

PRECONCENTRATION OF TRACE METAL IONS FROM NATURAL
WATERS: STUDIES ON THE APPLICATION OF AN
ACRYLIC ESTER MACRORETICULAR RESIN

By

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ABSTRACT

A new preconcentration method has been developed for the determination of trace metals from natural waters. The method is based on the direct uptake of metal ions on a column packed with the macroporous acrylic ester resin, XAD-7, after interfering humic substances are removed on a XAD-7 precolumn. The retained metal ions are subsequently eluted with 1% v/v HNO_3 and the trace metals determined by graphite-furnace atomic absorption spectroscopy. The effects of various parameters such as pH, ionic strength, anions, organic substances, flow rate, column bed-size and resin particle size on the adsorption and elution of metal ions were examined. Based on these investigations, optimal conditions for the group preconcentration of Cr, Fe, Cd, Co, Cu, Mn, Ni and Pb were established.

The method was successfully applied to various natural waters and was found to be simpler and less susceptible to contamination than the Chelex-100 method. In addition, a larger preconcentration factor was obtained. The accuracy and precision of the XAD-7 method were found to be at least competitive with the Chelex-100 method.

The mechanism of adsorption was investigated and adsorption isotherms and distribution ratios of selected metal ions were measured. The adsorption process is complex and likely involves charge-dipole interactions.

A simple model was developed to illustrate the rationale of the method of standard additions in a preconcentration procedure. It was shown that a high degree of spike reaction with the sample matrix

and a reasonable degree of analyte separation are vital for the successful application of standard additions. If the degree of separation is very high, the method of standard additions is not required and only a simple calibration curve is necessary.

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I. INTRODUCTION

I.1 General

Over the years, growth in world population and in industrialization has introduced an increasing number and amount of waste materials into the natural environment. For various reasons, efforts to control the resulting pollution have not kept pace and severe contamination of land, water and air has occurred in various locations on the globe.

This thesis is concerned with the determination of trace heavy metals in natural waters since contamination of rivers, lakes and coastal waters is of particular interest. The detrimental effects of waste materials are significant in inland water systems because of the traditional roles of these systems as sources of water supply for human activities and as receiving bodies for effluents. Many of the pollutants enter the biological food chain and are concentrated in fish and other edible aquatic organisms. Since rivers carry pollutants either in dissolved, colloidal or particulate form to oceans, there is a concern with coastal waters as well, especially at a time when the oceans are becoming important suppliers of protein for the growing world population (1,2).

There are various sources of pollution in the aquatic ecosystem. Pollutants can be introduced directly into the aquatic environment from industrial, domestic and agricultural effluents as well as from waterborne chemical spills. In addition, atmospheric emissions such as acid rain and pest-control sprays are also important sources of aquatic pollutants.

Some pollutants can upset the ecosystem without being directly harmful to human beings. Others, such as polycyclic aromatic hydrocarbons, pesticides, radioactive materials and trace heavy metals can place human life at risk.

Trace heavy metals* are of significance in two respects. First, trace metals, in contrast to many organic pollutants, are not usually eliminated in waters by natural processes such as biodegradation and evaporation. Second, most trace metals can be accumulated in bio-organic substances through chemical and biological processes. These accumulated trace metals enter and often move up the biological food chain and endanger human health. To facilitate the development of preventative and corrective measures for metal pollution in the aquatic environment, it is important to monitor trace metals in the aquatic ecosystem. This importance is reflected by the rapid growth of studies pertaining to their concentrations (horizontal, vertical and seasonal) and speciation in natural waters. The trace metals of primary significance in aquatic studies and to which reference is often made (e.g., 1-5) are cadmium, copper, chromium, iron, lead, manganese, mercury, nickel, tin and zinc.

* Trace metals are conventionally considered to be those which exist at concentrations lower than 1 mg/L (1) in the aquatic environment. The term "heavy metals" is used in the connotation of toxicity. Thus, even the toxic element Be (atomic number = 4) is classified as a heavy metal (3). Since heavy metals exist at trace levels in natural waters, the terms "trace metals" and "heavy metals" are often used synonymously (4). For purposes of this thesis, the term "trace metals" will be used to mean "trace heavy metals".

I.2 Determination of Total (Soluble) Trace Metals in Natural Waters

In natural waters, metal ions are distributed between "soluble" and particulate phases. "Soluble" constituents, as defined by Stumm and Bilinski (6), are those that are not retained on a 0.45 μm membrane filter ($1 \mu\text{m} = 10^{-4} \text{ cm}$). Soluble metal constituents include free aquated metal ions, inorganic metal-ion complexes, oxygenated metal anions, inorganic ion pairs, low and high molecular-weight complexes (e.g., complexes of humic and fulvic acids) and highly-dispersed colloids. The sum of these "soluble" species for copper, for example, is referred to as total (soluble) copper. Many studies on trace metals in aquatic systems are concerned with the total (soluble) metal content regardless of the chemical forms into which the metal ion is speciated. This section is concerned with the quantitative determination of total (soluble) trace metals.

A particular metal-ion species may have more environmental impact than the total (soluble) metal ion concentration (7) and a considerable effort has been made (e.g., 8-11) to estimate the concentrations of "soluble" metal ion present in particular forms. These studies are briefly described in Section I.3.

The concentrations of trace metals in natural waters can vary with surface location, depth and season and are often distorted by localized pollution effects. In general, trace metal abundances are highest and show the largest variation in nearshore mid-latitude fresh water systems where the bulk of human activities is located; concentrations are the lowest and most stable in open ocean deep seawater (1,4).

It is now recognised by investigators that errors associated with analytical methodology have, in the past, resulted in the reporting of "high" values for trace metal ions in natural waters. These high values were mainly the effects of contamination arising from sampling and storage techniques, impurities in chemical reagents used and inadequate detection limits of the analytical measurement methods. Table I illustrates the general decline in reported trace metal concentrations in seawaters in the last two decades. The trend to lower values is mainly the result of reduced contamination (i.e., lower analytical sample blanks) and lower detection limits which arise from lower blanks and improved instrumentation. The subjects of sampling and storage of water samples and of contamination control are well-documented (1,18,19).

Because of the low concentrations of trace metals that can prevail in natural waters, particularly in open seawater ($\mu\text{g/L}$ and lower), few analytical techniques are useful for the direct determination. Neutron activation analysis (1) and anodic stripping (20-22) are exceptions but nuclear reactors for the former are not routinely available and anodic stripping is not highly selective. These methods are used less frequently than spectroscopic methods.

At the present time, the two most important techniques for the determination of trace metals in natural waters are graphite furnace atomic absorption spectrophotometry (GFAAS) and inductively-coupled plasma atomic emission spectrometry (ICPAES). These techniques are most frequently used in conjunction with a "preconcentration" step in which the trace elements are both isolated from the matrix and concentrated, prior to measurement.

TABLE I. Decline in the Reported Concentrations of Trace
Metals in Seawaters, 1962 - 1981

Element	Concentration ($\mu\text{g/L}$)					
	a	b	c	d	e	f
	1962(12)	1967(13)	1972(14)	1978(15)	1980(16)	1981(17)
Cu	1.8	2.8	2.03	0.50	0.71	1.03
Fe	6.7	10.8	-	0.58	1.00	1.0
Cd	-	-	1.38	0.05	0.049	0.020
Ni	-	1.5	0.78	0.65	0.17	0.33
Zn	-	13.8	11.8	10.8	4.51	0.44
Co	-	1.2	< 0.01	< 0.01	<0.02	0.018
Pb	-	3.8	0.90	-	0.49	0.22
Mn	4.0	-	-	-	-	0.71

a, Atlantic Ocean deep seawater ($31^{\circ}47'N$, $65^{\circ}11'W$)

b, Pacific coastal water (Southern California coast)

c, Atlantic coastal water (Liverpool Bay)

d, Indian Ocean deep seawater (Gulf of Aden)

e, Atlantic coastal water (Nova Scotia)

f, Nearshore seawater (Nova Scotia)

Occasionally, GFAAS has been used for the direct determination of metals such as Fe, Cu, Mn, Cd, Cr and Zn in natural waters, when the concentrations lie within the instrumental detection limits. However, the direct approach is generally limited to freshwater samples. In seawater, not only are concentrations generally lower but also matrix interferences arising from non-specific absorption (e.g., light-scattering from covolatization of salt) renders direct analysis by GFAAS almost impossible (23). Attempts to compensate for salt-matrix interference by techniques like matrix modification (24), selective volatization (25) and capacitive discharge (26) often impoverish the sensitivities and detection limits, and precision and accuracy are often poor.

ICPAES is less sensitive and less specific than GFAAS. Consequently; detection limits for various trace metals by ICPAES (27,28) are about one order of magnitude poorer than by GFAAS (29). This limitation effectively precludes the application of ICPAES to the direct determination of trace metals in natural waters. Detection limits for some trace metals by ICPAES and GFAAS are shown in Table II, together with concentrations in two water samples.

The lack of analytical instrumental techniques which offer the necessary sensitivity and/or freedom from matrix interferences for the direct determination of trace metals in natural waters has led to the use of chemical preconcentration procedures. These are discussed below.

(i) Methods of Preconcentration

The term "preconcentration" in analytical chemistry describes a process by which the concentrations of analyte elements in a sample are

TABLE II. Detection Limits of Some Trace Metals by
ICPAES and GFAAS and Comparison to
Concentrations in Two Natural Water Samples

Element	Detection limits ($\mu\text{g/L}$)		Concentration ($\mu\text{g/L}$)	
	ICPAES(28) ^a	GFAAS(29) ^a	Niagara River (30)	Atlantic Ocean (17)
Cd	4.0	0.0025	0.052	0.033
Mn	1.0	0.14	2.84	0.018
Zn	2.0	0.030	1.42	0.28
Cu	3.0	0.38	3.5	0.12
Fe	3.0	0.33	86.7	0.20
Pb	2.0	0.65	0.59	0.095
Ni	10.0	1.0	1.56	0.27
Co	6.0	0.80	0.21	0.003

^a Based on 20- μL volume injection, pyrolytic graphite furnace .
tube and interrupt-flow mode, data converted from $\text{pg/l}\%$
adsorption to $\mu\text{g/L}$ (ppb).

enriched to make possible their quantitative measurement with reduced error. Some methods of preconcentration also provide isolation of the analytes from the matrix which, in general, is desirable. For example, in the determination of trace metals in seawater by GFAAS or by ICPAES, isolation of the trace metals from the salt matrix is a prerequisite. Also, chemical techniques used in preconcentration can lead to simple matrix-matching of the analyte sample to the calibration standards; this, of course, is a very favourable condition. The need for preconcentration in trace element analysis has led not only to the application of existing methods of preconcentration but also to the development of new ones, which is the main topic of this thesis.

The preconcentration methods used for trace metal determination in natural waters are outlined below. Excellent and more extensive reviews are provided by Leyden (31), van Grieken (31a) and by Bachmann (32).

(a) Volume reduction. Solvent evaporation is an obvious preconcentration method. The technique has been applied to the arc-emission spectrographic (33) and X-ray spectrometric (34) determination of trace metals in freshwaters. Since matrix problems are amplified by evaporation, the method offers little applicability, especially for seawater analysis.

(b) Coprecipitation/cocrystallization. All precipitates tend to carry down substances which would otherwise be soluble under the conditions of the precipitation. This phenomenon has been applied to the preconcentration of trace metals from natural waters (35): The analytically useful precipitation methods are of two types; cocrystallization and coprecipitation. In cocrystallization, the trace metals are incorpor-

ated into the lattice of the precipitates. This process is often very specific, although cocrystallization techniques using reagents such as thionalide (35) and 5,7-dibromo-8-hydroxyquinoline (36) have been found to simultaneously preconcentrate several elements at the trace level. In the case of coprecipitation, the trace metal ions are adsorbed onto the surface of a host (carrier) precipitate. Among host precipitates used for this purpose are the hydrous oxides of Fe(III), Al(III) and Mn(IV) and the sulphides of Cu(II) and Co(II) (37-39).

Theoretically, coprecipitation and cocrystallization methods offer large preconcentration factors. In practice, however, the net gain in concentration may not be large if the analyte must be stripped from the host precipitate before analytical measurement. Furthermore, it is often difficult to obtain a host precipitate relatively free from the element being concentrated. This problem of contamination is the major drawback of coprecipitation/cocrystallization techniques. For this and other reasons above, these methods have not been as widely used recently as in the past for trace-metal preconcentration.

(c) Electrodeposition. Electrodeposition has the advantages of providing large preconcentration factors and isolation of the analyte elements from the matrix. As well, few reagents are required and so contamination problems are reduced. Trace metals have been electrodeposited from various aqueous solutions onto a tungsten filament (40), a carbon rod (41), a hanging mercury drop (42), an iridium wire (43) and a graphite electrode (44), prior to measurement by GFAAS. Unfortunately, these techniques are characterized by poor reproducibility.

Anodic stripping voltammetry is the most widely used electrochemical technique for the direct preconcentration and subsequent measurement of trace metals from natural waters (20-22). In the preconcentration step, the trace metal ions are deposited cathodically (usually on a hanging mercury electrode); in the measurement step, the concentrated metals are oxidized and the anodic currents measured. Relatively poor selectivity is the major disadvantage of this technique.

(d) Solvent extraction. Solvent extraction (liquid-liquid) is an important technique for the preconcentration of trace metals and the method is well-known and understood (e.g., 45,46). A large variety of chelating agents are available as extractants, e.g., 8-hydroxyquinoline (oxine), diethyldithiocarbamate (DDTC), ammonium pyrrolidinedithiocarbamate (APDC), dithizone and acetylacetone (ACAC). These are unselective reagents and in a particular pH range will extract several metal ions simultaneously. Hence, such reagents are termed "group" extractants. The use of such group extractants, when combined with a highly selective measurement technique such as GFAAS, leads to high efficiency in trace metal determinations.

There are numerous examples of the application of solvent extraction to the preconcentration of trace metals from natural waters (e.g., 1,13,16,45-50). In general, preconcentration factors in the range of 10 to 20 are readily achievable but factors greater than 20 require rather high values of the distribution ratio, D , if the extraction is to remain above 90%. The well-known relationship among these factors is given by the following equation in which the precon-

centration factor is V_a/V_o , the ratio of the volumes of the aqueous and organic phases:

$$\% \text{ Extraction} = \frac{100 D}{D + V_a/V_o} \quad (1)$$

Preconcentration factors may be improved by back-extraction of the metal ions from the organic solvent into an aqueous solution of HNO_3 (16); however, this procedure may increase the analytical blank of the method, which is already susceptible to contamination owing to the several reagents (i.e., buffer, chelating agent, organic solvent) required in the extraction step. Problems caused by dissolution of the organic solvent (e.g., MIBK) in the aqueous phase are solved by the pre-saturation of the aqueous phase with the organic solvent (13,16,50).

(e) Ion-exchange. Ion exchange is another important preconcentration technique. Cation-exchange with sulfonic acid resins is of little value for the preconcentration of trace metals, owing to the presence of large amounts of Na^+ , K^+ , Ca(II) and Mg(II) in natural water systems. Anion-exchange procedures are useful for concentrating those metal ions which exist as chloro-anions in high chloride medium. This method is limited in scope (e.g., 51). The most useful ion-exchange resin for preconcentration has proven to be the chelating resin, Chelex-100, a copolymer of vinylbenzyliminodiacetic acid, styrene and divinylbenzene (16,52-55).

An important factor with chelating resins is that they must have a low affinity for the alkali and alkaline earth ions at the pH for preconcentration of the trace metals. Chelate ion-exchange methods

can be applied in either a batch-equilibration mode or, more often, in a column-percolation mode. The batch-equilibration approach is used mainly in conjunction with X-ray spectrometric (56) or neutron activation (57) analysis. The column approach is used primarily in conjunction with GFAAS (16,53) and ICPAES (54). Recently, a combination batch equilibration/column percolation technique was developed by Sturgeon and coworkers (16,52). This useful technique yields quantitative recoveries of the metal ions even at high percolation rates, owing to the prior batch equilibration of the sample with the resin.

Large preconcentration factors (e.g., 50 or higher) should be obtainable by chelate-ion exchange, being limited only by the size of sample available. However, the anticipated large factors have not been achieved generally, primarily because of the relatively large volume of eluant (e.g., 25 mL of 2.5 M HNO_3) required to strip the column quantitatively (16,58). This can be attributed to the rather strong interaction between the metal ions and the chelating groups. Furthermore, the use of relatively concentrated acid solution increases the reagent blank of the method.

Although a number of conventional chelate ion-exchange resin have been synthesized (59,60), a more recent approach to chelate ion-exchange has been through "ligand immobilization". In ligand immobilization, a chelating ligand is fixed (i.e., immobilized) on the surface of supporting substrates such as resins, activated charcoal or silica gel. The chelating agent can be appended either by adsorption or by chemical reaction. The ligand-immobilized substrate can then be used,

usually in a column configuration, to preconcentrate trace metals.

Among the more interesting studies involving adsorption immobilization are those in which commercially available resin beads such as Amberlite XAD-2 and XAD-4 (copolymers of styrene-divinylbenzene) (61,62) and polyurethane foam (63) were used to adsorb chelating agents such as a pyridyl-substituted triazine (61) and dithizone (63). A characteristic of such substrates is the low capacity (e.g., 1-100 μeq of metal ion/g of resin). Exchange capacities of 1 to 3 meq/g are typical for conventional chelate ion-exchange resins.

Several studies have been reported on the chemical immobilization of chelating agents on support materials and on the application of the resulting exchangers to the preconcentration of trace metals in natural waters (17,64-68). 8-Hydroxyquinoline is often used as the ligand (17,64,67) and typical substrates are silica gel (17,68), XAD-4 resin (66) and controlled pore glass (64). Immobilization by chemical reaction produces substrates with capacities in the high $\mu\text{eq/g}$ range.

Ligand-immobilized substrates and chelate ion-exchange resins have similar characteristics and as preconcentration media, they share similar advantages and disadvantages. The main differences are that ligand-immobilized exchangers can be tailored to special applications, but have lower capacities, especially those prepared by adsorption. The latter also suffer from bleeding of the ligand. However, in trace-metal preconcentration, a high exchange capacity is not required and since the ligand-immobilized substrates can be regenerated easily, bleeding may not always be a major problem.

(f) Adsorption. Preconcentration by adsorption is a less common method.

The mechanism is similar to that of coprecipitation but the solid substrate (adsorbent) is brought directly into contact with the sample solution, instead of being precipitated out of solution.

Activated charcoal and tungsten wire have been used as adsorbents. The adsorbed metal ions can be determined directly by neutron activation analysis or by GFAAS; alternatively, they can be stripped with acid and determined by GFAAS (69-72).

In another approach, metal complexes (e.g., oxinates) are formed in solution and then these complexes are preconcentrated by adsorption, usually by percolation through a column. Typical adsorbents are activated charcoal (73), silica gel (74), and XAD-2 resin (61,75).

(g) Other methods. There are a few miscellaneous preconcentration methods which do not warrant discussion here except by reference (e.g., 76,77).

Recently, studies pertaining to the comparison of preconcentration methods have been made (16,78,79). Based on these studies and the foregoing discussion, one concludes that a good preconcentration method should provide a large preconcentration factor; give a good separation from the sample matrix; be subject to minimal contamination; be able to concentrate several metals simultaneously (i.e., a "group" method); and be simple and inexpensive. Based on these criteria, it would appear that column percolation techniques based on chelate ion-exchange or adsorption are the most useful. Clearly, however, there is a need for the development of more advantageous preconcentration methods.

One final and fundamental point must be made about preconcentration, particularly with regard to water samples containing natural complexing agents such as humic and fulvic substances (1,8-11,80) and halides and carbonates (1,5,6). With such samples, each preconcentration method may lead to different analytical results because each method displaces the bound metal to a different extent. The degree of displacement depends on the relative stabilities and labilities of the natural complexes and of the complexes or species formed by the preconcentration process. As noted, the preconcentration process could involve coprecipitation, electrodeposition, chelate ion-exchange, solvent extraction or adsorption. Obviously, the presence of natural ligands poses a serious matrix problem. To compensate for effects of the complexing matrix in the preconcentration step, the standard additions method is often used. However, the standard additions method cannot be used without thought. This topic is discussed in the following section.

(ii) Method of Standard Additions: Effect of Incomplete Reaction of Spike

The standard additions method (SAM) is nowadays routinely used and reference to it can be found in many text books on instrumental analysis (81,82). The method, which is intended to compensate for any effect of the sample matrix on the analytical response, is based on the assumption that the analyte spike added in increasing amounts to aliquots of the sample behaves identically to the sample analyte throughout the analytical procedure and is affected to the same extent by any chemical interference. The blank value is determined in the absence

of the sample analyte in a closely matched matrix and is subtracted to yield the analytical result.

As mentioned previously, natural waters contain a multitude of ligands. Consequently, metal ions are highly speciated in forms that include the free (aquated) metal ions, metal complexes of various stabilities and labilities, and colloiddally adsorbed ions (1,5,7-11,80, 83-85). In such complicated systems, the analyte spike may not be completely equilibrated with the sample before the preconcentration step and as pointed out by others (8,9,16), the application of SAM in these circumstances can lead to an erroneous estimate of the total (soluble) analyte concentration. To date, however, the magnitude of the potential error has not been demonstrated. Since SAM is such an important calibration procedure in trace element determinations, study was given to this problem in the present work. In Section III.4.(iv), RESULTS AND DISCUSSION, the relationship between the analyte concentration taken, the analyte concentration recovered, and the degree of reaction of the spike with the matrix components is illustrated by means of a simple model.

I.3 Metal-Ion Speciation in Natural Waters

(i) Metal-Ion Species in Natural Waters

In natural waters, metal ions exist in many physico-chemical forms which together make up the total concentration (1,5,7-11,80,83-86). Some of the possible soluble forms of a divalent trace metal are shown in Table III. Since by convention (6), "soluble" metal is defined as all metal species which pass through a 0.45 μ m filter, most colloidal

TABLE III. Possible Physico-Chemical Forms of Metals in
Natural Waters (85)

Physico-chemical form	Examples	Approximate diameter (nm)
Particulates	retained by 0.45 μ m filter	> 450
Simple hydrated metal ions	$\text{Cd}(\text{H}_2\text{O})_6^{2+}$	0.8
Simple inorganic complexes	$\text{Pb}(\text{H}_2\text{O})_4\text{Cl}_2$	1
Simple organic complex	Cu-glycinate	1-2
Stable inorganic complexes	PbS, ZnCO_3	1-2
Stable organic complexes	Cu-fulvate	2-4
Adsorbed on inorganic colloids	Cu^{2+} - Fe_2O_3 , Pb^{2+} - MnO_2	10-500
Adsorbed on organic colloids	Cu^{2+} -humic substances	10-500
Adsorbed on mixed organic/inorganic colloids	Cu^{2+} -humic substances/ Fe_2O_3	10-500

particles will therefore be included in the soluble form.

It has been established that the potential toxicity of trace metals is controlled to a large extent by their physico-chemical forms and that the toxicity of a particular form is probably related to its ability to react with a biological membrane (3,4,7,86). For example, Cr(III) in trace amounts is an essential element while Cr(VI) is highly toxic; As(III) is much more toxic than As(V); and alkyl leads are dangerous because they are lipid-soluble. In natural waters, certain free (hydrated) metal ions are toxic to organisms because of their high mobility across a biological membrane while stable complexes and species associated with colloids are usually less toxic or non-toxic. Obviously, measurement of the total (soluble) concentration of trace metals in natural water, while important, does not provide adequate information about their environmental impact. Speciation measurements are thus necessary to establish metal toxicity on aquatic organisms.

(ii) Methods of Speciation

Trace-metal speciation in natural waters has been based on the use of two distinctly different techniques: computer modelling and experimental measurement (85,86).

Computer modelling involves the use of known stability-constant data, together with the known concentrations of various ions and suspended solids in natural waters, to compute the equilibrium concentrations of the various species (e.g., 87-89). However, there is doubt about the data obtained by computer modelling because of the lack of reliable thermodynamic data. For example, there is not much knowledge of metal ion interactions with many of the natural ligands; indeed, the

nature and concentration of these ligands are only partially known (8-11,80,83-86).

Accurate experimental measurement of trace metal species is a most difficult task because of the low concentrations involved and matrix interferences. Furthermore, because of such effects as localized pollution, the various species of a trace element may not be in equilibrium with each other. But even if they are, any procedure applied to the sample may disturb the various equilibria and alter speciation, although if the equilibrium changes are slow and the separation is rapid, the disturbance may be minimal (85,86). It is clear, then, that the results of speciation studies are method-dependent and for this reason, they are operationally defined.

The main procedures used to study trace metal speciation are anodic stripping voltammetry (ASV) (e.g., 8,20,22), chelate ion exchange (e.g., 8,9,84,90), dialysis (e.g., 91,92), bioassay (e.g., 93,94) and UV-irradiation (e.g., 8,84). A detailed discussion of individual speciation schemes is beyond the scope of this thesis. An example of a speciation scheme based on the complementary use of Chelex-100, ASV and UV-irradiation (8) illustrates the mechanics and concepts of trace-metal speciation in natural waters. This scheme involves ASV measurements of labile and total metal concentrations on samples of original natural water, water passed through a Chelex-100 column, UV-irradiated water, and UV irradiated water passed through a Chelex-100 column. It is assumed that metal ions in labile complexes are electroactive. Also, the assumption is made that upon oxidation with $\text{HClO}_4/\text{HNO}_3$, all metal species are made electroactive (i.e., the total metal concentration

can be determined by ASV). One function of the Chelex-100 separation step is to distinguish between metal species which are retained on the resin and those associated with colloidal particles, which are not retained. Any metal in a complex which is weaker than the Chelex-100 complex is assumed to be retained by Chelex-100. The purpose of UV-irradiation is to destroy organic matter, thereby releasing the organically bound metal species; metal species which are associated with inorganic colloids, however, would not be released by UV-irradiation.

A summary of the various classes of metal defined by the speciation scheme and of some metal species which correspond to each class is given in Table IV. Based on this table and on the ASV measurements on the four aforementioned water samples, concentrations of some individual metal species in natural water can be determined. A major drawback of this scheme is that pH adjustment is required for the ASV measurement (pH 4.7). This adjustment obviously will distort metal-speciation equilibria before the ASV measurement. However, the authors emphasize that the various metal classifications of the scheme are operational classifications and cannot be taken to represent the original sample exactly.

I.4. Adsorption and XAD-7, a Macroreticular Polymeric Adsorbent

Adsorption occurs as the result of surface forces between a solid adsorbent and an adsorbate (e.g., a gas, liquid, solute or colloid). The nature of these forces is not completely understood. The extent of adsorption depends on the physical and chemical characteristics of the adsorbent and the adsorbate.

Since the 18th-century observations of C. W. Scheele and Abbe F. Fortana on the adsorption of gases by charcoal, there have been many

TABLE IV. Summary of Speciation Scheme by Florence and Batley (8)

Metal ^a species	Electroactive		Removed By Chelex-100		Example of possible species
	before UV irradiation	after UV irradiation	before UV irradiation	after UV irradiation	
M, MA1 ML1	yes	yes	yes	yes	Zn ²⁺ , CdCl ₄ ²⁻ Cu-glycinate
MA2 ML2	yes	yes	no	no	Pb-Fe ₂ O ₃ ^b Cu-humic acid ^b
MA3 ML3	no	no	yes	yes	PbS, ZnCO ₃ Cu(OH) ₂ CO ₃
MA4 ML4	no	no	no	no	Pb-MnO ₂ ^b Cu-humic acid ^b

- ^a
- M : hydrated metal ions
 - ML1 : labile organic complexes
 - MA1 : labile inorganic complexes
 - ML2 : labile organic complexes + labile metal adsorbed on organics
 - MA2 : labile inorganic complexes + labile metal adsorbed on inorganics
 - ML3 : non-labile organic complexes
 - MA3 : non-labile inorganic complexes
 - ML4 : non-labile organic complexes + non-labile metal adsorbed on organics
 - MA4 : non-labile inorganic complexes + non-labile metal adsorbed on inorganics

^b Colloidal particles

attempts to develop a theoretical basis for adsorption. Experimentally, it is known that for a given gas and a unit weight of a given adsorbent, the amount of gas adsorbed at equilibrium is a function of the final (equilibrium) pressure and temperature:

$$\Gamma = F(P, T) \quad (2)$$

where Γ = the amount of adsorbed gas per gram of adsorbent

P = the equilibrium pressure

T = the absolute temperature

When the pressure of a gas is varied at constant temperature, a graph of the amount of gas adsorbed versus the equilibrium pressure is called an adsorption isotherm. It is often observed that at low pressure, adsorption increases linearly with pressure; as the pressure is increased, the amount adsorbed becomes proportional to a power of the equilibrium pressure smaller than unity. At still higher pressures, adsorption increases only slightly until a region is reached where adsorption is essentially independent of the pressure (Figure 1). The same situation is often observed in the adsorption of a solute from solution onto a solid surface. The convex nature of the adsorption isotherm has been described by the Freundlich equation (95):

$$\Gamma = k[M]^n \quad (n < 1) \quad (3)$$

or

$$\log \Gamma = \log k + n \log [M] \quad (4)$$

where k and n are characteristic constants, and $[M]$ is the equilibrium pressure or concentration.

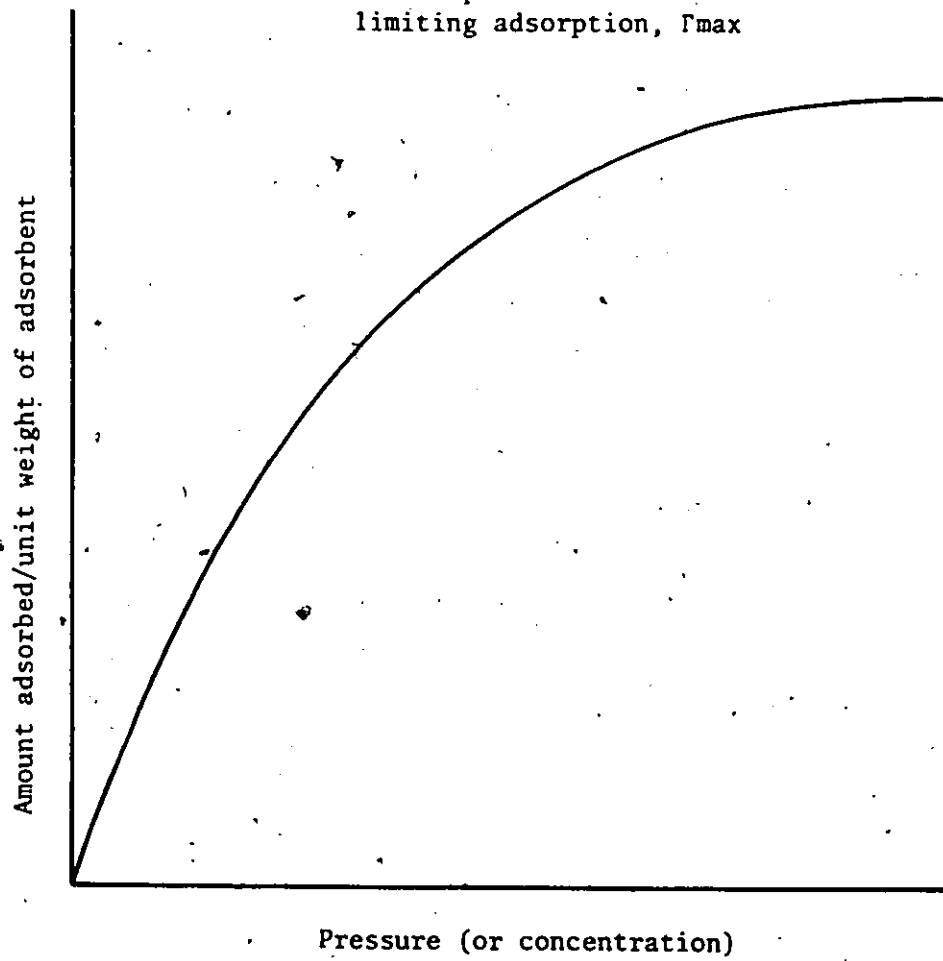


Figure 1. Adsorption isotherm

This simple equation is not exact in that it does not show that Γ approaches a linear function of $[M]$ at low pressure or concentration, a common experimental observation. Also, it does not yield a limiting value corresponding to Γ_{\max} , another common experimental observation. It is also insensitive and leads to imprecise results.

In 1916-18, Langmuir (96-98) proposed a theory for adsorption based on the following assumptions: (i) the forces in adsorption are similar in kind to those involved in chemical bonding; (ii) points of residual valency exist on the surface of a crystal; (iii) adsorption consists of fixing the adsorbates onto these points; and (iv) since these points of residual valency can hold one atom or molecule of the adsorbate, the adsorbed layer can be only one atom or molecule thick. Using these assumptions and the principle that at equilibrium the rate of adsorption and the rate of desorption are equal, Langmuir derived the well-known equation which bears his name:

$$\Gamma = \frac{\Gamma_{\max} [M]}{(1/K) + [M]} \quad (5)$$

Γ_{\max} is the limiting adsorption value and K is the heterogeneous equilibrium constant (i.e., the ratio of rate constants for adsorption and desorption, respectively). This equation can be written in six linearized forms (See Appendix I). One of these is shown here:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\max} K} + \frac{1}{\Gamma_{\max} [M]} \quad (6)$$

The Langmuir equation is superior to the Freundlich equation in that it mathematically describes the convex adsorption isotherm (Figure 1) well. From its general form (equation 5), it is seen that at low values of $[M]$ (i.e., $[M] \ll 1/K$), Γ approaches a linear function of $[M]$; at high values of $[M]$, Γ approaches a limiting value, Γ_{\max} . The equation can be rewritten into linearized forms from which values of Γ_{\max} and K can be easily obtained. For example, in equation (6), Γ_{\max} and K can be obtained from the slope ($1/\Gamma_{\max} \cdot K$) and intercept ($1/\Gamma_{\max}$) of the linear regression plot of $1/\Gamma$ vs $1/[M]$. Thermodynamic quantities for the experimental adsorption process can also be calculated from the temperature dependence of the K values, i.e.:

$$\Delta G^\circ = -RT \ln K \quad (7)$$

$$\frac{\Delta H^\circ}{R} = \frac{-\delta \ln K}{\delta(1/T)} \quad (8)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (9)$$

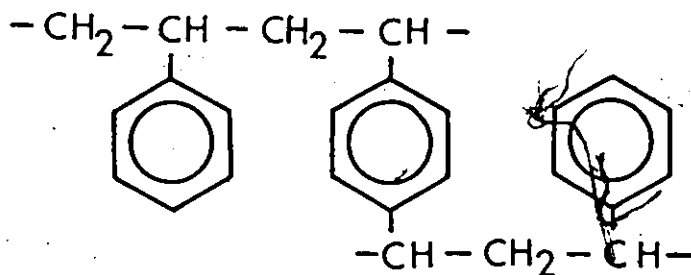
The Langmuir equation was originally developed and verified for gas-solid adsorption processes. Its application to solution adsorption processes may not be appropriate, however, since the solution adsorption process is much more complex. For example, the displacement of solvent molecules from the solute and adsorbent surface must surely be involved. A detailed discussion on the application of the Langmuir equation to solution adsorption is presented in Section III.2.(iv) of this thesis.

The phenomenon of adsorption is used for many practical purposes; for example, for the purification of drinking water, wines and oils; for the decolourization of liquids; for the removal of toxic and radioactive

materials from industrial wastes; and for the elimination of toxic gases (99-101).

Adsorption processes are also important in analytical chemistry. For example, silica gel, activated charcoal, alumina, Fuller's earth, carbonates and polymeric resins are often used as column-packing materials in adsorption chromatography (102-108), and as separation/preconcentration media in trace analysis (69-75, 109-116). The use of adsorbents as separation/preconcentration media differs from adsorption chromatography in that the latter involves the introduction of a sample onto a column where a continuous flow of mobile phase has been initiated. Separation of components having different partition coefficients is achieved by many adsorption/desorption steps down the length of the column. The separated components are carried out by the mobile phase and quantitated by a detection device. In the separation/preconcentration process, either a batch equilibration or a column percolation approach can be used to strip the analyte species from the sample matrix components. Often, many analyte species are stripped simultaneously, the separation being from the matrix rather than from each other. The concentrated analyte species are then either eluted from the adsorbent or are determined directly on the adsorbent. Air and water samples have been treated in this way (e.g., 69-75, 109-116).

Recently, a new class of adsorbents, macroporous organic resins, have found use in liquid chromatography and in separation/preconcentration (117, 118). These materials are cross-linked polymers and have no ionic functional groups. The most popular of these adsorbents are the commercial products XAD-2 and XAD-4 (polystyrene-divinylbenzene copolymers) and XAD-7 (a methylmethacrylate polymer). The structures of these resins are shown in Figure 2 and some physical and chemical properties



XAD-2, XAD-4 (see Table V for difference in properties)

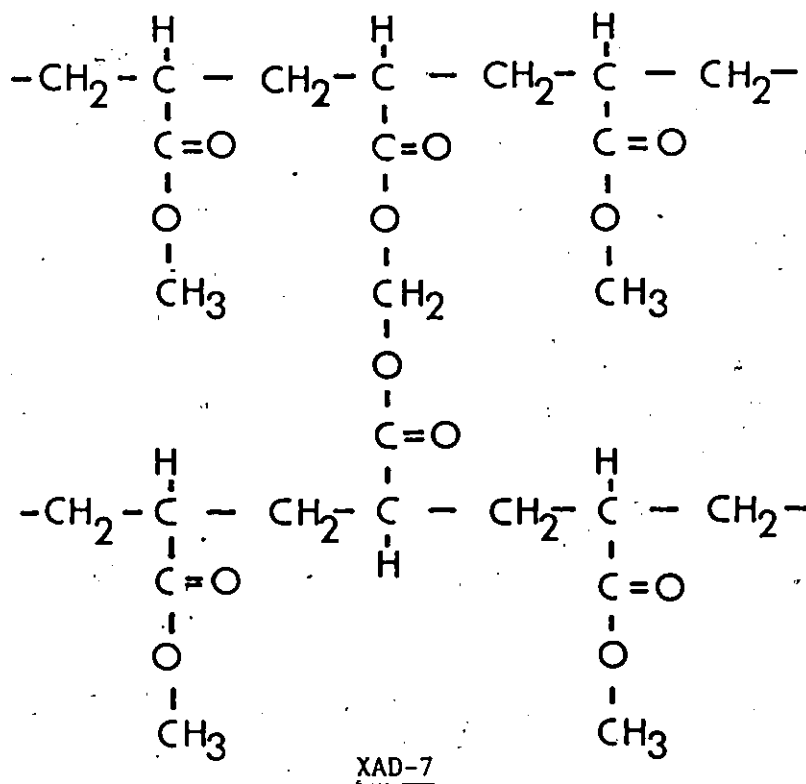


Figure 2. Structures of XAD-2, XAD-4 and XAD-7 resins (117,118)

of these resins are listed in Table V. These resins have good physical durability and thermal stability (up to 150°C for XAD-7 and 250°C for XAD-2 and XAD-4). They are stable over the entire pH range and are inert to organic solvents. In addition, they do not contract or expand with changes in solvent and have excellent flow characteristics. These are attractive characteristics for analytical column materials.

The adsorptive properties of the XAD resins are derived from a combination of macroreticular porosity, pore-size distribution and large surface area (117,118). The nature of the adsorptive forces is not completely understood. For XAD-2 and XAD-4, the π -electrons on the benzene rings (i.e., sites of residual valency) are likely involved. For XAD-7, the carbonyl or ester group could be the site of residual valency. In addition, adsorption could also be aided by van der Waals' forces between the surface of the resins and the adsorbates.

The XAD resins retain weak organic acids, and bases and ampholytes. Organic ions and dipolar ions are adsorbed and counter ions are retained as a diffuse double layer (119). Some examples of the analytical applications of the XAD resins are given in Table VI and Table VII. These resins have also found use in environmental applications (e.g., for the removal of organic pollutants from industrial effluents and natural waters (130-132)).

Of particular relevance to this work is the application of the XAD resins to the preconcentration of trace metals. Only a few studies have been reported (61,62,75,129). In all but one of these, trace metals were adsorbed either as preformed metal complexes (61,75) or were chelated to organic ligands which had been immobilized on the

TABLE V. Some Chemical and Physical Properties of the XAD Resins (117)

	Chemical nature	Polarity	Dipole moment (debye)	Average pore diameter(A)	Surface area(M ² /g)
XAD-2	Polystyrene divinylbenzene	hydrophobic	0.3	90	300
XAD-4	polystyrene divinylbenzene	hydrophobic	0.3	40	725
XAD-7	methyl- methacrylate	hydrophilic	1.8	90	450

TABLE VI. Application of XAD Resins in Adsorption Chromatography

Application	Resin	Analyte	Reference
Drug analysis	XAD-2	drugs of abuse	120
	XAD-2	narcotic antagonists	121
	XAD-7	analgesics	122
Separation of biological compounds	XAD-2	steroids	123
	XAD-2	cabalamines	124
	XAD-2	bile acids	125
Separation of organic compounds	XAD-2	benzene sulfonic acids	126
	XAD-2	substituted benzenes,	118
	XAD-4	anilines, phenols,	
	XAD-7	sulfonic acids	

TABLE VII. Application of XAD Resins as Separation/Preconcentration Agents in Trace Analysis

Application	Resin	Compounds Adsorbed	Reference
Air analysis	XAD-2	polychlorobiphenyls (PCBs)	111
	XAD-2 XAD-4 XAD-7	low molecular weight compounds such as benzene, acetone, heptane, butyl acids	114
	XAD-2	polynuclear aromatic hydrocarbons (PAHs)	115
Water analysis	XAD-4	halogenated hydrocarbons	116
	XAD-2 XAD-4 XAD-7	humic and fulvic substances	127,128
	XAD-2	preformed complexes of trace metals	61,75
	XAD-2 XAD-4	trace metals	61,62 ^a
	XAD-7	Au(III)	129

^a Resin precoated with chelating agents.

resin by adsorption (61,62). XAD-7 has not been used either for the adsorption of organic metal complexes or as a substrate for ligand immobilization. Presumably, this is because of the weaker adsorption of organic ligands on XAD-7. There is one report, however, on the adsorption of a metal (Au(III) in 1M HCl) onto XAD-7, without the mediation of an organic ligand (129).

1.5 Aim of Research

For ecological and environmental reasons, the concentrations of trace metals in aquatic systems need to be monitored. Because of low concentrations and interference problems from the matrix, the determination of these metals is not straight-forward. Therefore, prerequisite to the instrumental measurement is a preconcentration step that can alleviate both problems simultaneously. At the present time, there are only a few simple preconcentration methods applicable to trace metals in natural waters and each suffers from some disadvantages. Clearly, there is a need for the development of improved or new methods.

Previous work in this laboratory showed that the ligand meso-tetra(p-sulphophenyl)porphine (TPPS₄, Figure 3) reacts in neutral to basic solutions with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and that the resulting complexes can be extracted as a group into MIBK and then measured by GFAAS (49,50). In a preliminary study, it was found that TPPS₄ metal complexes could also be preconcentrated by adsorption onto XAD-7. In the course of this study, it was noticed that inorganically bound metal ions (e.g., aquo and chloro complexes) were directly retained on XAD-7 without the use of an organic ligand. This discovery was surprising and was deemed to be potentially significant.

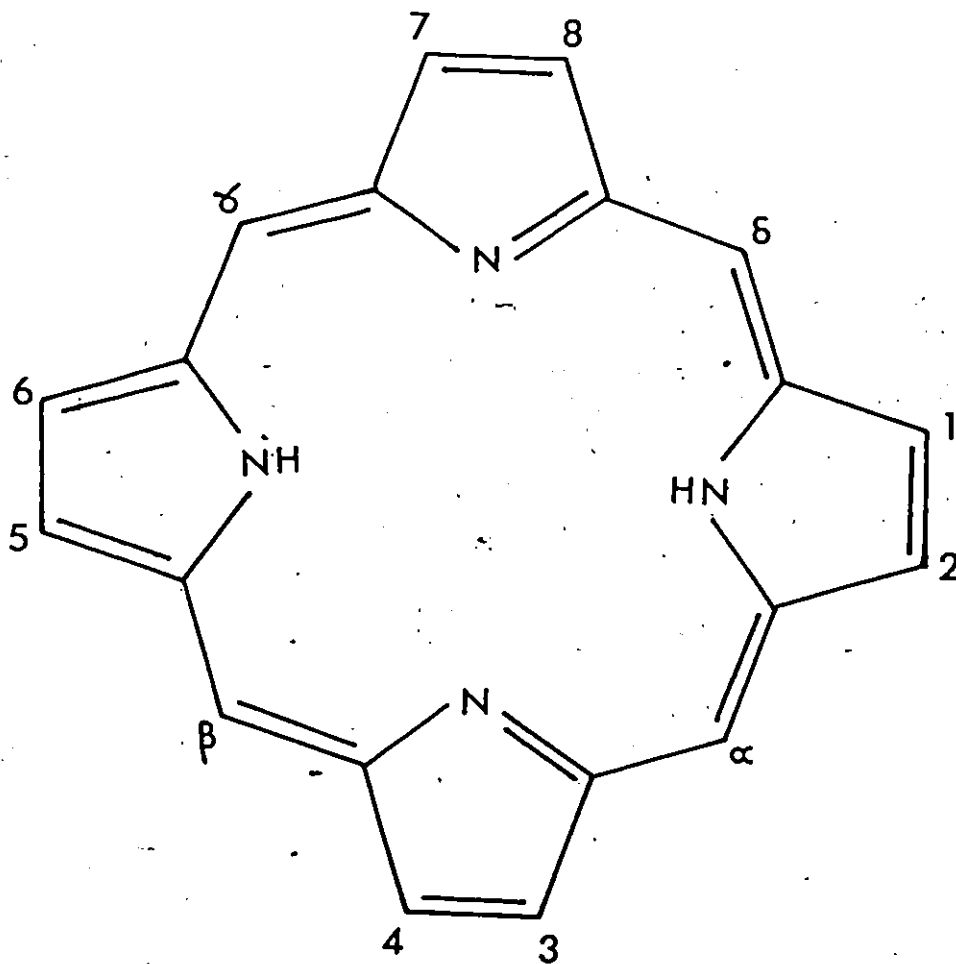



Figure 3. Structure of porphine. TPPS_4 has  substituted at α - δ positions

For example, preconcentration methods based on the direct uptake of metal ions onto XAD-7 would be very simple, efficient and economical. Also, the elimination of the ligand would reduce the risk of contamination which should also lead to improved accuracy, precision and detection limits. Consequently, it was decided to investigate the preconcentration of trace metals* by direct uptake onto XAD-7. The investigation involved four stages: (i) preliminary studies on the conditions for uptake of metal ions on XAD-7; (ii) studies on the mechanism of direct uptake onto XAD-7, (iii) studies on column operation; and (iv) application of the XAD-7 resin to preconcentration and speciation of metal ions in natural water samples.

These studies are described in the following Sections of this thesis.

*The trace metals were: Fe(III), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II). Zn(II) was excluded from this group because of problems arising from contamination from reagents and the laboratory environment.

II. EXPERIMENTAL SECTION

II.1 Laboratory Apparatus, Resins, Reagents, Test Solutions

Adsorption of trace metal ions from solution onto the walls of laboratory glass ware has been studied by several investigators (e.g., 133-135). The loss of trace metals to adsorption is more severe at lower concentrations and higher pH values. Adsorption loss is significantly lower if polypropylene or polyethylene laboratory ware is used. In view of the low concentrations ($\leq \mu\text{g/L}$) used in this work, polypropylene vessels such as volumetric flasks, beakers, funnels and test-tubes were employed whenever possible. Also, test water samples were stored in large polypropylene or polyethylene bottles and were adjusted to pH 1.6 - 1.7 (see below).

A horizontal laminar-flow work station (bench-top model, Canadian Cabinets, Ottawa, Ont.) was used to provide a clean-air working environment. The unit contains a high efficiency particulate air filter (HEPA filter) which is claimed to remove 99.97% of particles of 0.3 micron or larger. The preparation of solutions and the loading and stripping of columns were done in the work station.

The delivery of small volumes was made with Eppendorf pipettes (fixed-volume, multi-volume and continuous digital types). The accuracy of these pipettes ranges from 1.2% at 5 μL to 0.5% at 1000 μL ; the precision ranges from 0.5% at 5 μL to 0.15% at 1000 μL . Both accuracy and precision were adequate for the work of this thesis. The pipettes were calibrated periodically according to the manufacturer's instructions.

The borosilicate glass columns used for loading of resin were obtained from Bio-Rad Laboratories (Mississauga, Ont.). These Bio-Rad Econo-Columns were either 20 cm x 1.0 cm i.d. or 10 cm x 1.0 cm i.d. with a 35 μ m bed support and nylon stopcock. In normal use, metal ions were stripped from the resin-loaded column with 1% v/v HNO_3 and no memory effects from adsorbed ions could be detected.

The acrylic ester resins were either Amberlite[®] XAD-7 (Rohm and Haas, Philadelphia, Pennsylvania) or Bio-Beads SM 7 (Bio-Rad Laboratories). The latter resin is XAD-7 which has been further purified by Soxhlet extraction with methanol before marketing. Experimentally, no difference was observed in the adsorption characteristics between the two brands of resins. The hydrated resin is in the form of hard, opaque beads with particle size of 20-50 mesh. Smaller particle sizes of 60-80, 60-100, 80-100 and 100-200 mesh were obtained by grinding with a pestle and mortar and sieving through a series of Tyler sieves.

The XAD-7 resin and to a lesser extent the SM-7 resin are contaminated with polar organic and inorganic impurities (136,137) and must be further purified before use. The resins were washed batchwise with dilute HNO_3 (5% v/v) and the washings were checked for trace metal content by GFAAS. Washing was ceased when the Fe content in the effluent could no longer be distinguished from that in the HNO_3 ($\sim 0.1 - 0.2$ $\mu\text{g/L}$ Fe). The resin was then rinsed in turn with dilute aqueous ammonia (2-3% v/v) and distilled deionized water (DDW). Finally, it was washed by suction with methanol several times and dried in an oven at 90°C. The dried resin was stored in a bottle. After the batch

equilibration studies (see below), the resin was regenerated for future use by the above purification procedure. Procedures for packing, conditioning and regeneration of the columns are described in Section II.2.

The Chelex-100 resin (sodium-ion form 100-200 mesh) was obtained from Bio-Rad Laboratories. Its use is described in Section II.2.

All chemicals used in this work were of reagent grade or better*. Aqueous solutions were prepared with distilled deionized water. Distilled water was passed either through a Barnstead Ultrapure Cartridge (Sybron Corporation, Boston, Mass.) or a Milli-Q2[®] system (Millipore Corporation, Bedford, Mass.). The water was checked periodically for trace metal impurities by GFAAS.

Saline solutions (0.80, 0.75, 0.50 and 0.20 M NaCl) and electrolyte stock solutions (1.0 M NH₄OAc, 1.0 M NH₄Cl and 1.0 M NH₄NO₃) were prepared by dissolving the appropriate amounts of salts in DDW. The electrolyte solutions were used with either dilute HNO₃ or dilute aqueous ammonia for buffering purposes. Trace metals were removed from the saline and electrolyte solutions by passage through an XAD-7 or Chelex-100 column. The quality of these reagents with regard to trace metal impurities in the preparation of dilute working solutions was found to be satisfactory.

Atomic-absorption grade standard stock solutions of Cd(II),

* For example, HNO₃, HCl and ammonia were of Baker Instra-Analysed grade (Baker Chemical Company, Phillipsburg, New Jersey).

Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Fe(III) (1000 mg/L, 1% accuracy) were obtained from the Fisher Scientific Company (Toronto, Ont.) Cr(III), Na⁺ and Ca(II) standard stock solutions (1000 mg/L) were prepared from Cr(NO₃)₃, NaCl and CaCl₂. Metal-ion working solutions and calibration standards for GFAAS were then prepared by dilution of the above stock solutions.

Aqueous stock solutions of Cu(II)-TPPS₄, Co(II)-TPPS₄ and Pb(II)-TPPS₄ were prepared from the metal porphyrins previously synthesized and purified in this laboratory (49). Working solutions were prepared by appropriate dilution.

Humic substances (sodium salt) were obtained from the Aldrich Chemical Company (Milwaukee, Wisconsin). A stock solution of 10000 mg/L was prepared by dissolution of the appropriate amount of humic substances in dilute aqueous ammonia (~ pH 11). Stock solutions at other pH values (e.g., pH 8, pH 6, etc.,) were prepared by lowering the pH of the original stock solution with HNO₃. On standing, an undissolved fraction settled out and was removed by filtration (0.45 um membrane filter, HA, Millipore). Working solutions at various pH values were obtained by dilution.

The seawater reference material, NASS-1, was obtained from the National Research Council of Canada (Ottawa, Ont.). It is a Bermuda Atlantic Ocean (32°10'N, 64°30'W) deep seawater with a salinity of 35.07%. It was acidified to pH 1.6 to preserve the integrity of the trace metal content (18).

A Sandy Cove coastal seawater was obtained from the Atlantic Regional Laboratory (Halifax, Nova Scotia). This sample had been previously filtered through a white-sand filter and acidified to pH 1.7.

Three freshwater samples were obtained from the Canada Centre for Inland Water (CCIW) (Burlington, Ont.). These samples included a Hamilton Harbour sample and two lakewater samples, one a nearshore sample (Station 14) and the other an offshore sample (Station 302). The water samples were centrifuged to remove suspended particulates and acidified to pH 1.7.

II.2 Instrumentation and Techniques

(i) General

pH measurements were made with a Fisher Accumet 520 pH meter equipped with an Orion 91-05 combination electrode. The meter was standardized with appropriate Eisher (NBS) buffers prior to use.

Infrared spectra of purified XAD-7 and of XAD-7 treated with 1% v/v HNO_3 were obtained with a Perkin-Elmer Model 283 double-beam spectrophotometer. The resins were prepared as KBr discs.

(ii) Atomic Absorption and Flame Emission Measurements

Atomic spectrometric methods are the most frequently used instrumental methods for the determination of metals at trace levels. Several monographs (e.g., 138-140) which deal with the principles and the applications of atomic absorption/flame emission spectrometry are available.

In the present work, GFAAS was used to determine the percent adsorption and elution of metal ions on XAD-7 columns, and to obtain adsorption isotherms and distribution ratios in batch studies. GFAAS was also used as the analytical finish technique in the analysis of various natural waters.

The atomic absorption equipment consisted of a Perkin Elmer

Model 373 double-beam spectrophotometer with automatic D_2 -arc background correction and a 057-0705 premix burner-nebulizer, a Perkin Elmer Model 2200 graphite furnace atomizer/controller unit and a strip-chart recorder. Perkin Elmer Intensitron[®] hollow cathode lamps were used as the radiation sources.

For flame atomic absorption measurements, a premix air/acetylene flame was used with a regular single slot, 4-inch burner. The rate of nebulization was set at around 3 mL/min. For graphite-furnace operation, both regular and pyrolytic graphite tubes were used. The latter provide longer life and somewhat better sensitivities. The temperature settings for the drying, charring and atomization cycle, together with the analytical wavelengths for the eight elements of interest are given in Table VIII. The time settings for each individual step in the drying, charring and atomization cycle were selected according to the volume of the aqueous sample injected. For example, a 5- μ L or 10- μ L volume injection required 20 sec for drying, 20 sec for charring and 5 sec for atomization. For larger injections, moderately longer times were required (29). Volume injections of 50 μ L and higher were seldomly used owing to poor atomization reproducibility (29). Pre-purified argon was used as the purge gas and tap water was used as the furnace coolant.

Flame emission spectrometry was used to investigate the adsorption of alkali and alkaline-earth ions (Na^+ and $Mg(II)$) on XAD-7 and their effects on the adsorption of trace metal ions. The equipment consisted of the Perkin-Elmer 373 spectrophotometer with the 057-0705 burner-nebulizer. An air/acetylene flame was used.

TABLE VIII. Analytical Wavelength and Temperature Settings for the Drying, Charring and Atomization Cycle in GFAAS.

Element	Analytical Wavelength, nm	Temperature Settings, °C		
		Drying	Charring	Atomization
Fe	357.9	100	800	2500
Cr	248.3	100	800	2500
Ni	232.0	100	800	2600
Co	240.7	100	800	2600
Cu	324.8	100	800	2500
Mn	279.5	100	800	2500
Cd	228.8	100	250	2100
Pb	283.3 or 217.0	100	500	2300

(iii) Radioisotope Tracer Techniques

Radioisotopes were used as tracers in investigations on the adsorption behaviour of trace metal ions on XAD-7 from solutions of high NaCl concentrations (simulated and natural seawaters). The high salt content precluded the application of the GFAAS technique. Procedures for the use of tracer techniques are available in the literature (e.g., 141-143).

$^{64}\text{Cu}(\text{II})$ and $^{51}\text{Cr}(\text{III})$ were used as representative of divalent and trivalent ions, respectively. $^{51}\text{Cr}(\text{III})$ was prepared by reduction of a $4.2 \times 10^{-5} \text{ M } ^{51}\text{CrO}_4^{2-}$ in saline solution (Frosst Chemical Company, Montreal, Que.) with $\text{HCl}/\text{H}_2\text{O}_2$. $^{64}\text{Cu}(\text{II})$ was prepared by irradiation of $\text{Cu}(\text{NO}_3)_2$ in the McMaster Reactor (n, γ reaction). One hundred μL of a $\text{Cu}(\text{NO}_3)_2$ solution (1000 mg Cu/L) was evaporated to dryness in a quartz vial and irradiated for 6 hr at a flux of 2×10^{12} neutrons $\text{cm}^{-2} \text{ sec}^{-1}$. The sample was cooled for 18 hr. The $^{51}\text{Cr}(\text{III})$ and $^{64}\text{Cu}(\text{II})$ were dissolved and/or diluted to the appropriate concentrations with 1% v/v HNO_3 .

Activities were measured by gamma-ray spectrometry. A NaI well-counter in conjunction with a single-channel analyser (Nuclear Chicago) or a multichannel analyser (Canberra Model 30) was used. $^{64}\text{Cu}(\text{II})$ was detected by the 0.511 MeV γ -ray radiation associated with the positron annihilation process. $^{51}\text{Cr}(\text{III})$ was detected by the 0.323 MeV γ -ray radiation. Typical counting times were 100 sec. Corrections for background radiation and half-life were made.

(iv) Column Percolation Procedure

A column percolation procedure was used in preliminary studies

on the adsorption of metal ions on XAD-7. The conditions for the adsorption of metal ions were later optimized and the optimal XAD-7 column procedure was then used for the preconcentration of trace metal ions in the analysis of various natural water samples.

The packing and conditioning of the XAD-7 column was carried out as follows. A borosilicate glass column was slurry-loaded with an appropriate weight and mesh size of the purified XAD-7 resin in DDW. For a 1 x 3 cm bed, 0.5 g of resin were taken; for a 1 x 6 cm bed, 1 g were taken. For a new column, about 200 mL of 5% v/v HNO_3 were passed through the column to remove metal contaminants. The excess acid was removed by washing with 5% v/v aqueous ammonia and DDW until the effluent pH was 8-9. Next, the XAD-7 column was backwashed with DDW to achieve a uniform packing. Prior to the percolation of a sample or a test solution, the column was treated with about 50 mL of the appropriate buffer solution. Retained metal ions were eluted with dilute HNO_3 (see below). After completion of an experiment, the column was rinsed with aqueous ammonia and DDW and stored for the next experiment.

A column of Chelex-100 was also used as a preconcentration medium. Operation of this column was as described by Kingston (55) and Sturgeon (16). The resin was purified batchwise by washing successively with 5 M HNO_3 , 4 M HCl and DDW. It was converted to the ammonium ion form with 1 M ammonia and rinsed with DDW. The borosilicate column was then slurry-loaded to a bed size of 1 x 6 cm. Two 5-mL portions of 5M HNO_3 were passed through the column followed by two 5 mL portions of 4M HCl, 5 mL of DDW and 5 mL of 2 M ammonia.

The column was backflushed and then washed with DDW to remove excess base until the effluent pH was 8-9. Before percolation of a sample, the column was treated with about 50 mL of the appropriate buffer solution. After an experiment, the Chelex-100 column was rinsed with dilute ammonia and then DDW.

The configuration of the columns used in this work is shown in Figure 4.

(v) Elution Recovery Procedure

Dilute HNO_3 or HCl was used to strip the metal ions after their uptake on the XAD-7 column. The volume of the eluant required was dependent on the size of the column. The eluant was analyzed by GFAAS for metal ion recoveries on the test solutions and natural water samples.

(vi) Batch Equilibration Procedure

This procedure was used to obtain adsorption isotherms and distribution ratios of metal ions on XAD-7. Aliquots (25.0 mL) of the metal ion at various concentrations were placed in polypropylene test-tubes containing 0.500 g of the XAD-7 resin. The stoppered test-tubes were then agitated at room temperature on a Burrell mechanical shaker for 4 hr, which was shown to be adequate for the attainment of adsorption equilibrium. The aliquots were analysed by flame AAS or GFAAS to obtain equilibrium concentrations. The amounts of metal ions adsorbed were obtained by difference.

For proton adsorption on XAD-7, the procedure involved the addition of 0.500 or 2.00 g of XAD-7 resin to 100.0 mL of dilute HNO_3

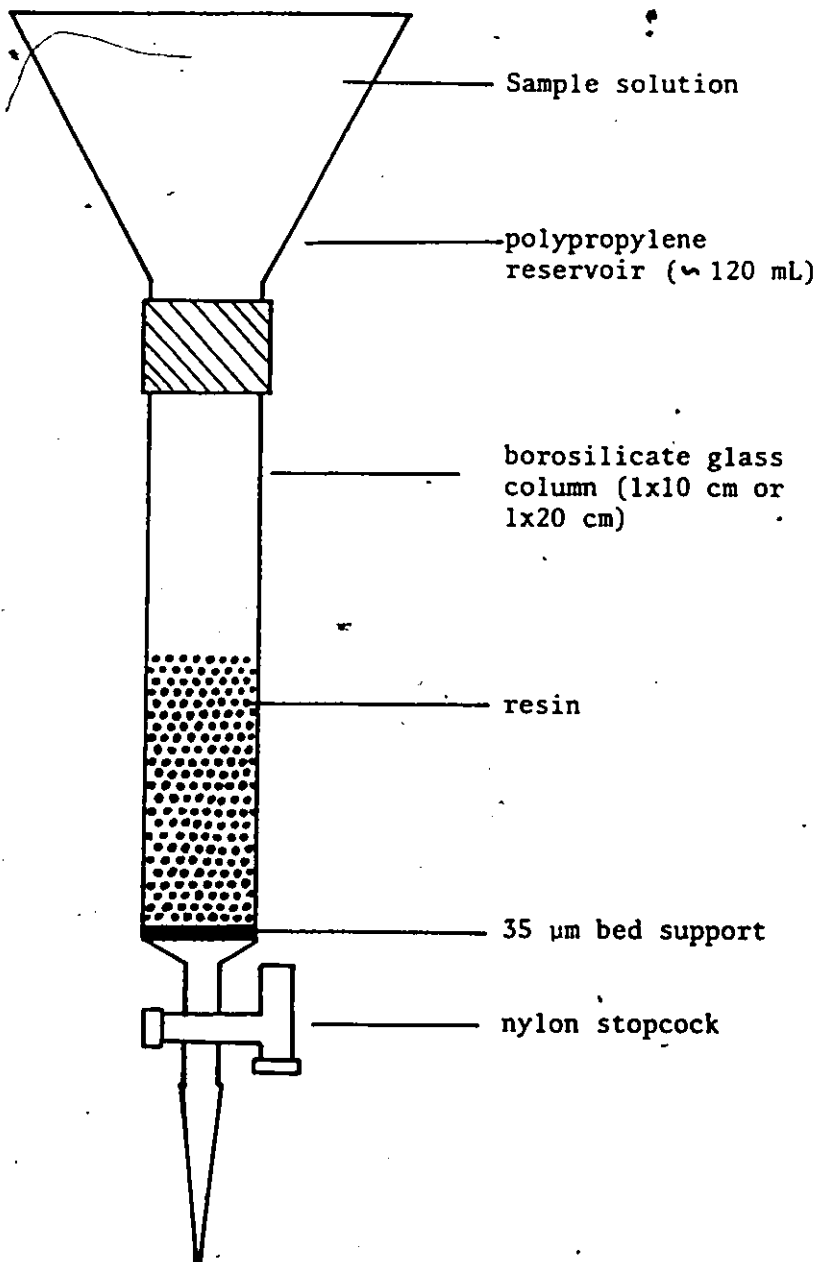


Figure 4. Column configuration

solutions (10^{-3} M to 10^{-5} M). Equilibrium was attained within 20 min. The amount of protons adsorbed was then calculated from the difference between the initial and equilibrium pH values. For these adsorption studies, a jacketed 250-mL Pyrex beaker fitted with a lucite cover with holes for electrodes, a N_2 inlet, and a thermometer was used. The solution was stirred at a constant rate and temperature control was provided by a GCA 250 water circulating system.

II.3 Preliminary Studies on Direct Preconcentration of Metal Ions on an XAD-7 Column

During work with the adsorption of metal-TPPS₄ complexes on XAD-7 (see Appendix II), it was discovered that uncomplexed metal ions were retained directly on the resin. Preliminary studies on the direct retention were then undertaken. The test ions and concentrations used were: Cd(II) and Mn(II), 1.00 μ g/L; Cu(II), Pb(II), Fe(II) and Cr(III), 5.00 μ g/L; Co(II), 10.0 μ g/L, Ni(II), 20.0 μ g/L; total metal ion concentration, 52.0 μ g/L. These concentrations were selected mainly on the basis of GFAAS sensitivity. Columns with 1 x 7 cm resin beds (1.3 g of 20-50 mesh XAD-7) were used.

(a) Effect of pH: 100.0-mL aliquots of 0.010 M NH_4OAc adjusted from pH 1.0 to 12.0 (with dilute HNO_3 , dilute $HOAc$, aqueous ammonia or dilute KOH) were spiked with trace metal ions to the desired concentrations. The test solutions were then passed through the columns at a flow rate of 1 mL/min. The column effluents were collected and analysed by GFAAS. The percent retention for each ion was calculated at each pH value.

(b) Effect of anions: The effect of NH_4OAc , NH_4NO_3 , NH_4Cl , NH_4SCN , NH_4Br (each 0.010 M) on the retention of metal ions was determined at various pH values. For example, 100.0-mL aliquots of the electrolyte solutions at pH 2.0 were spiked with the metal ions. The solutions were percolated and the column effluents collected and analysed by GFAAS as above. The percent retention was calculated for each ion. The experiment was repeated at pH 5.0, 8.0 and 9.0.

(c) Effect of flow rate: 100.0-mL aliquots of 0.010 M NH_4OAc at pH 5.0 were spiked with the metal ions and the solutions passed through the columns at flow rates ranging from 0.86 to 5.6 mL/min. The column effluents were collected and analysed by GFAAS and the percent retention was calculated at each flow rate. The experiment was repeated at pH 8.0.

(d) Elution of retained metal ions: Various solvents were tried: 25%, 10% and 1% v/v HNO_3 ; 1% v/v HCl ; 1% v/v NH_4NO_3 (elution rate: 1 mL/min). Elution profiles for the various metals were obtained and from these, the volume of eluant required for quantitative elution was determined. Although the percent recovery could be obtained from the elution profiles, the summation of errors over the aliquots could lead to a large overall error. Therefore, more accurate percent recovery values were obtained as follows. A test solution containing 0.200 $\mu\text{g/L}$ each of $\text{Cd}(\text{II})$ and $\text{Mn}(\text{II})$; 1.00 $\mu\text{g/L}$ each of $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$, and 2.00 $\mu\text{g/L}$ each of $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ in 0.010 M NH_4OAc at pH 8.0 was prepared. A 100.0-mL aliquot was passed through the column at 1 mL/min and the retained metal ions were eluted with 10.0 mL of 1% v/v HNO_3 (1 mL/min). The eluant was analysed by GFAAS to yield percent recovery of metal

ions. The experiment was repeated at pH 5.0.

II.4 Studies on Mechanism of Retention of Metal Ions on XAD-7

(i) Potentiometric Titrations

Potentiometric titrations with 0.1 F standard NaOH were done to reveal the possible presence of unesterified carboxylic or other acid functional groups on the resin. Such sites could account for metal-ion uptake. Extra caution was taken in the cleaning procedure of the resin to ensure complete removal of the HNO_3 (see Section II.1). Titrations were done in the jacketed vessel described earlier. DDW was boiled to remove dissolved CO_2 and a blanket of N_2 gas was maintained over the solution during the titration (at $22.0 \pm 0.5^\circ\text{C}$). Two types of titrations were done, a classical potentiometric and a single-point titration.

(a) Classical potentiometric titration: 100.0 mL of 1.045×10^{-2} F HNO_3 were titrated potentiometrically with 0.1055 F NaOH. This titration was followed immediately by the titration of 10.00 g of XAD-7 resin (100-200 mesh) suspended in exactly the same amount of HNO_3 . The rate of titrant addition in both titrations was 1.00 mL/2 min except in the neighbourhood of the endpoint (i.e., 90% to 110%) where the rate was 0.100 mL/5 min. The titrant was added by means of an Eppendorf pipette so that a fixed volume (i.e., 100 μL) could be delivered with a high degree of precision. The two titration curves obtained were compared to ascertain any difference in endpoint volumes that could be ascribed to the presence of free carboxylic (or other) acid groups.

(b) Single-point titration: Because the titration of HNO_3 in the presence of XAD-7 resin was not done under equilibrium conditions,

thereby creating ambiguity in interpretation, a single-point titration was done at the endpoint. To 10.00 g of XAD-7 (100-200 mesh) in 100.0 mL of 1.055×10^{-2} F HNO_3 , were added 10.52 mL of 0.1003 F NaOH. The solution was kept stirred under N_2 gas cover and the pH was measured with time until no further significant change occurred (i.e., until equilibrium was attained).

Interpretation of these potentiometric titration experiments is made under RESULTS AND DISCUSSION.

(ii) Infrared Studies

Infrared spectra of XAD-7 resin and XAD-7 resin treated with 1% v/v HNO_3 were obtained to show possible protonation of the carbonyl groups. Acid treatment of XAD-7 resin involved the following. To about 5 g of the XAD-7 resin were added 100 mL of 1% v/v HNO_3 , the mixture was stirred for one hr and then filtered. The resin was washed with about 150 mL of 1% v/v HNO_3 and portions were dried under vacuum at 80° or 20°C or simply in a desiccator. The acid-treated and untreated resin were prepared as KBr discs.

(iii) Adsorption Isotherm Studies

Cu(II) was chosen as the model ion for these studies. Because retained metal ions can be eluted readily with dilute acid solution, proton adsorption isotherms were also obtained. The batch-equilibration procedure (discussed earlier) was used in which aliquots of the test solutions (25.00 mL for Cu(II) and 100.0 mL for protons) at increasing concentration of the ions were required. The concentration range suitable for a particular set of adsorption conditions had to be determined experimentally in trial runs. The time required for adsorption

equilibrium for protons was established by monitoring the solution pH with time. For Cu(II), attainment of adsorption equilibrium was determined by withdrawal of small portions (e.g., 50 μ L) of the Cu(II) solution at fixed time intervals for GFAAS or flame AAS analysis. In general, 30 min was adequate for the attainment of equilibrium.

The Cu(II) adsorption isotherms were obtained at room temperature ($22 \pm 1^\circ\text{C}$). The effects of various parameters were determined as follows.

- (a) Effect of pH: 25.0-mL aliquots of 0.010 M NH_4OAc (at pH 6.0) were spiked with increasing concentrations of Cu(II). The test solutions were transferred to polypropylene test-tubes containing 0.500 g of XAD-7 (20-50 mesh). After agitation for 4 hr on a mechanical shaker, the test solutions were analysed by GFAAS or flame AAS for equilibrium Cu(II) concentrations, from which the adsorption isotherm could be obtained. The experiment was then repeated at pH 4.8 and pH 3.8.
- (b) Effect of anions: The experiment described in part (a) was repeated with Cu(II)-spiked aliquots of 0.010 M NH_4Cl and 0.010 M NH_4NO_3 each at pH 6.0.
- (c) Effect of ionic strength: 25.0-mL aliquots of 0.010 M NH_4OAc /0.050 M NH_4Cl (at pH 6.0) were spiked with increasing concentrations of Cu(II). From this point, the procedure was exactly as in part (a): The experiment was then repeated at higher concentrations of NH_4Cl (i.e., 0.10 M and 0.75 M).
- (d) Effect of particle size: The experiment of part (a) was repeated using 60-100 and 100-200 mesh XAD-7.

For proton adsorption, the following parameters were studied.

(a) Effect of particle size: 100.0-mL aliquots of dilute HNO_3 solutions of increasing concentration and 2.00-g portions of XAD-7 (20-50 mesh) were placed in a 250-mL jacketed Pyrex beaker with a lucite cover. The test solutions were kept under N_2 cover at 26.0°C and stirred at a constant rate. The proton adsorption isotherm was obtained from the differences between the initial pH values and the equilibrium pH values of the HNO_3 solutions. The experiment was repeated for 0.500 g of 60-100 and 100-200 mesh resin.

(b) Effect of temperature: The effect of temperature was determined with two different mesh sizes: (i) 20-50 mesh (2.00-g portions, temperature settings at 7.0 , 26.0 and 38.0°C); and (ii) 60-100 mesh (0.500-g portions at 11.0 , 26.0 and 42.0°C). The experiments were done as described in part (a) immediately above.

(iv) Distribution Ratios

To determine distribution ratios, the eight metal ions were divided into groups of four: Cr(III), Fe(III), Ni(II) and Co(II) in one group and Cu(II), Cd(II), Mn(II) and Pb(II) in the other. The concentration of each metal ion was $20 \mu\text{g/L}$. The total concentration of trace metals resembles that in natural waters. The distribution ratios were determined at various pH values for 20-50 and 60-100 mesh resin. The procedure involved was as follows: 25.0 mL aliquots of 0.010 M NH_4OAc (adjusted to pH ranging from 1.0 to 13.0 with dilute HNO_3 , dilute HOAc, aqueous ammonia, or dilute KOH) were spiked with the metal ions and transferred to polypropylene test-tubes containing 0.500 g of 20-50 or 60-100 mesh XAD-7. After 4 hr of agitation, the equilibrium concentrations of the metal ions were determined by GFAAS and the

distribution ratios calculated at each pH value.

II.5 Studies on the XAD-7 Column Operation

(i) Breakthrough Curves

A breakthrough curve is a graphical representation of [effluent concentration/initial concentration] x 100% versus effluent volume. Experimentally, these curves can be determined by analysis of small aliquots of effluent (e.g., 0.50 mL) for the analyte at various cumulative volumes of the effluent (e.g., 20 mL, 40 mL, 60 mL, etc.). The effects of various parameters on the breakthrough curves were determined.

(a) Effect of particle size and metal-ion concentration: Three solutions of 0.010 M NH_4Cl adjusted to pH 8.0 with aqueous ammonia were spiked with Cu(II) to concentrations of 5.00 $\mu\text{g/L}$ and 1.00 and 10.0 mg/L and were then passed through three 1.0-g (1 x 6 cm) XAD-7 columns (20-50 mesh) at a flow rate of 1 mL/min. The effluents were analysed by GFAAS at fixed volume intervals. The experiment was repeated with 60-100 mesh resin at the same bed size.

(b) Effect of flow rate: 0.010 M NH_4Cl at pH 8.0 was spiked with Cd(II), Co(II), Cu(II), Mn(II), Ni(II) and Pb(II) to a concentration of 5.00 $\mu\text{g/L}$ for each ion (total metal ion concentration: 30 $\mu\text{g/L}$) and was then passed through a 1.0 g (1 x 6 cm) XAD-7 column (20-50 mesh) at flow rates of 1 to 4 mL/min. Breakthrough curves were obtained for each metal ion at each flow rate. For Cr(III) and Fe(III), 0.010 M NH_4OAc (at pH 5.0) was spiked to a concentration of 5.00 $\mu\text{g/L}$ for each ion. Breakthrough curves for Cr(III) were also obtained at pH 4.3 and 6.3. For low concentrations of Cr(III) (0.50 $\mu\text{g/L}$), $^{51}\text{Cr(III)}$ was used to provide the required sensitivity.

- (c) Effect of alkali-metal and alkaline-earth salts (i.e., ionic strength, μ): Natural waters contain high concentrations of alkali-metal and alkaline-earth salts (i.e., $\mu \approx 0.70$ in seawater). The effect of ionic strength on adsorption of trace metal ions on XAD-7 was investigated. The high concentration of salt necessitated the use of a radioisotope traces. $^{64}\text{Cu}(\text{II})$ was chosen as the model ion. Three different experiments were done. (i) Test solutions of NaCl ($\mu = 0.01, 0.2, 0.5$ and 0.8 at pH 8.0) were spiked with $^{64}\text{Cu}(\text{II})$ ($1 \mu\text{g}/\text{L}$) and passed through columns (1×3 cm, 0.5 g, 80-100 mesh and 1×6 cm, 1.0 g, 20-50 mesh) at $1 \text{ mL}/\text{min}$. The breakthrough curve for each test solution was determined by measuring the γ activity of $^{64}\text{Cu}(\text{II})$ in the effluents. (ii) Test solutions of the same pH, ionic strength and $^{64}\text{Cu}(\text{II})$ concentration were spiked with humic substances to $10 \text{ mg}/\text{L}$. After equilibration for 12 hr, the solutions were passed through columns at $1 \text{ mL}/\text{min}$ and the breakthrough curves determined as above. (iii) Natural seawater from which humic substances had been removed (see Section II.5. (ii)) was used to prepare test solutions by dilution with DDW to 2, 10, 25 and 50%. These solutions and an undiluted (100%) solution were adjusted to pH 8.0 and spiked with $^{64}\text{Cu}(\text{II})$ to $1 \mu\text{g}/\text{L}$. After 12 hr, the solutions were passed through columns at a rate of $1 \text{ mL}/\text{min}$ and the breakthrough curves determined.
- (d) Breakthrough curves for alkali and alkaline-earth ions: Test solutions containing $10 \text{ mg}/\text{L}$ each of Na^+ and $\text{Ca}(\text{II})$ in $0.010 \text{ M NH}_4\text{Cl}$ (at pH 8.0) were passed through 1.0 g (1×6 cm) 60-100 mesh and 0.5 g (1×3 cm) 80-100 mesh columns at a flow rate of $1 \text{ mL}/\text{min}$. Breakthrough curves for Na^+ and $\text{Ca}(\text{II})$ for each column were determined by flame emission spectrometry.
- (e) Effect of humic substances: Because natural waters contain organic

materials collectively known as humic substances at relatively high concentrations (e.g., 10 mg/L) (80), the effect of this matrix constituent on the column adsorption of metal ions was investigated. NH_4Cl (0.010 M, pH 8.0) was spiked with Cd(II), Co(II), Cu(II), Mn(II), Ni(II) and Pb(II) to concentrations of 5.00 $\mu\text{g/L}$ for each ion (total metal ion concentration: 30.0 $\mu\text{g/L}$). Humic material was added to a final concentration of 10 mg/L and the solutions were left to equilibrate for at least 24 hr. The test solution was then passed through a 1.0 g (1 x 6 cm) XAD-7 column (20-50 mesh) at 2 mL/min. Breakthrough curves for each metal ion were obtained. The experiment was repeated at pH 6.3 for Cr(III) and Fe(III) (5.00 $\mu\text{g/L}$ of each).

(ii) The Two-Column Technique

From the above experiments it was observed that the presence of humic substances has a large negative effect on the adsorption of metal ions on XAD-7. It is necessary to remove this matrix interference before the XAD-7 column can be applied to the preconcentration of trace metals in natural water samples. This was accomplished by the following two-column procedure. In this procedure, the humic substances are first removed by the percolation of the preacidified sample through a precolumn of the XAD-7-resin at pH 1.6-1.7 (144). The effluent containing the trace metals is then buffered to pH 8.0 and passed through the XAD-7 analytical column to preconcentrate the trace metals. The following experiments were performed to demonstrate the application of the two-column approach. Aliquots of 0.010 M NH_4Cl (at pH 8.0, 100.0 mL) were spiked to a concentration of 20 $\mu\text{g/L}$ with each of Cr(III), Fe(III),

Cd(II), Co(II), Cu(II), Mn(II), Ni(II) and Pb(II) (total metal ion concentration: 160 $\mu\text{g/L}$). The solutions were also spiked with humic substances to a concentration of 10 mg/L and were left to equilibrate for 48 hr. After acidification to pH 1.7, the solutions were allowed to stand for another 48 hr to ensure dissociation of the metal humates, just as is done for real samples. Preconcentration at 1 mL/min through a pre-column (1.0 g, 1 x 6 cm, 60-100 mesh) followed. The pH of the effluents was adjusted to 6.3 for the trivalent and 8.0 for the divalent ions and the effluents were immediately passed through analytical columns (1.0 g, 1 x 6 cm, 60-100 mesh) at a flow rate of 1 mL/min. The adsorbed metal ions were then eluted with 10.0 mL of 1% v/v HNO_3 (1 mL/min). The percent recovery for the various metal ions was obtained by GFAAS analysis of the acid eluant. The experiment was repeated but without acidification of the test solutions and without the pre-column treatment. The two sets of recovery data were then compared to show the effect of pre-column treatment on recovery of the metal ions in the presence of humic substances.

(iii) Elution Recovery and Preconcentration Factor

The elution volume is important in determining the preconcentration factor that can be attained. Therefore, the effect of column bed size and resin mesh size on the elution volume was studied.

(a) Effect of column bed size: 100.0 mL aliquots of 0.010 M NH_4OAc (at pH 8.0) were spiked to 1.00 $\mu\text{g/L}$ of Cd(II) and Mn(II), 2.00 $\mu\text{g/L}$ of Pb(II), Cu(II), Cr(III) and Fe(III) and 5.00 $\mu\text{g/L}$ of Co(II) and Ni(II) (total metal ion concentration: 20.0 $\mu\text{g/L}$). The solutions were percolated through columns at a rate of 1 mL/min. Three sizes of

column bed were used: 0.5 g (1 x 3 cm), 80-100 mesh; 1.3 g (1 x 7 cm), 80-100 mesh; 2.7 g (1 x 15 cm), 80-100 mesh. The eluant was 1% v/v HNO_3 or HCl (1 mL/min) and was collected in 0.50-mL aliquots. The aliquots were analysed by GFAAS to yield elution profiles for each column.

(b) Effect of particle size: The test solutions were prepared exactly as in the previous section. They were passed through 1 x 6 cm (1.0 g) columns containing resin of mesh size 20-50, 60-80 or 80-100. The eluant was 1% v/v HNO_3 or HCl. The 0.50 mL aliquots were analysed by GFAAS as above to obtain elution profiles.

(c) Removal of entrained salts from XAD-7 columns. The above elution procedures are applicable to freshwater samples. For seawater, the salt content entrained in the void volume of the column requires removal before the elution of the metal ions and GFAAS measurement. NH_4NO_3 (0.010 M) at pH 8.0 was used to rinse the columns after percolation of 50.0-mL of seawater samples previously buffered to pH 8.0 with NH_4Cl /ammonia. The samples were percolated through a 1 x 3 cm (80-100 mesh) column at a flow rate of 1 mL/min. The entrained salts were then eluted with the NH_4NO_3 solution (1 mL/min) which was collected in 0.50-mL aliquots and analysed by flame emission spectrometry for Na^+ . In this way the volume of NH_4NO_3 required to rinse the column free of entrained salts could be determined.

(d) Effect of NH_4NO_3 rinsing on recovery and elution profile. It was necessary to show the effect, if any, that rinsing with NH_4NO_3 has on the recovery and elution profile of ions adsorbed from solutions of high ionic strength. An aliquot (200.0 mL) of 0.70 M NaCl at pH 8.0 was spiked with $^{64}\text{Cu}(\text{II})$ to 1 $\mu\text{g}/\text{mL}$ and passed through a 1 x 3 cm

(80-100 mesh) column at a rate of 1 mL/min. The column was then rinsed with 10 mL of 0.010 M NH_4NO_3 (at pH 8.0) and the $^{64}\text{Cu(II)}$ eluted with 1% v/v HNO_3 (1 mL/min). The eluant was collected in 0.50 mL portions and analysed by γ -ray spectrometry to yield the elution profile for $^{64}\text{Cu(II)}$.

II.6 Applications

(i) Application to Lakewater

Before application to natural freshwater samples, the two-column XAD-7 method was tested with a synthetic sample. The synthetic sample contained 10 mg/L of humic substances; 0.100 $\mu\text{g/L}$ of Cd(II) and Mn(II) ; and 1.00 $\mu\text{g/L}$ each of Cr(III) , Fe(III) , Ni(II) , Co(II) , Cu(II) and Pb(II) (total metal ion concentration: 6.20 $\mu\text{g/L}$). The solution also contained NH_4Cl (0.010 M) and was set at pH 8.0. After standing for 48 hr, it was acidified to pH 1.7 and left to stand for an additional 48 hr. Both the precolumn and the analytical column contained 0.50 g of 80-100 mesh XAD-7 resin (1 x 3 cm bed). Aliquots (200.0 mL) of the acidified synthetic solution were percolated through the precolumn at 1 mL/min to remove humic substances. The effluents were then adjusted to pH 8.0 with aqueous ammonia and passed through the analytical column at 1 mL/min. The adsorbed metal ions were eluted with 5.00 mL of 1% v/v HNO_3 and the eluants were analysed by GFAAS to obtain the percent recovery of each metal ion.

Three freshwater samples were obtained from the Canada Centre for Inland Water (CCIW). These samples included a Hamilton Harbour sample and two Lake Ontario samples, one a nearshore sample (Station 14) and the other an offshore sample (Station 302). The water samples were centrifuged to remove suspended particulates, acidified to pH 1.7 and

stored in polypropylene bottles. Three different analytical procedures were applied in the analysis of these samples. Direct GFAAS was used when permitted by the metal ion concentrations. The other two procedures involved preconcentration by Chelex-100 and the XAD-7 two-column method.

(a) Chelex-100 method: Purification of the Chelex-100 resin and column packing and conditioning have been previously described (Section II.1 and Section II.2.(i)). The resin was used in the NH_4^+ form in a 1 x 6 cm resin-bed column. Aliquots (200.0 mL) of the Station 14 and 302 samples were buffered to pH 5.4 with 0.010 M $\text{NH}_4\text{OAc}/\text{HOAc}$ and passed through Chelex-100 columns at a flow rate of 1 mL/min. The retained metal ions were eluted at 1 mL/min with 25.0 mL of 14% v/v HNO_3 . The eluants were analysed by GFAAS with reference to standard calibration curves to give the concentrations of the trace metals.

(b) XAD-7 two-column method: The precolumn and analytical column were as previously described for the synthetic samples. Aliquots (200.0 mL) of the two preacidified lakewater samples were passed through the precolumn to remove humic substances. The effluents were adjusted to pH 8.0 and passed through the analytical column. The adsorbed metal ions were eluted with 5.00 mL of 1% v/v HNO_3 . As usual, flow rates were 1 mL/min. The eluants were analysed by GFAAS using standard calibration curves. The analysis was then repeated using the method of standard additions. The standard spikes were added to the aliquots of acidified lakewater before they were passed through the precolumn.

(ii) Application to Seawater

The seawater reference material NASS-1 (see Section II.1), was

used to test the two-column method for natural waters of high salinity. The sample had been previously acidified to pH 1.7 and stored in polypropylene bottles. The procedure for processing the sample was as described previously for the lakewater samples (XAD-7 two-column method) except that 500.0 mL aliquots were used for the Co(II) determination and 10 mL of 0.010 M NH_4NO_3 were used to rinse the analytical column of entrained salts prior to elution of the absorbed trace metals. The method of standard additions was not applied to NASS-1 owing to the restriction on sample availability.

An Atlantic coastal seawater (Sandy Cove, Nova Scotia) was also analysed. This sample had been filtered and acidified to pH 1.7 as described previously. For purposes of comparison, both the Chelex-100 and XAD-7 two-column methods were used. The Chelex-100 procedure was as described previously except that the method of standard additions was used, wherein the standard metal spikes were added to the acidified seawater aliquots before pH adjustment for the Chelex-100 column. Also, prior to elution of the ions with 14% v/v HNO_3 , the column was rinsed with 10 mL of DDW, followed by 10 mL of the pH 5.4 buffer.

The XAD-7 two-column procedure was as described for the NASS-1 reference material except that 200.0-mL aliquots of the Sandy Cove sample were used throughout. Both the standard calibration curve and standard additions methods were used.

(iii) The Analytical Blank

In trace metal determinations, a "blank" control must be obtained to give validity to the analytical data. Ideally, the "blank" samples should be identical to the test sample except that

the analyte is not present. All sample matrix components and chemical reagents should be present in the blank. However, as pointed out by others (145-147), it is difficult to match the matrix components of natural water samples and therefore an approximation is necessitated. Often, a volume of DDW equal to the sample volume is taken and subjected to the same amounts of external chemical reagents and chemical and instrumental procedures as the sample. This approximation was used in the present work. For example, with the XAD-7 two-column procedure, the DDW blank aliquot was acidified to pH 1.7 and passed through the precolumn. The effluent was then buffered to the appropriate pH and passed through the analytical column. The analytical column was stripped with 1% v/v HNO_3 and the acid eluant was analysed by GFAAS to obtain the level of metal-ion contamination (i.e., the "blank" values). These solution "blank" values were then used to correct the trace metal concentrations obtained for the natural water samples. For the "blank" solutions corresponding to the seawater samples, it was not necessary to approximate the salt matrix because the sample eluant from the analytical column is essentially a solution of the trace metals in 1% v/v HNO_3 , as is the "blank" solution.

III. RESULTS AND DISCUSSION

III.1. Preliminary Studies on Direct Preconcentration of Metal Ions on an XAD-7 Column

During the initial studies on the preconcentration of metal-TPPS₄ complexes on XAD-7 by adsorption (see Appendix II), it was noticed that uncomplexed metal ions were directly retained on the resin. This discovery was surprising and in a subsequent search of the literature, one report was found on the direct retention of metal ions on XAD-7. In this work, Fritz and Millen (129) reported the extraction of Au(III) from 1 M HCl onto the resin. Recently, Aiken and Walton (108,127) suggested that XAD-7 possesses a low capacity (in the order of 10 µeq/g) for inorganic ions but follow-up studies were not reported.

The direct retention of metal ions on XAD-7 was deemed not only interesting but also potentially significant, especially with regard to preconcentration of trace metal ions. For example, direct preconcentration on XAD-7 could be simple in that no organic chelating agent would be required; it could yield large preconcentration factors because a column approach would be feasible; low detection limits should be achievable because a simple approach should lead to less contamination; and it should be economical. Consequently it was decided to investigate XAD-7 as a medium for the direct preconcentration of trace metals. The effect of pH, anions and flow rate, on metal-ion retention and the means of elution of retained metal

ions are discussed below. Complementary studies done by batch equilibration are described later in Section III.2.

(a) Effect of pH. The effect of pH on the retention of metal ions on a column of XAD-7 resin is summarized in Table IX. For a divalent ion; maximum retention (85-100%) occurred in the pH range 7-9, for tri-valent ions (Fe(III) and Cr(III)), maximum retention (> 85%) occurred in the pH range 4-6, although even up to pH 10 retention was better than 80%. In Figure 5, the effect of pH on the retention of Ni(II), Pb(II), Cr(III) and Fe(III) is shown.

Solution pH can affect retention in two ways: (1) by alteration of the distribution of simple, complexed species among $M(H_2O)_x^{+n}$, $M(OH)_x^{+n-x}$, $M(\text{acetate})_x^{+n-x}$ and $M(NH_3)_x^{+n}$, each of which may have a different affinity for the resin, and/or (ii) by alteration of the resin in a way to affect its retention properties, for example, by occupation of retention sites by protons at low pH and by hydroxyl ions at high pH. The effect of pH is most significant in the pH range 2-6. The general decline in retention above pH 10 may be caused by displacement of metal ion species from retention sites by hydroxyl ions, or by formation of colloidal metal-hydroxide species which are not retained on the column, even by physical entrainment. The decline is most notable for Pb(II), for reasons not known at this time.

(b) Effect of anions. Whether at pH 2.0, 5.0 or 8.0, the effect of various anions is small (Table X), with the unexplained exception of the effect of NH_4CNS on the retention of Fe(III) at pH 2.0. This fact suggests that the affinity of the resin for various simple complexes of the metal ions is about the same at a particular pH.

TABLE IX. Percent Retention of Metal Ions
on a XAD-7 Column at Various Solution pH Values^a

pH	Retention ^a (%)							
	Fe(III)	Cr(III)	Cu(II)	Pb(II)	Ni(II)	Co(II)	Mn(II)	Cd(II)
2.0	26±3	11±2	11±1	26±5	4±2	9±2	15±3	6±5
3.0	84±2	56±2	33±5	39±6	20±2	20±3	23±5	36±2
4.0	93±3	91±7	80±6	53±4	30±5	39±3	36±4	40±2
5.0	89±1	86±2	95±1	91±5	56±5	53±7	51±7	57±9
6.0	85±4	85±5	92±3	97±2	96±4	88±5	78±2	83±11
7.0	79±3	82±1	88±1	100±1	100±1	100±1	94±6	93±7
8.0	82±3	80±2	88±1	100±1	100±1	100±1	97±2	100±1
9.0	83±4	79±4	88±3	93±4	100±1	92±2	98±4	100±1
10.0	85±1	81±5	92±1	90±3	93±6	87±1	85±2	91±3
11.0	76±2	78±2	79±10	53±6	85±5	79±3	78±5	81±6
12.0	61±3	68±2	75±1	14±3	78±2	74±2	64±2	79±3

^a 1 x 7 cm XAD-7 column (20-50 mesh); 100 mL of test solution containing 1 to 20 µg/L of the metal ions in 0.010 M NH₄OAc; flow rate 1 mL/min. Data represent average of at least three results.

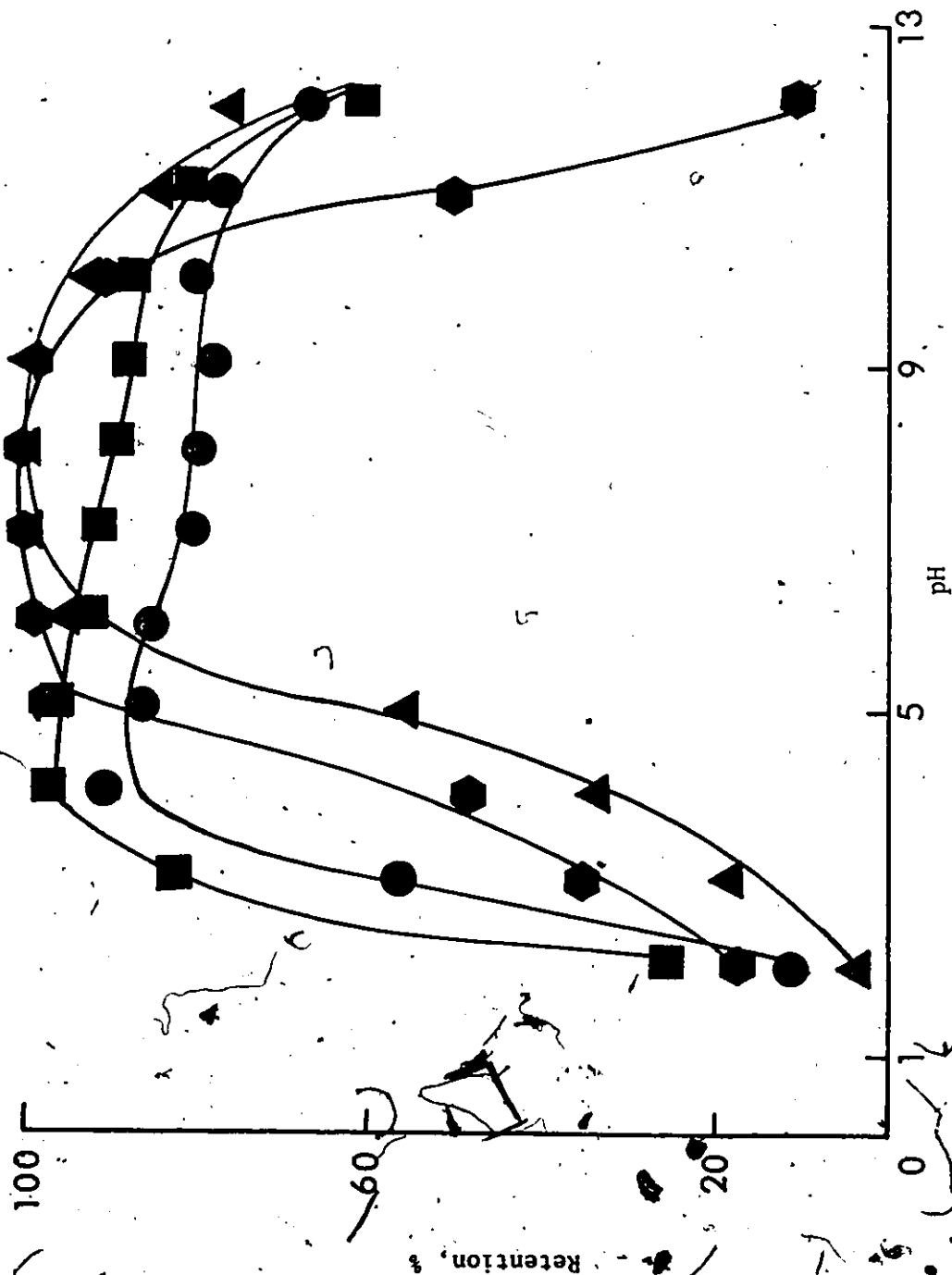


Figure 5. Effect on pH on the retention of Ni(II) (▲, 20 µg/L), Pb(II) (●, 5 µg/L), Cr(III) (●, 5 µg/L) and Fe(III) (■, 5 µg/L)

on a 1x7 cm XAD-7 column (20-50 mesh). Flow rate = 1ml/min.

TABLE X. Effect of Anions on Percent Retention of
Metal Ions on XAD-7 Column at pH 2.0, 5.0 and 8.0^a

	<u>Retention (%)</u>							
	<u>Fe(III)</u>	<u>Cr(III)</u>	<u>Cu(II)</u>	<u>Pb(II)</u>	<u>Ni(II)</u>	<u>Co(II)</u>	<u>Mn(II)</u>	<u>Cd(II)</u>
<u>Matrix(pH2.0)</u>								
0.010MNH ₄ OAC	26±3	11±2	11±2	26±5	3±2	9±2	15±3	6±5
0.010MNH ₄ NO ₃	11±4	19±5	5±3	5±4	8±3	8±6	4±2	4±2
0.010MNH ₄ CNS	<u>53±6</u>	28±4	11±2	14±8	9±3	8±3	15±2	6±3
0.010MNH ₄ Cl	16±7	16±1	13±6	9±3	4±2	3±2	15±3	8±3
0.010MNH ₄ Br	20±7	16±3	7±5	3±1	11±4	9±4	14±7	8±1
<u>Matrix(pH5.0)</u>								
0.010MNH ₄ OAc	93±3	91±1	80±6	73±4	30±6	39±3	36±4	40±2
0.010MNH ₄ NO ₃	94±2	93±1	91±4	50±2	33±9	41±2	42±4	37±2
0.010MNH ₄ CNS	82±7	93±1	92±4	88±1	52±2	55±1	55±5	40±3
0.010MNH ₄ Cl	87±2	89±3	90±4	50±5	37±3	37±3	39±2	31±2
0.010MNH ₄ Br	94±2	92±2	91±4	44±9	39±2	39±2	38±6	35±1
<u>Matrix(pH8.0)</u>								
0.010MNH ₄ OAC	82±2	81±2	89±1	100±0	100±1	100±1	97±2	98±3
0.010MNH ₄ NO ₃	78±5	84±4	84±2	88±3	93±1	100±1	100±1	96±5
0.010MNH ₄ CNS	87±1	85±3	86±4	94±2	93±2	100±1	100±1	96±3
0.010MNH ₄ Cl	84±7	81±2	88±1	89±9	97±1	100±1	100±1	97±2
0.010MNH ₄ Br	83±5	79±3	88±4	82±6	100±1	100±1	100±1	100±1

^a 1 x 7 cm XAD-7 column (20-50 mesh), 100 mL of test solution containing 1 to 20 µg/L of the metal ions; flow rate = 1 mL/min. Data represent average of at least three results.

The much reduced retention at pH 2 indicates that the interaction of protons with the resin is the overriding factor in strongly acidic solutions.

(c) Effect of flow rate. The effect of flow rate (percolation rate) of the sample is illustrated in Figure 6. It appears that the flow rate, when varied from 0.8 to 5.6 mL/min, has little effect on percent retention, provided that the pH is in the optimal range for the particular charge-type ion (pH 7-9 for divalent ions and pH 4-6 for trivalent ions). At pH 8, only 50-70% of Cr(III) and Fe(III) was retained at flow rates of 1.3-5.6 mL/min compared to 80-85% at flow rates of 0.8-1.0 mL/min. These values represent overall retention over 100 mL of sample, without regard to breakthrough volumes. Breakthrough studies are described in Section III.3, (i).

Although the flow rate has no effect in the appropriate pH range for quantitative retention, it may well play a role at low and high pH values, in conjunction with the high concentration of hydrogen and hydroxyl ions referred to in (a). The time required to reach equilibrium is about 20-30 min and is invariant with pH (see Section III.2(iii) below). Since the holdup volume of the column is 4 mL, and the dead volume 1 mL, the flow rates of 0.8 to 5.6 mL/min represent residence times of 4 to 0.5 min, times far short of equilibrium conditions. Therefore, slower flow rates (e.g., 1 mL/30 min) could well increase the percent retention at the extremes of the pH range. Such slow flow rates are impractical, however, and were not examined.

(d) Elution of retained metal ions. As described before, little retention of metal ions occurs below pH 2.0. Therefore, a solution of dilute mineral acid should be effective for the elution of metal ions retained at higher pH. Elution profiles for various metal ions with 1% v/v HNO₃ are shown in Figure 7. In general, quantitative elution of all metal ions

* The 4 mL holdup volume represents the sum of the void volume, pore volume and dead volume of the column.

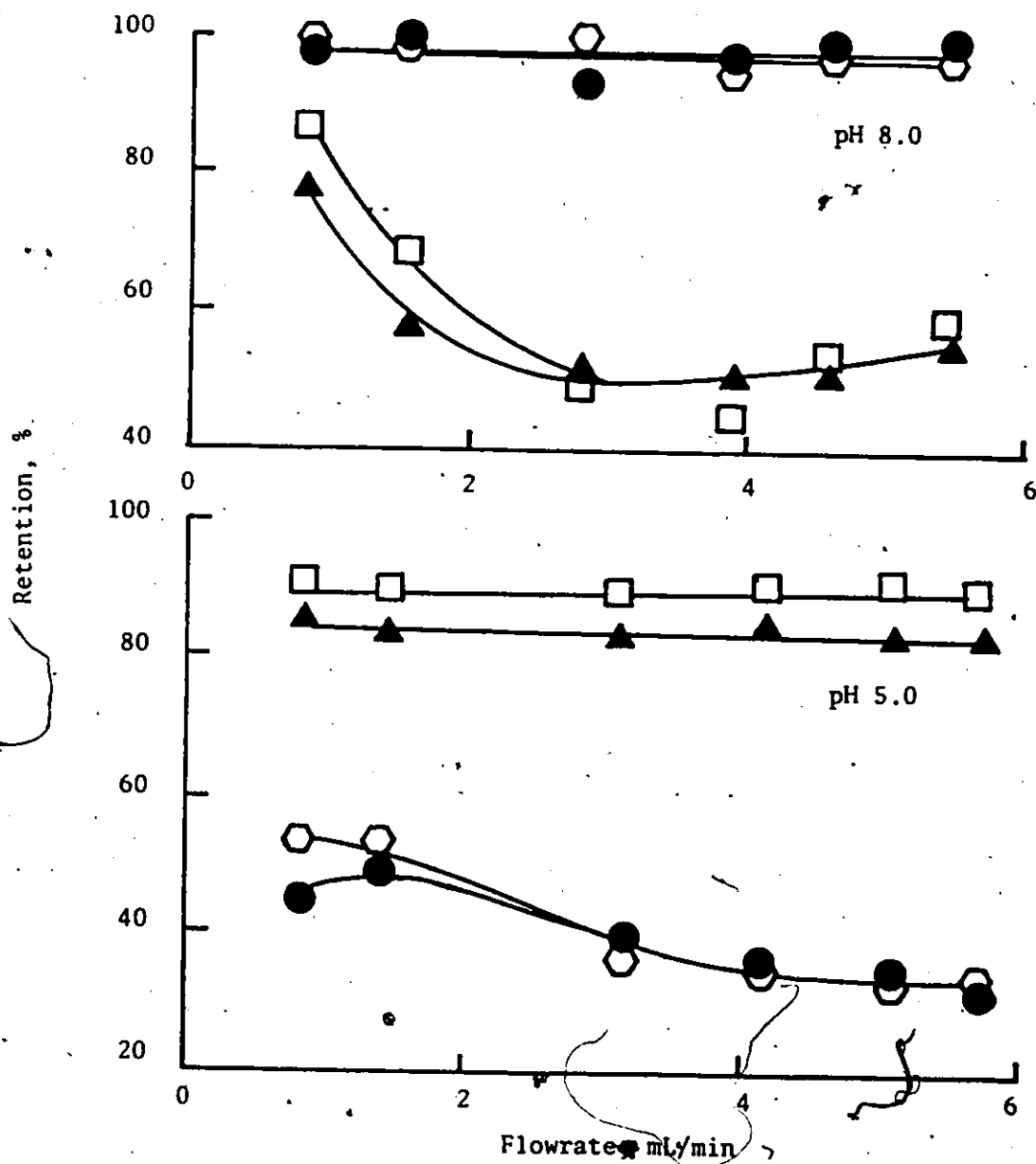


Figure 6. Effect of flow rate on the retention of Fe(III) (□, 5 μ g/L), Cr(III) (▲, 5 μ g/L), Mn(II) (○, 1 μ g/L) and Cd(II) (●, 1 μ g/L) on a 1x7 cm XAD-7 column (20-50 mesh). 100 mL of test solution (0.010MNH₄DAC) was taken.

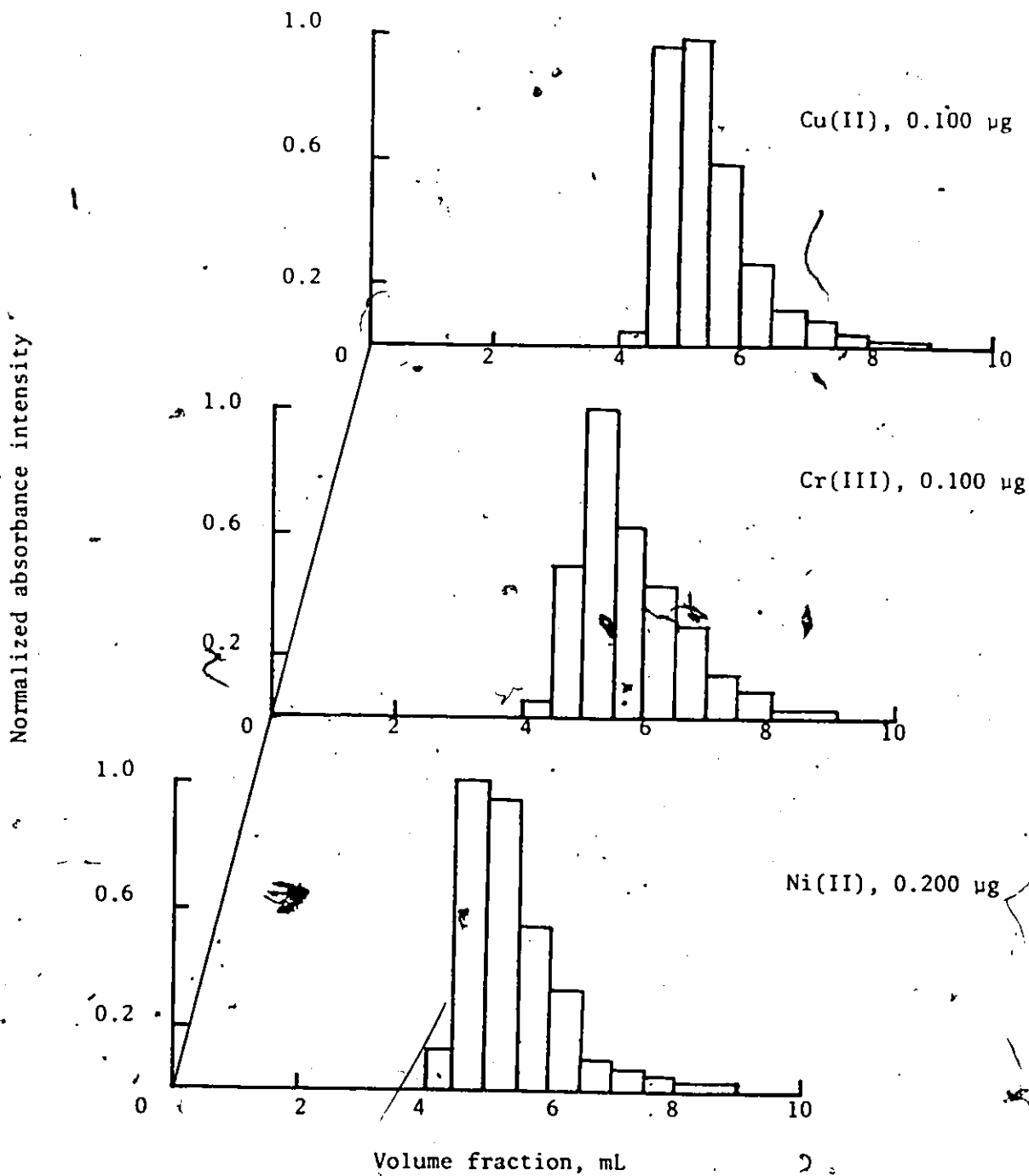


Figure 7. Profiles for the elution of some metal ions from a 1x7 cm XAD-7 column (20-50 mesh) by 1% v/v HNO_3 . Elution rate = 1 mL/min.

could be accomplished within a relatively small volume interval (e.g., 4.0 to 9.0 mL) for a 1 x 7 cm column. This fact indicates that large preconcentration factors could probably be achieved.

Higher concentrations of HNO_3 (10 and 25% v/v) were unsatisfactory owing to the high blank values. The metal ions could also be eluted efficiently with 1% v/v HCl but not with 1% v/v NH_4NO_3 . These observations suggest that elution is proton specific, which is in accord with the effect of pH on direct retention.

The final aspect of the preliminary work involved testing the complete retention/elution cycle with a 0.01M NH_4OAc solution spiked with known quantities of all of the metal ions (0.2 to 2.0 $\mu\text{g/L}$) together. The recovery values (Table XI) are quite satisfactory, pointing to the potential usefulness of XAD-7 for the preconcentration of trace metals, at least for simple aqueous solutions. Natural waters, however, contain a multitude of organic and inorganic ligands which might compete with the preconcentration medium for trace metals, thereby significantly reducing the retention of metal ions. The effects of such complexing matrices on retention and recovery of metal ions are discussed later in Sections III.3.(i) and III.3.(ii).

The data in Table XI represent a preconcentration factor of 10. This factor is somewhat arbitrary since it is dependent on the sample size as well as on the eluant volume. Thus, a larger sample size would lead to a larger preconcentration factor provided that the sample volume does not exceed the breakthrough volume for the metal ion of interest. The volume of eluant in this study was 10 mL but smaller volumes could be used by discarding the 4 mL holdup volume and/or by using a smaller resin bed and smaller resin particles. Optimization of the process is discussed in Section III.3.(iii).

TABLE XI. Percent Recovery of Metal Ion Spikes in DDW^a

Metal ion	Recovery (%)
Fe(III)	95±10
Cr(III)	95± 2
Cu(II)	95± 6
Pb(II)	95± 8
Ni(II)	103±10
Co(II)	99± 8
Mn(II)	95± 6
Cd(II)	100±12

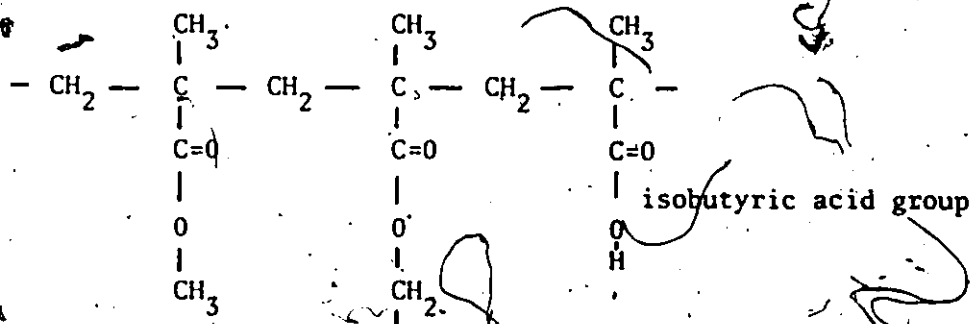
^a 1 x 7 cm XAD-7 column (20-50 mesh); 100 mL of test solution containing 0.2 to 2 µg/L of the metal ions in 0.010M NH₄OAc was used, pH 5.0 for trivalent ions, 8.0⁴ for the divalent ions; flow rate for retention and elution was 1 mL/min; 10.0 mL of 1% v/v HNO₃ was used as the eluant. Data represent average of at least three results.

III.2. Studies on Mechanism of Retention of Metal Ions on XAD-7

Based on the fact that the resin is a polymeric ester (117-119) and that the retention and elution of the metal ions is strongly dependent on pH, the following possible mechanisms for the uptake of metal ions can be envisaged.

- (i) Cation exchange. XAD-7 is a methyl methacrylate polymer. If the synthesis of the ester resulted in incomplete methylation, the resin would contain isobutyric acid groups* which could function as cation exchange sites. Since the capacity of the resin is low (see Section III.2.(iii)), the degree of incomplete methylation would not have to be large.
- (ii) Coordination. Assuming no residual free carboxylic acid groups, the carboxyl groups could act as donors in coordination with metal ions.
- (iii) Adsorption. Metal ions could be adsorbed as simple inorganic complexes on the surface of the resin and held by van der Waals forces; or metal ions could be adsorbed on sites of residual valency (e.g., the carboxyl groups) and held by an ion-dipole interaction. The latter mechanism is similar to coordination but the forces of interaction differ by degree.

For all these mechanisms, retention and elution of metal ions



would be sensitive to pH. The results of experiments to delineate the most probable mechanism are discussed below.

(i) Potentiometric Titration

Attempts to identify the presence of carboxylic acid groups on the resin by potentiometric titration were made. The error (precision) in endpoint detection of these titrations was about 0.5 mL of 0.10 F NaOH. Figure 8 shows the titration of 10.00 g of XAD-7 resin in 100.0 mL of 0.01045F HNO₃ with 0.1055F NaOH. The main feature of Figure 8 is the displacement in pH between the titration curves for the resin (O) and solution blank (Δ) at equal volumes of NaOH. In acid solution, the elevated pH readings in the titration of the resin is due to retention of protons by the resin. After addition of each increment of NaOH, sufficient time was not allowed for neutralization of the retained protons (as evidenced by a continuous downward drift in pH for each titration point). Similarly, in basic solutions, the lower pH for equal volumes of NaOH is due to retention of hydroxyl ions by the resin. It is obvious that the resin titration was not done under equilibrium conditions. Whereas the endpoint volume for the blank titration was 9.90 mL of standard NaOH to obtain pH 7.00, the same volume gave a non-equilibrium pH of 7.9 in the presence of resin. If no carboxylic acid groups are present, the equilibrium pH at 9.90 mL should be 7.00; if, however, free carboxylic acid groups are present, the endpoint volume should be greater than 9.90 mL. Furthermore, the equilibrium pH at 9.90 mL should be around 4.0, considerably lower than 7.00, as shown by the hypothetical curve (dotted line) in Figure 8. This curve is

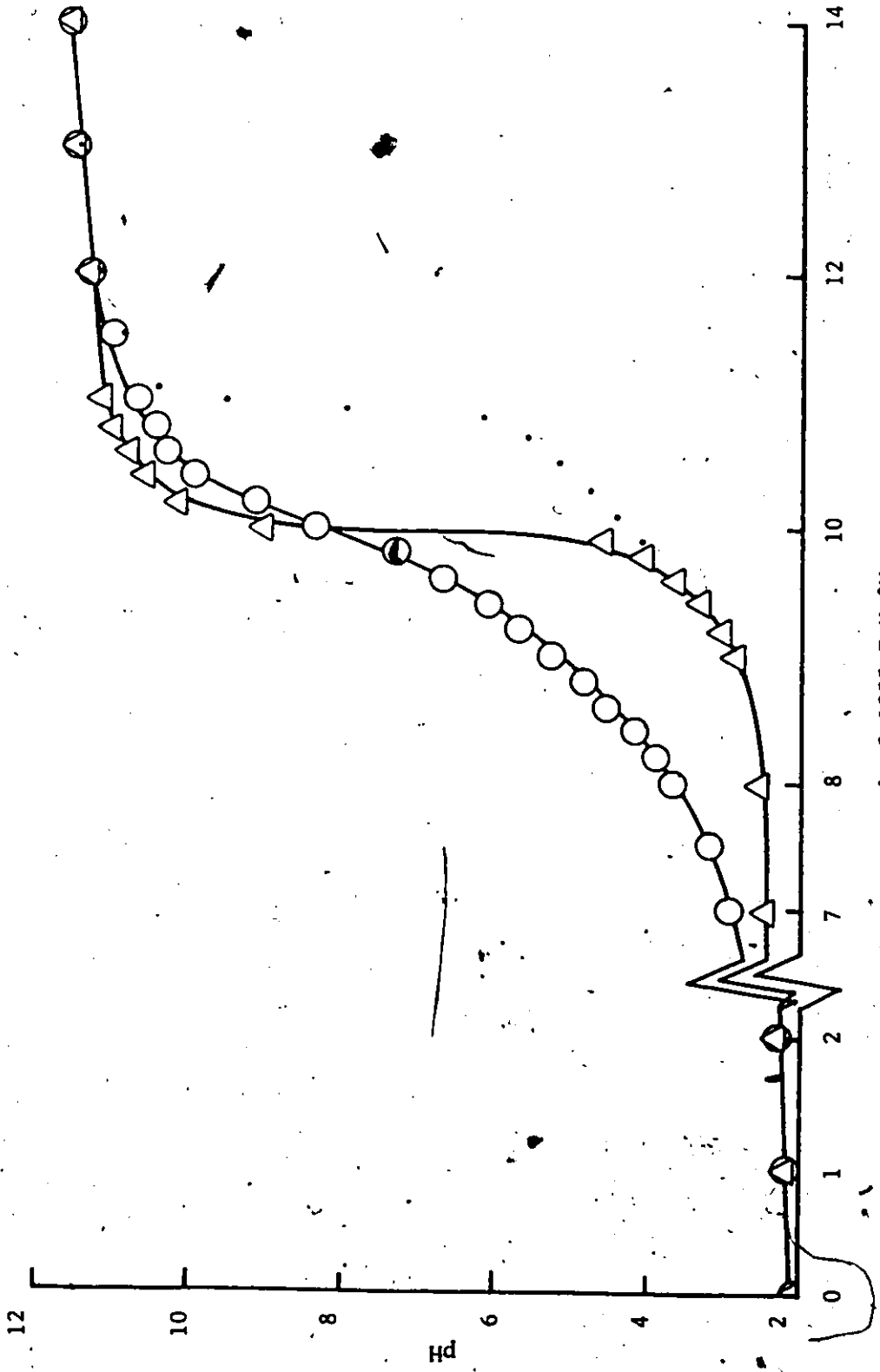


Figure 8. Curves for the titration of (i) 10.00 g of XAD-7 in 100.0 mL of 0.01045F HNO₃ (O); (ii) 100.0 mL of 0.01045F HNO₃ blank (Δ). Dotted line is calculated for the presence of isobutyric acid corresponding to a capacity of 10 μeq of metal ion per gram of resin.

calculated for free isobutyric acid ($pK_a = 4.84$) corresponding to a resin capacity of 10 μeq of metal ion per gram of resin.

The slowness in achieving equilibrium in the titration of the resin was not anticipated. To do a complete titration under equilibrium conditions, it was estimated that 24 hours would be required. Because such a titration is not practical, a single-point titration was devised to show whether or not the endpoint in the titration of XAD-7 in HNO_3 would indeed reach an equilibrium pH-value of 7.00. The titration curve is shown in Figure 9 which represents a pH/time profile for the addition of 10.52 mL of 0.1003 F NaOH (i.e., the calculated endpoint volume) to 10.00 g of XAD-7 in 100.0 mL of 0.01055 F HNO_3 . This figure indicates the following. Immediately after the titrant addition, protons in solution are neutralized but protons retained on the resin are not. As the retained protons are desorbed and neutralized with time, the pH decreases to its equilibrium value of 7.00. This result shows that there is no measurable amount of carboxylic acid in the 10 g of resin taken for analysis. Even a generous error of 0.10 mL in the endpoint volume would correspond to only 1.0 μmole of free acid per gram of resin ($0.1003 \times 0.10 \times 10^{-3} / 10.0$). Since the capacity of the resin for metal ions is in the order of 10 $\mu\text{mole/g}$ (see Section III.2.(iii)), it is not likely that retention of metal ions is by cation exchange involving carboxylic acid groups.

(ii) Infrared Studies

If metal ions are retained on XAD-7 by coordination to the carbonyl groups, then elution of the metal ions by 1% v/v HNO_3 should result in protonation of the resin at the carbonyl groups. Accord-

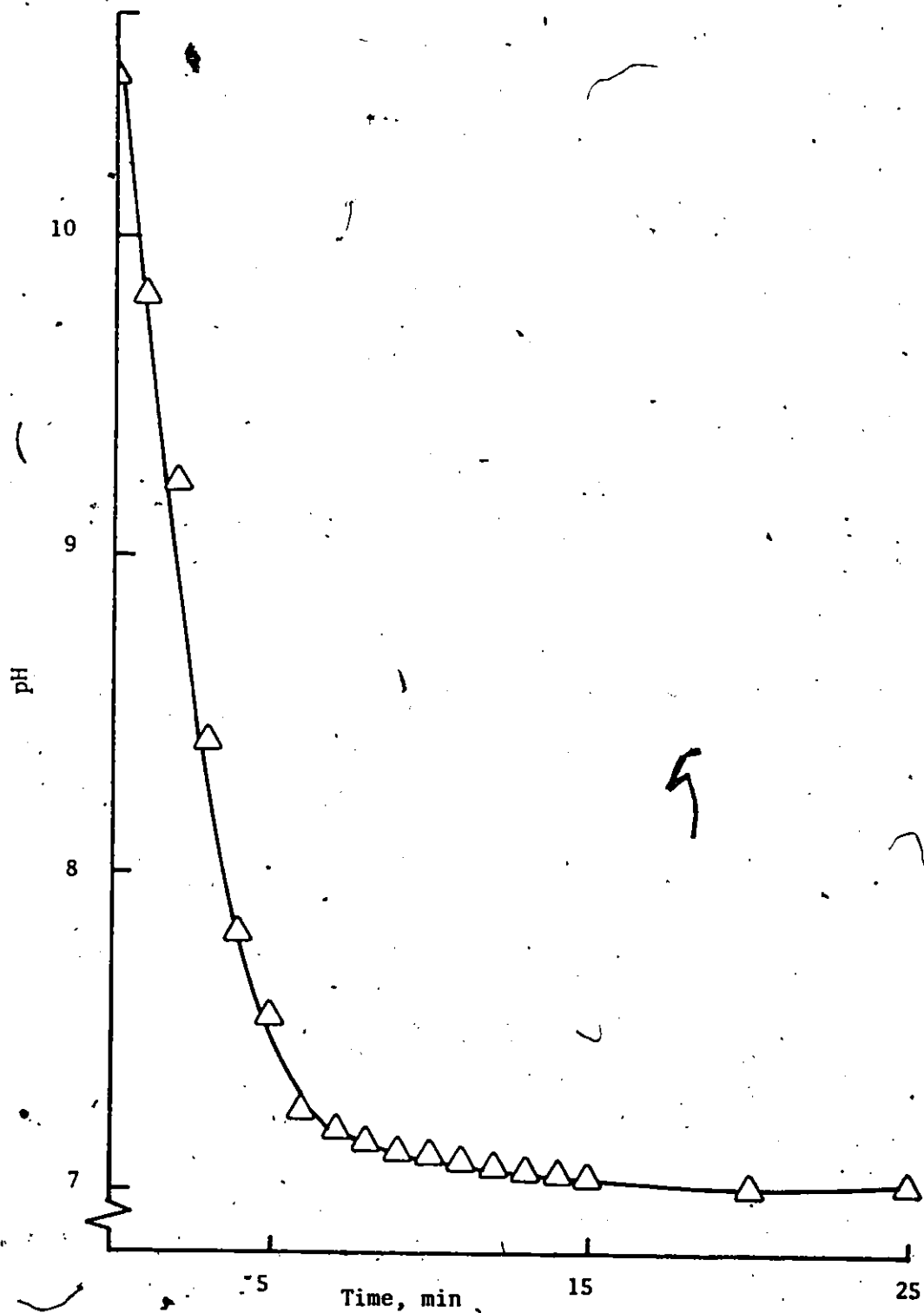


Figure 9. pH/Time profile for a single point-endpoint titration of 10.00 g of XAD-7 in 100.0 mL of 0.01055 F HNO_3 with 10.52 mL of 0.1003 F NaOH.

ingly, evidence of protonation was sought by infrared spectroscopy. The infrared spectra of untreated resin and of resin treated with 1% v/v HNO_3 are shown in Figure 10. The spectra are identical and no shift in the carbonyl band is observed (i.e., no C=O-H band). If protonation by 1% v/v HNO_3 does not occur, then the carbonyl oxygen would be too weak a donor to coordinate the metal ions. However, as shown in the following section, the proton capacity is only 9 $\mu\text{mole/g}$ of resin (20-50 mesh) and this appears to be too low to allow detection of protonated carbonyl by conventional infrared analysis. Therefore, this experiment is inconclusive. Nevertheless, the fact that the proton capacity represents only about 0.1% of the carbonyl groups does suggest that the forces binding the protons to the resin are considerably weaker than covalent forces and may involve longer range dipole-charge interactions, more consistent with adsorption.

(iii) Adsorption Isotherm Studies

The XAD resins are widely used as separation/concentration media for organic compounds (111, 114-116, 118-128). Recent studies have suggested that for the non-polar XAD-1, XAD-2 and XAD-4 resins, organic molecules are adsorbed and held by van der Waals forces. For XAD-7, which is of intermediate polarity, adsorption forces involve both van der Waals and polar interactions (e.g., dipole-dipole) (117-119, 127, 148-150). Based on these known adsorptive properties of XAD-7 resin, it seems that metal ions could be adsorbed as simple inorganic complexes and/or hydrated ions and held either by van der Waals forces or by ion-dipole interactions at the sites of residual valency (i.e., the carbonyl groups). To further investigate the interaction between metal ions and the resin, adsorption isotherm studies were conducted.

(a). Adsorption isotherm for Cu(II) and protons. Cu(II) was chosen as the model metal ion for the adsorption isotherm studies. Quali-

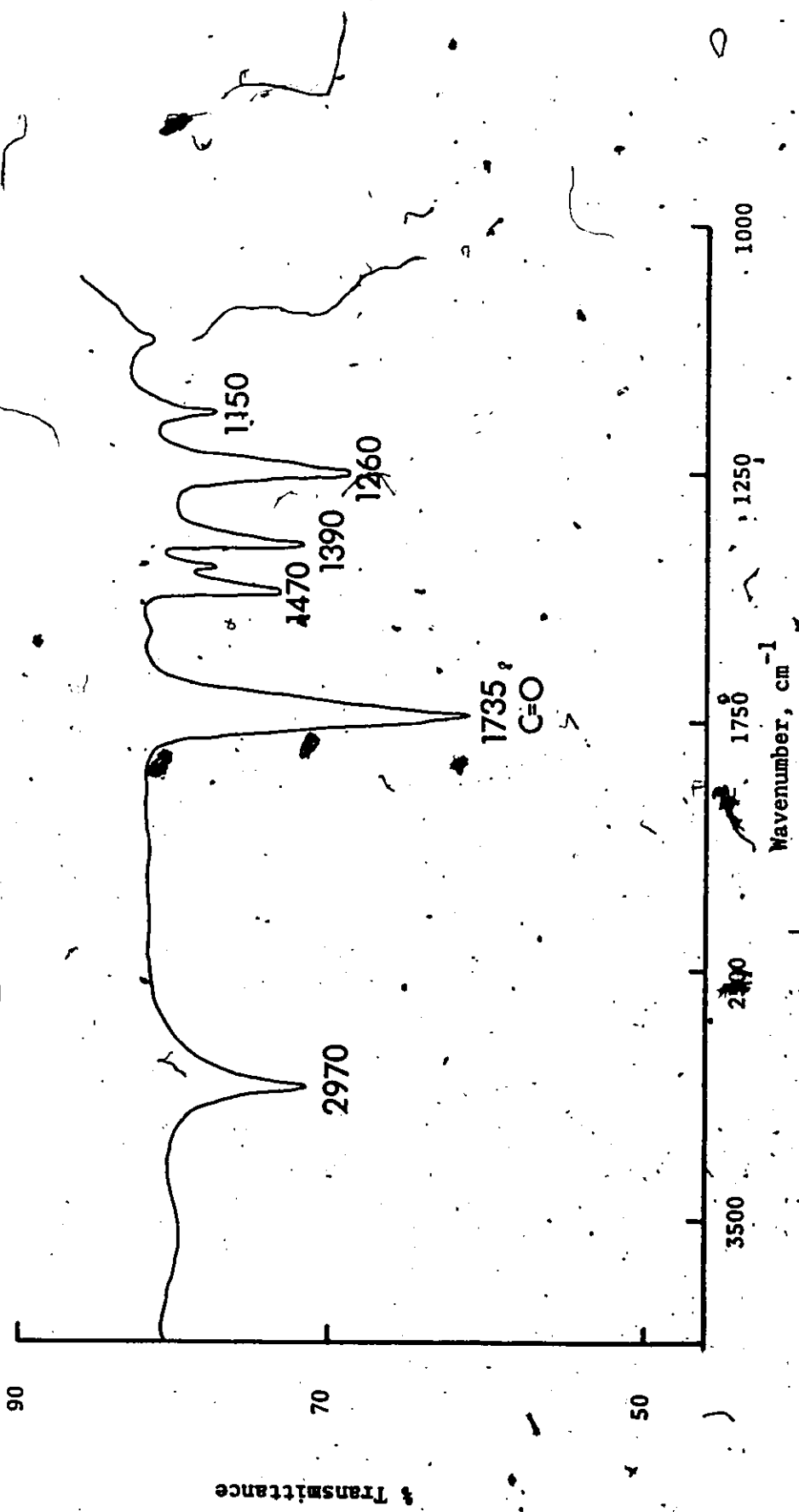


Figure 10. Infrared spectrum of XAD-7 resin. The spectrum of resin treated with 1% v/v HNO₃ is identical to that of the untreated resin.

tatively, the rate of adsorption of hydrated and weakly complexed Cu(II) on XAD-7 was found to be fairly rapid (Figure 11). In general, adsorption equilibrium was attained in less than 30 min. Adsorption isotherms were obtained at pH 3.8, 4.8 and 6.0. Above pH 6.0, isotherms could not be obtained owing to precipitation of colloidal copper hydroxide from test solutions at the higher Cu(II) concentrations. The isotherms are convex in shape (see example in Figure 12). Γ_{\max} , the adsorption maximum (and also resin capacity), was found to be strongly pH dependent (Table XII). This observation indicates a competition between Cu(II) ions and protons for adsorption sites on the resin and that the mechanisms for adsorption of Cu(II) and protons are similar.

The rate of adsorption of protons is also quite fast, with equilibrium being attained within 20 min. The convex isotherm (Figure 13) yields a Γ_{\max} value of about 9 $\mu\text{mole/g}$ for proton adsorption on 20-50 mesh XAD-7. These capacities for protons and Cu(II) correspond to the value of around 10 $\mu\text{eq/g}$ mentioned by Aiken and Walton (108,117).

In view of the large surface area of the macroporous XAD-7 resin ($\sim 450 \text{ M}^2/\text{g}$) (117, 118), the rather low capacities for Cu(II) and proton adsorption are surprising. This fact raises the question that trace impurities on the structure of the resin could be responsible for ion retention. Although no carboxylic acid impurity sites were detected, other impurity sites with donor atoms such as nitrogen or sulphur might perhaps be involved. Alternatively, perhaps adsorption involves only the exterior surface of the resin, i.e., Cu(II) and protons do not penetrate into the vast interior surface of the

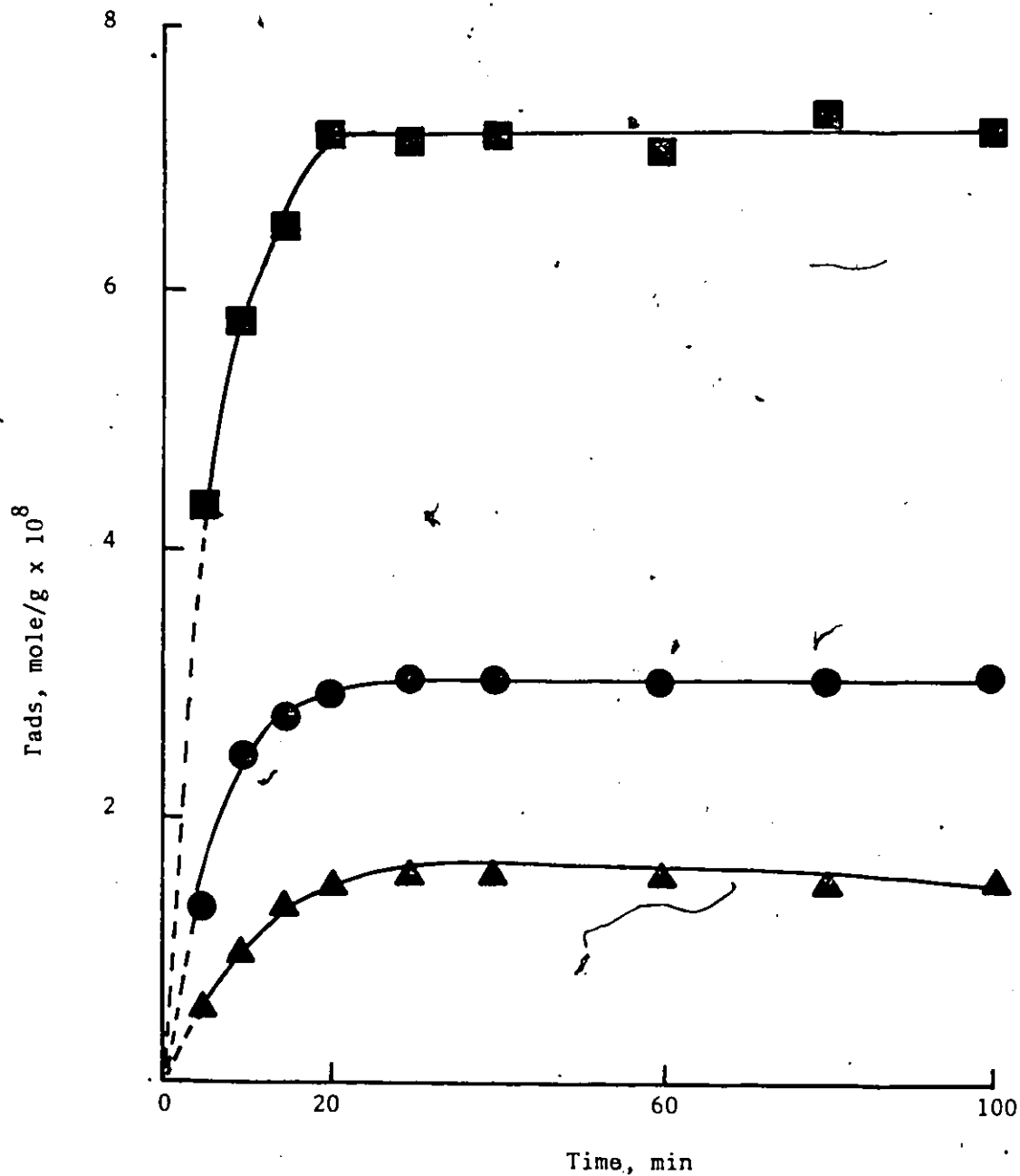


Figure 11. Rate of adsorption of Cu(II) on XAD-7 (20-50 mesh); 30 $\mu\text{g/L}$ (\blacktriangle), 60 $\mu\text{g/L}$ (\bullet) and 200 $\mu\text{g/L}$ (\blacksquare) of Cu(II) in 0.010 M NH_4OAc , pH 4.8. Similar adsorption rates were obtained at pH 3.8 and 6.0 despite of differences in Rads values.

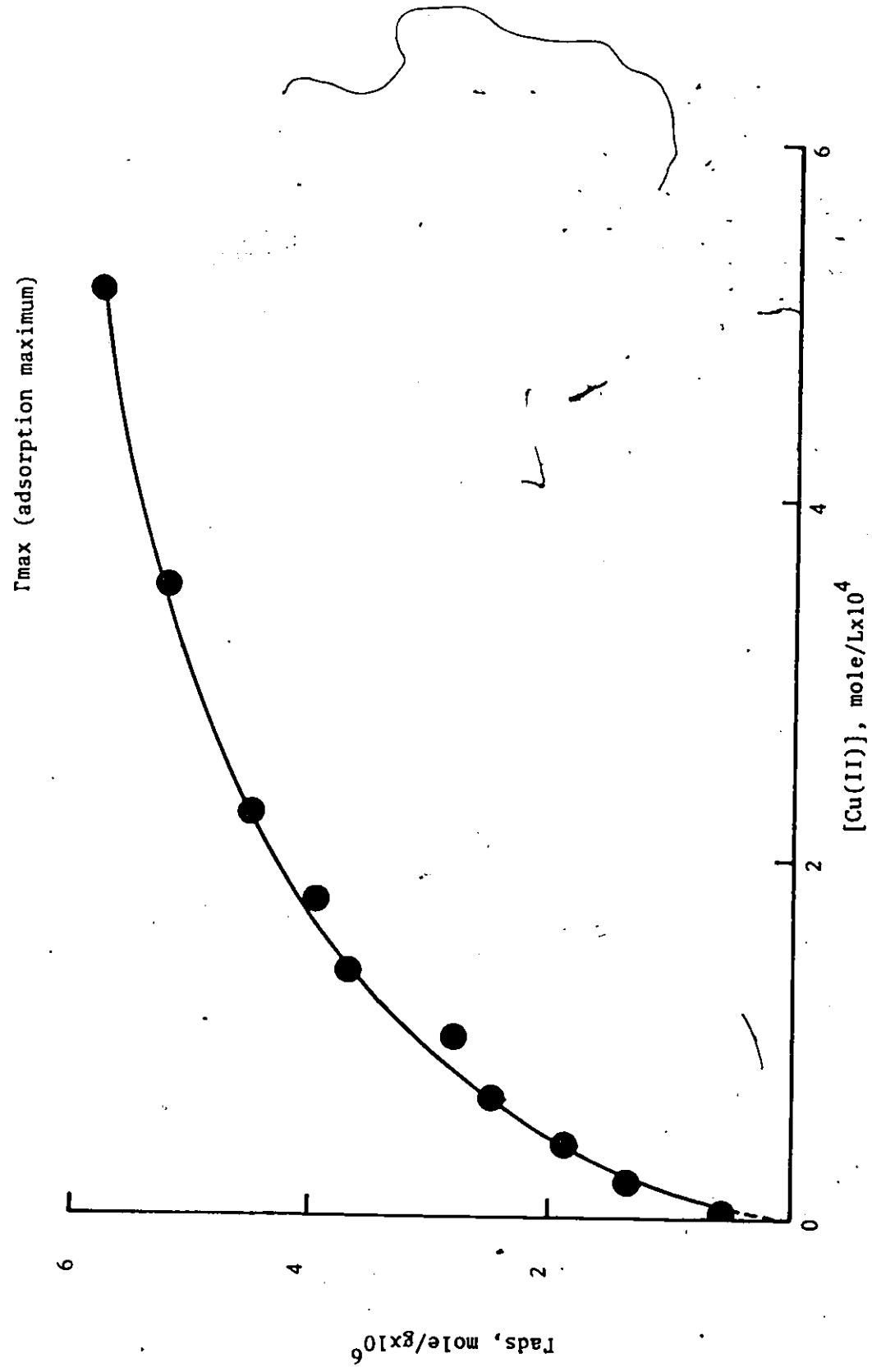


Figure 12. Adsorption isotherm for Cu(II) on XAD-7 (20-50 mesh) from 0.010 M NH_4OAc , pH 6.0, $22 \pm 1^\circ\text{C}$.

TABLE XII. Γ_{\max} (Resin Capacity) for the Adsorption of Cu(II) on 20-50 Mesh XAD-7 at Various pH Values^a

pH	Γ_{\max} (mole/g)
3.8	1.7×10^{-9}
4.8	1.5×10^{-7}
6.0	6.0×10^{-6}

^a Values of Γ_{\max} were obtained from the convex isotherms by extrapolation.

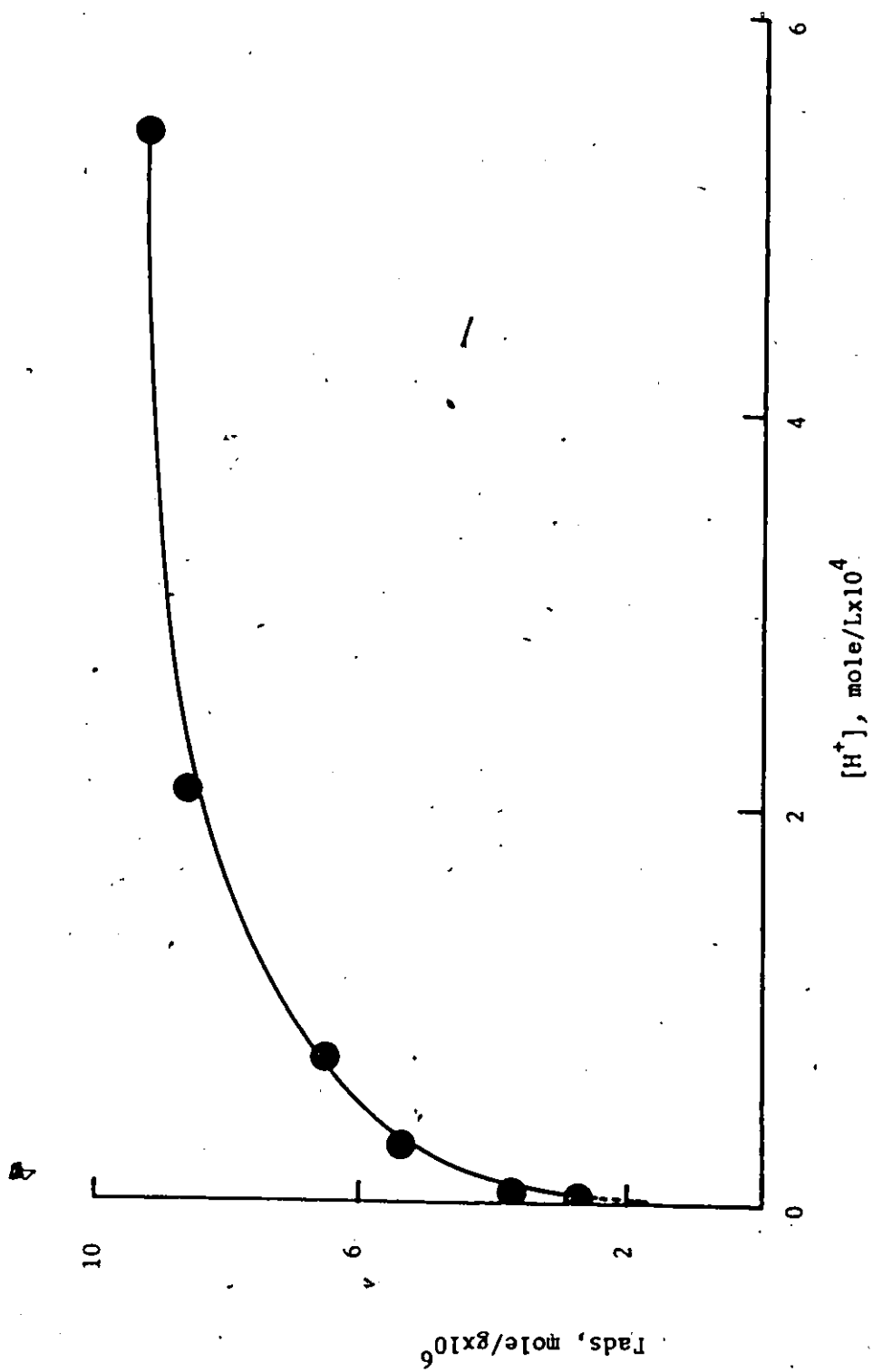


Figure 13. Proton adsorption isotherm on XAD-7 (20-50 mesh), 26.0°C.

resin. If the exterior surface is important and the interior surface is not, then adsorption should increase as the resin particle size decreases. Accordingly, the effect of particle size was investigated.

(b) Effect of particle size on adsorption. Isotherms for the adsorption of protons and Cu(II) on mesh sizes 20-50, 60-100 and 100-200 were obtained. These mesh sizes correspond to particle size ranges of 850-300, 250-150 and 150-75 μm , respectively. Figures 14 and 15 show that Γ_{max} increases significantly with decreasing particle size. The increase is approximately in proportion to the decrease in the radius of the particle (Table XIII). For a given weight of resin the smaller particle size means an increase in the exterior surface area but since this increase is small compared to the interior surface area, the increase in overall surface area should be small. Therefore, if adsorption occurs on both the exterior and the interior surfaces, the effect of mesh size should not be very significant. The data in Table XIII, however, show that the effect of mesh size is indeed significant. However, a rough calculation shows that the number of carbonyl groups (possible adsorption sites) on the exterior surface is about 20 times lower than the moles of ions adsorbed per gram of resin. Since the calculation was based on perfectly spherical particles, the actual exterior surface would be considerably higher than calculated because of flaws and surface irregularities. Therefore, the lower factor is expected because the minimal surface area was used in the calculation. Overall,

these observations support the interpretation that adsorption must occur primarily on the exterior surface and that the protons and metal ions (free and weakly complexed) do not penetrate the resin surface to reach interior sites. Limited penetration may arise because adsorption involves only a weak interaction which may not in itself provide much driving force for these hydrated cationic adsorbates to enter the largely non-polar cavities of the resin. The degree of penetration does not increase with time since, as described earlier, constant adsorption (i.e., presumably adsorption equilibrium) is attained within 30 min or less.

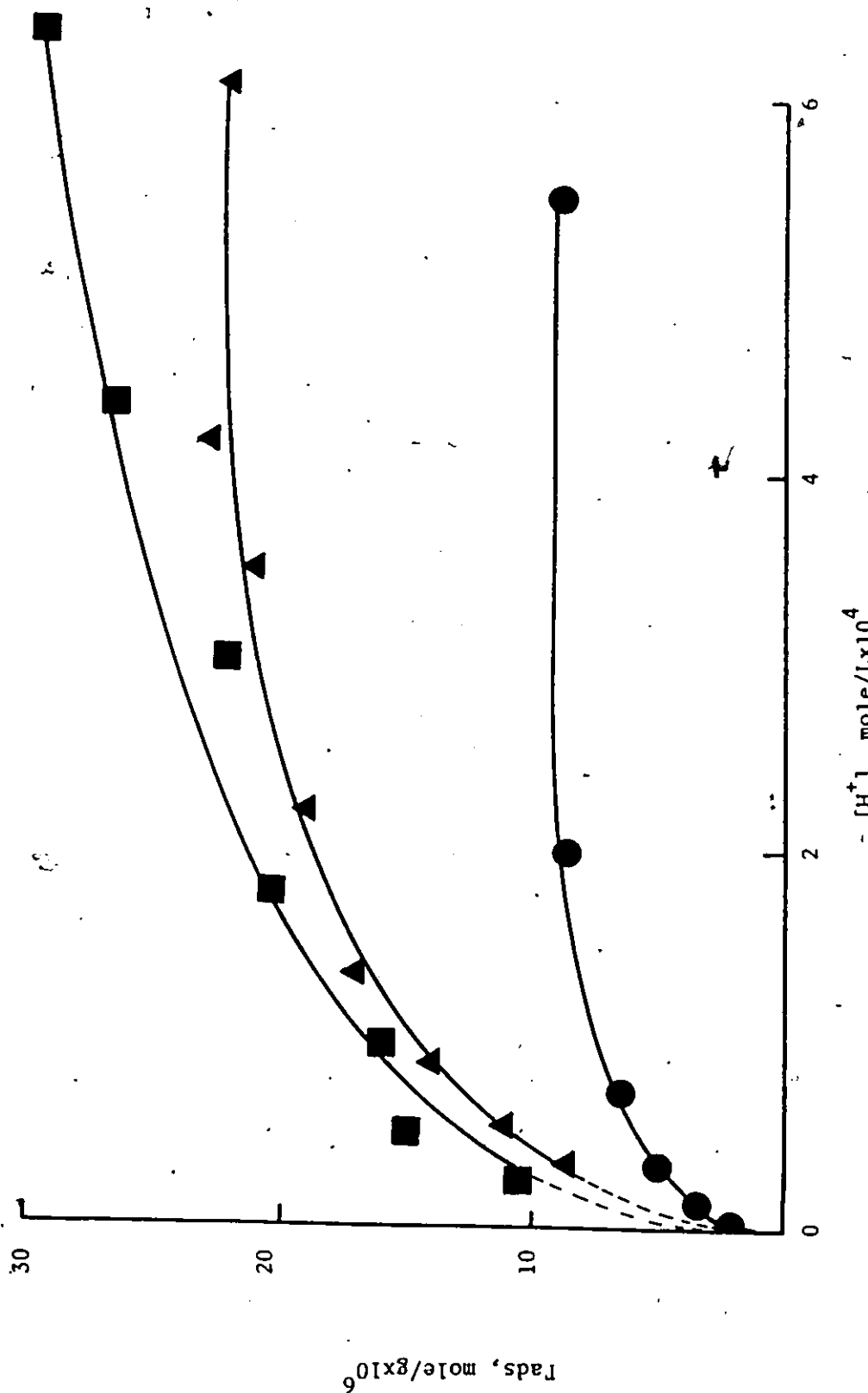


Figure 14. Isotherms for the adsorption of protons on XAD-7 20-50 mesh (●), 60-100 mesh (▲) and 100-200 mesh (■), 26.0°C.

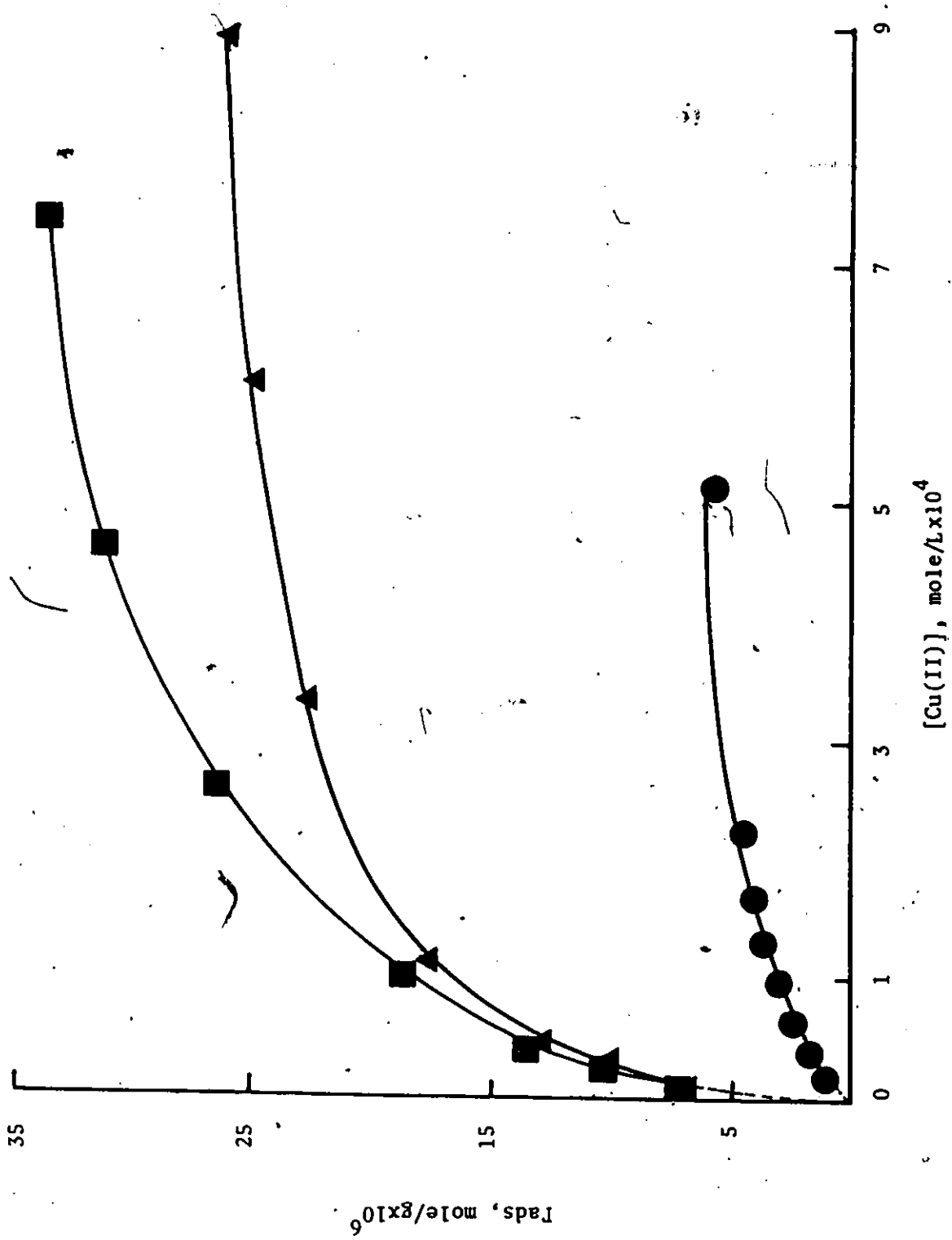


Figure 14. Isotherms for the adsorption of Cu(II) on XAD-7, 20-50 mesh (●), 60-100 mesh (▲) and 100-200 mesh (■), 0.010M NH₄OAc, pH 6.0, 22±1°C.

TABLE XIII. Γ_{\max} (Resin Capacity) for Protons and Cu(II) as a Function of Particle Size

Mesh size	Particle diameter (μm)	Approx. mean radius (μm)	$\Gamma_{\max}(\text{Cu(II)})^a$ ($\mu\text{mole/g}$)	$\Gamma_{\max}(\text{H}^+)^b$ ($\mu\text{mole/g}$)	Approx. ^c exterior surface area (M^2/g)	Number of c=O groups on exterior surface ($\mu\text{mole/g}$)
20-50	850-300	~ 300	~ 5	~ 9	~ 0.016	~ 0.35
60-100	250-150	~ 100	~ 25	~ 24	~ 0.048	~ 1.1
100-200	150-75	~ 60	~ 34	~ 30	~ 0.080	~ 1.7

^a For 0.010M NH_4OAc , pH 6.0, $22 \pm 1^\circ\text{C}$ ^b For 26°C

^c Calculated based on the assumption that all particles are perfectly spherical and the fact that one gram of resin has a total surface area of 450 M^2 and contains 10 mmoles of carbonyl groups (117).

i.e., Density of dry resin = 0.62 g/mL (117), therefore volume of 1 g = 1.6 mL(c.c.) or $1.6 \times 10^{-6} \text{ M}^3$.
 Volume of 1 g is also given by $\frac{4}{3} \pi r^3 \cdot n$, where n is the number of particles in 1 g.

From r (approx. mean radius) and $3 \times 10^{-6} \text{ M}^3$, one can calculate n; and from n, one can calculate the total exterior surface in 1 g (i.e., $A = 4 \pi r^2 \cdot n$).

e.g., $r = 300 \mu\text{m} (3 \times 10^{-4} \text{ M})$, $n = \frac{3 \times 1.6 \times 10^{-6}}{4 \times \pi \times (3 \times 10^{-4})^3} = 1.41 \times 10^4$.

and $A = 4 \times \pi \times (3 \times 10^{-4})^2 \times 1.41 \times 10^4 = 0.016 \text{ M}^2$.

Number of c=O groups on exterior surface in 1 g of resin is simply given by

$\frac{0.016}{450} \times 10 \times 10^3 \mu\text{mole} = 0.35 \mu\text{mole}$.

Accepting that adsorption takes place on the exterior surface, the question remains as to whether the adsorption sites are the exterior carbonyl groups or exterior sites of some impurity. Simple calculation, however, shows that the latter situation is unlikely because it would mean a high level of impurity. For example, if exterior impurity sites are responsible for adsorption, there would be about 30 μ mole of them on the exterior surface in one gram of 100-200 mesh XAD-7 (Table XIII). Since the exterior surface is estimated to be 0.02 % of the total surface (Table XIII), this would mean a total of $30 \times 5000 = 150000 \mu$ mole/g of impurities on the resin, and such a value is extremely high.

(c) Effect of anions. The effect of anions (i.e., 0.010 M acetate, chloride and nitrate as ammonium salts) on the adsorption isotherm of Cu(II) was found to be negligible. No significant effect was observed at pH 3.8, 4.8 and 6.0 (Figure 16). Therefore, the fact that acetate, chloride and nitrate have different complexing abilities towards metal ions does not seem to be important. The formation of acetic acid from acetate in acid solution also has little effect on the adsorption of Cu(II). These isotherm results (by batch equilibration) are consistent with those from the preliminary studies in which no anion affect was observed on the retention of metal ions on an XAD-7 column.

(d) Effect of ionic strength on Cu(II) adsorption. This study was done in anticipation of the use of the XAD-7 column for the preconcentration of trace metal ions from seawater. Because of the alkali-salt matrix interference on atomic absorption measurements, ammonium chloride instead of sodium chloride was used for the adjustment of ionic strength. Experimentally, it was observed that for ionic strength

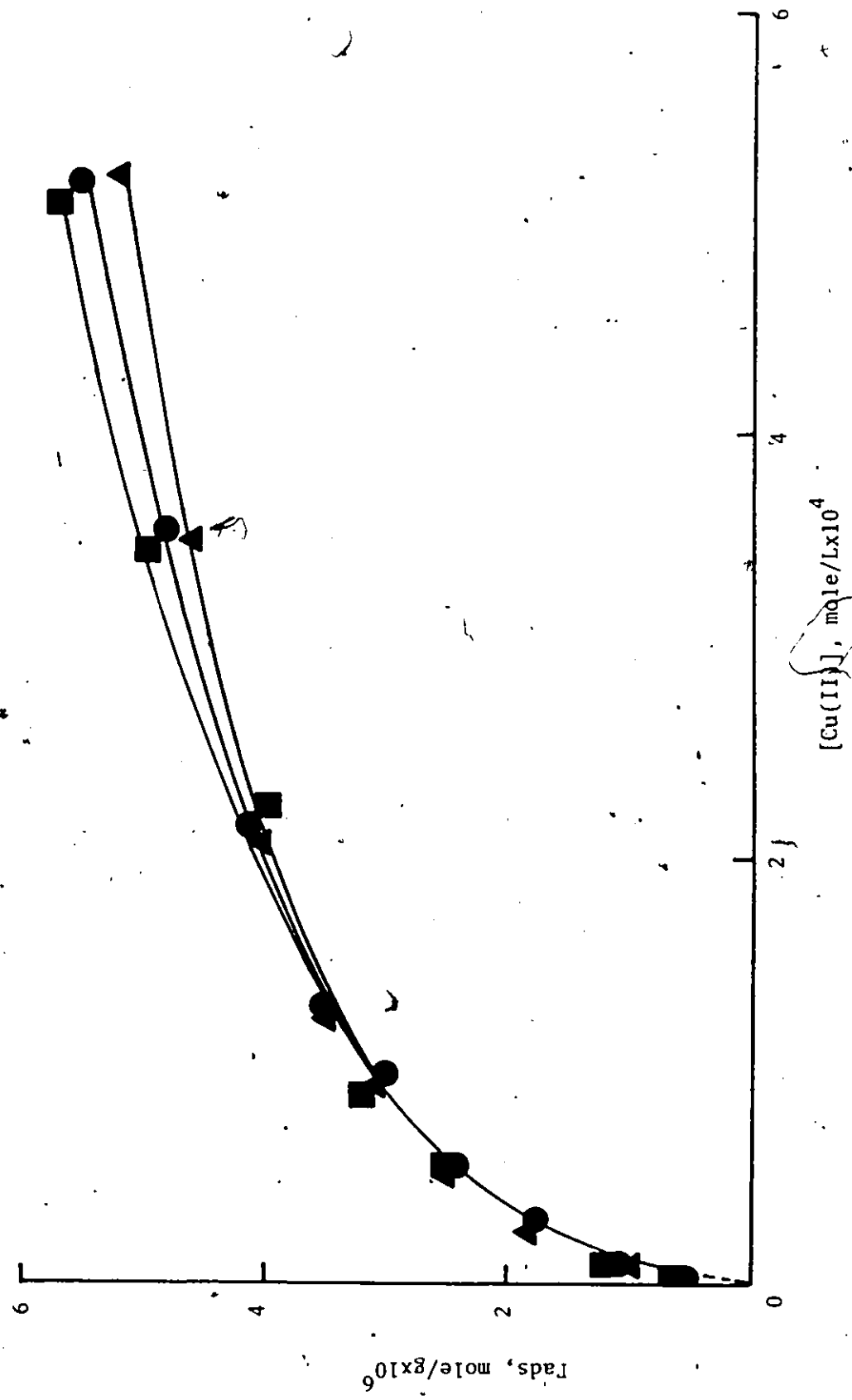


Figure 16. Adsorption isotherms for Cu(II) on XAD-7 (20-50 mesh) from 0.010M NH₄OAc (●), 0.010 M NH₄Cl (▲) and 0.010 M NH₄NO₃ (■), at pH 6.0, 22±1°C.

varying from 0.01 to 0.76, the adsorption capacity of Cu(II) on XAD-7 resin (20-50 mesh) decreases from about 6 to 1.5 $\mu\text{mole/g}$ (Figure 17). This effect is opposite to that observed by Cantwell and Pion~~e~~ (119) who reported that adsorption of the organic diphenylguanidium cation (DPGH⁺) on a non-polar styrene-divinylbenzene resin (XAD-2) increases with increasing ionic strength. They attributed this observation to the stabilization of the Helmholtz double layer formed by the adsorbed cations, the hydration sheath, and the counter ions. In the present case, the decrease in Cu(II) adsorption with ionic strength indicates that there is little double-layer stabilization at higher ionic strengths, or that the double-layer stabilization effect is outweighed by increased formation of metal-ion chloro complexes at higher chloride concentrations, i.e., there is a shift in equilibrium from metal-ion adsorption to complexation. Another possibility is the increased competition from ammonium ion for carbonyl sites. The microscopic adsorption model for the Cu(II)/XAD-7 process will be discussed in further detail in Section III.2.(v).

From a practical viewpoint, the reduced resin capacities at higher ionic strengths are still adequate for metal-ion preconcentration in seawater where the combined trace metal content is only of the order of 10^{-7} mole/L.

(e). Effect of temperature on adsorption. The effect of temperature on adsorption of protons is shown in Figure 18. Adsorption decreases with an increase in temperature. This fact probably corresponds to a weakening of the attractive force between protons and the XAD-7 adsorption sites, i.e., the position of equilibrium is displaced in

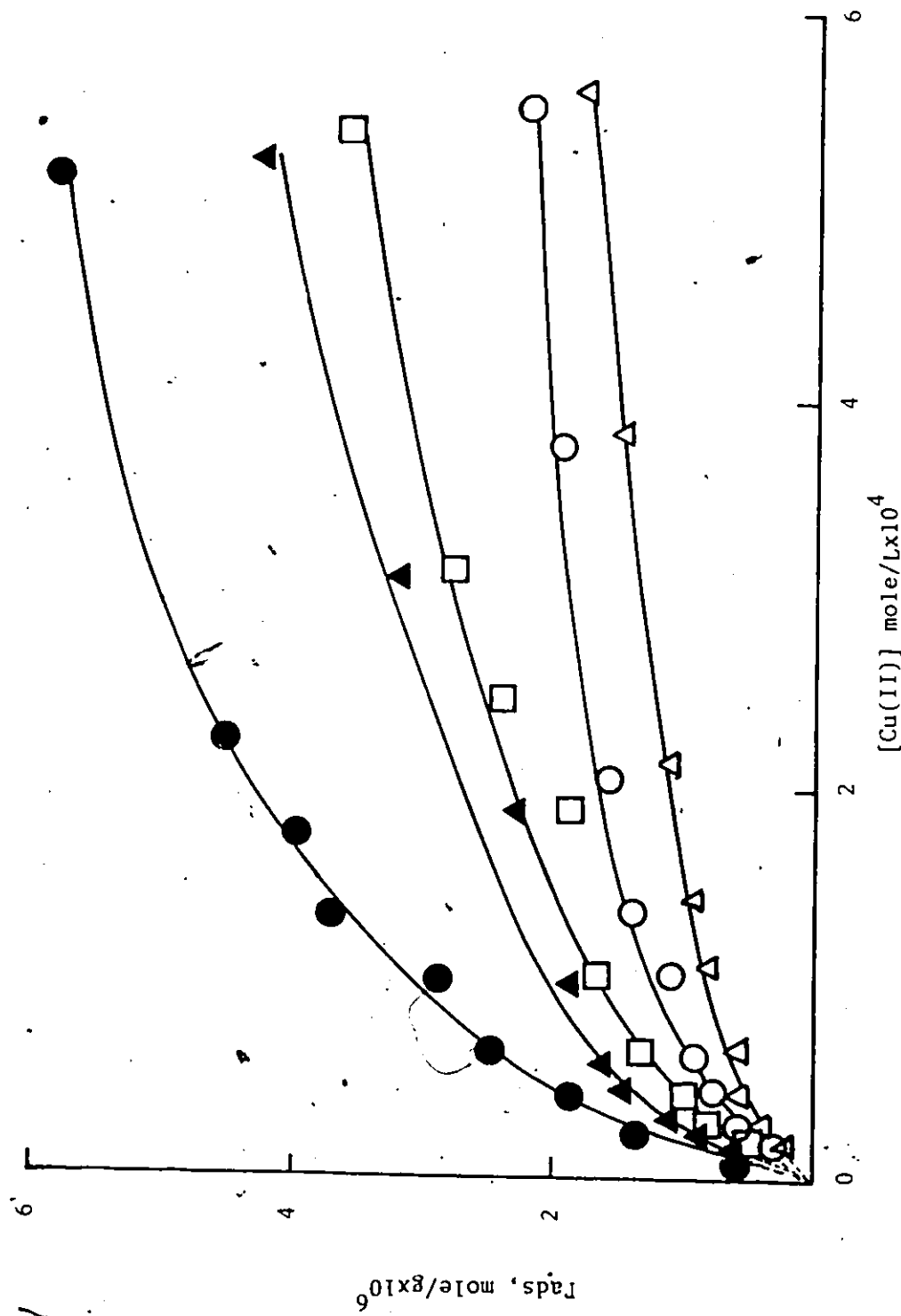


Figure 17. Isotherms for the adsorption of Cu(II) on XAD-7 (20-50 mesh) from 0.010 M NH₄OAc, pH 6.0, with different bulk solution concentrations of NH₄Cl: 0.00M(●), 0.05M(▲), 0.10M(□), 0.25M(○) and 0.75M(Δ).

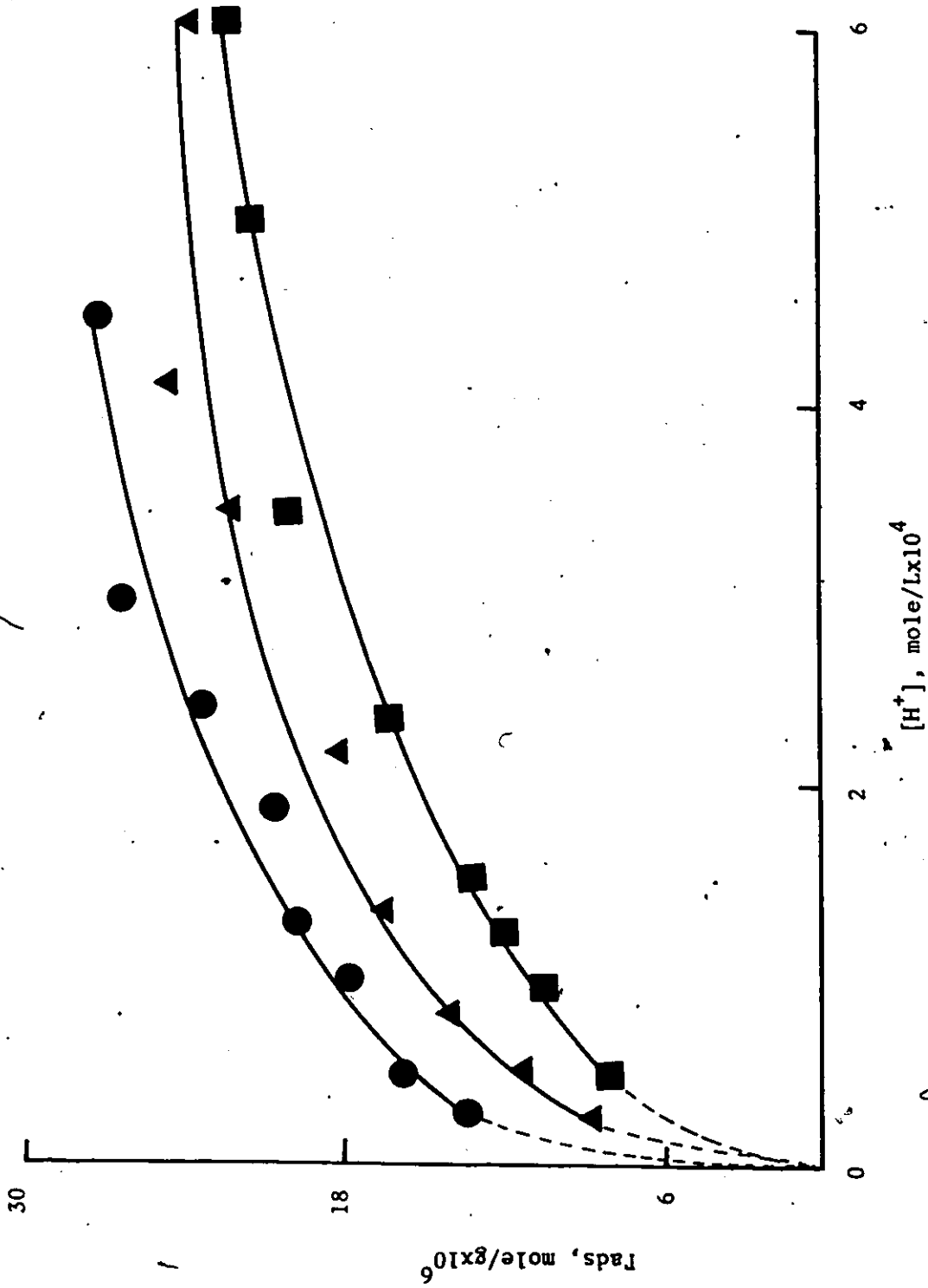


Figure 18. Isotherms for the adsorption of protons on XAD-7 (60-100 mesh) at 11.0°C (●), 26.0°C (▲) and 42.0°C (■).

favour of the solution at elevated temperatures. The dependence of Cu(II) adsorption on temperature was not determined but is expected to be similar to that for proton adsorption.

Various thermodynamic quantities can be obtained from the temperature dependence of an adsorption process, using the Langmuir and the Van't Hoff equations (see Section I.4., INTRODUCTION). These thermodynamic quantities can then be used to interpret the nature of the adsorption interaction. Such studies are routinely made for gas-solid adsorption processes. However, adsorption from solution is a much more complicated process. For example, in the present study, solution parameters such as pH and ionic strength affect the extent of Cu(II) adsorption. Furthermore, the adsorption process involves solvent participation. For such a complicated process, fundamental assumptions in the Langmuir equation might not be valid and, furthermore, derived enthalpy, entropy and free energy values would at best be empirical and not easily related to a discrete known adsorption reaction. For these reasons, thermodynamic parameters were not determined in this work, as explained in part (iv) immediately following.

(iv) Langmuir Equation and Adsorption in Solution

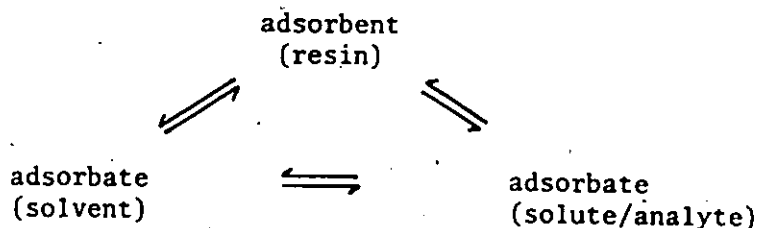
The Langmuir equation (96-98)

$$\Gamma = \frac{\Gamma_{\text{max.}} [M]}{(1/K) + [M]} \quad (5)$$

is often used to describe experimental data obtained from solution adsorption studies. Since, however, the solution

adsorption process is more complex than the gas-solid adsorption process (for which the Langmuir equation was derived), inappropriate interpretation of the results can arise. In this section, the chemical, mathematical and statistical implications of the Langmuir equation are discussed and some comments on the application of the equation to solution adsorption, including the adsorption of metal ions and protons on XAD-7 resin, are presented.

(a) Chemical implications. The derivation of the Langmuir equation involves several implicit assumptions: (i) the adsorbate behaves ideally; (ii) the adsorption surface is homogeneous, i.e., all adsorption sites are geometrically and chemically equivalent; (iii) the only interaction involved is that between the adsorbent and the adsorbate, i.e., there are no interactions with a third species and no lateral interactions between the adsorbed molecules; and (iv) the adsorbate is confined to a monolayer. While some of these assumptions are often difficult to fulfill for a gas-solid adsorption process, it is obvious that some, particularly (iii), cannot be realized for a solution process. In solution, the participation of solvent complicates the process since more than one type of interaction is involved, as shown diagrammatically below:



The solvent may compete with the solute for adsorption sites and with

the adsorbent for solute through solvation. The Langmuir equation does not account for the participation of solvent. Furthermore, a solution-adsorption process could also be influenced by parameters such as pH, ionic strength, and the possible presence of other adsorbates. Thus, adsorption from solution is, indeed, a complicated process and the Langmuir parameters (i.e., Γ_{\max} and K) obtained from the application of the equation should be regarded as empirical constants. As suggested by Hiemenz (151) and Rubin (152), there may not be any justification for further interpretation of these parameters in terms of thermodynamic significance. For example, the calculation of the heat of adsorption (ΔH°) - an often sought quantity - from the temperature dependence of the K value may not be at all valid. Unfortunately, there exist in the literature several examples of solution adsorption studies for which interpretation of thermodynamic quantities has been extended beyond validity (e.g., 61, 153).

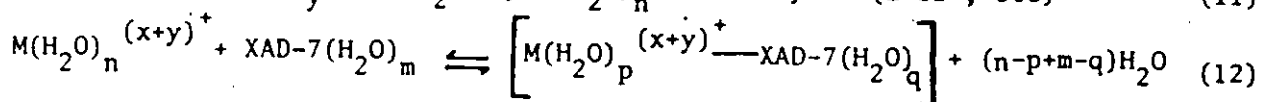
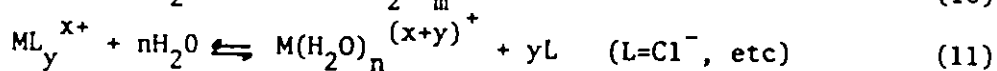
(b) Statistical and mathematical implications.

Application of the Langmuir equation involves a reciprocal plot of the data. Such a plot is susceptible to errors which arise from improper inclusion or rejection of experimental data. In addition, a reciprocal plot tends to give uneven statistical weight to individual datum points. For these reasons, improper application of the Langmuir equation to experimental data could lead to erroneous results. Details of the statistical and mathematical implications of the Langmuir equation are discussed in Appendix II.

(c) Application of the Langmuir equation to adsorption on XAD-7.

So far, the studies in this work have shown that metal-ion adsorption

on XAD-7 is quite complicated and that the process is affected by several solution parameters. Solvent (water) participation in the adsorption process must occur. Solvent interaction with XAD-7 is demonstrated by the degree of swelling (2:1) of the resin. Thus, adsorption of metal ions almost certainly involves competition with water for the adsorption sites. This situation is depicted below:



Obviously, the simple Langmuir equation could not possibly describe the above complicated situation and interpretation of the extracted K values is opened to question. For example, in the studies on proton adsorption on XAD-7, K values were obtained as a function of temperature (Table XIV). All six linearized transformations of the Langmuir equations (see Appendix II) were used and the K values were averaged. These average K values appear to be reliable in the sense that agreement among them is satisfactory and the calculated Γ_{max} values agree well with the experimental Γ_{max} values. However, the adsorption reaction to which these K values correspond is not known and it does not seem fruitful to calculate ΔG° , ΔS° and ΔH° values.

In summary, adsorption from solution is a complex process. Application of the Langmuir equation should be regarded as an empirical approach and the Langmuir parameters as merely empirical constants. Furthermore, the reciprocal linear plots are error prone and inclusion and/or rejection of data for such plots should be done prudently. More than one transformation of the Langmuir equation should be employed, and the experimental Γ_{max} value should be used to assess the validity of the Γ_{max} values obtained from the reciprocal Langmuir plots.

TABLE XIV. Langmuir Parameters for the Adsorption of Protons
on XAD-2 (60-80 Mesh) as a Function of Temperature

Transformation used ^a		Temperature					
		11°C		26°C		42°C	
		Γ_{\max}^b	K^c	Γ_{\max}^b	K^c	Γ_{\max}^b	K^c
$\frac{1}{\Gamma}$	vs $\frac{1}{[M]}$	26.0	3.17	26.0	1.60	22.8	1.02
$\frac{[M]}{\Gamma}$	vs $[M]$	30.3	1.63	26.6	1.01	27.7	0.633
Γ	vs $\frac{\Gamma}{[M]}$	26.7	2.79	25.9	1.53	24.6	0.861
$\frac{1}{[M]}$	vs $\frac{1}{\Gamma}$	27.0	2.72	25.7	1.56	23.9	0.908
$[M]$	vs $\frac{[M]}{\Gamma}$	29.8	1.74	26.5	1.42	27.5	0.648
$\frac{\Gamma}{[M]}$	vs Γ	28.5	2.18	26.2	1.47	26.2	0.738
Average		28.0 ± 1.7	2.37 ± 0.62	26.1 ± 0.4	1.43 ± 0.21	25.4 ± 2.0	0.80 ± 0.15
Experimental Γ_{\max}^d		26	-	24	-	23	-

^a See Appendix II for transformations.

^b in $\mu\text{mole/g}$

^c $(\text{L/mole}) \times 10^4$

^d From extrapolation of the experimental adsorption isotherms (Figure 18).

(v) Microscopic Model for the Adsorption of Metal-Ions

The results above have shown that pH has a pronounced effect on the adsorption of metal ions on XAD-7 and that the effect of other parameters such as ionic strength, resin particle size, anions and temperature are less significant. Consistent with these macroscopic observations is the microscopic model for the adsorption of metal ions presented in Figure 19. The metal ion is shown held by a charge-dipole interaction between the metal ion and the carbonyl groups, or between the metal ion and water molecules on the hydrated resin surface. Another interaction is a dipole-dipole attraction between the carbonyl group and water molecules on the hydrated metal. Anions are attracted to the zone of hydration to compete the Helmholtz double layer. At higher ionic strengths, water molecules in the hydration layer may be replaced by coordinating anions such as chloride, hydroxyl and carbonate and the complexes which result could lower the adsorption of metal ions. Desorption of metal ions occurs when saturation of the adsorption sites by protons is approached, or when precipitation of colloidal metal hydroxides or occupation of adsorption sites by hydroxyl ions takes place.

(vi) Distribution Ratios

Methods of separation are characterized by several parameters, an important one being the distribution ratio, D_R . The distribution ratio here is defined as the ratio of moles of metal ion adsorbed per kilogram of resin to moles of unadsorbed metal ion per litre of solution.

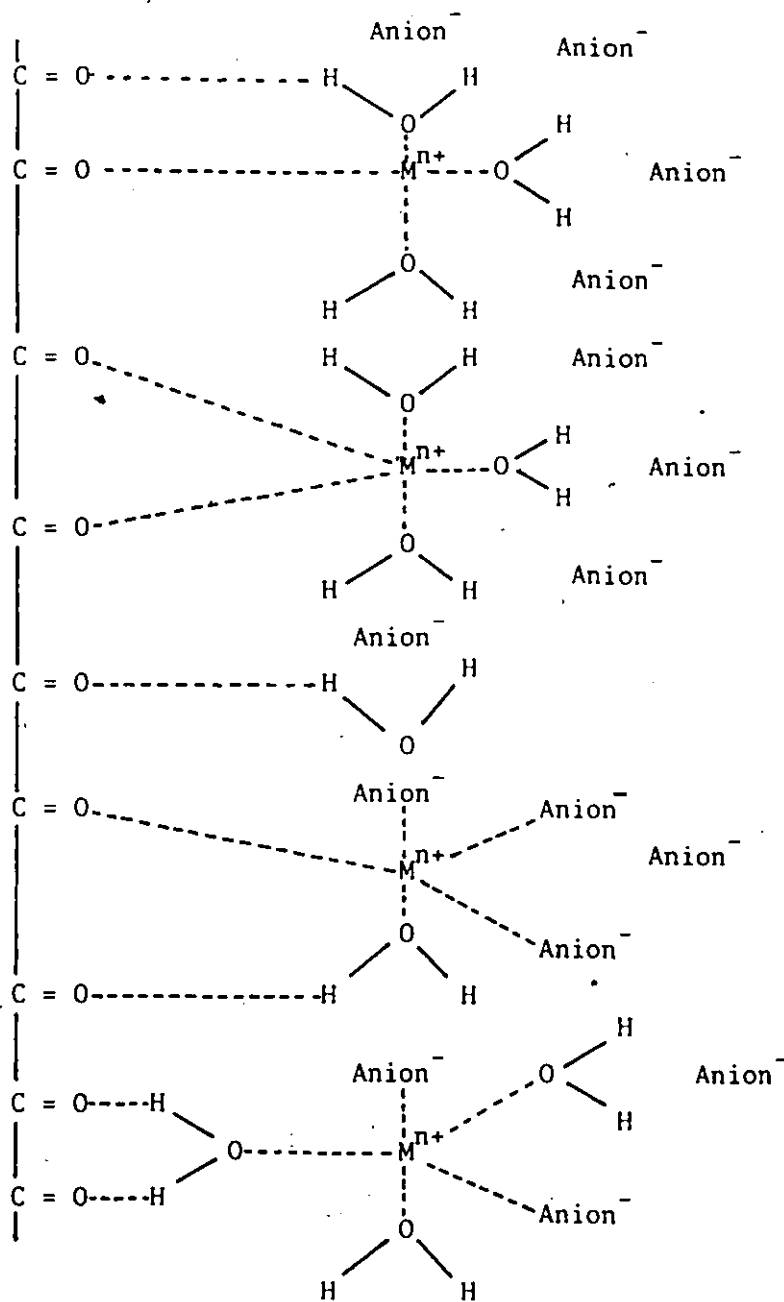


Figure 19. Proposed microscopic model for the adsorption of metal ions on XAD-7.

Figures 20 and 21 show D_R values as a function of pH for eight metal ions. The concentration of each metal was 20 $\mu\text{g/L}$, much lower than the concentrations required for the adsorption isotherm studies and so higher pH values could be reached. The two test solutions contained groups of four metal ions each, i.e., four sets of D_R values could be determined simultaneously. The resin mesh size was 60-100.

The maximum D_R values (i.e., maximum absorption) for the divalent ions occur in the range pH 7-9, and for the trivalent ions, pH 5-6. These pH ranges are in good agreement with the previous findings on the effect of pH on column adsorption of the trace metal ions (Section III.1.). D_R values for resin of larger particle size (20-50 mesh) were also determined and the pH values for maximum adsorption of metal ions were found to be the same as for 60-100 mesh resin. The numerical values of D_R , however, are lower for the larger particle size resin (Table XV). This fact is in agreement with the earlier observation that adsorption of metal ions increases with decreasing particle size.

The decrease in D_R with decreasing pH can be ascribed to increased proton adsorption and the eventual saturation of adsorption sites by protons. D_R values for the adsorption of protons (analytical concentration, 10^{-5} M) on 20-50 mesh and 60-100 mesh XAD-7 were determined to be 869 and 1912, respectively. These values are higher than the maximum D_R values for the various metal ions at the corresponding mesh size (Table XV). The stronger adsorption of protons on XAD-7 compared to metal ions may be a consequence of the higher

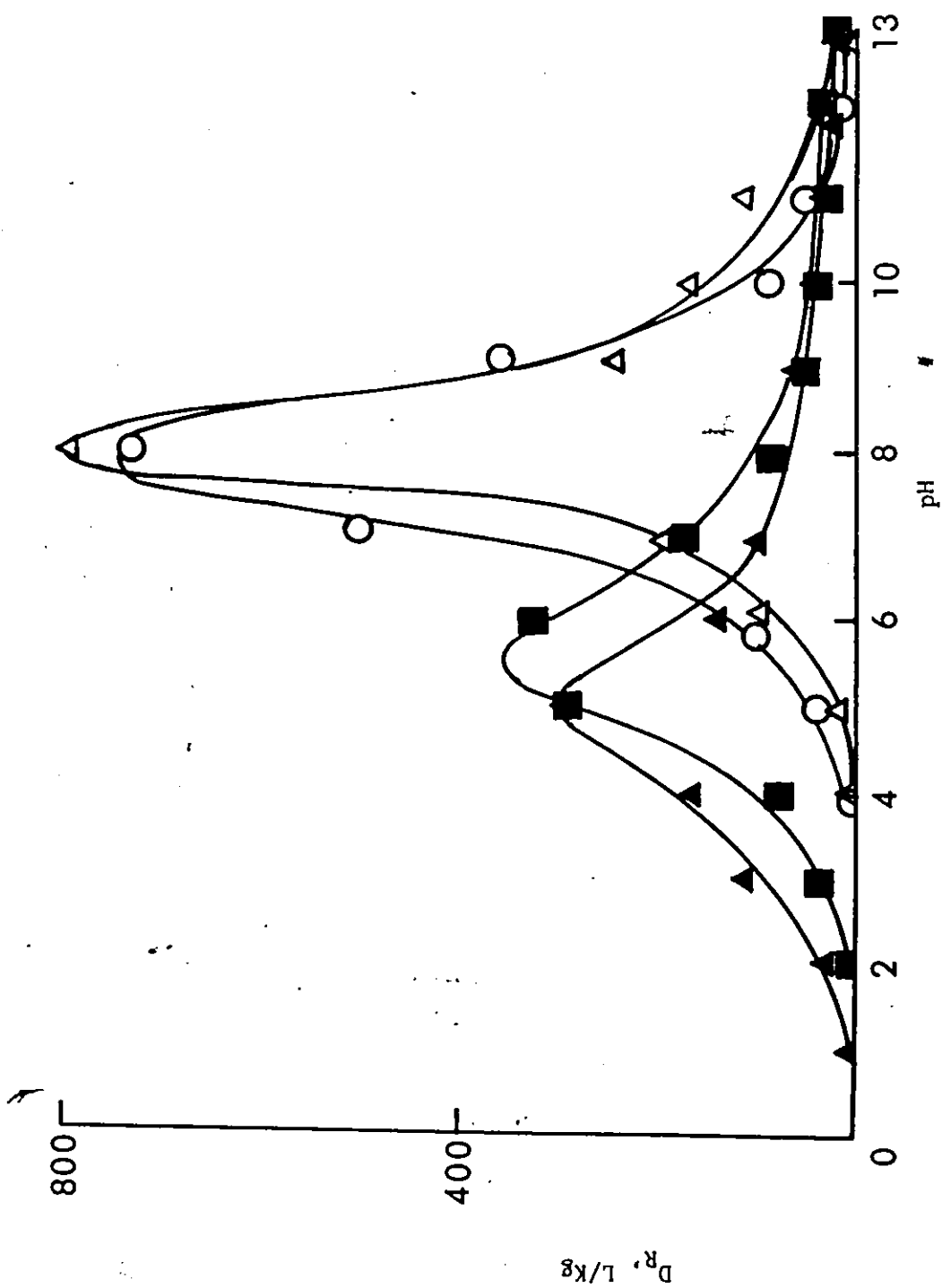


Figure 20. Distribution ratios as function of pH for the adsorption of Fe(III) (▲), Cr(III) (■), Mn(II) (○) and Co(II) (△) on XAD-7 (60-100 mesh). Metal ion concentration, 20 µg/L.

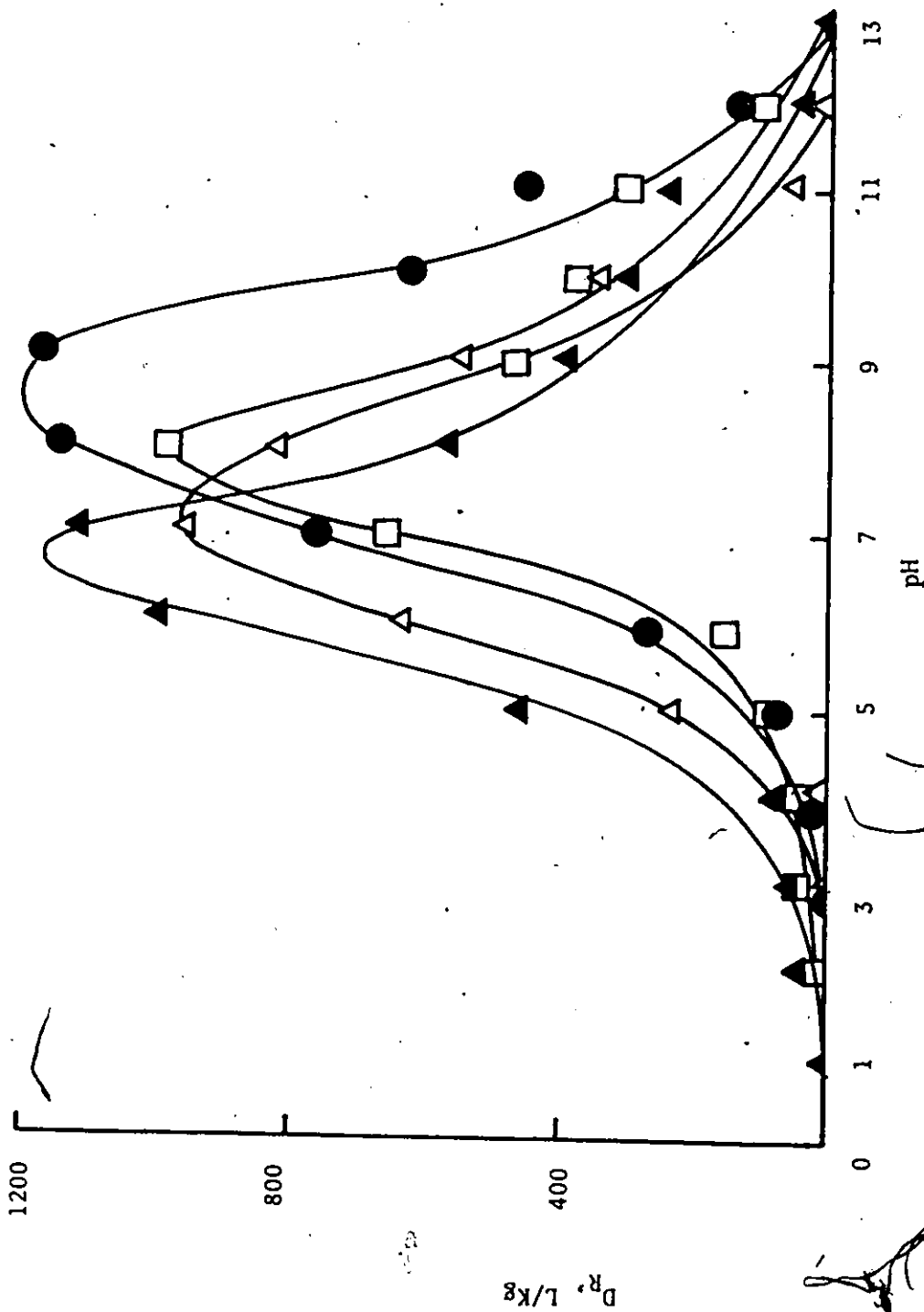


Figure 21. Distribution ratios as function of pH for the adsorption of Cu(II) (▲), Ni(II) (□), Cd(II) (●) and Pb(II) (△) on XAD-7 (60-100 mesh). Metal ion concentration, 20 µg/L.

TABLE XV. Maximum D_R Values for the Adsorption
of Metal Ions on XAD-7.

Metal Ion	pH ^b	D_R (L/Kg) ^a	
		20-50 mesh	60-100 mesh
Fe(III)	5.0	142	295
Cr(III)	6.0	209	320
Cu(II)	7.0	329	1086
Pb(II)	8.0	369	827
Ni(II)	8.0	422	930
Co(II)	8.0	234	797
Cd(II)	8.0	697	1168
Mn(II)	8.0	142	708

^a D_R values of four metal ions were determined simultaneously; total metal ion concentration in test solution was 80 $\mu\text{g/L}$.

^b pH at which maximum adsorption occurs.

charge density of the proton and therefore stronger charge-dipole interaction. Charge density considerations probably explain the adsorption of trivalent ions at pH values lower than those of the divalent ions, since the trivalent ions could compete better with protons for adsorption sites.

At higher pH, the adsorption of metal ions declines with increasing pH (Figures 20 and 21). At these pH values, there is an increase in the concentration of species such as $M(OH)_n$, $M(OH)_x^{+n-x}$, $M(\text{acetate})_x^{+n-x}$ and $M(NH_3)_x^{+n}$. Of these species, it is likely that the zero-charged insoluble hydroxides ($M(OH)_n$) mainly account for the decrease in D_R . In Figures 22 and 23, the D_R/pH profiles are shown in comparison to the fraction (α) of metal ion present as zero-charged hydroxides as a function of pH. The α diagrams were calculated for $10^{-5} M$ metal ion (154). The concentrations used to obtain the D_R values were about $10^{-6} M$. Although changes in the analytical concentration of metal ion do cause shifts along the pH axis, a 10-fold difference would result in shifts of no larger than ± 0.5 pH units. Thus, the decline in D_R values and the increase in the fraction of the colloidal zeroed-charged hydroxide species with pH may be more than coincidence. Also, the decrease in D_R values may be partly the result of increased adsorption of hydroxyl ions.

In summary, the D_R/pH profiles are shaped by the competitive interaction of protons and hydroxyl ions with the XAD-7 resin, by the charge density of species and by hydrolysis of the metal ions.

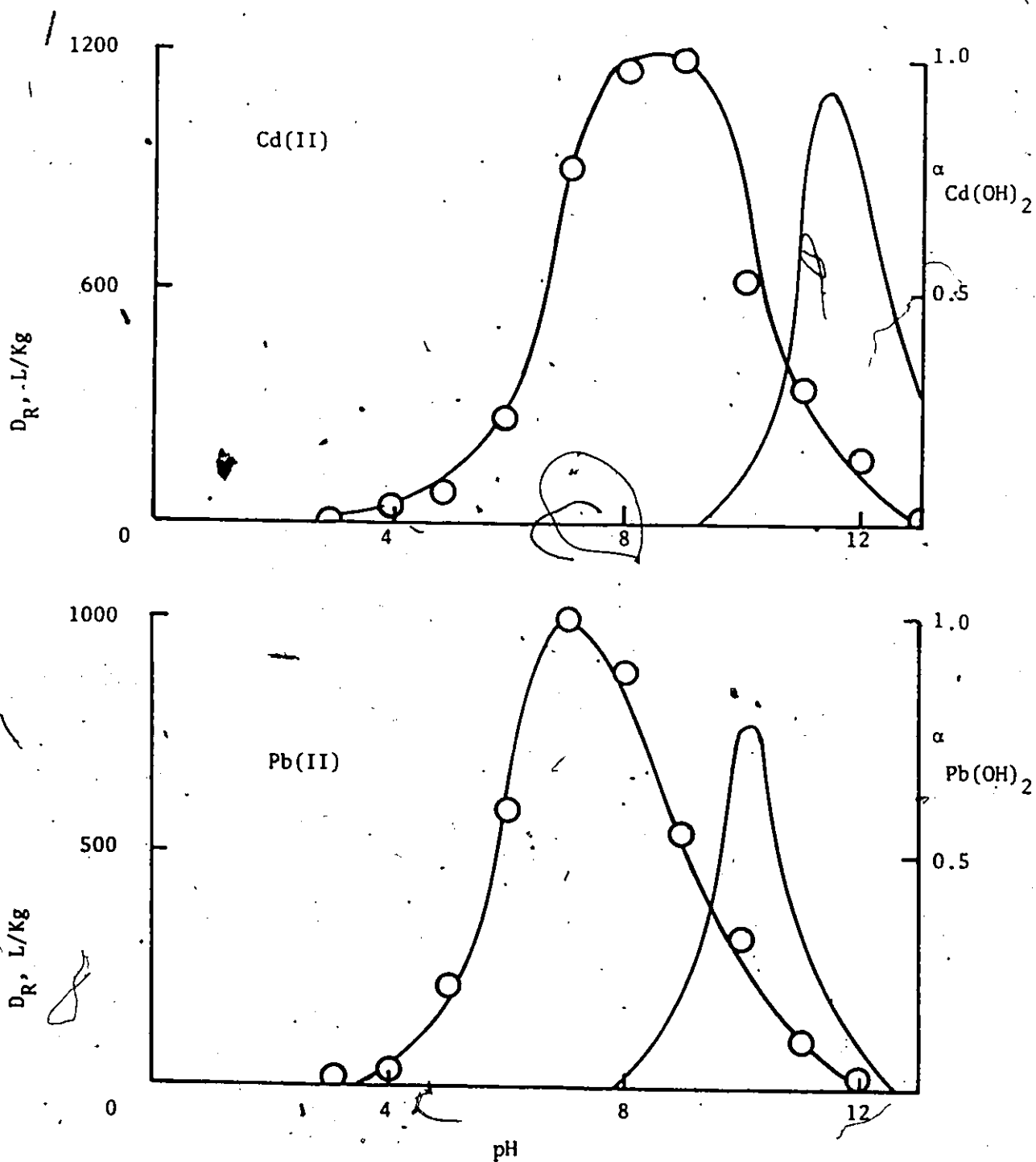


Figure 22. D_R /pH profiles for Cd(II) and Pb(II) adsorption on XAD-7 (80-100 mesh) (O) and α diagrams for $Cd(OH)_2$ and $Pb(OH)_2$ (—).

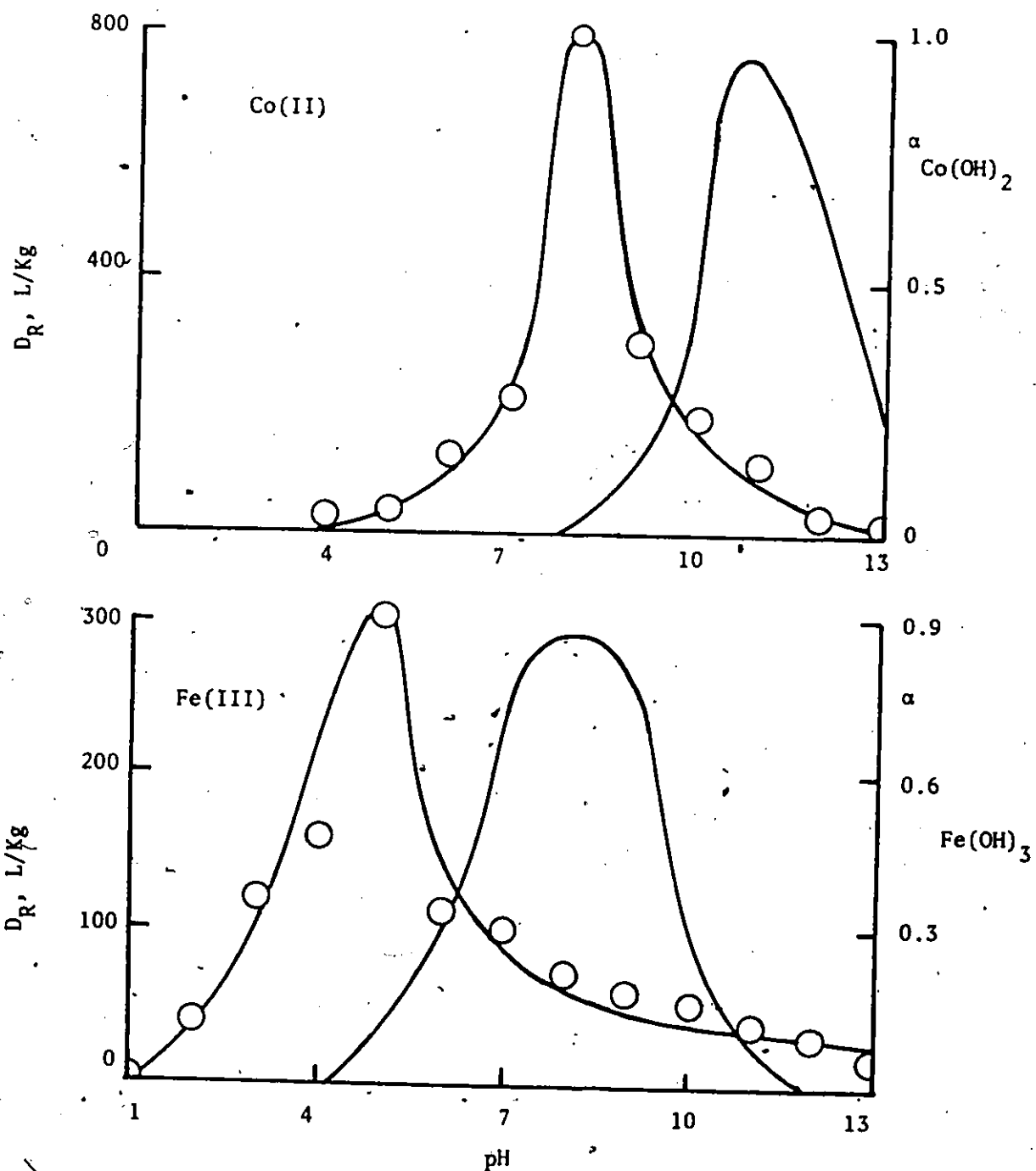


Figure 23. D_R /pH profiles for Co(II) and Fe(III) adsorption on XAD-7 (80-100 mesh) (O) and α diagrams for Co(OH)_2 and Fe(OH)_3 (—).

III.3 Studies on XAD-7 Column Operation

(i) Breakthrough Curves

The percent retention (adsorption) values reported in the preliminary studies represent an average extent of adsorption of metal ions in a fixed volume (i.e., 100 mL) of the test solution. A thorough study of column operation must include the breakthrough curve, which is a graphical representation of percent unretained metal ion (i.e., breakthrough) versus summed aliquots of sample volume, where the aliquots can be, say, 10 or 20 mL. The effects of particle size, metal-ion concentration, flow rate, organic ligands such as humic substances and (high) ionic strength on the breakthrough curve are discussed below.

(a) Effect of particle size and metal-ion concentration. In the preliminary work on column adsorption, only one particle size (20-50 mesh) of XAD-7 was used. Subsequent batch-adsorption studies showed that the resin capacity increases with a decrease in particle size. The effect of particle size on the breakthrough curve of Cu(II) is consistent with this observation. The results in Table XVI show that a higher breakthrough volume can be attained if resin of smaller particle size is used. In these studies, rather high concentrations of Cu(II) were used in order to reach breakthrough within a reasonable volume of sample. For practical purposes, however, the XAD-7 procedure is developed for the preconcentration of $\mu\text{g/L}$ levels of metals. At these levels, a very large volume of solution would be required to reach breakthrough. The experiment was terminated if no breakthrough was observed after 2.5 L of the sample had been percolated. In practice, the availability of sample and time restrictions almost always limit

TABLE XVI. Breakthrough Volumes for Cu(II) on 1 x 6 cm XAD-7 Column^a

Conc. of Cu(II), (mg/L)	Breakthrough volume (mL)	
	20-50 mesh	60-100 mesh
0.005	Not observed	Not observed
1.0	Not observed	Not observed
10	180	450

^a Column contains 1:0 g XAD-7, flow rate = 1.0 mL/min.

the volume of sample to less than 500 mL.

(b) Effect of flow rate. The concentration of metal ions used in this study was 5 $\mu\text{g/L}$. For the divalent ions (Cd, Co, Cu, Mn, Ni and Pb), the pH was 8.0; for the trivalent ions (Cr, Fe), the pH was 5.0. The preliminary work had shown that at these pH values, the flow rate for 100-mL test samples had little effect on percent adsorption.

With the exception of Cr(III), no breakthrough was observed for sample volumes of up to 500 mL at flowrates of 1 to 4 mL/min. Thus, for practical purposes, the flow rate of sample percolation can be as high as 4 mL/min for 20-50 mesh resin. For 80-100 mesh resin, however, a flow rate greater than 1 mL/min can not be attained by gravity feed because of column packing.

The effect of flow rate on the breakthrough of Cr(III) was further studied at pH 4.3, 5.0 and 6.3 and two concentrations of Cr(III) (0.5 and 5.0 $\mu\text{g/L}$). Whereas these Cr(III) concentrations had little effect on the breakthrough volume at a fixed flow rate, the effect of pH was found to be large (Figure 24). At a fixed pH (6.3) the flow rate also has an effect, although smaller (Figure 25). Over the pH range 4.3 to 6.3 and for flow rates from 1.0 to 4.5 mL/min, the breakthrough volume is highest at pH 6.3 and 1.0 mL/min. These data likely reflect the lower competition for resin sites by protons at pH 6.3 and the longer time for interaction with the resin at 1.0 mL/min.

The above results are somewhat different from those obtained in the preliminary studies (see Section III.1) which showed that percent retention of Cr(III) was highest and constant over the pH range 4 to 6 and that the effect of flow rate was minimal. The

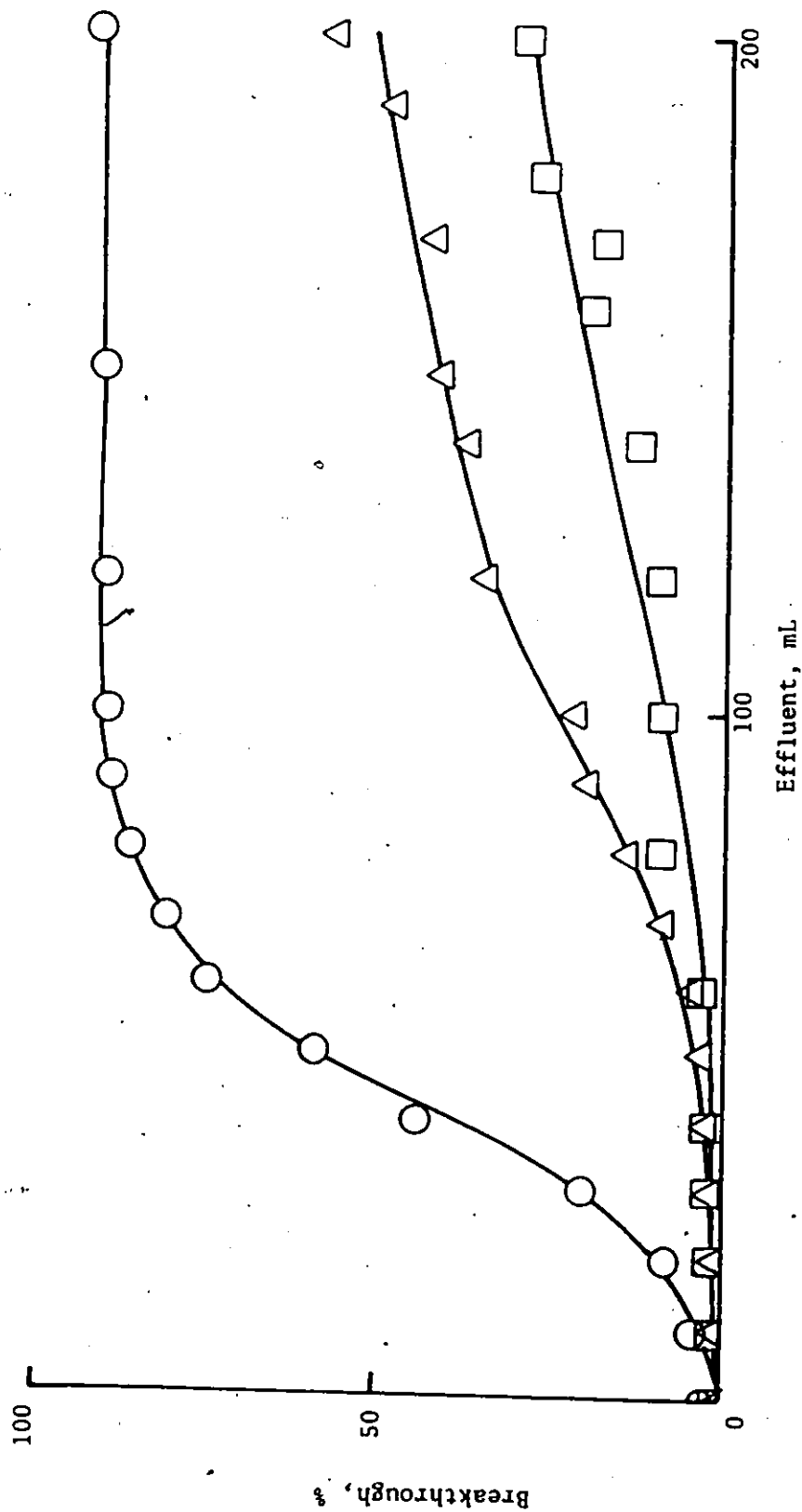


Figure 24. Breakthrough curves for solution of 5 $\mu\text{g/L}$ of Cr(III) at pH 4.3 (O), 5.0 (Δ) and 6.3 (\square). A 1x6 cm XAD-7 column (20-50 mesh) was used. Flow rate = 1 mL/min.

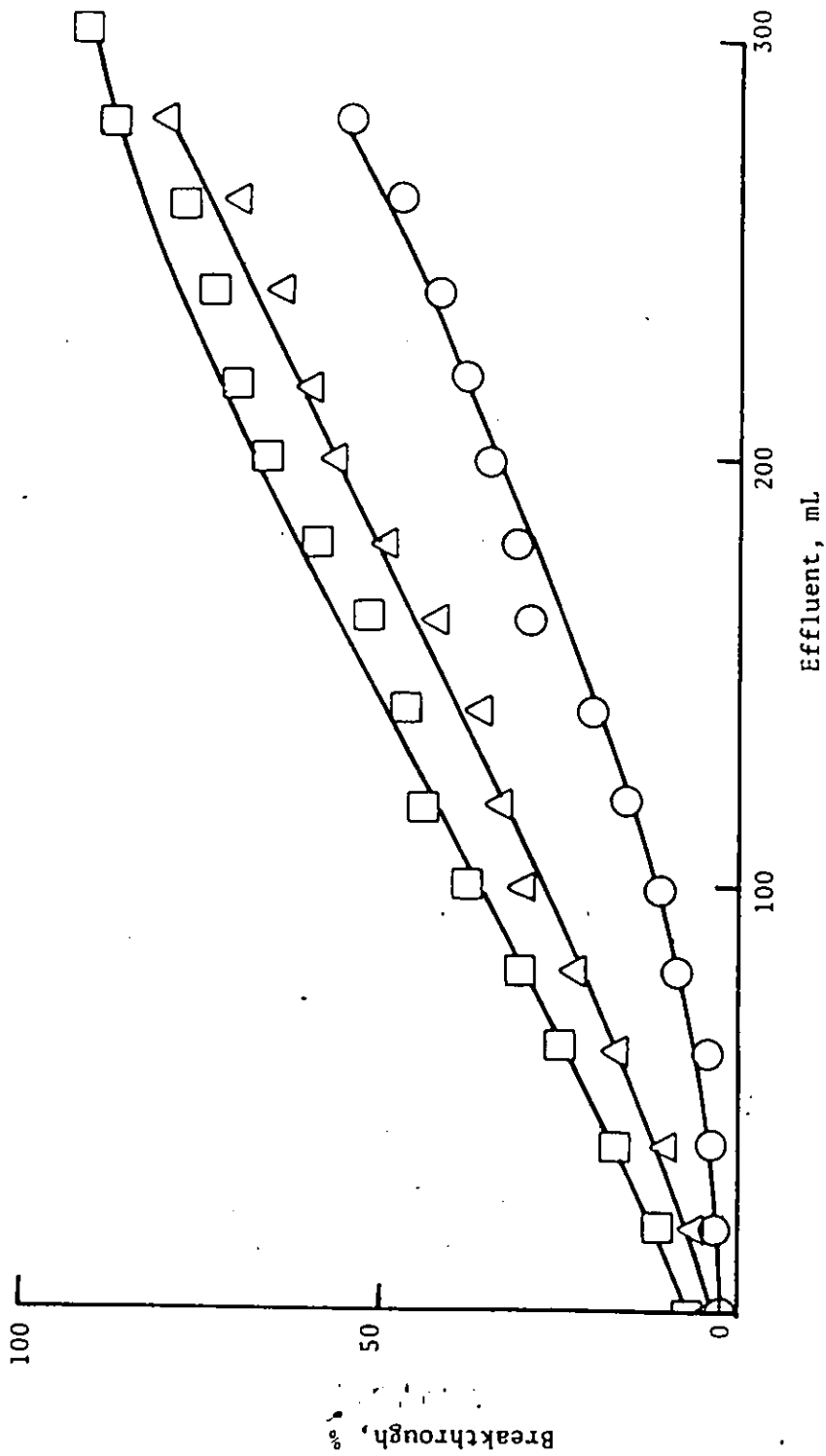


Figure 25. Breakthrough curves for solutions of 5 $\mu\text{g/L}$ of Cr(III) (pH 6.3) at flow rates of 4.5 mL/min (\square), 2.7 mL/min (Δ) and 1.0 mL/min (\circ). A 1x6 cm XAD-7 column (20-50 mesh) was used.

breakthrough curves show that pH 6.3 is optimal and that flow rate has an effect. The difference might be due partly to the fact that a larger column (1.3 g, 1 x 7 cm) and smaller sample (100 mL) were used in the preliminary studies, thus reducing the effect of flow rate.

The kinetic problems associated with the determination of Cr(III) are well-documented (155-159) and the low breakthrough volume for Cr(III) compared to Fe(III) and the divalent ions likely results from a kinetic factor. In the analysis of water samples described later, the flow rate was set at 1 mL/min to allow for better adsorption of Cr(III). Although breakthrough would still occur, the method of standard additions would still permit the determination of Cr(III), although with reduced sensitivity.

(c) Effect of ionic strength. The adsorption isotherm studies showed that as the ionic strength increases, the adsorption of Cu(II) drops to a lower level (see Section II.2 (iii) and Figure 17). Therefore, it was necessary to study the effect of ionic strength on the breakthrough volume in anticipation of the preconcentration of trace metal ions from seawater.

Solutions of NaCl adjusted to ionic strengths 0.01, 0.2, 0.5 and 0.8 at pH 8 were spiked with 1 µg/L of ⁶⁴Cu and the breakthrough volume for each solution was determined on both a 1 x 6 cm (20-50 mesh) and 1 x 3 cm (80-100 mesh) XAD-7 column, at a flow rate of 1 mL/min. No breakthrough could be detected at any ionic strength after passage of up to 500 mL of the solutions. This suggests that high concentrations of NaCl do not pose a serious problem.

In addition to NaCl, seawater contains other alkali-metal and

alkaline-earth salts. To examine their effect, the experiment was repeated with test solutions containing natural seawater diluted with DDW. The percentage of natural seawater was 2, 10, 25, 50 and 100. Humic substances were first removed to eliminate their effect on the adsorption of Cu(II) by XAD-7 (see Section (e) below). Each solution was adjusted to pH 8.0 and spiked with 1 $\mu\text{g/L}$ of $^{64}\text{Cu(II)}$. No breakthrough could be detected even after passage of up to 500 mL of any of the test solutions through the 1 x 3 cm column. The results of this experiment show that the salts in seawater do not seriously affect the capacity of a 1 x 3 cm column for the trace metal ions present in up to 500 mL of seawater.

(d) Breakthrough curves of alkali-metal and alkali-earth ions. In the preconcentration and GFAAS determination of trace metals in natural waters, it is desirable that alkali-metal and alkaline-earth salts not be preconcentrated to a large degree with the trace metals. Significant preconcentrations of these high-concentration cations would not only reduce the number of resin sites for adsorption of trace metals (as implied in the previous section) but a high concentration of these salts in the acid eluant would also be detrimental to GFAAS measurement of the trace metals.

In this experiment, NaCl and CaCl_2 , each at 10 mg/L, were used to represent alkali-metal and alkaline-earth salts. The breakthrough volume at pH 8 for each ion was determined for a 1 x 3 cm (80-100 mesh) and a 1 x 6 cm (60-100 mesh) XAD-7 column. For Na^+ ,

the breakthrough volume for each column was less than 5 mL; for Ca(II), it was about 20 mL and 30 mL, respectively - much lower than that of metal ions such as Cu(II) under the same experimental conditions (Figure 26). The breakthrough volume for Na⁺ probably represents physical entrainment of dissolved NaCl in the void volume of the column rather than adsorption of the ion on the resin. The low breakthrough volume of Ca(II) suggests that it competes less favourably for adsorption sites than Cu(II). Thus, once the alkali-metal and alkaline-earth salts entrained in the void volume of the column have been removed, the acid eluent containing the trace metals should be relatively free from salt-matrix interference for GFAAS measurements.

(e) Effect of organic (humic) substances. The bulk of organic matter in natural waters consists of humic substances (7-11, 80, 83-85). These are amorphous, hydrophilic, polyacidic materials of molecular weight ranging from several hundred to tens of thousands. These substances are strong complexing agents and their presence in natural waters could have a strong effect on the adsorption of trace metals on an XAD-7 column. Indeed, it was found that in the presence of humic substances (10 mg/L), the breakthrough volumes for metal ions are quite low, even at their optimal adsorption conditions (Figure 27).

In a separate experiment in which Cu(II) was used as a model ion, solutions ranging in ionic strength from 0.01 to 0.8 (pH 8) were spiked with 10 mg/L of humic materials. At all ionic strengths, almost immediate breakthrough of Cu(II) was observed. This experiment illustrates the detrimental effect of humic substances in solutions of ionic strength comparable to seawater (i.e., ~ 0.70 (1)).

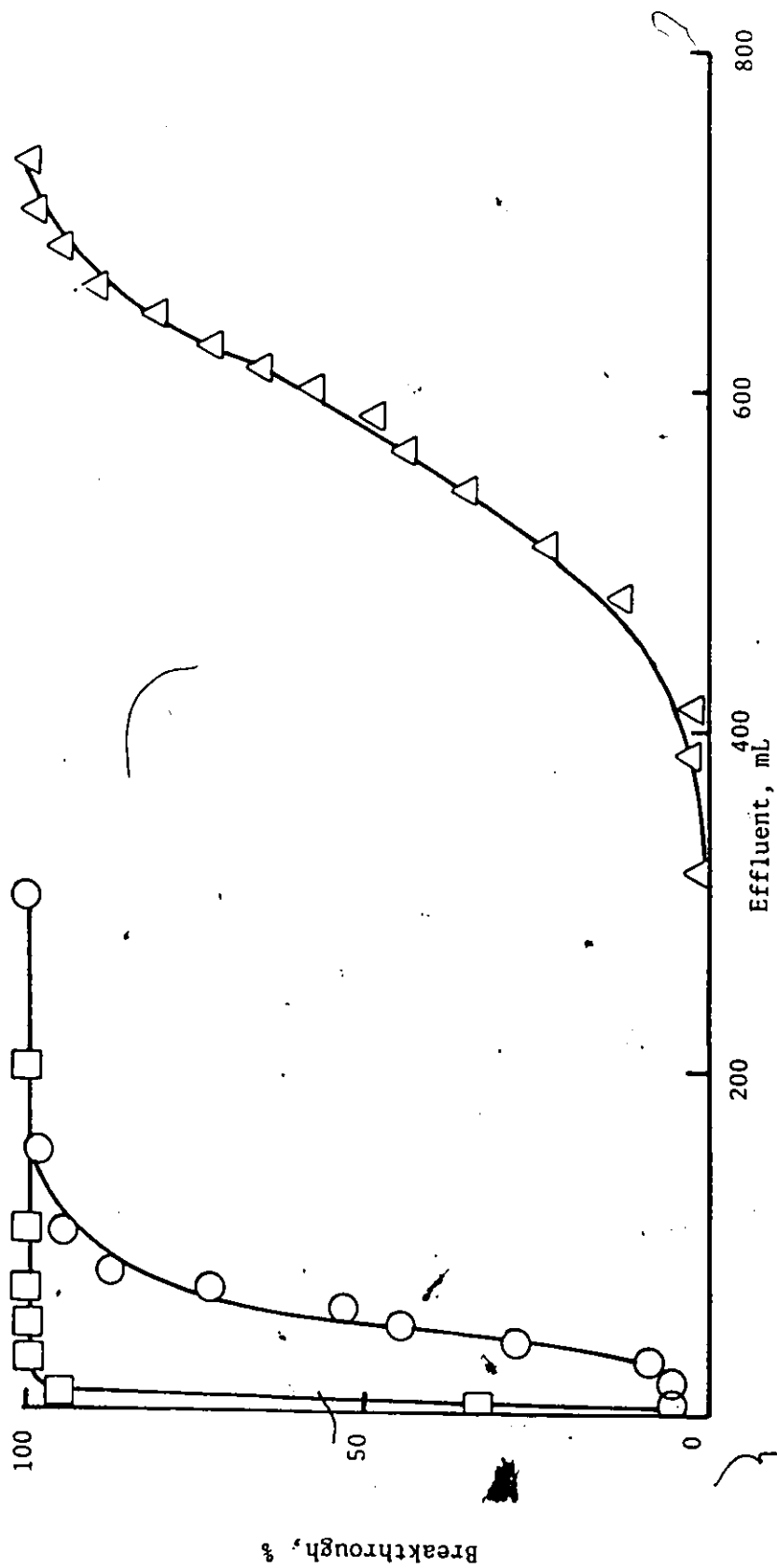
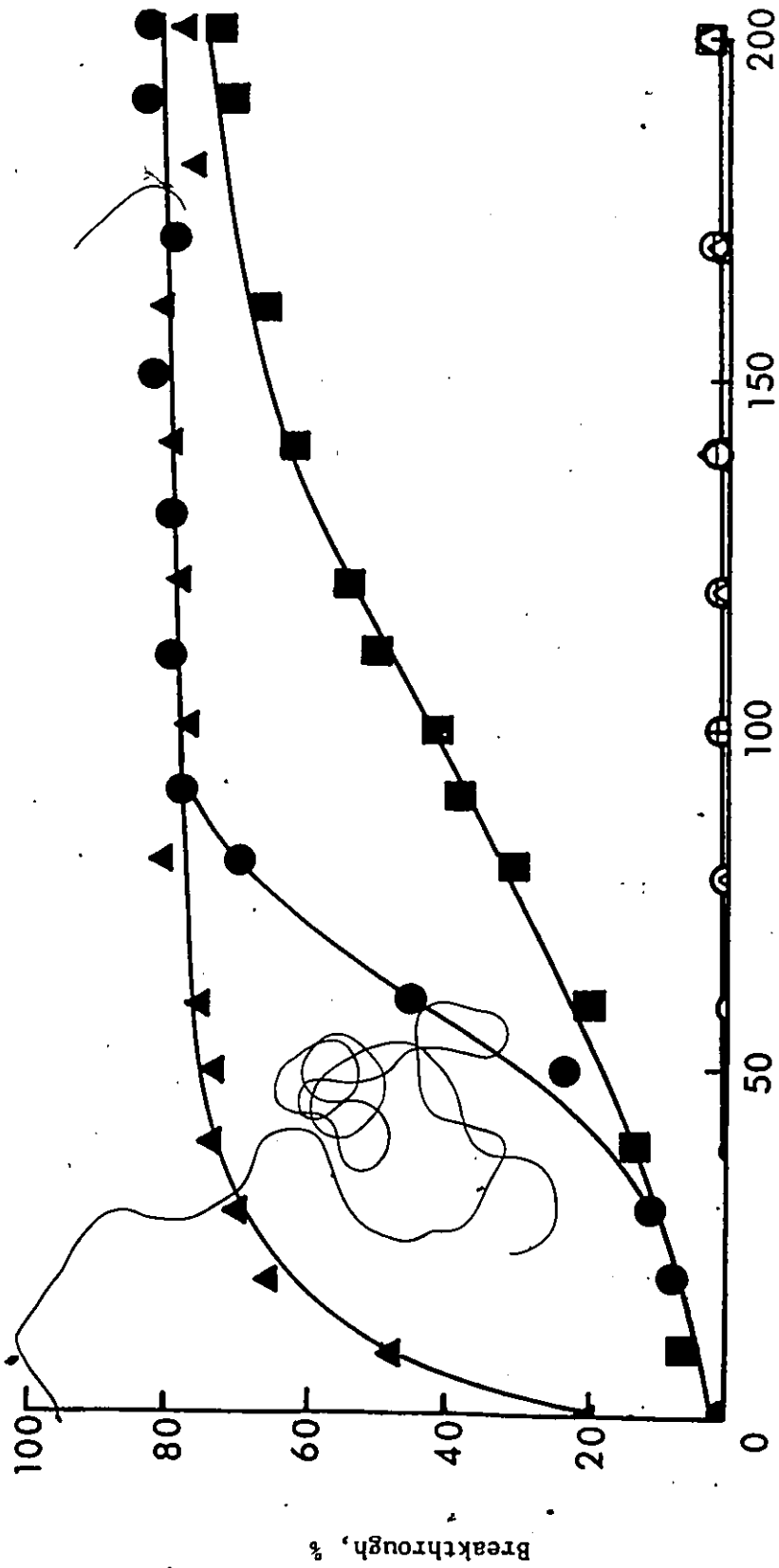


Figure 26. Breakthrough curves for solutions of 10 mg/L of Cu(II) (Δ), of Na⁺ (O) and of Ca(II) (O) on a 1x6 cm XAD-7 column (60-100 mesh). Flow rate = 1 mL/min.



Effluent, mL

Figure 27. Breakthrough curves for Fe(III) (Δ), Cu(II) (\circ) and Mn(II) (\square) in the absence of humic substances; for Fe(III) (\blacktriangle), Cu(II) (\bullet) and Mn(II) (\blacksquare) in the presence of 10 mg/L of humic substances. A 1x6 cm XAD-7 column (20-50 mesh) was used; flow rate = 2mL/min; metal ion concentration = 5 μ g/L each, pH = 6.3 for Fe(III), 8.0 for Cu(II) and Mn(II).

The effect of the humic materials on breakthrough volumes is a thermodynamic one, rather than a kinetic effect relating to possible low lability of the humate complexes. If the latter is true, then adsorption of metal ions should increase with time to essentially the same level obtained in the absence of the humics. This was not observed, however, when a test solution (25.0 mL) at pH 8 containing 30 µg/L of Cu(II) and 10 µg/L of humics was batch-contacted with XAD-7 resin.* Adsorption of Cu(II) reached 30% after about 30 min and remained at this level for up to 48 hr. The distribution ratio was 21, which is much lower than the value of 329 obtained for Cu(II) in the absence of humic materials. The rates of adsorption in both cases were about the same. Similar observations were made for Co(II), Cd(II) and Mn(II). Therefore, it is concluded that the adsorption forces are too weak to cause complete displacement of the metal ions from their humate complexes and thus the breakthrough volume is substantially lowered.

To overcome the detrimental effect of humic substances in the application of the XAD-7 procedure to the preconcentration of trace metal ions from natural waters, a two-column technique described in the following section was devised.

(ii) The Two-Column Technique

As shown by the results above (and by low results for a Lake Ontario water analyzed in this laboratory (160)), humic substances must

*Before use, the solution was allowed to stand for 48 hr to permit equilibration of the Cu(II) and humics; 0.500 g of XAD-7 (20-50 mesh) was then added and the mixture was stirred and sampled for up to 48 hr.

be removed from the natural water matrix before preconcentration by the XAD-7 procedure*.

Previous work in this laboratory (144) and by others (127, 128) had shown that humic substances in acid solution (i.e., pH < 2) can be removed by passage through a XAD-7 column. Since metal ions are not adsorbed on XAD-7 at this low pH, a two-column preconcentration technique was developed in which the humic substances are first removed by percolation of the acidified water sample through a precolumn of XAD-7, and the trace metals in the effluent are then preconcentrated (after adjustment to pH 8) on an XAD-7 analytical column.

The effectiveness of this two-column technique is demonstrated in Table XVII, in which the recovery of metal ions from a synthetic solution by the two-column method and by the conventional single-column method are compared. The effect of humic-substance removal is quite dramatic. Since natural water samples are stored at pH 1.6-1.7, percolation through the precolumn is the only additional step involved and so the simplicity of the XAD-7 procedure is not significantly compromised.

(iii) Elution Recovery and Preconcentration Factor

In the context of the low concentrations pertinent to this work, the breakthrough volumes on the XAD-7 column are high in the absence of humic substances. Therefore, to obtain large preconcentration factors,

* Although water samples are stored at pH 1.6-1.7, at which acidity the metal humates and fulvates are dissociated, readjustment to pH 8 for preconcentration on the XAD-7 column would cause at least partial reformation of the complexes. Therefore, the humic substances must be removed.

TABLE XVII. Recovery of Metal Ions from Aqueous Solutions Containing Humic Substances by Single and Two-column Method^a.

Element	Recovery (%) ^b	
	Single-column	Two-column
Fe(III)	58	88
Cr(III)	37	81
Cu(II)	77	97
Pb(II)	69	94
Ni(II)	81	101
Co(II)	72	99
Mn(II)	93	97
Cd(II)	73	99

^a For 1 x 6 cm (60-100) mesh XAD-7 columns and 100 mL of test solutions containing 20 µg/L of each metal ion and 10 mg/L of humic substances. Flow rate = 1 mL/min; pH = 6.3 and 8.0 for the trivalent and divalent ions, respectively. Metal ions were eluted with 10 mL of 1% v/v HCl (preconcentration factor = 10).

^b Results represent single determination only.

tration factors, one can simply use a large sample size (e.g., ≥ 1 litre). Sample availability and time restrictions, however, often limit the sample volume to 100 or 200 mL. A more fruitful approach is to reduce the solvent elution volume. In this regard, the effects of column size and of resin particle size on the elution volume were investigated.

(a) Effect of column-bed size. Elution profiles (i.e., fractional chromatograms) for several metal ions were determined as a function of column-bed size. A resin mesh size of 80-100 was used and the eluant was either 1% v/v HNO_3 or 1% v/v HCl .

In Figure 28, the effect of column-bed size is demonstrated with Cu(II) . Similar elution profiles were obtained for the other metal ions. The volume of eluant required for quantitative elution is reduced as column size decreases. With a 1 x 3 cm column, 4.5 mL of the eluant is adequate (5 mL in practice). No attempt was made to reduce the volume to less than 4.5 mL by use of an even smaller column, so as not to compromise the breakthrough volume and to avoid significant volumetric errors in the collection of small volumes.

(b) Effect of particle size. Elution profiles for several metal ions were determined as a function of resin particle size. A 1 x 6 cm XAD-7 column was used and the eluant was either 1% v/v HNO_3 or 1% v/v HCl .

The effect of particle size on elution is demonstrated with Cu(II) in Figure 29. Similar elution profiles were obtained for the other metal ions. The elution chromatograms are essentially independent of particle size and elution is quantitative between 3 to 8 mL. The difference in interstitial volume due to the difference in particle size is hardly significant and does not affect the elution profile.

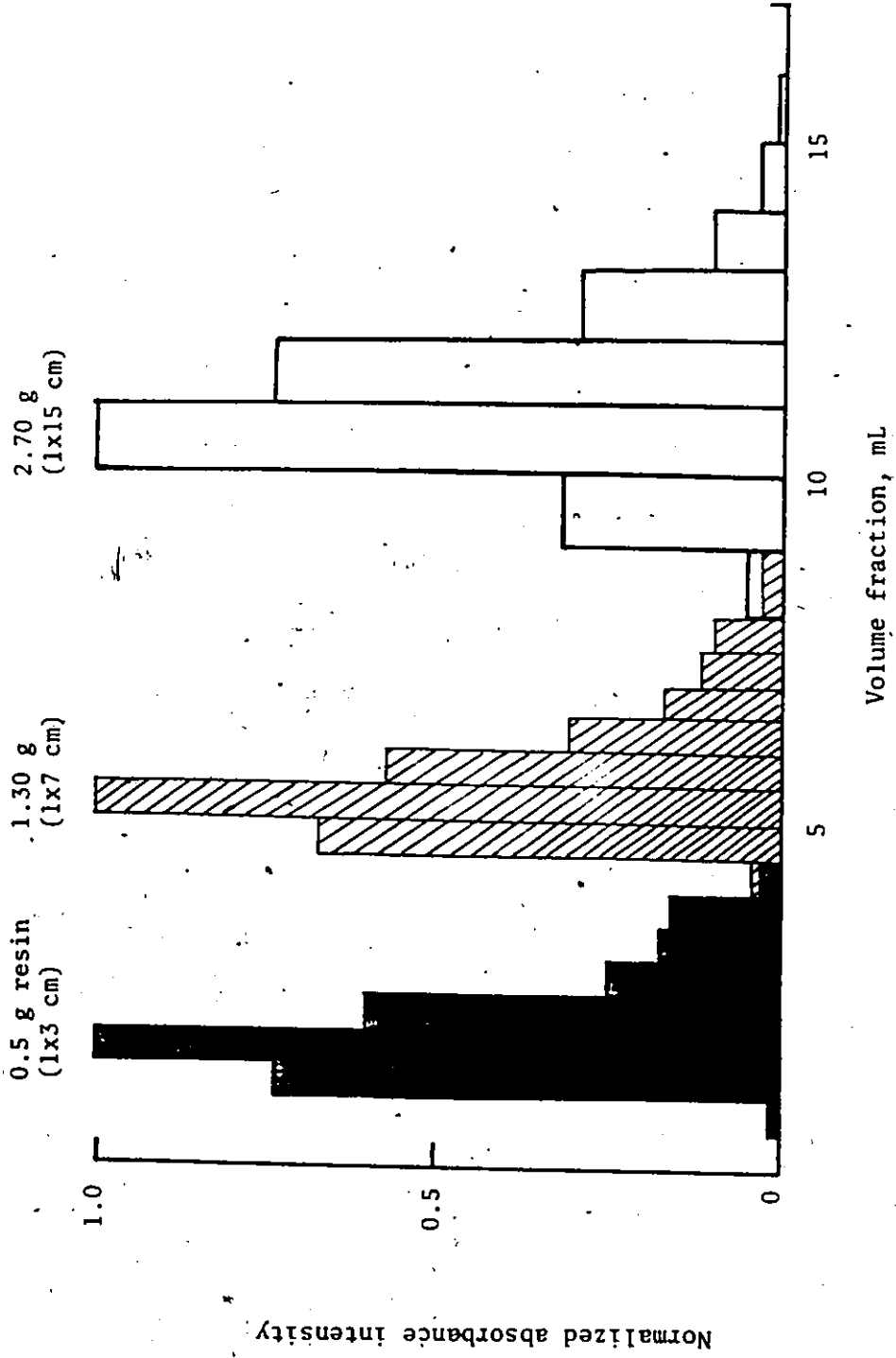


Figure 28. Elution profiles of Cu(II) from columns of different bed size, 80-100 mesh. Total mass of metal ions on column, 2 µg; mass of Cu(II) on column, 0.2 µg; elution rate = 1 mL/min; eluant, 1% v/v HNO₃ or HCl.

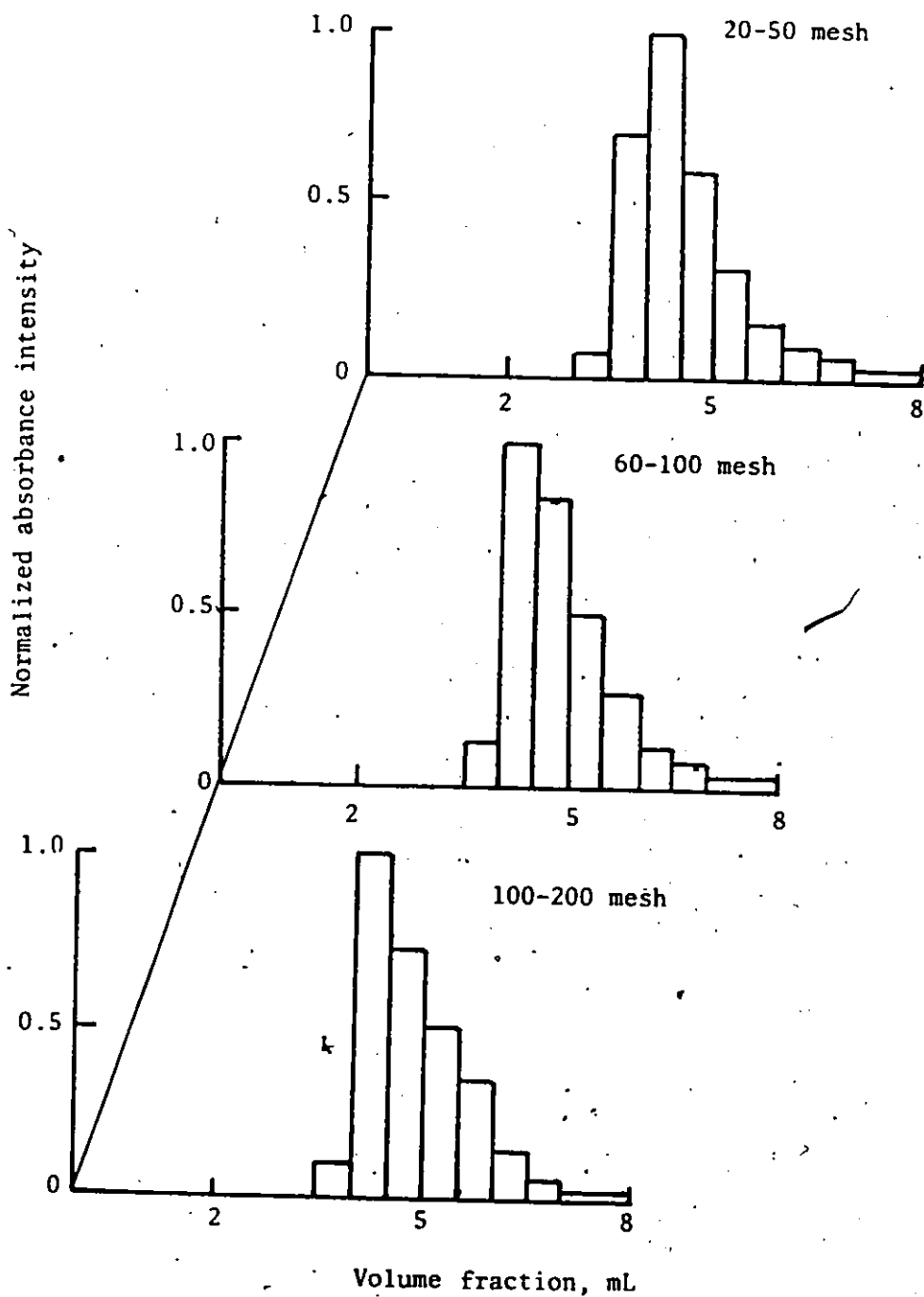


Figure 29.4 Elution profiles of Cu(II) from columns of different particle sizes. Total mass of metal ions on column, $2 \mu\text{g}$; mass of Cu(II) on column, $0.2 \mu\text{g}$; eluant, 1% v/v HNO_3 or HCl ; column size $1 \times 6 \text{ cm}$, elution rate = 1 mL/min .

(c) Removal of entrained sodium salt from the column. In the analysis of solutions of high ionic strength by GFAAS, matrix interference by light scattering from covolatilized sodium salts (i.e., non-specific adsorption) is often encountered (23-26). In seawater, NaCl accounts for over 90% of the salt matrix and analyte isolation from NaCl is therefore a prerequisite.

Previously, it was demonstrated that Na^+ is not adsorbed on an XAD-7 column. Nevertheless, a significant amount of NaCl would be trapped in the column void-volume and should be removed prior to elution of the trace metal ions. Obviously, washing of the column should not lead to premature elution of metal ions. Because 0.01 M NH_4NO_3 (pH 8.0) does not cause elution of the metal ions from the column (Section III.1), it was used here to rinse NaCl from the column (Figure 30). About 10 mL of the rinsing agent is quite adequate for removal of the entrained NaCl. No salt matrix interference was encountered in the subsequent GFAAS measurement of the acid eluant.

Figure 31 shows the elution of Cu(II) (in 0.70 M NaCl) is not affected by prior rinsing of the NaCl with 10 mL of the NH_4NO_3 solution. The elution profile is essentially the same as that in Figure 28.

III.4 Applications

The XAD-7 two-column method was applied to both lakewater and seawater samples. Optimal conditions for adsorption, elution and preconcentration were selected in accordance with the foregoing discussion. Thus, the column bed-size was 1 x 3 cm, which allows quantitative elution with 5 mL of 1% v/v nitric acid. The resin

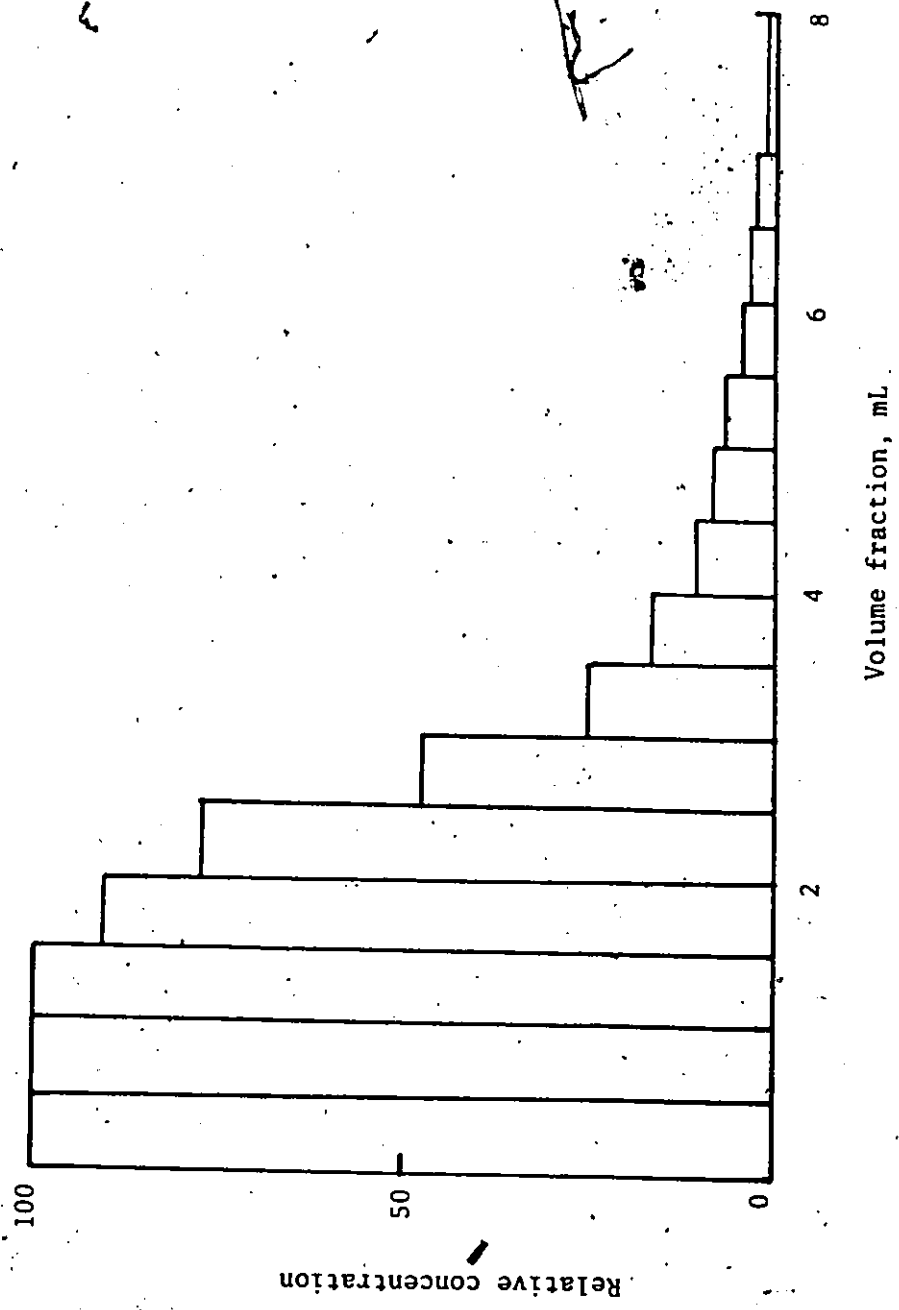


Figure 30. Rinsing of entrapped NaCl from a 1x3 cm XAD-7 column (80-100 mesh) by 0.01M NH_4NO_3 at pH 8.0, after percolation of 50 mL of seawater. Flow rate = 1 mL/min.

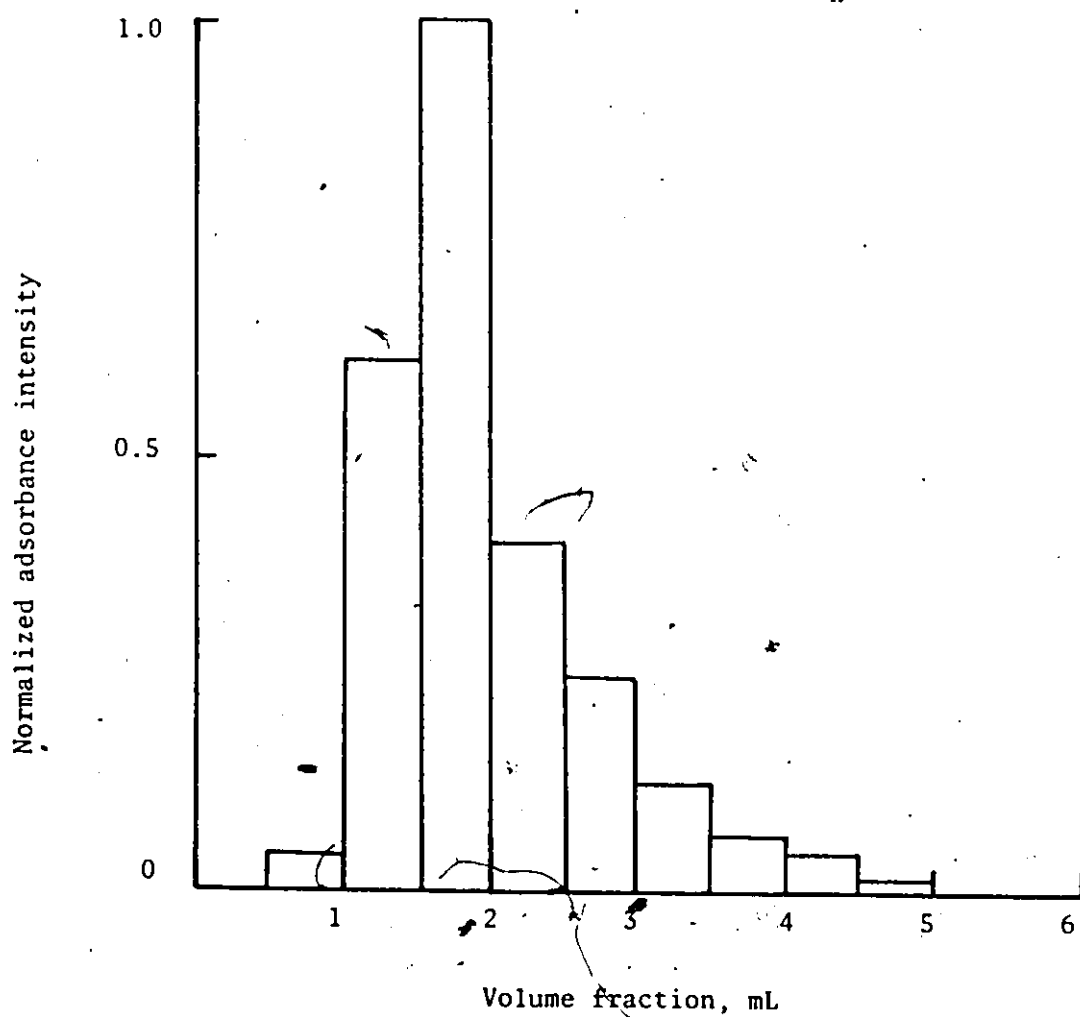


Figure 31. Elution of Cu(II) from 1x3 cm XAD-7 column (80-100 mesh) by 1% v/v HNO₃, after rinsing column with 10 mL of 0.01M NH₄NO₃. Mass of Cu(II) on column = 0.2 µg; flow rate = 1 mL/min.

mesh size was 80-100, which allows a higher column capacity and superior packing (due to a narrower size range). Flow rates for adsorption and elution were 1 mL/min. Resin sizes smaller than 100 mesh result in flow rates that are too low to be practical. The test solution was adjusted to pH 8 which is optimal for the divalent ions and a little less so for the trivalent ions. A separate aliquot adjusted to about pH 6.3 yields a higher recovery of the trivalent ions but requires more time and sample.

The water samples were stored at pH 1.6-1.7 in polypropylene bottles. Little adsorption of metal ions onto container walls occurs at this pH over long periods of time. Also, organic complexes (mainly humates and fulvates) of the trace metals are effectively dissociated. As noted above, the sample is ready for passage through the precolumn to remove the humic substances.

(i) Application to Lakewater

Before application to natural lakewater, the two-column procedure was tested on a synthetic freshwater sample. Recovery of the various trace metals in the synthetic lakewater is shown in Table XVIII. The results for the divalent ions are, in general, satisfactory. The result for Fe is somewhat high and not within experimental error of GFAAS. It is likely the result of contamination. The result for Cr is low. The determination of Cr by the XAD-7 procedure is a general problem, and is addressed in more detail below.

The two-column method was next applied to two Lake Ontario water samples, identified by the Canadian Center for Inland Waters (CCIW) as taken from Station 302 and Station 14. They were preconcentrated

TABLE XVIII. Analysis of Synthetic Freshwater by XAD-7 Two-Column Method^a

Element	Mass added to 200 mL(ng)	Mass recovered (ng)
Fe	200	265 ± 17
Cr	200	92 ± 9
Cu	200	240 ± 40
Pb	200	224 ± 58
Ni	200	196 ± 17
Co	200	180 ± 6
Mn	20.0	18.0 ± 1.5
Cd	20.0	18.3 ± 2.3

^a The precolumn and analytical columns were 1 x 3 cm (80-100 mesh); test solution, 200 mL containing 10 mg/L of humic substances, electrolyte, 0.01 M NH₄Cl at pH 8.0; elution, 5.0 mL of 1% v/v HNO₃ (preconcentration factor: 40.0); flow rates = 1 mL/min. Results and standard deviations are based on triplicate determination. A standard calibration curve was used.

trated 40-fold (200 mL to 5 mL) and measured by GFAAS. Both the standard calibration curve method and the method of standard additions were used. For comparison purposes, these samples were also preconcentrated (8-fold) by the accepted Chelex-100 method prior to GFAAS measurement (by calibration curve). As an additional check, those metal ions of sufficiently high concentration were measured directly by GFAAS (calibration curve method) without preconcentration. The data are given in Tables XIX and XX. Except for Cr and Mn, the results by the various methods are in satisfactory agreement, considering the low levels of concentrations under consideration.

A point of note is that the 8-fold preconcentration factor associated with the Chelex-100 method is not adequate for the low level of Co in the samples. The low preconcentration factor is a direct consequence of the large volume (i.e., 25 mL) of 14% v/v HNO_3 required for elution of the metal ions from the column.

With regard to the XAD-7 two-column method, the data obtained by the method of standard additions confirms the data obtained by the calibration curve method (except for Cr and Mn). This is a significant result because the use of the calibration curve method is obviously preferable since considerable amounts of both sample and time are spared. These are often major considerations. The reason that the calibration curve method can be used with the XAD-7 column is due to the prior removal of humic substances by the precolumn. The humics are not present to cause interference in the subsequent preconcentration step carried out on the analytical column. In this respect,

TABLE XIX. Analysis of Lake Ontario Water, CCIW Station 302

Element	Concentration ($\mu\text{g/L}$) ^a			
	Direct GFAAS ^b	Chelex-100 ^c	Calibration Curve	XAD-7 Two-Column Method ^d SAM
Fe	5.14 \pm 0.31	5.53 \pm 0.72	4.94 \pm 0.55	5.60 \pm 0.48
Cr	1.13 \pm 0.19	0.31 \pm 0.07	0.50 \pm 0.12	1.00 \pm 0.12
Cu	1.18 \pm 0.19	2.17 \pm 0.41	1.95 \pm 0.07	1.41 \pm 0.22
Pb	< 1	0.41 \pm 0.04	0.64 \pm 0.18	0.78 \pm 0.09
Ni	< 3	1.38 \pm 0.11	1.47 \pm 0.26	1.71 \pm 0.06
Co	< 1	< 0.1	0.093 \pm 0.017	0.085 \pm 0.018
Mn	0.89 \pm 0.08	0.72 \pm 0.04	0.125 \pm 0.011	0.80 \pm 0.02
Cd	< 0.1	0.031 \pm 0.002	0.038 \pm 0.004	0.047 \pm 0.010

^a Means and standard deviations are based on triplicate determinations.

^b The symbol < means less than the concentration which corresponds to 0.013 absorbance units (i.e., 3 times the absolute sensitivity, 0.0044, of GFAAS).

^c A 1 x 6 cm (100-200 mesh, NH_4^+ form) Chelex-100 column and 200 mL of sample were used. 0.01M NH_4OAc at pH 5.4 was used as the buffer electrolyte. Metal ions were eluted with 25.0 mL of 14% v/v HNO_3 (preconcentration factor 8.0). Flow rates = 1 mL/min.

^d Experimental conditions were the same as those described for Table XVIII.

TABLE XX. Analysis of Lake Ontario Water, CCIW Station 14

Element	Concentration ($\mu\text{g/L}$) ^a			
	Direct GFAAS ^b	Chelex-100 ^c	XAD-7 Two-Column Method ^d	
			Calibration Curve	SAM
Fe	4.29 \pm 0.32	4.51 \pm 0.40	4.20 \pm 0.18	5.50 \pm 0.86
Cr	1.56 \pm 0.23	0.46 \pm 0.07	0.57 \pm 0.03	1.17 \pm 0.04
Cu	7.40 \pm 0.11	6.67 \pm 0.66	6.75 \pm 0.18	6.39 \pm 0.23
Pb	1	0.28 \pm 0.04	0.38 \pm 0.06	0.34 \pm 0.01
Ni	< 3	2.32 \pm 0.32	2.30 \pm 0.18	1.83 \pm 0.22
Co	< 1	< 0.1	0.032 \pm 0.002	0.031 \pm 0.019
Mn	1.26 \pm 0.14	1.13 \pm 0.03	0.148 \pm 0.028	1.07 \pm 0.02
Cd	< 0.1	0.026 \pm 0.002	0.033 \pm 0.011	0.032 \pm 0.017

^a Means and standard deviations are based on triplicate determinations.

^b The symbol < means less than the concentration which corresponds to 0.013 absorbance units (i.e., 3 times the absolute sensitivity, 0.0044, of GFAAS).

^c Experimental conditions were the same as those described for Table XIX.

^d Experimental conditions were the same as those described for Table XVIII.

it is interesting to note that the calibration curve was also used in the Chelex-100 procedure. The standard practice in preconcentration by Chelex-100 is to use standard additions but here again, the data suggest that standard additions may not be necessary. In the future, it would be good practice for investigators to try both calibration procedures and if the results yielded by both are in reasonable agreement, to continue with only the calibration curve method, which is more convenient by far.

The results of the direct analysis for (total) Cr and Mn provided a basis to assess recovery of these metals by the various preconcentration methods. From Tables XIX and XX, it is obvious that Cr can not be quantitatively recovered by either the XAD-7 calibration curve or Chelex-100 method*. Several investigators have attributed low Cr recovery to slow reaction kinetics (155-159) and have recommended the method of standard additions as a means of compensation. With the XAD-7 method, application of the standard additions method does yield improved data (compare direct GFAAS and SAM results in Tables XIX and XX). For chromium preconcentration, the standard additions method is mandatory.

While problems with the preconcentration of Cr(III) are well recognised, the real surprise was the data for Mn (see Tables XIX and

* In natural waters, Cr(III) exists in equilibrium with Cr(VI). In acidic waters, however, Cr exists as Cr(III) (155-159,161).

XX). The XAD-7 calibration-curve method yields very low Mn recovery (11-15%) compared to the results by Chelex-100 and direct GFAAS. Significantly, the XAD-7 calibration curve method yields good recoveries of Mn(II) in the seawater samples discussed in the following section. This observation indicates that special circumstances obtain in the lakewater samples which affect the XAD-7 calibration curve method but not the Chelex-100 calibration curve method. Because the XAD-7 preconcentration with standard additions is a compensating procedure, the effect is not observed when this calibration method is used.

It is tempting to suggest that the Mn(II) in the lakewater is partially bound by a ligand giving a Mn(II) complex which is thermodynamically or kinetically inert to XAD-7 but not to Chelex-100. This would have to be a ligand which is not removed from the acidified sample by the precolumn and which would reform the complex when the pH is raised for the analytical column. Also, the ligand would need to be specific for Mn(II) because the other ions are not affected. It is difficult to imagine such a specific ligand and so this possibility does not seem to be a likely one.

A better possibility is that a higher oxidation state(s) of Mn is involved. For example, oxidation to MnO_2 or to Mn(III) followed by disproportionation to Mn(II) and Mn(IV), are processes consistent with the oxic nature of the western basin of Lake Ontario from where the samples were taken. Presumably, MnO_2 is held by Chelex-100 but not by XAD-7.

The Mn preconcentration problem is interesting and worthwhile elucidating because important implications with regard to speciation

are involved. Thus, the different results by Chelex-100 and the XAD-7 calibration curve method indicate speciation of Mn. Speciation is also indicated by the different results from the XAD-7 calibration curve and XAD-7 standard additions procedures. Once the exact nature of the Mn speciation is discovered, then the general applicability of these speciating devices could be tested. The outcome could provide an important contribution to speciation studies.

(ii) Application to Seawater

The two-column method was tested with Seawater Reference Material, NRC NASS-1. A calibration curve rather than standard additions was used. Volume of sample ranged from 200 to 500 mL to give preconcentration factors of 40 to 100, respectively. Preconcentration by 100 is required especially for Co. The preconcentration was done at pH 8.

The results are given in Table XXI, together with the NRC reference data. The NRC data represent the weighted average of results obtained by several different methods of preconcentration and measurement. Except for Cr, the results by XAD-7 preconcentration are in good agreement with the NRC data. The optimal pH for the trivalent ions is 6 but the Cr result at pH 6 is not significantly improved. The method of standard additions is required for Cr but was not used here because of the high cost of the reference material.

As pointed out in the previous section, the two-column calibration method returns a reliable value for Mn in seawater. This observation is also apparent in the analysis of the Nova Scotia (Sandy Cove) coastal seawater (Table XXII), in which the three results

TABLE XXI. Analysis of Seawater Reference Material,
NRC NASS-1, by XAD-7 Two-Column Calibration Curve Method

Element	Concentration ^a (µg/L)	NRC data ^b (µg/L)
Fe	0.233 ± 0.016 (0.214 ± 0.050, pH 6.0)	0.192 ± 0.036
Cr	0.077 ± 0.008 (0.084 ± 0.002, pH 6.0)	0.186 ± 0.016
Cu	0.108 ± 0.018	0.099 ± 0.010
Pb	0.043 ± 0.005	0.039 ± 0.006
Ni	0.245 ± 0.044	0.257 ± 0.027
Co	0.007 ± 0.002	0.004 ± 0.001
Mn	0.025 ± 0.004	0.022 ± 0.007
Cd	0.025 ± 0.003	0.029 ± 0.004

^a Experimental conditions were the same as those described in Table XVIII except that the analytical columns were rinsed with 10 mL of 0.01 M NH_4NO_3 prior to elution. The results represent the mean and standard deviation for four results, two each with a preconcentration factor of 40 and 100.

^b Results expressed as mean ± 1.96 standard deviations.

for Mn are in reasonably good agreement. Since economy was not a factor for this particular sample, analytical checks were done by the XAD-7 two-column standard additions and the Chelex-100 standard addition methods. Presumably, in the seawater samples, the oxidizing (or complexing) interference(s) in Lake Ontario waters is not present. The analytical data in Table XXII for the other metals are also in good agreement, except for the Cr value obtained by the XAD-7 calibration curve procedure. The standard additions procedure with Chelex-100 and XAD-7 yield Cr values in good agreement.

In summary, with the exception of Cr and Mn in lakewater and Cr in seawater, the XAD-7 two-column technique using a standard calibration curve yields reliable data for total (soluble metal) in these natural waters. Furthermore, a combination of preconcentration media (i.e., Chelex-100 and XAD-7 resins) and calibration methods (calibration curve and standard additions) can indicate speciation of a metal. Compared to the Chelex-100 method, the XAD-7 column is cheaper and easier to pack and condition, the resin does not shrink or swell with changes in pH or ionic strength, is stable over the entire pH range and does not deteriorate with time. Also, the smaller volume and lower concentration required for elution (5 mL of 1% v/v HNO_3 versus 25 mL of 14% HNO_3 for a 1 x 6 cm Chelex-100 column), leads to larger preconcentration factors and lower blank values. The technique is especially attractive for the preconcentration of unpolluted natural waters (e.g., open-ocean seawater) where trace metals exist at very low levels (e.g., ng/L levels).

Table XXII. Analysis of Nova Scotia. (Sandy Cove) Coastal Seawater

Element	Concentration ($\mu\text{g/L}$) ^a		
	Chelex-100 ^b SAM	XAD-7 Two-Column ^c Calibration curve	SAM
Fe	3.96 \pm 0.08	3.49 \pm 0.36 (pH 8.0)	4.20 \pm 0.23
Cr	0.52 \pm 0.02	0.15 \pm 0.02 (pH 8.0)	0.45 \pm 0.06
Cu	1.10 \pm 0.10	1.14 \pm 0.06	1.18 \pm 0.06
Pb	0.34 \pm 0.08	0.35 \pm 0.07	0.36 \pm 0.02
Ni	0.43 \pm 0.04	0.42 \pm 0.04	0.37 \pm 0.04
Co	<0.2	0.011 \pm 0.003	0.017 \pm 0.005
Mn	0.95 \pm 0.04	0.83 \pm 0.08	0.78 \pm 0.08
Cd	0.038 \pm 0.006	0.044 \pm 0.004	0.048 \pm 0.007

^a Means and standard deviations based on triplicate determinations.

^b Experimental conditions were the same as those described in Table XX, except that the analytical columns were rinsed with 10 mL of DDW and 10 mL of 0.01M NH_4OAc (pH 5.4) prior to acid elution.

^c Experimental conditions were the same as those described in Table XXI.

(iii) Statistical Analysis of the XAD-7 Two-Column Method

(a) Detection limits and analytical blanks. The detection limit is the smallest amount of concentration that can be measured with a high degree of certainty. The instrumental detection limit is often defined as the analyte concentration that gives a signal to noise ratio of 2 (162, 163).

For a complete analytical procedure involving several steps such as separation or preconcentration plus instrumental measurement, the detection limit of the overall chemical procedure is more useful and is defined as that concentration that corresponds to the blank signal plus three standard deviations of the signal (19, 163)*. After subtraction of the blank, the detection limit is that concentration that corresponds to three standard deviations of the blank signal. Thus, in trace and ultra-trace analysis, the detection limit of a particular chemical procedure is often governed by the analytical blank (i.e., the level of contamination) and proper use and interpretation of analytical blanks are important in such work.

In this work, analytical blanks were obtained by subjecting appropriate aliquots of distilled deionized water (DDW) to the same chemical preconcentration procedure as the aliquots of the real sample. The standard calibration curve or standard additions method was used in the GFAAS measurement and the blank values so obtained were then used for correction of the analytical results. Values of the analytical blanks for the XAD-7 two-column and the Chelex-100 procedures are shown in Table XXIII. The values are the average of many determinations over a span of about eight months and represent the average level of contamination that can be expected for the corresponding preconcentration method performed in this laboratory.

The significantly lower values of the XAD-7 method are probably a

* Mathematically, the detection limit is: $D.L.(conc.) = \frac{(\text{Blank Signal}) \times 3S}{\text{Slope}}$

TABLE XXIII. Analytical Blank Values for XAD-7
Two-Column and Chelex-100 Procedures

Element	Concentration ($\mu\text{g/L}$)		Detection limit of ^a XAD-7 method
	Chelex-100	XAD-7	
Fe	1.3 \pm 0.2	0.20 \pm 0.07	0.21
Cr	0.16 \pm 0.08	0.02 \pm 0.01	0.03
Cu	0.4 \pm 0.1	0.09 \pm 0.02	0.06
Pb	0.4 \pm 0.1	0.03 \pm 0.01	0.03
Ni	0.6 \pm 0.1	0.06 \pm 0.02	0.06
Co	-	0.004 \pm 0.001	0.003
Mn	0.2 \pm 0.1	0.008 \pm 0.003	0.009
Cd	0.02 \pm 0.01	0.004 \pm 0.001	0.003

^a Detection limit is defined as three standard deviations of the blank value.

consequence of the lower amounts of reagents required. For the XAD-7 method, the environment is probably a significant contributor to contamination. The analytical work was performed in a laboratory equipped with a laminar flow clean-air station (see EXPERIMENTAL SECTION) and some environmental contamination should be reflected in the results. If a clean-room facility yielding a "class-100" environment was available, lower blank values would be expected (19,164). Although the detection limits of the XAD-7 method (Table XXIII) lie well below the concentrations of metal in the lakewater and coastal seawater, they approach in some cases the concentration in open ocean (deep) seawater and indicate clearly the requirement of a clean-room facility for such levels.

(b) Precision. In general, the analytical results by the XAD-7 two-column method with GFAAS measurement carry uncertainties of around 10-20% (based on one standard deviation of triplicate or quadruplicate determinations). If the analyte concentrations are extremely low as in the NASS-1 seawater reference (Table XXI), the uncertainties are near the upper end of the range (i.e., 20%). If the analyte concentrations are relatively high as in the Lake Ontario sample (Tables XIX and XX), the uncertainties are closer to 10%. The magnitude of these uncertainties is of the same order as those by other preconcentration methods such as chelating ion-exchange (16,51-58) or solvent extraction (16,45-50), in trace metal applications.

(c) Accuracy. Since the XAD-7 two column method has been applied to a seawater reference material (i.e., NASS-1), the accuracy of the method can be assessed using the Student's t test, where

$$t = \frac{|\bar{x} - \mu| \cdot \sqrt{n}}{s} \quad (13)$$

and \bar{x} = the average value of the finite series;

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

s = the standard deviation of the finite series;

n = the number of measurement in the finite series.

Table XXIV shows that with the exception of Cr, all XAD-7 results are acceptable at the 99% confidence level and, with the exception of Fe and Cr, at the 95% confidence level; that is, the NASS-1 values with the exceptions noted fall within the range defined by the mean XAD-7 result $\pm \frac{ts}{n}$ for the 99 and 95% confidence levels.

(d) Test of significant difference between methods. In Sections III.4 (i) and 4. (ii), comparisons were made between results obtained by the Chelex-100 method and by the XAD-7 method, as well as between results obtained by the XAD-7 calibration curve and the standard additions methods (see Tables XIX, XX, XXII). While comparison can be made based on experience and common sense, it is desirable to establish a statistical criterion. Accordingly, a test of significant difference between methods was done using the Student's t test. The two means under consideration are \bar{x}_1 and \bar{x}_2 and the associated standard deviations for the two series are s_1 and s_2 . The respective number of measurements made in each series is given by n_1 and n_2 . For the two series, a

Table XXIV. Test for Accuracy of XAD-7 Two-Column
Method Using Calibration Curve

Element	Concentration ($\mu\text{g/L}$)		t calculated ^a
	XAD-7 two-column	NASS-1	
Fe	0.233 \pm 0.016	0.192	5.12
Cr	0.077 \pm 0.008	0.184	26.8
Cu	0.108 \pm 0.018	0.099	1.00
Pb	0.043 \pm 0.005	0.039	1.60
Ni	0.245 \pm 0.044	0.257	0.54
Co	0.007 \pm 0.002	0.004	3.00
Mn	0.025 \pm 0.004	0.022	1.50
Cd	0.025 \pm 0.003	0.029	2.67

^a Value of t = 3.18 at 95% confidence level and n = 4; t = 5.84 at 99% level and n = 4.

value of t is found from

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{S} \cdot \frac{n_1 n_2}{n_1 + n_2} \quad (14)$$

where the value of a pooled S is given by

$$S = \frac{\sum(x_{i,1} - \bar{x}_1)^2 + \sum(x_{i,2} - \bar{x}_2)^2}{n_1 + n_2 - 2} \quad (15)$$

In the above procedure, it is required that the values of s_1 and s_2 are shown not to be significantly different by the F test, where

$$F = \frac{s_1^2}{s_2^2} \quad (16)$$

The F test and the t test were used to compare the results for the Lake Ontario water (Station 302) obtained by the XAD-7 standard additions and the calibration curve methods (Table XXV). Also, the results for the Sandy Cove coastal seawater by the Chelex-100 method and both XAD-7 methods were compared (Tables XXVI and XXVII).

As expected, Table XXV shows that the means for Cr and Mn obtained by the calibration curve method differ significantly from those obtained by the method of standard additions. The reasons for this have been discussed earlier. Otherwise, there is no significant difference in the means (t test) and the standard deviations (F test) obtained by the two calibration methods at the 99% confidence level (and, with the exception of Cu, at the 95% confidence level). A similar comparison was made for the Station 14 Lake Ontario water. With the exception of Cr and Mn, there is no significant difference

TABLE XXV. Comparison of Analytical Data for Lake Ontario
Water (Station 302) by XAD-7 Calibration Curve and Standard
Additions Methods: Test of Significant Difference

Element	Concentration ($\mu\text{g/L}$)		F calculated ^a	t calculated ^b
	Calibration curve	Standard additions		
Fe	4.94 \pm 0.55	5.60 \pm 0.48	1.56	1.55
Cr	0.50 \pm 0.12	1.00 \pm 0.12	1	5.10
Cu	1.95 \pm 0.07	1.41 \pm 0.22	9.88	3.13
Pb	0.64 \pm 0.18	0.78 \pm 0.09	4.00	1.22
Ni	1.47 \pm 0.26	1.71 \pm 0.06	18.8	1.54
Co	0.093 \pm 0.017	0.085 \pm 0.018	1.12	0.54
Mn	0.125 \pm 0.011	0.80 \pm 0.02	3.30	51.6
Cd	0.038 \pm 0.004	0.047 \pm 0.010	6.25	1.38

^a Values of F with reference to confidence levels of 95% ($n_1, n_2 = 3, 3$): 19.0; 99% ($n_1, n_2 = 3, 3$): 99.0.

^b Values of t with reference to confidence levels of 95% ($n_1 + n_2 = 6$): 2.78; 99% ($n_1 + n_2 = 6$): 4.60.

TABLE XXVI. Test of Significant Difference between Chelex-100 Standard Additions and XAD-7 Standard Additions for Sandy Cove Seawater

Element	Concentration ($\mu\text{g/L}$)			
	Chelex-100 (SAM)	XAD-7 (SAM)	F calculated ^a	t calculated ^b
Fe	3.96 ± 0.08	4.20 ± 0.23	8.26	1.72
Cr	0.52 ± 0.02	0.45 ± 0.06	9.00	1.92
Cu	1.10 ± 0.10	1.18 ± 0.06	2.78	1.19
Pb	0.34 ± 0.08	0.36 ± 0.02	16.0	0.42
Ni	0.43 ± 0.04	0.37 ± 0.04	1.00	1.83
Co	<0.2	0.017 ± 0.005	-	-
Mn	0.95 ± 0.04	0.78 ± 0.08	4.00	3.30
Cd	0.038 ± 0.006	0.048 ± 0.007	1.36	1.88

^a Values of F with reference to confidence levels of 95% ($n_1, n_2 = 3, 3$): 19.0; 99% ($n_1, n_2 = 3, 3$): 99.0.

^b Values of t with reference to confidence levels of 95% ($n_1 + n_2 = 6$): 2.98; 99% ($n_1 + n_2 = 6$): 4.60.

TABLE XXVII. Test of Significant Difference between Chelex-100 Standard Additions and XAD-7 Calibration Curves for Sandy Cove Seawater

Element	Concentration ($\mu\text{g/L}$)		F calculated ^a	t calculated ^b
	Chelex-100 (SAM)	XAD-7 (calibration curve)		
Fe	3.96 \pm 0.08	3.49 \pm 0.16	4.00	2.53
Cr	0.52 \pm 0.02	0.15 \pm 0.02	1.00	22.7
Cu	1.10 \pm 0.10	1.14 \pm 0.06	2.75	0.62
Pb	0.34 \pm 0.08	0.35 \pm 0.07	1.30	0.18
Ni	0.43 \pm 0.04	0.42 \pm 0.04	1.00	0.31
Co	<0.2	0.011 \pm 0.003	-	-
Mn	0.95 \pm 0.04	0.83 \pm 0.08	4.00	2.46
Cd	0.038 \pm 0.006	0.044 \pm 0.004	2.25	1.48

^a Values of F with reference to confidence levels of 95% ($n_1, n_2 = 3, 3$): 19.0, 99% ($n_1, n_2 = 3, 3$): 99.0.

^b Values of t with reference to confidence levels of 95% ($n_1 + n_2 = 6$): 2.78; 99% ($n_1 + n_2 = 6$): 4.60.

at the 99 and 95% confidence levels. Therefore, the apparent significant difference for the Station-302 Cu mean at the 95% confidence level is inconclusive.

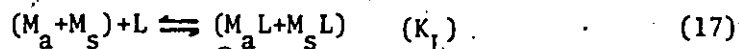
As indicated by Table XXVI for the analysis of the Sandy Cove coastal seawater by the Chelex-100 and XAD-7 standard additions methods, there is no difference in the means and standard deviations at the 99% confidence level and, with the exception of Mn, at the 95% confidence level. Finally, Table XXVII shows that for the analysis of the same water sample the mean for Cr obtained by the Chelex-100 SAM method differs significantly (as expected) from that obtained by the XAD-7 calibration curve method. Otherwise, there is no difference in the two sets of results at both the 99 and 95% confidence levels.

(iv) Method of Standard Additions: Effect of Incomplete Reaction of Spike

In the INTRODUCTION, it was noted that the method of standard additions (SAM) cannot be used without care in the preconcentration of trace metals from natural waters. In natural water samples, the analyte spike may not be completely equilibrated with the sample matrix before the preconcentration step. The application of SAM in these circumstances could lead to an erroneous estimation of the total (soluble) metal concentration. In this Section, the relationship between analyte concentration-taken, the analyte concentration recovered, and the degree of reaction of the spike with the matrix components is illustrated by means of a simple model. This model takes into account the fraction of reacted spike plus the original analyte transferred to the preconcentration phase.

In the model, the sample solution is assigned a total analyte metal (M_a) concentration of 1.00 $\mu\text{g/L}$. The analyte metal is assumed to be distributed between the ionic (i.e., free) and complexed forms.

Four aliquots of the sample solution are taken and after being spiked with a known amount (M_s) of the analyte metal, contain final spike concentrations of 0.00, 1.00, 2.00 and 3.00 $\mu\text{g/L}$. The total analyte (M_a plus M_s) is then subjected to a preconcentration procedure. It is between the time of spike addition and completion of the preconcentration step that M_s can react with matrix components. The model is concerned particularly with the degree of reaction of the spike with a ligand, L, during this time interval. In a real sample, several different ligands can be present that form metal complexes of various stabilities but to keep the model simple, only a single ligand, L, is considered. For the time interval, the following degrees of spike reaction (DSR) with L are assigned: 0, 25, 50, 75 and 100%. For DSR = 0, none of the M_s has yet reacted with L; for DSR = 100%, M_s has come to complete equilibrium with L (whether the equilibrium constant be high or low) and is no longer distinguishable from M_a . The following reaction (charges omitted) depicts this situation:



For intermediate values of DSR, only a portion of M_s has participated in the reaction with L. Thus, for DSR = 50%, half of the M_s ions have "seen" L and are either bound to L or have dissociated from $M_s L$ and so are indistinguishable from M_a . The remaining half have not been complexed to L at all and in this sense are distinguishable

from M_a ions.

In the calculation of the combined amount of added spike and original analyte that is recovered in the preconcentration step, the portion of spike unreacted with L is differentiated from the portion of reacted spike (and from the original analyte); it is assumed that the separation method is efficient enough to achieve quantitative separation of unreacted spike. In contrast, for the portion of reacted spike and for the original analyte, the degree of separation is unknown, because it will depend on the stability constants, concentrations and rates of reaction of the species involved, as well as temperature, pH and other reaction conditions. Therefore, in the model the total amount of added spike and original analyte that is separated at each value of DSR is simply calculated for a range of fractions (F_t) of reacted spike plus original analyte transferred in the separation step. Nine values of F_t have been chosen (from 0.001 to 0.999) and so nine standard-additions plots can be constructed for each value of DSR. Table XXVIII shows the calculation for the construction of the line represented by DSR = 50% and $F_t = 0.50$. A plot of the combined recovery (last column) against spike concentration added (first column) gives a SAM line that yields 0.67 $\mu\text{g/L}$ as the original concentration of analyte (1.00 $\mu\text{g/L}$ actually present) when extrapolated to the X axis. For simplicity, the instrument response is assumed to be a linear function of concentration and is plotted as combined spike and analyte concentration found. The degree of preconcentration is not included in the calculation since it would simply involve multiplication and eventual division of the same number (the preconcentration

Table XXVIII. Calculation of Combined Spike and Analyte Recovery
for DSR=50%, $F_t=0.50$; Original Analyte Concentration = $1.00\mu\text{g/L}$

Spike added ^c	Concentration ($\mu\text{g/L}$)			
	Unreacted spike recovered	Reacted spiked recovered	Analyte recovered	Combined spike and analyte recovered
0	0	0	1.00×0.50^c	0.50
1.00	0.50^a	0.50×0.50^b	0.50	1.25
2.00	1.00	1.00×0.50	0.50	2.00
3.00	1.50	1.50×0.50	0.50	2.75

^a For DSR = 50%, reacted spike = $0.50 \mu\text{g/L}$ and so unreacted spike = $0.50 \mu\text{g/L}$. 100% recovery of unreacted spike gives $0.50 \mu\text{g/L}$.

^b For $F_t = 0.50$, recovery of reacted spike = 0.50×0.50 .

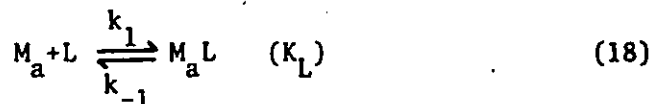
^c For $F_t = 0.50$, analyte recovery = 1.00×0.50 .

factor).

Table XXIX records the analytical estimates of the original analyte concentration for various combinations of DSR and F_t . Each value is derived from calculations as shown in Table XXVIII and the corresponding SAM plot. It should be noted that the range of F_t values corresponds, for example, to distribution ratios ranging from 10^{-3} to 10^3 for a solvent extraction process* involving equal phase volumes. Strictly speaking, however, F_t is the fraction of reacted spike and original analyte transferred to the second phase in any two-phase separation procedure, whether or not equilibrium exists.

As already observed, complexing species in natural waters range from simple unidentate ligands such as chloride and hydroxide to amino-acids and high molecular-weight polyfunctional molecules such as polypeptides and humic materials. Trace metals exist in these media as aquated ions and as labile, moderately labile, and non-labile complexes and as colloiddally-bound metal (inert).

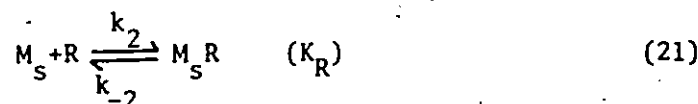
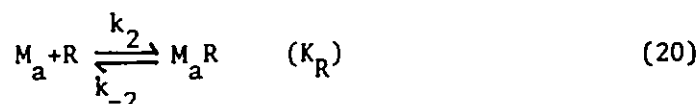
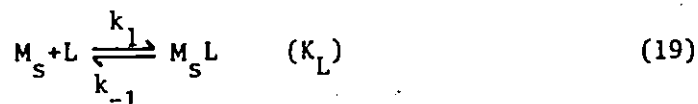
In the analysis of natural waters for the total (soluble) concentration of a particular trace metal, the determination is frequently made by GFAAS or by ICPAES in conjunction with SAM and a preconcentration step. The relevant equilibria can be depicted simply as:



*Solvent extraction is often used as a preconcentration technique, as stated in the INTRODUCTION.

Table XXIX. Recovery ($\mu\text{g/L}$) of Original Analyte ($1.00 \mu\text{g/L}$)
as a Function of DSR and F_t

F_t	DSR (%)				
	0	25	50	75	100
0.001	0.001	0.001	0.002	0.004	1.00
0.010	0.010	0.013	0.020	0.038	1.00
0.091	0.091	0.12	0.17	0.28	1.00
0.24	0.24	0.30	0.39	0.56	1.00
0.50	0.50	0.57	0.67	0.80	1.00
0.76	0.76	0.80	0.86	0.93	1.00
0.91	0.91	0.93	0.95	0.98	1.00
0.99 ⁰	0.99 ⁰	0.99 ²	0.99 ⁴	1.00	1.00
0.99 ⁹	0.99 ⁹	0.99 ⁹	0.99 ⁹	1.00	1.00



where L denotes a natural ligand, R the separation agent (e.g., a solvent-extraction reagent or an ion-exchange resin or XAD-7), K_L and K_R are the relevant equilibrium constants and k_1 , etc., represent the appropriate rate constants.

The main concern in total trace metal determination is the problem of whether M_s has reached complete equilibration with the complexing matrix component (L) before completion of the preconcentration. The degree of spike reaction with L will decide the accuracy of the analysis. In Table XXIX, the recovery of analyte metal, present originally at 1.00 $\mu\text{g/L}$, is shown for various degrees of spike reaction with L. At each value of DSR, the recovery has been calculated as a function of the fraction of reacted spike plus original analyte transferred to the second phase. The effect of DSR is illustrated by the data for $F_t = 0.50$ and the corresponding SAM plots (Figure 32). Note that quantitative recovery of the analyte is possible only if the spike has completely equilibrated with L (DSR = 100%). If the spike has not reacted at all with L (DSR = 0), only 50% of the original analyte is recovered (i.e., 0.5 $\mu\text{g/L}$). Also of interest is the fact that although the accuracy is diminished as DSR is decreased, the sensitivity is increased (Figure 32). This arises because the

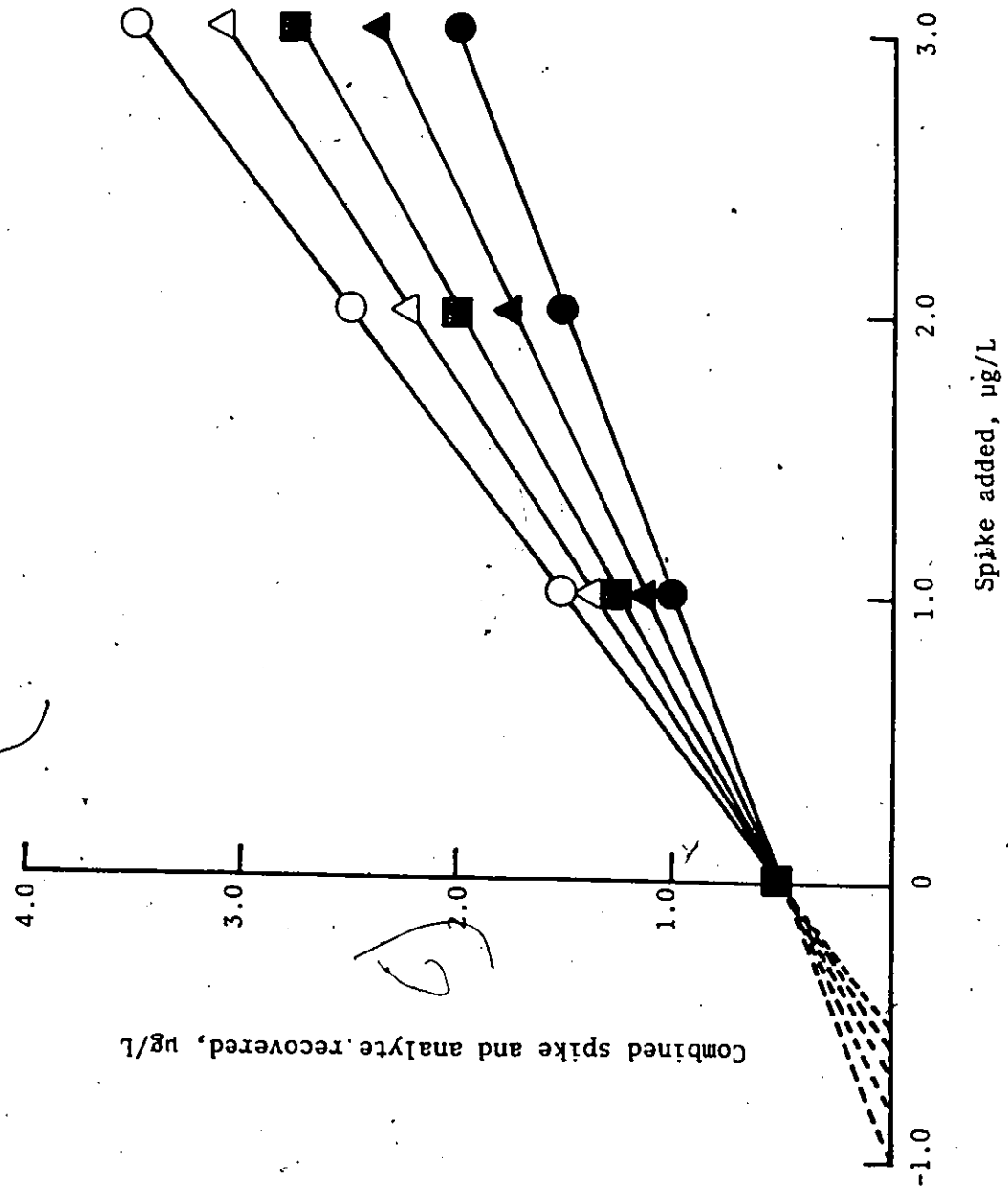


Figure 32. Effect of DSR on analytical recovery of original metal analyte (1.00 µg/L), at Ft = 0.50. DSR = 0 (O); 25% (Δ); 50% (■); 75% (▲); 100% (●).

the calculation is made on the basis that unreacted spike is quantitatively transferred and that the parameter F_t applies only to reacted spike and original analyte. At $DSR = 0$, the basis of the calculation is certainly valid since this situation merely corresponds to the case in which the rate constant k_1 is so small that in the time interval between spiking and the completion of preconcentration (usually only some minutes), no M_s has entered reaction with L . At the other extreme ($DSR = 100\%$), k_1 is large enough to allow complete equilibration in the experimental time interval and no unreacted spike exists.

Several other features in Table XXIX are noteworthy.

(i) If $DSR = 100\%$, the analytical recovery of the analyte metal will be complete, regardless of the value of F_t (last column and Figure 33). The effect of F_t on sensitivity, however, is great and for the examples illustrated here, values of $F_t < 0.50$ are not practical (Figure 33). For higher concentrations of analyte and spike, lower F_t values could be tolerated. (ii) No matter what the value of DSR , complete recovery of the analyte metals is possible if F_t is sufficiently large (last two rows of Table XXIX, where $F_t = 0.99$ and 0.999). These values corresponds to distribution ratios of 10^2 and 10^3 .

In fact, if the preconcentration reaction is sufficiently powerful to remove the analyte element quantitatively from its matrix, the application of SAM, which is a method of calibration of a chemical procedure

*It is assumed, of course, that the dissociation kinetics for $M L$ ($M L$) and the formation kinetics for $M_a R$ ($M_s R$) are favourable for the time interval involved.

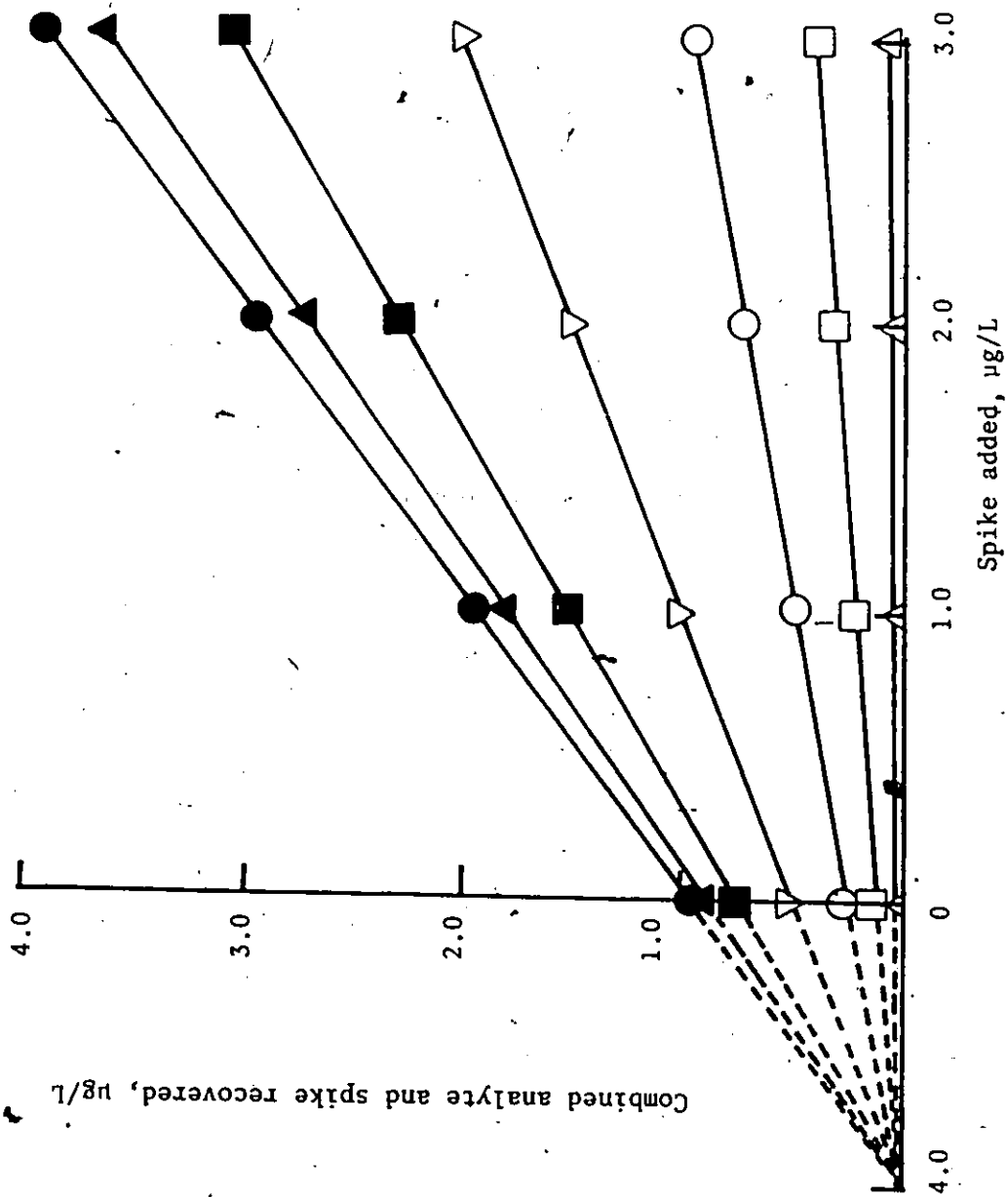


Figure 33. Effect of F on analytical recovery of original metal analyte (1.00 $\mu\text{g/L}$), at DSR = 100%. $F_t = 0.99$ (●); 0.91 (▲); 0.76 (■); 0.50 (▽); 0.24 (○); 0.091 (□); 0.010 (△).

and not merely of an instrument, is not necessary, because chemical interference from matrix components will not occur in the preconcentration step. A simple calibration graph would suffice. In this regard, it is interesting to observe that in a study of the preconcentration of trace elements from seawater with silica-immobilized 8-hydroxyquinoline (17), calibration was done by addition of a standard spike to the solution obtained after elution of the analyte element from the column. (iii) For the examples shown (Figure 33), the application of SAM is most practical for $F_t = 0.50, 0.76$ and 0.91 . It should be stressed that quantitative separation of the spike and analyte element ($F_t \geq 0.99$) is not a prerequisite for a good analytical result. What is a prerequisite is knowledge that the spike has fully equilibrated with the matrix components. Very infrequently do investigators possess this knowledge. Indeed, complete recovery of the spike is not sufficient evidence that the analytical result is to be trusted, as such a recovery could simply be the result of unfavourable kinetics (i.e., $DSR = 0$), with little or no recovery of the analyte.

In summary, suitable combinations of thermodynamic and kinetic factors are required for SAM to yield reliable results. Two combinations are: (i) K_R sufficiently greater than K_L for F_t to be large enough to be practical, and k_1, k_{-1}, k_2 ($\gg k_{-2}$) sufficiently large to allow complete spike equilibration and rapid formation of $M_a R$ ($M_s R$) (ii) K_R large and $\gg K_L$, to give complete separation of the spike and analyte element ($F_t = 0.99 - 0.999$); here k_1 can vary from a small value ($DSR = 0$) to a high value ($DSR = 100\%$) but $M_a L$

($M_S L$) should be labile (k_{-1} large) and $M_a R$ ($M_S R$) should form quickly.

In the analysis of natural waters, investigators do not have enough knowledge of all the relevant thermodynamic and kinetic parameters to be certain that complete spike equilibrium has occurred and to know the extent of separation of the analyte in the sample. It would seem prudent, therefore, to use powerful preconcentration/separation methods - for example, solvent extraction systems that employ strong chelating agents which give complexes having good solubility in organic solvents, or strong chelating ion-exchange media, even more powerful than Chelex-100 (16,51-54). If quantitative separation of spike and analyte cannot be assured, then complete equilibration of the spike should be promoted, e.g., by heating the spiked aliquot and allowing a reasonable amount of standing time before the preconcentration step. For storage of water samples, many investigators acidify the sample with nitric acid to pH 1-2 (1,18,19). This practice is effective in minimizing adsorption of trace elements on the container walls. It is also an appropriate way to promote equilibration of the spike, in that organometallic complexes should be effectively dissociated at low pH. Thus, on the upward adjustment of pH for preconcentration, M_S and M_a should be indistinguishable, even if the complexes reform. Finally, more drastic measures such as destruction of matrix components (e.g., by ultra-violet irradiation) can be used when deemed necessary.

For the determination of total (soluble) metal in the lake and seawater samples reported in this thesis, the water samples were acidified to pH 1.6 - 1.7 and left standing for at least seven days

before an aliquot was spiked. The spike was added to the acidified sample before the pH was adjusted upwards for the preconcentration step. On the assumption* that the organic-metal complexes were effectively dissociated on prolonged standing at pH 1.6 - 1.7, one can have high confidence that the spike and sample analyte metal were indistinguishable in the preconcentration procedure.

For the two-column procedure described in this work, the standard additions method was found to be unnecessary for the preconcentration of all trace metals except Cr and Mn. As already observed, the analytical results obtained for the metal ions by the calibration curve method were the same as those by SAM (see Tables XIX, XX and XXII), because the interfering humic substances were removed by the precolumn prior to preconcentration of the trace metals.

III.5 Summary

1. A new preconcentration method has been developed for the determination of trace metals from natural waters. The method is based on the direct uptake of metal ions on a column packed with the macroporous acrylic ester resin XAD-7, after prior removal of the interfering humic substances* by a precolumn of XAD-7 resin. The retained metal ions are subsequently eluted with 1% v/v HNO₃ and the trace metals are determined by GFAAS.

*There is considerable evidence in the literature (1,5,80,83-86) that humate and fulvate complexes are essentially fully dissociated at pH 1.6-1.7.

2. The method has been applied successfully to the preconcentration of trace metals from synthetic samples and natural lakewater and nearshore and open-ocean seawater. The XAD-7 method has several advantages over other preconcentration methods (i.e., solvent extraction and chelate-ion exchange). It is simple and requires few reagents, thus reducing the risk of contamination. The resin is also inexpensive. The two-column approach provides a matrix relatively free of organic ligands for preconcentration of metal ions on the analytical column. Thus, a simple calibration-curve method can be used in place of the more time- and sample-consuming method of standard additions. Because the retained metal ions can be eluted easily with a small volume of dilute acid, large preconcentration factors (40 or greater) can be achieved. The main disadvantage is that the capacity of the resin for metal ions is rather low (i.e., in the $\mu\text{mole/g}$ range); this fact limits the method to trace concentrations of about the magnitude illustrated in this work.

3. The mechanism of metal-ion retention on XAD-7 likely involves charge-dipole interactions rather than coordination to sites such as carboxylate groups or ion-exchange at impurity sites.

4. Adsorption isotherms and distribution ratios for several environmentally important metal ions have been determined. The effect on adsorption of pH, ionic strength, resin particle size and temperature have been illustrated. The adsorption process is complex and the participation of solvent (water) molecules is likely involved. Because the adsorption reaction is not known, the Langmuir equation, which is used to describe gaseous-solid adsorption

processes, was not applied to the metal-ion/XAD-7 adsorption process.

5. A simple model has been developed to illustrate the concepts and mechanics of the method of standard additions, with regard to its ability to compensate for matrix interference in a chemical separation-preconcentration procedure. It has been shown that a high degree of spike reaction with the sample matrix and a reasonable degree of analyte separation ($F_t > 0.50$) are of utmost importance for the successful application of the standard additions method. If the degree of analyte separation is very high ($F_t > 0.99$), the method of standard additions is not required; a simple calibration curve is sufficient.

IV. SUGGESTIONS FOR FUTURE WORK

1. In the INTRODUCTION (Section 1.2), reference was made to a rather recent approach to preconcentration by immobilization of ion-exchange chelating agents on the surface of supporting materials. The XAD-2 and XAD-4 resins have already been used as substrates in such applications (61,62,66). Perhaps the XAD-7 resin can be used in a similar approach with the chelating agent appended either by adsorption or by chemical reaction. A major disadvantage of the ligand-immobilized XAD-2 and XAD-4 resins in aqueous solution is the low wettability and poor packing owing to the hydrophobicity of the resins. The use of the more hydrophilic XAD-7 resin as a substrate could alleviate this problem.

2. This work has shown that without prior removal of humic substances, recovery of trace metals by the XAD-7 column method is

less than quantitative (Section III.3.(ii)). Humic-bound metal ions are both too stable for and non-labile to the XAD-7 column and are not recoverable. This fact suggests that an operational speciation scheme could be developed based on a three-column XAD-7 scheme. The first column would remove free (ionic) metal. The second and third columns would operate as the usual two-column method described in this thesis. This scheme could be an improvement on that developed by Florence and Batley (8,9,83-86). The working pH range for the adsorption of trace metal ions on the resin is 6 to 9, which encompasses the natural pH of waters, unlike the Florence and Batley scheme (pH 5). Therefore, pH adjustment of the natural water would probably not be required, which is a definite advantage. Furthermore, if the lability of the metal humates is low relative to the time of passage on the first XAD-7 column, the equilibria between the metal ions and the natural ligands might not be greatly disturbed, and organically bound metal ions could then be speciated from ionic metal. The weak interaction between the resin and metal ions is an additional factor in favour of this order of speciation.

3. The problem with the preconcentration of Cr(III) on XAD-7 was discussed in Sections III.3 and III.4. The method of standard additions compensates for the kinetic and thermodynamic factors associated with low recovery but at the expense of reduced sensitivity. Better means for the preconcentration of chromium (and for speciation of Cr(III) and Cr(VI)) should be investigated in view of the biological importance of this element. Further investigation of the low recovery of Mn in Lake Ontario water appears worthwhile, in

that fruitful information concerning the speciation of Mn could be gained.

APPENDICES

I. Mathematical and Statistical Implications of the Langmuir Equation

The general form of the Langmuir equation

$$\Gamma = \frac{\Gamma_{\max} \cdot [M]}{(1/K) + [M]} \quad (5)$$

can be rearranged into six linearized forms, from which Γ_{\max} and K can be obtained graphically or by linear regression.

For example, equation (5) can be readily rearranged to the following linear form by taking the reciprocal of both sides:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\max} \cdot K} \cdot \frac{1}{[M]} + \frac{1}{\Gamma_{\max}} \quad (6)$$

Multiplication of equation (6) by $[M]$, followed by rearrangement, yields a second linear form:

$$\frac{[M]}{\Gamma} = \frac{1}{\Gamma_{\max}} \cdot [M] + \frac{1}{\Gamma_{\max} \cdot K} \quad (22)$$

Multiplication of equation (6) by $\Gamma \cdot \Gamma_{\max}$ and rearrangement leads to a third linear form:

$$\Gamma = \frac{-1}{K} \cdot \frac{\Gamma}{[M]} + \Gamma_{\max} \quad (23)$$

Similarly, multiplication of equation (6) by $\Gamma_{\max} \cdot K$ followed by rearrangement yields:

$$\frac{1}{[M]} = \Gamma_{\max} \cdot K \cdot \frac{1}{\Gamma} + K \quad (24)$$

Multiplication of equation (22) by Γ_{\max} and rearrangement gives:

$$[M] = \Gamma_{\max} \cdot \frac{[M]}{\Gamma} - \frac{1}{K} \quad (25)$$

Lastly, multiplication of equation (23) by $-K$ followed by rearrangement results in the equation:

$$\frac{\Gamma}{[M]} = -K \cdot \Gamma + \Gamma_{\max} \cdot K \quad (26)$$

Application of the Langmuir equation involves a reciprocal plot of data using the above transformations. A reciprocal plot tends to give uneven error weight to an individual datum point (i.e., the lowest numerical values of Γ and $[M]$ are associated with the highest uncertainties in the reciprocal plot whilst the highest values of Γ and $[M]$, which dictate the value of Γ_{\max} , have the lowest). Since data with the lowest and the highest numerical values are important, improper inclusion or rejection of such data may greatly affect the reciprocal plot. Furthermore, the error susceptibility of different transformation differs by degree, depending on the nature of the transformation and the distribution and scatter of datum points. As a consequence, application of different transformations to the same set of data could yield Langmuir parameters (i.e., Γ_{\max} and K) of different numerical values.

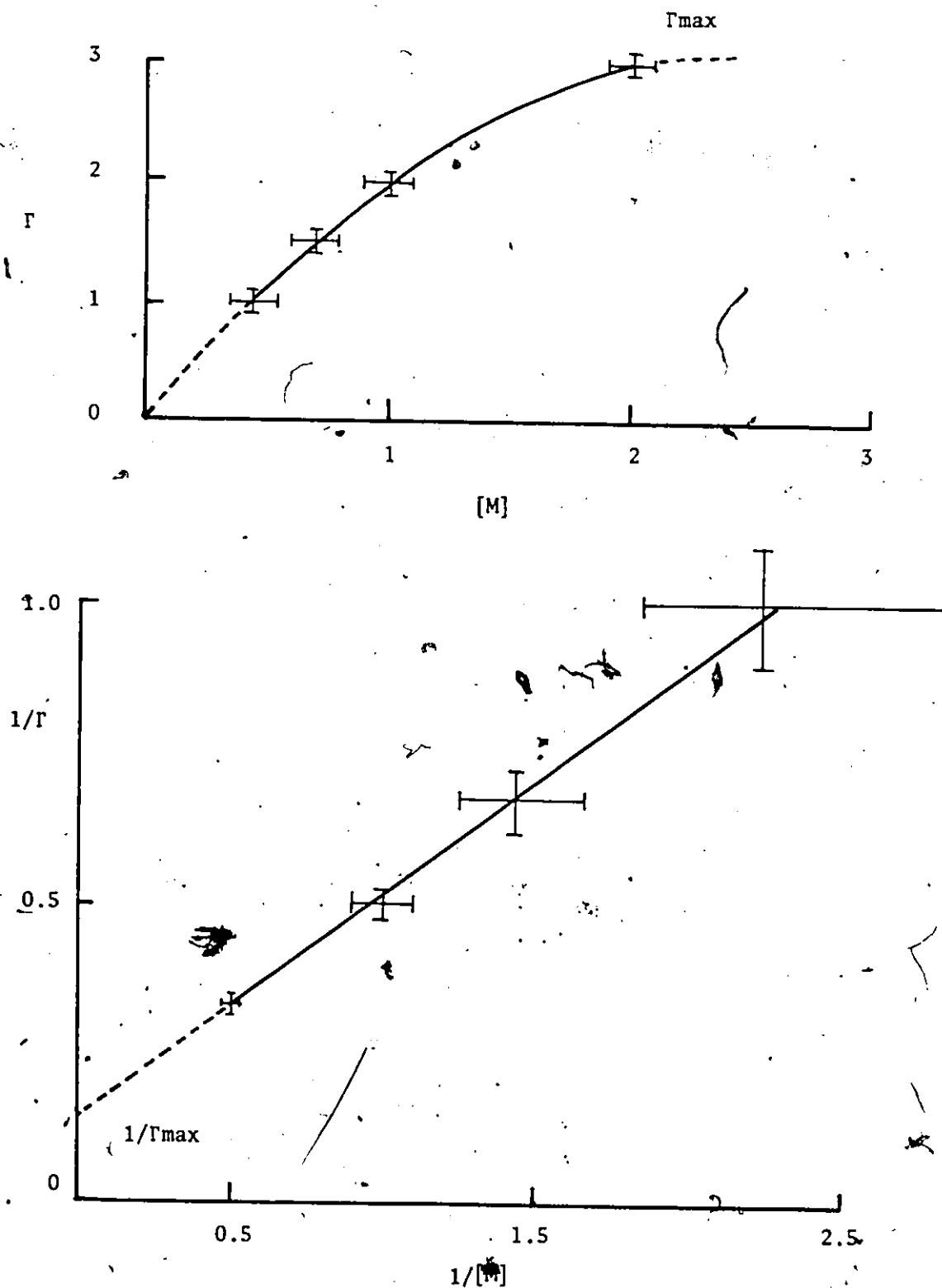


Figure 34. Langmuir plot (top) and corresponding reciprocal plot (bottom) (eq. 6) showing error weight distribution of data. Dimension of error bars represents the magnitude of uncertainties. Arbitrary data are used.

II. Adsorption of Metal Complexes of Meso-tetra(p-sulphophenyl)porphine (TPPS₄) on an XAD-7 Column.

Previous work in this laboratory showed that the ligand, meso-tetra(p-sulphonphenyl)porphine (TPPS₄), reacts in neutral to basic solutions with Co(II), Cu(II), Pb(II), Mn(II) and Zn(II). The resulting complexes can be extracted as a group with methylisobutylketone (MIBK) and the metal contents in the organic phase subsequently measured by GFAAS (49,50). Based on this work, an alternate approach to the pre-concentration of the group of metal ions was attempted in which the complexes were preconcentrated by adsorption on an XAD-7 column. It was during this work that the direct retention of metal ions by XAD-7, discussed in the main body of the thesis, was observed. The work with the metal-TPPS₄ complexes is described here.

Procedure

Aqueous stock solutions of Co(II), Cu(II) and Pb(II) complexes of TPPS₄ ($>10^{-3}$ M) were prepared in this laboratory by Herrmann and coworkers (49) and used in this work. Borosilicate glass columns were slurry-packed with 2.7 g of XAD-7 (20-50-mesh) to give a bed size of 1 x 15 cm. Test solutions of the Co(II), Cu(II) and Pb(II)-TPPS₄ complexes containing 10.0 µg/L of each metal ion in 0.010M NH₄OAc were prepared and the pH was adjusted to cover the range 4.0 to 11.0. Adjustment of pH was made with dilute HNO₃, dilute acetic acid or aqueous ammonia. A 100-mL aliquot was then transferred to the reservoir at the top of the XAD-7 column and percolated at a flow rate of 2 mL/min. The uptake of each complex was determined from the

difference between the known initial concentration of the metal ion and its concentration in the effluent, measured by GFAAS. For example, if the initial concentration was 10.0 $\mu\text{g/L}$ and the effluent concentration was 35.0 $\mu\text{g/L}$, the percent retention was 65.0%.

To elute the complexes, 10% v/v HNO_3 and 35 to 95% v/v methanol/DDW were tried (elution rate, 1 mL/min). Elution profiles were obtained by plotting the concentration of the metal in a fixed volume of the eluant against the summed increments. The recovery was calculated from the preconcentration factor, the initial concentration and the eluted concentration. Thus, for a 100.0 mL sample at 10.0 $\mu\text{g/L}$ and 10.0 mL of eluant at 85.0 $\mu\text{g/L}$, the percent recovery is 85.0%.

Results and Discussion

The effect of pH on the uptake of the TPPS_4 complexes of Co(II), Cu(II) and Pb(II) on the XAD-7 column is shown in Figure 35. The results for Pb(II) were surprising since in solution, below pH 7-8, the Pb(II)- TPPS_4 complex decomposes to Pb(II) and free TPPS_4 (49,50). According to Figure 35, however, there is still a large percentage of Pb(II) on the column below pH 7. This observation suggested that free Pb(II) is retained directly on XAD-7.

To elute the metal- TPPS_4 complexes from the column, 10% v/v HNO_3 was tried initially as an eluant. It was expected that dissociation of the metal- TPPS_4 complexes would occur and that the liberated metal ions would be eluted. It was found, however, that quantitative elution could not be achieved with a small volume (e.g., 10.0 mL) of the acid eluant, a prerequisite for a good column preconcentration method. This observation is very likely a consequence of the slow

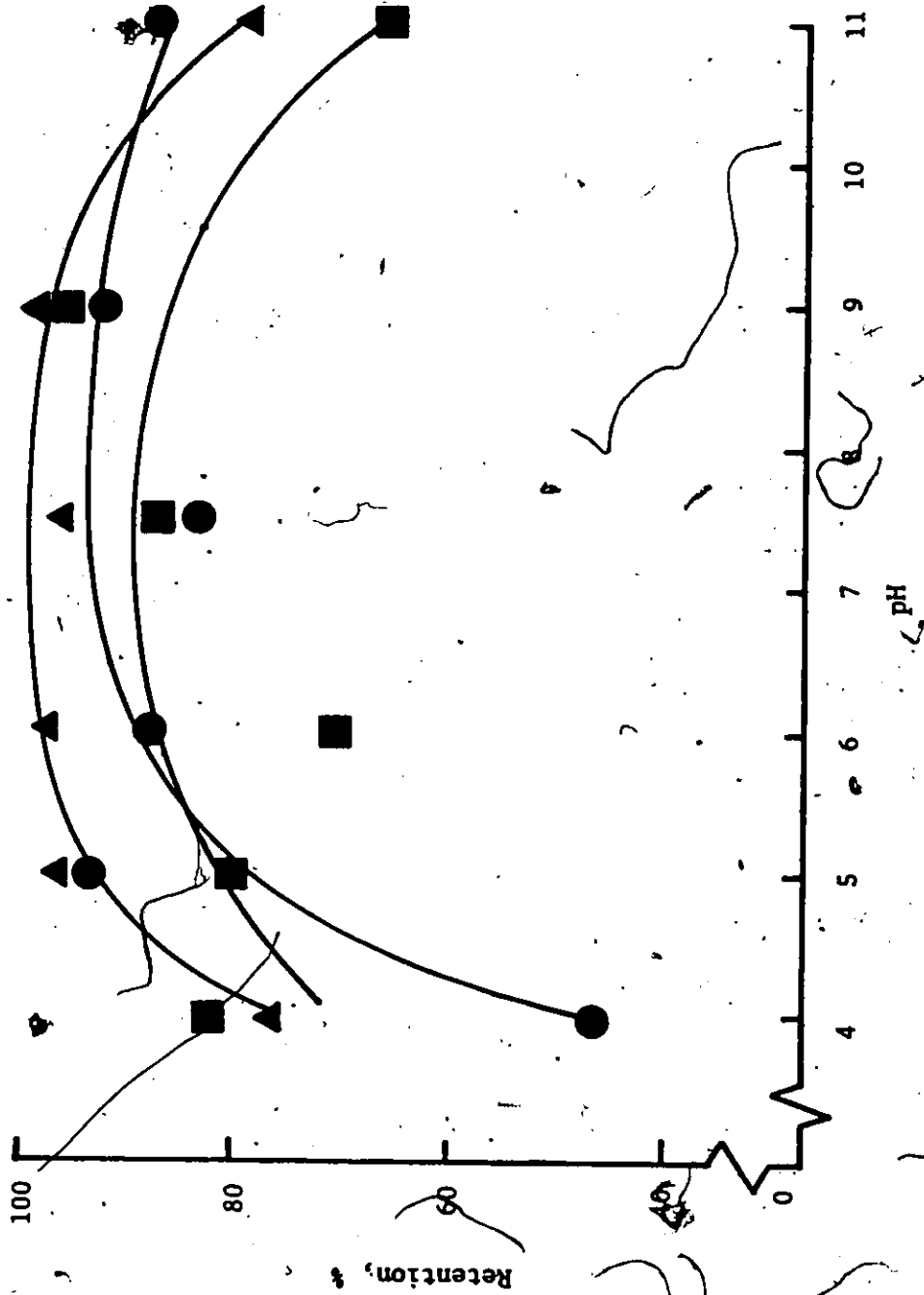


Figure 35. Percent retention of TPPS₄ complexes of Cu(II) (●), Co(II) (□) and Pb(II) (Δ) on a 1x15-cm XAD-7 column (20-50 mesh) as a function of pH. 100 mL of test solutions containing 10 μg/L each of Cu(II), Co(II) and Pb(II) in 0.01M NH₄OAc were used. Flow rate = 1 mL/min.

dissociation rate of the metal-TPPS₄ complexes (50), especially of CuTPPS₄, even in acidic medium. It was found, however, that the complexes were quantitatively eluted with methanol/DDW (in which the methanol content is >75% by volume). The profile (fractional chromatogram) for the elution of 0.500 µg of Cu(II) (as Cu-TPPS₄) from the XAD-7 column by 95% v/v methanol/DDW is shown in Figure 36.

At this point, it was decided that the direction of the research work should be focused on the development of a preconcentration technique based on the direct retention of metal ions on XAD-7. Consequently, the adsorption of metal-TPPS₄ complexes was not studied further.

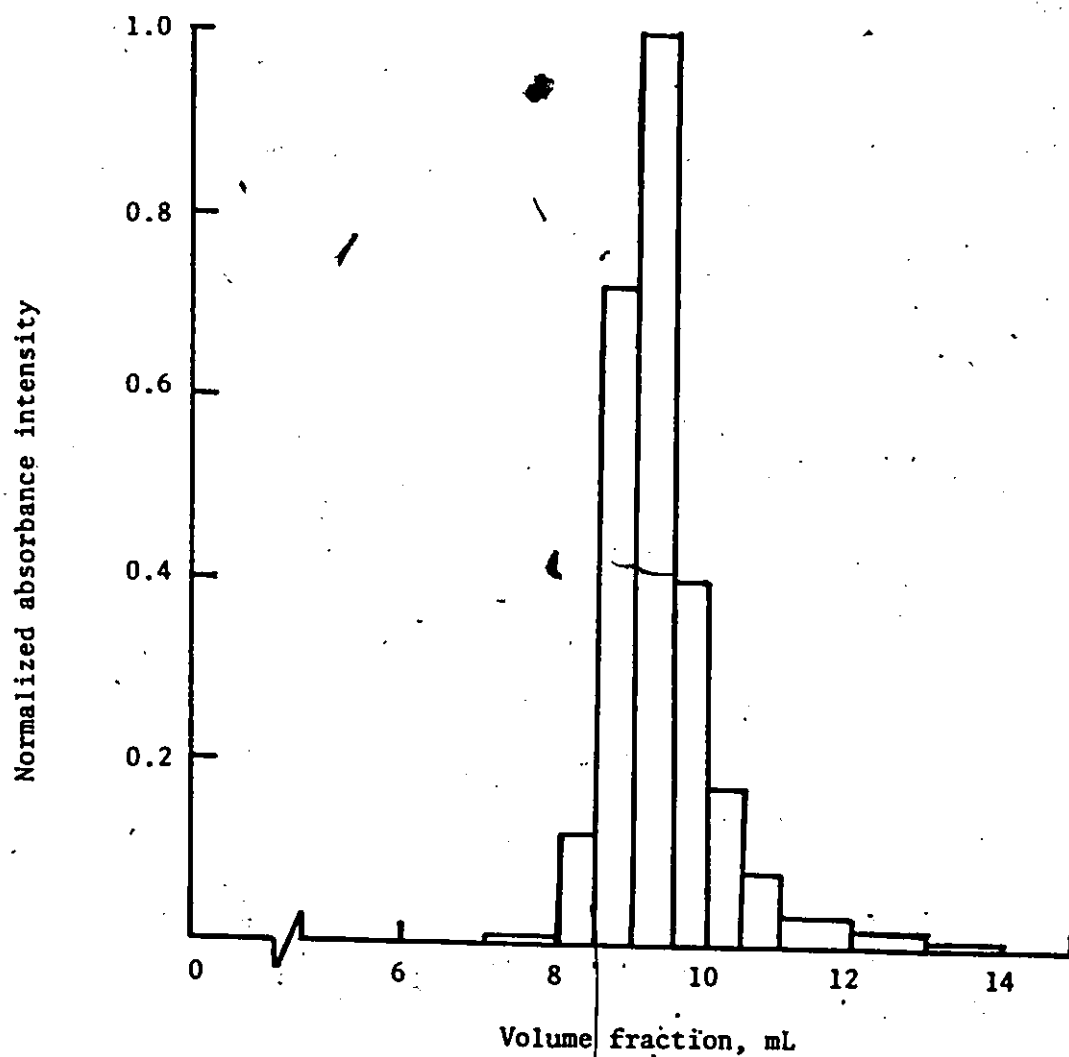


Figure 36. Profile for the elution of 0.500 μg of Cu(II) (as Cu TPPS₄) from a 1x15 cm XAD-7 column (20-50 mesh) by 95% methanol/DDW. Elution rate = 1 mL/min.

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