PRECONCENTRATION OF TRACE METALS WITH KELEX 100

SOLVENT EXTRACTION PRECONCENTRATION OF TRACE METAL IONS FROM NATURAL WATERS WITH AN ALKYLATED OXINE DERIVATIVE

By

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A Thesis

Submitted to the School of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Science

McMaster University

MASTER OF SCIENCE (1989) McMASTER UNIVERSITY
(Chemistry) Hamilton, Ontario

TITLE: Solvent Extraction Preconcentration of Trace Metal Ions from Natural Waters with an Alkylated Oxine Derivative

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NUMBER OF PAGES: xii, 138

TO

MY PARENTS

WHOSE

LOVE

FAITH AND UNDERSTANDING

MADE THIS EFFORT

POSSIBLE

ABSTRACT

A method for the simultaneous preconcentration by solvent extraction of a group of trace metal ions from natural waters has been developed. The procedure makes use of a proprietary "liquid cation-exchanger", Kelex 100, the primary component of which is an alkylated oxine (8-quinolinol) derivative, 7-(4-ethyl-1-methyloctyl)-8-quinolinol (HL). After purification of HL from the commercial mixture, the extraction of ten environmentally-significant trace metal ions from artificial seawater into toluene solution was studied as a function of pH. From these investigations, the optimal conditions for the extraction of Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) from natural waters were established. The conditions for quantitative back-extraction of the metal ions were then investigated. With the exception of cobalt, the metal ions were quantitatively back-extracted into a small volume of nitric acid, simplifying the matrix and providing additional analyte enrichment. The optimized forward- and back-extraction technique was subsequently applied to the determination of total (soluble) Cd, Cu, Mn, Ni and Pb in a coastal seawater reference standard by graphite-furnace atomic absorption spectroscopy (GFAAS). The quantitative recovery of the analytes and the uncomplicated matrix of analysis enabled quantitation to be

carried out by external calibration. Compared to the method of standard additions, external calibration has advantages in overall analysis time and sample consumption. Satisfactory agreement was obtained between the experimental and reference values, although Cu(II) blanks were high due to trace Cu(II) contamination of HL and the stability of the Cu(II)-HL chelate.

The lipophilicity of HL and its metal chelates provided high metal chelate distribution ratios which, in turn, permitted preconcentration factors of up to 500 in a single batch-extraction. Additionally, studies on the recovery of radiotracer spikes from lakewater and seawater suggested that HL is an effective extractant for stripping metal ions from variously-bound forms from natural waters.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Dr. A. Corsini, for starting me on this research for which I may someday forgive him, and for his unswerving, if often unwarranted, faith in my abilities over the course of these many years. His help in the preparation of the thesis was most appreciated.

I gratefully acknowledge the invaluable assistance of Dr. J. Harvey and the staff of Health Physics for providing me with much-needed laboratory space. I would also like to thank Dr. S. Landsberger for helping me initiate the radio-tracer work, and Ms. A.E. Pidruzcny, Ms. V. Vermette and Mr. A. Kabir for helping me to complete it. The advice and assistance of Mr. P.C. Ersnt, Mr. M.P. Butler and Mr. C. LoPresti in the production and use of the radio-isotopes involved in this study were gratefully appreciated, as was the boundless cooperation and patience of the operators of the McMaster Nuclear Reactor who had to deal with me and my voluminous irradiation requests on a daily (and nightly) basis.

I would also like to thank Dr. R. Smith, Dr. B.E. McCarry, Mr. F.A. Ramelan, Mr. J.T. Kapron and Mr. J. Chan for obtaining the GC/MS spectra and helping me to interpret their significance.

Special thanks are due to my research group, friends and associates, Mr. P.A. Thomson, Mr. M.H. Brown, Mr. M.G. Malott, Mr. D.S. Mitchell and Ms. T.R. Bryar, who also had to deal with me on a daily basis but were not remunerated for it. Their company was most welcomed and I made frequent use of their valuable suggestions regarding my research and Ms. Bryar's shoulder during times of adversity.

Most of all, I would like to acknowledge the assistance of the late Mr. Ian McKee, whose unparalleled aid in matters academic and otherwise during the early phases of this work was instrumental in bringing it about. He was a good friend and a respected colleague and he will be missed.

Finally, I must thank my family for putting up with me for twenty-five years. Their unreserved support and understanding helped keep me going throughout the past four years, and enabled me to throw common sense to the wind and finish what I had started. This thesis is dedicated to them with love.

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I.1 Trace metal ions in natural waters

The presence of metal ions in natural waters from both natural and anthropogenic sources has long been an area of concern and interest to environmental scientists and toxicologists. Certain waterborne metals such as Hg, Pb and Cd are known to be inimical to human health at very low concentrations while others, including Zn, Co, Cu, Cr, Mn and Ni, are essential to life but can promote deleterious effects if present in excess or insufficient concentrations [*e.g.*, 1-3].

Many biologically important metal ions are present in natural waters only at trace (μg/mL, ppm) or ultra-trace (ng/mL, ppb) levels and numerous attempts have been made at classifying them with respect to their potential toxicity. Burrell [4] has used the term "heavy metals" to denote all elements in the Periodic Table having specific gravities of 4.5 to 22.5 inclusive, while more recently, Nieboer and co-workers [2,5] have adapted the hard/soft acid and base (HSAB) convention of Pearson [6] in an attempt to classify metal ions on the basis of their biological reactivity (Table 1). In this scheme, class (b) metal ions or soft acids and borderline Lewis acids are generally considered to be more

Table 1. Classification of metal ions*

Class (a)	Borderline	Class (b)
Inert gas electron configuration; low polarizability; "hard spheres"	One to nine outer shell electrons; not spherically symmetric	10 to 12 outer shell electrons; high polarizability; low electronegativity; "soft spheres"
(H^+), Li^+, Na^+, K^+,	V^{2+}, Cr^{2+}, Mn^{2+},	Cu^+, Ag^+, Au^+,
Be^{2+}, Mg^{2+}, Ca^{2+},	Fe^{2+}, Co^{2+}, Ni^{2+},	Tl^+, Ga^+, Zn^{2+},
Sr^{2+}, Al^{3+}, Sc^{3+},	Cu^{2+}, Ti^{3+}, V^{3+},	Cd^{2+}, Hg^{2+}, Pb^{2+},
La^{3+}, Si^{4+}, Ti^{4+},	Cr^{3+}, Mn^{3+}, Fe^{3+},	Sn^{2+}, Tl^{3+}, Au^{3+},
Zr^{4+}, Th^{4+}	Co^{3+}	In^{3+}, Bi^{3+}

* Adapted from reference [7].

toxic than class (a) metal ions or hard acids, principally because of their greater affinity for sulphydryl (-SH) groups in biomolecules which are critical to their integrity [2,5]. Additionally, class (b) and borderline metal ions can displace essential metal ions from biomolecules, resulting in an alteration of activity [2,5,8].

The toxicity of a given metal ion to a particular organism is, of course, dependent to a large extent on its bioavailability, the method and kinetics of its uptake, and the concentrations of its various species. For example, lead and mercury can form lipophilic organic species which are able to readily cross biological membranes and concentrate in cells [5], whereas for other metal ions, stable complexes and species associated with colloids are less toxic than the free (hydrated) metal. Furthermore, trace metal ions, unlike some organic pollutants, are not easily eliminated in waters by biodegradation, may be further mobilized by acid precipitation and have the capability to bio-accumulate [3,9]. These facts make the monitoring of natural waters increasingly important.

Because the toxicity of a given metal ion is strongly dependent on its chemical and physical form, speciation studies have become increasingly important in providing meaningful toxicological information [*e.g.*, 10-12]. Such studies, however, are either operationally-defined or involve complex computer modelling and, since many government regula-

tions on water quality are based on total metal concentration [*e.g.*, 13,14], the determination of total (soluble) metal in natural waters also merits investigation.

I.2 Determination of total (soluble) metal in natural waters

Total metal concentration in water refers to the sum of the metal concentrations in the soluble and particulate phases. By convention [15], total (soluble) metal is defined as that portion which is not retained on a 0.45-μm membrane filter. Components of this fraction include inorganic metal complexes, ion pairs, low and high molecular weight complexes (such as metal bound to humic and fulvic acids), and highly dispersed colloids [9].

Direct analysis of natural waters is preferable to chemical pretreatment as it entails little or no sample manipulation, thus reducing the potential for contamination, and eliminates the need for the analytical blank otherwise required in all chemical pretreatment methods [16]. The often low concentrations ($\leq$ng/mL) of environmentally significant metal ions in natural waters coupled with the high levels of coexisting interfering matrix components inhibits direct analysis by conventional instrumental techniques, however [17]. Direct analysis of trace metals in natural waters has, nevertheless, been achieved by neutron activation analysis (NAA) [18] and anodic stripping voltammetry (ASV) [19-21].

The former technique often requires specialized irradiation facilities capable of producing high neutron fluxes, in addition to long irradiation and decay times. For ultra-trace analysis, instrumental NAA is applicable only to elements whose activation products have relatively long half-lives (months to years) because the interference from the high activity produced by activation products (specifically ^{24}Na, ^{38}Cl, ^{82}Br and ^{42}K) of the major components of the natural water matrix precludes early analysis [18]. ASV permits measurement of speciated forms and has the necessary sensitivity for the direct determination of a few elements, but is not very selective, being beset with difficulties arising from inter-element interferences [3,18].

Commonly-used spectroscopic techniques such as graphite-furnace atomic absorption spectroscopy (GFAAS), inductively-coupled plasma atomic emission spectroscopy (ICPAES) and inductively-coupled plasma/mass spectrometry (ICP/MS) suffer from either matrix interferences or inadequate sensitivity for the direct analysis of natural water samples. The presence of major amounts of alkali and alkaline earth salts often precludes the direct application of GFAAS to the analysis of natural water samples. This is primarily due to non-specific absorption resulting from the co-volatilization of salts, loss of analyte as volatile chlorides at relatively low furnace temperatures, and the suppression of analyte absorption due to incomplete

dissociation of thermally-stable monochlorides in the gas phase [22]. Attempts to alleviate these matrix interferences by techniques such as matrix modification [*e.g.*, 23-26] or selective volatilization [27] often result in a decrease in sensitivity as well as in the range of metals that can be determined. Additionally, environmentally significant metal ions in natural waters are often present at concentrations below the detection limit of GFAAS. Nevertheless, GFAAS still has advantages over the other spectroscopic techniques noted above in terms of lower detection limits, higher sensitivity, and the capacity for handling small sample volumes. In order to fully exploit these advantages for natural water analysis, however, a preconcentration step which both enhances analyte concentration and separates interfering matrix components is required. Such a step is valuable since it lowers the effective detection limits of analytical instruments and simplifies the matrix.

I.3 Methods of preconcentration

Preconcentration may be absolute, in which the mass or volume of sample is decreased, or relative, in which there is an increase in the mass ratio of trace components to matrix components coupled with a decrease in the mass or volume of sample [28]. Mizuike [29] has defined the

preconcentration or enrichment factor, F, in terms of mass as follows:

$$F = \frac{Q_T/Q_M}{Q_T^o/Q_M^o} \qquad (I.1)$$

Above, Q_M^o, Q_T^o, Q_M and Q_T represent the amounts of matrix and trace element before and after preconcentration, respectively.

While a plethora of routine preconcentration techniques exist, the method of choice will usually be determined by the nature of the sample matrix and the instrument chosen for analysis. Generally, simultaneous multielement preconcentration is preferable since most modern instrumental analytical techniques are selective. Furthermore, the number of steps in the analysis is reduced which, in turn, minimizes analysis time and the likelihood of contamination. Typically, recoveries of greater than 90 or 95% are required for inorganic trace analysis although lower recoveries, if sufficiently reproducible, are sometimes satisfactory [29].

In short, the general characteristics of an "ideal" preconcentration procedure would include simultaneous multielement enrichment, high enrichment factors, negligible contamination effects and essentially quantitative analyte recovery. If possible, the technique should have the capability of being interfaced to the final method of analysis, enabling automation of the entire preconcentration/

analysis procedure. Commonly-employed preconcentration techniques include solvent evaporation, coprecipitation, electrodeposition, ion-exchange chromatography and solvent extraction.

Solvent evaporation is a simple absolute preconcentration technique which has been applied to the analysis of freshwater by arc-spark emission [30] and x-ray spectroscopy [31]. The large sample volumes required to achieve suitable precision at the ng/mL level and the tendency of evaporation to magnify matrix effects renders it unattractive for natural waters, especially seawater.

Coprecipitation of trace elements from large volumes of natural water samples in the presence of milligram quantities of a carrier precipitate is a classic preconcentration technique which can yield high ($\sim 10^3$) preconcentration factors, provide greater than 90% recovery of the analyte, and remove most alkali and alkaline earth salts [29]. If the instrumental technique employed for analysis requires a liquid matrix, however, the potentially high preconcentration factors of coprecipitation may be offset somewhat. One drawback to coprecipitation is the difficulty of obtaining carriers which are free of the trace elements of interest.

Electrodeposition, particularly anodic stripping analysis, is an important preconcentration technique for saline natural waters. The preconcentration step takes the form of the deposition of metals onto the mercury cathode,

while analysis occurs when the mercury electrode is scanned in the anodic direction and the deposited metals are oxidized [32]. High preconcentration factors and analyte recoveries are possible. Unless the current-carrying capacity of the sample is low (such as in freshwater), few reagents need to be added, reducing the risk of contamination. The primary disadvantages of electrodeposition techniques lie in their inherent slowness, their limitation to samples of high current-carrying capacity (since the addition of a supporting electrolyte can increase contamination), and their relatively low selectivity [32].

Ion-exchange chromatography has become increasingly popular over the past decade [*e.g.*, 12, 33-35], primarily because of the large preconcentration factors attainable. Analyte retention is dependent upon the distribution ratio of the metal ion between the ion-exchange material and the solution [32]. If the distribution ratio is sufficiently high, the attainable preconcentration factors are limited only by the volume of water sample available, the capacity of the ion-exchange material, and the volume of eluent required to strip the adsorbed metal ions. Preconcentration factors of 500 and greater have been obtained [36]. The ion-exchange material can also be analyzed directly after adsorption of metal ions [37], eliminating the need for an eluent. For the purposes of natural water preconcentration, it is desirable that the large amounts of existing alkali and alkaline earth

ions not be retained along with the analyte metal ions. This requirement has precluded the use of many classical cation-exchange resins (such as those containing sulphonic acid moieties), although some successful applications of such resins have been reported [38-40].

Applications of Amberlite XAD-2, XAD-4, and XAD-7 as ion-exchange resins have been promising. Wan *et al.* [34] found that XAD-7, a methylmethacrylate polymer, contains carboxylic acid impurities which enable it to act as a low-capacity (~0.06 meq/g) cation-exchange resin. The resin was used for the simultaneous preconcentration of Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) and Pb(II) from natural waters [34]. XAD-2 and XAD-4, both styrene-divinylbenzene copolymers differing only in pore size and surface area, have also exhibited cation-exchange characteristics, but of lower capacity than XAD-7 [41,42].

Chelate ion-exchange has been more frequently used in preconcentration from natural waters, but while many resins have been synthesized, few are commercially available. One proprietary resin whose use has been well-documented [*e.g.*, 12,33,43] is Chelex 100, a cross-linked styrene-divinylbenzene polymer with iminodiacetic acid moieties. Chelex 100 has been used for the simultaneous preconcentration of Cd(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II) and Zn(II) from seawater [33] but suffers from limited preconcentration factors due to the large volume of eluent

(*e.g.*, 25 mL of 2.5*M* HNO_3) required to strip the retained metal ions. As well, alkali and alkaline earth ions are concomitantly retained and sometimes must be differentially eluted from the resin, which may bring about the loss of some trace metal ions [44]. Chelating ion-exchange resins which have been synthesized include propylenediaminetetraacetic acid groups [45] and n-butylamide groups [46] bound to XAD-4, while oxine has been chemically immobilized onto a number of substrates, including silica gel [47] and controlled pore glass [48]. The exchange capacities of these resins are of the order of 4 meq/g. Synthesis of chelating ion-exchange resins is often long and involved and their relatively high stability constants with metal ions usually requires a high concentration of acid for elution.

In an attempt to circumvent the sometimes long and tedious process of synthesizing chelating ion-exchange resins, the practise of immobilizing chelating agents by adsorption onto suitable substrates has been investigated. While the lower capacity (μeq/g) of these resins is not a drawback since the metal ions of interest are normally present at trace or sub-trace levels, "ligand bleeding" can present serious problems [49]. Recently, Isshiki *et al.* [36] adsorbed the alkylated oxine derivative 7-(1-ethenyl-3,3,5,5-

tetramethylhexyl)-8-quinolinol* onto XAD-4 for the simultaneous preconcentration of trace metal ions from sea-water. This compound has also been adsorbed on XAD-7 for the recovery of copper from 5% (w/v) sodium chloride solution [50] and Ge(IV) from acidic aqueous solution [51].

Solvent (liquid-liquid) extraction and ion-exchange chromatography represent the two most commonly-used preconcentration techniques for the determination of total (soluble) metal in natural water samples. Extraction of metal ions from aqueous solution into an organic solvent can take place by two mechanisms: (i) the formation of an extractable metal chelate with an organic ligand; and (ii) the formation of a neutral ion associate between an anionic metal complex in solution and a lipophilic organic counter-cation. As with ion-exchange chromatography, significant amounts of alkali and alkaline earth ions must not be extracted with the trace metal ions of interest.

Classic solvent extraction preconcentration procedures have involved the formation of metal chelates of ammonium pyrrolidinedithiocarbamate (APDC) [*e.g.*, 16, 52-54], and sodium diethyldithiocarbamate (NaDDC) [*e.g.*, 54-58]. Since these extractants coordinate through sulphur, they would generally have a strong affinity towards class (b)

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* Up to 1976, 7-(1-ethenyl-3,3,5,5-tetramethylhexyl-8-quinolinol was the active component of the proprietary extractant, Kelex 100 (see Section I.5).

metal ions, many of which are toxic [2,5]. Ag(I), Cd(II), Cr(III), Cu(II), Fe(III), Ni(II), Pb(II), and Zn(II) have been simultaneously preconcentrated from seawater into a solution of APDC in methyl isobutyl ketone (MIBK) [59]. Also, APDC, NaDDC, and oxine have been used in mixed extraction systems [16,58]. APDC extractions are simple and well-understood but suffer from instability of metal chelates in the organic phase [60], with substantial decomposition of Pb(II), Zn(II), and Fe(III) chelates occurring within 16 hours of the initial extraction [54]. To overcome this limitation, a back-extraction step is sometimes employed, most commonly into nitric acid which destroys the metal-APDC complexes [16,59] and, less frequently, into a solution of Hg(II) at pH 1.6 which displaces most metal-APDC complexes due to its high stability with APDC [58]. A further limitation is the relatively low preconcentration factors attainable in APDC extractions. These low factors often result from low metal chelate distribution ratios ($\sim 10^2$) which do not permit the use of high phase volume ratios [53]. In fact, preconcentration factors of about 20-50 are likely the maximum that can be achieved if the extraction is to remain essentially quantitative [16,53,58].

A relatively recent extraction method which overcomes some of the limitations of the APDC method involves the formation of anionic metal complexes of meso-tetra(p-sulphonatophenyl)porphine ($TPPS_4$) in aqueous solution and their

extraction into MIBK as ion associates of the quaternary ammonium salt, tricaprylmethylammonium chloride [61]. Simultaneous preconcentration of Ag(I), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) from seawater was achieved and the lipophilicity of the quaternary ammonium salt enabled the attainment of about 135-fold single-batch preconcentration factors. The method was complicated, however, by the necessity of heating the aqueous phase at 90-98°C for 90 minutes to promote complex formation with $TPPS_4$ prior to extraction.

The synthesis of new, highly lipophilic chelating agents is an area that warrants investigation in analytical chemistry. A long alkyl chain with an EDTA-type moiety could be powerful enough to completely remove the analyte metal ion from organic and inorganic complexing agents in the aqueous matrix, while the lipophilicity of the extractant and its metal chelates would likely result in high metal chelate distribution ratios and, hence, higher preconcentration factors than are presently routinely achievable in a single batch-extraction. The development of a solvent extraction preconcentration technique utilizing a highly lipophilic extractant could potentially rival ion-exchange chromatography since, in both cases, the attainable pre-concentration factors would effectively be limited only by the volume of sample available, while the solvent extraction

procedure would have the advantages of simplicity and fewer steps.

I.4 Principles of solvent extraction

I.4.1 Extraction fundamentals

Solvent (liquid-liquid) extraction involves the distribution of a solute between two mutually immiscible phases, usually water and an organic solvent. This partition can be expressed by the ratio of the activities of a solute, M, in the organic and aqueous phases, provided that the solute exists in the same chemical form in both phases;

$$K_D^T = \frac{\overline{\{M\}}}{\{M\}} \qquad (I.2)$$

K_D^T represents the thermodynamic distribution constant, the brace brackets activities and bars the organic phase. Equation (I.2) can be expressed in terms of concentrations and activity coefficients, where the concentration ratio represents the stoichiometric distribution constant, K_D;

$$K_D^T = \frac{\overline{\gamma_M}\,\overline{[M]}}{\gamma_M[M]} = \frac{\overline{\gamma_M}}{\gamma_M} \cdot K_D \qquad (I.3)$$

If the ionic strength of the aqueous phase is kept constant and significantly higher than the concentration of

the solute in that phase and if changes in the activity coefficient of the nonelectrolyte solute are small, then the ratio of the activity coefficients, and therefore K_D, will remain reasonably constant [62]. The stoichiometric distribution constant represents the ratio of the concentrations of the solute in the organic and aqueous phases, provided the solute is present in the same chemical form in both phases. This situation rarely exists in practice and it is often more useful to express the distribution of all forms of the solute between the two phases by the distribution ratio, D;

$$D = \frac{\Sigma[M]}{\Sigma[M]} \qquad (I.4)$$

Another practical expression for the distribution ratio in terms of the percent extraction, %E, and the aqueous to organic phase ratio, $V/\overline{V}$, can be written as follows:

$$D = \frac{\%E}{100 - \%E} \cdot \frac{V}{\overline{V}} \qquad (I.5)$$

Equation (I.5) can be rearranged to determine the percent extraction, or extraction efficiency;

$$\%E = \frac{100\ D}{D + V/\overline{V}} \qquad (I.6)$$

Although the distribution ratio may be a more rigorous expression of solute partition, the extraction efficiency is more useful analytically to assess the efficacy of a particular extraction. Generally, an extraction can be said to be quantitative if %E=99 and not to occur at all if %E≤1 [63]. Another important aspect of Equation (I.6) is that it permits expression of the preconcentration or enrichment factor, F, in terms of the percent extraction and the aqueous to organic phase ratio [64];

$$F = (\%E/100) \cdot (V/\overline{V}) \qquad (I.7)$$

Generally, it is desirable to obtain quantitative recovery of the analyte from a sample matrix in a single batch-extraction [64]. With the extraction efficiency known for a particular analyte, the enrichment factor for that analyte may be adjusted to obtain the desired concentration of analyte in the organic phase simply by manipulating the ratio of the organic and aqueous phases.

I.4.2 Metal chelate extraction equilibria

The general mechanism for the extraction of metal ions, M^{n+}, with a lipophilic* chelating acid, HA, can be visualized as follows [65]:

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* For a lipophilic chelating acid, $K_{DR} \gg 1$.

$$M^{n+} + n\overline{HA} \rightleftharpoons \overline{MA_n} + nH^+ \qquad (I.8)$$

for which the extraction constant is;

$$K_{ex} = \frac{\overline{[MA_n]}\,[H^+]^n}{[M^{n+}]\,\overline{[HA]}^n} \qquad (I.9)$$

In the most simple case, if it is assumed that there is no hydrolysis of the metal ion, that no stable complexes form between the metal ion and secondary aqueous complexing agents, that MA_n and M^{n+} are the only metal species in the organic and aqueous phases, respectively, and that the concentration of intermediate metal-ligand complexes is minimal, then the distribution ratio for the metal chelate formed simplifies to the following expessions:

$$D_M = \frac{\overline{[MA_n]}}{[M^{n+}]} \qquad (I.10)$$

$$D_M = K_{ex} \cdot \frac{\overline{[HA]}^n}{[H^+]^n} \qquad (I.11)$$

Equation (I.10) is an oversimplification and, to provide a more complete description of the chemical equilibria involved in metal chelate extractions, it is convenient to consider complex formation with the extractant in the aqueous phase and subsequent distribution of the metal

chelate formed into the organic phase, although this may not occur to a significant extent if a highly lipophilic chelating extractant is employed. Such a consideration generally involves the following reactions:

(i) Distribution of the extractant into the aqueous phase;

$$\overline{HA} \rightleftharpoons HA \qquad K_{DR} = \frac{\overline{[HA]}}{[HA]} \qquad (I.12)$$

(ii) Dissociation of the extractant in the aqueous phase;

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]} \qquad (1.13)$$

(iii) Complexation with the metal ion in the aqueous phase;

$$M^{n+} + nA^- \rightleftharpoons MA_n \qquad \beta_n = \frac{[MA_n]}{[M^{n+}][A^-]^n} \qquad (I.14)$$

(iv) Distribution of the complex into the organic phase;

$$MA_n \rightleftharpoons \overline{MA_n} \qquad K_{DC} = \frac{\overline{[MA_n]}}{[MA_n]} \qquad (1.15)$$

Above, K_{DR} and K_{DC} are the stoichiometric extraction constants of the extracting reagent and the metal chelate, respectively; K_a is the acid dissociation constant of the extractant; and β_n is the overall stability constant for the nth metal-ligand complex. On the basis of the earlier assumptions, the distribution ratio can then be rewritten as follows:

$$D_M = \frac{\overline{[MA_n]}}{[M^{n+}] + [MA_n]} \qquad (I.16)$$

Rearrangement of Equation (I.16) in terms of the constants in Equations (I.12) to (I.15) yields the following:

$$D_M = \frac{\beta_n K_{DC} K_a^n}{K_{DR}^n} \cdot \frac{\overline{[HA]^n}}{[H^+]^n} \qquad (I.17)$$

Equation (I.17) is the same as (I.11) where

$$K_{ex} = \frac{\beta_n K_{DC} K_a^n}{K_{DR}^n} \qquad (I.18)$$

In the case of extraction of a metal ion of charge n and coordination number 2n with a bidentate ligand, a coordination-saturated chelate is formed and the relevant extraction equilibrium, metal chelate distribution ratio and extraction constant are given by Equations (I.8), (I.17) and (I.18), respectively. When the coordination number exceeds 2n, however, coordination-unsaturated or adduct chelates form. These complexes may simply contain excess molecules of the neutral extractant (self-adduct chelates) or may be adducts to an additional ligand (*i.e.*, Lewis base) added to the organic phase. Adduct formation generally enhances the hydrophobicity of a metal chelate and, hence, its extraction.

The extraction equilibrium and metal chelate distribution ratio for a self-addcut chelate are provided in Equations (I.19) and (I.20) below;

$$M^{n+} + \overline{(n+r)HA} \rightleftharpoons \overline{MA_n \cdot rHA} + nH^+ \qquad (I.19)$$

$$D_M = \frac{\beta_{n,r} K_{DC} K_a^n}{K_{DR}^{n+r}} \cdot \frac{\overline{[HA]^n}}{[H^+]^n} \qquad (I.20)$$

From Equations (I.11), (I.17) and (I.20), it is clear that the distribution ratio is dependent upon the pH of the aqueous phase as well as the equilibrium concentration of the extractant in the organic phase. In most extractions involving lipophilic chelating extractants, the initial concentration of the extractant can be equated to the equilibrium concentration if the extractant is present in large excess of the metal ion concentration so that the large majority of the extractant is not bound to the metal.

Equation (I.16) illustrates an idealized form of the distribution ratio, in that metal ion species other than the free metal and the metal chelate were ignored. In practice, however, it is usually impossible to disregard metal ion hydrolysis or the formation of complexes between the metal ion and ligands in the aqueous phase, particularly in natural waters which contain numerous inorganic and organic complexing agents. If chelate compounds are mononuclear in

each phase, D_M is independent of metal ion concentration, provided it does not exceed ~$10^{-3}M$ [66]. Sometimes, polymerization occurs in the organic phase, particularly with organophosphorous acid extractants. In such circumstances, D_M will depend on metal ion concentration. Additionally, intermediate metal-ligand complexes may be present in significant concentrations and, thus, cannot be overlooked. A more rigorous expression of the metal chelate distribution ratio in light of these phenomena can, therefore, be given by the following expression:

$$D_M = \frac{\overline{[MA_n]}}{[M^{n+}] + \sum_{i=1}^{n} [MA_i^{n-i}] + \sum_{i=1}^{p} [M(OH)_i^{p-i}] + \sum_{i=1}^{j} [MX_i^{j-i}]} \quad \text{(I.21)}$$

In Equation (I.21), $\Sigma[MA]$ represents the sum of the concentrations of the metal-extractant complexes, $\Sigma[M(OH)]$ represents the sum of the concentrations of hydroxide species, and $\Sigma[MX]$ represents the sum of the concentrations of complexes with secondary aqueous complexing agents. The term $[MA_n]$ represents the neutral metal chelate extracted into the organic phase. If polymeric species of the neutral chelate form in the organic phase, appropriate concentration terms would have to be added to the numerator.

I.4.3 Effect of organic solvent

Organic solvent effects will vary in magnitude with the mechanism of extraction and the form of the extracted complex. Generally, solvent effects are more pronounced in ion association than in metal chelate extractions and in the extraction of hydrated, coordination-unsaturated complexes in comparison to coordination-saturated chelates [63,66]. Moreover, the choice of a suitable solvent for a metal chelate extraction depends not only on the physical and chemical properties of the solvent and the extracted complex, but also upon the eventual method of elemental analysis [66]. For the purposes of trace metal preconcentration, it is desirable, if possible, to utilize a solvent which is essentially completely immiscible with water to ensure that the phase volume ratio remains constant throughout the extraction. This ideal is not always possible, particularly with oxygenated solvents, and presaturation of the aqueous phase with a small quantity of the solvent to be used is sometimes required [61].

Physical properties of the solvent which also warrant consideration include density, viscosity and surface tension, which are responsible for clean phase separation, as well as dielectric constant, polarity, polarizability, acid/base strength and hydrogen bonding ability, which influence

solvent-solvent, solute-solute and solute-solvent interactions [64].

Attempts to classify solvents according to all or some of these properties abound in the literature. "Active" and "inert" are adjectives which are often used in this regard. Although no rigorous definition exists, "inert" solvents are typically non-polar and do not themselves participate in the extraction, whereas "active" solvents are normally oxygenated and, when protonated, can participate in the extraction process through the formation of ion associates, or as adducts (solvates) when unprotonated.

A classification of solvents on the basis of their proton and/or electron donating characteristics was proposed by Pimental and McClellan [67]. Chloroform and other halogenated hydrocarbons were classified as proton donors; ketones, aldehydes and olefins as electron donors; water and alcohols as both proton and electron donors; and saturated hydrocarbons and carbon tetrachloride as non-donors.

For certain metal chelates, the nature of the solvent has been found to have a profound effect on the extraction. For example, chelates with free hydroxyl groups, such as those of 4-pyridylazo-1-recorcinol (PAR), were found to be preferentially extracted with oxygenated solvents [66]. For metal chelate extractions with highly lipophilic extractants, however, organic solvent effects would appear to be minimal, since not only the extractants but the metal chelates formed

should be readily soluble in a wide range of solvents. Sekine and Hasegawa concluded that the extraction efficiencies of metal ions with a given chelating agent in different organic solvents are similar if the extraction mechanism involves little or no complex formation in the aqueous phase [65].

I.4.4 Extraction kinetics

The establishment of equilibrium in metal chelate extractions is, typically, slower than in ion association extractions, ranging from a few minutes to several hours [66]. Thus, a general knowledge of metal chelate extraction kinetics for a given system is necessary not only for practical considerations such as the duration of phase agitation, but also because the site of complex formation may be inferred (*e.g.*, at the solvent interface or in the bulk aqueous phase).

In general, the rate of extraction depends upon the identity of the organic solvent, metal ion and extractant, the pH and composition of the aqueous phase, and the concentration of the extractant and the metal ion [66]. Generally, the extraction rate increases with increasing pH (in the absence of hydrolysis), due to the increase in extractant anion, A^-, available for complex formation at the interface or in the aqueous phase. The extraction rate has also been found to increase with increasing equilibrium

extractant concentration and to decrease in the presence of external aqueous complexing agents [66]. Freiser and colleagues [68-71] studied the rate of extraction of chelates of dithizone and its derivatives and concluded that the extraction rate was proportional to the metal ion concentration, the pH and the equilibrium concentration of the extractant in the organic phase.

The kinetics of a solvent extraction process can depend on the rate of chemical reaction, the rate of mass transfer, or both [63]. Which of the above steps is rate-determining is decided by the rate of phase agitation. If the agitation rate is slow, mass transfer becomes the rate-determining step and the extraction rate will vary with the shaking intensity. If the agitation rate is sufficiently fast, the rate of chemical reaction (complex formation) will be rate-determining and further increase in the shaking intensity will not affect the extraction rate [66].

An increase in the rate of extraction due to phase agitation could result from increased phase intermixing, the dispersion of one liquid phase into another as small particles, and an increase in the interfacial area through which the solute molecules enter the organic phase. Diffusion through the interface can occur in the absence of phase agitation and is affected by factors such as viscosity, surface tension, extractant concentration, the area of the interface, and the size of the solvent and solute

molecules [65]. When the rate-determining step is complex formation at the interface, the rate of extraction is often enhanced by increased shaking intensity as this will increase the area of the interface and hence the probability of the collision of molecules in the two phases at the interface.

The actual site of complex formation will affect the kinetics of extraction, if complexation is the rate-determining step. If complex formation occurs primarily in the aqueous phase, then at a constant pH and initial organic phase extractant concentration, the rate of extraction will increase with increasing concentration of the extractant in the aqueous phase. Thus, the extraction rate will increase if an organic solvent is used in which the extractant is less soluble (lower K_{DR}). Conversely, if complex formation at the interface predominates, then at a constant pH, the extraction rate will increase with increasing extractant concentration in the organic phase. In this case, the extraction rate will increase if a solvent is used in which the extractant has a higher K_{DR} and, hence, is more soluble [66].

It is sometimes analytically desirable to strip the extracted metals from their complexes in the organic phase into a simpler matrix, such as an aqueous acid. Such a stripping or back-extraction step often affords a simplified matrix and an additional enrichment factor if the organic phase is back-extracted into an aqueous phase of smaller volume. Few systematic studies have been carried out on the

kinetics of back-extraction, however. The rate of back-extraction can sometimes be slower than that of a forward-extraction. The rate-determining step in such extractions often is the replacement of complexed ligand anions by water molecules to form the hydrated metal ion [65].

I.4.5 Effect of electrolytes

Since natural waters contain a high concentration of dissolved salts (~0.7*M* NaCl in seawater), the effects of extraneous salts and electrolytes must be considered in the extraction of metal ions from such aqueous phases.

Salt effects are varied and much of the data concerning them is purely empirical in nature. For example, the anion of the salt may bind to the metal ion, impeding the extraction, or the salt may act as a dehydrating agent and, thus, assist in the formation of chelate compounds, enhancing both the extraction efficiency and the extraction rate [66]. Primarily, salts will increase the ionic strength of the aqueous phase, bringing about an alteration in all of the stoichiometric extraction equilibrium constants that describe the system. For example, the metal chelate distribution constant, K_{DC}, has been found to increase as the ionic strength of the aqueous phase increases (the "salting-out" effect [65]).

Increasing the ionic strength of the aqueous phase will, of course, decrease its dielectric constant. The high dielectric constant of pure water ($\varepsilon \approx 83$ at 25°C) is responsible for its strong capacity for the solvation of charged species. The extraction of charged species is only observed after their charge has been neutralized by chelation or ion association and any remaining coordinated water molecules have been displaced by organic solvent or Lewis bases therein [65]. The depression of the dielectric constant of water by electrolytes is therefore favourable for the extraction of metal ions.

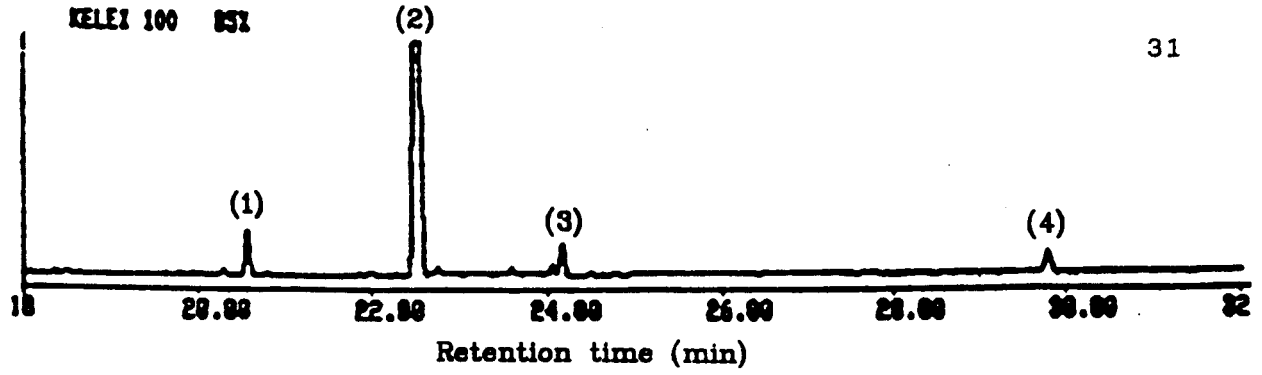
I.5 Rationale for research

I.5.1 Selection of Kelex 100 as the extractant

Highly lipophilic chelating agents, commonly known as "liquid cation-exchangers", have been extensively used in industry for the recovery of metals because their hydrophobicity permits them to stay in the organic phase to a greater degree than conventional chelating agents, particularly under the conditions of high acidity or alkalinity often required. Their analytical applications have been limited, although their potentially high metal chelate distribution ratios make them attractive with regard to trace metal preconcentration.

One such extractant is Kelex 100, a proprietary product whose primary component, up to 1976, was the

alkylated oxine derivative, 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol. Until a recent study in which the purified active component was impregnated on XAD-4 resin for the preconcentration of trace metals from seawater [36], the primary applications of the compound have been confined to hydrometallurgical studies [*e.g.*, 72-77] and fundamental investigations [*e.g.*, 78-85]. With a change in the manufacturing process in 1976, the active component in present-day Kelex 100 has been identified [86-89] as 7-(4-ethyl-1-methyloctyl)-8-quinolinol (HL) and no applications of the purified component to the preconcentration of trace metals from natural waters have been have been reported, although the compound has been adsorbed on XAD-7 for the recovery of Ga(III) from aqueous solution [89]. The active component, HL, comprises only about 85 wt % of Kelex 100, with the remainder consisting of organic impurities and by-products. The composition of a representative sample of Kelex 100 is given in Figure 1, as reported in private communications [86,87]. The expected unselective complex-forming characteristics of HL, coupled with its lipophilicity, should make it a potentially attractive extractant for multielement trace metal preconcentration from natural waters.



(1) 5,13-diethyl-10-methyl-8-heptadecanone (~8 wt %)

(2) 7-(4-ethyl-1-methyloctyl)-8-quinolinol (~85 wt %)

(3) C_9-alkylated furoquinoline (~4 wt %)

(4) C_{22}-alkylated oxine homologue (~3 wt %) and/or

oxine (not shown above) (≤0.5 wt %)

Figure 1. Gas chromatogram and components of a Kelex 100 sample similar to that used in this work [86,87].

I.5.2 Previous work

The ethenyl derivative of HL has been successfully applied to the extraction of numerous metal ions from a variety of matrices, including Ni(II) from perchlorate media [85], Cu(II) [81] and Co(II) [77] from sulphate solution, Cd(II) and Zn(II) from chloride matrices of neutral pH [90], Pb(II) and Ga(III) from sodium hydroxide solution [91], Fe(III) [92] and Ge(IV) [93] from acidic sulphate solution, Pd(II) from 2*M* HCl [94], and Pr(III), Eu(III), Yb(III) [78] and UO_2^{2+} [82] from neutral aqueous solution. Additionally, Ag(I), Al(III), Bi(III), Cd(II), Cu(II), Fe(III), Ga(III), Mn(II), Ni(II), Pb(II) and Ti(IV) have been extracted from 0.1*M* $NaClO_4$ [36].

The parent compound, oxine, extracts over 30 metal ions through the formation of both coordination-saturated and coordination-unsaturated (self-adduct) chelates (see Section I.4.2). While Co(II), Zn(II), Cd(II) and Sr(II) have been found to form adduct chelates of the type $MA_2 \cdot 2HA$, and Ag(I) of the type MA·HA, Cu(II), Mn(II), Ni(II), Pb(II), Pd(II) and Fe(III) form only conventional chelates with oxine [75,95]. Extractions with 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol have, on the whole, exhibited similar extraction stoichiometry. Cu(II) [83,96], Ni(II) [79,85], Pd(II) [94], Pb(II) and Zn(II) [91] have been extracted as coordination-saturated ML_2 chelates, while Co(II) has been observed to

form the adduct $CoL_2 \cdot 2HL$ [77,84]. The extraction stoichiometry of Cd(II) has indicated the formation of the $CdL_2 \cdot HL$ adduct [90] and that observed for UO_2^{2+} in the absence of acetate was found to be $UO_2L_2 \cdot HL$ [82].

The primary difference between the structure of HL and oxine is, obviously, the 7-alkyl substituent, which would not only increase the distribution constant of the reagent, K_{DR}, but also its Brønsted acidity, hence affecting the pK values of the heterocyclic nitrogen and the hydroxyl proton on the oxine ring. The values for the pK_{NH} and pK_{OH} of the ethenyl derivative of HL and of oxine in 50% (v/v) dioxane/ water are provided in Table 2. The higher pK_{OH} of the ethenyl derivative is due to the negative inductive effect of the electron-donating alkyl group in the 7-position. The decreased pK_{NH} is likely the result of steric hindrance by the 7-alkyl substituent, resulting either in displacement of the hydroxyl group towards the nitrogen to hinder protonation [97], or in hindrance to solvation of the protonated ring nitrogen [98]. Whereas the pK_{NH} of 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol is about 1.4 units more acidic than oxine, the pK_{OH} is about 1.5 units more basic. Thus, on the basis of Brønsted basicity, the stability constants of their metal chelates are expected to be of similar magnitude. The same is expected to prevail for 7-(4-ethyl-1-methyl-octyl)-8-quinolinol (HL) in terms of ligand basicity and chelate stability. The stability constants of several metal

Table 2. Acid dissociation constants of oxine (8-quinolinol) and the ethenyl derivative of HL

Ligand	pK_{NH}	pK_{OH}	
8-quinolinol	4.48	10.80	*
7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol	3.05±0.05	12.30±0.05	†

* Obtained in 50% (v/v) aqueous dioxane containing 0.3*M* $NaClO_4$ at 20°C, reference [100].

† Obtained in 50% (v/v) aqueous dioxane, reference [81].

Table 3. Stability constants of various metal ions with oxine (8-quinolinol)

Metal Ion	log β_2	Conditions
Cu^{2+}	23.0	I=0.1*M*; T=25°C; ref. [101]
Cd^{2+}	13.4	I=0.1*M*; T=20-25°C; ref. [101]
Co^{2+}	17.52	0.1*M* $(Na^+,H^+)ClO_4^-$; T=25°C; ref. [102]
Ni^{2+}	19.2	0.1*M* $(Na^+,H^+)ClO_4^-$; T=20°C; ref. [103]
Zn^{2+}	17.10	0.1*M* $(Na^+,H^+)ClO_4^-$; T=20°C; ref. [104]
Mn^{2+}	15.46	50% (v/v) dioxane; T=25°C; ref. [105]
Pb^{2+}	17.34	50% (v/v) dioxane-0.1*M* $NaClO_4$; T=25°C; ref. [106,107]
Fe^{3+}	($\log\beta_3$=36.95)	I=0.1-0.5*M*; T=25°C; ref. [101]
Ag^+	9.56	0.1*M* $(Na^+,H^+)ClO_4^-$; T=18-22°C; ref. [108]
Mg^{2+}	8.3	I=0.1*M*; T=25°C; ref. [101]
Ca^{2+}	13.2	70% (v/v) dioxane; T=30°C; ref. [109]

oxinates are provided in Table 3 as a matter of reference.

Bag and Freiser [81] have determined the extractant distribution constant, K_{DR}, for 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol between water and chloroform to be $10^{5.52}$. These workers also determined the metal chelate distribution constant for the Cu(II) chelate to be $10^{9.5}$, which is significantly higher than that of the Cu(II) oxinate, $10^{4.58}$ [81]. In view of the structural similarity between the present-day active component of Kelex 100, 7-(4-ethyl-1-methyloctyl)-8-quinolinol (HL), and its ethenyl derivative, similarly high distribution constants are to be expected for HL and its metal chelates.

The low aqueous solubility of the ethenyl derivative ($<3 \times 10^{-6} M$) [99] coupled with its high distribution constant suggests that complex formation at the phase interface, rather than in the bulk aqueous phase, would predominate. Although the actual site of chelate formation does not affect the final distribution equilibrium, it may affect the kinetics of extraction, as was pointed out in Section I.4.4 [66]. Freiser and co-workers found that the ligand anion of the ethenyl derivative of HL is surface-active and is strongly adsorbed at the phase interface, while the neutral form of the compound is not [79,85]. In the extraction of Ni(II) by the ethenyl derivative, they suggested concurrent reaction pathways which are strongly pH-dependent [79,85]. At lower pH values, the neutral form of the ligand predominates

and the extraction proceeds primarily through reaction between the neutral ligand and the metal ion in the bulk aqueous phase. At higher pH values, the formation of the ligand anion, as noted above, is predominantly at the interface and the extraction proceeds primarily through interfacial reaction between the ligand anion and the metal ion [79,85]. Flett and co-workers, on the other hand, have proposed the existence of a purely interfacial mechanism for the extraction of Cu(II) and Co(II) by the ethenyl derivative of HL [83,84]. An interfacial extraction mechanism may favour more rapid extraction kinetics, particularly in extraction from aqueous solutions of high ionic strength, since the dielectric constant of the interface (which should have a value between that of the bulk solvents and significantly lower than that of the bulk aqueous phase [85]) would be further depressed and, hence, could be a more conducive site for complex formation.

Since HL coordinates through nitrogen and oxygen, it should form extractable complexes with most class (a) metal ions as well as some class (b) metal ions. This expected reactivity makes HL attractive to the preconcentration of many environmentally significant trace metal ions, which primarily represent borderline and class (b) cations. Natural waters also contain salts of alkali and alkaline earth elements (class (a) metal ions) as major components. While oxine does not form extractable complexes with alkali metals,

it can form Mg(II) and Ca(II) complexes, particularly at alkaline pH. Mg(II) has been extracted by 0.1-0.2*M* oxine in chloroform [95,110] and in methyl isobutyl ketone (MIBK) [111], in the pH range 9-10.5. Ca(II) is also extractable with 0.5*M* oxine in chloroform at pH>10.7 [111]. Concomitant extraction of large amounts of these alkaline earth elements would be undesirable in a preconcentration scheme, particularly one involving GFAAS measurement, for the reasons outlined in Section I.3.

I.6 Aim of research

The major emphasis of this work was the development of a solvent extraction preconcentration procedure which could be applied to the GFAAS determination of total (soluble) metal in natural waters. The aim was to develop a method which would afford simultaneous multielement enrichment, quantitative analyte recovery, and an uncomplicated final matrix which would enable quantitation to be carried out by external calibration rather than by the method of standard additions, which consumes more time and sample. Additionally, a straightforward method was desired, involving few reagents and steps, to minimize the potential for external contamination.

Because of its ability to extract a wide variety of metal ions from a number of different aqueous matrices,

7-(4-ethyl-1-methyloctyl)-8-quinolinol, the active component of Kelex 100, was selected as the extractant for these studies. The relatively unselective nature of HL should make possible multielement preconcentration at a single pH, and its lipophilicity should afford high metal chelate distribution ratios. Since the metal-ligand stability constants of HL are expected to be comparable to those with oxine, it should be possible to strip metal ions from variously-bound forms in natural waters, enabling quantitative analyte recovery from the aqueous matrix. Quantitative back-extraction into aqueous acid would simplify the matrix for GFAAS analysis by external calibration and further concentrate the analyte.

In order to achieve these goals, it was first necessary to purify Kelex 100 on a preparative scale. The product contains various organic impurities, some of which have been identified as chelating agents which likely would interfere with the extraction of metal ions by HL [86-88]. After purification, the optimal forward- and back-extraction conditions were determined using radioisotopes of a number of environmentally significant trace metal ions in an artificial seawater matrix. The recovery of radiotracer spikes from natural water samples was used to assess the efficacy of HL in the extraction of both free and bound metal ion forms. The optimized extraction procedure was then applied to the GFAAS determination of trace metals in a reference seawater material to assess the utility of the technique.

II. EXPERIMENTAL

II.1 Apparatus and reagents

To minimize trace metal losses due to adsorption on glass surfaces [112-114], polypropylene or Teflon laboratory ware was used as much as possible (*e.g.*, separatory funnels, beakers, storage bottles). Prior to use, all glass and plastic-ware was soaked in 10% (v/v) nitric acid to remove trace metals and then rinsed with distilled deionized water (DDW).

The delivery of microlitre quantities of aqueous solutions was accomplished with continuous digital, fixed-volume, or multi-volume Eppendorf pipettes which ranged in accuracy and precision from 1.2% and 0.5% at 5 μL to 0.5% and 0.15% at 1000 μL, respectively. The accuracy and precision were found to be adequate for this work.

The Nalgene® Teflon FEP separatory funnels (125, 250, or 500 mL) used to carry out all the extractions described in this work were obtained from Sargent-Welch Scientific of Canada, Limited (Weston, Ontario). Borosilicate glass columns (20 x 1.0 cm i.d. with 35-μm bed support and nylon stopcock) were used for the loading of Chelex 100 resin (1 x 6 cm bed, 200-400 mesh). Both the columns and the resin were obtained from Bio-Rad Laboratories (Mississauga, Ontario). The general

operation of a Chelex 100 column is described by Kingston *et al.* [33]. The resin was purified of trace metals by successive batch washes with 5*M* HNO_3, 4*M* HCl and DDW, after which it was converted to the ammonium form with 1*M* NH_4OH and rinsed with DDW. It was then slurry-loaded into the borosilicate column to a bed size of 1 x 6 cm and was further cleaned by percolation of 50 mL each of 5*M* HNO_3, 4*M* HCl, DDW and 2*M* NH_4OH. To ensure even packing, the column was then backflushed with DDW until the effluent pH was 8-9. Before percolation of a sample, the column was conditioned with 50 mL of the appropriate buffer solution and, when sample elution was complete, it was rinsed with 50 mL aliquots of 5*M* HNO_3, 2*M* NH_4OH and DDW for storage [3,9].

Distilled deionized water (DDW; 18 MΩ) was used throughout and was prepared by passage of distilled water through a Barnstead NANOpure three-cartridge system (Sybron Corporation, Boston, Massachusetts). Baker Ultrex® or Instra-Analyzed® acids and bases (J.T. Baker Chemical Company, Phillipsburg, New Jersey) were used for pH adjustment and the preparation of buffer solutions. For GFAAS analysis, buffer and electrolyte solutions were further purified from trace metals by passage through a Chelex 100 column at alkaline pH at 1 mL/min. All other chemicals were analytical reagent grade and of sufficient purity for the purpose intended.

To simulate the salinity and major inorganic ions in seawater, an artificial seawater matrix containing 0.77*M*

NaCl, 0.053*M* $MgCl_2$ and 0.010*M* $CaCl_2$ (ionic strength=0.96*M*; $[Cl^-] \approx 0.9M$) was prepared. Natural water samples consisted of the National Research Council of Canada Nearshore Seawater Reference Material, CASS-1 (Ottawa, Ontario); a coastal seawater sample from Sandy Cove, Nova Scotia (obtained from the Atlantic Regional Laboratory, NRC, Halifax, Nova Scotia); and, an offshore freshwater sample from Lake Ontario (Station 302, Western Basin, obtained from the Canada Centre for Inland Waters, Burlington, Ontario). The CASS-1 standard was collected at the 15-metre level, 400 to 800 metres off the Nova Scotia shore and had a salinity of 31.8 parts per thousand. It was filtered through 0.45-μm porosity filters to remove particulate matter and acidified to pH 1.6 with nitric acid to preserve trace metal content. The Sandy Cove sample had been passed through a white-sand filter and acidified to pH 1.7, while the Lake Ontario sample had been centrifuged to remove suspended particulates, passed through a 0.45-μm filter and acidified to pH 1.7.

Kelex 100® (lot number 3349-72; manufactured by the Sherex Chemical Company, Incorporated, Dublin, Ohio) was kindly donated through Henley Chemicals (Scarborough, Ontario). The commercial product contained several organic and inorganic impurities, the removal of which is covered in Section II.3.1.

Metal ion solutions were prepared by dilution of Fisher standard atomic absorption solutions (1000 mg/L,

1% accuracy, obtained from the Fisher Scientific Company, Toronto, Ontario).

Radioisotopes were generated at the McMaster Nuclear Reactor through irradiation of the appropriate metal nitrates in the reactor core. A known volume (*e.g.*, 250 or 1000 μL) of the appropriate Fisher atomic absorption solution was pipetted either into a 1.0 x 3.0 cm quartz sample vial for irradiations of longer than five hours, or into a 1.0 x 2.5 cm polyethylene sample vial for shorter irradiations, and the solution was evaporated to dryness under a heat lamp. The sample vials had been previously acid-washed to remove trace metal impurities and, before irradiation, the polyethylene vials were heat-sealed and the quartz vials wrapped in aluminum foil to prevent the loss of target material. The samples were then encapsulated in aluminum containers and irradiated in a thermal neutron flux of either 4.5×10^{13} or 1.4×10^{13} n/cm^2/s for a specified time. The nuclear reactions, radioisotope half-lives, neutron fluxes and irradiation times are provided in Table 4. After irradiation, the radioisotopes were allowed to decay for 6 hours to 2 days, depending on the irradiation time and isotope half-life, to reduce the activity from ^{24}Na ($t_{½}$=15.4 hr) created from the aluminum capsule through the ^{27}Al(n,α)^{24}Na reaction. The radioactive salts were then dissolved in ~1 mL of 2*M* HNO_3 or 2*M* HCl and stock solutions of 10 or 50 μg/mL were prepared by dilution with DDW.

Table 4. Conditions for the generation of the radioisotopes used

Nuclear Reaction	Half-life	Irradiation Time	Neutron Flux ($n/cm^2/s$)
$^{109}Ag\ (n,\gamma)\ ^{110m}Ag$	253 days	5 days	4.5×10^{13}
$^{114}Cd\ (n,\gamma)\ ^{115}Cd$	2.3 days	20 hours	4.5×10^{13}
$^{59}Co\ (n,\gamma)\ ^{60}Co$	5.24 years	2 days	1.4×10^{13}
$^{63}Cu\ (n,\gamma)\ ^{64}Cu$	12.8 hours	4 hours	1.4×10^{13}
$^{58}Fe\ (n,\gamma)\ ^{59}Fe$	45.1 days	45 days	4.5×10^{13}
$^{202}Hg\ (n,\gamma)\ ^{203}Hg$	46.9 days	5 days	1.4×10^{13}
$^{55}Mn\ (n,\gamma)\ ^{56}Mn$	2.58 hours	4 hours	1.4×10^{13}
$^{64}Ni\ (n,\gamma)\ ^{65}Ni$	2.56 hours	4 hours	1.4×10^{13}
$^{64}Zn\ (n,\gamma)\ ^{65}Zn$	245 days	15 days	4.5×10^{13}

II.2 Instrumentation

Gamma-ray spectroscopy was employed to study the extraction efficiencies of HL with the radiotracers listed in Table 4. Measurements of γ-ray energies were made with an APTEC coaxial Ge(Li) detector interfaced to a Canberra Series 90 multichannel analyzer having both dead time correction and pile-up rejection units. The detector had a resolution of 1.9 keV at the ^{60}Co 1332-keV photopeak and an efficiency of 28% relative to a NaI(Tl) detector (3 x 3 inch cylinder). The resolution of the detector made possible the simultaneous counting of a group of radioisotopes provided no overlapping photopeaks were present. The radiotracers were analyzed in the following groups: ^{110m}Ag, ^{115}Cd, ^{60}Co, ^{59}Fe, ^{203}Hg, ^{65}Zn (long-lived, $t_{1/2} \geq 20$ hr); and ^{64}Cu, ^{56}Mn, ^{65}Ni (short-lived, $t_{1/2} \leq 13$ hr). No overlapping photopeaks were found within each of these two groups. All counting dead times were less than 11% and all counts were corrected for background. Short-lived radiotracers were also corrected for half-life decay. Samples were counted until a minimum of 10,000 background-corrected counts were obtained for each isotope; the associated counting uncertainty was less than 10%. Typical counting times were 3,000 seconds.

Both graphite-furnace and flame atomic absorption spectroscopy were employed in this work. Graphite-furnace atomic absorption spectroscopy (GFAAS) was used for the

determination of trace metals in the coastal seawater reference material, CASS-1. The graphite-furnace equipment consisted of a Perkin-Elmer Model 373 double-beam atomic absorption spectrophotometer equipped with a deuterium-arc background corrector, a Perkin-Elmer HGA-2200 graphite-furnace atomizer/controller and strip-chart recorder. Either Perkin-Elmer Intensitron® or Cathodeon (Cathodeon Ltd., Cambridge, England) hollow cathode lamps were used as radiation sources and pyrolytically-coated graphite tubes were used throughout. Samples were injected manually using 20-μL Eppendorf pipettes. Argon, the purge gas, was used in the "interrupt" mode in view of the low analyte concentrations involved. The wavelengths, slit-widths, lamp currents and temperature programmes selected were those recommended in the applications manual [115]. A summary of the drying, charring and atomizing temperatures is given in Table 5. The drying time is dependent upon the volume of sample injected. For a 20-μL injection, a drying time of 25 seconds, a charring time of 20 seconds and an atomization time of 5 seconds were found to be satisfactory. Flame atomic absorption spectroscopy was used to investigate the extraction of Mg(II), Ca(II) and Pb(II) from artificial seawater with HL as a function of pH. An Instrumentation Laboratory Model 251 spectrophotometer with a regular single-slot, four-inch laminar-flow burner and an air/acetylene flame was employed, together with Instrumentation Laboratory hollow cathode

Table 5. Analytical conditions* for GFAAS determination of trace metals in acidic media in pyrolytically-coated graphite tubes

Element	Analytical Wavelength (nm)	Temperature Settings (°C)		
		Drying	Charring	Atomization
Cd	228.8	100	250	1700
Cu	324.7	100	900	2700
Mn	279.5	100	1000	2600
Ni	232.0	100	1000	2700
Pb	283.3	100	500	2100

* Adapted from reference [115].

lamps. The nebulization rate was set at 5 mL/min. The slit-widths, lamp currents and wavelengths were those recommended in the applications manual [116].

Gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) were used to determine the organic components of Kelex 100. The GC equipment consisted of a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and a 10-metre Hewlett-Packard Series 530 μ fused silica column (DB-1 stationary phase). A temperature programme of 100-300°C at 5°C/min with a 15-minute hold at the maximum column temperature (300°C) was employed. Injector and detector temperatures were 250 and 300°C, respectively. Nitrogen (60 p.s.i.) was used as the carrier gas at a flow rate of 10 mL/min. GC/MS analysis was carried out under the same conditions using a gas chromatograph identical to that described above interfaced either to a Vacuum Generators (VG) Micromass 7070F or ZAB-E mass spectrometer. Mass spectrometric determinations with the above instruments were also made with a sample probe. Both electron impact and chemical ionization (with methane or ammonia as the reagent gas) were used at an electron energy of 70 eV and an accelerating voltage of 8 kV. The ion source was heated to 200°C.

A Hewlett-Packard Model HP 8451 diode array spectrophotometer was used to monitor the aqueous phase for the HCl (1*M*) extraction of the impurity, oxine, from the

Kelex 100 mixture [77]. Absorption measurements were made with Hellma quartz cells (1 cm).

The pH of the aqueous phase before and after extraction was measured with a Fisher Accumet 520 digital pH/ion meter equipped with a Ross model 81-55 combination electrode. The meter was standardized with the appropriate Fisher (NBS) buffers prior to use.

A Burrell Model 75 wrist-action shaker was used for prolonged phase agitation.

II.3 Procedures

II.3.1 Purification of Kelex 100

Commercial Kelex 100 was purified from organic impurities (see Figure 1, page 31) by the following procedure. Oxine was removed from the mixture by five extractions of a 30% (w/v) solution of Kelex 100 in toluene with a equal volumes of 1*M* HCl [77]. The presence of protonated oxine in the aqueous phase was monitored by ultra-violet/visible spectroscopy and was deemed to be complete when the absorption peaks were no longer observed. The extractant was then neutralized by a four-stage water wash with DDW at pH 7, after which the toluene was evaporated.

The Kelex 100 mixture was purified of remaining hydrophobic organic impurities by a four-pass fractional vacuum distillation. A short-path still with a seven-inch

Vigreux column and a three-neck sample collector was used in conjunction with a Sargent-Welch DuoSeal® Model 1400 vacuum pump, which provided an internal pressure of 0.1 mm Hg. The distillation flask was heated by a mantle controlled by a set point controller (Omega Model 22M). The flask temperature was monitored by a K thermocouple. The maximum flask temperature was approximately 350°C and no thermal decomposition of the Kelex 100 was noticed. Under the above conditions of pressure, a green-yellow material began to slowly distill at a vapour temperature of about 128°C and continued distilling until a vapour temperature of 134°C was reached. At this point, the distillation rate was observed to increase, and the distillate was more pale yellow in colour with the major portion of the material distilling in the 134-136°C range. As the temperature was raised above 136°C, the distillation rate was observed to decrease, and the distillate became progressively darker yellow in colour. At 140°C, distillation essentially ceased, leaving ~10 wt % of material in the distillation flask. In the initial distillation, the distillate was collected primarily in the 134-136°C range. This fraction was redistilled and the material coming off at about 136-138°C was collected, providing a distillate freer of the more volatile organic impurities. In turn, this latter fraction was distilled and the distillate at about 132-134°C, now reduced in the less volatile impurities, was obtained. A fourth and final distillation at 134-136°C increased the

purity of HL in the distillate to 98%, as determined by gas chromatography using area normalization.

Kelex 100 also possessed trace metal impurities, the most significant of which was Cu(II), which was found by GFAAS to be present at a concentration of approximately 65 ng/mL in the vacuum-distilled material. Thus, after vacuum distillation, the extractant was purified from the majority of trace metal impurities by extraction of a 0.25*M* toluene solution of HL with equal volumes of 10% (v/v) nitric acid and DDW, and then four times with 0.1*M* EDTA at pH 7. The EDTA had been previously purified from trace metal contaminants by recrystallization at pH 0-1. Even at this point, the level of Cu(II) contamination was still sufficient to give appreciable blank values in the GFAAS determination of Cu(II) in seawater (see Section III.7.2).

II.3.2 Radiotracer study of extraction efficiencies

The extraction efficiencies of metal ions with HL were determined for an artificial seawater matrix (Section II.1) spiked with radiotracers in the groups outlined in Section II.2. The concentration of each radiotracer in the aqueous phase along with the photopeaks monitored are provided in Table 6. The buffers used in this work were acetic acid/ammonium acetate in the pH range 4-6, and ammonia/ammonium acetate in the pH range 8-10. For pH values

Table 6. Radiotracers used and γ-rays monitored

Radiotracer	Concentration Employed (*ng/mL*)	γ-ray Energy (*keV*)
^{115}Cd	5	527.7, 492.5
^{60}Co	5	1173.1, 1332.4
^{65}Zn	5	1115.4
^{59}Fe	20	1098.6, 1291.5
^{203}Hg	20	279.1
^{110m}Ag	5	657.8
^{64}Cu	5	511.0, 1345.5
^{56}Mn	5	846.9, 1810.7
^{65}Ni	50	1481.7, 1115.4

of 1-3, dilute HNO_3 was used. Although acetate could form complexes with the metal ions in the artificial seawater matrix, their formation constants are significantly lower than those for oxine [101, 117-121] and, thus, presumably for HL. Therefore, the presence of acetate should not interfere with the extraction of the metal ions of interest in this study. The pH of the aqueous phase (95 mL) was adjusted with 0.6 mL of the appropriate buffer solution, and then saturated with a small volume of the organic solvent (*e.g.*, 100 μL of toluene) prior to extraction to ensure that the phase volume ratio remained constant. The aqueous phase was then extracted with 5.0 mL of the organic phase. After complete phase clarification (2-3 hours), the phases were separated and a 4.0-mL aliquot of each was counted. The percent extraction (extraction efficiency) of a metal ion was obtained as the ratio of the counting rate in the organic phase (corrected to 5.0 mL) to that of a 4.0-mL standard representing the activity added to the aqueous phase before extraction. The percent metal ion remaining in the aqueous phase was similarly calculated as the ratio of the counting rate in a 4.0-mL aliquot of the aqueous phase (corrected to 95 mL) to that of the standard. In all cases, the sum of the activities in the organic and aqueous phases accounted for 100±5% of the original activity of each radiotracer.

Initial tests were made with kerosene as the organic solvent at an HL concentration of 0.025*M*, but when this

organic phase was back-extracted with 16% (v/v) HNO_3 or other aqueous acids, the formation of a third phase resulted. To avoid this, the organic solvent was changed to toluene, which did not exhibit third phase formation on back-extraction with acids. Toluene, therefore, was used in all subsequent experiments. No significant difference in the extraction efficiencies of any of the radiotracers was observed when kerosene was replaced by toluene. Studies on the extraction of radiotracers from artificial seawater were then conducted using HL concentrations of 0.025, 0.25, 0.50, and 1.0*M*. Incomplete extraction of radiotracers was observed at HL concentrations of less than 0.25*M*, and this extractant concentration was employed in all subsequent experiments.

The time required for the attainment of equilibrium for all radiotracers was determined by varying the period of vigorous phase agitation from 10 minutes to 48 hours. Artificial seawater, Lake Ontario water (Station 302, Western Basin) and coastal seawater (Sandy Cove, Nova Scotia) comprised the aqueous phases, while the organic phase was a 0.25*M* solution of HL in toluene. The extraction efficiencies for each radiotracer were constant after 10-15 minutes of shaking and a 15-minute agitation time was adopted for all subsequent extractions.

II.3.3 Aqueous to organic phase ratio

In solvent extraction, the extent of analyte preconcentration is determined by the ratio of aqueous to organic phase and the percent extraction (Equation I.7). Since previous studies [80,81] have indicated that the ethenyl derivative of HL has a high distribution ratio, the attainment of high preconcentration factors with HL in a single batch-extraction should be possible. To determine the practical preconcentration factors attainable, the volume ratio of artificial seawater to organic phase was varied. Prior to extraction, the aqueous phase was adjusted to the optimal pH of 9.3 (Section III.2.3) with *4M* ammonia/0.*4M* ammonium acetate buffer and saturated with toluene. Single batch-extractions were then carried out as described in Section II.3.2, with 1.0 mL of 0.25*M* HL in toluene on aqueous phases of 100, 200, or 500 mL containing the radiotracers in the groups specified in Section II.2. After clarification, 500 μL of the organic and one-half the volume of the aqueous phase was counted. In view of the large aqueous phase volumes used, larger aqueous phase volumes were counted to obtain more precise counting statistics on the activities of the radiotracers in the aqueous phase after extraction. This procedure ensured a more precise activity-balance. Again, the sum of the activities in the organic and aqueous phases represented 100±5% of the initial activity. The percent

extraction was obtained (*e.g.*, see Section II.3.2) as the ratio of the counting rate in the organic phase (corrected to 1.0 mL) to that of a 1.0-mL standard containing the activity added to the aqueous phase before extraction. The percent metal ion remaining in the aqueous phase was determined as the ratio of the counting rate in the aqueous phase to that of a standard of the same volume as the aqueous phase counted.

II.3.4 Radiotracer study of back-extraction

It is often desirable to simplify the final matrix of analysis, particularly when the analytical sample is complicated and contains many potential interfering matrix components. In solvent extraction preconcentration procedures, this is often accomplished through the incorporation of a back-extraction step which quantitatively strips the complexed metals from the organic phase into a suitable aqueous acid [16,57,59,122]. After forward-extraction of the aqueous phase containing radiotracers as described in Section II.3.2, 4.0 mL of the organic phase was pipetted into a 125-mL Teflon® FEP separatory funnel into which 2.0 mL of aqueous acid was added. The funnel was shaken for 15 minutes and the phases were completely clear within 1 hour. The organic and aqueous phases (1.0 mL each) were counted and the

percent back-extraction was determined in an analogous manner to that of the forward-extraction outlined in Section II.3.2.

II.3.5 Recovery of radiotracer spikes from natural waters

In addition to numerous inorganic ions, natural waters contain from 0.1 to 10 mg/L of dissolved organic matter [7], some of this in the form of complexing agents such as humic and fulvic acids. To assess the efficacy of HL as an extractant for metal ions in free and variously-bound forms from seawater and freshwater, 95 mL of coastal seawater (Sandy Cove, Nova Scotia) and a Lake Ontario water sample (Station 302, Western Basin) were spiked with radiotracers, buffered to pH 9.3, allowed to equilibrate for at least 2 hours, presaturated with toluene, and extracted with 5.0 mL of a 0.25*M* solution of HL in toluene. Extraction efficiencies were obtained by the procedure outlined in Section II.3.2.

II.3.6 Flame AAS determination of the extraction efficiencies of Pb(II), Mg(II), and Ca(II)

The extraction efficiency of Pb(II) with HL was determined because of the well-documented toxicity of lead [*e.g.*, 123]. The study of the extraction efficiencies of Ca(II) and Mg(II) with HL was undertaken to investigate the extractability of alkaline earth ions which are major constituents of natural waters. Since a suitable radioisotope

of Pb could not be generated by (n,γ) reactions at the McMaster Nuclear Reactor, its extraction efficiency from artificial seawater with HL over the pH range 3-10 was evaluated by flame AAS. The γ-emitting radioisotopes of Ca and Mg that could be generated at the reactor possess very short half-lives (8.8 min for ^{49}Ca, and 9.45 min for ^{27}Mg) which precluded their use, so their extraction efficiencies with HL as a function of pH were also obtained by flame AAS.

Artificial seawater (Section II.1) was used as the aqueous phase and was spiked with 5 μg/mL of Pb(II). This solution (95 mL) was treated with 0.6 mL of the appropriate buffer, presaturated with toluene, and extracted as in Section II.3.2 into a 0.25*M* solution of HL in toluene. After extraction, 4.0 mL of the organic phase was back-extracted with 2.0 mL of 16% (v/v) nitric acid as described in Section II.3.4. A 650-μL portion of this aqueous phase was diluted to 25 mL with DDW to provide a final solution which would be 5 μg/mL in Pb(II) if analyte recovery was quantitative, and this sample was analyzed by flame AAS using external calibration. The above dilution was necessitated to bring the Pb(II) concentration in the linear working range of the calibration curve. The Pb(II) blank consisted of unspiked artificial seawater and was carried through the same procedure.

Mg(II) and Ca(II) extractions were performed in the same manner from artificial seawater containing accurately-

determined concentrations of $MgCl_2$ and $CaCl_2$. Mg(II) was diluted 2.5 x 10^6-fold, and Ca(II) 2 x 10^4-fold prior to analysis by flame AAS. A solution of 0.77*M* NaCl in DDW was used as the blank and was carried through the same procedure as the samples.

II.3.7 Analysis of CASS-1 seawater

CASS-1 was analyzed for Cd(II), Cu(II), Mn(II), Ni(II) and Pb(II) by GFAAS to assess the utility of the solvent extraction preconcentration method developed. A 0.25*M* solution of HL in toluene was purified from most trace metal contaminants by extraction with 10% (v/v) nitric acid, DDW and 0.1*M* EDTA (Section II.3.1). The aqueous phase (95 mL) was buffered to pH 9.3, presaturated, and extracted with 5.0 mL of 0.25*M* HL in toluene as outlined in Section II.3.2. This provided a preconcentration factor of 19. A 4.0-mL aliquot of the organic phase was then back-extracted with 2.0 mL of 16% (v/v) nitric acid (described in Section II.3.4). This enriched the analyte concentration an additional 2-fold for an overall preconcentration factor of 38. The phase volume ratios and, thus, the preconcentration factors were chosen on the basis of GFAAS sensitivity for the analytes. Quantitation was carried out by external calibration with metal ion standards made up in 16% (v/v) nitric acid on the assumption that analyte recovery was quantitative.

Blank control is important to the detection limits and accuracy of trace metal determinations insofar as it serves as an indicator of any trace metal components added to the sample by contamination from added reagents or the laboratory environment. Ideally, the blank solution should be identical to the sample except for the presence of the analytes; *i.e.*, it should contain all sample matrix components as well as all chemical reagents. In practise, however, it is often difficult to produce a representative synthetic blank which both matches the matrix of the natural water sample and the level of trace element contamination from reagents added to the sample. If, for example, the blank was more contaminated than the sample, the final result would be erroneously low since the blank values would be erroneously high. To circumvent this potential problem, some researchers have used highly pure (*i.e.*, distilled deionized) water [16,124] without matrix-matching. Accordingly, DDW (Section II.1) was used in place of the natural water sample for all trace metal determinations by GFAAS and was carried through the same procedure. The absorbance of the blank was then used to correct that of the sample. The trace metal content of DDW was measured periodically by GFAAS and Zn(II) was the only metal ion that could be detected by direct injection (absorbance≈0.24). As a consequence, Zn(II) blanks were high and irreproducible, precluding its determination in the CASS-1 sample.

III. RESULTS AND DISCUSSION

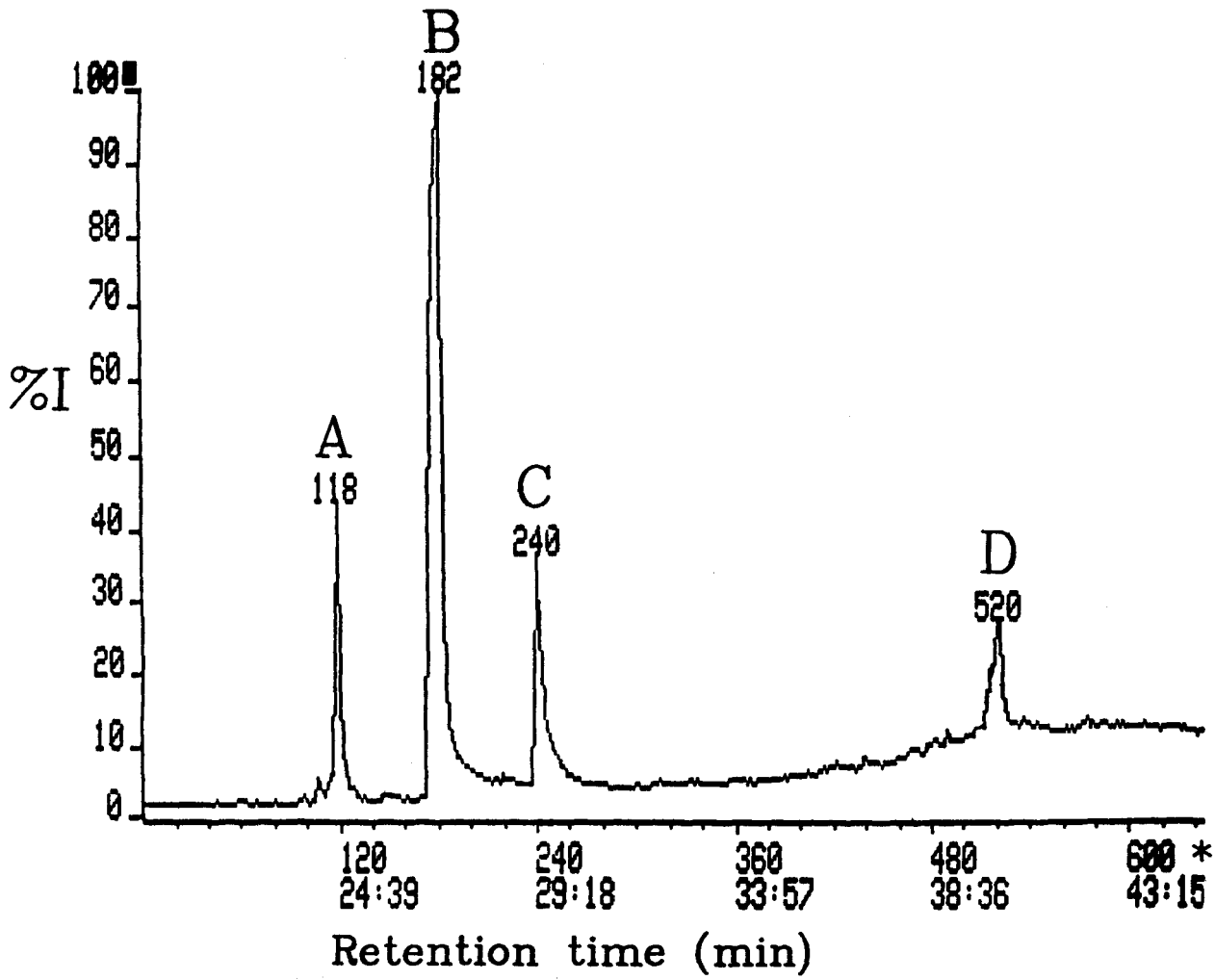
III.1 Removal of organic impurities from Kelex 100

Since 1976, the composition of Kelex 100 has changed significantly [88]. Up to 1976, the active component was 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol which comprised approximately 78 wt % of the commercial mixture. The remainder of the material consisted of an unspecified dark fluorescent material (presumed to be a decomposition product of the active component) and about 4 wt % of oxine [125]. After a change in the manufacturing process, the active agent has been identified as 7-(4-ethyl-1-methyl-octyl)-8-quinolinol (HL) by FT-IR spectroscopy as well as ^{1}H and ^{13}C nmr studies [88,89]. It comprises about 85 wt % of the commercial mixture with the remainder consisting of a number of different organic impurities [86]. Internal documents [86,87] and an external study [88] have identified the organic impurities contained in Kelex 100 as oxine, a C_{22}-alkylated ketone, a C_9-alkylated furoquinoline, and a C_{22}-alkylated oxine derivative (see Figure 1, page 31). Of these, only oxine and its C_{22}-alkylated homologue would present potential problems in the preconcentration of metal ions as they may compete with HL by complexation in the extraction. Although the non-chelating furoquinoline and

ketone impurities would not pose this problem, their presence in significant amounts in the final product would lower the effective concentration of the active component, necessitating corrections in the preparation of standard solutions. Additionally, variations in the manufacturing process may cause different samples of Kelex 100 to exhibit different concentrations of the active component and impurities. Past researchers [*e.g.*, 77,91,125] have employed a variety of techniques to purify the ethenyl derivative of HL which have lead to both differing impurity levels and concentration of the active component. For the purposes of this work, a purification procedure was required which would produce HL of high purity, free from chelating impurities, at the multi-gram quantities needed for subsequent solvent extraction studies. The procedure should also be rapid, involving a minimum number of steps and chemical reactions to avoid chemical alteration of the components of the mixture, and should minimize trace metal contamination.

To ascertain the major organic impurities likely to be present in the Kelex 100 sample used in this study, a sample of the material as supplied was analyzed by gas chromatography/mass spectrometry (GC/MS). The total ion chromatogram (TIC) is provided in Figure 2 and shows a four-component mixture.

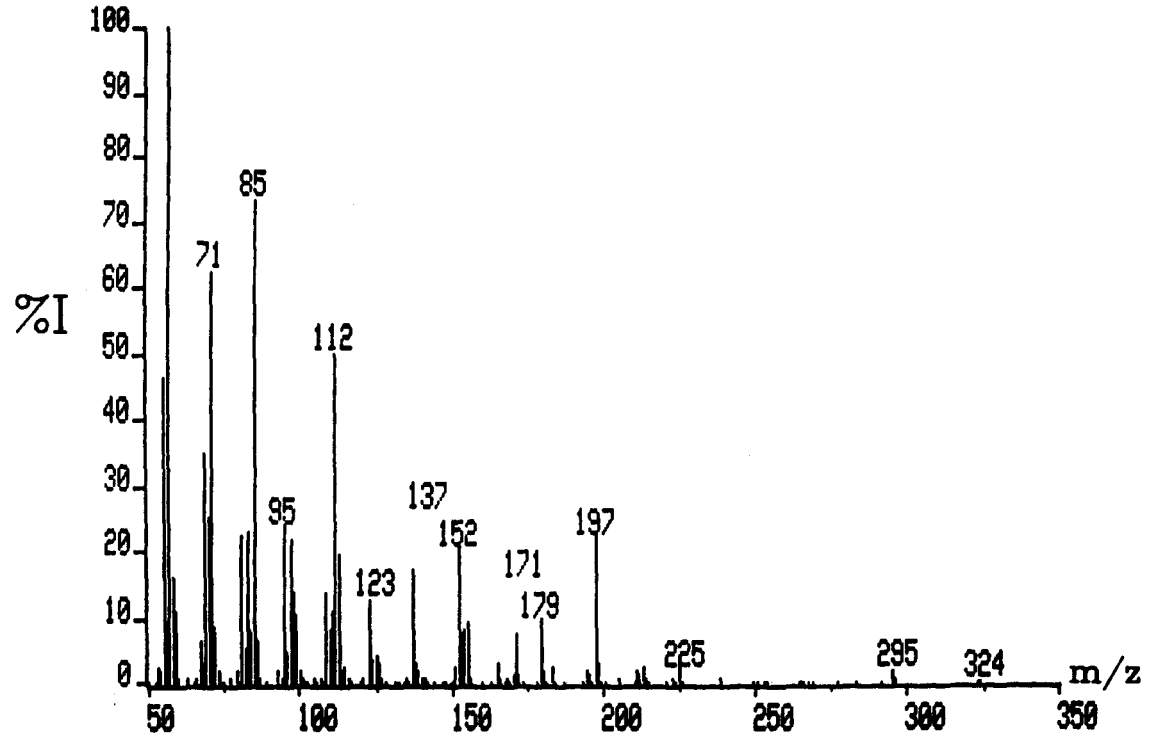
The mass spectrum of component A (Figure 3) strongly resembles that obtained by Graefe and Richter [87] for the



* scan number

Figure 2. Total ion chromatogram (TIC) of unpurified Kelex 100.

Figure 3. Mass spectrum of component A.



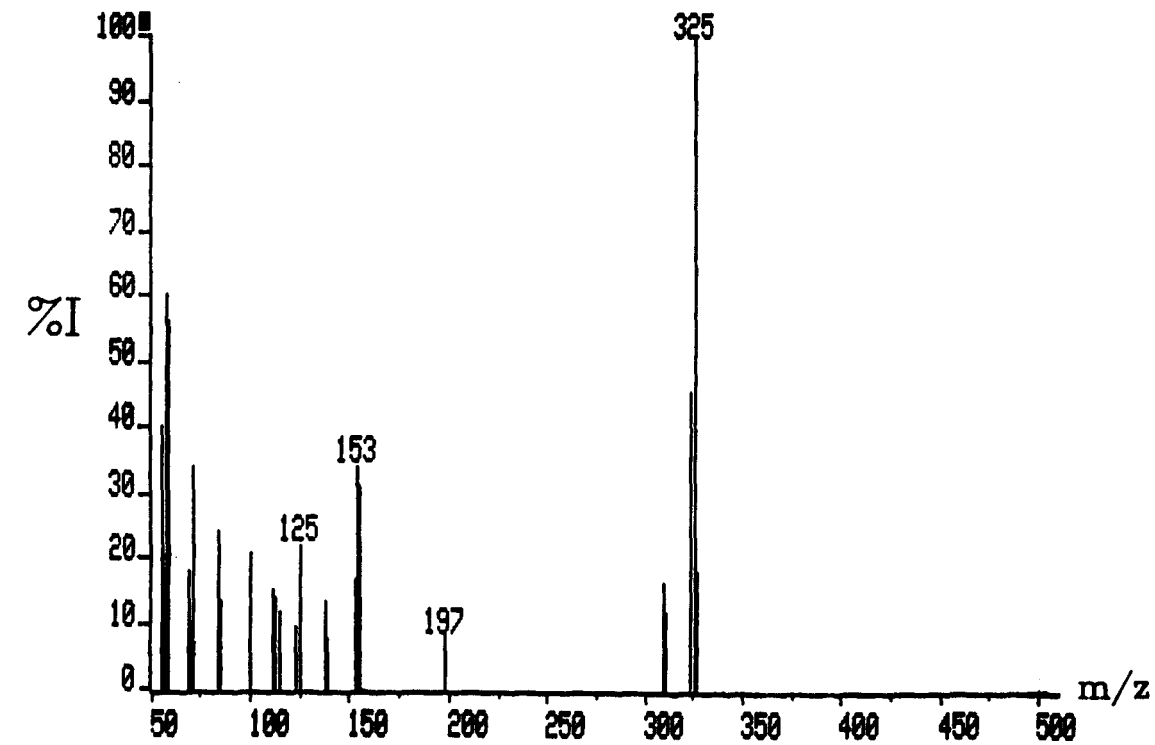
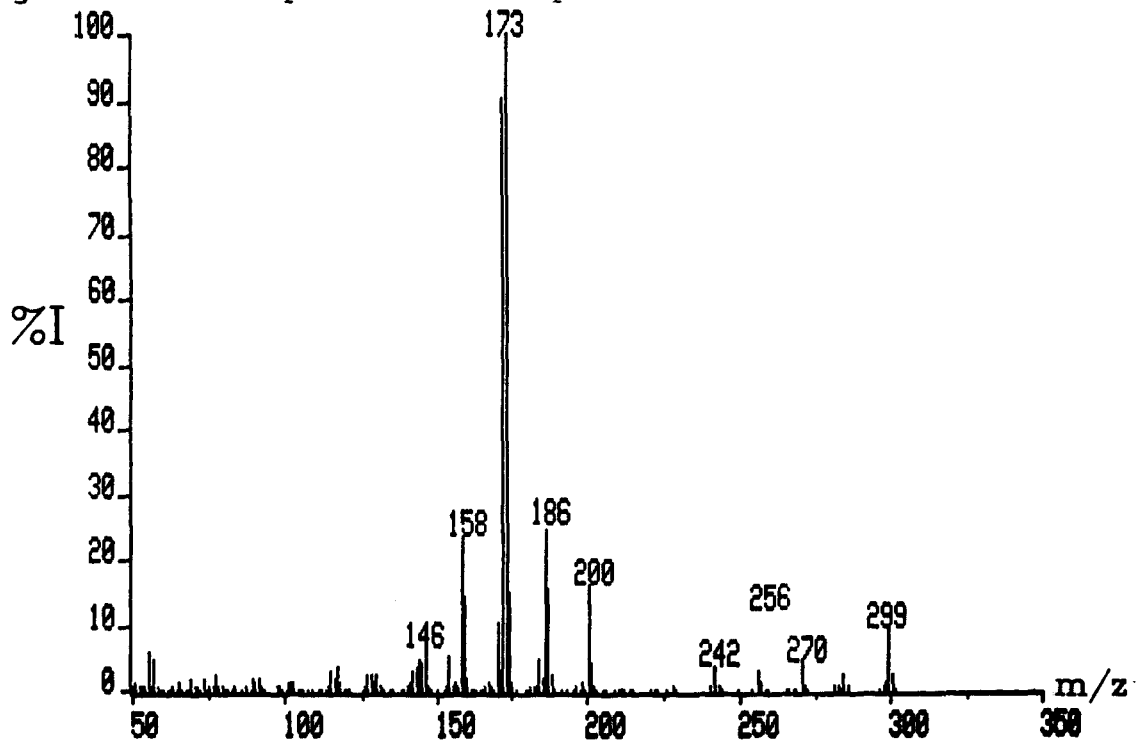


Figure 4. Chemical ionization mass spectrum of component A using methane as the reagent gas.

Figure 5. Mass spectrum of component B.



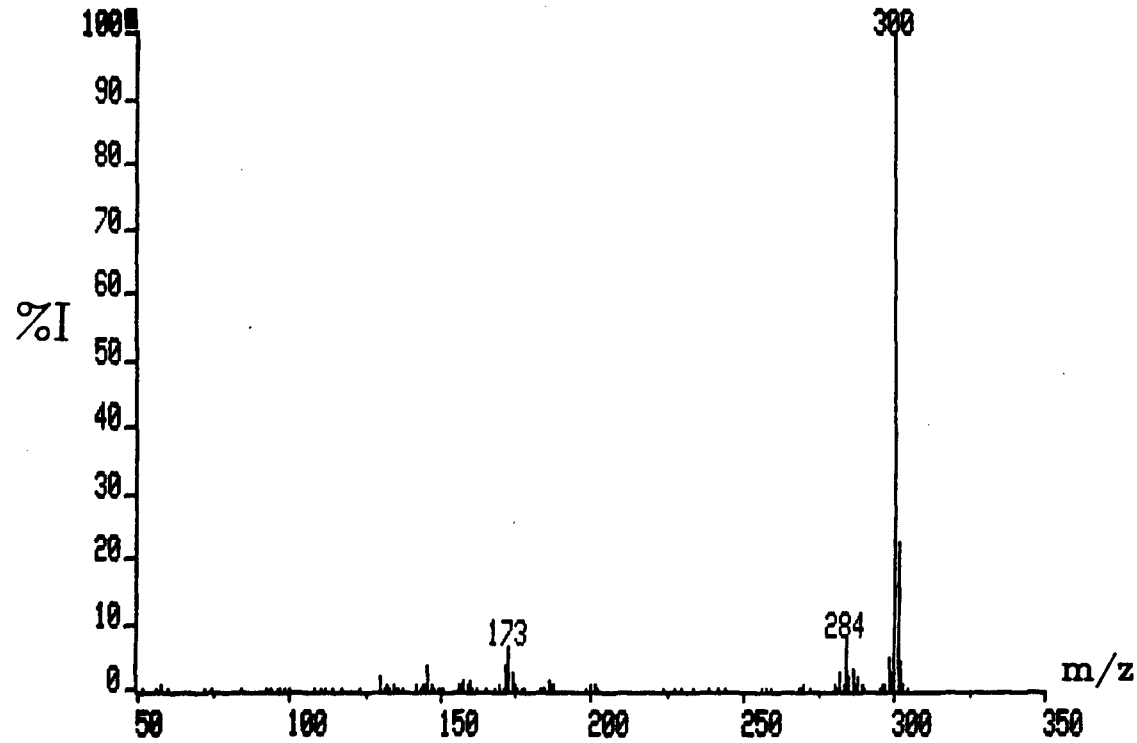


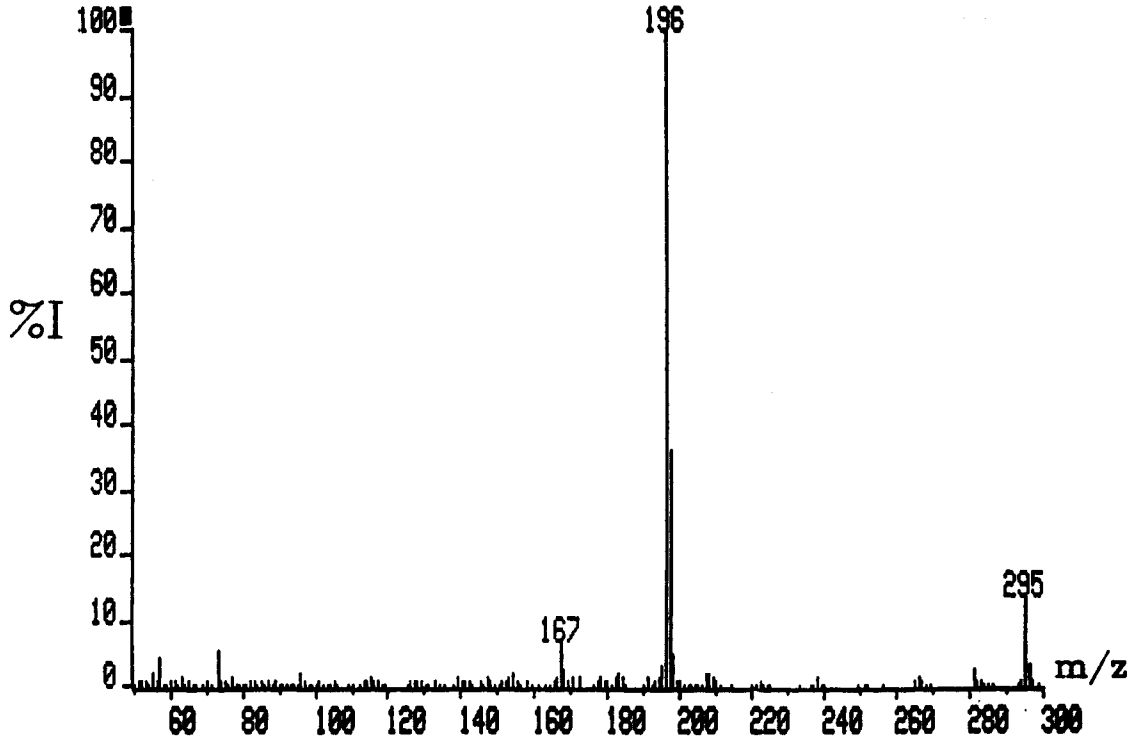
Figure 6. Chemical ionization mass spectrum of component B using ammonia as the reagent gas.

first-eluting component of a similar Kelex 100 sample. They identified this compound as 5,13-diethyl-10-methyl-8-heptadecanone, a C_{22}-alkylated ketone of molecular weight 324 (Appendix, page 125, Figure 1 [87]). The low-intensity apparent molecular ion at m/z 324 of component A (Figure 2) was further substantiated by the presence of an $(M+H)^+$ ion at m/z 325 in the chemical ionization (C.I.) GC/MS of Kelex 100 using methane as the reagent gas (Figure 4).

The mass spectrum of the major constituent of the mixture, component B (Figure 5), strongly resembles that of the active component, 7-(4-ethyl-1-methyloctyl)-8-quinolinol (Appendix, page 126, Figure 2 [87]). Confirmation of the molecular ion at m/z 299 (Figure 5) was obtained by C.I. GC/MS using ammonia as the reagent gas; an intense $(M+H)^+$ ion at m/z 300 is observed (Figure 6). High resolution MS on the m/z 299 ion provided the elemental composition $C_{20}H_{29}NO$ (observed mass, 299.22497; calculated mass, 299.22490), which is consistent with the elemental formula of 7-(4-ethyl-1-methyloctyl)-8-quinolinol. Since the structure of the active component has been verified by independent workers [88,89] and, in view of the fact that it is the major constituent of the Kelex 100 sample, component B can be identified as 7-(4-ethyl-1-methyloctyl)-8-quinolinol.

The mass spectrum of component C (Figure 7) is very similar to that obtained for the third-eluting component of a similar sample of Kelex 100 analyzed by others [87];

Figure 7. Mass spectrum of component C.



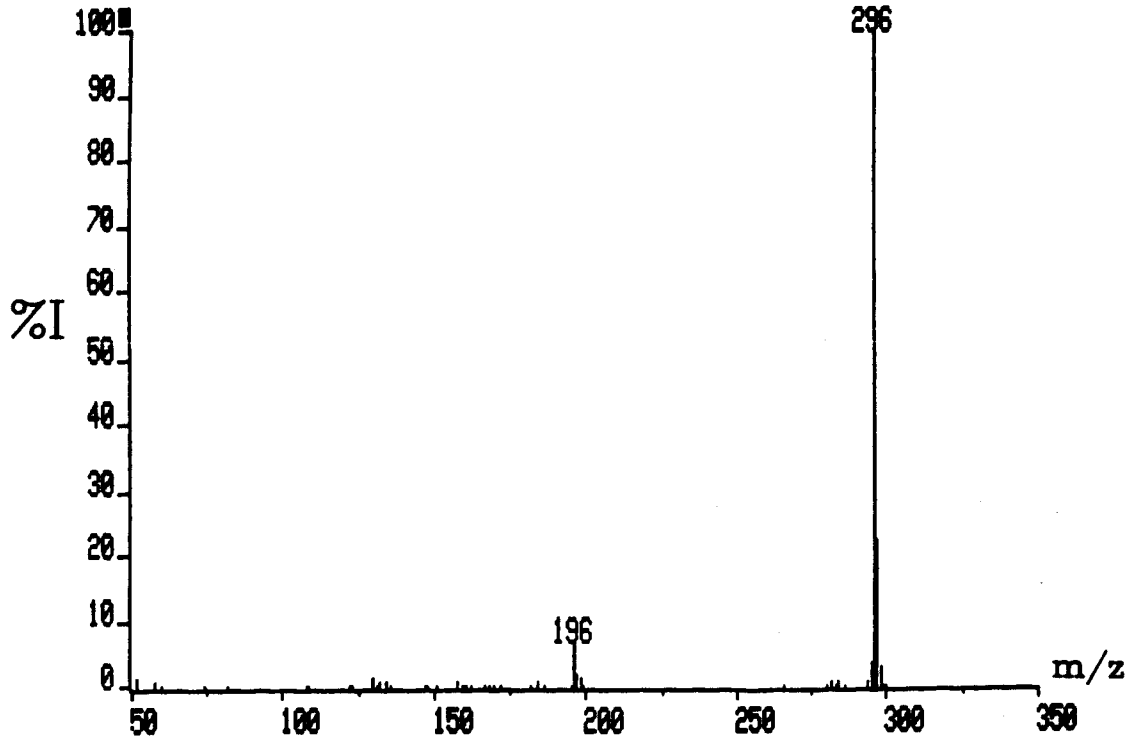
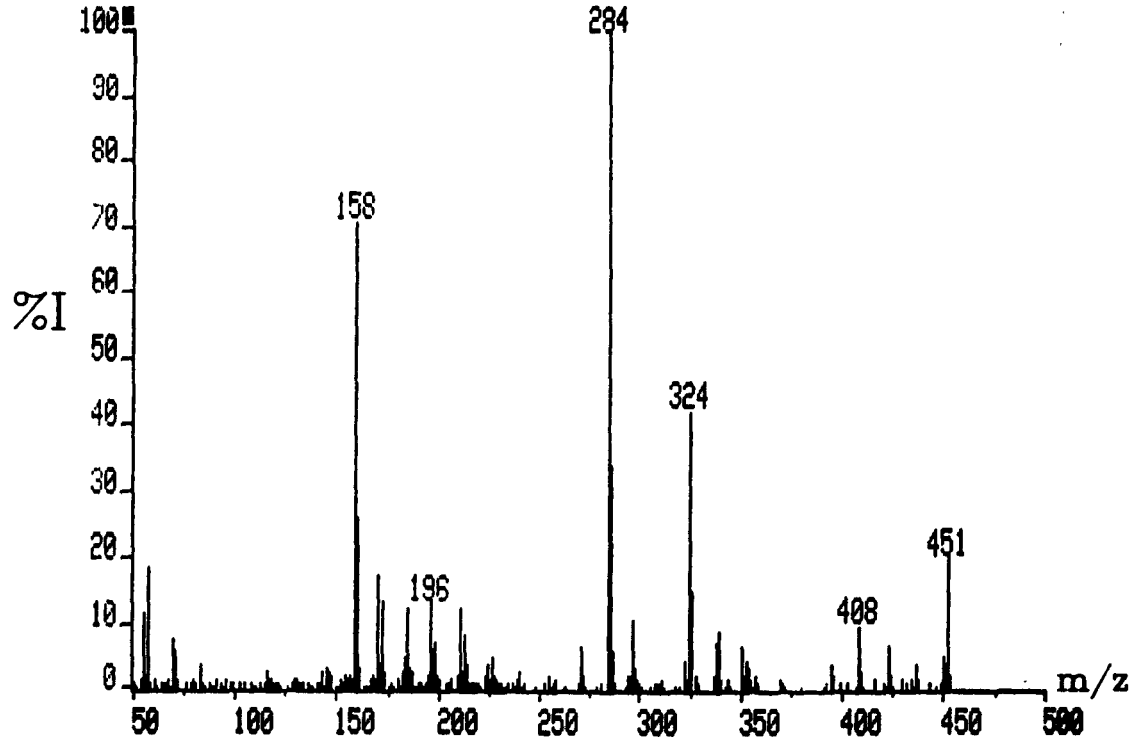


Figure 8. Chemical ionization mass spectrum of component C using ammonia as the reagent gas.

component C has been identified as a C_9-alkylated furoquinoline (Appendix, page 127, Figure 3 [87]). The apparent molecular ion at m/z 295 was confirmed by C.I. GC/MS (ammonia reagent gas) which yielded an intense $(M+H)^+$ ion at m/z 296 (Figure 8).

The late elution of component D is indicative of a relatively involatile compound of high molecular weight. Other studies have indicated the presence of a C_{22}-alkylated oxine homologue of molecular weight 453, which has been identified as 5,7-di-(4-ethyl-1-methyloctyl)-8-quinolinol [87]. In the present study, GC/MS analysis revealed an apparent molecular ion at m/z 451 (Figure 9), which was further substantiated by the $(M+H)^+$ ion detected by probe C.I. MS (Figure 10). No higher mass ions were detected. High resolution MS on the molecular ion at m/z 451 provided the elemental composition $C_{31}H_{49}NO$ (observed mass, 451.3818; calculated mass, 451.3814) which is consistent with the elemental formula of an unsaturated C_{22}-alkylated oxine derivative. Data obtained [86] on sample of Kelex 100 of a lot number similar to that used in this study noted the presence of a C_{22}-alkylated oxine derivative but did not specify whether the alkyl chain was saturated, or substituted in one or more positions on the oxine ring (see Figure 1, page 31). In view of variations in the by-products likely to occur in different samples of Kelex 100, the presence of an

Figure 9. Mass spectrum of component D.



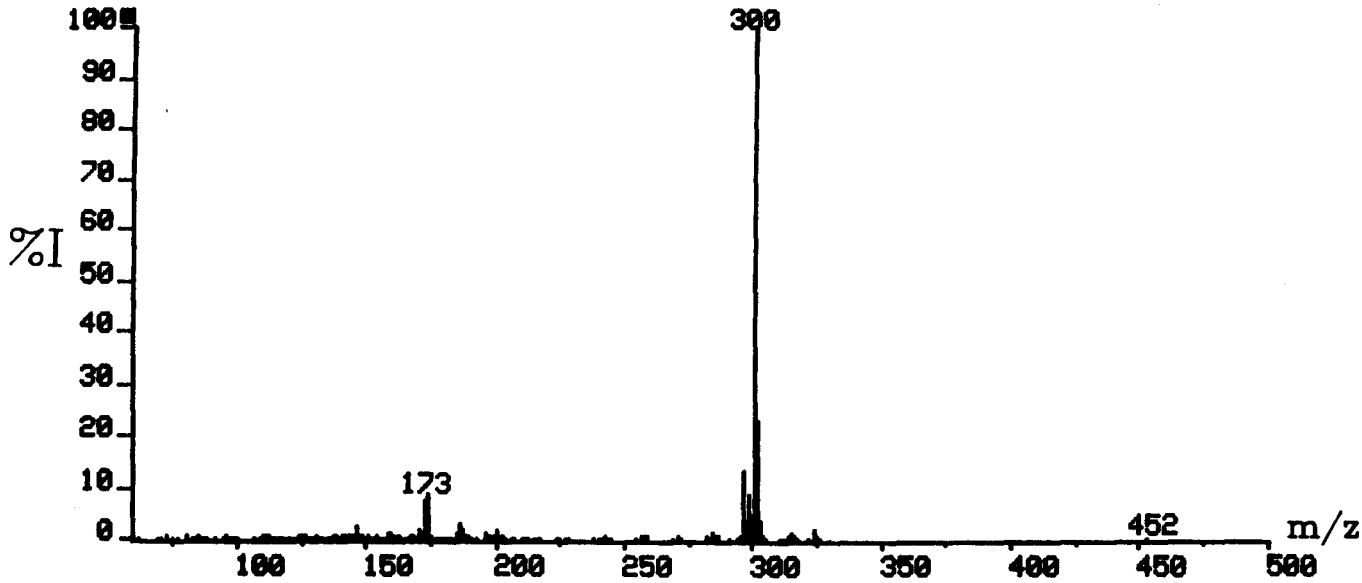


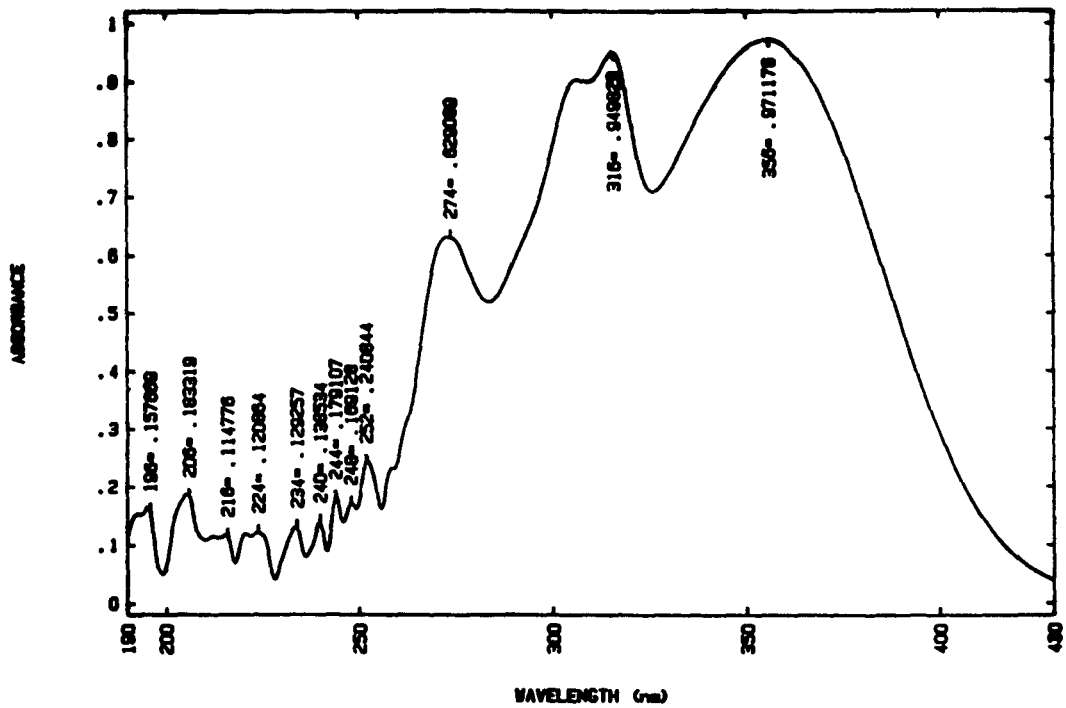
Figure 10. Probe chemical ionization mass spectrum of unpurified Kelex 100 mixture using ammonia as the reagent gas.

unsaturated C_{22}-alkylated oxine derivative, while not conclusively proven, cannot be ruled out.

The general agreement between the gas chromatographic and mass spectral results of this work and those of independent studies on Kelex 100 [86-89] strongly suggests the presence of the impurities 5,13-diethyl-10-methyl-8-heptadecanone, a C_9-alkylated furoquinoline, and a C_{22}-alkylated oxine homologue. It must be emphasized, however, that in the absence of standard library spectra or pure samples of the compounds in question from which accurate mass spectra could be obtained, the above assignments are tentative and are used in the remainder of this thesis for the sake of convenience.

A rapid, preparative purification procedure was then sought which would remove most if not all of the organic impurities from Kelex 100. In particular, the potential chelating impurities oxine and its high molecular weight homologue would have to be removed. Although oxine was not detected by GC or GC/MS, likely due to its volatility and reportedly low concentration in Kelex 100 ($\leq$0.5 wt %) [86,88], its presence in the mixture was probable and steps were taken to remove it. This was accomplished by the acid extraction procedure outlined in Section II.3.1. The absorption spectra of the first and fifth acidic aqueous fractions are provided in Figures 11 and 12; a spectrum of oxine in 1*M* HCl used as a reference is given in the Appendix, page 128, Figure 4. The

Figure 11. UV/visible spectrum of the first acidic fraction in the extraction of Kelex 100 with 1*M* HCl.



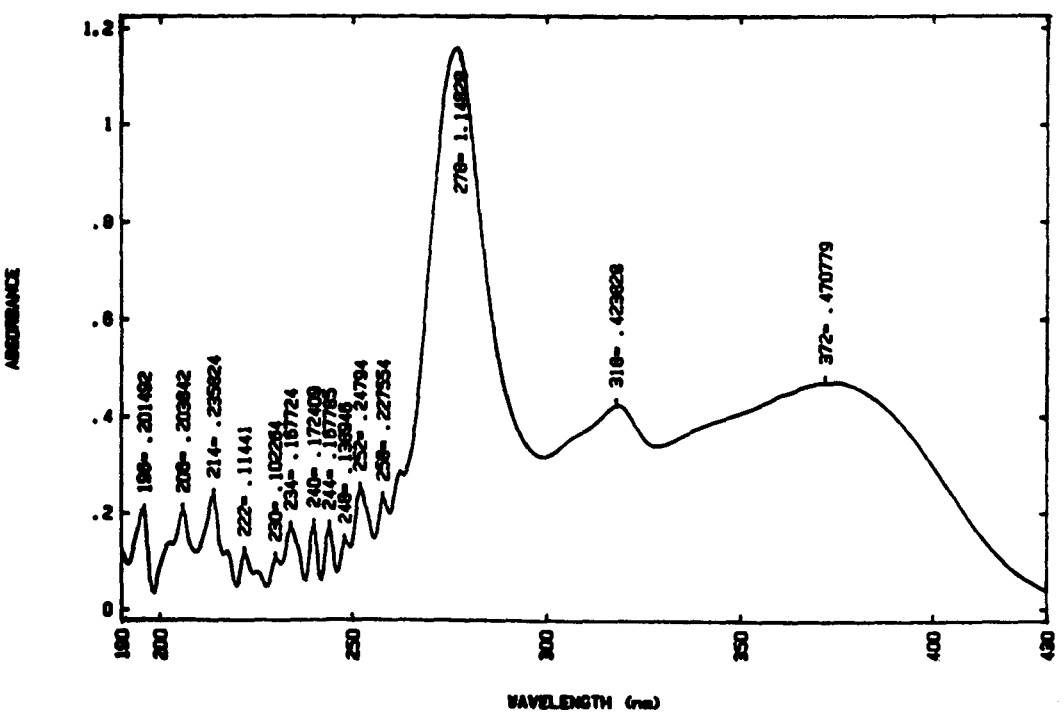


Figure 12. UV/visible spectrum of the fifth acidic fraction in the extraction of Kelex 100 with 1*M* HCl.

shoulder at 306 nm in the first fraction (Figure 11) is essentially absent in the fifth (Figure 12), while the strong absorption peaks at 316 and 356 nm are substantially reduced. These absorption maxima are generally consistent with those observed for protonated oxine [126]. This would indicate that the removal of oxine from Kelex 100 is essentially complete after five washings with 1*M* HCl.

The washed (neutralized) Kelex 100 was thereafter fractionally distilled under vacuum to remove the remaining organic impurities. A four-pass vacuum distillation was found to be sufficient to upgrade the reagent to 98% purity (Section II.3.1). The first distillation reduced the Kelex 100 sample to a three-component mixture which was found by GC to contain approximately 90% HL, 10% 5,13-diethyl-10-methyl-8-heptadecanone and 3% C_9-alkylated furoquinoline. Significantly, E.I. probe MS on the distillate detected no ion at m/z 451 or 453. Thus, the probable absence of any high molecular weight potential chelating agents was indicated. The second distillation removed much of the 5,13-diethyl-10-methyl-8-heptadecanone and the third distillation nearly all of the C_9-alkylated furoquinoline impurity. The distillate from the fourth and final pass was found by GC and GC/MS to contain 98% HL and 2% of the non-chelating impurity, 5,13-diethyl-10-methyl-8-heptadecanone. The yield for the first distillation was approximately 60% and about 80% for each of the subsequent distillations. Although the procedure provides

an overall yield of HL of only about 30%, this limitation may be easily overcome by using large (~250 g) quantities of starting material.

A purification procedure [89] which produced essentially 100% HL by vacuum distillation, precipitation and recrystallization of the Pb(II) complex of HL, regeneration of HL, followed by a final vacuum distillation was avoided because the removal of trace metal ions from HL is tedious and difficult (see Section III.7.1), and more sample treatment is involved. Although the final yield was not specified, such a procedure would likely result in an even lower overall yield than that obtained in this work.

III.2 Radiotracer study of extraction efficiencies

III.2.1 Selection of aqueous and organic phases

The extraction efficiencies (%E) of metal ions from artificial seawater with HL (Section II.3.2) were determined with radiotracers grouped as noted in Section II.2. The resolution of the Ge(Li) detector permitted simultaneous multielement analysis at the trace metal concentrations typically found in natural waters (ng/mL) without the attendant risk of contamination. Thus, the effect of any change in experimental parameters (*e.g.*, HL concentration and shaking time) could be simultaneously observed for each metal ion. The composition of the artificial seawater matrix from

which the metal ions were extracted was selected primarily to simulate the typical salinity of natural seawater. Chloride ion is by far the most prevalent inorganic ligand in seawater and is likely to act as the primary inorganic complexing agent; therefore, no attempt was made to duplicate the smaller concentrations of sulphate, bicarbonate, bromide or natural organic ligands likely to be present. The effect of these species on the extraction of trace metals from natural waters with HL was, however, taken into account in separate experiments which involved the extraction of radiotracer spikes from natural lakewater and seawater (Section III.5) and also in the analysis of natural seawater by extraction/ GFAAS (Section III.7.2). Magnesium and calcium chloride were present in the artificial seawater at their typical natural seawater concentrations (approximately 0.053*M* and 0.010*M*, respectively) to observe whether a substantial amount of HL would be consumed through complexation with these ions. Although the stability constants of Mg(II) and Ca(II) with oxine are significantly smaller than those of the transition metal ions (see Table 3, page 34 and references [101,120,121]), the extraction of these ions with oxine at alkaline pH has been documented [95,110,111], and it is not unreasonable to assume that HL would behave in a similar manner to its parent compound. The extraction of Ca(II) and Mg(II) from artificial seawater with HL is discussed in Section III.6.

Initially, kerosene was selected as the organic solvent but was abandoned when back-extraction with aqueous acid resulted in the formation of a viscous third phase, which likely contained protonated HL. Third phase formation has also been observed in stripping of kerosene solutions of the ethenyl derivative of HL with aqueous phases of pH<0.5 [80,127]. Therefore, the solvent was changed to toluene, in which HL appeared to be more soluble. A third phase was not observed on back-extraction of a toluene solution of HL with any of the aqueous acids noted in Section III.4 and the extraction efficiencies for metal ions with HL in toluene were identical, within the limits of experimental error, to those obtained with kerosene.

III.2.2 Optimization of equilibration time and extractant concentration

The time required for the attainment of equilibrium for all radiotracers was determined to be within 15 minutes (Section II.3.2). This equilibration time is longer than that required for the extraction of metal ions from 0.1*M* $KClO_4$ into 0.1*M* oxine in chloroform observed by Starý [95], but is somewhat shorter than that reported by Isshiki *et al.* [36] for extraction from 0.1*M* $NaClO_4$ into a 0.04*M* toluene solution of the ethenyl derivative of HL. In the former report, equilibrium was reached within 2-3 minutes for most of the metal ions investigated with the exception of Ni(II), which

required 6 hours. In the latter study, 30-minute extraction times were required except for Ni(II), Fe(III), and Ti(IV) which needed about six hours for equilibrium to be established. While the longer equilibration times for HL relative to oxine can be rationalized in terms of the enhanced hydrophobicity of HL, the discrepancy between the data of this work and that of Isshiki *et al.* is not insignificant.

As was pointed out in Section I.4.4, the rate of a metal chelate extraction is dependent upon many parameters including shaking intensity, pH, extractant concentration, extraction mechanism, and metal ion species. Generally, the rate increases with increasing pH (in the absence of hydrolysis or secondary complex formation) and extractant concentration. Obviously, differences in some of these conditions between the present study and that of Isshiki *et al.* account for the more rapid equilibration time observed here. Conditions (where ascertainable) are listed in Table 7 for both studies. Assuming that the minor differences in extractant structure have little bearing on the rate of attainment of extraction equilibrium, several of the conditions used in the present study favour a faster equilibration time; specifically, higher ionic strength of the aqueous phase and higher extractant concentration in the organic phase. Furthermore, the alkaline aqueous phase pH is reported to favour a predominantly interfacial extraction

Table 7. Conditions for the extraction of metal ions from artificial seawater

Experimental Parameter	This Work	Isshiki *et al.* [36]
HL	7-(4-ethyl-1-methyl-octyl)-8-quinolinol	7-(1-ethenyl-3,3,5,5-tetramethyl-hexyl)-8-quinolinol
Organic solvent	toluene	toluene
$[HL]_{initial}$	0.25*M*	0.04*M*
pH range for simultaneous extraction	9.0-9.5	8.0-9.0
Ionic strength of aqueous phase	0.96*M*	0.1*M*
Main electrolyte in aqueous phase	NaCl	$NaClO_4$

Table 8. Effect of varying HL concentration in toluene on extraction efficiencies of radiotracers from artificial seawater in the pH range 9.0-9.5*

	% Extraction			
Radiotracer	[HL]=0.025*M*	[HL]=0.25*M*	[HL]=0.50*M*	[HL]=1.0*M*
^{115}Cd	3±1	99±6	99±1	96±3
^{64}Cu	100±3	100±1	101±3	99±3
^{56}Mn	88±2	100±4	94±2	95±2
^{65}Ni	85±3	103±2	100±4	97±2
^{65}Zn	100±2	97±3	95±1	101±2
^{60}Co	95±2	98±3	98±5	100±5
^{59}Fe	16±4	24±2	22±5	28±4
^{203}Hg	<1	32±4	44±5	46±6
^{110m}Ag	<1	<1	<1	<1

* Results represent the mean ± the standard deviation of 3-5 determinations; $V/\overline{V}=19$; ionic strength of artificial seawater=0.96*M*.

mechanism [79,85] (Section I.5.2). This, combined with the low dielectric constant of the artificial seawater of the present study, could, in turn, favour more rapid complex formation.

The effect of initial concentration of HL in the organic phase was investigated and the data are supplied in Table 8. At 0.025*M* HL, simultaneous extraction of ^{60}Co(II), ^{64}Cu(II), ^{56}Mn(II), and ^{65}Zn(II) occurred in the pH range 9.0-9.5 but only ^{60}Co(II), ^{64}Cu(II) and ^{65}Zn(II) extracted quantitatively and the extraction of ^{115}Cd(II) and ^{203}Hg(II) was negligible. At 0.25*M* HL, the extraction of ^{115}Cd(II), ^{56}Mn(II) and ^{65}Ni(II) was quantitative and that of ^{59}Fe(III) and ^{203}Hg(II) increased but was still not quantitative. Since negligible improvement was obtained at 0.50 and 1.0*M* HL, the extractant concentration selected for subsequent extractions was 0.25*M*, and Hg(II) was excluded from the group.

III.2.3 Extraction efficiencies of metal ions as a function of pH

The extraction efficiencies as a function of the pH of the artificial seawater for ^{115}Cd(II), ^{60}Co(II), ^{64}Cu(II), ^{56}Mn(II), ^{65}Ni(II), ^{65}Zn(II), ^{203}Hg(II) and ^{59}Fe(III) are illustrated in Figures 13 to 21. The aqueous phase volume was 95 mL and the organic phase volume was 5.0 mL ($V/\bar{V}$=19); the organic phase was 0.25*M* HL in toluene. Near-quantitative extraction of ^{115}Cd(II), ^{64}Cu(II), ^{56}Mn(II), ^{65}Ni(II), and

$^{65}Zn(II)$ occurred in the pH range 9.0-9.5. The extraction of Pb(II) (Figure 19) was also quantitative in this pH range, as determined by flame AAS. A pH of 9.3 was selected as optimal for multielement extraction since it maximized the extraction efficiencies of the analytes while avoiding losses due to metal ion hydrolysis. Of the nine radiotracers investigated, only $^{110m}Ag(I)$, $^{59}Fe(III)$ and $^{203}Hg(II)$ did not extract quantitatively over the pH range 9.0-9.5. In fact, $^{110m}Ag(I)$ did not extract from artificial seawater at any pH, while the extraction of $^{203}Hg(II)$ in the pH range 9.0-9.5 was only 32±4% (Table 8 and Figure 20). $^{59}Fe(III)$ was extracted nearly quantitatively at pH 4.0, after which the extraction efficiency decreased as the pH was raised (Figure 21). Evaluation of the reasons for the poor extraction of these metal ions with HL at the optimum pH necessitates consideration of the nature of the metal ion species present in the aqueous phase as a function of pH and some knowledge of stability constants with ligands present in the aqueous phase, as well as knowledge of stability constants with HL. However, since no detailed stability constant data for HL or its ethenyl derivative presently exist, its metal chelate stability constants will be equated to those of oxine (Table 3, page 34) as a first approximation. Inorganic ligands present in the aqueous phase (artificial seawater) include chloride (~0.9*M*), acetate and ammonia from the buffers, and hydroxide. As the pH of the aqueous phase is changed, the

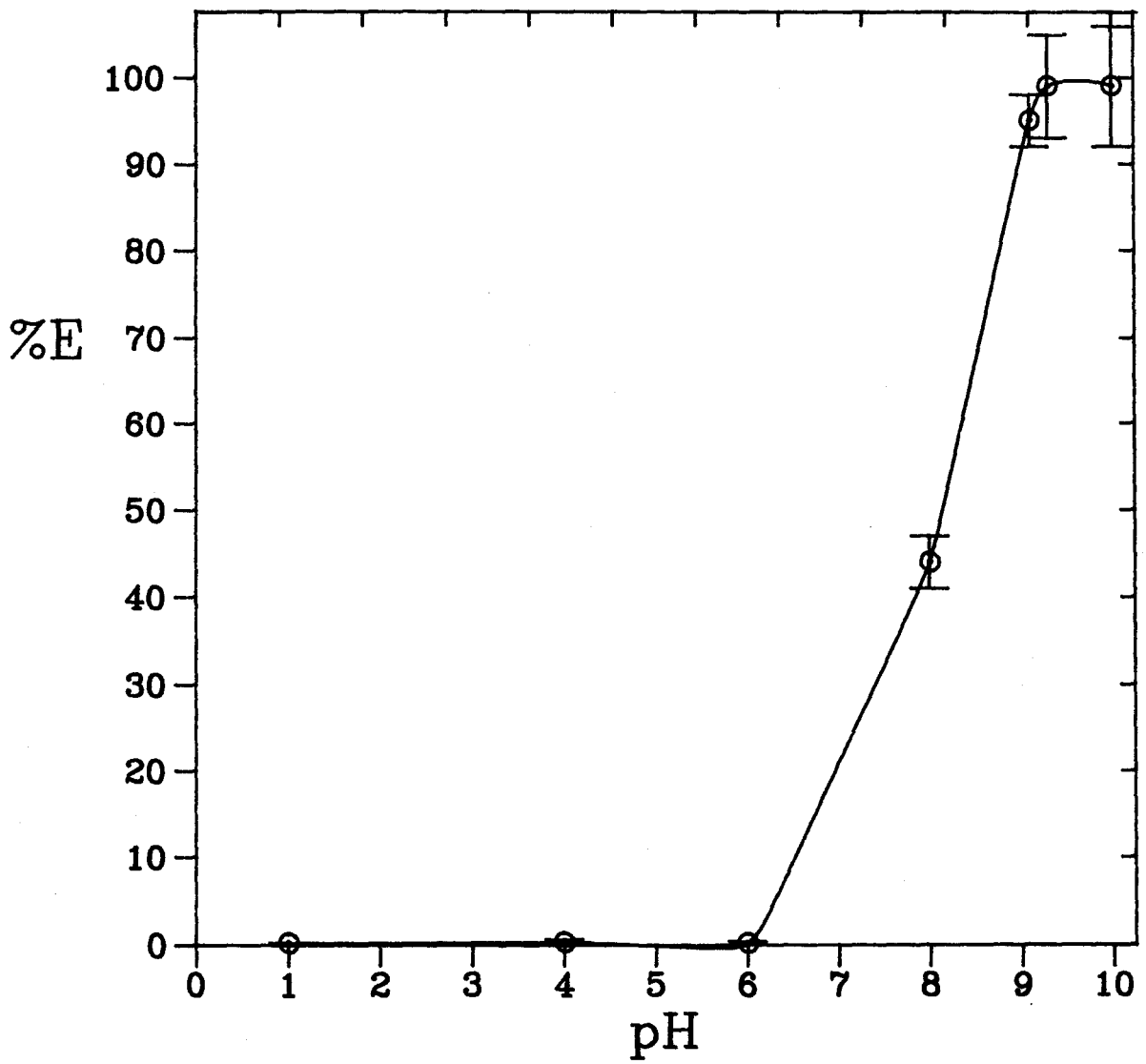


Figure 13. Extraction efficiency of $^{115}Cd(II)$ with 0.25*M* HL in toluene as a function of pH.

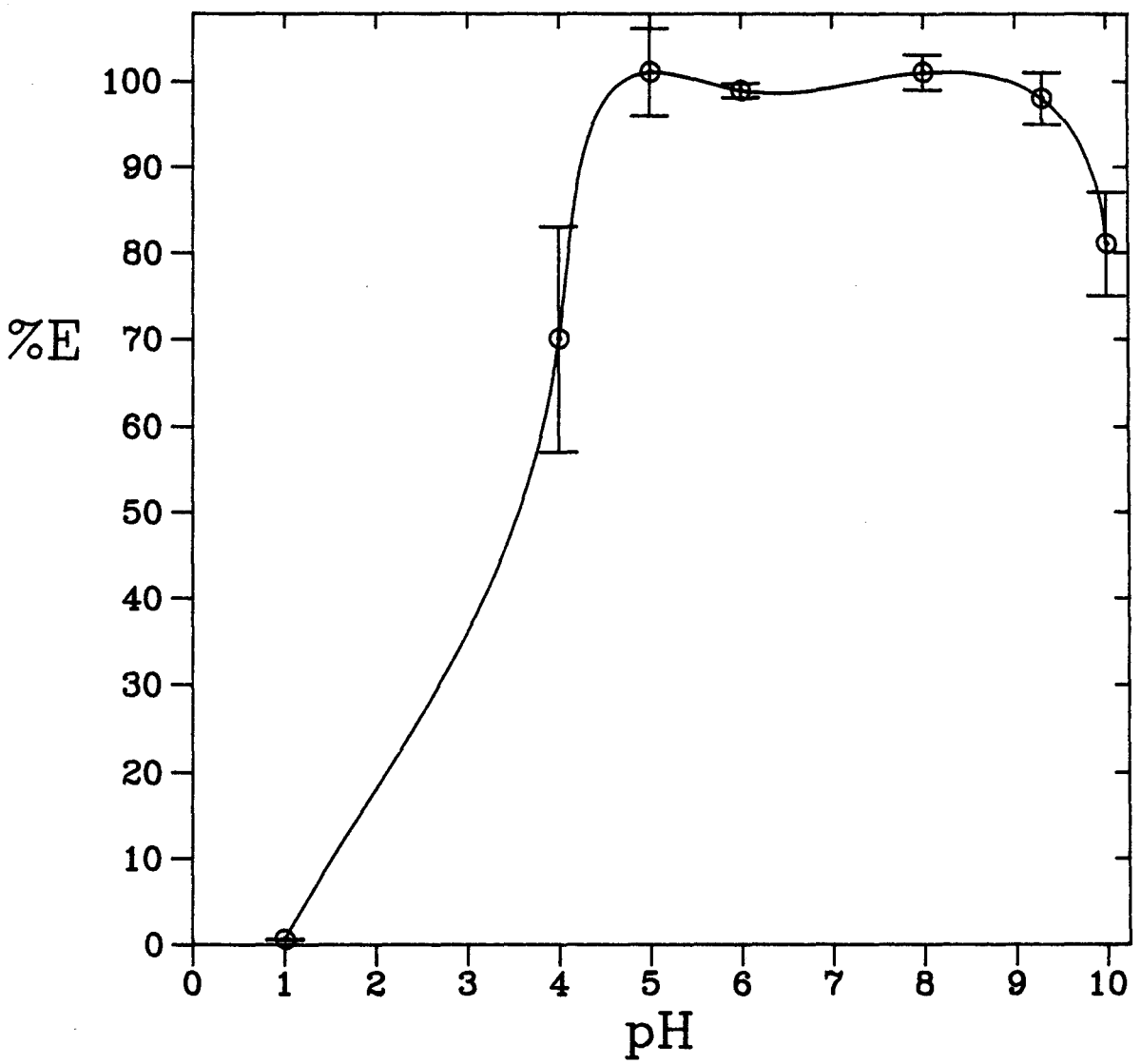


Figure 14. Extraction efficiency of $^{60}Co(II)$ with 0.25*M* HL in toluene as a function of pH.

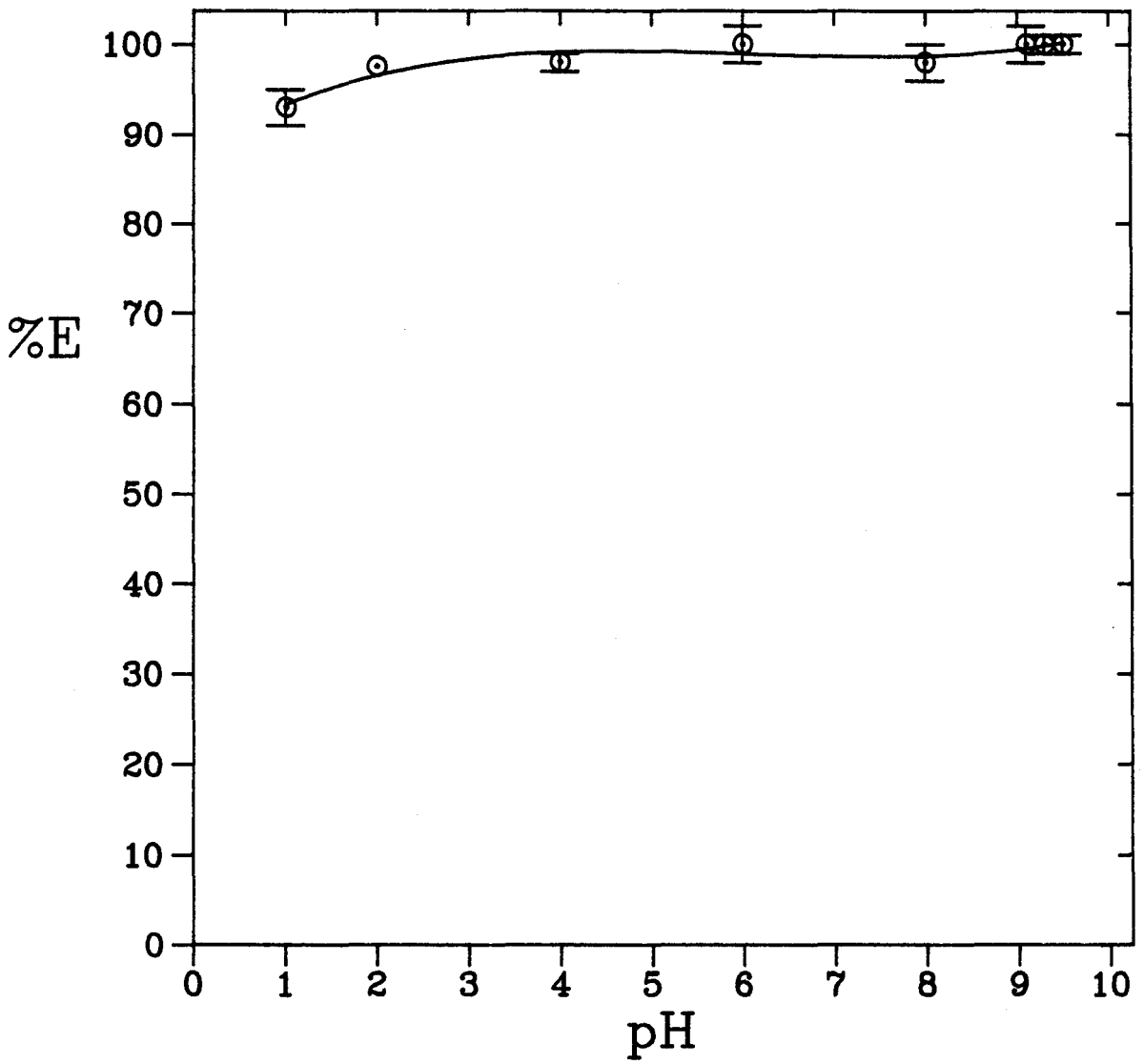


Figure 15. Extraction efficiency of $^{64}Cu(II)$ with 0.25*M* HL in toluene as a function of pH.

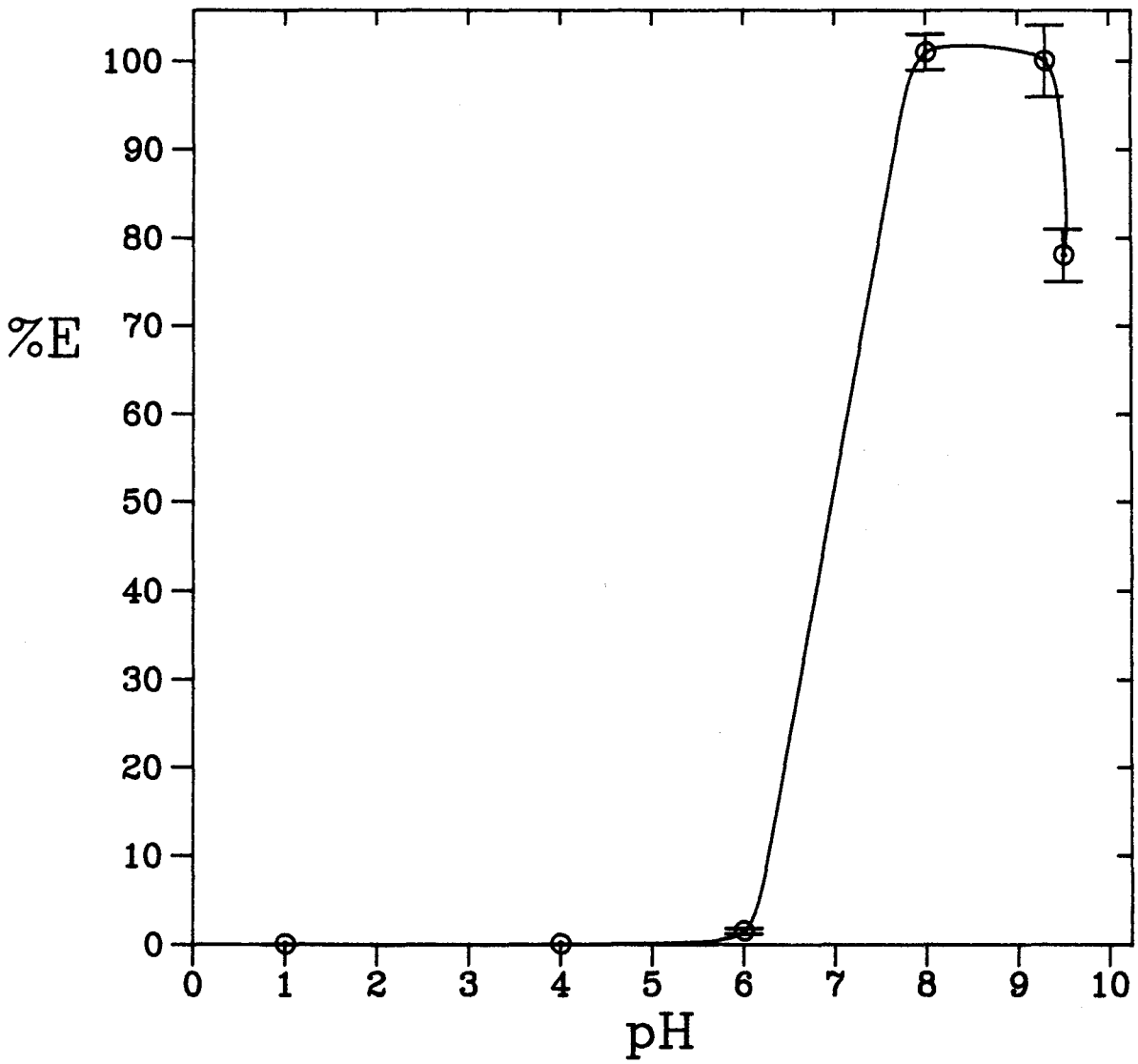


Figure 16. Extraction efficiency of $^{56}Mn(II)$ with 0.25*M* HL in toluene as a function of pH.

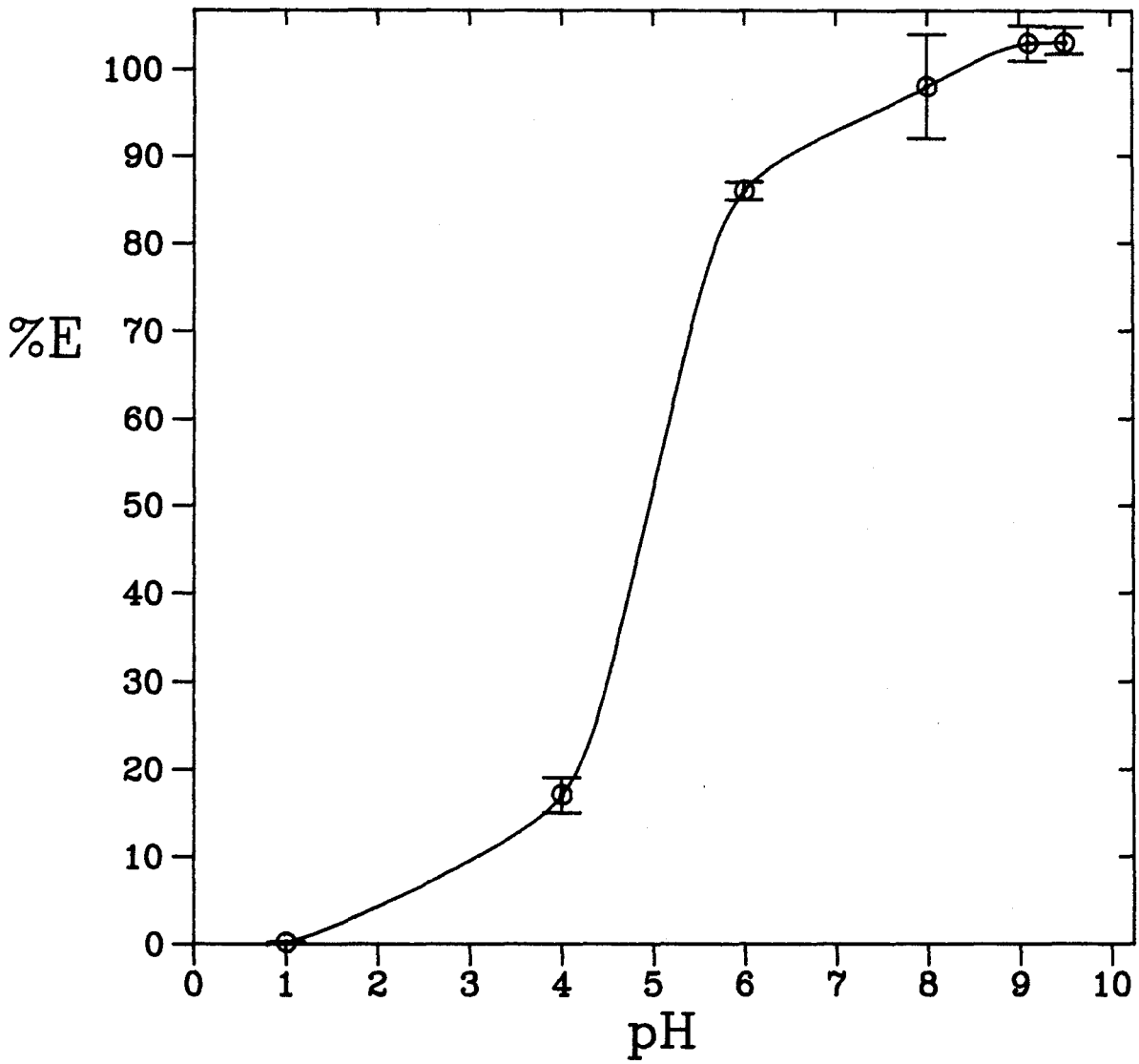


Figure 17. Extraction efficiency of $^{65}Ni(II)$ with 0.25*M* HL in toluene as a function of pH.

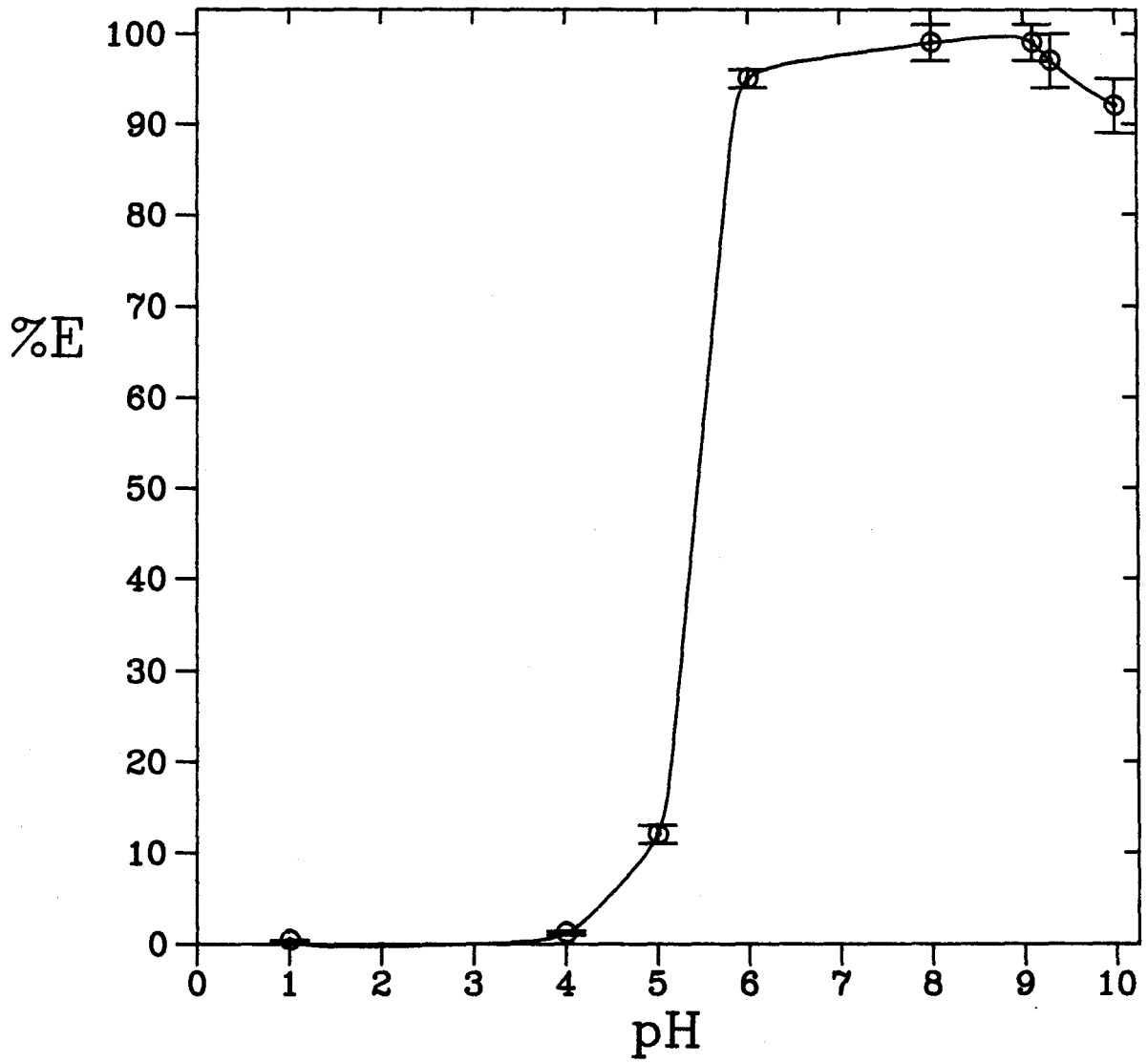


Figure 18. Extraction efficiency of $^{65}Zn(II)$ with 0.25*M* HL in toluene as a function of pH.

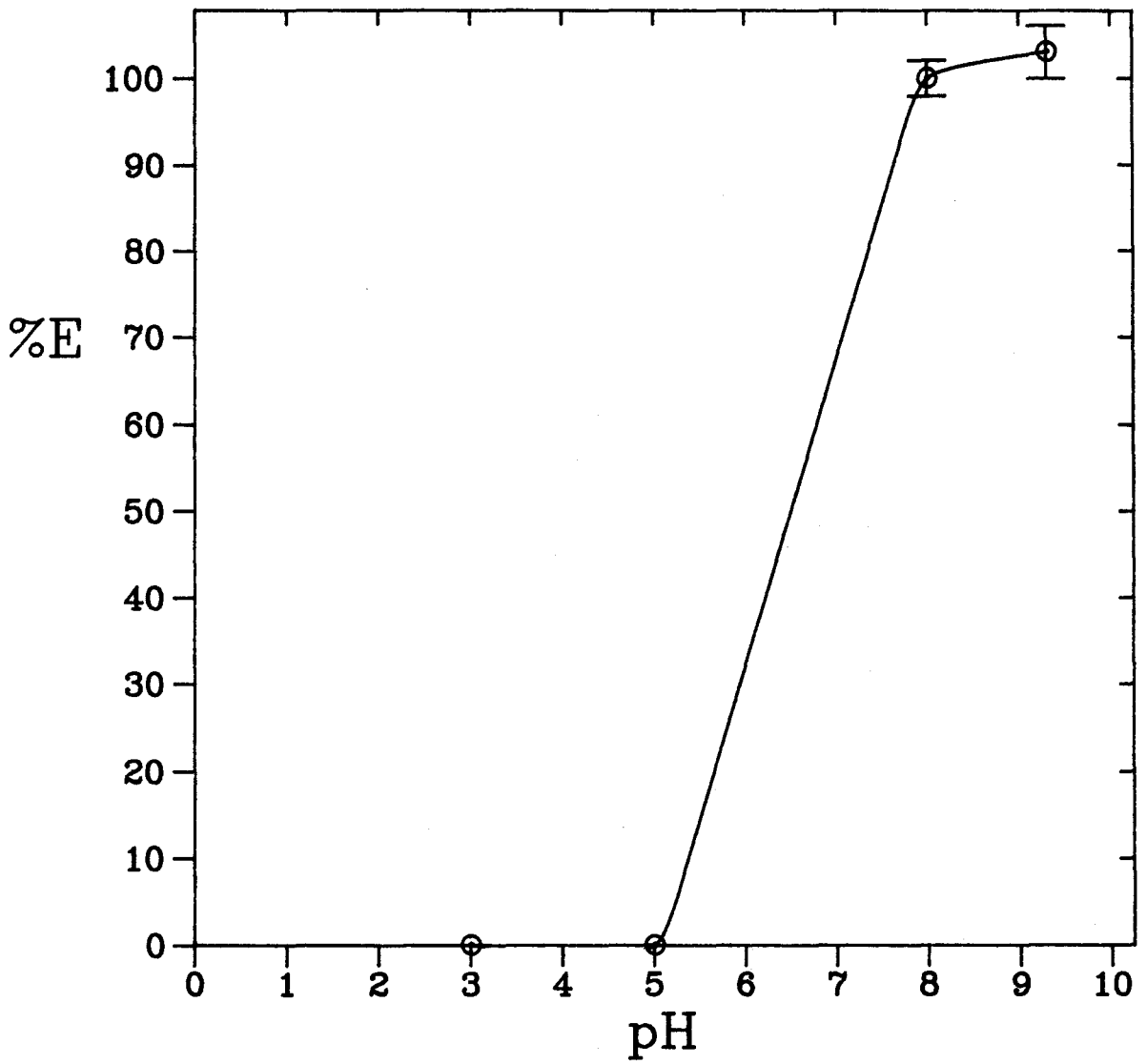


Figure 19. Extraction efficiency of Pb(II) with 0.25*M* HL in toluene as a function of pH.

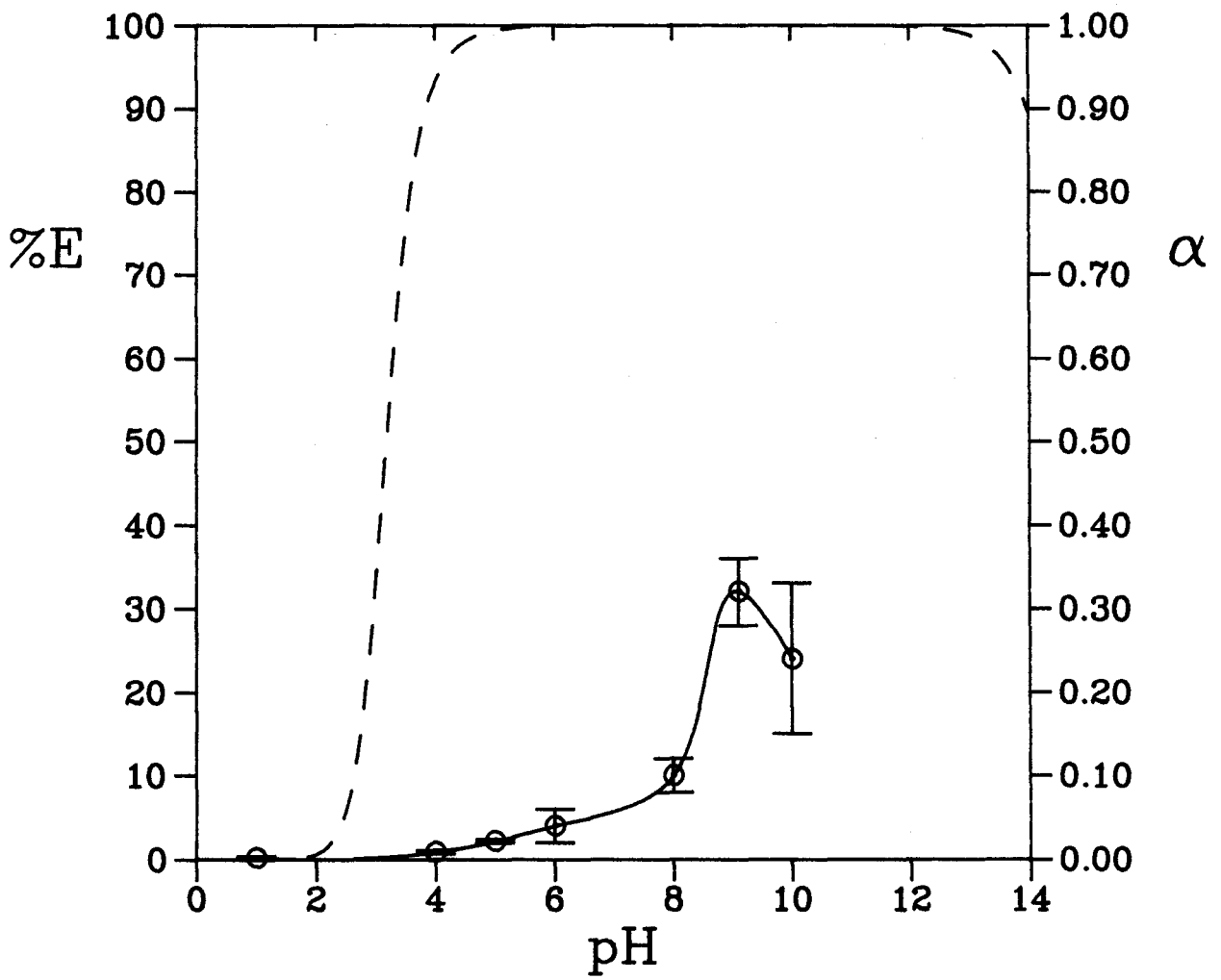


Figure 20. Extraction efficiency of $^{203}Hg(II)$ with 0.25*M* HL in toluene and calculated fraction (α) of $Hg(OH)_2$ (---) as a function of pH [128].

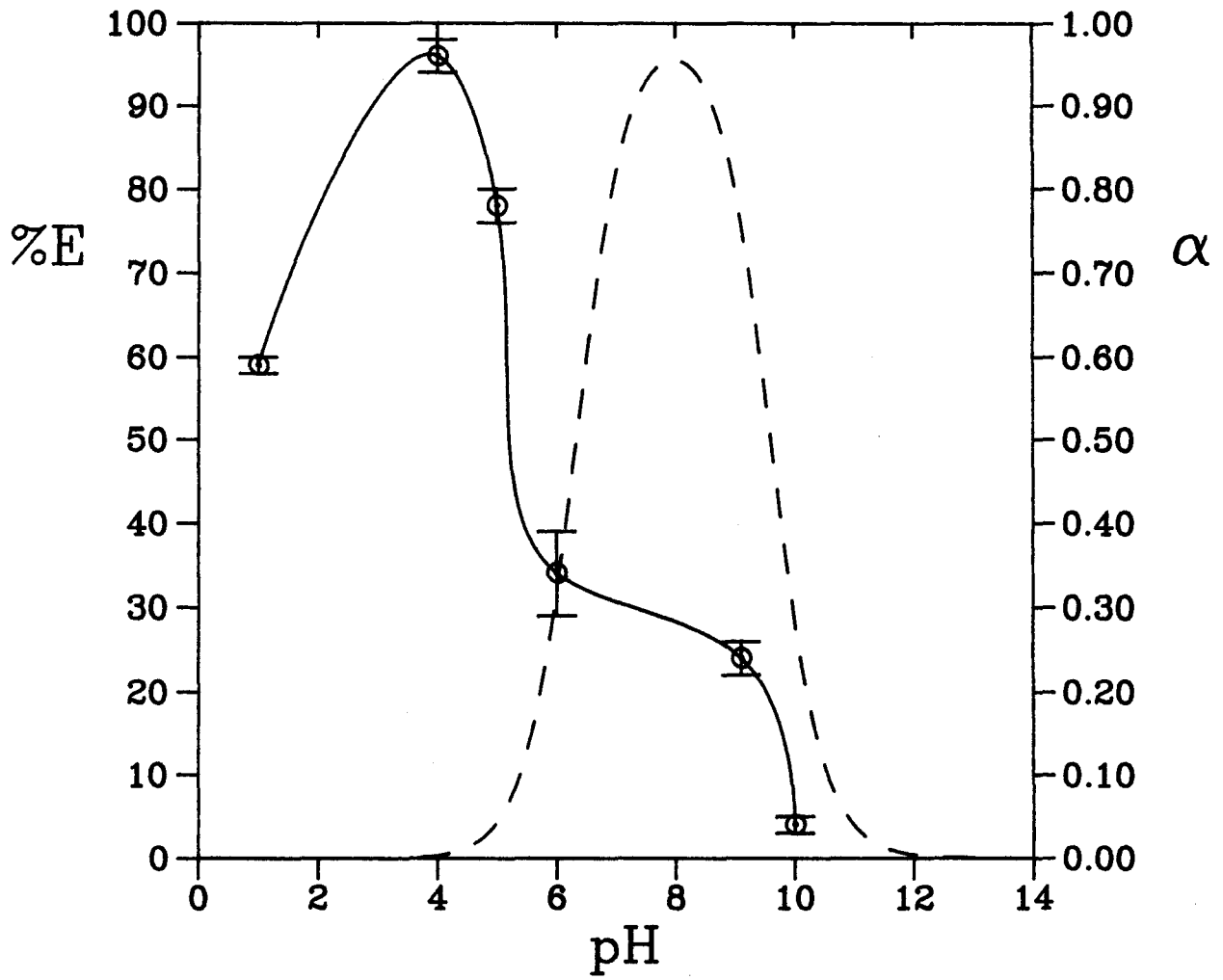


Figure 21. Extraction efficiency of $^{59}Fe(III)$ with 0.25*M* HL in toluene and calculated fraction (α) of $Fe(OH)_3$ (---) as a function of pH [128].

distribution of the simple complexed species $M(H_2O)_x^{+n}$, $M(OH)_p^{+n-p}$, $M(Cl)_q^{+n-q}$, $M(OAc)_r^{+n-r}$, and $M(NH_3)_x^{+n}$ would be affected. The stability constants of the metal ions in this study with ammonia and acetate are sufficiently low in comparison to those of the corresponding metal oxinates [101, 117-119] that they should not interfere in the extraction and can be ignored (although acetate has been found to form a mixed-ligand complex with the ethenyl derivative in the extraction of uranyl ion into chloroform [82]).

The lack of extraction of $^{110m}Ag(I)$ by HL can be ascribed primarily to the formation of anionic and neutral chloride complexes in the aqueous phase and the relatively low stability constant of Ag(I) with oxine [108]. In the aqueous phase, silver ion could be present as AgCl, $AgCl_2^-$, $AgCl_3^{2-}$ and $AgCl_4^{3-}$, the stability constants for which are provided in Table 9, together with the stability constant for silver oxinate. Considering the solubility product alone, and using the silver ion concentration of this work (5 ng/mL or $5 \times 10^{-8} M$), a chloride ion concentration of $>4 \times 10^{-3} M$ would be sufficient for formation of an (unextractable) AgCl precipitate. This concentration is well below that of the artificial seawater ($\sim 0.9 M$) and is comparable to that found in freshwater ($\sim 2 \times 10^{-4} M$). Based on the formation of this precipitate alone, the solvent extraction preconcentration of Ag(I) with HL from seawater (and possibly from freshwater) does not appear feasible. Furthermore, the anionic silver

Table 9. Stability constants for silver with oxine and chloride as ligands

Complex	log β_2^*	log $\beta_n^\dagger$	$K_{sp}^\ddagger$
Ag oxinate	9.56		
AgCl		3.36	1.82×10^{-10}
$AgCl_2^-$		5.20	
$AgCl_3^{2-}$		6.0	
$AgCl_4^{3-}$		6.0	

* Determined at 0.1*M* $(Na^+,H^+)ClO_4^-$; T=18-20°C; reference [108].

† Obtained at 25°C, I=1.0*M* ; reference [118].

‡ Obtained from reference [129].

chloride complexes have stability constants comparable to silver oxinate, and their formation would also inhibit the extraction of $^{110m}Ag(I)$ by HL. By contrast, the extraction of Ag(I) from 0.1*M* $NaClO_4$ into a 0.04*M* toluene solution of the ethenyl derivative of HL was found to be quantitative at pH 9.0 [36].

Unlike Ag(I), the aqueous chemistry of Hg(II) is complicated by strong complex formation with hydroxide as well as chloride and by the formation of the mixed complex, HgOHCl. Considering only these inorganic ligands, the actual species of mercury formed in aqueous solution is governed by the chloride ion concentration and the pH, as illustrated in the predominance diagram in Figure 22 [128]. Of the possible species existing in the artificial seawater phase at pH 9.0-9.5, at which the maximum extraction of $^{203}Hg(II)$ was observed, $HgCl_4^{2-}$ and $Hg(OH)_2$ would predominate at the chloride ion concentration used (~0.9*M*; log $[Cl^-] \approx -0.05$). $HgCl_4^{2-}$ is quite stable (log β_4=15.42 [128]) and would undoubtedly inhibit the extraction of mercury, as would the presence of the neutral insoluble hydroxide, $Hg(OH)_2$ ($K_{sp} \sim 4 \times 10^{-26}$ [118,119]). Even in the absence of chloride, the hydrolysis of Hg(II) alone, which begins at ~pH 3, would likely be sufficient to impede the extraction. The distribution of $Hg(OH)_2$ is plotted in Figure 20 as a function of pH [128]. The findings in this thesis with regard to the poor extraction of mercury by HL are consistent with those of

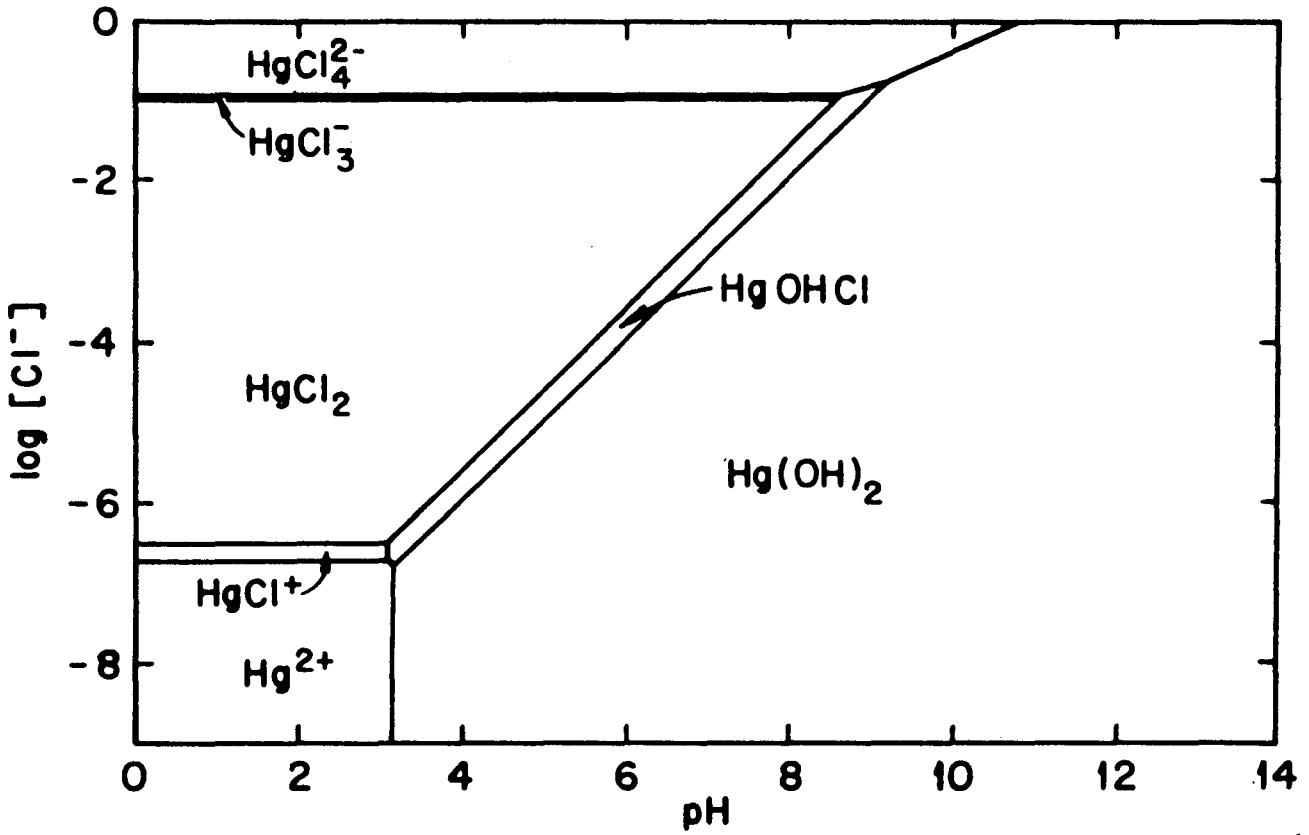


Figure 22. Predominance diagram for the Hg^{2+}-OH^--Cl^- species at 25°C and I=1*M*; adapted from reference [128].

Starý [95] and others [101] who ascribed the incomplete extraction of Hg(II) at pH>3 by oxine to hydrolysis.

The extraction of $^{59}Fe(III)$ with HL from artificial seawater (Figure 21) differs from both $^{110m}Ag(I)$ and $^{203}Hg(II)$ in that near-quantitative extraction was achieved at pH 4.0, above which the extraction efficiency steadily decreased, becoming unacceptably low (24±2%) at pH 9.3. The stability constants of iron chloride complexes are sufficiently low in comparison to that of Fe(III) oxinate [101, 118-120] that their effect on the extraction can be ignored even at the high chloride concentrations used; indeed, the extraction of $^{59}Fe(III)$ was quantitative at pH 4.0. Hydrolysis of Fe(III), however, is well-known and begins at about pH 1, with insoluble $Fe(OH)_3$ ($K_{sp}=4 \times 10^{-38}$ [129]) forming at about pH 5 [128]. The distribution of this species as a function of pH is plotted in Figure 21 [128]. The calculated increase of $Fe(OH)_3$ in solution corresponds well with the decrease in extraction of $^{59}Fe(III)$ with increasing pH. A similar decrease in the distribution ratio of Fe(III) adsorbed on XAD-7 was reported by Chiang [9] at pH>5. In contrast, a study of the extraction of Fe(III) from 0.1*M* $NaClO_4$ solution into a 0.04*M* toluene solution of the ethenyl derivative of HL found that extraction was quantitative even at pH 8 [36]. This result, at first, seems incongruous in light of the low extraction of $^{59}Fe(III)$ observed at alkaline pH in the present work, but even at

pH 8, D_M for $^{59}Fe(III)$ was found to be ≈8. Although this value of D_M yields an extraction efficiency of about 30% at $V/\bar{V}$=19, (see Figure 21), it is still large enough to provide an extraction efficiency of 80% at the phase volume ratio employed by Isshiki *et al.* ($V/\bar{V}$=2). This is in reasonable agreement with the near-quantitative extraction reported by these researchers at pH 8, within the limits of experimental error.

III.3 Distribution ratios and preconcentration factors

Solvent extraction preconcentration techniques generally exhibit lower preconcentration (enrichment) factors than ion-exchange chromatography because of lower metal chelate distribution ratios. Distribution ratios for the commonly-used APDC/MIBK extraction are of the order of 100-600 at $V/\bar{V}$=37.5 [53], whereas that obtained for the sorption of Au(III) from dilute HCl solutions by XAD-7 resin is at least ten times higher [130]. In solvent extraction, the preconcentration factor, F, is related directly to the phase volume ratio and the extraction efficiency, as shown by Equation (I.6). If the extraction is essentially quantitative for the ratio used, then $F \approx V/\bar{V}$. For an APDC/MIBK extraction, at $D_M \approx 600$, the usable phase volume ratios would be limited to ≤50 for the extraction to remain essentially quantitative [53]. Furthermore, if extraction is incomplete, calibration

by the method of standard additions would be required, rather than external calibration, which is preferred.

Because six radiotracers were quantitatively extracted from artificial seawater at pH 9.3 into 0.25*M* HL in toluene at $V/\overline{V}$=19 (Section II.2.3), the extractions were repeated from the same aqueous matrix under the same experimental conditions, but at the increased phase volume ratios of 100, 250, and 500 to determine the practical preconcentration factors attainable. High extraction at these phase volume ratios was also suggested by the lipophilicity of the extractant as exemplified by the high reagent and metal chelate distribution constants ($10^{5.52}$ and $10^{9.5}$) obtained by Bag and Freiser [81] for the extraction of Cu(II) by the ethenyl derivative. The extraction efficiencies and distribution ratios obtained are provided in Table 10.

As is readily seen, all the extraction efficiencies are greater than 90% at all phase volume ratios and, in fact, are essentially quantitative for the phase volume ratios 100 and 250. The metal chelate distribution ratios range from 1.62×10^4 for the extraction of Cd(II) to 5.0×10^3 for Co(II) at $V/\overline{V}$=500, and are at least ten times higher than those observed by Brooks *et al.* for extractions of metal ions with APDC [53]. At $V/\overline{V}$=500, the lowest extraction efficiency (91% for Co(II)) still represents a 455-fold enrichment for a single batch-extraction, while preconcentration factors of almost 500 would be obtained for the remaining metal ions,

Table 10. Effect of varying aqueous to organic phase ratio at pH 9.3 on extraction efficiency with 0.25*M* HL in toluene

	% Extraction*				
Radiotracer	$V/\bar{V}$=19	$V/\bar{V}$=100	$V/\bar{V}$=250	$V/\bar{V}$=500	D_M†
^{115}Cd	99±6	99±4	99±3	97±2	(1.62±0.05) x 10^4
^{64}Cu	100±1	98±3	98±2	96±2	(1.20±0.04) x 10^4
^{56}Mn	100±4	100±3	96±3	95±5	(9.5±0.7) x 10^3
^{65}Ni	103±2	98±2	99±2	93±4	(6.6±0.4) x 10^3
^{65}Zn	97±3	96±4	97±3	92±3	(5.8±0.3) x 10^3
^{60}Co	98±3	97±3	96±5	91±4	(5.0±0.3) x 10^3

* Results represent the mean ± the standard deviation of 3-5 determinations; ionic strength of artificial seawater=0.96*M*.

† Calculated for $V/\bar{V}$=500.

whose extraction efficiencies are nearly quantitative. This is particularly significant; because of the extremely high D_M values, a solvent extraction preconcentration procedure is now possible which is essentially limited only by the volume of water sample available. High preconcentration factors and near-quantitative extraction of the metal ions in question not only widen the instrumental applicability of the technique but also provide the potential for determining total (soluble) metal in natural waters at levels which are presently considered to be sub-toxic, a feature of environmental analysis which has gained importance in pollution control studies. Practical considerations, however, such as the consumption of large volumes of water samples and the physical difficulty in the agitation and separation of large volume of aqueous phase in the presence of a smaller organic phase may limit the use of the higher range of preconcentration factors reported in this work.

III.4 Back-extraction

Direct analysis of the organic phase from a solvent extraction preconcentration procedure by spectroscopic techniques can be complicated by several factors. First, the applicability of the procedure is limited to instrumental methods which are capable of dealing with complex organic matrices, such as GFAAS. Even if such an instrumental method

is employed, quantitation could not be achieved simply by external calibration with matrix-matched aqueous standard solutions since the analytical response from organometallic compounds is often different from that of inorganic salts [131]. To compensate for the complicated organic matrix, either organometallic standards would have to be prepared in the same solvent used for the extraction, or an alternative method of quantitation would have to be used. In GFAAS, the method of standard additions is frequently employed when the organic phase is to be analyzed [16,61]. This method of quantitation compensates both for incomplete extraction and aqueous and organic matrix effects, provided that sufficient time is allowed for spike and analyte equilibration [132]; however, it consumes more sample and increases overall analysis time compared to external calibration. Analysis of the organic phase would be further complicated by the necessity of altering standard instrumental parameters such as the furnace programme to compensate for the effects of the organic phase, possible pre-atomization losses of particularly volatile metal chelates or their decomposition products [133,134], and significant background absorption from "smoke" particles produced in the atomization step, particularly if the extractant is present in large excess, as is often required.

A quantitative back-extraction into a suitable aqueous acid can overcome many of these problems and provide

a simple matrix which can be readily matched against aqueous calibration standards. Furthermore, back-extraction can yield additional analyte preconcentration if the volume of acid used is less than that of the organic phase. These benefits far outweigh the inconvenience of additional sample manipulation and small attendant risk of contamination [16].

For these reasons, a back-extraction was incorporated into the overall preconcentration procedure. A factor that influences the type of acid selected for a back-extraction is the mode of analysis to be employed. In GFAAS, HCl is usually avoided because of the potential formation of volatile metal chloride salts which can lead to pre-atomization losses of the analyte [33,135], or to suppressed analyte absorption due to the formation of thermally stable monochlorides in the gas phase [22]. Furthermore, it is desirable to use the lowest practicable acid concentration as high concentrations of acid decrease graphite tube life and can increase the analytical blank. The acids tested in this study were HNO_3, H_2SO_4 and HCl at concentrations ranging from about 1 to 40%. A summary of the data is provided in Table 11. With the exception of ^{60}Co, which was not stripped to a significant extent by any of the acids investigated, quantitative recovery of the radiotracers was accomplished with 16% (v/v) nitric acid. Pb(II), determined by AAS, was also quantitatively stripped with this acid.

Table 11. Back-extraction of radiotracers into various aqueous acids*

Radiotracer	% Stripped		
	6% HCl†	10% HNO_3†	16% HNO_3†
^{115}Cd	86±3	93±2	96±3
^{64}Cu	23±2	37±4	99±4
^{56}Mn	79±3	99±3	99±2
^{65}Ni	88±2	98±2	97±3
^{65}Zn	84±2	93±3	100±2
^{60}Co	2.1±0.5	2.3±0.4	4.8±0.6

* Results represent the mean ± the standard deviation of 3-5 determinations; $\overline{V}/V=2$.

† Percentages on a (v/v) basis.

The resistance to stripping of cobalt by aqueous acids has also been observed in the extraction of Co(II) by oxine [16,136,137] and 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol [77,84,137], and has been ascribed to air oxidation of the extracted Co(II) complex to the stable and non-labile Co(III) chelate at the phase interface [84]. Data [137] suggest that oxidation of the extracted Co(II) oxinate is largely complete after two hours, while the oxidation of the Co(II)-ethenyl complex is about as fast as the extraction (~20 minutes). Although there is some discord in the literature, there are indications [77,84] that the formation of a coordination-unsaturated Co(II)-ethenyl chelate occurs which is rapidly oxidized at the phase interface as follows:

$$Co^{2+} + 4\,\overline{HL} \rightleftharpoons \overline{CoL_2 \cdot 2HL} + 2\,H^+ \qquad \text{(III.1)}$$

$$\overline{CoL_2 \cdot 2HL} + \tfrac{1}{4}\,O_2 \rightleftharpoons \overline{CoL_3} + \overline{HL} + \tfrac{1}{2}\,H_2O \qquad \text{(III.2)}$$

Some evidence suggests that cobalt oxidation can be depressed if the extraction with the ethenyl derivative is performed in the presence of a large excess of a hydrophobic aliphatic carboxylic acid (*i.e.*, Versatic 911, HR, an alkylated monocarboxylic acid). Apparently, a mixed Co(II) complex, $CoL_2(H_2R_2)$, which can be stripped by aqueous acid, forms at the interface [77,84]. The precise role of HR in reducing the rate of oxidation of the Co(II)-ethenyl chelate

is unclear [84,137]. Since a mixed extraction system could affect the simultaneous extraction of metal ions by HL in an unknown and possibly adverse manner, it was not undertaken in this work. The determination of cobalt by GFAAS in aqueous samples is still feasible using only the forward-extraction and, in view of the high preconcentration factors attainable in a single batch-extraction (Section III.3), low aqueous Co(II) levels could still be measured. Because of the complicated matrix, however, calibration by the method of standard additions would be necessary.

As evidenced by the nearly quantitative forward-extraction of $^{64}Cu(II)$ even at ~pH 1 (Figure 15), the Cu(II)-HL chelate is highly stable; thus, it was not dissociated by the more dilute acids listed in Table 11. An estimate of the stability constant of the Cu(II)-HL complex can be made from the data of Bag and Freiser [81] for the extraction of Cu(II) with the ethenyl derivative of HL. They concluded that Cu(II) is extracted into chloroform as the coordination-saturated chelate, in agreement with the stoichiometry of Cu(II)-ethenyl chelate as determined by others [83,96,138] and with that of Cu(II) oxinate [95,101]. Bag and Freiser [81] experimentally determined the extractant (reagent) distribution constant (K_{DR}) to be $10^{5.52}$; the metal chelate distribution constant (K_{DC}) $10^{9.5}$; the acid dissociation constant (K_a) $10^{-10.40}$; and, the extraction constant (K_{ex}) $10^{1.09}$. If these values are substituted into Equation (I.18),

where n=2, the stability constant for the Cu(II)-ethenyl chelate can be calculated to be $10^{23.4}$, which is in reasonable agreement with that of Cu(II) oxinate, $10^{23.0}$ [101].

III.5 Recovery of radiotracer spikes from natural waters

Natural waters contain numerous natural complexing agents including halides, carbonates and humic substances. These ligands can pose serious problems to total (soluble) metal determinations since the amount of bound metal ion displaced from these ligands is dependent not only on the preconcentration procedure employed but also upon the relative stabilities and labilities of all the complexes involved [34]. Quantitative recovery of the analyte is one of the requisite conditions for the application of external calibration as a method of quantitation [34] and constituted an important goal in the development of the preconcentration procedure of this work. The efficacy of the extractant to strip metal ions from variously-bound forms from both fresh-water and seawater matrices was determined by spiking a Lake Ontario water sample (Station 302, Western Basin) and a coastal seawater sample (Sandy Cove, Nova Scotia) with radio-tracers and determining the extraction efficiencies after the samples had been allowed to equilibrate (Section II.3.5). These water samples were selected for investigation because

an earlier speciation study [139] on similar samples (Sandy Cove coastal seawater and nearshore Lake Ontario water, Station 14, Western Basin) indicated the presence of natural organic complexing agents in addition to the inorganic ligands typically found in such systems. It was found that 74% of the copper, 45% of the manganese and 60% of the lead were organically-bound in the seawater sample and that 46% of the copper and 42% of the lead were organically-bound in the lakewater sample, while cadmium and nickel were largely present as uncomplexed species in both water samples.

Data from the radiotracer experiments are provided in Table 12. With the exception of ^{110m}Ag(I), ^{59}Fe(III) and ^{203}Hg(II), the radiotracer spikes were quantitatively recovered from both aqueous matrices (~90% of the ^{60}Co(II) spike was recovered from lakewater). The low extraction of ^{110m}Ag(I), ^{59}Fe(III) and ^{203}Hg(II) from both natural water samples is consistent with the observation made for artificial seawater and can be explained by the formation of chloride and hydroxide species (see Section III.2.3), with the $Hg(OH)_2$ species predominating over chloride species in lakewater.

The concentration of total dissolved organic matter in natural waters ranges from 0.1 μg/mL in seawater and unproductive freshwater to 10 μg/mL in lakes, streams and estuaries [7]. Between 6 and 30% of the total organic matter in seawater is believed to be present as humic substances

Table 12. Extraction of radiotracer spikes from natural waters at pH 9.3 with 0.25*M* HL in toluene*

Radiotracer	% Extraction	
	Sandy Cove Coastal Seawater	Lake Ontario Freshwater
^{115}Cd	98±1	96±1
^{64}Cu	99±3	98±2
^{56}Mn	100±2	98±3
^{65}Ni	98±4	96±3
^{65}Zn	100±1	98±6
^{60}Co	94±5	88±2

* Results represent the mean ± the standard deviation of 3-5 determinations; $V/\overline{V}=19$.

[140], which are polymers of molecular weight 300-30,000 containing phenolic and aliphatic hydroxyl groups and carboxylic acid moieties [7]. Humic substances are classified into three operationally-defined fractions whose structures are similar but which differ in both molecular weight and functional group content [141]: humic acid, which is soluble in alkaline solution but precipitates in acidic media; fulvic acid, which is the humic fraction that remains soluble in both acidic and basic solution; and, humin, which is that fraction that cannot be extracted by acid or base. The stabilities of metal complexes with fulvic acid are expected to be of the same magnitude as those of its closest monomeric analogues, carboxylic acids, salicylic acid, phthalic acid and dihydroxybenzoic acid [142-146]. Despite their relatively low concentrations in natural waters, organic complexing agents still have the potential of altering the speciation of trace metals, which are present at even lower concentrations. Principally due to these low metal ion and ligand concentrations, little direct evidence exists for the existence of soluble metal chelate complexes in natural waters [7]. In a speciation study of seawater, Florence and Batley [12] assumed that the fraction of metal not directly retained on a Chelex 100 column or not extracted into an MIBK solution of APDC was present as soluble chelates or adsorbed on organic or inorganic colloids, while other workers [147] have concluded that, with the exception of Cu(II), trace metals in

seawater are present exclusively as inorganic species. In freshwater, the effect of natural organic ligands may be more pronounced due to the higher concentration of dissolved organic matter and the lower concentration of Group I and II chloride salts.

In this work, the effect of natural aquatic ligands was determined indirectly by measuring the recovery of radiotracer spikes from lakewater and seawater. In general, when dealing with spiked natural water samples, it is difficult to state with certainty that the spikes have equilibrated with the matrix components of the sample; if this is not the case, the recovery of an ionic spike would bear no relation to the recovery of the metal naturally present in the sample [12,16]. In the present work, the water samples had been passed through 0.45-μm or white sand filters to remove particulate matter and adjusted to pH 1.7 for storage, but colloidal species could still be present with which the radiotracer spikes would have to equilibrate. Previous work [34] has demonstrated that organic complexes such as humates are dissociated at pH 1-2. The radiotracer spikes were added to the sample at pH 1.7, at which the analyte metal ions would be present in organically-free form. Thus, both the analyte and radiotracer ions would be present in non-organic form at this point. Prior to extraction, the pH was raised to 9.3 and the solution was allowed to stand for at least two hours (Section II.3.4).

If it is assumed that the radiotracer spikes reached equilibrium with inorganic and organic ligands in both natural water samples on pH adjustment and standing, then the quantitative recovery of the spikes (Table 12) suggests that HL can displace natural aquatic ligands from metal ions in both seawater and freshwater. In this case, the radiotracer spikes then behave in exactly the same way as the analyte metal ions towards the components of the natural water matrix. Of course, it has not been proven conclusively that the spikes reached equilibrium with the natural ligands prior to extraction, but it is reasonable to suppose that equilibrium with at least inorganic ligands (*i.e.*, chloride) was attained. Evidence for this equilibration is provided in Section III.7.2 below in which the quantitative extraction of naturally-occurring trace metals in a reference seawater sample (CASS-1) is reported.

III.6 Extraction of alkaline earth ions Mg(II) and Ca(II) from artificial seawater

Significant extraction of the substantial amounts of alkali and alkaline earth ions present in natural waters would obviously be deleterious to any solvent extraction procedure for the preconcentration of trace metal ions, since not only would a large portion of the extracting reagent be consumed but also interference with the eventual determination of the analyte could occur. As mentioned earlier, in

GFAAS, halogen-containing species such as NaCl, $MgCl_2$ and $CaCl_2$ are severe sources of interference. Furthermore, the resulting complex matrix would not be easily matched, which is one of the requisite conditions for calibration by external standards. Since the development of a solvent extraction preconcentration procedure which yields a simple matrix was a major emphasis of this work, the potential interference from alkaline earth salts in the final matrix was investigated.

Because Mg(II) and Ca(II) are extracted from aqueous solution at pH ~9-11 with oxine (~0.1-0.5*M*) [95,110,111], the extraction of these ions from artificial seawater by HL was investigated over a rather broad pH range of 5-9.3 (Section II.3.6). It was found that Ca(II) did not extract over this pH range but Mg(II) extracted to the extent of 3% at pH 9.3. Although this extraction efficiency is very small, it is, nonetheless, significant considering that typical concentrations of Mg(II) in natural waters (~1,300 μg/mL in seawater and ~6 μg/mL in freshwater) are much higher than those of trace metals. On the basis of the forward- and back-extraction technique of Section II.3.7, an overall preconcentration factor for Mg(II) of 1.14 (0.03 x 38) is obtained. If the aqueous phase originally contained about 1,300 μg/mL of Mg(II), the final matrix would contain approximately 1,500 μg/mL of Mg(II). The injection of a 20-μL aliquot of this solution into the furnace would provide 30 μg of Mg(II) in

the graphite tube. Since 16% (v/v) nitric acid is used as the back-extracting medium, any Mg(II) extracted by HL would be present as $Mg(NO_3)_2$ in the final matrix. Unlike $MgCl_2$, $Mg(NO_3)_2$ is not a significant cause of interference in GFAAS analysis [135] and, indeed, has been used in larger amounts as a matrix modifier in the determination of manganese [24,25]. The thermal stabilization of manganese in the furnace is thought to be the result of the formation of MgO on which Mn becomes imbedded, permitting the use of higher charring temperatures to remove interfering matrix components without loss of manganese. In the present work, however, the use of elevated charring temperatures was not required because of the simple matrix and the fact that all the analytes in the final matrix were present as nitrate salts which are readily decomposed under the conditions specified in Table 5 (page 46). Thus, the presence of small amounts of Mg(II) in the final matrix would be unlikely to significantly alter the atomization behaviour of the analyte metals or interfere with quantitation and, as such, would not require compensation in the external calibration standards.

The ion pair extraction of Na^+ by the ligand anion of the ethenyl derivative of HL has only been found to occur from $\geq 1M$ NaOH solutions (pH$\geq$14) at high extractant concentration ($0.32M$) [93]. In the present study, the extraction was carried out at a pH of 9.3 and it is highly improbable that Na^+ or other alkali metal ions would be significantly

extracted. If significant extraction occurred, much of the extractant would be consumed and precipitation of the sodium salt in the organic phase would likely occur, but this was not observed. Even slight extraction of the Na^+ present (0.77*M*) in the artificial seawater would be sufficient to impart a yellow colour to the flame used in AAS measurement of Ca(II), Mg(II) and Pb(II). Since no such colour was detected, it is safe to conclude that ion pair extraction of Na^+ by L^- is negligible.

III.7 Application of the preconcentration procedure to the analysis of a natural water sample by GFAAS

III.7.1 Removal of trace metal impurities from purified Kelex 100

Although Kelex 100 was purified from much of the organic impurities and by-products as described previously (Sections III.1 and II.3.1), the extractant still required significant purification from existing trace metal impurities prior to its application to the analysis of natural water samples. In a study of the ethenyl derivative [125], the presence of iron, nickel, copper, manganese and molybdenum was detected, suggesting contamination from the use of stainless-steel reaction vessels in the manufacturing process. Since metallic impurities in HL would presumably exist as chelates, a means of dissociation of these species

was sought by back-extraction of an organic solution of HL with aqueous acid. The protonated extractant, H_2L^+, would then be free from trace metal species and could be neutralized by successive washings with DDW at pH 7.

On the basis of the data in Table 11 (page 100), 16% (v/v) nitric acid was initially employed in an attempt to remove trace metal impurities from HL. When, however, a 0.25*M* toluene solution of HL was stripped with an equal volume of 16% (2.5*M*) HNO_3, the extractant in the organic phase appeared to be degraded. Qualitatively, the organic phase took on a dark yellow colour and did not regain the colourless appearance associated with neutral HL when it was subsequently contacted with equal volumes of DDW. Indeed, the organic phase formed a stable emulsion on contact with DDW and this poor phase-transfer characteristic made it unsuitable for further use. Although the precise effect of the 16% HNO_3 on the observed degradation of HL was not investigated, oxidation or nitration of the 8-quinolinol ring are possibilities. Mild oxidation of 8-quinolinol by nitric acid is known to produce 2,3-pyridinedicarboxylic acid (quinolinic acid) [148]. Phenols are readily nitrated by ~20% HNO_3 at room temperature, producing tarry by-products resulting from ring oxidation [149], and nitration of 8-quinolinol N-oxide occurs at the 5-position on the ring under more vigorous conditions [150].

To avoid the potential problems of an acid-wash procedure, it was decided to attempt the stripping of associated trace metals from HL with a 0.1*M* solution of EDTA (trace metal free) at pH 7 (Section II.3.1). EDTA generally forms more stable complexes with metal ions than does oxine [101,119,151]. Thus, washing a 0.25*M* toluene solution of HL with an equal volume of EDTA resulted in low blank values (≤10% of sample absorbance signal) for all the metal ions except Cu(II) (~50% of sample absorbance signal). This high background signal is due to the high stability of the CuL_2 complex (calculated log $\beta_2 \approx 23.4$) which exceeds that of Cu-EDTA (log K=18.8, [151]). The procedure was then modified to include a one-step acid wash with an equal volume of 10% (1.5*M*) HNO_3, followed by neutralization with DDW at pH 7 and four washings with 0.1*M* EDTA. This clean-up procedure resulted in no significant degradation of the extractant and lowered the blank values for Cu to ~30% of the final signal.

III.7.2 Analysis of the seawater reference material CASS-1

The optimized forward- and back-extraction procedure was applied to the GFAAS determination of total (soluble) Cd(II), Cu(II), Mn(II), Ni(II) and Pb(II) in the coastal seawater reference standard CASS-1. The data are presented in Table 13. Co(II) was not measured because it did not back-extract quantitatively in 16% HNO_3 (Section III.4) although,

Table 13. Determination of total (soluble) metals in CASS-1 by GFAAS using the solvent extraction procedure developed

Element	Concentration (*ng/mL*)		$t^{\ddagger}_{calc.}$
	This Work*	Reference Values†	
Cd	0.024±0.009	0.026±0.005	0.385
Pb	0.31±0.07	0.251±0.027	1.46
Mn	2.7±0.7	2.27±0.17	1.1
Ni	0.35±0.04	0.290±0.031	2.60
Cu	0.36±0.06	0.291±0.027	1.99

* Results represent the mean ± the standard deviation of 3 determinations.

† Data represent the pooled results from several analytical procedures and the 95% confidence level.

‡ Literature t-values for n=3 are as follows: t=9.92 at the 99% confidence level; t=4.30 at the 95% confidence level; and t=2.92 at the 90% confidence level.

if desired, it could be determined in the organic phase by the method of standard additions. Zn(II) was also excluded from the group of metals because its high ambient background levels resulted in high and irreproducible blank values (Section II.3.7). Since the radiotracer study indicated that recovery of the analytes was quantitative within the limits of experimental error and because the final matrix consisted primarily of trace metals in 16% HNO_3, quantitation was carried out using matrix-matched calibration standards.

In general, the agreement between the experimental and reference values is reasonable, particularly in view of the low analyte concentrations involved, the relatively small experimental data set, and the fact that the reference data represent the pooled results of several analytical procedures. For a statistical comparison between the empirical and reference values, Student's t-test [152-155] was applied; *i.e.*,

$$t = \frac{|\bar{x}-\mu| \cdot \sqrt{n}}{s} \qquad \text{(III.3)}$$

where μ = the average value of the infinite series (*i.e.*, the standard reference result);

$\bar{x}$ = the average value of the finite series (*i.e.*, the empirical result);

n = the number of measurements of the finite series;

s = the standard deviation of the finite series.

The calculated and expected t-values for the metal ions of interest at the 99%, 95% and 90% confidence levels appear in Table 13. Since $t_{calc.} < t_{lit.}$ for all metal ions at these confidence levels, the means of the two sets of data cannot be said to be significantly different at these confidence levels even though examination of the data shows that, for most elements, the experimental values are greater than the reference values. This may indicate a small systematic error not indicated by the t-test. A comparison of the precision the of the two data sets was not possible because the NRC reference data represented the pooled results of several different analytical procedures with an unknown number of degrees of freedom.

The general agreement of the two data sets also seems to validate the initial assumption, suggested by the earlier radiotracer studies (Sections III.2.3 and III.5), that analyte recovery is quantitative and substantiates the efficacy of HL for stripping metal ions from inorganic and organic complexing agents present in CASS-1. Indeed, the general validity of the radiotracer model in predicting the actual extraction behaviour of the analyte metal ions from natural waters would seem to be justified. Nevertheless, additional GFAAS application of the procedure to a lakewater standard would be beneficial to further test the validity of the radiotracer work.

III.8 Critical evaluation of the solvent extraction preconcentration procedure developed

Because metal chelate distribution ratios are generally of the order of 10^2, solvent extraction techniques have traditionally been limited to preconcentration factors of about 20-50. On the other hand, ion-exchange chromatography, because of its inherently higher distribution ratios, has been limited only by sample size. In the past decade, there has been a growing interest in the application of "ligand-immobilized" systems which offer the advantages of chelating ion-exchange resins without the necessity of complicated synthesis. For example, in a relatively recent paper [36], the adsorption of the ethenyl derivative of HL onto XAD-4 resin for the recovery of trace metals from seawater was described. In light of this development, it is of interest to compare this technique with the solvent extraction preconcentration procedure developed in this work. In the former study, preconcentration factors of 500 were claimed and minimal bleeding (0.01%) of the adsorbed ligand was reported. The preconcentration procedure involved loading of the impregnated resin with 500 mL of seawater, stripping the metal ions with 8 mL of 2*M* HCl, followed by collection and subsequent evaporation of the effluent. The effluent was then treated with concentrated nitric acid and 30% H_2O_2 to decompose unspecified organic residue before the remaining

material was dissolved in 0.1*M* HNO_3 for eventual GFAAS measurement by external calibration.

This procedure offers no advantage of either simplicity or time over the solvent extraction technique described in this work. In fact, more reagents are used and a greater number of steps are involved, both of which increase the likelihood of contamination. The solvent extraction procedure involves only a forward- and back-extraction. The former concentrates the metal ions in the organic phase with enrichment factors of up to 500 and removes interfering components from the sample matrix; the latter further simplifies the matrix and also increases the overall enrichment factor. Like the ligand-immobilized resin [36], the solvent extraction method is essentially limited only by the sample size.

Discrepancies between the two methods do exist, most notably in the recovery of Ag(I) and Fe(III) from natural and artificial seawater. Isshiki *et al.* [36] reported quantitative retention of Fe(III) and 73% retention of Ag(I) at pH 8 by the ligand-immobilized resin. This contrasts markedly with the low extraction (~24%) obtained for ^{59}Fe(III) and the negligible extraction of ^{110m}Ag(I) observed from artificial seawater over the pH range 8.0-9.5 in this work. These discordant results can be rationalized, however, in view of the small but significant capacity for sorption of metal ions of the XAD-4 resin itself, used as a substrate for the

ethenyl derivative of HL. In an investigation of XAD-4 (and the chemically identical resin, XAD-2), Mackey [42] concluded that the resins contain a number of different impurity sites which cause them to act as low-capacity cation-exchange resins. Additionally, the adsorption of metal ions as simple inorganic complexes on the surface of the resin by van der Waals forces cannot be ruled out; Au(III) is apparently adsorbed from chloride solution as $AuCl_3$ on the methyl-methacrylate polymer, XAD-7, in this manner [130]. Thus, the recovery of Ag(I) from artificial seawater reported by Isshiki *et al.* [36] could involve a number of mechanisms; namely, the sorption of AgCl on the XAD-4 resin, cation-exchange with the resin, and complex formation with the ethenyl derivative of HL. The quantitative recovery of Fe(III) at pH 8 by the impregnated resin would likely involve the same kind of mechanisms.

III.9 Conclusions

A new solvent extraction procedure has been developed for the simultaneous preconcentration of the divalent metal ions Cd, Co, Cu, Mn, Ni, Pb and Zn from natural waters. It involves a forward-extraction into a toluene solution of 7-(4-ethyl-1-methyloctyl)-8-quinolinol, the active component of the proprietary "liquid-cation exchanger" Kelex 100, followed by a back-extraction into a small volume of nitric

acid. The forward-extraction is quantitative for all the metal ions of interest. The back-extraction is quantitative for all the analytes except cobalt, which is thought to be rapidly oxidized by dissolved oxygen in the organic phase to form a stable, non-labile Co(III) chelate. The lipophilicity of the extractant and its metal chelates enables preconcentration factors of up to 500 to be attained in a single batch-extraction, while the back-extraction simplifies the final matrix and provides additional analyte enrichment. The quantitative analyte recovery and the uncomplicated matrix enable the determination of total (soluble) metal from natural waters by GFAAS using easily matrix-matched external calibration standards. This calibration procedure is more advantageous, both in terms of analysis time and sample consumption, than the method of standard additions. Furthermore, the large amounts of alkali and alkaline earth ions present in natural waters are not significantly extracted by HL and, as such, do not consume a large amount of the extractant or interfere with GFAAS analysis of the natural water sample. Additionally, HL appears to be an effective extractant in stripping metal ions from variously-bound forms from both seawater and lakewater. In this study, however, high atmospheric levels of zinc precluded its determination.

Kelex 100, as supplied commercially, requires considerable purification because of the presence of organic and trace metal impurities. The majority of the organic

impurities was removed on a preparative scale by fractional vacuum distillation, while the bulk of the associated trace metals was removed by an acid/DDW/aqueous EDTA stripping procedure. The purified product still retained sufficient sub-trace levels of Cu(II) to cause a high analytical blank for this element.

III.10 Suggestions for future work

1. Restrictions of time precluded more thorough testing of the solvent extraction preconcentration procedure on other reference water samples. The method should be applied at least to a reference lakewater standard.

2. Also because of time considerations, a fundamental investigation into the mechanism of extraction for the analyte metal ions was not undertaken in this work. Such a study would be particularly useful in determining the stoichiometry of the extracted metal chelates as well as the extraction constant for the reaction, K_{ex}. These data, together with the reagent and metal chelate distribution constants (K_{DR} and K_{DC}, respectively) would, in turn, permit the calculation of the stability constants of the metal chelates. The compilation of such fundamental extraction data for HL with the wide variety of metal ions studied in this work has not yet appeared in the literature and, as such,

would serve as a useful comparison to the large amount of analogous data already accumulated for oxine.

3. Flow-injection solvent extraction systems are becoming attractive as preconcentration techniques for routine analysis because of their ease of automation and large sample-handling capabilities. An ideal flow-injection extraction system would be fully automated, employing on-line reagent purification, and would produce a simple matrix which could then be immediately analyzed (*e.g.*, by prompt injection into a graphite furnace by means of an autosampler). Such an arrangement would allow the entire analysis to be performed in a closed system, thus greatly reducing or eliminating atmospheric contamination. Although a method exploiting all the above potential advantages has not yet been developed, a promising step has been made by Bengtsson and Johansson [156] who extracted Cd(II), Co(II), Cu(II), Ni(II) and Pb(II) from aqueous solution as carbamate complexes into trichlorotrifluoroethane, and subsequently back-extracted the analytes into an acidic Hg(II) matrix for eventual measurement by GFAAS. This rather encouraging result suggests that the feasibility of applying the flow-injection technique to the preconcentration procedure developed in this work should be examined.

4. Some of the discouraging results of this work included the lack of extraction of ^{110m}Ag(I), ^{203}Hg(II) and ^{59}Fe(III) at

the alkaline pH required for simultaneous extraction of the remaining metal ions. EDTA forms strong complexes with a large number of metal ions, including Fe(III) and Hg(II), at more acidic pH values than HL and, hence, could in principle avoid some of the problems of metal ion hydrolysis encountered in this study. Since the anionic EDTA chelates so formed are appreciably hydrophilic, they could only be extracted into an organic solvent as the ion associate of a lipophilic counter-cation. Before commencing the Kelex 100 project, preliminary attempts were made (not reported here) to extract metal-EDTA complexes from the aqueous phase into organic solvents using a long-chain quaternary ammonium salt. While extraction from deionized water was possible, extraction from artificial and natural seawater and lakewater did not occur because of strong competition for the counter-cation by inorganic anions in the aqueous matrix, particularly chloride [157]. This problem could be overcome by the synthesis of a long-chain alkylated EDTA derivative which would function as a "liquid cation-exchanger" in much the same way as HL, but at a sufficiently low pH to avoid extensive hydrolysis of the acidic cations Hg(II) and Fe(III).

IV. APPENDICES

IV.1 Independent GC/MS analysis of a similar Kelex 100 sample

The following material represents the results of independent analysis by gas chromatography/mass spectrometry on a sample of Kelex 100 of similar lot number to that used in this study. The annotations, assignments of structure and proposed fragmentation patterns are those of the original workers and were kindly supplied in a private communication [87].

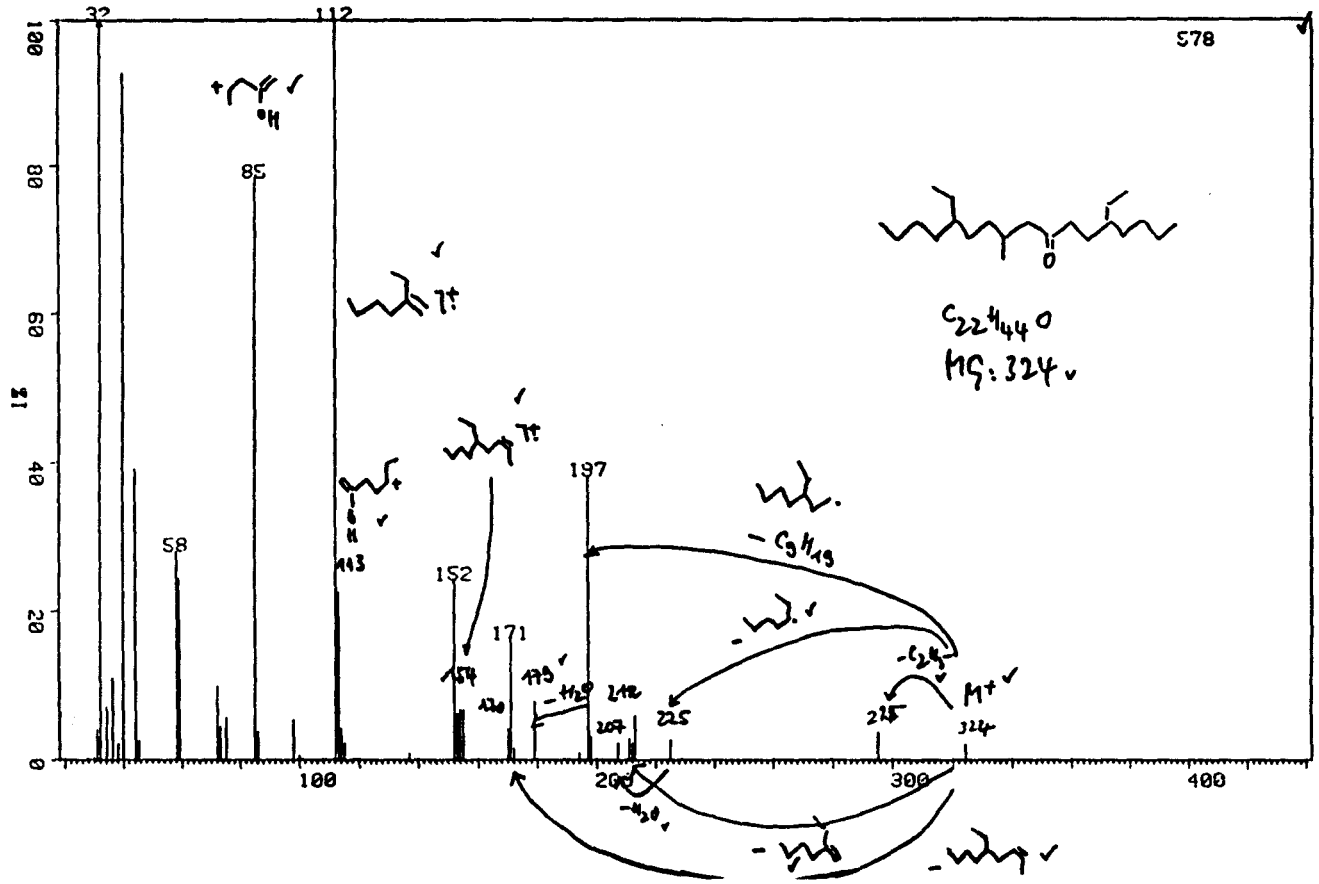


Figure 1. Mass spectrum of 5,13-diethyl-10-methyl-8-heptadecanone [87].

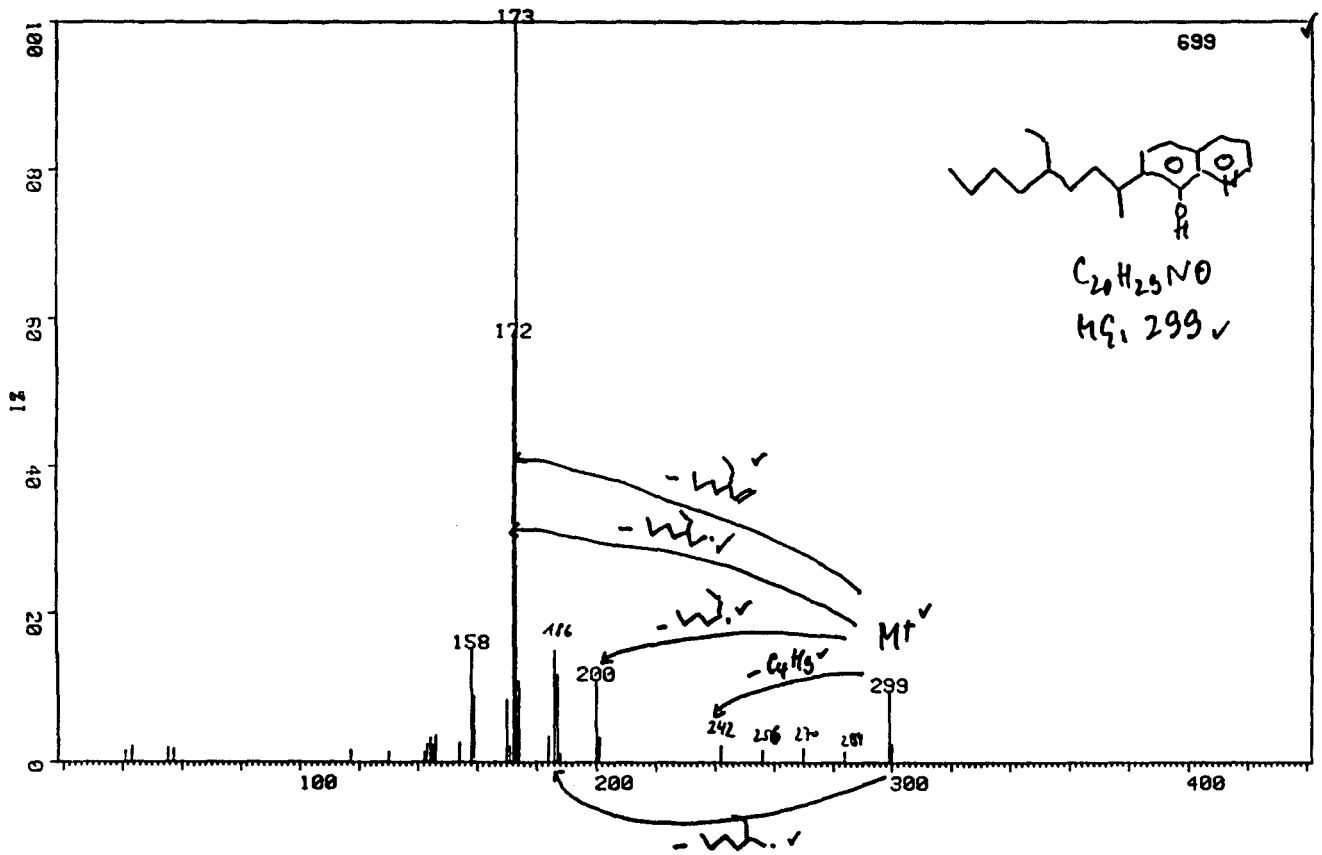


Figure 2. Mass spectrum of 7-(4-ethyl-1-methyloctyl)-8-quinolinol [87].

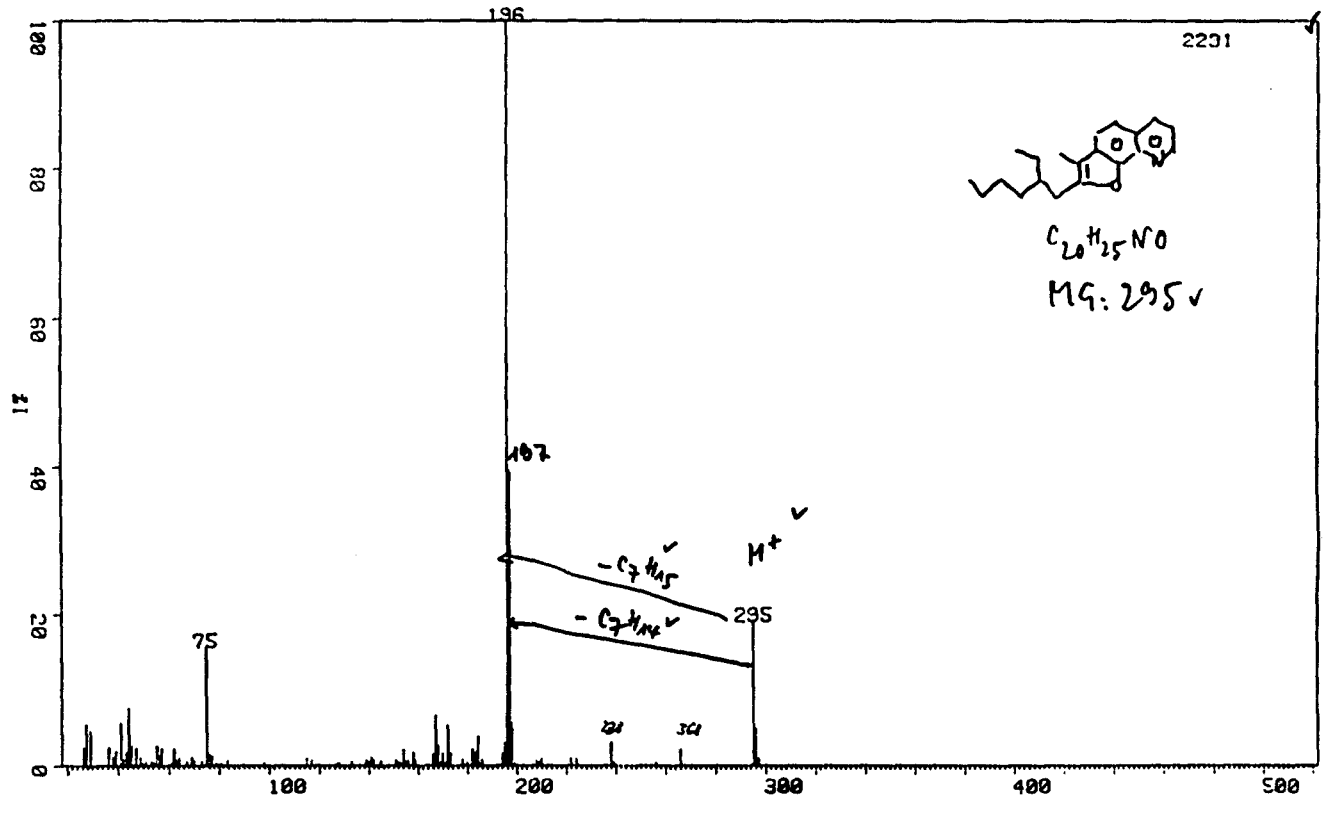


Figure 3. Mass spectrum of C_9-alkylated furoquinoline [87].

IV.2 UV/visible spectrum of oxine in 1*M* HCl

The following spectrum was taken with a Hewlett-Packard Model HP 8451 diode array spectrophotometer for comparison to the acidic fractions obtained in the extraction of Kelex 100 with 1*M* HCl.

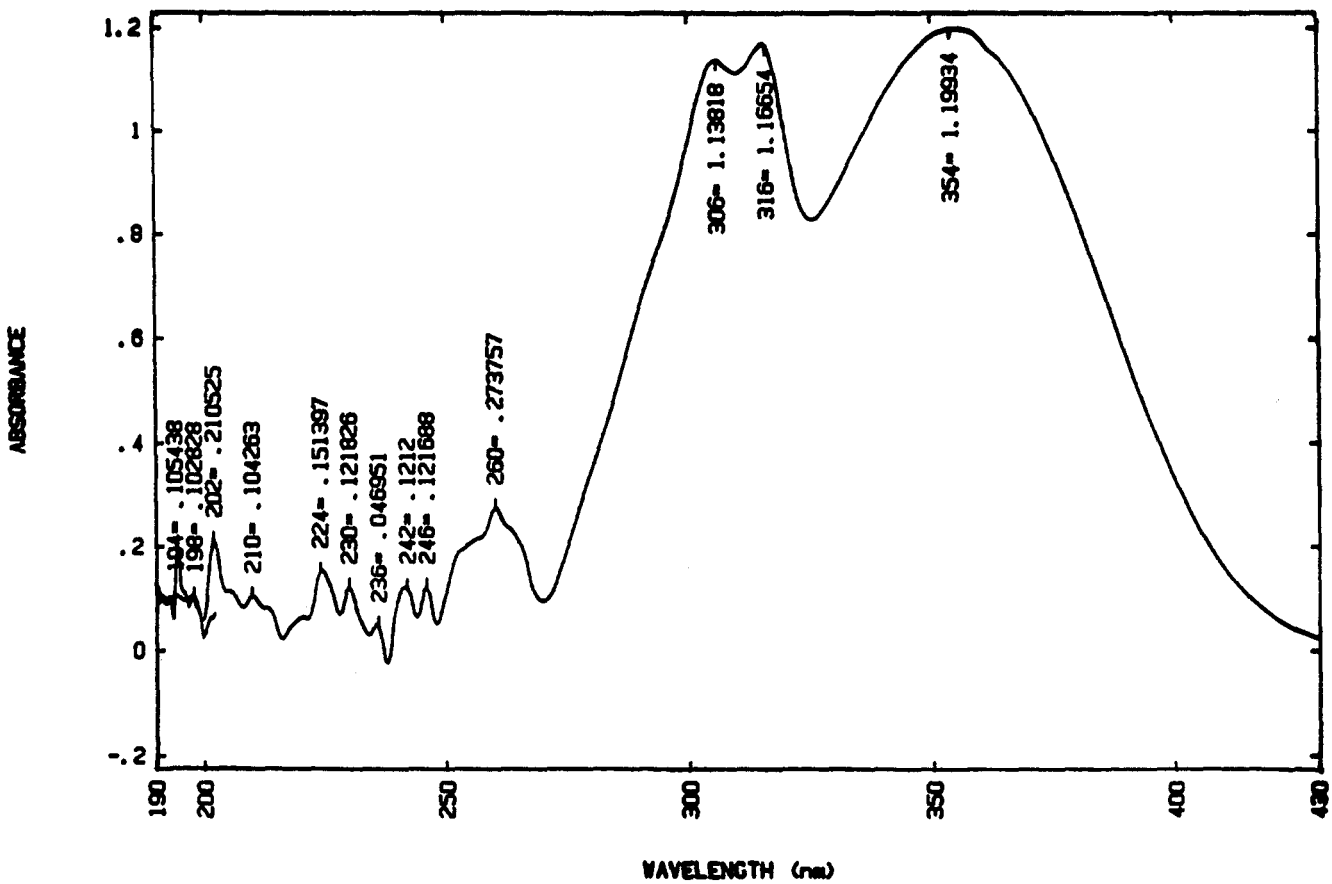


Figure 4. UV/visible spectrum of oxine (~8 x 10^{-4}*M*) in 1*M* HCl.

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