitative metal analysis[1,2]. While typically β-diketones are ligands of choice for the GC of trivalent hexa-coordinate metals such as Cr(III) and Al(III)[3–5], the problems of solvation, polymerization and oxidation exhibited by β-diketonates of divalent transition metals in particular[6] have prompted the search for alternative chelate systems for these metals. Of particular note have been the studies of chelates of β-thioketones[7–9] and bidentate and tetradentate β-ketoamine analogs of β-diketones[10–12].

In general, the development of metal chelate GC has seen the increased application of fluorinated chelates, this being the result of a number of favorable factors including their frequently increased volatility and thermal stability as compared with their non-fluorinated analogs[1], less deleterious column interactions and, when electron capture detection is employed, the enhanced sensitivity deriving from the incorporation of fluorine atoms into the already strongly electron capturing ring systems[13]. Thus non-fluorinated β-diketonates have found few GC applications to the present time.

In the area of tetradentate β-ketoamine complexes of such metals as Cu(II), Ni(II) and Pd(II), the situation is less clear-cut, however. First, in contrast to β-diketonates and bidentate β-ketoamine chelates, thermogravimetry has shown the non-fluorinated tetradentate complexes to be generally more volatile than their fluorinated counterparts, an effect not as yet readily understood[11]. Secondly the non-fluorinated ligands are usually easier to prepare and also react more rapidly with

transition metal ions in solution. Thirdly, thermogravimetry indicates greater volatility differences between different metal chelates of the same ligand than are seen for the fluorinated systems. These features indicate these chelates to be worthy of GC study, but this area has to date been little explored owing primarily to unfavorable column interactions and sample decomposition especially at low concentrations.

The present paper describes a re-examination of these ligands with respect to their potential for quantitative derivatization and GC analysis of divalent transition metals, notably Cu(II), Ni(II) and Pd(II). The improved GC characteristics of recently developed GC substrates is shown to make their application practicable in certain cases.

EXPERIMENTAL

General nomenclature

A nomenclature based primarily upon appropriate abbreviations of trivial names of ligands and complexes is used in the text. These names are given in Table I.

TABLE I

GENERAL NOMENCLATURE

Systematic name	*Trivial name*	*Complex*
N,N′-Ethylenebis(acetylacetoneimine)	bis(acetylacetone)ethylenediimine	$H_2(enAA_2)$
N,N′-Propylenebis(acetylacetoneimine)	bis(acetylacetone)propylenediimine	$H_2(pnAA_2)$
N,N′-Ethylenebis(trifluoroacetyl-acetoneimine)	bis(trifluoroacetylacetone)ethylenedi-imine	$H_2(enTFA_2)$
N,N′-Propylenebis(trifluoroacetyl-acetoneimine)	bis(trifluoroacetylacetone)propylene-diimine)	$H_2(pnTFA_2)$

Preparation of ligands

β-Ketoamine ligands were prepared from β-diketones by condensation with the appropriate diamine as previously described[11,12]. The non-fluorinated ligands were purified by recrystallization from *n*-hexane and the fluorinated ligands from ethanol.

Preparation of metal chelates

Pure samples of chelates were prepared for GC evaluation. The method used was as described previously[12]; for copper and nickel chelates an acetone solution of the ligand was reacted with the appropriate freshly prepared metal hydroxide; palladium chelates were prepared by reacting an acetone solution of the ligand with the palladium dichloride bis(benzonitrile) complex. Purification was by recrystallization and vacuum sublimation.

Sample preparation and reaction procedure for quantitative determinations

The high solubilities of the non-fluorinated tetradentate β-ketoamine ligands in water as compared to the fluorinated analogs enables them to be used in aqueous solution. The following is a typical procedure as used for the determination of the noble metal "matte" samples discussed in this paper. A solution of $H_2(pnAA_2)$ of

concentration 7.8 mg/ml was prepared in 5% sodium carbonate (aqueous). (Generally the sodium carbonate concentration should be sufficient to neutralize any acid present in the sample and to bring it to high pH; strongly acidic samples should be partially neutralized prior to addition of ligand, *n*-docosane or *n*-tetracosane internal standards may be dissolved in the chloroform to be used for the extraction of the complexes.)

The sample to be analyzed is placed in a sample vial and the ligand solution added followed by warming on a hot plate for 5 min, care being taken to ensure that the sample does not boil. After cooling to room temperature chloroform is added to extract the complex, this being effected by a few seconds of brisk shaking. At very high metal concentrations, the aqueous sample will cloud due to precipitation of the complex but after extraction both aqueous and organic phases should be clear. In the typical case of the "matte 2" sample quantities were as follows, 127 μl of the sample was placed in the weighed vial, 4.0 ml of ligand solution were added and complete extraction effected into 209 μl of chloroform.

Gas chromatography

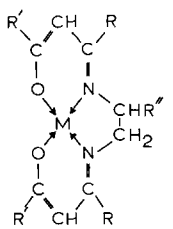
A Varian Associates Model 2440 instrument was used for this study, hydrogen flame ionization being employed. 1/8-in.-O.D. stainless-steel columns were used, substrates and column conditions being as reported in the text.

Thermal analysis

Thermogravimetric curves were recorded on a Perkin-Elmer TGS 1 thermogravimetric analyzer with *ca.* 2-mg samples at scan rates of 10°/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Previous studies of the tetradentate β-ketoamine complexes shown below have made it clear that the behavior of the non-fluorinated chelates on a range of available stationary phases and supports has been unsuitable for analytical purposes.



M = Cu, Ni, Pd
R = CH_3
R′ = CH_3, CF_3
R″ = H, CH_3

For example, in Fig. 1, the GC behavior of Cu(enAA$_2$) on an Apiezon L column at 250° is seen to change erratically with successive samples, degradation being evident. Typical silicone oil phases on silanized supports show similar behavior. While Ni(enAA$_2$), Pd(enAA$_2$) and the analogous propylenediamine derivatives show some-

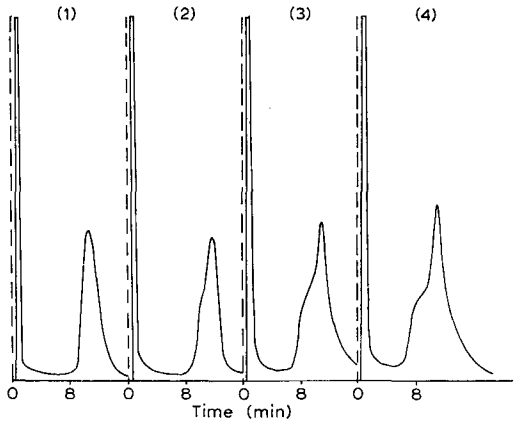


Fig. 1. A consecutive series of gas chromatograms for analytically pure $Cu(enAA_2)$ illustrating sample degradation. Column, 6 ft. × 1/8 in. O.D. stainless steel packed with 5% Apiezon L on Anakrom ABS (80–100 mesh). Column temperature, 250°; injector and detector temperature, 260°.

what improved behavior, quantitative elution of these complexes has not previously been achieved below the 100-ng level. It has been considered that these problems have resulted from a combination of marginal thermal stability coupled with deleterious interactions with column materials, supports or stationary phases. Even so, interest in these systems has been maintained for the reasons already noted: (i) their unexpectedly greater volatility than that of their fluorinated analogs, this being contrasted with the behavior of bidentate chelates in general; (ii) their potentially increased resolution of copper and nickel chelates as compared to the fluorinated complexes. These features are clear from the thermogravimetric curves presented in Figs. 2 and 3. Fig. 2 indicates comparable thermograms for the series of copper and palladium chelates, while Fig. 3 shows the markedly greater volatility difference for copper and nickel chelates of the non-fluorinated ligands.

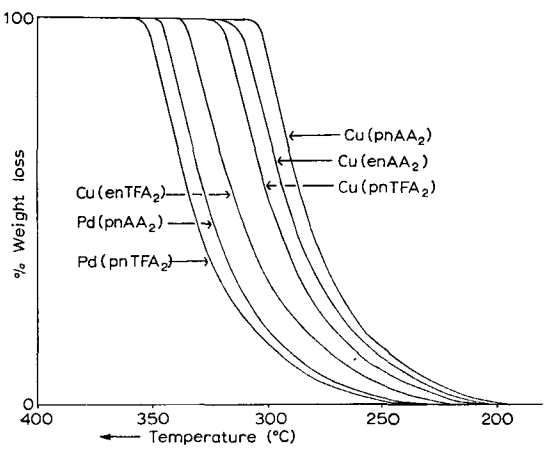


Fig. 2. Thermograms of tetradentate fluorinated and non-fluorinated Cu(II) and Pd(II) β-ketoamine chelates.

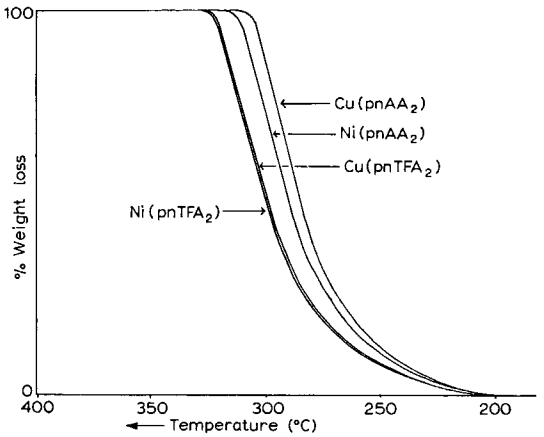


Fig. 3. Thermograms illustrating the volatility differences between Cu(II) and Ni(II) chelates of $H_2(pnAA_2)$ and $H_2(pnTFA_2)$.

Furthermore, the much more rapid chelate formation exhibited by these ligands in solution is a considerable experimental advantage over their fluorinated analogs. It seems probable that in the case of the $H_2(pnAA_2)$ complexes, which would be predicted to be of greater analytical potential than the $H_2(enAA_2)$ series because of their greater volatilities and thermal stabilities, there is an improved chance of GC resolution of copper and nickel chelates provided that they can be eluted without degradation.

The continual search for improved GC substrates in recent years has produced many new supports and stationary phases. In the area of supports, improved methods of silanization and deactivation have given more and more inert substrates. Recently, an improved grade of diatomite, derived according to the manufacturers from purer natural sources than previously used, has become available (Chromosorb 750; Johns-Manville, Celite Division, Denver, Colo., U.S.A.). We have assessed this substrate as obtained directly from the manufacturers and found it to give substantially improved GC behavior for these chelates. We describe in this paper data obtained for a stationary phase comprising 2% Dexsil 300GC coated on Chromosorb 750. The successful use of Dexsil 300GC columns for GC of relatively unstable metal chelates has been well established by Burgett in his recent study of mixed ligand complexes of divalent cations[14]. The column was conditioned before use according to the following procedure: with a nitrogen flow-rate of 45 ml/min, the column was held isothermal at 150° overnight, programmed at 4°/min to 300° and held at 300° for 4 h; it was found that alternative conditioning procedures gave much inferior results. While it is not certain as yet that data similar to those described below could not be obtained for other stationary phases on Chromosorb 750 or for Dexsil 300GC on other substrates, present evidence suggests this to be the case.

Fig. 4 shows the elution of $Cu(enAA_2)$ and $Ni(enAA_2)$ at the μg level from the Dexsil 300GC column at 220°. It can be seen that both chelates now exhibit excellent peak characteristics. No deterioration of peak shape is evident after numerous sample injections. Particularly in the case of the somewhat marginally stable $Cu(enAA_2)$ it is encouraging that the complex can be successfully eluted under these conditions to

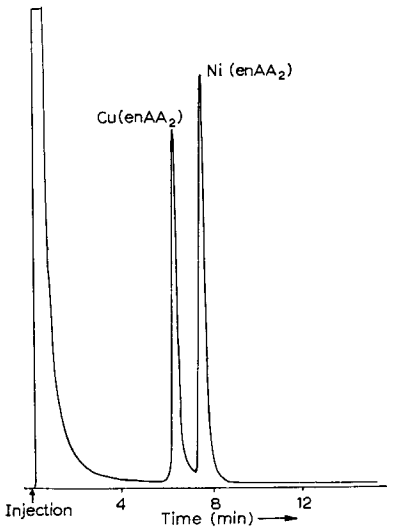


Fig. 4. GC separation of $Cu(enAA_2)$ and $Ni(enAA_2)$ on a 6-ft. × 1/8-in.-O.D. stainless-steel column filled with 2% Dexsil 300GC on Chromosorb 750. Injector temperature, 225°; column temperature, 220°; detector temperature, 230°.

the limits of flame ionization detection. The virtual baseline resolution of the two peaks also bears out the prediction of separability indicated by their thermograms.

The only conditions under which a parallel separation has been approached for tetradentate copper and nickel β-ketoamine chelates has been for the $H_2(pnTFA_2)$ chelates by utilizing fluorosilicone stationary phases such as QF-1 to impart selectivity and to resolve these virtually identically volatile species[11]. Such phases are, however, limited as to temperature when electron capture detection is employed, 215° being the effective limit. Even with flame ionization detection, where 230° may be tolerated, the poorer peak shapes of the non-fluorinated chelates exhibited on the QF-1 columns mean that their shorter retention times cannot be exploited analytically nor useful resolution achieved.

Fig. 5 shows the even greater resolution exhibited by the chelates of $H_2(pnAA_2)$ under similar conditions. The resolution of the non-fluorinated chelates as compared to the fluorinated species is apparent as also is the acceptable peak shape for the palladium complex. These chelates of the $H_2(pnAA_2)$ series were chosen to establish calibration curves over the flame ionization detection range for the chelates from *ca.* 20 ng/μl to *ca.* 4000 ng/μl. One microliter of chloroform solution was injected using the solvent flush technique, the standards being made by derivatizing metal ion solutions of known concentration according to the method described above. *n*-Tetracosane was included in the chloroform solution as an internal standard and concentrations normalized to this to accomodate injection errors.

Fig. 6 shows a calibration plot of detector current *vs.* concentration of metal chelate obtained as described. Good linearity is seen over the 20-ng to 400-ng range for the copper and nickel calibrations although insufficient replicate data are yet available to establish precision of individual points or of the slope.

There is some discrepancy, as yet unresolved, for the palladium chelate points.

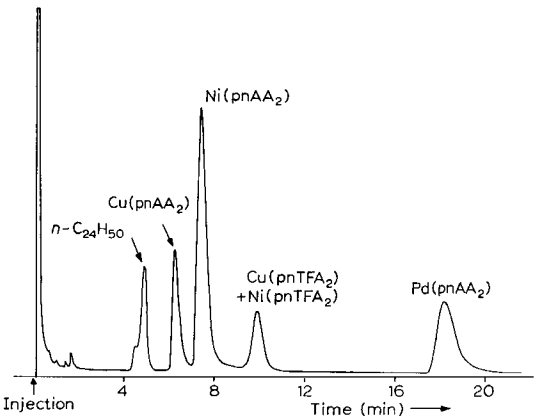


Fig. 5. Typical gas chromatogram of Cu(II), Ni(II) and Pd(II) chelates of $H_2(pnAA_2)$ and $H_2(pnTFA_2)$. Column, as Fig. 5. Injector and detector temperature, 230°; column temperature, 210°.

It would be predicted that the flame ionization response for this would be very close to that of the copper and nickel complexes, which are essentially identical. Points obtained at around the 500-ng region using pure chelate solutions do fall within the scatter of the copper and nickel points, but at lower values a diminished response is seen both for peaks corresponding to pure chelate solutions and for peaks derivatized as described from palladium "black" standards. This is possibly due to sample loss on the column, but appears more to be the result of peak tailing at the column temperature employed to establish reasonable retention times to enable copper and nickel resolution. This tentative conclusion is borne out by the improved peak shape for the palladium chelate peak obtained on temperature programming this portion of the chromatogram (Fig. 7).

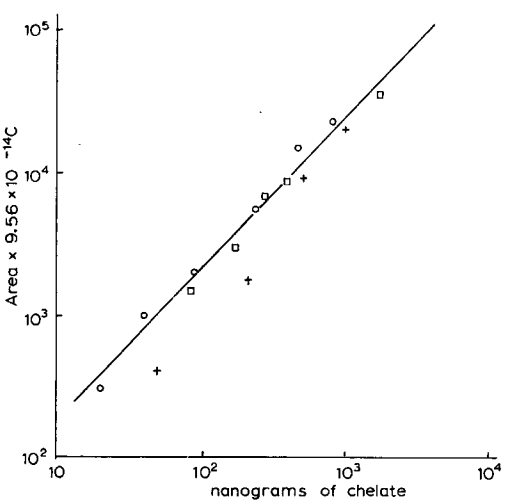


Fig. 6. Calibration plot for sample size (ng of metal chelate) *vs.* flame ionization detector response for $Cu(pnAA_2)$ (○), $Ni(pnAA_2)$ (□), and $Pd(pnAA_2)$ (+).

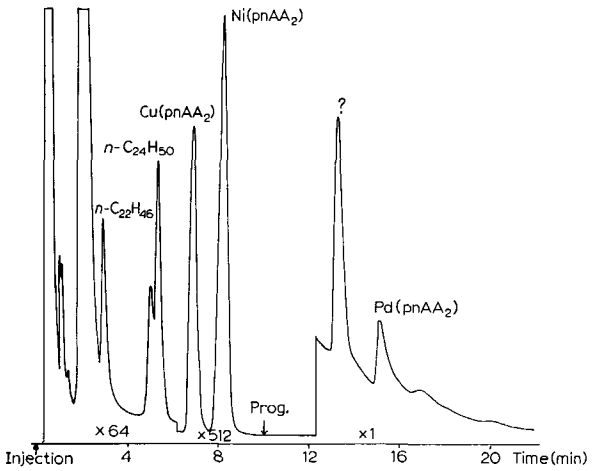


Fig. 7. Typical gas chromatogram derived from the solution of the "matte 2" sample. Column, as Fig. 5. Column isothermal at 210° for 10 min, then programmed at 20°/min, held at 230°. Current range, 10^{-11} A; attenuated as shown.

The applicability of the calibration plot was investigated for the analysis of two copper–nickel–"matte" samples (Falconbridge Nikkelverk, Kristiansands, Norway). These samples contained copper, nickel and sulfur as major components and iron, selenium, silver, gold, platinum, palladium, rhodium, ruthenium, and iridium as minor or trace components. The metal "mattes" were treated as follows: *ca.* 2 g samples were dissolved in approximately 150 ml of *aqua regia* and evaporated to dryness, the residue was taken up in concentrated hydrochloric acid and evaporated to dryness again, this procedure being repeated twice more in order to destroy any interfering nitrosyl complexes. The final residue was then dissolved in a minimal quantity of concentrated HCl (*ca.* 50 ml) and made up to 100 ml with distilled water. These samples were both derivatized directly and diluted as noted.

A typical gas chromatogram of a "matte" sample ("matte 2") derivatized from aqueous solution without dilution is shown in Fig. 7. It is noted that the great concentration difference between copper and nickel and palladium can be accomodated by suitable attenuation of the signal while still remaining within the linearity range of the detector. Values obtained directly from this chromatogram are included in Table II for comparison purposes on the assumption that linearity of response is retained to the level of *ca.* 30 μg, this not appearing likely to exceed the linearity range of column or detector. Also noteworthy in this chromatogram is the appearance of a peak before the palladium complex; this is at present unidentified but may possibly be due to a metal complex formed from one of the other metals in the sample.

Further results are given in Table II for copper and nickel determinations on diluted samples whose values fall in the calibrated region of the curve. In all cases results are higher than reported by Atomic Absorption (as supplied by Falconbridge Nikkelverk). Greater disparity is seen for copper than for nickel but at present in neither case is there evidence of GC interferences. It is unlikely that the higher values arise from high blank values as these have been shown by independent electron capture GC investigation to be well below the levels of concentration met with here[15]. Positive

TABLE II

COMPARISON OF GAS CHROMATOGRAPHIC RESULTS FOR COPPER, NICKEL AND PALLADIUM DETERMINATIONS ON NOBLE METAL "MATTE" SAMPLES WITH ATOMIC ABSORPTION DATA

Gas chromatography carried out on a 6-ft × 1/8-in.-O.D. stainless-steel column packed with 2% Dexsil 300GC on Chromosorb 750. Injector temperature, 225°; column temperature, 220°; detector temperature, 230°. Atomic Absorption data from Falconbridge Nikkelverk.

Sample	*Weight taken (g)*	*Atomic Absorption (ppm)*			*GC (ppm)*		
		Cu	*Ni*	*Pd*	*Cu*	*Ni*	*Pd*
Matte 1*	2.2224	96.9	211	—	186	239	—
Matte 2*	2.0270	114	195	0.3	166	249	—***
Matte 2**	2.0270	3453	5911	9.1	3980	5140	14.5

* Dilution of aqueous sample × 50 for analysis.

** Direct analysis of aqueous sample, calibration curve extrapolated by *ca.* one order of magnitude.

*** Below the limit of flame ionization detector response.

interference may result from chelate formation with other metals present in the sample and this will be further investigated as it has clear implications for the analysis of other noble metals by GC. However, at present there is no clear explanation for the discrepancies between the methods.

The value obtained for palladium is listed using the linear calibration plot for the determination. This value is also somewhat higher than that reported by Atomic Absorption, but it must be noted that the latter is quoted for a sample carried through a multi-stage separation and purification procedure. It is believed that the palladium value as listed is a reasonably valid one, rather than that obtained by employing the calibration curve which gives lower response for palladium as derived from palladium black standards. This approach is taken because of the superior peak shape exhibited by the palladium complex in the derivatized "matte" sample extract.

Clearly, considerably more results need to be obtained for samples of this type before full reliance can be placed on the method. The present data are presented primarily to indicate the potential of the GC procedures for the direct analysis of these metals at widely differing concentration levels without tedious work-up procedures. Efforts are currently being made to explore the electron capture detection characteristics of these non-fluorinated chelates and also, as stated previously, to investigate the broader determination of a wider range of noble metals by GC derivatization methods.

ACKNOWLEDGEMENTS

We wish to acknowledge "matte" samples obtained from Mr. H. Zachariasen of the Falconbridge Nikkelverk, Kristiansand, Norway. Our thanks are also due to Dr. C. A. Burgett of the Hewlett-Packard Corporation for valuable discussions on the use of Dexsil 300GC stationary phases for metal chelate GC. This work was supported by the National Science Foundation by Grants GP 31749 and GP 41168X and by the Research Corporation.

REFERENCES

1 R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon Press, Oxford, 1965.
2 G. Guiochon and C. Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Sci. Publ., Ann Arbor, 1973, Ch. VIII.
3 W. D. Ross and R. E. Sievers, *Anal. Chem.*, 41 (1969) 1109.
4 J. Savory, P. Mushak, F. W. Sunderman, Jr., R. Estes and N. Roszel, *Anal. Chem.*, 42 (1970) 294.
5 H. Veening, W. E. Bachmann and D. M. Wilkinson, *J. Gas Chromatogr.*, 5 (1967) 248.
6 D. F. Graddon, *Coord. Chem. Rev.*, 4 (1969) 1.
7 R. Belcher, W. I. Stephen, I. J. Thomson and P. C. Uden, *J. Inorg. Nucl. Chem.*, 33 (1971) 1851.
8 R. Belcher, W. I. Stephen, I. J. Thomson and P. C. Uden, *J. Inorg. Nucl. Chem.*, 34 (1972) 1017.
9 E. Bayer, H. P. Muller and R. E. Sievers, *Anal. Chem.*, 43 (1971) 2012.
10 R. H. Holm, G. W. Everett, Jr. and A. Chakravorty, *Progr. Inorg. Chem.*, 7 (1966) 83.
11 R. Belcher, K. Blessel, T. Cardwell, M. Pravica, W. I. Stephen and P. C. Uden, *J. Inorg. Nucl. Chem.*, 35 (1973) 1127.
12 R. Belcher, D. E. Henderson, A. Kamalizad, R. J. Martin, W. I. Stephen and P. C. Uden, *Anal. Chem.*, 45 (1973) 1197.
13 K. J. Eisentraut, D. J. Griest and R. E. Sievers, *Anal. Chem.*, 43 (1971) 2003.
14 C. A. Burgett, *J. Chromatogr. Sci.*, 11 (1973) 611.
15 P. C. Uden, D. E. Henderson and A. Kamalizad, *J. Chromatogr. Sci.*, in press.