INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600

PRECONCENTRATION NEUTRON ACTIVATION ANALYSIS OF TRACE ELEMENTS WITH 1-(2-THIAZOLYLAZO)-2-NAPHTHOL USING REVERSED-PHASE EXTRACTION CHROMATOGRAPHY

Wayne E. Goodwin

Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy
at
Dalhousie University
Halifax, Nova Scotia
1997 July

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

0-612-24741-4

Canadä

DALHOUSIE UNIVERSITY

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "Preconcentration Neutron Activation Analysis of Trace Elements with 1-(2-Thiazolylazo)-2-Naphthol Using Reversed-Phase Extraction Chromatography"

by Wayne Eldon Goodwin

in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dated: August 28, 1997

External Examiner [redacted]

Research Supervisor

Examining Committee

Dalhousie University

Author: **Wayne E. Goodwin**

Title: **Preconcentration Neutron Activation Analysis of Trace Elements with 1-(2-Thiazolylazo)-2-Naphthol Using Reversed-Phase Extraction Chromatography**

Department: Chemistry
Degree: Ph.D.
Convocation: 1997 Fall

Permission is herewith granted to Dalhousie University to circulate and have copied for non-commercial purposes, at its discretion, the above title upon the request of individuals and institutions.

[redacted]

Signature of Author

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

The author attests that permission has been obtained for the use of any copyrighted material appearing in this thesis (other than brief excerpts requiring only proper acknowledgement in scholarly writing) and that all such use is clearly acknowledged.

Dedicated to my father, and to the memory of
my uncle Lorne, who passed away August 2, 1997

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure page

Figure page

Figure page

ABSTRACT

Reversed-phase extraction chromatographic (RPEC) methods have been developed for the simultaneous determination of trace elements in natural and potable water samples. The elements are collected on a column of Amberlite XAD-4 resin impregnated with 1-(2-thiazolylazo)-2-naphthol (TAN), and then determined by neutron activation analysis (NAA).

The synthesis of the resin involves the equilibration of precleaned XAD-4 resin with a solution of TAN in methanol for two hours, followed by the addition of water to the mixture and a second two-hour equilibration. The adsorption isotherms for TAN on XAD-4 have been evaluated using a variety of solvent systems. The various factors such as solvent polarity, concentration of TAN in solution, and shaking time, which control the loading of TAN on the resin have been investigated. An optimized synthesis procedure has been developed which yields a high-capacity TAN-XAD-4 resin reproducibly. The TAN-loaded support has a copper exchange capacity of 0.1-0.2 mmol g^{-1} resin, and is therefore suitable for the concentration of trace elements from water samples.

Several parameters which can influence the recovery of trace elements have been studied in detail. These include pH, flow rate, column height, and salinity. It has been found that cadmium, cobalt, copper, manganese, mercury, nickel, and zinc can be simultaneously and quantitatively recovered from solutions of pH > 7.5. Silver (pH 6.1-7.3) and uranium (pH 4.5-5.5) were also quantitatively retained by the resin at appropriate pH. The preconcentration NAA (PNAA) method developed is simple, rapid, and provides a solid sample free of major and interfering elements such as Na and Mg, so that quantification of trace elements in saline samples such as seawater is also feasible.

An internal quality assessment procedure of the PNAA method has been devised. Various steps of the method have been critically examined using comparator standards. All chemicals and reagents used have been analyzed for elemental contaminants. Procedural blanks have been routinely determined. The precision of the method has been evaluated by replicate analysis of spiked samples and tap water, and found to be generally within ± 6% RSD. External quality assessment of the PNAA procedure has been carried out by analyzing reference materials. The results obtained in this study are in good agreement with the certified values, generally within ± 10%. The detection limits of the PNAA methods have been found to range between 0.014 μg for uranium and 7.57 μg for nickel. Enrichment and decontamination factors for the PNAA method have been calculated.

One of the main advantages of coupling the RPEC procedure to NAA is the ability to quantify elements in a solid sample. Consequently, the resin can be irradiated directly, thereby eliminating the need for an elution step which can give irreproducible recoveries and high reagent blanks. The PNAA method has been applied to the determination of trace elements in river water and tap water to demonstrate its practical applicability.

LIST OF ABBREVIATIONS AND SYMBOLS

ANS	8-amino-naphthalene-2-sulfonic acid
ASV	anodic stripping voltammetry
AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
M	atomic mass
N	Avogadro's number
ATPS	azothiopyrine sulfonic acid
b	barns
BCS	bathocuproine disulfonic acid
μ_B	blank counts
γ	branching ratio
CRM	certified reference material
CAS	Chrome Azurol S
CV	coefficient of variation
CPG	controlled pore glass
t_c	counting time
C	counts
L_C	critical level
Φ	cross-section for a neutron capture reaction
d	day
λ	decay constant
t_d	decay time
DDW	deionized distilled water
L_D	detection limit
L_Q	determination limit
Tiron	1,2-dihydroxybenzene-3,5-disulfonic acid
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DW	distilled water
Dz	dithizone
Dz-XAD-4	dithizone loaded onto Amberlite XAD-4 resin

ϵ	detector efficiency
DPTH	2,2'-dipyridyl-4-amino-3-hydrazino-5-mercapto-1,2,4 triazolehydrazone
K_D	distribution coefficient
Dz	dithizone
DVB	divinylbenzene
EBBR	Eriochrome Blue-Black R
Θ	fractional abundance
k	Freundlich constant
γ	gamma
GMA	glycidyl methacrylate
GFAAS	graphite furnace atomic absorption spectroscopy
$t_{1/2}$	half-life
h	hour
HAP	hydrated antimony pentoxide
HMD	hydrated manganese dioxide
HEPES	n-[2-hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid]
oxine	8-hydroxyquinoline
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
INAA	instrumental neutron activation analysis
i.d.	internal diameter
IQA	internal quality assessment
IHQS	7-iodo-8-hydroxyquinoline-5-sulfonic acid
t_i	irradiation time
keV	kiloelectronvolt
m	mass of element
MIBK	methyl isobutyl ketone
min	minute
MES	2-[N-morpholino]ethanesulfonic acid
NBS	National Bureau of Standards
NIST	National Institute of Standards and Technology
NRC	National Research Council (of Canada)
NAA	neutron activation analysis

σ	neutron flux
NTA	nitrilotriacetic acid
NRS	Nitroso-R-salt
ND	not determined
PIPES	piperazine,N,N'-bis[2-ethanesulfonic acid]
PNAA	preconcentration neutron activation analysis
PAPH	2-pyridinecarboxyaldehyde phenylhydrazone
PAN	1-(2-pyridylazo)-2-naphthol
PAR	4-(2-pyridylazo)-resorcinol
PV	Pyrocatechol Violet
PDTC	pyrrolidine dithiocarbamate
QC	quality control
RNAA	radiochemical neutron activation analysis
REE	rare earth element
RM	reference material
RSD	relative standard deviation
RPEC	reversed-phase extraction chromatography (ic)
I-8-HOQ	silica-immobilized 8-hydroxyquinoline
K_1, K_2, β_2	stability constants for metal complex formation
SRM	standard reference material
SPADNS	2-(*p*-sulfonato)-1,8-dihydroxy-3,6-naphthalene disulfonic acid
DzS	(4-sulfophenyl)-1-[2-(4-sulfophenyl)hydrazide]diazenecarbothioate
T-azo-R	1-(tetrazolylazo)-2-hydroxynaphthalene-3,6-disulfonic acid
TAC	2-(2-thiazolylazo)-*p*-cresol
TAN	1-(2-thiazolylazo)-2-naphthol
TAN-XAD-4	TAN loaded onto Amberlite XAD-4 resin
$[\mathrm{TAN}]_s$	TAN concentration in solution
$[\mathrm{TAN}]_r$	TAN concentration on resin
TOPO	trioctylphosphine oxide
TOPO-XAD-4	TOPO loaded on Amberlite XAD-4 resin
TRIS, THAM	tris[hydroxymethyl]aminomethane (also TRIZMA base)
XRF	X-ray fluorescence
XO	Xylenol Orange

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Prof. Amares Chatt, for providing the opportunity to work in his research group. His patience, hard work, and enthusiasm have been indispensable to the completion of this thesis. Thanks also to the staff of the SLOWPOKE-2 facility, Dr. R.R. Rao, Dr. Jiri (George) Holzbecher and Mr. Blaine Zwicker. George and Blaine were responsible for the countless sample irradiations needed to generate the results obtained in this work, and always handled this task in a co-operative and professional manner. Raghu was a postdoctoral fellow in the research group when I first arrived, and was a tremendous help in developing the framework of this project. These three gentlemen always made the facility an interesting and pleasant place to work. During my time here, Raghu and Blaine have left the SLOWPOKE-2 group, and I wish them all the best in their future endeavours.

A general thanks to the other students in Prof. Chatt's research group and the professors, staff, and students of the Chemistry department at Dalhousie. I have drawn on the knowledge of many members of the department and have derived much, in matters scientific and otherwise. Special thanks go to P. Beazley, B. Jewett, R. Schurko, H. Maguire, C. Macdonald, C. Brown, P. Bessonette, P. Delijser, and P. Losier for helpful discussions.

Finally, I wish to thank the people closest to me from outside of my scientific circle. To my father, Eldon, and my family, your unwavering support has been appreciated beyond words, and is a debt I shall be hard-pressed to repay. To my friends, you have made life interesting and you have given me cause to laugh. I hope I have served you as well.

CHAPTER 1. INTRODUCTION

1.1. The Need for Preconcentration in Water Analysis

With the advent of improved chemical instrumentation, the quantification of trace elements in water samples by direct instrumental techniques has become feasible. Water samples, including seawater, have been analyzed by atomic fluorescence spectroscopy [1], graphite furnace atomic absorption spectroscopy (GFAAS) [2,3], inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [4], inductively coupled plasma-mass spectrometry ICP-MS [5-7], neutron activation analysis (NAA) [8], photon activation analysis [9], and voltammetry [10,11]. The choice of instrumental technique is based on such factors as sensitivity, ease and speed of analysis, potential for automation, availability, and cost.

Direct analysis is preferred because analytical procedures involving sample pretreatment prior to the determination step are often time consuming and may lead to elevated and irreproducible reagent blanks, due to the introduction of chemicals and glassware to the system [12]. However, as trace elements are typically present at levels at or below the detection limits of many instrumental techniques, their determination by direct analysis may not be feasible. The ability to quantify such elements in seawater and other saline media is further compromised by the presence of major as well as potentially interfering elements such as chlorine and sodium. Correspondingly, numerous preconcentration schemes have been devised for the determination of trace elements in water, in order to concentrate the elements of interest and simultaneously remove potentially interfering elements prior to the instrumental analysis step.

The importance of the preconcentration step was demonstrated by Sturgeon *et al.* [13], who analyzed nine trace elements in coastal seawater by direct GFAAS and compared the results with those obtained using GFAAS preceded by a separation step using either chelating ion-exchange or solvent extraction. The results show good agreement for cadmium, iron, manganese, and zinc. However, five other metals, namely chromium, cobalt, copper, lead, and nickel, could not be quantified without preconcentration.

One of the objectives of present work is to develop a preconcentration method for simultaneous multielement determination. The ideal preconcentration method should display several favorable characteristics, most importantly a high enrichment factor for the elements of interest and a high decontamination factor with respect to interfering elements [13]. The method should also be relatively simple, requiring the fewest steps possible and a modicum of reagents and handling, in order to minimize contamination of the sample [14].

The choice of a preconcentration step can be tailored depending on the degree of selectivity required and the need for a solid or liquid sample for analysis [15]. The most popular techniques currently in practice include physical preconcentration (*i.e.* evaporation and freeze-drying), solvent extraction, coprecipitation, ion-exchange, electrodeposition, and collection of metals or metal chelates on solid supports [15,16]. The latter group of preconcentration techniques are generally carried out by column separation, which is of interest to this thesis. An overview of column separation procedures is presented in the following section.

1.2 Preconcentration Methods Utilizing a Column Separation

A review of the literature reveals numerous studies incorporating a column separation step which serves to concentrate or isolate the elements of interest prior to their analysis in aqueous samples. In this thesis, a distinction is drawn among five related yet disparate column preconcentration techniques, namely, ion-exchange, chelating ion-exchange, ligand-immobilized and ligand-impregnated reversed-phase extraction, and chelation-adsorption. These techniques are characterized by the nature of the solid phase used to carry out the separation.

An ion-exchange resin is a high molecular weight polymer bearing numerous ionic functional groups [17]. Typically, cation-exchange resins may be either a strong-acid type (*e.g.* bearing sulfonic acid groups) or a weak-acid type (*e.g.* bearing carboxylic acid groups). Anion-exchange resins generally contain amine groups; a strongly basic anion exchanger contains quarternary amine moieties, while secondary or tertiary amine groups are characteristic of weakly-basic exchangers. Ion-exchange materials suffer from a relative lack of selectivity, especially with respect to separating transition and other metals from alkali and alkaline earth metals [18]. As a result, numerous column reagents have been developed as more selective alternatives to conventional ion-exchange resins [19].

A chelating resin [18] resembles an ion-exchange resin in structure, but differs in that the active groups responsible for metal uptake are chelating units which tend to display good selectivity for certain metal ions over alkali and alkaline earth metals. The chelating resin is considered a type of ion-exchange resin and trace elements are said to be collected by chelating ion-exchange [20]. The most commonly employed chelating resin is the commercially available Chelex-100 [21], which is composed of a cross-linked polystyrene matrix bearing iminodiacetate functional groups. While Chelex-100 has been widely used for the preconcentration of trace elements from seawater, it suffers from some drawbacks. Most notably, the separation of trace elements from one another is difficult to execute because Chelex-100 displays such favorable retention characteristics toward a large number of elements [18]. A minor reported disadvantage of Chelex-100 is the fact that the resin tends to shrink or swell depending on the nature of the solution passing through the column [22]. This led to the development of alternative solid exchangers.

In reversed-phase extraction chromatography (RPEC), the stationary phase consists of an inert solid matrix bearing an organic complexing agent which is responsible for the uptake of trace elements from aqueous solution. There are two types of RPEC, characterized by the manner in which the organic ligand is fixed to the support. If the complexing ligand is attached by a covalent bond to the support, the reagent is said to be ligand-immobilized [23,24]. A ligand-impregnated resin [23,24] consists of a solid matrix bearing a complexing agent which is not chemically bound, but rather adsorbed onto its surface. Many authors use the label "ligand-loaded resin" [19,25] in the discussion of ligand-impregnated resins; these two terms shall be used interchangeably throughout this thesis. While the focus of this research has been on the application of ligand-impregnated resins, both types of RPEC supports have been extensively reviewed in the literature survey (Chapter 2).

A special type of ligand-immobilized reagent is produced by condensation of polymers in the presence of a chelating agent. The product, a copolymer with the complexing ligand incorporated into the matrix, is known as a condensation resin [26] and shall be included in the discussion of ligand-immobilized resins.

At first glance, chelating resins and ligand-immobilized resins would appear to be similar; however, for the purpose of this thesis the two shall be distinguished. Chelating resins such as Chelex-100 are commercially available in various mesh sizes and reproducible in terms of structure, performance, and purity from one batch to another [20]. This is essential to obtaining reproducible results for a given study, and critical in attempting to repeat results from other laboratories. In contrast, since ligand-immobilized resins are generally synthesized in individual laboratories following different synthetic routes, they may display vastly different analytical characteristics [26-29].

The preparation of ligand-immobilized reagents allows the complexing group to be fixed to alternative substrates, including non-conventional resin supports such as cellulose. Problems may be encountered with the inert support, with respect to stability in a variety of media, swelling properties, or trace element contamination. A ligand-immobilized resin exhibiting such unfavorable characteristics can be modified by simply bonding the complexing agent to a more suitable support. This option is not always available with commercially available chelating resins.

The other column preconcentration technique is chelation-adsorption, in which a chelating agent is added directly to an aqueous solution containing the trace elements of interest. The metal chelates formed are collected by passage of the aqueous solution through a column of solid adsorbent material. Chelation-adsorption is closely related to ligand-impregnated RPEC in that the adsorptive processes which govern the uptake of metal chelates tend to be similar to those for the adsorption of the uncomplexed ligand in the preparation of the reversed-phase reagent. In the strictest sense, chelation-adsorption is a type of RPEC, as the stationary phase is less polar than the aqueous mobile phase [30]. Yet, the techniques are sufficiently different to justify the use of distinguishing terms. Sarzanini *et al.* [31], for example, applied pyrocatechol violet as a reagent for ligand-impregnated RPEC and chelation-adsorption studies, and differentiated between "chelating agent loaded resin" and "precomplexation anion exchange".

Care should be taken when reviewing the literature, since there appears to be little uniformity with respect to terminology in the discussion of RPEC. The terms "chelating resin" and "ligand-immobilized resin" have frequently been used to characterize a reagent which in this context is to be considered a ligand-impregnated resin [32,33]. As the focus of this thesis is to develop a preconcentration method using RPEC, a brief description of the technique is provided in the following section.

1.3 Reversed-Phase Extraction Chromatography

Reversed-phase chromatography was first introduced by Howard and Martin [34] in the early 1950's as a method for separating long-chain fatty acids. The procedure was so termed because, unlike the existing chromatographic procedures, a non-polar stationary phase and a more polar mobile phase were used. Until this time, chromatographers generally made use of a mobile phase which was less polar than the stationary phase. The rationale behind performing reversed-phase separations was that with a wider selection of solvent systems, more selective and flexible methods could be developed.

As the term implies, reversed-phase extraction chromatography (RPEC) may be viewed as a marriage of solvent extraction and chromatographic techniques. The relationship between RPEC and solvent extraction, and the importance of the chromatographic separation, are described below.

When a solute, S, is introduced into a system of two immiscible solvents, the solute may distribute itself in equilibrium between the two phases; this equilibrium may be represented by

$$S_1 \rightleftharpoons S_2 \qquad [1.1]$$

where 1 and 2 denote the two solvent phases. In trace metal analysis, the extraction procedure will almost certainly make use of water as one of the two solvent phases. The second phase would then be an organic solvent which is immiscible with water.

The equilibrium is governed by the distribution law: at constant temperature and pressure, the ratio of the concentrations of S in each phase is a constant. This constant is termed the distribution coefficient, K_D, and defined by:

$$K_D = [S]_2 / [S]_1 \qquad [1.2]$$

The value of K_D is dependent on temperature as well as the nature of the solute and solvents, but the most important consequence of equation [1.2] is that K_D is independent of the total concentration of S.

As previously noted, the levels of trace metals in aqueous solutions are low enough to demand a preconcentration step. It would be advantageous, then, to devise an extraction procedure in which metal ions in a dilute aqueous sample could be concentrated in an organic phase. However, a problem exists in that metal ion salts display negligible solubility in organic media. This problem can be overcome by forming a neutral metal chelate which is generally soluble in organic solvents.

Solvent extraction of metal chelates holds numerous advantages for trace metal preconcentration. Most important is the fact that metal chelates, once formed, are difficult to break up without a change in pH. This is a marked advantage over conventional ion-exchange which suffers from the potential problem of preferential adsorption onto the resin. A metal ion bound on an ion-exchange resin would be displaced by a metal ion for which the active group has a higher affinity. The more weakly-bound ions are pushed down the column, and may pass through the column altogether. These weakly-bound metal ions could also be eluted by washing the column with fresh solvent.

Chelation also suppresses the interference of alkali metals, and sometimes alkaline earth metals. Many chelating ligands tend to display a high affinity for transition and heavy metals, but not for alkalis and alkaline earths. This would be especially important in the separation of trace elements from the many-fold excess of sodium chloride in seawater and other saline samples.

There are, however, some problems inherent in the preconcentration of metals from aqueous solution using solvent extraction. It is apparent that if the metals present are to be concentrated by extraction into an organic solvent, the volume of organic phase should be kept small. Difficulties may arise in the attempt to separate a small volume of organic solvent from a much larger volume of water. Adhesion of the organic phase to the walls of the separation vessel requires a rinsing step which lowers the enrichment factor. Furthermore, if the solvents emulsify, a clean separation becomes nearly impossible. Solvent extraction also tends to be time- and labor-intensive in comparison to some other preconcentration procedures [35].

It would thus be practical to devise a method which incorporates the strong binding of chelation solvent extraction while circumventing the problems faced at the liquid-liquid partition. One way is to introduce a column separation step. In RPEC, trace elements are extracted from dilute aqueous solution with a chelating agent fixed to a resin support. The analogy to solvent extraction lies in the distribution of the element between two phases: aqueous, as ions in solution, and organic, while bound to the chelating agent. The difference is that the metal chelate is not extracted into an organic solvent, but rather, is held on the solid support as the mobile phase is eluted from the column. Compared to solvent extraction, RPEC introduces several beneficial characteristics, including ease and speed of handling, reduced health hazard, and higher efficiency. The latter advantage is due to the multiple equilibrations afforded by a chromatographic separation.

As a preconcentration technique, RPEC displays numerous positive characteristics. A major advantage is a high enrichment factor, as the trace elements present in a rather large volume of aqueous sample can be concentrated onto a resin phase which is typically no more than a few grams of solid [19]. As with other chromatographic separations, RPEC is relatively fast [36], and is amenable to automated [37] as well as on-site [38] separations. With the choice of a suitable support, chelating agent, and experimental conditions, it is possible to obtain a desirable selectivity with respect to particular elements or groups of elements. For these reasons, RPEC has been increasingly applied to trace element separation in recent years [19,39-44].

A problem commonly encountered in the use of ligand-impregnated resins is bleeding of the stationary phase, especially when using acidic, basic, or saline media [45] or mixed aqueous and organic solvents [46]. This can be overcome by attaching the chelating agent to the solid support with a chemical bond (*i.e.* with the use of a ligand-immobilized resin). However, ligand-immobilized resins may suffer from complicated, time-consuming, and expensive preparation methods. Many laboratories have proposed using ligand-impregnated resins as a suitable alternative [47]. Adsorption of a complexing agent onto a solid support generally can be carried out more rapidly and with fewer and smaller quantities of reagents than would be required to chemically immobilize the ligand.

It would be preferable that the chelating characteristics of the reversed-phase resin would be dependent mainly on the chelating agent used rather than the manner in which this ligand is held on the solid support. Lee *et al.* [24] loaded 8-hydroxyquinoline (oxine) onto Amberlite XAD-2 resin, and compared its performance with that of two oxine-immobilized resins, namely, the silica-immobilized oxine prepared by Sturgeon *et al.* [48] and an XAD-2-immobilized oxine resin reported by Sugii *et al.* [49]. The loading of XAD resins with oxine or an oxine derivative could be carried out using a single 1-h equilibration. The oxine-impregnated XAD-2 resin displayed similar characteristics to the two ligand-immobilized resins with respect to percent recovery of trace copper and nickel, the pH at which quantitative recoveries of these elements was observed, the metal ion capacity, and the nature of the eluent required to release the metal ions from the column. The authors noted that the leaching of the chelating agent is a major disadvantage of ligand-impregnated RPEC but showed that oxine-loaded XAD-4 resin was stable in solutions of pH 5-10 [24].

1.4 Complexing Agents Used in Ligand-Impregnated RPEC

While the major advantage of ligand-impregnated RPEC lies in its easier synthesis, another benefit is the wider choice of ligands that are available compared to the ligand-immobilized RPEC. Ligand impregnation does not involve formation of a chemical bond between the ligand and the solid support; the choice of a suitable complexing agent is limited only by the requirement of suitable hydrophobicity, in order to minimize bleeding of the stationary phase into the aqueous mobile phase. To this end, most impregnated chelating agents contain at least one aromatic ring. Once the problem of leaching of the ligand has been eliminated, the choice of ligand can be made based on the desired selectivity. As noted by Naghmush *et al.* [50] and Chikuma *et al.* [45], it is possible to freely substitute the ligand to prepare a variety of reversed-phase resins, as long as the ligand-loaded resins are sufficiently stable to aqueous media.

A detailed review of ligand-impregnated RPEC is presented in Section 2.3. Torre and Marina [19] noted the types of ligands which have been most frequently used.

These include sulfonated compounds such as nitroso-R-Salt and pyrocatechol violet, especially when loaded onto anion-exchange supports; oxine and oxine derivatives; and azo dyes such as 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)-resorcinol (PAR).

The chelating agent chosen for the majority of the work done in this thesis is 1-(2-thiazolylazo)-2-naphthol (TAN). This ligand is an azo dye which displays chelating characteristics similar to those of PAN. Previous investigations with TAN, especially in solvent extraction studies, suggest that the ligand should be useful for the simultaneous extraction of several trace elements.

1.5 Use of TAN as the Chelating Agent for RPEC

First synthesized in the late 1950's [51], TAN was originally used as a chelating agent for solvent extraction followed by spectrophotometric determination of trace metals. The structure of TAN [52] is shown in Fig. 1.1. The stability constants of TAN-metal complexes have been reported to be of the order of 10^8 to 10^{11} for several of the trace elements of interest to this study. These values are given in Table 1.1.

The use of TAN as a reagent in trace element quantification has been reviewed in Section 2.4. While TAN has been applied largely to solvent extraction studies, there are a few examples in the literature in which TAN-loaded supports have been utilized.

Brykina *et al.* loaded TAN onto ion-exchange resins for the extraction of copper [53] and cadmium, copper, nickel and zinc [54]. In the latter study, the four trace elements were collected on the TAN-loaded resin at pH 8.3 prior to their determination by

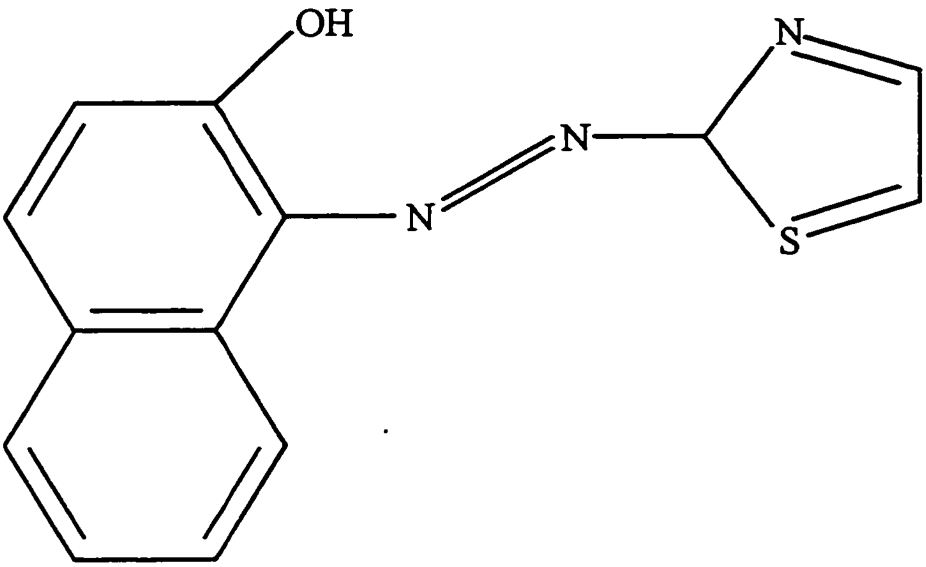


Figure 1.1. Structure of 1-(2-thiazolylazo)-2-naphthol (TAN).

Table 1.1. Stability constants for TAN-metal complexes.

Element	log K_1	log β_2	Reference
Ag	8.67		55
Cd	9.18	17.88	56
Co	9.50	19.00	56
Cu	10.92	22.52	55
Th	8.62[a]		57
U	9.32[a]		58
Zn	9.87	19.74	55

a. Complexes were reported to have the M:L ratio 1:2, but only the K_1 values were given by the authors

X-ray fluorescence (XRF) spectrometry. These four elements are also of interest to the present work.

The retention of uranium by TAN-loaded resins has been reported. Ueda *et al.* [59] impregnated silica gel with TAN for the collection of uranyl ion from solution at pH 5-7. The maximum recovery of uranium by the resin was 93%. Uranium was eluted with 25 mL acetone/nitric acid (9:1 v/v) and determined spectrophotometrically. Vácha and Sommer [60] reported the collection of uranium on TAN-loaded XAD-4 (TAN-XAD-4) resin prepared by a column method. At pH 6.1-6.3, uranium was quantitatively retained at moderately high flow rates, but it was necessary to use resin beads of 0.10-0.20 mm grain size. The authors reported that the efficiency of the column was inversely proportional to the grain size of the resin beads. The determination of uranium using TAN is also of interest in this thesis.

Ivanov and co-workers loaded TAN onto C-18 silica gel [61] and silica gel [62] for the chromatographic separation of palladium from other metals. The separation of palladium or rhodium from cobalt, copper, and nickel was developed [63] and applied to the determination of the two elements in the presence of a 100-200 fold excess of copper, iron, and nickel [64].

Sarzanini *et al.* [65] loaded PAN or TAN onto Amberlite XAD-2 or XAD-4 resin and studied the kinetics of ligand adsorption onto the solid supports. A method was developed for the on-line determination of cadmium, copper, iron, manganese, nickel, and zinc from seawater [66]. Amberlite XAD-2 was impregnated with TAN by a column procedure and the elements were collected on the column at pH 8.4 prior to elution with acid and determination by ICP-AES.

Ide and co-workers [67] loaded polystyrene beads with TAN or PAN to investigate the retention of cadmium, cobalt, copper, manganese, nickel, and zinc. With the exception of nickel, all elements were retained by both resins. Copper and zinc were quantitatively eluted from the columns using 1 M HCl, but this treatment did not remove cadmium and manganese. Using 1 M HCl as the eluent, cobalt could be removed from the TAN column but not the PAN column. Such elution steps and their inherent problems can be eliminated if the resin can be directly processed for elemental determinations. Neutron activation analysis can be used for such purposes.

1.6 Neutron Activation Analysis

Activation analysis was first proposed as a potential analytical technique by Hevesy and Levi in the late 1930's [68,69]. In general, the technique involves the bombardment of a sample with radiation or particles. If the energy of the radiation or particles exceeds the threshold energy, a nuclear reaction will occur. Stable isotopes in the sample may be converted to radionuclides, which then undergo radioactive decay, a process accompanied by the emission of radiation. Detection of this radiation permits identification and determination of the elements present in the sample.

In order to quantify a particular element in a sample, it is necessary to relate the amount of that element to some measurable quantity. In NAA, this quantity is the number of counts (C), taken as the number of γ-ray occurrences detected at a particular energy value.

An irradiated sample is placed on a γ-detector and counted for a discrete period. The number of counts, C, registered during this counting period is given by the activation equation [70]:

$$C = (Nm/M)\ \Phi\sigma\Theta\epsilon\gamma\ [1-e^{-\lambda t_i}][e^{-\lambda t_d}][1-e^{-\lambda t_c}] \qquad [1.3]$$

where C is the total number of counts registered,
N is Avogadro's number,
m is the mass of the element (g),
M is the atomic mass of this isotope (g mol^{-1}),
Φ is the cross-section for the neutron capture reaction (cm^2),
σ is the neutron flux to which the sample is exposed (neutrons $\text{cm}^{-2}\ \text{s}^{-1}$),
Θ is the fractional abundance of the parent isotope,
ϵ is the detector efficiency,
γ is the gamma branching ratio,
λ is the decay constant of the nuclide (units of reciprocal time), and
t_i, t_d, and t_c are the irradiation, decay, and counting times.

The activation equation can be used for elemental assay only if all of these terms can be accurately determined. Since this is not always the case, the comparator method is generally employed. In this procedure, a comparator standard containing a known amount of the element to be determined is irradiated and counted under identical conditions as the sample of unknown composition. Under said conditions, the terms N, M, Φ,σ,Θ,ϵ,γ, λ, t_i, t_d, and t_c all cancel. The only terms remaining from equation [1.3] are C and m; since the number of counts is proportional to the mass of the element present, all that remains is the simple relationship:

$$C_{\text{unknown}}/C_{\text{standard}} = m_{\text{unknown}}/m_{\text{standard}} \qquad [1.4]$$

Throughout this research project, the comparator method was used to determine the elemental content of samples. Using selected timing schemes, several elements can be determined from a single sample. It is important that all parameters be kept as similar as possible for samples and standards; this is achieved in this work by duplicating sample size, sample container, homogeneity, and counting geometry. Since irreproducible sample geometry can adversely affect the precision and accuracy of the method, significant attention was devoted to avoid this problem. Equation [1.4] is only valid if the values of t_i, t_d, and t_c are kept constant as well. However, corrections for different timing schemes can be made, if necessary.

Neutron activation analysis techniques can be subdivided into three distinct classes. In instrumental NAA (INAA), the sample is irradiated without any chemical treatment and the quantification is performed directly. This is the simplest form of NAA and preferred for most analyses. The lack of chemical separation steps minimizes the risk of contamination inherent to sample handling. However, if the elements of interest are present at concentrations at or below the detection limits of INAA, or if matrix or major element interference is a severe problem, a concentration step may be necessary. In preconcentration NAA (PNAA) this is carried out before irradiation, while in the radiochemical NAA (RNAA) technique the chemical treatment takes place after the sample is irradiated.

Activation analysis in general offers many advantages including excellent sensitivity; many elements can be detected at the parts-per-billion (ppb) level or below [71,72]. There are other techniques which offer comparable sensitivity, but activation analysis has other important benefits such as high selectivity and simultaneous multielement capability

[72], arising from the fact that radionuclides decay with characteristic half-lives and γ-ray energies. Nuclides can generally be selectively determined on the basis of their unique γ-ray energies, so a single irradiation of a sample can often yield data for several elements at once. In the event of interferences due to overlapping photopeaks, the desired selectivity can usually be achieved with the proper choice of timing parameters. Consequently, the appropriate nuclides can be individually quantified without the need to physically isolate the elements under investigation.

Another advantage of NAA is that the analysis can be performed on a solid sample. Many instrumental techniques require a liquid sample; to that end, most RPEC procedures include a sample digestion [73] or an elution step, in order to remove the trace elements from the column prior to analysis. Typically, elements are stripped from the column with acid or an organic solvent prior to quantification by AAS [74], AES [31], ICP-MS [75,76] or visible spectrophotometry [59,77].

The elution step is disadvantageous in that it tends to lower the attainable concentration factor of the preconcentration procedure and may not always be quantitative or reproducible. Furthermore, the additional step may introduce an elevated or irreproducible blank value. When NAA is used, the solid resin containing the trace elements can be analyzed directly, precluding the need for the elution step and eliminating these potential problems.

This has been demonstrated by researchers who have applied NAA to quantify trace elements collected on a solid resin phase. Van der Sloot [78] preconcentrated chromium from fresh water and seawater samples buffered to pH 8 on a column of activated carbon. The carbon was subsequently washed with doubly distilled water, dried, irradiated, and counted in order to ascertain the chromium content. The method was applied as a multielement preconcentration procedure for the determination of cadmium, chromium, cobalt, copper, mercury, molybdenum, selenium, tungsten, uranium, vanadium, and zinc in natural water samples [79,80].

Greenberg *et al.* [81,82] reported the preconcentration of aluminum, copper, manganese, and vanadium from biological samples on a Chelex-100 column, followed by irradiation of the resin for the determination of the elements of interest. Milley and Chatt [83] applied a similar method to the preconcentration of fifteen trace elements in acid rain.

Blotcky and co-workers [84] collected aluminum from urine samples on an ion-exchange column prior to irradiation of the resin. Preconcentration by chelation-adsorption techniques, followed by irradiation of the solid phase containing the collected metal chelates, was shown to be effective in the determination of trace elements. Devi and Rama Krishna Naidu collected chelates of cadmium [85] and cadmium, cobalt, copper, mercury, and zinc [86] on activated carbon. Shah and Wai [87] determined five trace elements in natural waters by collecting their chelates on C18 silica gel and irradiating the solid phase.

Preconcentration using ligand-impregnated reversed-phase resins has not been frequently combined with NAA determination. Akaiwa [88] collected cadmium, cobalt, copper, manganese, nickel, and zinc on an ion-exchange resin loaded with oxine-5-sulfonic acid, and applied other resins impregnated with sulfonated ligands to the preconcentration of copper, lead, mercury, and zinc, or copper and mercury. The elements were quantified by irradiation and counting of the resin phase. Using a similar procedure, Rao *et al.* [14] loaded oxine on Amberlite XAD-2 and applied the reagent to the determination of cadmium, cobalt, copper, mercury, vanadium, and zinc in tap water and acid rain.

1.7 Summary of Objectives

The principal purpose of this research was to develop a reversed-phase extraction chromatographic preconcentration method for the determination of trace elements (namely, antimony, arsenic, cadmium, chromium, cobalt, copper, gold, manganese, mercury, nickel, silver, thorium, uranium, vanadium, and zinc) in water samples.

One of the main experimental objectives of this work was to optimize the conditions for the synthesis of the TAN-XAD-4 resin with respect to the amount of TAN which could be loaded onto the solid substrate, as well as the metal ion exchange capacity of the ligand-loaded resin. Another important goal of the research project was to evaluate the experimental conditions which control the uptake of trace elements on the TAN-XAD-4 resin, such as pH, particle size and quantity of resin, and flow rate, and in so doing, to determine optimal conditions leading to the quantitative uptake of trace elements from aqueous media.

With the optimization completed, the next objective was to perform quality assessment of the PNAA method. Individual reagent blanks and procedural blanks will be measured. Internal and external quality assessment will be carried out using elemental comparator standards and reference materials, respectively. The precision of the PNAA method will be evaluated through replicate analysis of real and spiked solutions. The method will be applied to the determination of trace elements in potable water samples and solutions of high salinity. Detection limits, as well as enrichment and decontamination factors will be calculated.

In order to evaluate the utility of other chelating agents as RPEC reagents, preliminary experiments will be carried out with two other chelating agents, dithizone and trioctylphosphine oxide.

A survey of the literature is given in Chapter 2. Column extractions in general and coupled to NAA, ligand-immobilized and ligand-impregnated RPEC, and the use of TAN as an analytical reagent have been thoroughly reviewed here. The experimental methods and results obtained are discussed in detail in Chapters 3 and 4, respectively.

CHAPTER 2. LITERATURE SURVEY

In this chapter, solid phase preconcentration methods in general, and RPEC in particular, are extensively reviewed. Examples of such separations in conjunction with NAA are also discussed. Literature in which TAN has been used as an analytical reagent for the determination of trace elements is reviewed.

2.1 Historical Background: Solid Supports Bearing Chelating Groups

The use of chelating agents in the column extraction of trace metals from aqueous solution dates back to the work of Erlenmeyer and Dahn [89], who separated nine metal ions on a column of powdered 8-hydroxyquinoline (oxine). By a similar method, Burriel-Marti and Perez [90] used solid dimethylglyoxime to separate traces of nickel from iron, palladium, and cobalt. In both of these systems, however, the separation is attributed to precipitation rather than to RPEC [91].

In 1952, the Chemical Research Laboratory in Teddington, U.K., presented "a novel form of reversed-phase partition chromatography" [92]. A solid support was prepared by soaking polystyrene beads in a carbon tetrachloride solution of dithizone. Over the next decade, several laboratories reported the use of dithizone loaded onto cellulose acetate and silica gel supports for the isolation of cadmium, cobalt, copper, indium, lead, manganese, mercury, and zinc from a variety of matrices [93-98].

A review article by Vernon and Eccles [26] credited Gregor and co-workers [99] with the synthesis in the early 1950's of a "new class of ion-exchange resins", namely, a pair of condensation resins consisting of *o*-aminophenol or anthranilic acid incorporated into a phenol-formaldehyde polymer. These chelating agents had certain desirable properties such as the ability to be incorporated into the resin matrix and the stability to withstand the polymerization process [26,100].

Oxine satisfies these requirements, and was the first widely studied chelating agent utilized in RPEC. In 1955, Parrish [101] reported the preparation of a resorcinol-formaldehyde condensation resin with oxine which exhibited favorable chelating properties but extremely low exchange capacity. Parrish also described a modification of the *o*-aminophenol resin of Gregor *et al.* [99] in which the amino group was reduced, diazotized, and coupled with 2-naphthol. Having identified the high degree of cross-linking as the probable cause of the low capacity of the resin, Parrish suggested that binding the oxine unit to a polystyrene matrix *via* an azo bridge could alleviate the problem. This proved to be an important finding in the development of reversed-phase resins. Subsequent studies by Parrish [102,103] and Davies *et al.* [104] demonstrated the utility of the azo-linkage in improving the performance of ligand-immobilized supports.

Reports of the use of chelating resins began to appear in the literature in the late 1950's. Dowex A-1, a styrene-divinylbenzene iminodiacetate chelating resin became commercially available at that time and was cited for its improved selectivity for divalent and trivalent cations with respect to alkali and alkaline earth metals [105]. In the late 1960's, Riley and Taylor [18] were among the first to report the use of Chelex-100, a purified form of Dowex A-1 marketed by Bio-Rad Laboratories, for the determination of trace elements in seawater [18,106]. The performance of Chelex-100 was far superior to that exhibited by conventional ion-exchange resins. Subsequently, Chelex-100 was applied quite successfully as a preconcentrating resin [107-111]. While numerous studies on Chelex-100 showed its utility in this capacity, some shortcomings were reported, most notably the inability to separate trace elements from one another [18]. Consequently, several researchers began to prepare new, more selective ligand-impregnated supports for the preconcentration of trace elements.

In the late 1960's Cerrai and Ghersini [112] loaded cellulose with a commercial liquid extractant, Lix-64, which was used to chromatographically separate copper from other metal ions, namely chromium, cobalt, iron, manganese, and nickel. The authors termed this procedure "reversed-phase extraction chromatography" and praised the excellent selectivity of the method for copper. Following this work, many researchers synthesized novel ligand-loaded supports including α-hydroxyoximes on Amberlyst XAD-2 resin [113,114], ethylene glycol dibutyl ether on XAD-2 [115], α-benzoinoxime on Algoflon "F" [116], 2-thenoyltrifluoro-acetone on cellulose acetate [117] or Porapak Q [118], and neotridecano-hydroxamic acid on Microthene-710 [119].

In the early 1970's Brajter and co-workers [120-122] were among the first to report the use of complexing agents bearing sulfonic acid groups with anion-exchange resins. The selectivity of conventional anion-exchangers was improved with ferroin [120], nitroso R-salt [121], bromopyrogallol red [122], alizarin red S [122], and chromotropic acid [122] as chelation-adsorption reagents. Over the past twenty years, Brajter and co-workers have reported a variety of ligand- impregnated RPEC reagents, generally using anion-exchange resins loaded with sulfonate-bearing chelating agents.

In the early 1970's, Hill [123] cited the need for solid chromatographic adsorbents with greater selectivity than the commercially available iminodiacetate chelating resins, and reported the preparation of silica-immobilized oxine. Since then, silica-immobilized oxine has become the most frequently studied ligand- immobilized RPEC reagent.

These studies constitute the earliest examples of solid phase extractions applied to the preconcentration of trace elements from water samples. Reversed-phase reagents, developed largely as more selective alternatives to commercial chelating resins, began to appear in the literature with increasing frequency in the mid-1970's, and are discussed in greater detail in the following two sections.

2.2 Ligand-Immobilized Reversed-Phase Extraction Chromatography

An overview of recent developments in the field of ligand-immobilized RPEC is presented in Table 2.1. There are a few examples in the literature where the reagent is prepared by copolymerization of an active chelating group with such binding agents as naphthalene [36,124] or formaldehyde [125]. Fujinaga *et al.* [126] developed a method for concentrating copper by liquid-liquid extraction at 90°C using oxine, followed by a solid-liquid separation at room temperature. The authors modified this procedure for the

Table 2.1. Preconcentration of trace elements by ligand immobilization and reversed-phase extraction chromatography.

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Acetoacetanilide	Styrene-DVB	Al, Co, Cu, Fe, Ni, Ti, U	spiked	AAS; spectrometry	Fe, U, and Ti were collected on the resin at pH 2-3, the other elements at pH > 4. A method was developed for the separation of Ti from Al, Ca, Co, Cu, Mg, and Ni.	127
Alizarin Red	XAD-2	Cd, Ni, Pb, Zn	well	AAS	The average recovery of all four metals was ≥ 95% in the pH range 3-6. The precision of the method was much higher than that reported for Chelex-100.	128
Aminophosphoric acid	XAD-4	Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn	bottled, mineral	AAS	All elements studied were retained quantitatively at pH 5; trace elements in bottled mineral water were determined in the presence of mg/L levels of Ca and Mg.	129
Aminophosphoric acid	XAD-4	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	potable	AAS	A microcolumn containing 0.02 g of resin was used, compared to 2-3 g in a previous study. The method was applied to an on-line preconcentration procedure.	130
Bicine	XAD-4	Co, Cu, Fe, Hg, Ni, Pb, Zn	spiked	AAS	All seven elements were quantitatively retained at the optimum pH, typically in the pH range 5-9.	131

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Diethylamino-acetalaldoxime	polystyrene-DVB	Cu	spiked	titrimetry	The resin displayed high selectivity for Cu with respect to other transition elements such as Co, Fe, Ni, and Zn.	132
Dithiocarbamate	polyethylene-imine-poly-methylene	Cr, Fe, Mo, Os, Th, Ti, V, W, rare earth elements	spiked	AES	All of the elements investigated were retained in the pH range 2-6. The resin was shown to recover Cr(VI) and Fe(III), but not Cr(III) and Fe(II).	133
Dithizone	polystyrene	Au, Cu, Fe, Hg, Ir, Ni, Os, Pd, Pt, Rh, Ru	spiked	AES	The poor selectivity of dithizone was was overcome by attaching the ligand to the resin support *via* the S atom.	134
Dithizone	poly(vinyl-pyridine)	Au, Cu, Hg, Pt	spiked	spectro-photometry	All four elements were quantitatively retained at pH 5; Au was isolated from the other elements with appropriate selection of eluents.	135
Dithizone	styrene-DVB	Ag, Bi, Cd, Co, Cu, Ni, Pb, Zn	river water	AAS	Ag was the only element studied to be quantitatively retained from 1 M nitric acid; the other seven elements were completely recovered at pH > 5.	136

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Ethylenediamine tetraacetic acid	cellulose	Ca, Cd, Co, Cu, Fe, Hg, Mg, Ni, Pb, Zn	spiked	AES	The resin recovered > 90% Cd, Cu, Fe, and Pb at pH 3, but also displayed a high affinity for Ca (88%) and Mg (80%).	137
8-Hydroxyquinoline	CPG	Cu	natural	AAS	Cu was collected at pH 4.6. The CPG-oxine displayed superior performance compared to a conventional ion-exchanger.	37
8-Hydroxyquinoline	Porasil B	Cd, Co, Cu, Gd, La, Mn, Ni, Pb, Yb, Zn	spiked	spectro-photometry	The Porasil-immobilized oxine was applied to the chromatographic separations of metal ions using a gradient elution technique.	138
8-Hydroxyquinoline	silica	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	seawater	AAS	Metal recoveries on I-8-HOQ were at least 92% from solution of pH 8.0, with the exception of Co (74 ± 1%).	48
8-Hydroxyquinoline	Amberlite XE-305	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	seawater	AAS	This resin was easier to prepare, and had a much lower Fe blank, than the I-8-HOQ of Sturgeon *et al.* (ref. 48).	139
8-Hydroxyquinoline	silica	Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	seawater	AAS	The procedure of Sturgeon *et al.* (ref. 48) was used with ICP-MS in order to test the applicability of the instrumental technique.	140

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
8-Hydroxyquinoline	silica	Co, Cu, Fe, Ni	spiked	AAS	The authors had previously reported a "more efficient" synthesis of I-8-HOQ [142]; this resin retained all four elements quantitatively at pH ≥ 4.	141
8-Hydroxyquinoline	silica	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	seawater	AAS	The method of Sturgeon *et al.* (ref. 48) was modified; use of a microcolumn permitted use of smaller samples (50 mL).	143
8-Hydroxyquinoline	silica	Cd, Cu, Mo, Ni, Pb, U, Zn	seawater RMs	ICP-MS	The resin and procedure of Sturgeon *et al.* (ref. 48) were utilized.	144
8-Hydroxyquinoline	silica	Al, Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn	spiked	spectrophotometry; AAS	Specific attention was devoted to the back extraction of the chelated metals.	145
8-Hydroxyquinoline	silica	Co, Cu, Mn, Ni, Pb, U	river, seawater RMs	ICP-MS	The column of Nakashima *et al.* (ref. 143) was used in an on-line procedure, further reducing the sample volume to 10 mL.	76
8-Hydroxyquinoline	silica	Al, Cu, Fe, Pb Zn	tap water	AAS	Selectivity for lead was improved by using masking agents.	146

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
8-Hydroxyquinoline	silica	Bi, Cd, Cu, In, Pb, Zn	seawater	ASV	Elements were concentrated using seawater samples as small as 10 mL.	147
8-Hydroxyquinoline	silica	Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, U, Zn	seawater RMs	ICP-MS	Following Sturgeon *et al.* (ref. 48), the trace elements were collected at pH 8; Fe and Mo were preconcentrated at pH 3.	148
8-Hydroxyquinoline	silica	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	seawater RMs	ICP-MS	For an on-line procedure, a mini-column of 40 mg I-8-HOQ (ref. 48) had a lower blank than a commercial iminodiacetate column, so 5-mL samples could be used.	149
8-Hydroxyquinoline	silica	Cd, Cu, Ni	seawater RM	AES	The authors used a resin prepared in-house [151] to collect Cd, Cu, and Ni at pH 6.5 using an on-line method.	150
8-Hydroxyquinoline	CPG	Al, Ga, In	river, seawater	AAS	All three elements are quantitatively retained from pH 10 malonate buffer; only In is recovered from pH 10 picolinate buffer.	152
8-Hydroxyquinoline	cellulose	Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Pd, Zn	synthetic solutions	AAS	All elements except Pd were recovered quantitatively at pH ≥ 10.	153

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
8-Hydroxyquinoline	CPG	Cr	seawater	AAS	The recovery of Cr(III) was quantitative from an acetate solution buffered to pH 9.	154
8-Hydroxy-quinoline	resorcinol/formaldehyde or resorcinol/hydroquinone	Co, Cu, Ni, Pb, Zn	spiked	AAS	An eluent switching technique was used to separate Cu from Ni, Pb, or Ni and Co.	155
8-Hydroxy-quinoline	resorcinol/formaldehyde/2-furaldehyde/hydroquinone/benzaldehyde	Ni	spiked	spectro-photometry	Five combinations of cross-linking agents were studied; the five displayed similar characteristics, including a Ni capacity of 0.5-0.7 mmol/g for each resin.	156
8-Hydroxy-quinoline	resorcinol/formaldehyde/2-furaldehyde/hydroquinone/benzaldehyde	Cd, Co, Cu, Zn	spiked	spectro-photometry	All four elements were retained at pH 4; a flow-injection system was applied to the separation of Cd or Zn from mixtures containing the other elements.	157
8-Hydroxyquinoline	silica	Cu, Ni, Zn	spiked	AAS	A novel method for the synthesis of I-8-HOQ was presented; this resin has a higher Cu capacity than other oxine resins.	158

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
8-Hydroxyquinoline	silica	rare earth elements	seawater, natural	ICP-MS	The retention of REE's by the resin varied from 90-93% for seawater, to 81-84% for groundwater, to < 50% for river water.	159
8-Hydroxyquinoline	XAD-2	Mg	spiked	AAS	Free Mg(II) ion was determined in the presence of Mg complexes.	160
8-Hydroxyquinoline	vinyl polymer	Mn	seawater	spectro-photometry	Mn was determined by an on-line preconcentration procedure using flow-injection analysis.	161
8-Hydroxyquinoline	Fractogel TSK	Al, Cd, Co, Cu, Fe, Mn, Zn	seawater, natural	AAS	As I-8-HOQ is unstable in solutions of high pH, the authors proposed bonding oxine to Fractogel TSK.	162
Lysine-N^{α},N^{α}-di-acetic acid	GMA gel	rare earth elements	spiked	ICP-MS, spectro-photometry	Elements loaded on resin in 0.02 M nitric acid were separated by gradient elution.	163
Mercapto groups	silica	As	seawater	AAS	The mercapto-immobilized resin has no affinity for As(V), but the recovery of As(III) is ≥ 90% over the pH range 1-9.	164

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
2-Mercaptobenzothiazole	naphthalene	Cu	spiked	AAS	After metal uptake, the solid column contents were dissolved in 10 mL *n*-butylamine-DMF prior to AAS.	36
Nitrilotriacetic acid, thiourea, cysteine	cellulose filters	Al, Ca, Cd, Co, Cu, Fe, Hg, Mg, Ni, Pb, Zn	spiked	AES	All 11 elements studied were retained quantitatively on the NTA filters in the pH range 4-8; the metal recoveries were good for the other filters, generally at pH ≥ 7.	165
1-Nitroso-2-naphthol	polystyrene-DVB	Co, Cu, Fe, Ni, Pd, U	spiked	AAS, spectrophotometry	This was one of the first reported attempts to apply the ligand to RPEC; theory had suggested that the compound would display little tendency to couple with a diazo group.	166
1-Nitroso-2-naphthol	silica	Al, Cd, Co, Cu, Hg, Pb, Zn	spiked	AES	Co and Hg were retained quantitatively, Cu ≈ 90%; the other elements displayed poor uptake. Co(II) was isolated as Co could not be eluted even with 5M HCl.	167
PAPH	silica	Cd, Co, Cu, Fe, Mn, Pb, Zn	spiked	spectrophotometry	All seven elements were retained on the resin at pH 4.5, then separated using a variety of eluents. The method was applied to the determination of Fe, Mn, and Zn in NBS Tomato Leaves.	168

Table 2.1. (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Salicylaldoxime	formaldehyde	Cd, Co, Cu, Fe, Mn, Ni, Pb, Pd, Zn	spiked	AAS	Pd was separated from other metal ions; the optimum pH for adsorption of Pd was 3.5-4.0, compared to pH > 6.7 for the other 8 elements.	125
Salicylic acid	XAD-2	Cd, Ni, Pb, Zn	well water	AAS	Quantitative recovery of Pb and Zn was found to occur at pH ≈ 5; the maximum attainable recovery of Cd and Ni was ≈ 55%.	169
Thioglycolate	XAD-4	Cd, Ni, Pb, Zn	artificial seawater	AAS	The resin was prepared following the synthesis of Phillips and Fritz [171]; all four elements were completely recovered from buffer solutions of pH 7-9, but the retention of Ni and Zn from artificial seawater samples was non-quantitative.	170

Abbreviations used: AAS = atomic absorption spectrometry; AES = atomic emission spectrometry; ASV = anodic stripping voltammetry; CRM = certified reference material; DMF = dimethylformamide; DVB = divinylbenzene; GMA gel = glycidyl methacrylate gel; ICP-MS = inductively coupled plasma mass spectrometry; NBS = National Bureau of Standards; PAN = 1-(2-pyridylazo)-2-naphthol; PAPH = 2-pyridinecarboxyaldehyde phenylhydrazone; PAR = 4-(2-pyridylazo)resorcinol; REE = rare earth elements; RM = reference material; RPEC = reversed-phase extraction chromatography; SRM = standard reference material concentration of palladium using dimethylglyoxime and naphthalene [172]. In a later study by the same group, naphthalene doped with 1-(2-thiazolylazo)-2-naphthol (TAN) was prepared by warming TAN and naphthalene in distilled water [124]. After cooling, the TAN-naphthalene solid was filtered and ground into a powder, and used to extract nickel from solution. In contrast to the previous reports, the extraction step was carried out at room temperature, so the naphthalene powder remained in the solid phase throughout the separation. After equilibration, the powder was removed by filtration and analyzed for nickel by XRF.

Satake *et al.* [36] produced naphthalene loaded with 2-mercaptobenzothiazole for the determination of copper by AAS. Recently, Purohit and Devi [157] prepared several condensation resins utilizing oxine and cross-linking agents such as hydroquinone and furaldehyde in an attempt to improve their stability and exchange kinetics. These reagents were applied to an on-line determination of copper in aqueous solution [155] and nickel in chocolate [156].

Studies involving a ligand-immobilized reagent usually employ a system in which the ligand is chemically grafted to a solid surface. Oxine has been the most commonly used chelating agent in ligand-immobilization studies [37,48,138-162]. In particular, silica-immobilized oxine, abbreviated I-8-HOQ [48], has found extensive application in the preconcentration of trace elements.

The majority of this work incorporated an oxine-immobilized support prepared by one of the two following methods [142]. The classical synthetic procedure for the preparation of I-8-HOQ was reported by Hill [123], by treating silica gel with 3-aminopropyl triethoxy silane, acylation of the amine with *p*-nitrobenzoyl chloride, reduction of the $-NO_2$ group to $-NH_2$, diazotization with sodium nitrite, and coupling of oxine to the diazotized support. An alternative method was presented by Sugawara *et al.* [173], in which oxine was immobilized on Controlled Pore Glass (CPG) *via* a phenylazo linkage.

Several researchers have devoted efforts either to provide more expeditious syntheses of I-8-HOQ [142,151,158], or to immobilize oxine on supports other than silica, *e.g.* CPG [152,154], Amberlite XE-305 [139], XAD-2 [160], vinyl polymer [161], cellulose [153], and Fractogel TSK [162], as summarized in Table 2.1. Much of the extensive literature devoted to oxine-immobilized substrates has focussed on improving the performance of the method, through the use of microcolumns [143,149] and flow injection systems [76,149,161].

Sturgeon *et al.* [48] utilized about 600 mg of Porasil-oxine substrate to preconcentrate trace elements from up to 1 L of seawater prior to AAS determination. McLaren *et al.* [140,144,174] employed this method with ICP-MS. Nakashima *et al.* [143] used a microcolumn containing less than 100 mg of I-8-HOQ and smaller volume of eluent so that seawater of 50 mL can be analyzed by AAS. Later, Beauchemin and Berman [76] utilized this technique in an on-line preconcentration of trace elements from 10 mL of seawater by ICP-MS. Mohammad *et al.* [152] further reduced the quantity of reagent by about half, using oxine-CPG.

In comparison with the large body of work devoted to reagents bearing immobilized oxine, the use of other chelating agents has not been as exhaustively explored. Most groups reporting the use of novel ligand-immobilized reagents did not attempt to improve upon studies utilizing oxine; rather, such reagents are proposed as a more selective alternative to iminodiacetate resins [131] or as a means to further exploit well-known organic chelating agents [127,166]. For the most part, such ligand-immobilized resins have been prepared following similar synthetic procedures as those proposed for oxine.

As presented in Table 2.1 some of the ligand-immobilized supports which have been used in RPEC are: 1-nitroso-2-naphthol on polystyrene-divinylbenzene [166] and silica [167]; thiourea, cysteine, or nitrilotriacetic acid (NTA) on cellulose [165]; dithizone and dehydrodithizone on polystyrene [133,134]; dithizone on styrene-divinylbenzene [135]; thioglycolate groups bound to Amberlite XAD-4 [170,171]; salicylic acid coupled to Amberlite XAD-2 [169]; Alizarin Red-S onto XAD-2 [128]; and aminophosphonic acid groups on Amberlite XAD-4 [129,130]. Other such examples include: silica-immobilized 2-pyridinecarboxyaldehyde phenylhydrazone [168,175]; styrene-divinylbenzene polymer beads bearing fixed acetoacetanilide groups [127]; EDTA groups bound to cellulose filter discs [137]; polystyrene-divinylbenzene with oxime and diethylamino groups [132]; lysine-N^{α}-N^{α}-diacetic acid bound to a cross-linked polymer gel [163]; and bicine groups attached to Amberlite XAD-4 [131].

The development of ligand-immobilized RPEC methods highlights the two major advantages of reversed-phase reagents with respect to chelating resins such as Chelex-100. The active component, the chelating agent bound to the inert matrix, can be readily changed to meet a variety of analytical needs. As exhibited for oxine-immobilized supports, the silica gel or other matrix can be replaced by a more suitable solid as required, without compromising the ability of the ligand-immobilized resin to concentrate trace elements from solution. These advantages should also hold for ligand-impregnated resins, which are discussed in detail in the next section, and summarized in Table 2.2.

2.3 Ligand-Impregnated Reversed-Phase Extraction Chromatography

A large body of work has been devoted to the synthesis and characterization of ligand-impregnated resins composed of conventional anion- exchange resins modified with ligands bearing sulfonic acid groups. Brajter and co-workers [120-122] introduced the use of sulfonate compounds to chelation-adsorption studies in the late 1960's, and subsequently applied these reagents to RPEC. The synthesis of such RPEC resins generally involves equilibrating an anion-exchange resin with an aqueous solution of the desired chelating agent, then filtering, washing, and drying the product. The metal-chelating characteristics of a wide variety of these resins have been investigated. This work highlights one of the major advantages of ligand-impregnated RPEC. Once a general method for the synthesis of the ligand-loaded resin has been developed, the complexing agent can be freely changed to meet a variety of analytical requirements.

Brajter and Dabek-Zlotorzynska [176] described the preparation of anion-exchange resins Amberlyst A-26 and Amberlite IRA 400 loaded with 1,2-dihydroxy-benzene-3,5-disulfonic acid (Tiron). Nine elements (Table 2.2) were quantitatively retained from neutral solution, but cadmium, copper, and zinc were poorly retained (< 50%) and chromium, cobalt, manganese, and nickel were not recovered at all at pH ≤ 6.

Table 2.2. Preconcentration of trace elements by ligand impregnation and reversed-phase extraction chromatography.

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
8-Amino-naphthalene-2-sulfonic acid	Amberlyst A-26	Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	spiked	AAS	All elements studied except Zn are quantitatively recovered; the method is selective for Ag in 0.1 M HNO_3.	177
Azothiopyrine disulfonic acid	Amberlite IRA-400	Cd, Cu, Hg	spiked	AAS	All three elements are quantitatively retained at pH $\geq$ 6.5; only Hg is retained at pH $\leq$ 2.	178
Bathocuproine disulfonic acid	Dowex 1X4	Cu, Hg	river	NAA	The method is specific for Hg at pH 0.5-1.0; Cu is retained quantitatively at pH >3.	88
Bismuthiol-II	Amberlite IRA-400	Se	river, seawater	spectro-photometry	Se is collected on the resin from 0.3 M HCl and can be eluted either with 6-13 M HNO_3 or pH 5 buffer containing 0.1 M penicillamine.	179
Calmagite	Dowex 1-X8 XAD-2,4	Co, Mg, Mn, Zn	spiked	spectro-photometry	Calmagite was found to be less suitable for separations than other ligands investigated in this study.	180,181
Chrome Azurol S	Dowex 1-X8, XAD-2,4, PLRP-S	Ba, Ca, Cd, Co, Cu, Mg, Mn, Ni, Pb, Sr, Zn	spiked	spectro-photometry	The coated PLRP-S resin is used to effect a quantitative separation of transition metals from alkaline earths.	180,181

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Chromotrope 2B	AG 1-X8	Al	tap water	spectro-photometry	Al was separated from Ca, Cd, Mg, Ni, Pb, and Zn.	182
Chromotrope 2B	AG 1-X8	Al	tap water, dialysis fluid	fluorometry	Al collected from 185-μL sample is eluted with 100 μL 0.1 M HCl, then complexed with 5,7-dibromo-8-hydroxyquinoline for fluorescence detection.	183
Chromotrope 2B	AG 1-X8	Al	tap water	ICP-MS, AAS	A microcolumn of (50 x 3 mm i.d.) of Chromotrope 2B was used in a flow injection system.	76
Chromotropic acid	Dowex 1-X8	Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	spiked	AAS	At pH 4.3, Cr(VI) is retained, but Cu(II), Mn(II), and Pb(II) are not.	184
Dithizone	XAD resins	Hg	seawater, natural	AAS	The authors consider the loading of dithizone on the resin to be due mainly to precipitation on the resin surface, rather than adsorption.	185
7-Dodecenyl-8-quinolinol	XAD-4	Ag, Al, Bi, Cd, Cu, Fe, Ga, Mg, Mg, Ni, Pb, Ti	seawater	AAS	The resin displays no affinity for Mg, but all other elements are quantitatively retained at pH 8.	23

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
DPTH	silica gel	Cd, Co, Cu, Ni, Pb, Zn	seawater, tap water	AAS	Ca was found to suppress the uptake of trace elements on the column.	186
DzS	Amberlite IRA-400	As, Co, Cu, Ge, Ni, Pb, Se	spring water	AAS	As, Ge, and Se are not retained by the resin, but Co, Cu, and Ni are taken up along with Pb and may interfere.	187
Eriochrome Blue-Black R	XAD-2, Amberlyst A-26	Bi, Co, Cr, Cu, Fe, Ga, In, Ni, Pb, Zn	spiked	AAS	The EBBR-A-26 resin was shown to be superior to the EBBR-XAD-2 resin in terms of higher loading of EBBR (3.7 to 0.6 mmol g^{-1}) and larger number of metals completely retained (7 to 5).	188
HDEHP, TBP, TTA	polyurethane foam	Sr	spiked	γ-spectrometry	Foam cylinders were loaded with one of the ligands by a batch method; the recovery of Sr for the loaded and unloaded foams were compared.	189
8-Hydroxyquinoline	XAD-2	Cd, Co, Cu, Hg, V, Zn	tapwater, rain water	NAA	Metals adsorbed on the resin were quantified by direct analysis on the resin with no elution step.	14
8-Hydroxyquinoline and derivatives	XAD-2,4, 7,8	Cd, Cu, Fe, Hg, Ni, Pb, Zn	seawater	AAS	Separation of Cd, Cu, Fe, and Pb was carried out with a pH gradient.	24

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
8-hydroxyquinoline-5-sulfonic acid	Diaion SA #100	As, Cd, Cu, Fe, Hg, Mn, Zn	river water	NAA	The elements were quantified by direct analysis of the resin, without need for an elution step.	190
8-hydroxyquinoline-5-sulfonic acid	Diaion SA #100	Zn	river water	γ-spectrometry	Interfering elements such as Cu and Fe were removed by extraction with dithizone.	191
8-hydroxyquinoline-5-sulfonic acid	Diaion SA #100	As, Cd, Co, Cu, Fe, Hg, Mn, Zn	river water	NAA	The elements were quantified by direct analysis of the resin, without need for an elution step.	88
8-hydroxyquinoline-5-sulfonic acid	Diaion SA #100	Co, Ni	spiked	AAS	The kinetics of metal uptake were investigated.	192
IHQS	Dowex 1-X8	Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	spiked	AAS	Cu and Pb are completely recovered at pH 4. The resin was applied to the determination of Cu or Pb in the presence of the other elements.	184
1-Nitroso-2-naphthol	silica gel	Co	seawater	AAS, γ-spectrometry	The recovery of Co is not hindered by the presence of Cu, Fe, Ni, U, or anions such as cyanide or tartrate.	46

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Nitroso-R-Salt	alumina	Ca, Cd, Co, Cr, Cu, Fe, Ir, Mg, Mn, Ni, Pb, Pd, Pt, Rh, Zn	spiked	AAS	Seven sulfonated aromatic chelating agents were investigated as reagents for loading on alumina. Nitroso-R-Salt was chosen as a representative ligand for further experiments.	193
Nitroso-R-Salt	alumina	Co	spiked	AAS	An on-line method was developed; in sequence, a solution of NRS (5 mM), the sample (pH 2), and eluent (0.1 M NaOH) were passed through the column.	194
Orange II	Varion AT-400	Al, Cd, Co, Cu, Mn, Ni, Pb, Zn	spiked	AAS	Separation of ions such as Al-Ni and Al-Pb-Zn-Ni was accomplished.	195
PDT	XAD-2	Co, Cu, Fe, Ni, Zn	seawater	AAS except spectrophotometry (Fe)	Other chelating agents, including 1,10-phenanthroline and 2,2'-bipyridine were studied; PDT was chosen for further experiments as the Fe-PDT complex has the highest rate of adsorption.	47
1-(2-Pyridylazo)-2-naphthol	polyurethane foam	Co	spiked	spectrophotometry	Interfering elements are removed by masking agents and ion-exchange.	196

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
1-(2-Pyridylazo)-2-naphthol	XAD-4	Cd, Cu, Fe, Ni Pb, Zn	river water, synthetic tap water	AAS	Metal recovery is > 90% in spiked buffer, but falls to 70-80% in synthetic drinking water.	197
1-(2-pyridylazo)-2-naphthol	Dowex 50W	Cu	spiked	spectro-photometry	Cu loaded onto the column at pH 4-6 was eluted with thioglycollic acid.	198
4-(2-Pyridylazo)-resorcinol	XAD-2	Ag, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Zn, Zr	spiked	AAS	All elements except Sb are retained by the resin at pH 2-8; with the use of tetren as a masking agent, Ag can be separated from Cu and other elements at pH 7.2-7.7.	199
Pyrocatechol Violet	XAD-2	Cu	tap water, river	AAS	Eriochrome Blue-Black R and 4-(pyridylazo)resorcinol were also studied; PV was used in the optimized procedure for natural water samples. Cu was quantitatively retained at pH 8.0.	50
Pyrocatechol Violet	AG MP-1	Al	tap water	AES	Reversed-phase extraction on the ligand-impregnated resin displays inferior performance compared to precomplexation and adsorption of the anionic Al-PV complex on AG MP-1.	31

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Pyrocatechol Violet	XAD-2	Pb	tapwater, natural	AAS	The results were compared to other sorbents, and the capacity was found to be less than that of the cationic sorbent Cellex P. The optimum pH for Pb retention was found to be 7-10.	200
Pyrocatechol Violet	XAD-2	Bi, Co, Cu, In, In, Ni, Pb	tapwater	AAS	Concentration factors of 80-500 were obtained for Pb in tapwater.	33
Pyrocatechol Violet	Dowex-2	Cd, Cu	river water	AAS	Recoveries of Cd and Cu are >95% in spiked buffer at pH 9, but fall to 80% or less at elevated NaCl levels.	74
Pyrogallolsulfonic acid	Seralite SRA-400	Be, Cu, Fe, Mn, Mo, Ni, V	spiked	AES; spectrophotometry	The separation of Mn-Cu-Fe using a pH gradient was achieved.	201
SPADNS	Amberlyst A-26	Al, Bi, Co, Cu, Fe, Ni, Zn, Zr	spiked	AAS	Bi can be separated from other ions such as Cd, Cr, Mn, Ni, and Zn.	195
5-Sulfosalicylic acid	PXPi	Cu, Mn, Ni, Pb, Zn	spiked	ASV	The PXPi resin was synthesized by the authors, and loaded with the chelating agent by a batch procedure. Filter paper strips were impregnated with this resin and used for metal separations.	202

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
5-Sulfosalicylic acid	Dowex 1-X8	Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	spiked	AAS	Fe can be separated from Cu, Mn, Ni, Pb, and Zn.	184
T-azo-R	AG MP-1	Ga	spiked	ASV	The resin was applied to the determination of trace Ga in a solution of Al.	203
Tiron	Amberlyst A-26	Ag, Al, Bi, Cd, Cr, Cu, Fe, Ga, In, Pb, Ni, Ti, V, Zn	spiked	AAS	The method was applied to the separation of elements, *e.g.* Al-Ga, using an eluent switching technique. The authors proposed that the method could be applied to analysis of alloys.	176
Xylenol Orange	Amberlyst A-26	In	spiked	AAS	The resin was used in determination of trace In in metallic Zn and Pb.	204
Xylenol Orange	Dowex 1-X8, XAD-2,4, PLRP-S	Ba, Ca, Cd, Co, Cu, Mg, Mn, Ni, Pb, Sr, Zn	spiked	spectro-photometry	The coated PLRP-S resin was used to separate alkaline earths from Pb and transition metals.	180,181
Xylenol Orange	Dowex 1-X8	Ba, Ca, Mg, Sr	brine	inverse spectro-photometry	The elements are retained at pH 10-11, then eluted with a solution containing lactic acid and ethylenediamine at pH 2.8.	205

Table 2.2 (continued).

Complexing Agent	Support	Elements Studied	Water	Technique	Remarks	Ref.
Xylenol Orange	Amberlyst A-26	Al, Cd, Co, Cr, Cu, Fe, Ga, In, Ir, Mn, Ni, Pb, Rh, Zn	spiked	AAS	All elements studied except Cr and Mn were at least 80% retained. The resin was applied to the chromatographic separation of In-Mn-Cu, Al-In-Zn, and In-Ga.	206
Xylenol Orange	polystyrene-DVB	Cu, Mn, Ni, Pb, Zn	seawater	spectrophotometry	The ligand was loaded on a high-performance resin support; and used to separate and quantify trace metals.	207
Zincon	Diaion SA #100	Co, Cu, Hg, Mn, Pb, Zn	river	NAA	Cu, Hg, Pb, and Zn are completely recovered, while Co and Mn are only partially retained.	88

ABBREVIATIONS: AAS = atomic absorption spectroscopy; AES = atomic emission spectroscopy; ASV = anodic stripping voltammetry; DPTH = 2,2'-dipyridyl-4-amino-3-hydrazino-5-mercapto-1,2,4-triazolehydrazone; DzS = (4-sulfophenyl)-1-[2-(4-sulfophenyl)-hydrazide]diazenecarbothioate; EBBR = Eriochrome Blue-Black R; HDEHP = *bis*-(2-ethylhexyl)-*o*-phosphoric acid; IHQS = 7-iodo-8-hydroxyquinoline-5-sulfonic acid; NAA = neutron activation analysis; NRS = Nitroso-R-Salt; PDT = 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; PV = Pyrocatechol Violet; SPADNS = 2-(*p*-sulfonato)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid; T-azo-R = 1-(tetrazolylazo)-2-hydroxynaphthalene-3,6-disulphonic acid; TBP = tri-*n*-butyl phosphate; TTA = 1-(2-theonyl)-3,3,3-trifluoroacetone

The same authors reported the synthesis of Xylenol Orange (XO) loaded on Amberlyst A-26 resin [206]. Many of the fourteen elements studied were completely retained (Table 2.2). The differences in optimal pH for complete uptake of each metal were exploited in order to separate indium from aluminum, gallium, or zinc, and copper from manganese. The XO-A-26 resin was subsequently used to quantify trace amounts of indium in zinc-indium and lead-indium alloys [204].

The anion-exchange resins Amberlyst A-26 and Varion AT-400 were impregnated with SPADNS, Orange II, or Nitroso R-salt (NRS) [195], and were applied to the extraction of twelve cations from aqueous solution (Table 2.2). A similar resin was prepared by equilibrating Amberlyst A-26 resin with a solution of 8-aminonaphthalene-2-sulfonic acid (ANS) [177]. The retention of ANS was attributed to a combination of ion-exchange and adsorptive mechanisms.

The chelating agent Eriochrome Blue-Black R (EBBR) was loaded onto the anion-exchanger Amberlyst A-26 and the non-ionic sorbent Amberlite XAD-2 [188]. Two experimental procedures, namely a chelation-adsorption batch extraction and an RPEC separation, for trace element preconcentration were compared using EBBR. RPEC methods, with only a few exceptions, displayed superior metal chelating characteristics. The most encouraging results were obtained for the RPEC separation of nickel on EBBR-XAD-2, and this resin was used to selectively extract nickel from seawater.

Brajter and co-workers also reported the impregnation of Amberlite XAD-2 resin with pyrocatechol violet (PV) [33] and a non-sulfonated chelating agent, 4-(2-pyridylazo)resorcinol (PAR) [199]. The PV-XAD-2 and PAR-XAD-2 resins had capacities of 0.10-0.12 mmol PV g^{-1} and 0.04 mmol PAR g^{-1} resin, respectively. The PV-XAD-2 resin was applied to the determination of lead in tap water. The PAR resin was employed to concentrate trace silver from copper ores prior to determination by AAS.

Akaiwa and co-workers [88,190-192] can be credited for some of the earliest reports of trace element preconcentration by RPEC. A report published in 1975 discussed the preparation of Diaion SA #100 anion-exchange resin loaded with oxine-5-sulfonic acid [25] which was applied to the preconcentration of cadmium, copper, iron, manganese, mercury, and zinc from river water samples adjusted to pH 7 [190]. The method can be made selective for zinc by performing the separation at pH 4.0-4.8 and using dithizone to mask copper and iron [191].

This work is of particular interest to this study because in some of the reports by Akaiwa and co-workers the trace metal analysis was carried out by PNAA [88, 190]. After the passage of the sample through the column, the resin was washed, placed in an ampoule and irradiated at a neutron flux of 2×10^{13} n $cm^{-2} s^{-1}$ for 1 hour. The column contents were then analyzed by γ-ray spectrometry after a decay period of 1-15 days [190]. The elements were thus quantified by direct NAA of the resin, without the need for an elution step. The same approach has been utilized in this thesis.

A similar procedure was used to analyze the uptake of several trace elements from river water [88]. The performance of three ligand-loaded resins was compared, with 8-hydroxyquinoline-5-sulfonic acid, Zincon, and bathocuproine disulfonic acid (BCS) as the active groups. The latter two ligands were found to be more selective than 8-hydroxyquinoline-5-sulfonic acid, which exhibits complete recovery for cadmium, cobalt, copper, manganese, nickel, and zinc at pH ≥ 3. The BCS resin completely retains copper and mercury at pH ≥ 3, and mercury alone at pH 1, but displays no affinity for cadmium, cobalt, iron, nickel, and zinc under these conditions. The Zincon resin quantitatively extracts copper, mercury, lead, and zinc at pH ≥ 4, but does not extract cadmium over the pH range 3-8. The 8-hydroxyquinoline-5-sulfonic acid resin was proposed as a useful reagent for simultaneous group extraction, while the other two resins were cited for their utility in metal separations.

Several other researchers have followed the work of Brajter and Akaiwa in developing new ligand-impregnated RPEC reagents using sulfonate-bearing chelating agents. Tanaka *et al.* [77] prepared a disulfonic acid derivative of dithizone (DzS) which was loaded on Amberlite IRA 400 resin to concentrate mercury from aqueous solution. Chikuma and Aoki [187] showed that the DzS-loaded resin was effective for the preconcentration of lead at pH 6.3-10 from spring water.

Chikuma *et al.* [208] introduced azothiopyrine sulfonic acid (ATPS), the first reported chelating agent bearing azo and mercapto groups, and impregnated an anion-exchange resin with ATPS. The ATPS-loaded resin was found to be effective for the adsorption of mercury (II) ion from acidic solution. Later, the same authors investigated the chelating properties of this resin in greater detail [178]. Copper, cadmium, and mercury are quantitatively recovered from 0.5 M NaCl solution at pH 6; at pH 1, only mercury is retained. The removal of mercury from the column using various eluting agents was also investigated. Mercury is completely eluted with 8 M nitric acid, but such harsh treatment also results in stripping of the ligand from the resin. In this thesis, such elution steps were avoided and the resin was directly analyzed by NAA for mercury.

Lee *et al.* [184] loaded chromotropic acid on Dowex 1-X8 resin and investigated its chelating characteristics toward a number of transition metals. The resin proved to be selective for chromium (VI) ion, which was quantitatively retained at pH >3; chromium (III) was not retained at any pH value. Pesavento *et al.* [182] loaded 2-(4-nitrophenylazo)chromotropic acid (Chromotrope 2B) on AG 1-X8 resin and found that aluminum is fully recovered at pH 6. The resin was used to preconcentrate aluminum from tap water samples. Fernández *et al.* followed this work by using a microcolumn of Chromotope 2B resin to preconcentrate aluminum using a flow-injection system. The method was used to determine aluminum in tap water, dialysis fluid, and tomato samples by fluorometry [183] and in tap water and dialysis solutions by AAS and ICP-MS [76].

Challenger et al. [180,181] examined the chelating properties of reversed-phase resins produced by loading Calmagite, Chrome Azurol S (CAS), or Xylenol Orange (XO) on a variety of supports as given in Table 2.2. Further, XO and CAS were loaded onto the small particle size (8 μm) PLRP-S resin for group separation of several transition elements and lead from alkaline earth metals. The authors used XO-impregnated Dowex 1-X8 to monitor alkaline earths in the feed brines used in the chloro-alkali industry [205]. A high-performance XO-PLPR-S resin prepared by Paull *et al.* [207] retains copper, lead, manganese, nickel, and zinc, but not calcium and magnesium, at pH 6; the method was applied to river and seawater analysis.

Pyrocatechol Violet (PV) has been loaded onto XAD-2 [50,200] and Dowex-2 [74] for the preconcentration of cadmium, copper, and lead from tap, well, and river water samples. Nakayama *et al.* [179] loaded bismuthiol-II on Amberlite IRA-400 for the determination of selenium (IV) in marine and river water samples. Trojanowicz and Pyrzynska [194] loaded Nitroso-R-salt, a disulfonated derivative of 1-nitroso-2-naphthol, onto alumina. A flow-injection system was developed for the determination of cobalt in tobacco leaves.

There are also many examples in the literature of RPEC reagents prepared by loading neutral chelating agents on non-ionic supports, and some of them are cited in Table 2.2. Howard and Arbab-Zabar [185] loaded dithizone on each of five Amberlite XAD resins for the preconcentration of mercury from sea water in the pH range 1-10. The recovery of mercury is quantitative regardless of the choice of support. De Oliveira and Narayanaswamy [32] loaded dithizone on Amberlite XAD-2, XAD-4, and XAD-7 resins for the collection of lead from solution at pH 8.

Terada and Nakamura [46] equilibrated silica gel with a solution of 1-nitroso-2-naphthol in acetone. The silica-impregnated 1-nitroso-2-naphthol was effective for the extraction of cobalt at pH >3. Ide and Haraguchi [209] loaded styrene-divinylbenzene with 1-nitroso-2-naphthol in chlorobenzene. This resin was shown to collect cadmium, cobalt, copper, manganese, nickel, and zinc under appropriate pH conditions. Cobalt and copper are selectively retained over the pH range of 3.3-4.8. Maksimova and Morosanova [210] applied C_{16} silica-impregnated 1-nitroso-2-naphthol to the simultaneous determination of cobalt and nickel.

Samara and Kouimtzis [186] prepared a new chelating agent, 2-2'-dipyridyl-4-amino-3-hydrazino-5-mercapto-1,2,4-triazolenydrazone (DPTH), and used DPTH-loaded silica gel to collect cadmium, cobalt, copper, lead, nickel, and zinc from solutions of pH >6. In tap and seawater samples, however, as little as 3 ppm calcium was found to prevent the quantitative recovery of these elements.

Chwastowska and Mozer [197] loaded PAN onto Amberlite XAD-4 for the preconcentration of lead and 5 transition elements (Table 2.2) from aqueous buffer at pH 8.5. Braun and Abbas [196] loaded PAN on polyurethane foam for the determination of trace cobalt at pH 5 buffer. The use of ligand-loaded polyurethane foam allowed flow rates as high as 100 mL min^{-1}. The reagent was prepared by soaking foam cylinders in solutions of PAN in chloroform. The poor selectivity of PAN with respect to other trace elements was cited.

Polyurethane foam was used as the stationary phase in the RPEC separation of strontium [189]. The performance of the untreated foam cylinders was compared to that exhibited by foams loaded with tri-*n*-butyl phosphate (TBP), 1-(2-theonyl)-3,3,3,-trifluoroacetone (TTA), or bis(2-ethylhexyl)-*o*-phosphoric acid (HDEHP). The unloaded foam partially retains strontium at pH 10, while the foam cylinders treated with any of the three chelating agents quantitatively collect strontium at optimum pH values.

The reports summarized in this section present an overview of the potential application of ligand-impregnated supports to trace element preconcentration methods. Such reagents should be considered a favorable alternative where commercial chelating resins or ligand-immobilized resins are found to display inferior performance.

For the present work, the principal chelating agent selected is TAN. The use of TAN-impregnated resins, as well as other examples in which TAN has been applied in trace element determination, will be discussed in the next section.

2.4 TAN as an Analytical Reagent

The chelating agent 1-(2-thiazolylazo)-2-naphthol (TAN) was first reported to be synthesized in the mid-1950's by Boni and Hemmeler [51] as one of a series of azo derivatives of thiazole. Colored complexes of TAN were shown to form with cobalt, copper, and zinc; it was postulated that TAN and related compounds might be suitable for trace metal determination and for usage as titrimetric indicators [211]. There are a few examples in the literature in which TAN has been used as an indicator [212-215].

However, most of the studies prior to the mid-1970's investigated the properties of TAN as a reagent for chelation-solvent extraction or colorimetry. Kawase [216-220], Navratil [56,221-224], Wada and Nakagawa [225,226], and Busev *et al.* [227-230] were among the first to report methods employing TAN in this role. In the 1970's, Kurahashi reported the X-ray crystal structures of several TAN-metal chelates, including the 1:2 (M:L) complexes of nickel [231], cobalt(III) [232], and iron [233,234], and the 1:1 complex of copper, as $Cu[(TAN)(OH_2)_2]ClO_4$ [235]. In each structure, TAN coordinates to the metal ion through the deprotonated naphthol oxygen, the nitrogen of the thiazole ring, and the azo nitrogen adjacent to the naphthol ring. The structures of the TAN-metal chelates, reprinted from the original references, are presented in Figs. 2.1-2.4.

In the late 1970's Miura and co-workers described the determination of nickel using TAN and the nonionic surfactant Triton X-100 [236,237]. Nickel chelates were extracted at pH 7 into the surfactant phase which precipitated out of solution at 5 °C. After redissolving the surfactant phase in a small volume of supernatent at room temperature, nickel

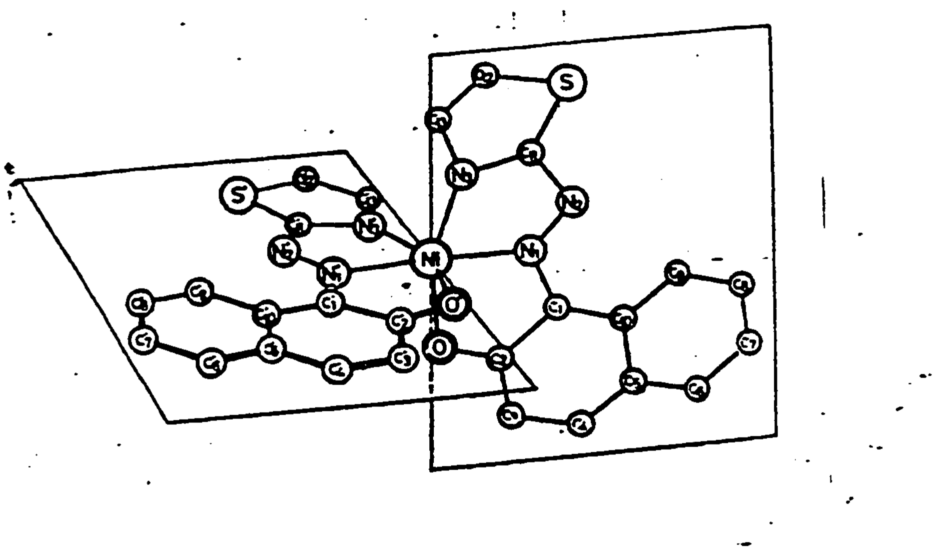


Figure 2.1. Crystal structure of $Ni(TAN)_2$, reprinted from ref. 231.

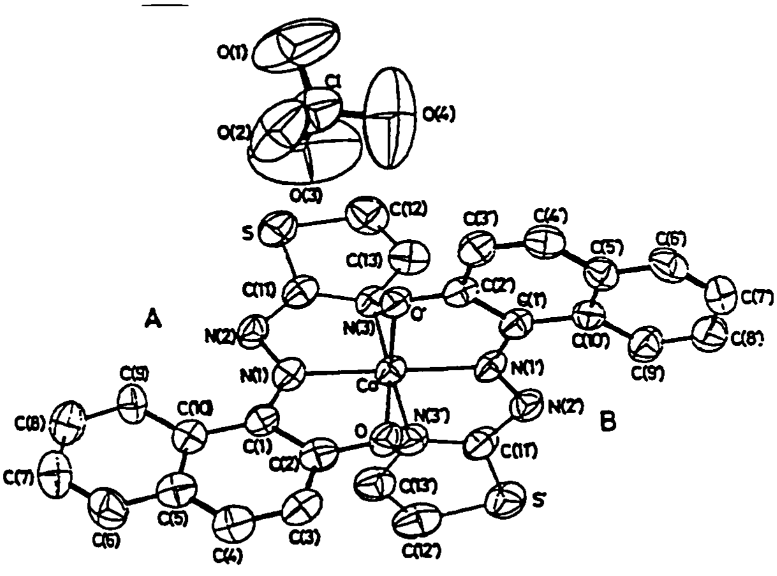


Figure 2.2. Crystal structure of $[Co^{III}(TAN)_2]ClO_4$, reprinted from ref. 232;

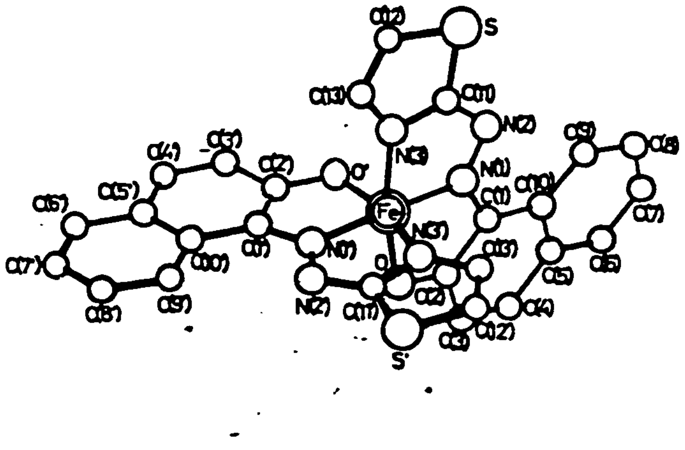


Figure 2.3. Crystal structure of Fe(TAN)$_2$, reprinted from ref. 234.

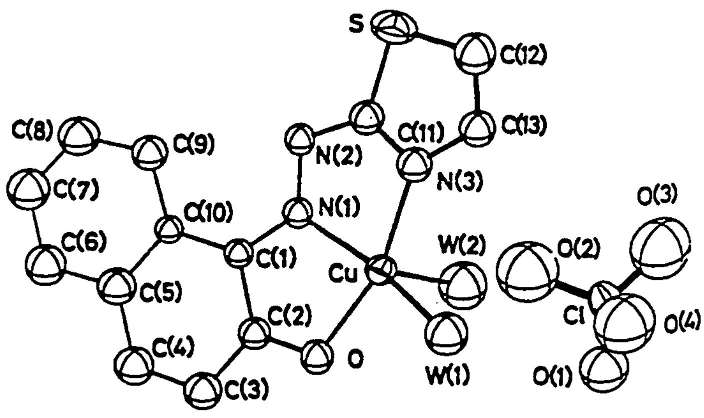


Figure 2.4. Crystal structure of [Cu(TAN)(OH$_2$)$_2$]$^+$, reprinted from ref. 235.

was determined by measuring the absorbance at 585 nm. In a later report, a modified procedure yielded concentration factors as high as 30 and was applied to the determination of nickel in soils [238]. Miura and Satake [239] described a solid-liquid separation method in which the nickel-TAN chelates were extracted into molten naphthalene at elevated temperature. Upon cooling, the solid naphthalene crystals containing the chelate were filtered and dissolved in dioxane. The absorbance of the nickel-TAN chelate was measured at 595 nm. The results of this study led the authors to synthesize a TAN-doped naphthalene powder [124] which was equilibrated with an aqueous solution of nickel adjusted to pH 6.9, then filtered and pressed into a disk for analysis by XRF.

Tanaka *et al.* [240] prepared a TAN-loaded polyvinyl chloride film which changes color when immersed in a metal ion solution buffered to pH 8.5. This film was used to quantify cadmium, cobalt, copper, mercury, nickel, and zinc in waste water.

The first examples of TAN-loaded resin supports appeared in the literature in the late 1970's. Brykina *et al.* [241] equilibrated the ion exchange resins KU-2 X 8 (Na^+ form) and AV-17 X 8 (Cl^- form) with a solution of TAN in aqueous methanol. The authors applied the AV-17 X 8 ion exchanger modified with TAN to the analysis of copper in steel [53] and cadmium, copper, nickel, and zinc in soil samples [54].

Ide *et al.* [67] loaded TAN on polystyrene-divinylbenzene using chlorobenzene as the solvent for the column extraction of cadmium, cobalt, copper, manganese, and zinc. It was noted that 1 M HCl was sufficient to quantitatively elute cobalt from this column in contrast to a similarly-prepared PAN-loaded column.

Silica gel was equilibrated with TAN, PAN, or an azophenol in acetone for 24 hours, and applied to the preconcentration of uranyl ion by Ueda *et al.* [59]. The recovery of uranyl ion is quantitative at pH 6 using silica gel loaded with PAN, TAR, or 2-(2-thiazolylazo)-*p*-cresol (TAC) and >90% for the TAN-loaded silica gel.

Isshiki and Nakayama [242] preconcentrated cobalt by adding TAN or one of 13 other chelating agents to a sample of seawater, then passing the solution through a column of Amberlite XAD-4 resin. The cobalt was then eluted for determination by GFAAS. The use of TAN as a reagent for chelation adsorption was discouraged owing to its very low solubility in water; some of the cobalt collected onto the undissolved ligand which adhered to the various parts of the column. The authors were able to obtain a quantitative recovery of cobalt using TAN, however. The significant fraction of cobalt adsorbed onto the sold TAN, estimated to be 15-50%, was recovered by rinsing the apparatus with a chloroform-methanol mixture.

Li *et al.* [243] used TAN-modified silica gel to preconcentrate cobalt and copper from aqueous solution. Both metals were quantitatively retained and determined by spectrophotometry after elution with HCl and 10:1 v/v acetone:HCl, respectively.

Sarzanini *et al.* [65] loaded PAN and TAN onto Amberlite XAD-2 and XAD-4 resins and found that the rate of adsorption of TAN to be the higher than that for PAN. Subsequently, a solution of TAN in 1:1(v/v) water:methanol was passed through a column of Amberlite XAD-2 resin. The modified resin was then used to preconcentrate cadmium, copper, iron, manganese, nickel, and zinc from seawater, and the elements were determined by ICP-AES after elution [66].

Vácha and Sommer [60] modified Amberlite XAD-4 with PAN or TAN and applied these resins to the recovery of uranyl ion from natural and potable water. Uranium was eluted with nitric acid and determined spectrophotometrically using PAR.

Ivanov *et al.* recently reported the chromatographic separation of palladium from aqueous solution using columns of TAN-loaded silica gel [62] or C-18 silica gel [61]. Palladium was eluted with acetone and determined spectrophotometrically with concentration factors as high as 100. A later report described the determination of palladium or rhodium in the presence of cobalt, copper, and nickel [63], and copper, iron, and nickel [64].

There are a few recent examples in the literature of TAN used in other analytical methods. Eshwar and co-workers reported the use of TAN in the spectrophotometric determination of cerium [244], vanadium [245], zirconium and hafnium [246], gallium [247], thorium [57], lead [248], and scandium [249] in mixtures of aqueous and organic solvents, as well as chromium [250], uranium [58], and beryllium [251] in surfactant solutions. Ferreira and Nano [252] recently reported the rapid spectrophotometric determination of iron using TAN and Triton X-100.

TAN has been used as a reagent in the solvent extraction-spectrophotometric determination of zirconium and hafnium [253] and nickel [254], and, along with cupferron and ammonium pyrrolidine dithiocarbamate, as a coprecipitating agent for the preconcentration of eight trace elements from seawater [255].

It is evident from the above survey that TAN has not been extensively studied. The main objective of this thesis is to develop a method for the preconcentration of trace elements using TAN. The chelating characteristics of a TAN-loaded resin will be investigated. This resin should display a high affinity as well as high capacity for a number of trace elements, a low affinity for alkali and alkaline earth metals, and favorable characteristics with respect to resin stability.

2.5 Solid Phase Separations in RNAA and PNAA

In this section, PNAA and RNAA utilizing solid-phase separations such as ion-exchange, chelating ion-exchange, RPEC, and chelation-adsorption will be reviewed. While a variety of procedures will be discussed, emphasis will be placed on the PNAA separations where the solid phase is analyzed rather than the eluate. The separation step should be designed to perform two tasks, namely to concentrate the elements of interest and to simultaneously remove interfering elements.

However, there are reports in the literature on PNAA involving evaporation or freeze-drying of water samples. Hamilton and Chatt [256] reported the analysis of rain water for 31 elements following evaporation or freeze-drying. Such physical separations concentrate all elements but can be disadvantageous if interfering elements are present in high concentrations. For example, Sharma *et al.* [257] analyzed drinking water from India by evaporating 1-L samples to dryness and irradiating the residue for one week at a flux of 10^{12} n cm^{-2} s^{-1}. Decay times ranging from 2-90 days, necessary to reduce activities from chlorine and sodium nuclides, allowed the determination of 25 elements but shorter lived nuclides such as aluminum, copper, and vanadium could not be detected. Piper and Goles [258] reported a method in which seawater samples were freeze-dried and the solid irradiated for one week to determine nine elements. Due to the high levels of bromine and sodium in the samples, a decay period of four to five weeks was deemed necessary.

The analysis of trace elements in certain biological materials (*i.e.* blood) by INAA may not always be feasible, in part due to their low levels but also due to the potential for a predominant activity of ^{24}Na in the irradiated sample. An RNAA method for the selective removal of sodium from biological matrices was introduced in the late 1960's by Girardi and Sabbioni [259] using hydrated antimony pentoxide (HAP) in a column. The use of HAP in the removal of sodium for NAA determinations is still quite common [260].

Bilewicz *et al.* [261] identified some of the difficulties encountered with the above RNAA method, namely poor exchange kinetics, resistance to flow rate, and poor mechanical stability of the solid HAP. They prepared a condensation resin of HAP implanted in a phenol-formaldehyde matrix which eliminated these problems. The authors later prepared another condensation resin of HAP bound into a polystyrene-divinylbenzene matrix [262] which was more stable in strongly acidic media than the phenol-HAP resin.

In the late 1960's Samsahl [263] proposed an automated radiochemical separation scheme for the determination of antimony, arsenic, bromine, mercury, and selenium in tissue samples using distillation and three sequential anion-exchange columns containing Dowex 2 resins. Samsahl later proposed a more elaborate separation scheme employing seven columns of different ion-exchange resins and three columns of Chelex-100 [264]. Of the forty elements investigated, 32 were quantitatively retained (>95%). Iyengar [265] reported a number of modifications to these schemes which were applied to the determination of cadmium, chromium, cobalt, copper, manganese, and molybdenum in blood serum, milk, hair, and other biological samples.

Woittiez and De La Cruz Tangonan [266] used a two-column system, based on the work of Samsahl, to determine cadmium and molybdenum in acidic solution using Bio-Rad AG 2X8 ion-exchange resin, and chromium and cobalt in solution buffered to pH 4 on Chelex-100. Tracer experiments showed the recovery of each element to be greater than 97.8%. The method was applied to NBS SRM 1577 (Bovine Liver) and a series of candidate reference materials prepared by Agriculture Canada.

Büttner *et al.* [267] developed a procedure for chromium determination in urine and blood serum by RNAA. Chromium was quantitatively retained (99%) at pH 1.3 on Cellex P ion-exchange resin while alkali metals and anions passed through the column. The column was washed free of impurities with dilute nitric acid, then chromium was eluted with 5 mL of 8 M nitric acid and counted.

Gallorini *et al.* [268] developed an RNAA method using a column of hydrated manganese dioxide (HMD) to separate antimony, arsenic, chromium, and selenium in standard reference materials NBS SRM 1571 (Orchard Leaves) and NBS SRM 1577 (Bovine Liver). Sodium was not retained by the HMD column; therefore, the resin can be counted without the need of any elution. Greenberg [269] used a modification of this procedure to concentrate the same four elements, as well as silver and molybdenum, on a column of HMD. These elements were determined in the NBS SRM 1549 (Milk Powder).

The abundance of RNAA studies can be attributed to the major advantage of the method, namely, the absence of a reagent blank. Pietra *et al.* [270] examined the utility of Chelex-100 as a reagent for both PNAA and RNAA. The authors analyzed the trace element content of Chelex-100, and concluded that Chelex-100 could be applied to PNAA only if all background contamination is evaluated. A PNAA procedure was used to determine the trace element content of mineral water, dialysis fluid, and honey. The authors, however, claimed superior results for a radiochemical separation, owing to the elimination of analytical blanks, and determined the trace element content of human bone, urine, and NIST SRM 1575 (Pine Needles) by RNAA.

The advantages of RNAA notwithstanding, it is of particular interest to this thesis to examine reports in which a preconcentration step is employed. The PNAA method has particular benefits which make it an attractive alternative to RNAA. Greenberg *et al.* [82] as well as Milley and Chatt [83] have discussed the merits of separating the elements of interest from the matrix prior to irradiation. A PNAA procedure reduces the background radiation attributable to elements present in the matrix, thereby lowering the detection limits for the elements of interest. Some elements which produce short-lived nuclides cannot be conveniently analyzed by RNAA because the nuclides could decay considerably in the time required to carry out the separation. The total activity of the sample upon retrieval from the reactor is also greatly reduced if elements such as sodium, chlorine, and bromine are removed prior to irradiation, so personnel are not required to handle highly radioactive samples.

It should also be noted that there are very few studies in which liquid water samples have been analyzed by RNAA. The volume of the liquid sample is limited by the volume of the irradiation vial which is typically less than 30 mL. Moreover, liquid samples cannot be irradiated for long periods due to the potential for problems associated with radiolysis. Such restrictions generally make the analysis of even freshwater samples for trace elements by INAA or RNAA impractical [271].

Lee *et al.* [272] described a method for the preconcentration of fifteen trace elements in seawater using Chelex-100. The elements were eluted prior to their determinations by NAA.. Hirose and co-workers reported a scheme of preconcentration on Chelex-100 followed by irradiation of the resin and radiochemical separation of lanthanides and transition metals from river water [273] and uranium from seawater [274]. In a radiotracer study, Arunachalam and Gangadharan [275] applied a Chelex-100 separation to the determination of copper, nickel, zinc, and five other elements in gallium and its compounds.

Xilei *et al.* [276] described the PNAA determination of gallium in biological materials. Gallium was collected on the cation exchanger Dowex AG 50W-X8, eluted with 1.9 M HF into a polyethylene vial, and irradiated. A separation scheme for the determination of ppb levels of thorium and uranium in tantalum metal was developed by Sasaki *et al.* [277]. The dissolved sample was passed through a column of cation exchanger AG 50WX8: thorium and uranium were retained on the resin while tantalum was not. Thorium and uranium were quantitatively eluted with 0.5 M HF, the effluent was evaporated to dryness and the residue dissolved in a small amount of nitric acid which was sealed in a quartz ampoule and irradiated.

Aluminum was determined in a biological SRM and human brain tissue after preconcentration by anion-exchange and NAA of the eluate [278]. Blotcky and co-workers [279] presented a preconcentration procedure for the determination of vanadium in shellfish samples. The acid-digested sample was passed through a column of AG 50W-X8 cation exchange resin, vanadium was eluted with 4 M ammonia solution and two 3-mL aliquots of the eluate were irradiated. Another method for the determination of vanadium in blood serum

[280] employed a column of AG 1X8 anion exchanger. Vanadium was eluted with dilute nitric acid and quantified by NAA.

While most researchers applied HAP to the radiochemical separation of sodium, Nyarku and Chatt [281] reported a preconcentration procedure for seawater using HAP. The eluate from the HAP column was evaporated to dryness and the residue was irradiated. However, the presence of antimony in the eluate residue prevented the determination of the trace elements of interest. In order to remove antimony, the authors added a second column extraction step, in which the eluate from the HAP column was passed through a column of tin dioxide or aluminum oxide. The eluate from the second column was treated to remove bromine and chlorine, then dried and irradiated. The determination of 14 trace elements in seawater was carried out following this method.

Devi and Naidu [85] preconcentrated cadmium from spiked distilled water by a chelation-adsorption procedure. The cadmium complex with potassium ethyl xanthate was collected on activated carbon after a batch equilibration. The carbon was filtered and irradiated. A similar procedure was used to quantitatively preconcentrate cadmium, cobalt, copper, mercury, and zinc from water samples [86]. The analysis was carried out either by irradiating and counting the solid phase directly or by eluting the trace elements with 1.5 M nitric acid prior to determination by AAS. In general, there was good agreement between the two methods.

Rama Devi *et al.* [282] utilized a poly(acrylamidoxime) condensation resin to preconcentrate cadmium, cobalt, copper, and zinc by batch extraction at pH 6 followed by determination using NAA and AAS. The authors noted that the enrichment factor of the

PNAA method was 400 compared to 40 for AAS.

Greenberg and Kingston [271] reviewed the use of Chelex-100 to preconcentrate trace elements from seawater up to the late 1970's. They noted that the procedure suffered from two major disadvantages, namely, the partial retention of alkali and alkaline earth metals, and the incomplete or irreproducible elution of certain trace elements of interest. A washing procedure outlined by Kingston *et al.* [283] yielded excellent separation of the elements of interest from alkali and alkaline earth metals, and the use of NAA to analyze the resin directly eliminated the problems associated with the elution step. The PNAA method utilizing Chelex-100 was applied to the determination of 14 trace elements in seawater samples [271].

Greenberg *et al.* [81] determined aluminum, copper, manganese, and vanadium in the NIST SRM 8419 (Bovine Serum) by PNAA using Chelex-100 at pH 5.3-5.9. These elements produce short- to medium-lived nuclides which can be more conveniently determined by PNAA than RNAA.. Following this method, these four elements were determined in human blood serum and three biological NIST SRMs [82].

Milley and Chatt [83] utilized a column separation on Chelex-100 to preconcentrate fifteen trace elements from acid rain prior to the direct NAA of the resin. The authors described an acid washing procedure for cleaning the Chelex-100 resin which lowered the blank.

Trace gold and iridium were preconcentrated on a column of PS2606 anion-exchange resin from steel [284]. Matrix elements such as iron, manganese, nickel, and chromium were washed out prior to ashing of the resin and subsequent irradiation. Blotcky *et al.* [84] developed a PNAA method to separate aluminum from acidified urine samples on a column of AG 50W-X8 cation exchanger followed by irradiation and counting of the resin.

Shah and Wai [87] determined gold, palladium, platinum, tungsten, and uranium in seawater by complexation with pyrrolidine dithiocarbamate (PDTC) at pH 2. The metal-PDTC complexes were collected on a column of C_{18} silica gel which was irradiated and counted. The authors noted high silica gel blanks.

There have been very few reported examples of preconcentration of trace elements on a ligand-impregnated resin prior to NAA. As previously discussed, Akaiwa [88] prepared three ligand-impregnated reagents with sulfonate-bearing chelating agents loaded on anion-exchange resins. After passage of the sample solution through the column, the resin was washed with distilled water, dried, and transferred to a polyethylene vial for irradiation. The trace elements adsorbed on the resin were quantified by counting the irradiated resin directly. In this fashion, a resin composed of oxine-5-sulfonic acid loaded on Diaion SA #100 was found to quantitatively retain cadmium, cobalt, copper, manganese, nickel, and zinc at pH >3. A Zincon-loaded resin extracted copper, lead, mercury, and zinc at pH >4, and bathocuproine disulfonic acid loaded on Dowex 1X4 selectively extracted mercury at pH ≥ 1 and copper at pH >3.

Using a similar procedure, Rao *et al.* [14] loaded oxine on Amberlite XAD-2 and applied the reagent to trace element determination by PNAA. By passage of samples through the column at pH 6.0, cadmium, cobalt, copper, mercury, vanadium, and zinc were quantitatively retained while calcium and magnesium were largely removed (>83%). After irradiating and counting the resin directly, ppb levels of the six transition metals were determined in tap water, acid rain, and NIST SRMs.

The preconcentration of trace elements on a solid resin phase, followed by direct irradiation and counting of the resin holds promise, given that NAA is amenable to the analysis of a solid sample. The reports reviewed in this section indicate that a separation step is generally mandatory for the trace analysis of biological and environmental samples. Despite the major advantage of radiochemical separations, namely the absence of a blank contribution, PNAA is favorable for the analysis of elements with short-lived nuclides and for trace analysis of water samples. Most of the methods incorporating a group separation on a column utilize Chelex-100. The use of ligand-impregnated RPEC as a preconcentration method in conjunction with NAA has not been extensively investigated. The experimental details of the PNAA procedure are provided in the following chapter.

CHAPTER 3. EXPERIMENTAL

In this chapter, details of the experiments done are discussed. The chemical reagents and equipment used are described. Procedures for the preparation and characterization of the ligand-impregnated resin are outlined. The preparations of samples and standards are given, as well as the irradiation and counting schemes used for the quantification of elements.

3.1 Irradiation and Counting

All irradiations were performed at the Dalhousie University SLOWPOKE-2 Reactor Facility. Samples are placed in one of the available irradiation sites by means of a pneumatic tube. The reactor has three types of irradiation sites, each characterized by the flux and energy of the neutrons available. Most sample irradiations were performed in one of the five inner sites, where the samples are subjected to the highest possible flux. Under normal operating power of 8 kW, the thermal neutron flux in the inner site is 5×10^{11} n cm^{-2} s^{-1}. The flux in the inner site is very stable; results reported by Ryan *et al.* [285] show that the flux has been highly reproducible since the installation of the reactor in 1977, and that the flux is independent of the position of the sample in the site and the specific inner site used.

There are two regular outer sites, which hold larger sample vials than the inner sites. The flux in the outer sites is approximately half that of the inner sites. While this flux has also proven to be highly reproducible over time with respect to choice of site, there is a significant variation with respect to position of the sample in the site. As reported by Ryan *et al.* [285], the variation in vertical homogeneity is less than 1% cm^{-1}, whereas the variation in radial homogeneity may be as high as 5% cm^{-1}. By comparison, the flux in the inner site is stable to within 1% cm^{-1} in any direction.

There is one additional outer site which is shielded with a 0.8-mm-thick layer of cadmium. The cadmium shield absorbs most of the thermal neutrons but is much less effective for higher-energy epithermal neutrons. As a result, samples irradiated in this site are essentially exposed to epithermal neutrons. As is the case for the regular outer site, the flux differs with cross-sectional position. The flux gradient in the outer sites is not problematic as long as samples and standards are prepared using similar geometry and placement in the irradiation vial.

The elements of interest were assayed by using different irradiation schemes. Medium-lived nuclides, *i.e.* those with a half-life ($t_{1/2}$) of less than a few hours (nuclides of Ag, Al, Br, Cl, Co, Cu, Mg, Mn, S, Th, U, and V), as well as sodium ($t_{1/2}$ = 14.959 h), were typically determined after a 10-minute irradiation, 1-minute decay, and 10-minute counting period. Nuclear data for these nuclides are provided in Table 3.1. The samples were allowed to stand for at least 3 days, then reirradiated for assay of the longer-lived nuclides, *i.e.* those with $t_{1/2}$ longer than several hours (nuclides of Ag, As, Au, Br, Cd, Co, Cr, Hg, Na, Sb, and Zn). The samples were irradiated for 7 hours, allowed to decay for 12-48 hours, and counted for 1 hour in order to evaluate the activities of nuclides with $t_{1/2}$ ranging from several hours to 3 days (nuclides of As, Au, Br, Cd, Na, Sb, and Zn). Nuclear data for these nuclides are given in Table 3.2. After a decay period of 14 days or longer, the samples were recounted

Table 3.1. Nuclear data for the elements of interest quantified using $t_i:t_d:t_c$ = 10:1:10 min [286,287].

Element	Target Isotope	% Abundance	Cross-section (b)	Nuclide Produced	Half-life	γ-ray used (keV)
Ag	^{107}Ag	51.839	35	^{108}Ag	2.37 min	434.0, 633.0
Al	^{27}Al	100	0.232	^{28}Al	2.241 min	1779.0
Br	^{79}Br	50.69	148 ± 4	^{80}Br	17.68 min	616.8
Cl	^{37}Cl	24.23	0.428 ± 0.005	^{38}Cl	37.2 min	1642.7
Co	^{59}Co	100	20 ± 2	^{60m}Co	10.467 min	58.6
Cu	^{65}Cu	30.9	2.17 ± 0.03	^{66}Cu	5.09 min	1039.2
Mg	^{26}Mg	11.01	0.0382 ± 0.0008	^{27}Mg	9.46 min	843.8, 1014.4
Mn	^{55}Mn	100	13.3 ± 0.2	^{56}Mn	2.5785 h	846.8, 1810.7
Na	^{23}Na	100	0 530 ± 0.005	^{24}Na	14.959 h	1368.6, 2754.0
S	^{36}S	0.015	0.150 ± 0.030	^{37}S	5.06 min	3103.4
Th	^{232}Th	100	7.40 ± 0.08	^{233}Th	22.2 min	86.5
U	^{238}U	99.2739	2.70 ± 0.02	^{239}U	23.45 min	74.7
V	^{51}V	99.75	4.88 ± 0.04	^{52}V	3.743 min	1434.1

Table 3.2. Nuclear data for the elements of interest quantified using $t_i:t_d:t_c = 7:24:1$ h [286,287].

Element	Target Isotope	% Abundance	Cross-section (b)	Nuclide Produced	Half-life	γ-ray used (keV)
As	^{75}As	100	43 ± 1	^{76}As	1.078 d	559.1
Au	^{197}Au	100	98.8 ± 0.3	^{198}Au	2.695 d	411.8
Br	^{81}Br	49.31	2.69 ± 0.09	^{82}Br	35.3 h	698.4, 776.5
Cd	^{114}Cd	28.8	0.300 ± 0.015	^{115}Cd	53.5 h	336.2
Na	^{23}Na	100	0.530 ± 0.005	^{24}Na	14.959 h	1368.6, 2754.0
Sb	^{121}Sb	57.25	6.25 ± 0.2	^{122}Sb	2.7238 d	564.1
Zn	^{68}Zn	18.6	0.072 ± 0.004	^{69m}Zn	13.8 h	438.6

for 2 hours to quantify nuclides with $t_{1/2}$ of several days or more (nuclides of Ag, Co, Cr, Fe, Hg, Ni, Sn, and Zn). The nuclear data for these elements is given in Table 3.3. Decay time (t_d) corrections were required for these irradiation schemes; decay times were typically corrected to $t_d = 24$ hours for the 1-hour count and $t_d = 21$ days for the 2-hour count. While these combinations of timing parameters were the most commonly employed, others were used in specific applications. The use of alternative irradiation, decay, and counting times will be highlighted where appropriate.

The samples and comparator standards were counted under identical geometry using a 60 cm^3 APTEC Ge(Li) semiconductor detector with a resolution of 1.9 keV at the 1332-keV photopeak of ^{60}Co, a peak-to-Compton ratio of 35:1, and an efficiency of 9.5%. The detector was used in conjunction with an APTEC multichannel analyzer.

3.2 Chemical Reagents

All chemicals used in this work were of analytical or better quality unless otherwise specified. Amberlite XAD-2, XAD-4, and XAD-7 resins, ammonium acetate, 2-[N-morpholino]ethanesulfonic acid (MES), piperazine-N,N'-bis[2-ethanesulfonic acid] (PIPES), tris[hydroxymethyl]aminomethane (TRIZMA base), and n-[2-hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid] (HEPES) were purchased from Sigma Chemical Company. Reagent grade 1-(2-thiazolylazo)-2-naphthol (TAN) was obtained from Eastman Kodak and Fluka. High purity TAN was purchased from TCI American. Ultrex acetic acid was purchased from J.T. Baker Chemicals. Ultrapure grade

Table 3.3. Nuclear data for the elements of interest quantified using $t_i:t_d:t_c = 7$ h:21 d:2 h [286,287].

Element	Target Isotope	% Abundance	Cross-section (b)	Nuclide Produced	Half-life	γ-ray used (keV)
Ag	^{109}Ag	48.17	49 ± 1	^{110m}Ag	250.4 d	657.8, 884.7
Co	^{59}Co	100	17 ± 2	^{60}Co	5.272 a	1173.5, 1332.5
Cr	^{50}Cr	4.35	15.9 ± 0.2	^{51}Cr	27.71 d	320.1
Hg	^{202}Hg	29.7	4.9 ± 0.1	^{203}Hg	46.6 d	279.2
Ni	^{58}Ni	67.88	0.113 ± 0.007	^{58}Co	70.82 d	810.8
Sb	^{123}Sb	42.75	4.28 ± 0.16	^{124}Sb	60.20 d	602.7
Zn	^{64}Zn	48.9	0.78 ± 0.02	^{65}Zn	243.7 d	1115.5

nitric acid and ammonia were purchased from Seastar Chemical Co. High purity plasma emission standard solutions of elements (typically 1000 ppm) were purchased from SPEX Industries. Methanol and sulfur flowers were obtained from Anachemia. Laboratory grade acetone, chloroform, and dimethyl sulfoxide were purchased from Fisher Scientific Company.

Deionized distilled water (DDW) was prepared by passing quartz-distilled water through a mixed-bed deionizing column from Fisher Scientific Company. Buffer solutions used in this study were prepared using the appropriate organic buffer and made up to the desired pH with dilute nitric acid or ammonia. The multi-element stock solutions used in this work were prepared by adding the appropriate amounts of the elemental standard solutions in 0.2 M ultrapure nitric acid. Concentrated stock copper solutions were generally prepared by dissolving copper wire in nitric acid and diluting with DDW; otherwise, $Cu(NO_3)_2{\cdot}5H_2O$ was dissolved in 0.1 M nitric acid. The resulting copper solutions contained 0.1-1.0 mg Cu mL^{-1}.

3.3 Equipment and General Apparatus

All samples analyzed during the course of this study were irradiated in polyethylene vials (Olympic Plastics Company, Inc.). The vials come in three sizes, with approximate volumes of 1.1 mL (small), 7 mL (medium) and 27 mL (large). The vials were generally cleaned by soaking in 1 M ultrapure nitric acid for 1-2 days, rinsing thoroughly with DDW and drying at 30°C. The precleaned vials were stored in a clean sealed polyethylene bag prior to use.

In order to adhere to strict radiation safety guidelines, all samples had to be doubly heat-sealed prior to irradiation. Thus, if one of the seals were to break during irradiation, the other would prevent the sample from spilling out and contaminating the site. Consequently, the samples were irradiated using one of three modes, as shown in Figure 3.1. A medium vial, trimmed for height, was sealed and placed in a large vial, held in place by a polyethylene spacer (Figure 3.1a). Two sealed small sample vials, or one sealed small sample vial and an empty small vial which acts as a place holder were placed in a sealed medium vial (Figure 3.1b). When the solid sample was too large to fit into a small vial, a double-seal was achieved in a medium vial by pushing a trimmed medium vial lid (a "spacer") onto the solid sample with a Teflon plunger, placing a piece of trimmed plastic slightly shorter than the headspace above the spacer to prevent the spacer from being forced out of position, and capping the top (Figure 3.1c).

Water samples were collected and stored in 1-L Nalgene high-density polyethylene bottles. All bottles and other laboratory ware were cleaned prior to use by soaking in dilute laboratory-grade nitric acid for 24 hours, washing thoroughly with ion-free detergent and tap water, and rinsing with dilute ultrapure nitric acid and DDW.

3.4 Column Apparatus

The column apparatus designed for use in this study is shown in Figure 3.2. A Bio-Rad Econo-Column (Stock No. 737-0711) of 10-cm length and a 7-mm internal diameter was used. The bottom of the column was fitted with a fluoropolymer frit and the

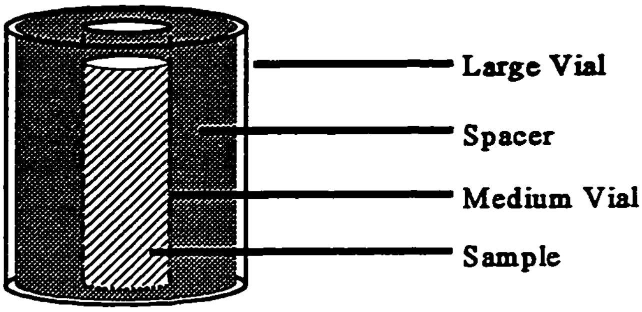


Figure 3.1a

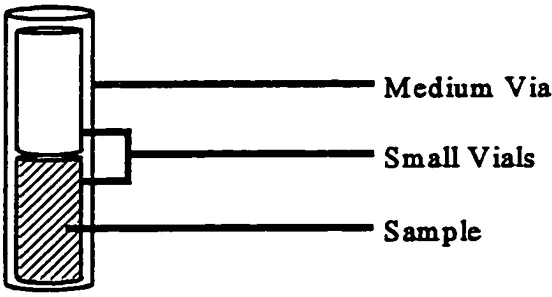


Figure 3.1b

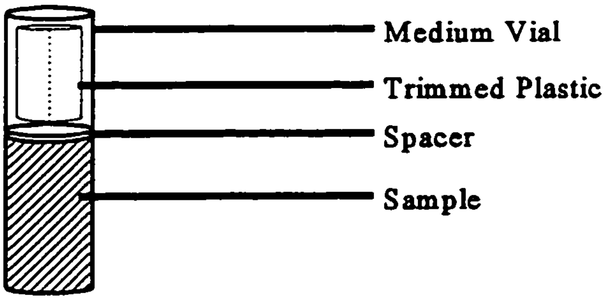


Figure 3.1c

Figure 3.1. Sample vial geometries for irradiation.

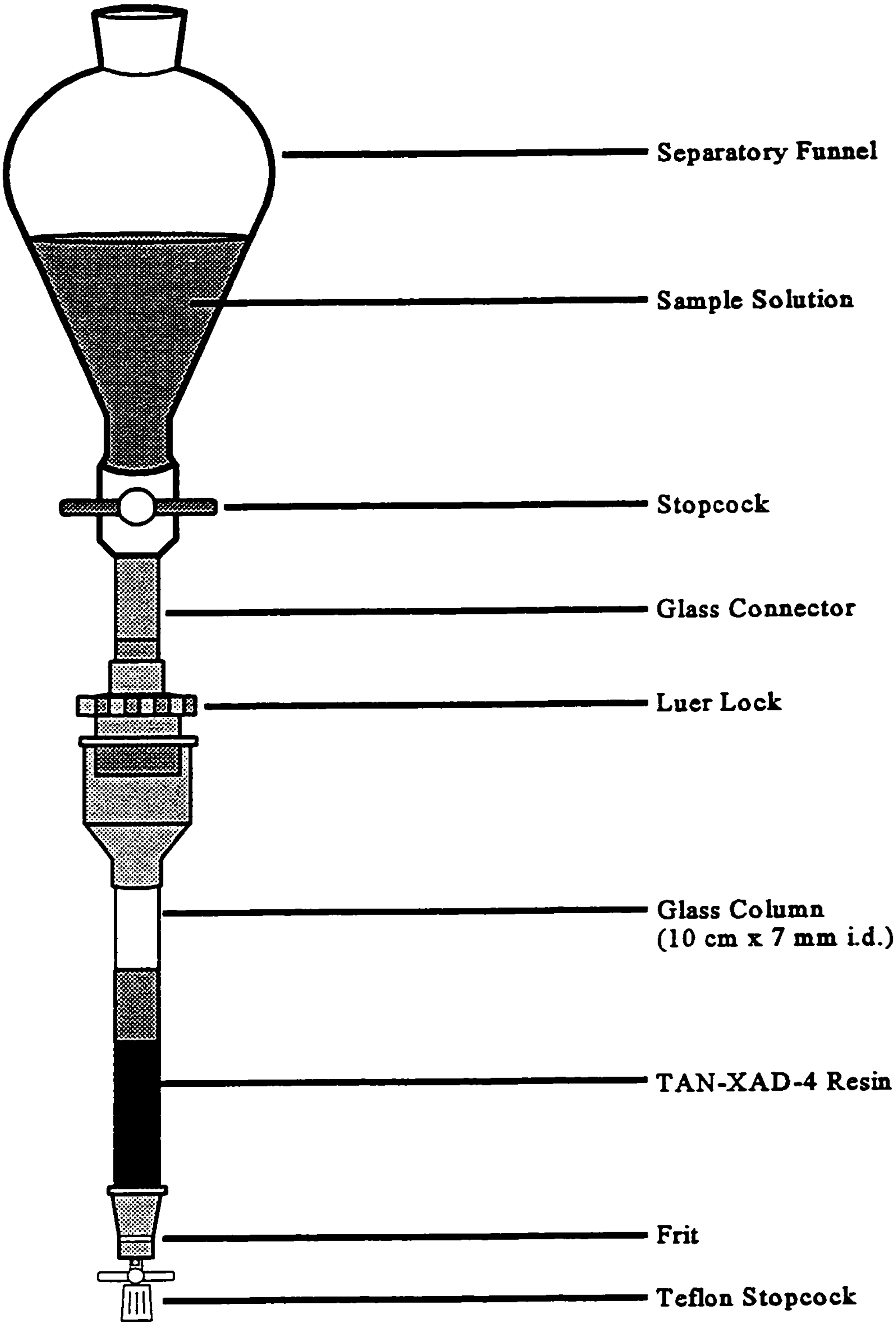


Figure 3.2. Column apparatus for RPEC.

top with a Luer lock connector. The flow rate was controlled using a removable Teflon stopcock (Bio-Rad Stock No. 7328102). A 100-mL, 250-mL, or 500-mL glass separatory funnel served as the reservoir for feeding the aqueous solution to the column. The separatory funnel was connected to the head of the column using a glass connector made in-house. This connector, approximately 5 cm long with a 1-cm bore, had ground-glass joints at both ends, in order to fit snugly with a standard Teflon stopcock and the Luer Lock at the head of the column. When necessary, Teflon tape was used to ensure a watertight seal between the Teflon stopcock and the glass connector. All components of the column were washed with an ion-free detergent and tap water, rinsed with dilute ultrapure nitric acid and DDW, and air-dried prior to use.

3.5 Cleaning of XAD-4 Resin

Approximately 150 g of the resin (wet weight) were distributed to each of two 1-L Nalgene screw-cap bottles. Approximately 0.6 L of 2 M laboratory grade nitric acid were added to each bottle. The bottles were capped, and the resin was equilibrated using a mechanical wrist action shaker. The bottles were shaken at a moderate rate for a period of 2 hours, then allowed to stand for 10 minutes.

The resin was filtered and the liquid phase discarded. The resin was returned to the bottles, then equilibrated, in succession, with approximately 0.6 L of the following solutions (times in parentheses indicate shaking times): DW (1 hour); 2 M NH_3 (1 hour); DW

(1 hour); 2 M ultrapure NH_3 (1 hour); DDW (1 hour); 2 M ultrapure HNO_3 (2 hours); DDW (1 hour); 3 M ultrapure HNO_3 (2 hours); DDW (1 hour); acetone (1 hour); DDW (1 hour); and DDW (1 hour).

Three samples of 0.4-1.0 g resin (dry weight) were collected in polyethylene irradiation vials and the extent of elemental contamination was determined by NAA. Once the purity of the resin was deemed satisfactory, the resin was oven dried at 80°C for 2 days and stored in a screw-cap glass bottle prior to coating with the chelating agent or for use in spotting standard solution spikes.

3.6 Adsorption Isotherm for TAN-XAD-4 System

The TAN-XAD-4 resin was prepared by equilibrating a sample of precleaned XAD-4 resin with a solution of TAN in batch mode. In order to ascertain the appropriate equilibration time, a water-driven magnetic stirrer was employed with a spectrophotometer. A quartz cuvette was filled with 3.00 mL methanolic solution of TAN, a small stirring bar was added and the absorbance of the solution measured. Once the absorbance measurement had stabilized (typically two consecutive measurements), 0.10 ± 0.01 g XAD-4 resin was added and the absorbance of the supernatant solution was sampled each minute for a period of several hours.

The effect of solvent and reagent concentration on the loading of TAN on the resin was tested using a variety of solvent systems, including acetone, methanol, ethanol, 95% ethanol and 9:1, 4:1, 7:3, 3:2, and 1:1 (v/v) methanol:water. A sample of 2.99-3.01 g dry

XAD-4 resin was weighed into a 125-mL Nalgene FEP bottle and 100.0 mL of TAN solution added. The contents were equilibrated for a period of at least 2 hours, after which time the TAN-loaded resin (TAN-XAD-4), a reddish-orange solid, was filtered, washed with several portions of DDW and stored in DDW in a screw-cap bottle. A sample of the coated resin was removed and dried at 50°C for at least 2 days, then transferred to a polyethylene irradiation vial in order to analyze the solid for sulfur content by NAA. Samples of the supernatant were taken before and after equilibration with the resin, in order to evaluate the concentration of TAN spectrophotometrically. The effect of initial TAN concentration in solution on the equilibrium TAN concentration on the resin was studied, as well as the effect of the choice of solvent.

3.7 Resin Characteristics

The stability of the TAN-XAD-4 resin was examined with respect to organic solvents, mineral acids and bases, and solutions of high ionic strength. A sample of TAN-XAD-4, approximately 0.5 g dry weight, was placed in a 20-mL screw-cap vial with 15 mL of the given liquid and equilibrated with moderate shaking for a period of at least 48 h. The relative loss of chelating agent, expressed in percent, was evaluated by measuring the TAN content in the supernatant by spectrophotometry and the sulfur content on the solid by NAA.

The analytical utility of the TAN-impregnated resins was evaluated with respect to the uptake of trace elements. The optimized column experiment indicates that copper is recovered quantitatively; the copper uptake of the various resins synthesized was calculated in order to ascertain the concentration limits at which the performance of the resins began to suffer.

The capacity of a TAN-impregnated resin was determined by passage of an excess of copper solution through a column of the resin. A sample of resin was slurry-packed into a Bio-Rad column and equilibrated with pH 6.0 buffer. A sample containing excess copper was prepared by adding 10.00 mL of the concentrated stock copper solution to appropriate amounts of MES buffer and DDW to yield a 50-mL sample of pH 6.0. This sample was passed through the column. After passage of the sample, the column apparatus and resin were washed with fresh pH 6.0 buffer. The resin sample was dried at 50°C for at least 2 days, and packed into a polyethylene vial for irradiation, in order to determine the amount of copper collected on the resin. The filtrate was transferred to a volumetric flask and the copper content evaluated by NAA after pipetting 1000 μL of the solution into a small irradiation vial.

3.8 Multielement Stock Solutions

Multielement stock solutions were required for use as comparator standards and for preparation of laboratory samples. Solutions were prepared using high-purity plasma emission standard solutions (SPEX Industries). Typically, a multielement stock solution was prepared in a 100.0-mL volumetric flask. Appropriate amounts of each standard were added, and the volume was made up to the mark with 2M HNO_3. The multielement solutions were prepared in such a manner as to contain the desired quantities of the elements of interest in a 200-μL aliquot.

3.9 Reference Materials

The accuracy of the PNAA procedure was evaluated through the analysis of five reference materials. Two standard reference materials (SRM) were supplied by the National Institute of Standards and Technology (NIST): Trace Elements in Water (1643a and 1643b) and three reference materials (RM) were supplied by the National Research Council (NRC): Riverine Water (SLRS-1), Estuarine Water (SLEW-1) and Seawater (NASS-2).

3.10 General Procedure for RPEC

The resin was slurry-packed in small portions into the Bio-Rad columns and the resin bed was agitated with a glass stirring rod to remove air bubbles from the column. The column was preconditioned to the appropriate pH by passing 50 mL of 0.05 M buffer solutions through the column at a flow rate of 1 mL min^{-1}. The column was considered to be adequately equilibrated when the pH of the effluent equalled the pH of the buffer. A 50-mL portion of buffer solution was generally sufficient to attain this condition.

The sample solution was prepared by dispensing 200 μL of the multielement stock solution into approximately 100 mL of buffer solution. The acidity of the spike caused the pH of the solution to fall; 1 M ultrapure NH_3 was added dropwise with stirring to restore the desired pH.

This solution was put into the separatory funnel reservoir and fed onto the column (Figure 3.2). The flow rate, as controlled by the stopcock at the bottom of the column, was held at 1 mL min^{-1}. After passage of the sample solution, the separatory funnel and the column contents were rinsed four times with 10-mL portions of the fresh buffer solution.

The column was drained, and the resin bed dried by passing compressed air down the column for several minutes. The dried resin was transferred to a polyethylene vial which was heat-sealed for irradiation and counting. In optimization studies involving medium-lived nuclides only, the geometry shown in Figure 3.1c was preferred. The top of the Bio-Rad column was of the appropriate diameter that a medium vial would fit snugly into it. Consequently, transfer of the dried resin from the column was carried out by tightly placing the empty vial at the head of the column and inverting the column, allowing the beads to flow into the vial without loss of sample. When long-lived nuclides were studied, the geometry shown in Figure 3.1b was preferred. Transfer of the resin beads to the small vial was more difficult than to the medium vial, but this geometry was considered advantageous in this case because with two small sample vials sealed inside a medium vial, the number of samples which can be exposed to a long irradiation time was maximized. Efficient use of neutrons requires running as many samples simultaneously as possible for a long irradiation time. This is not a concern for medium-lived nuclides; the relatively short half-lives of nuclides produced mandate that samples may only be run one at a time, so maximizing samples by use of the geometry depicted in Figure 3.1c was not necessary.

3.11 Optimization of Various Factors in RPEC

The RPEC procedure was optimized with respect to a number of experimental parameters in order to determine the conditions conducive to the most favorable performance of the TAN-impregnated resin.

The first parameter investigated was the effect of solution pH on the uptake of the trace elements of interest. A 100-mL solution, 0.05 M in the appropriate buffer, was spiked with a 200-μL aliquot of multi-element stock solution and the pH adjusted to the desired value with dropwise addition of dilute nitric acid or ammonia solution. The solution was passed through the column as previously described, and the elements collected on the resin were determined by NAA. The uptake of the elements of interest was investigated over the pH range of 3.0-9.0.

The effect of flow rate was investigated over the range 0.3-10 mL min^{-1}. The presence of chelating agent in the effluent was checked spectrophotometrically in order to estimate the degree of bleeding of TAN from the column.

The effect of column height was studied in order to ascertain the minimum amount of resin required to obtain quantitative recoveries of the elements of interest. Spiked solutions were passed through a column of TAN-loaded resin of height 0.5-10 cm. After washing and drying the column contents, precleaned XAD-4 resin was added to the column to normalize the column height to 10 cm. The resin was then transferred to a vial for irradiation.

The effect of particle size was studied for resin sizes of 20-60 mesh, 60-100 mesh, and 100-200 mesh. Resin samples, supplied by the manufacturer as 20-60 mesh beads, were cleaned, ground and sieved. The ground resin was loaded with TAN in the usual way, and the coated resins placed in a column and applied to the RPEC of trace elements.

3.12 Preparation of Spiked Standards

Comparator spiked standards were prepared by placing samples of precleaned XAD-4 resin into polyethylene vials (approximately 0.5 g resin in a small vial, or 0.7-1.0 g resin in a medium vial) and pipetting 200 μL of the multielement stock solution onto the resin with a calibrated Eppendorf pipette. A small amount of methanol was added, and the vials were loosely capped and allowed to stand overnight in a fume hood to allow the liquid to evaporate. Once the resin was dry, the vial was capped and shaken to equilibrate the sample, then heat-sealed and irradiated.

A typical experimental run featured three to ten sample replicates, as well as one or two blank runs and one or two spiked standards. In so doing, a large number of standards were analyzed over an extended period of time. The reproducibility of the standards was expressed in terms of quality control charts.

Comparator standards for sulfur were prepared by adding an accurately known mass of sulfur flowers to a vial containing a sample of clean XAD-4 resin. The vial was capped, equilibrated by shaking, then heat-sealed for irradiation.

3.13 Blank Studies

The elemental content of the blank was determined by NAA. Empty vials, cleaned resin, coated resin, and DDW were all irradiated and counted using the same schemes as used for the samples. None of the elements of interest were present in detectable amounts in any of the blank studies; the number of counts for each nuclide of interest in the samples was therefore considered to be entirely due to the sample and not to the reagents used in the experiment.

3.14 Precision and Accuracy

The reproducibility of the method was evaluated using three experimental systems. In each case, several replicates of aqueous samples were analyzed simultaneously, and the precision of the results determined. The three samples studied were spiked buffer solution, laboratory tap water, and spiked laboratory tap water. The accuracy of the method was tested by analyzing reference materials.

3.15 Trace Element Recovery from Solutions of High Salinity

A solution containing bromine, calcium, chlorine, magnesium, potassium, and sodium was prepared such that a 10-mL spike of this solution in a 100-mL sample would simulate the concentrations of these elements in seawater. The saline solution was buffered to pH 8.4 and passed first through a column of Chelex-100 and then through a column of TAN-XAD-4 in order to remove trace element impurities. The resulting solution was acidified with ultrapure nitric acid and stored in a screw-cap Nalgene bottle.

The sample solution was prepared by adding 10.0 mL of saline solution, 90 mL buffer solution, and a 200-μL spike of multielement stock solution. This was adjusted to pH 8.25 with ultrapure ammonia solution and passed through a column of TAN-XAD-4. The column apparatus and contents were then rinsed with seven 10-mL portions of fresh buffer solution. The effluents were collected in 10-mL fractions, and 1000 μL of each fraction was pipetted into a small vial in order to determine the elemental content of each fraction by NAA. By this method, the quantity of fresh buffer required to adequately remove these interfering elements from the column could be ascertained. Once the levels of sodium and chlorine, in particular, were lowered to acceptable levels, the resin was analyzed by NAA.

3.16 Environmental Water Samples

Samples (typically 0.5-2.0 L) of tap water or saline water such as river water were adjusted to pH 1.5 with ultrapure nitric acid and digested at 80°C for 20 minutes. After cooling to room temperature, the water samples were passed through a column of Amberlite XAD-7 resin to remove any dissolved organic matter. The samples were then adjusted to pH 8.25 and passed through a column of TAN-XAD-4 for trace element uptake as previously described. The column was rinsed with four 10-mL portions of buffer prior to drying the resin.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Reagent Blanks

The elemental content of all chemical reagents used in this work was evaluated by INAA. Prior to their use, precleaned XAD-4 resin, TAN-impregnated resin, and solid reagents such as organic buffers and chelating agents were irradiated and counted under the same experimental conditions as the samples. Liquid reagents, including organic solvents, mineral acids, distilled water, and deionized distilled water (DDW), were analyzed either by INAA of a 1-mL sample or by a PNAA method in which 25 mL of liquid was evaporated to dryness in a large vial under an infrared lamp prior to irradiation. In general, reagents containing any trace elements of interest or elevated levels of potentially interfering elements were either replaced or subjected to a cleaning procedure prior to use.

The levels of elemental contaminants present in the acid-washed polyethylene irradiation vials and the precleaned Amberlite XAD-4 resin were checked periodically. As fresh batches of clean vials and resin were processed, samples were taken to ensure their purity before proceeding to further experiments. Typically, three vials from a batch of approximately fifty cleaned small vials, and three 0.5-g samples of XAD-4 from a 100-g batch were taken. In one case, the resin samples were found to contain elevated levels of vanadium, which was almost completely removed by repeating the final five steps of the resin washing procedure described in Section 3.5. In general, the vials and resin did not contain any detectable amounts of the trace elements of interest. Levels of potentially interfering elements such as sodium and chlorine were significantly reduced by the cleaning methods described earlier.

The levels of elemental contaminants in the TAN samples supplied by three different manufacturers (Eastman Kodak, Fluka, and TCI American) were determined by INAA. The samples of TAN were not analyzed directly owing to the high cost of the reagent and the amount required for the analysis. Samples of Amberlite XAD-4 resin, TAN-loaded XAD-4 resins, and polyethylene vials were analyzed by INAA. A set of six 0.5-g samples of TAN-XAD-4 was analyzed for each of the three samples of TAN. Nine XAD-4 resin samples and six vials were evaluated. The results of this study are presented in Tables 4.1 and 4.2.

The data indicate that the reagent-grade TAN supplied by Eastman Kodak and Fluka exhibited higher elemental contamination than the TAN supplied by the TCI American. In particular, the levels of aluminum, iodine, and sodium were unacceptably high in the Eastman Kodak and Fluka samples. In addition, the Eastman Kodak TAN contained significant amounts of manganese and vanadium, two of the elements of interest in this study. It was therefore decided that all future experiments were to be performed with the ultrapure quality TAN supplied by the TCI American. It is evident from Table 4.2 that the observed elemental contamination of the TAN-XAD-4 prepared with the TCI TAN was due mainly to the resin and not the chelating agent. The presence of sulfur, as confirmed by the 3102-keV photopeak of ^{37}S, would be expected for the coated resin only, as TAN contains one sulfur atom per molecule (Fig. 1.1).

Throughout the course of this study, several sources of contamination of both major interfering elements and trace elements of interest were investigated, of which two are

Table 4.1. Elemental content (in counts) of the blank.

	Number of Counts				
Element	Empty Vial	Vial + Resin	Vial + (Kodak) TAN-coated Resin	Vial + (Fluka) TAN-coated Resin	Vial + (TCI) TAN-coated Resin
Al^a	335 ± 58	881 ± 293	1438 ± 135	1609 ± 423	862 ± 142
Br^a	95 ± 13	382 ± 124	551 ± 98	659 ± 135	283 ± 74
Cd^b	ND	ND	ND	ND	ND
Cl^a	203 ± 57	661 ± 72	758 ± 44	722 ± 127	575 ± 161
Co^a	ND	ND	ND	ND	ND
Cu^a	ND	ND	ND	ND	ND
I^a	24 ± 27	226 ± 44	670 ± 154	1093 ± 219	260 ± 34
Mg^a	ND	ND	ND	ND	ND
Mn^{b,c}	ND	ND	1098 ± 117	ND	ND
Na^a	83 ± 56	197 ± 83	7408 ± 402	6119 ± 767	226 ± 86
S^a	ND	ND	180 ± 6	198 ± 15	211 ± 12
V^a	ND	ND	2077 ± 102	ND	ND
Zn^d	ND	ND	ND	ND	ND

a. t_i:t_d:t_c = 10:1:10 min; b. t_i:t_d:t_c = 30:120:30 min; c. determined using the photopeak at 847 keV
d. t_i:t_d:t_c = 30:720:30 min; ND = not determined

Table 4.2. Elemental content of TAN-loaded resins;
Samples consisted of a small (1.1-mL) vial filled with dry resin (0.50 ± 0.03 g)

	Mass of element found in sample (µg)			
Element	Vial + Resin	TAN-coated Resin (Kodak)	TAN-coated Resin (Fluka)	TAN-coated Resin (TCI)
Al	1.35 ± 0.45	2.20 ± 0.22	2.46 ± 0.65	1.32 ± 0.22
Br	0.15 ± 0.05	0.21 ± 0.04	0.25 ± 0.05	0.11 ± 0.03
Cl	0.36 ± 0.04	0.41 ± 0.03	0.39 ± 0.07	0.31 ± 0.09
I	0.05 ± 0.01	0.16 ± 0.04	0.26 ± 0.05	0.06 ± 0.01
Mn	ND	0.05 ± 0.01	ND	ND
Na	1.34 ± 0.57	50.22 ± 4.45	41.49 ± 5.96	1.53 ± 0.59
S	ND	1484 ± 77	1632 ± 140	1739 ± 121
V	ND	0.09 ± 0.01	ND	ND

ND = not determined

of particular interest and merit discussion. The medium-size (7 mL) polyethylene vials contained measurable quantities of magnesium which could not be removed by acid washing. The 846.8-keV peak of ^{56}Mn (t_d = 2.578 h) could be interfered with by the 843.8-keV peak of ^{27}Mg (t_d = 9.462 min). For most of the experiments, the analysis of ^{56}Mn through its other major peak at 1810.7 keV was not feasible because this γ-ray had low population (28.7% relative to the 846.8-keV peak) and the counting statistics were rather poor. Instead of introducing an extra irradiation (1 h, for example), the 846.8-keV peak was measured using the 10-min irradiation and a longer decay time.

Another source of contamination encountered during this study was the presence of cobalt in the markers used to write sample numbers on vials. For a typical irradiation scheme of t_i:t_d:t_c = 10:1:10 min, a standard three-digit code written on a sample vial contributed from 400 to 1500 counts to the 58.6-keV photopeak of ^{60m}Co. In order to circumvent this problem while preventing errors in the identification of samples, sample numbers were etched into the vials using the tip of the heat-sealing iron. This modification eliminated the cobalt contamination to the system.

4.2 Calibration Curve for TAN Absorbance in Methanol

The value of λ_{max} for TAN in methanol was determined to be 484 nm. A calibration curve (Fig. 4.1) was constructed from data in Table 4.3, revealing that the plot of absorbance *vs.* concentration is linear over the range of concentrations studied, *i.e.* 6.0 x 10^{-6} to 1.2 x 10^{-4} M. The molar absorptivity for TAN in methanol solution was found to be

Table 4.3. Data for calibration curve for TAN absorbance in methanol.

	Absorbance at 484 nm	
[TAN] (M)	Individual Values	Average
1.188×10^{-4}	1.98715, 1.97580, 1.98344, 1.98058	1.982 ± 0.005
1.018×10^{-4}	1.72561, 1.72990, 1.73015, 1.72634	1.728 ± 0.002
9.528×10^{-5}	1.60627, 1.60887, 1.60231	1.606 ± 0.003
8.829×10^{-5}	1.48359, 1.48027, 1.47856	1.481 ± 0.003
7.713×10^{-5}	1.30755, 1.30278, 1.30366, 1.30359	1.304 ± 0.002
7.271×10^{-5}	1.21033, 1,21765, 1.21044	1.213 ± 0.004
7.247×10^{-5}	1.23109, 1.23568, 1.23487	1.234 ± 0.002
7.070×10^{-5}	1.20505, 1.18435, 1.19021	1.19 ± 0.01
5.940×10^{-5}	1.00905, 1.01129, 1.01307	1.011 ± 0.002
4.740×10^{-5}	0.80823, 0.80607, 0.80712	0.807 ± 0.001
4.526×10^{-5}	0.77234, 0.77291, 0.77021	0.772 ± 0.001
3.532×10^{-5}	0.61593, 0.61955, 0.61642	0.617 ± 0.002
3.291×10^{-5}	0.55702, 0.55260, 0.55318	0.554 ± 0.002
2.970×10^{-5}	0.50634, 0.50498, 0.50437	0.505 ± 0.001
2.828×10^{-5}	0.48618, 0.48539, 0.48313	0.485 ± 0.002
2.590×10^{-5}	0.43266, 0.42853, 0.42765, 0.42740	0.429 ± 0.002
1.414×10^{-5}	0.26065, 0.26497, 0.26412	0.263 ± 0.002
1.190×10^{-5}	0.21347, 0.21555, 0.21512	0.215 ± 0.001
6.060×10^{-6}	0.10708, 0.10256, 0.10434, 0.09957	0.103 ± 0.003

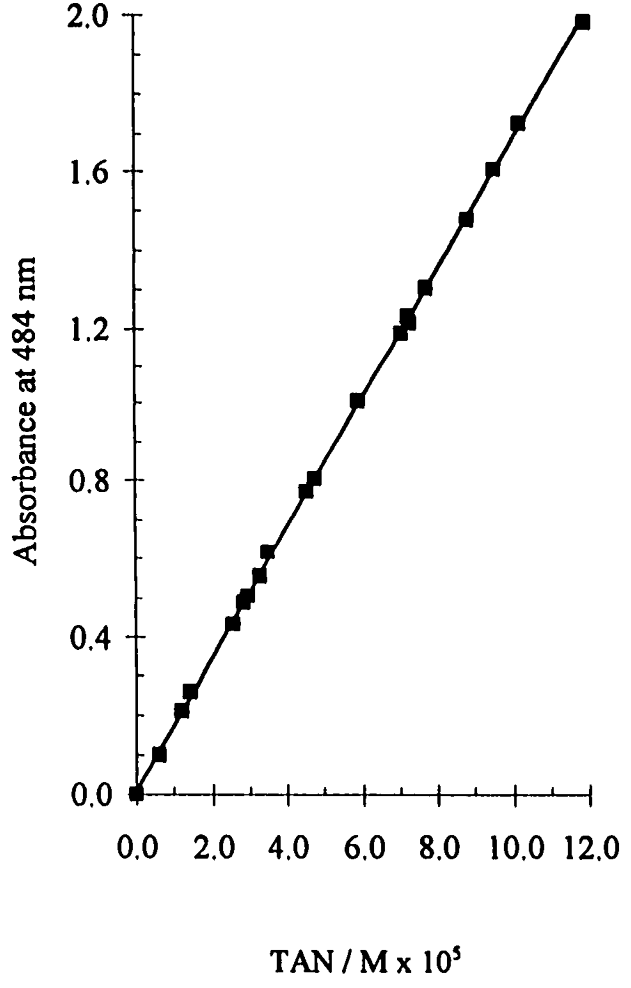


Figure 4.1. Plot of absorbance of TAN in methanol (484 nm) *vs.* TAN concentration.

1.68×10^4 M^{-1} cm^{-1}.

4.3 Adsorption of TAN on XAD-4 Resin

A solution of 3.00 mL of TAN in methanol (initial concentration of 10^{-5} - 10^{-4} M) was pipetted into a quartz cuvette. A small magnetic stirring bar was added to the cuvette which was placed in a magnetic stirring module. The stirrer was actuated at a moderate rate and a time-based absorbance at 484 nm scan was started. At $t = 60$ s, the second reading was taken (the first having been taken at $t = 0$ s); once this second reading had registered, 0.09-0.11 g of XAD-4 resin was added to the solution in the cuvette. The adsorption of TAN on the resin was estimated by measuring the absorbance of the supernatent solution every minute for 3 h.

A typical plot of absorbance *vs.* time is shown in Fig. 4.2a. The experiment was repeated 14 times; the absorbance values for each run were normalized by expressing them in terms of the percentage of TAN remaining in solution, *i.e.*, the ratio of solution concentration at time t to the initial concentration. The pooled results, shown in Fig. 4.2b, indicate that the system achieved equilibrium within 2 h. A shaking time of greater than 2 h did not lead to a significantly higher concentration of TAN on the resin.

In order to ensure that this equilibration time was suitable for more concentrated TAN solutions and larger quantities of resin, a set of four syntheses of TAN-XAD-4 was carried out. In each of four 125-mL Nalgene FEP bottles, between 2.99 and 3.01 g XAD-4 resin was equilibrated with a 100.0-mL aliquot of 0.0177 M TAN solution

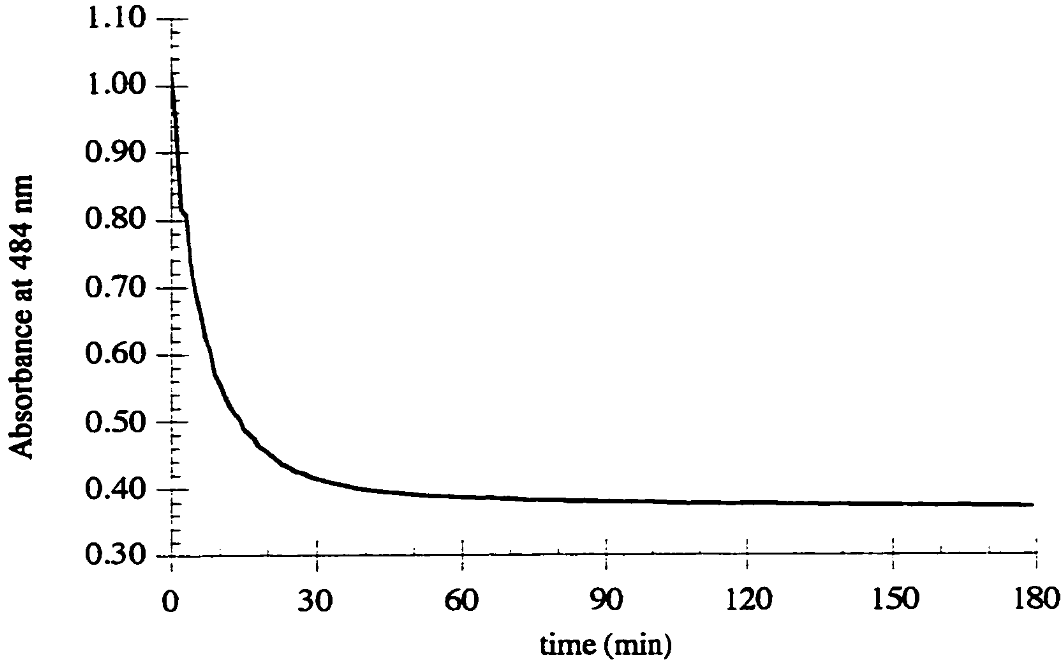


Figure 4.2a. Adsorption of TAN on XAD-4 resin, single run.

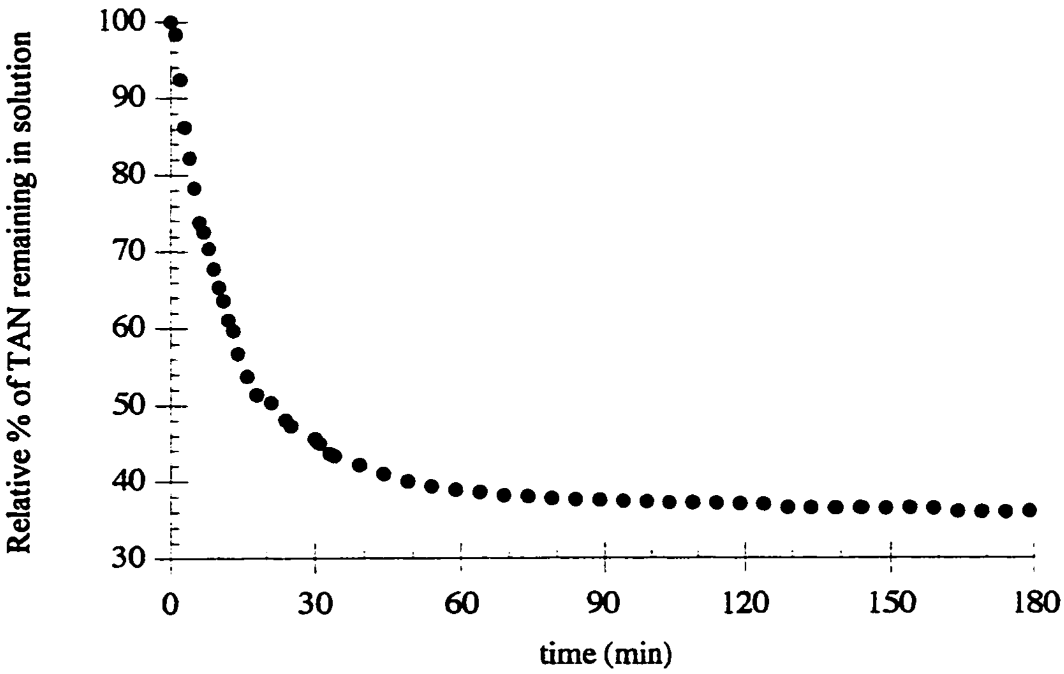


Figure 4.2b. Adsorption of TAN on XAD-4 resin, collective plot for N=15.

in methanol. The concentration of TAN in the supernatent was evaluated after 1, 2, 3, 4, and 5 h shaking time by removing 2.00 mL solution from each sample bottle for spectrophotometric determination. The results, as given in Table 4.4, show that the TAN concentration in the supernatent was essentially constant for $t \geq 2$ h. Therefore, a 2-h shaking time was employed for the preparation of the TAN-XAD-4 resins for further experiments. This choice of shaking time is consistent with the results obtained by other researchers. Most reported syntheses of ligand-impregnated resins describe a batch preparation method similar to that used in this work, in which a sample of solid resin is added to a solution of the chelating agent. Some experimenters simply allow the mixture to stand, with only occasional agitation, but this generally takes a day or longer [46,186]; in most cases, the mixture is stirred or shaken for a period of 30 min to 3 h [24,45,73,88,179,188].

There have been reports of preparations of ligand-loaded resins in which the equilibration time is much longer than this. Brajter *et al.* [195] reported that the impregnation of Amberlyst A-26 resin with SPADNS was not complete even after stirring for 24 h. Singh and Dhingra [74] noted that Dowex 2 resin could be saturated with xylenol orange (XO) in 2 h, but loading the same resin with pyrocatechol violet required shaking for 7 h or more. Handley *et al.* [205] loaded XO on Dowex 1-X8 by stirring for 2 days. Jones and co-workers [180] stirred a solution of XO or Chrome Azurol S overnight with XAD-2 or XAD-4 resin. These preparations, lengthy by ligand-impregnation standards, are still less time-consuming than many reported syntheses of ligand-immobilized resins, which may require several days to complete [134,151,166]. Furthermore, ligand-loaded resins can generally be prepared in a single step, which is preferable to the multi-step syntheses required for some chelating agent

Table 4.4. Effect of shaking time for $[TAN]_o$ = 0.01770 M

	TAN concentration in supernatent (M)			
Shaking Time (h)	A	B	C	D
1	0.01266	0.01264	0.01272	0.01283
2	0.01194	0.01191	0.01198	0.01207
3	0.01193	0.01181	0.01189	0.01196
4	0.01181	0.01176	0.01188	0.01196
5	0.01189	0.01181	0.01179	0.01192

immobilized reagents [128,131,162,163]. Compared to these reports, the present work is preferable because it involves only one step for the loading of the chelating agent and it takes only a 2-hour equilibration time.

Some authors have reported the synthesis of ligand-impregnated supports by a dynamic method, in which a solution of complexing agent is passed through a resin column. There are a few examples in the literature in which comparisons have been made between batch and dynamic preparations, and it has been generally shown that the quantity of complexing agent loaded onto the resin approximately the same no matter which method was used [195,197,188]. For this reason, the preparation of TAN-XAD-4 by this method was not attempted in the present work.

The loading of TAN onto Amberlite XAD-2 resin was also investigated. The absorbance *vs.* time plots were similar to that shown in Fig. 4.2a. A comparison of the adsorption of TAN on XAD-2 and XAD-4 resins is given in Table 4.5. It is apparent that initially, the adsorption of TAN by both resins proceeded rather quickly, and at approximately the same rate. However, as the systems approached equilibrium, and the relative adsorption rates decreased, the adsorption of TAN on XAD-4 resin was faster than that for XAD-2 resin. Furthermore, the relative quantity of TAN loaded on the resin was less for XAD-2 resin than for XAD-4. When Amberlite XAD-4 resin was loaded with TAN in dilute methanol solution (*i.e.* [TAN] $< 10^{-4}$ M), the equilibrium concentration in the supernatent was 37% of the initial TAN concentration. For XAD-2 resin, this figure was approximately 60%. These observations may be attributed to the higher surface area of XAD-4 compared to XAD-2 (800 $m^2 g^{-1}$ to 330 $m^2 g^{-1}$).

Table 4.5. Relative adsorption of TAN on XAD-2 and XAD-4 resins.

	Time Required (min)	
Relative % Adsorption of TAN	XAD-2	XAD-4
50	6	7
75	14	15
90	33	31
95	54	44
99	129	74

4.4 Chemical Stability of TAN-XAD-4 Resin

A 10-g batch of TAN-XAD-4 resin was prepared in *ca.* 0.01 M methanol solution and used throughout this study. The resin was loaded onto a column of 50 mm x 0.7 mm i.d. The resistance of the TAN-loaded resin to stripping of the ligand was investigated for a variety of organic solvents (acetone, methanol, ethanol, and methanol-water mixtures) and aqueous media (acids, bases, buffer solutions, and solutions of high salinity). A sample of 100 mL was passed through the column at a flow rate of 1 mL min^{-1}, then the concentration of TAN in the effluent was evaluated spectrophotometrically. When the amount of TAN found in the effluent was significant (*i.e.* 5% or more of the TAN initially present on the resin), the quantity of TAN left on the resin was determined by INAA. The results of this study are given in Table 4.6.

The resin was completely resistant (*i.e.* no perceptible bleeding of TAN into solution) in aqueous buffer solutions of pH 3-9, and 4 M NaCl, and relatively stable (< 1% loss of TAN to the effluent) in 6 M HNO_3, 2 M NH_3, 6 M NaOH, and methanol-water mixtures containing 50% methanol (v/v) or less. Therefore, TAN-XAD-4 can be applied to the preconcentration of trace elements from any of these media without a compromise in performance due to bleeding of the stationary phase. Eluents such as 6 M HNO_3 are generally sufficient to remove trace elements collected on the column. It is important for the resin to be able to withstand the conditions which permit removal of elements from the column, if the preconcentration method is to be coupled with an analytical technique which requires a liquid sample. The fact that TAN-XAD-4 is stable to such eluents suggests that the resin could be

Table 4.6. Chemical stability of TAN-XAD-4 resin; resin initially contains 0.118 mmol TAN g^{-1} resin

Medium	% TAN lost to solution				
HNO_3		2M	4M	6M	8M
		0.12	0.45	0.79	2.31
NH_3	1M	2M	4M	6M	8M
	0.12	0.25	1.79	2.12	3.14
NaOH			1M	3M	6M
			ND	0.01	0.06
NaCl			1M	2M	4M
			ND	ND	ND
Aqueous Buffer	pH 4	pH 5	pH 6	pH 7	pH 8
	ND	ND	ND	ND	ND
Organic Solvents		Acetone	Methanol		Ethanol
		100.0	49.00		48.34
Methanol/Water		30% (v/v) MeOH		40%	50%
		ND		0.01	0.92
Methanol/Water		60%	70%	80%	90%
		9.69	28.87	46.79	48.44

ND = no TAN detected in effluent

reused, if so desired. The elution of elements from the TAN-loaded resin and the reusability of the column are not as important to this research since the elements collected on the column are quantified directly by NAA. The advantages of circumventing the elution step, such as eliminating contamination by the eluent and avoidance of irreproducible elution, have been discussed in Section 1.6.

Passage of organic solvents or aqueous solutions containing elevated levels of methanol led to the bleeding of TAN from the resin; using acetone as the solvent, TAN was quantitatively removed from the column. Further investigation showed that passage of four 10-mL aliquots of acetone through the column was sufficient for this purpose. This could be an important consideration if an element collected on the column withstands elution by acidic media; in that event, the element can be completely removed from the column along with the chelating agent with acetone.

4.5 Solvent Effects on Adsorption of TAN on XAD-4 Resin

It has been proposed by Kipling [288] that the nature of the solvent may influence the adsorption of a solute onto a solid surface. To examine the effect of solvent on the uptake of TAN on XAD-4 resin, a series of TAN-loaded resins utilizing a variety of solvents was prepared. The chelating agent was loaded onto the resin in batch mode by equilibrating between 2.995 and 3.005 g XAD-4 with 100.0 mL solution of known TAN concentration in a Nalgene FEP bottle. The contents were equilibrated at a moderate rate for at least 2 h using a mechanical shaker. The concentration of TAN in the supernatent solution was then evaluated spectrophotometrically and the quantity of chelating agent on the resin was estimated by difference.

Whenever possible, the spectrophotometric data were corroborated with direct analyses of the resin samples by INAA. The TAN uptake on the resin was estimated by assaying the 3103.4-keV photopeak of ^{37}S. Based on the analysis of a series of sulfur standards (sulfur powder equilibrated with an appropriate quantity of XAD-4 resin), the sensitivity for sulfur following a 10-min irradiation, 1-min decay, and 10-min count was determined to be 121 ± 3 counts mg^{-1} S. Owing to this relative insensitivity, analysis of the sulfur content of TAN-loaded resins in which the TAN uptake was less than 10^{-2} mmol g^{-1} resin proved to be impractical. There was, however, good agreement between spectrophotometry and NAA in the determination of the loading of TAN on XAD-4 resin, as shown in Table 4.7, when there was sufficient TAN present on the resin. As $[TAN]_r$ decreased, the two experimentally determined values tended to diverge, due to the poor sensitivity of NAA for sulfur.

The adsorption isotherms for TAN on XAD-4 resin were determined in acetone, absolute ethanol, 95% ethanol, methanol, and mixtures of methanol and DDW containing 10%, 20%, and 40% (v/v) water. A typical adsorption isotherm for methanol is shown in Fig. 4.3, relating the concentration of TAN on the resin, $[TAN]_r$ (in mmol TAN g^{-1} resin), to the concentration of TAN in the supernatent solution at equilibrium, $[TAN]_s$ (in mmol mL^{-1}). The plot of $[TAN]_r$ *vs.* $[TAN]_s$ is not linear, nor does it fit a Langmuir-type curve in which $[TAN]_r$ tends to a limiting value for higher values of $[TAN]_s$. In order to derive a linear relationship, the experimental results were fitted to the Freundlich model.

Table 4.7. Calculation of loading of TAN on XAD-4 resin by NAA and spectrophotometry.

		NAA determination		spectrophotometric detn.	
Sample	$[TAN]_0$(M)	S counts/g	$[TAN]_r$ (mmol/g)	[TAN]s (M)	$[TAN]_r$ (mmol/g)
1	2.012×10^{-2}	734	1.89×10^{-1}	1.466×10^{-2}	1.821×10^{-1}
2	1.006×10^{-2}	410	1.06×10^{-1}	6.600×10^{-3}	1.153×10^{-1}
3	3.898×10^{-3}	179	4.61×10^{-2}	1.817×10^{-3}	4.163×10^{-2}
4	1.956×10^{-3}	70	1.80×10^{-2}	8.691×10^{-4}	2.174×10^{-2}
5	6.029×10^{-4}	35	9.02×10^{-3}	2.888×10^{-4}	1.047×10^{-2}
6	3.912×10^{-4}	25	6.44×10^{-3}	1.495×10^{-4}	4.834×10^{-3}
7	2.013×10^{-4}	8	2.06×10^{-3}	8.491×10^{-5}	3.880×10^{-3}

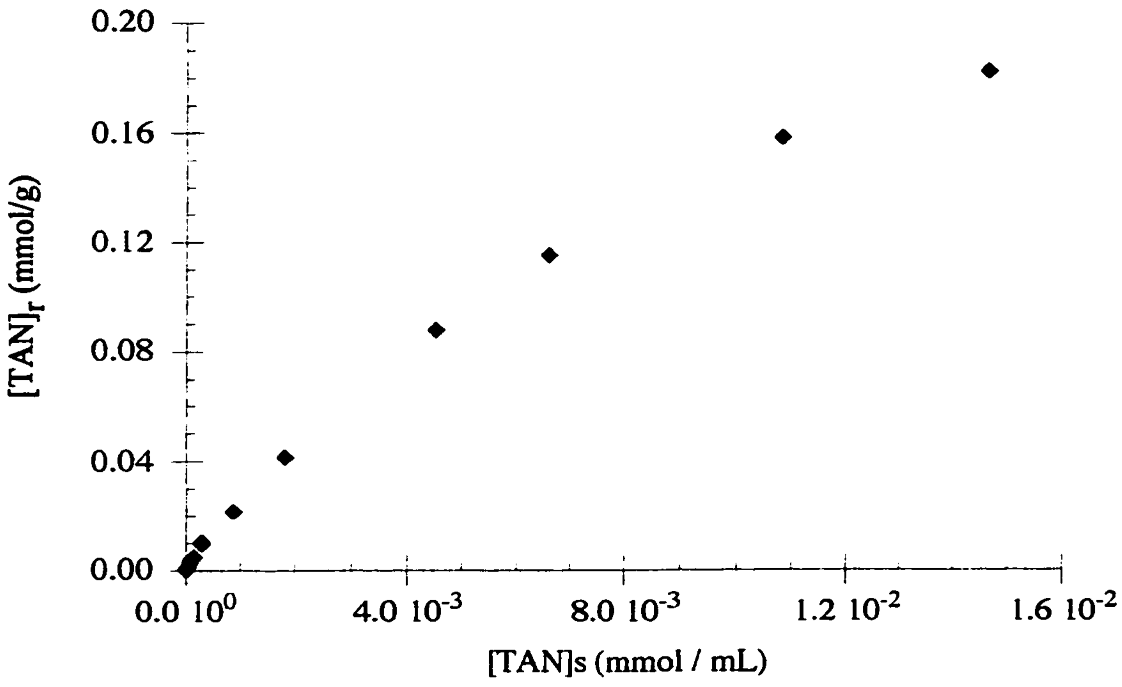


Figure 4.3. Plot of $[TAN]_r$ *vs.* $[TAN]_s$ for TAN-XAD-4 system in methanol.

According to this model, the concentrations on the solid phase and in solution are related by the Freundlich equation [289]:

$$[\mathrm{TAN}]_r = k([\mathrm{TAN}]_s)^n \qquad [4.1]$$

or:

$$\log\,[\mathrm{TAN}]_r = n \log\,[\mathrm{TAN}]_s + \log k \qquad [4.2]$$

where k is termed the Freundlich constant and n is a constant representative of the fact that a nonlinear relationship exists [290]. For adsorption isotherms, $n < 1$; this constant is sometimes expressed as $1/n$ in order to emphasize this fact [291].

The experimental data were treated according to equation [4.2]. The plots of log $[\mathrm{TAN}]_r$ *vs.* log $[\mathrm{TAN}]_s$ were linear, indicating a good agreement of the experimental results with the Freundlich isotherm model. The values for the constants n and log k are given in Table 4.8. The adsorption isotherms for seven solvent systems are shown in Fig. 4.4 through 4.6. Two general trends emerged from the series of adsorption isotherms, namely that the value for n was approximately constant for the seven solvent systems under investigation and that the value of log k increased with increasing solvent polarity.

Rearrangement of equation 4.1 yields an expression for k,

$$k = \frac{[TAN]^r}{[TAN]_s^n} \qquad [4.3]$$

Thus, the k value may be considered a type of partition coefficient which describes the

Table 4.8. Values for the Freundlich equation constants log *k* and *n*.

$$\log [TAN]_r = n \log [TAN]_s + \log k$$

Solvent	log *k*	*n*
acetone	0.241	0.866
abs. ethanol	0.567	0.788
95% ethanol	0.881	0.837
methanol	0.848	0.820
90% methanol	1.039	0.789
80% methanol	1.480	0.771
60% methanol	1.588	0.700

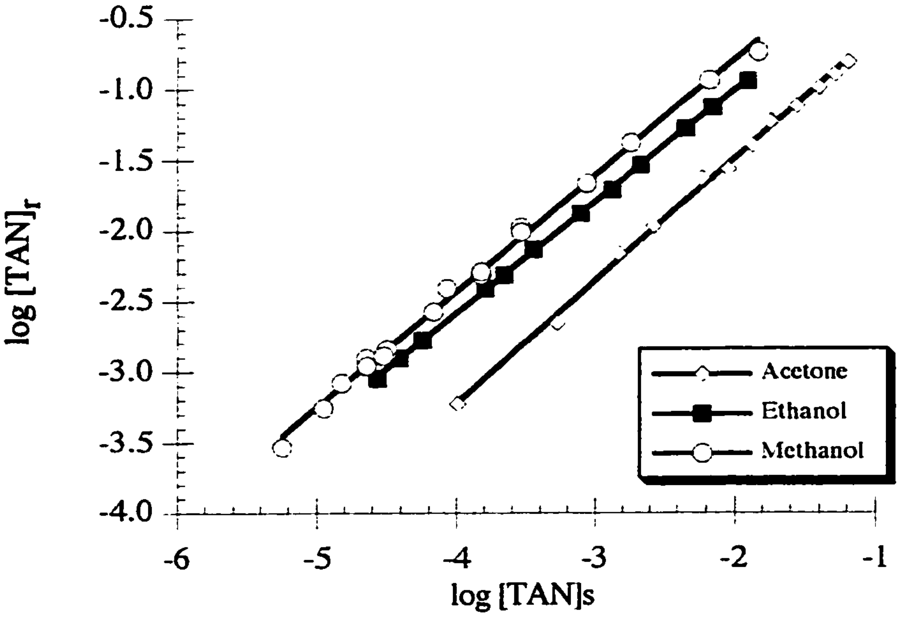


Figure 4.4. Freundlich adsorption isotherms: plots of log $[TAN]_r$ *vs.* log $[TAN]_s$ for TAN-XAD-4 system in acetone, absolute ethanol, and methanol.

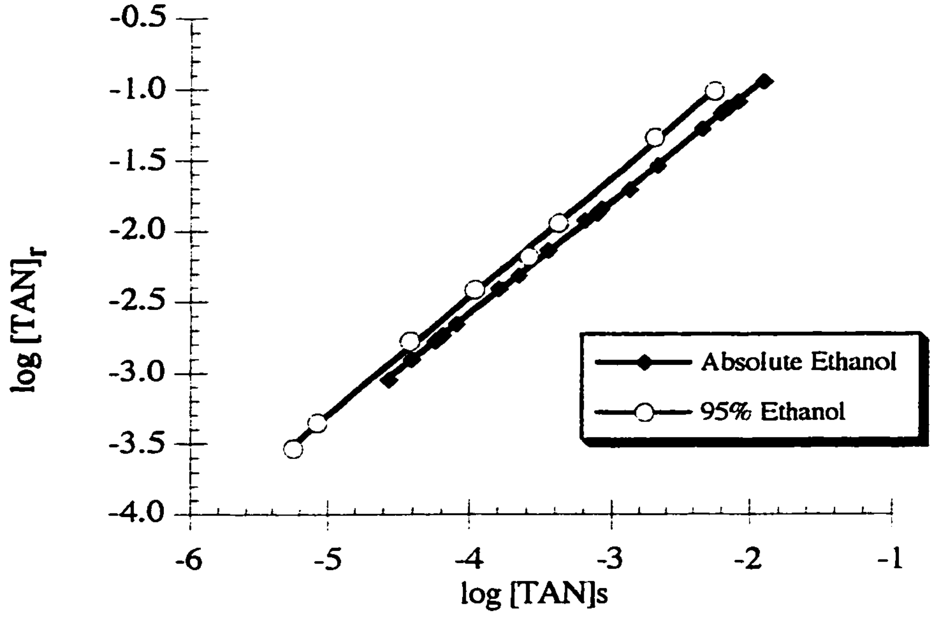


Figure 4.5. Freundlich adsorption isotherms: plots of log $[TAN]_r$ *vs.* log $[TAN]_s$ for TAN-XAD-4 system for absolute ethanol and 95% ethanol.

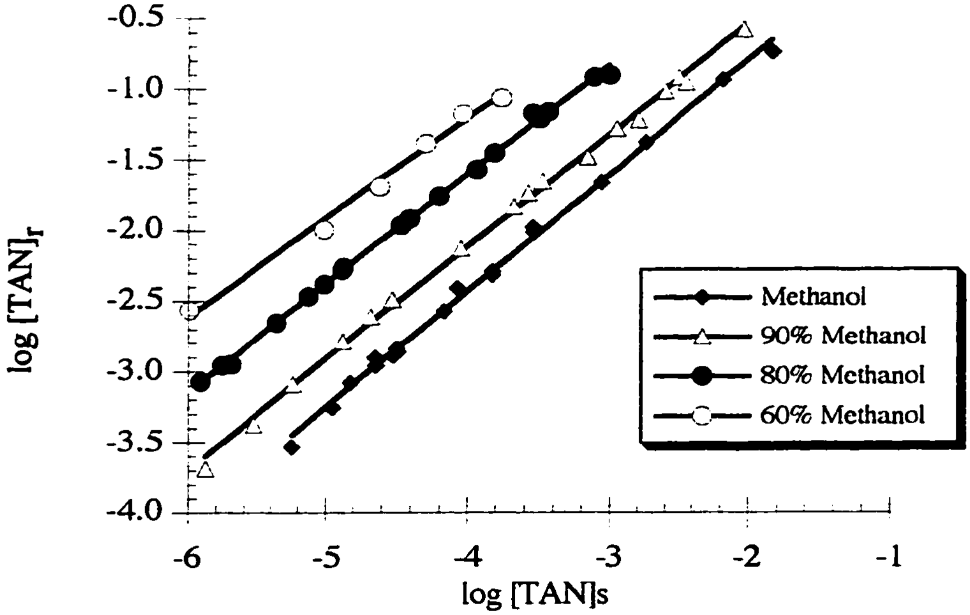


Figure 4.6. Freundlich adsorption isotherms: plots of log $[TAN]_r$ *vs.* log $[TAN]_s$ for TAN-XAD-4 system in methanol-water mixtures.

distribution of the solute between the solution and adsorbed phases. This value should depend on the affinity of the chelating agent for the resin and solution phases. From equation 4.3, it is apparent that an increase in *k* results in an increase in $[\text{TAN}]_r$ relative to $[\text{TAN}]_s$. Given the hydrophobic nature of both the chelating agent and the resin matrix, the solute should display a greater affinity for the resin, and a corresponding increase in *k*, when the polarity of the solution is increased. This is consistent with the experimental results shown in the adsorption isotherms in Figs. 4.4-4.6.

The construction of adsorption isotherms is limited by the solubility of TAN in water-methanol mixtures of elevated water content. The solubility of TAN in methanol is approximately 2×10^{-2} M; in methanol/water mixtures, this value falls from 7×10^{-3} M in 80% methanol, 5×10^{-3} M in 60% methanol, to 8×10^{-4} M in 50% methanol. This limitation made the analysis of the adsorption isotherm for 50% methanol impossible. The high solvent polarity served to shift the distribution of TAN almost completely to the resin. Consequently, the equilibrium concentration of TAN in the supernatent was so low that it could not be evaluated spectrophotometrically. This was true even at the solubility limit for TAN in this solvent. The higher initial concentrations necessary to yield a measurable value for $[\text{TAN}]_s$ could not be attained. Furthermore, the relative insensitivity of INAA for sulfur made an indirect determination of $[\text{TAN}]_r$ impossible, thereby precluding the possibility of obtaining a value for $[\text{TAN}]_s$ by difference.

It is apparent from the isotherms in Figs. 4.4 through 4.6 that to maximize the loading of TAN on the resin, it was beneficial to use a mixed methanol-water solvent. The presence of water increases the solvent polarity and served to shift the TAN equilibrium from the solution phase to the resin phase. For a given value of $[TAN]_s$, the quantity of TAN on the resin increased with increasing solvent polarity. However, mixed solvents of higher water content suffered due to the relatively low solubility of TAN in such media. Because of the lower attainable values for the initial concentration, $[TAN]_0$, resins prepared in these solvents did not display the maximum possible uptake of TAN. Optimization of the loading of TAN on the resin was achieved using solvents of more moderate polarity which permitted larger values of $[TAN]_0$.

In light of these considerations, a procedure was devised in order to further increase the loading of TAN onto XAD-4 resin. The resin sample was first equilibrated with a solution of TAN in methanol, rather than mixed methanol-water solvent; a higher value of $[TAN]_0$ was therefore possible than could be attained in mixed solvent. After an initial 2-h shaking time, water was added to the supernatent, thereby increasing the solvent polarity and increasing the amount of TAN taken up by the resin. The efficacy of this procedure was evaluated by comparison with the preparation of TAN-XAD-4 using methanol or acetone alone as the solvent.

A 250.0-mL solution of TAN in methanol was prepared and two 100.0-mL portions taken. Each aliquot was equilibrated as previously described for at least 2 h with 2.995 to 3.005 g XAD-4 resin. After this equilibration period, 20.0 mL of TAN solution was removed from one of the bottles and replaced with 20.0 mL DDW. The decision to add 20 mL of water was made based on the results shown in Fig. 4.6 and because larger volumes of water caused precipitation of the chelating agent from solution after the first equilibration period. Both samples were equilibrated for another 2 h. At the end of the second equilibration period, the TAN-loaded resin samples were filtered and the TAN uptake was evaluated by INAA of the impregnated resin. The results are given in Table 4.9. For comparative purposes, acetone solutions were prepared with the same values of $[TAN]_0$ as the methanol solutions; between 2.995 and 3.005 g of resin was equilibrated for 4 h with 100.0 mL of each acetone solution and the values of $[TAN]_r$ determined by NAA.

The results in Table 4.9 showed a general trend of increased ligand loading on the resin with increasing solvent polarity. As expected, for solutions of the same value of $[TAN]_0$, the uptake of TAN by the resin was lowest when acetone was used as the solvent, higher for methanol, and highest when water was added to the methanol solution. Compared to using methanol alone as the solvent, the addition of water to the system increased the value of $[TAN]_r$ by as much as a factor of 2. The effect seemed to be more pronounced at higher TAN concentrations. It should be noted that the uptake of TAN on the resin by this method was higher than that obtained by any of the solvent systems initially investigated and depicted in Figs. 4.4 through 4.6.

The optimized synthesis, utilizing $[TAN]_0 = 0.0218$ M and the addition of water to the system after the first equilibration, yielded a resin containing 0.439 mmol TAN per gram of resin. This figure compares favorably to other ligand-impregnated resins reported in the literature. Ueda *et al.* [59] loaded TAN onto silica gel using acetone as the solvent; the amount of TAN retained was approximately 0.040 mmol TAN g^{-1} silica gel. The PAN-XAD-4 resin of Chwastowska and Mozer [197], prepared in methanol, contained 0.054 mmol PAN g^{-1}. Brajter and Dabek-Zlotorzynska [199] loaded XAD-2 with PAR; an isotherm study showed that the maximum uptake of PAR by the resin was 0.2 mmol g^{-1}. Lundgren and Schilt

Table 4.9. Uptake of TAN on XAD-4 resin in acetone, methanol, and mixed methanol-water solvents.

	$[\mathrm{TAN}]_r$ (mmol g^{-1})		
$[\mathrm{TAN}]_o$ / M	acetone	methanol	methanol-water
2.18×10^{-2}	5.87×10^{-2}	2.25×10^{-1}	4.39×10^{-1}
2.00×10^{-2}	5.61×10^{-2}	2.09×10^{-1}	4.05×10^{-1}
1.33×10^{-2}	3.80×10^{-2}	1.47×10^{-1}	3.19×10^{-1}
1.00×10^{-2}	3.01×10^{-2}	1.12×10^{-1}	1.83×10^{-1}
5.01×10^{-3}	1.66×10^{-2}	6.84×10^{-2}	8.85×10^{-2}
2.50×10^{-3}	8.34×10^{-3}	3.19×10^{-2}	4.49×10^{-2}

[47] prepared PDT-XAD-2 in methanol with a capacity of 0.120 mmol PDT per gram of XAD-2 resin. Lee and co-workers [24] using acetone as the solvent, impregnated XAD-4 resin with oxine and its 5,7-diiodo derivative and reported ligand uptake of 0.0380 mmol g^{-1} and 0.0310 mmol g^{-1}, respectively. A modified XAD-4 resin containing 0.010 mmol dithizone g^{-1} resin was prepared by De Oliveira and Narayanaswamy [32]. In some of these reports, no apparent attempt was made to maximize the ligand loading on the reversed-phase resin. These resins were, however, successful in the collection of trace elements from solution.

The TAN-XAD-4 resin prepared in this work exhibited a higher degree of ligand uptake than other ligand-impregnated resins reported in the literature. Consequently, it would be expected that the TAN-loaded resin prepared here should be of relatively high metal exchange capacity, compared to other RPEC resins. The capacity of the TAN-XAD-4 resin with respect to copper has been investigated; the details are presented in the following section.

4.6 Solvent Effect on Copper Capacity of TAN-XAD-4 Resin

The TAN-impregnated XAD-4 resins prepared in the isotherm studies were evaluated for their retention capacities with respect to copper. A solution of $Cu(NO_3)_2 \cdot 5H_2O$ containing 0.5032 mg Cu mL^{-1} was prepared and buffered to pH 6.00 with MES-NH_3 buffer. A 20-mL portion of this copper solution was equilibrated by moderate shaking with 1.00 g of TAN-loaded XAD-4 resin in a screw-cap bottle for a period of at least 48 h. After this equilibration period, the supernatent solution was decanted and a fresh 20-mL sample of the copper solution was equilibrated with the TAN-loaded resin for an additional 48 h. At the end of the second shaking period, the resin sample was filtered, washed repeatedly with DDW, and transferred to a medium polyethylene vial for irradiation and counting. After a 30-s irradiation, 1-min decay, and 5-min counting period, the quantity of copper adsorbed on the resin was evaluated using the 1039.2-keV peak of ^{66}Cu. Comparator standards were prepared by adding a 1-mL spike of copper solution (ultrapure copper wire dissolved in nitric acid) to an appropriate quantity of clean XAD-4 resin in a medium vial. The copper capacity of the resin samples was plotted against $[\mathrm{TAN}]_r$ and the results are shown in Fig. 4.7.

The results indicate that the copper capacity of a TAN-impregnated XAD-4 resin was dependent on the value of $[\mathrm{TAN}]_r$ but not on the solvent used in the resin synthesis. The metal chelating capacity of the resin should be a reliable indicator of the ability of the resin to concentrate trace elements from solution. Consequently, it can be concluded that for the synthesis of TAN-XAD-4 resin, the choice of solvent used in the preparation should be based on maximizing the value of $[\mathrm{TAN}]_r$, which in turn should yield a ligand-impregnated resin of optimum metal-chelating performance.

Regression analysis of the linear relationship (Fig. 4.7) between the copper capacity (y) and $[\mathrm{TAN}]_r$ (x) yields an equation of the form:

$$y = 32.1x + 0.603 \qquad [4.4]$$

Given that the copper capacity was expressed in terms of mg Cu g^{-1} resin, the slope of 32.1 corresponds to a molar ratio of Cu to TAN of 1:2. The regression analysis yields a non-zero

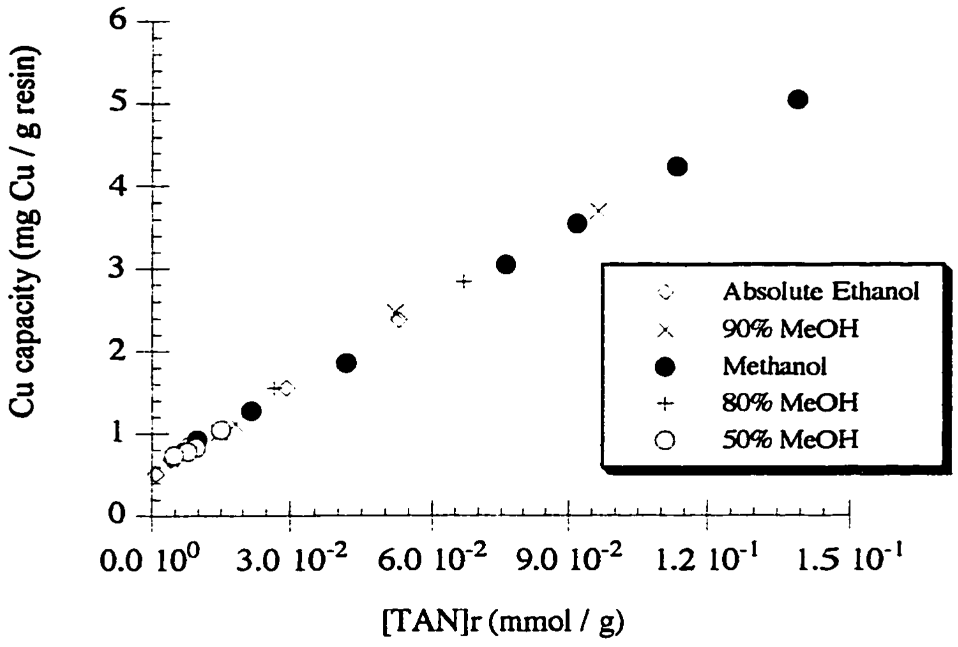


Figure 4.7. Plot of copper capacity of TAN-XAD-4 resins *vs.* $[TAN]_r$.

intercept, suggesting that the XAD-4 resin itself has some tendency to form metal complexes despite the absence of chelating functional groups.

The metal-chelating capacity of Amberlite XAD-4 resin has been investigated by Mackey [292,293], who reported that trace copper, iron, magnesium, and zinc were adsorbed on a variety of Amberlite resins from aqueous solution at pH 2.50. Koshima [294] collected iron from HCl solution on Amberlite XAD resins. Adsorption of iron on XAD-2 resin was poor but iron was successfully removed from solution by XAD-4, 7, and 8.

Subsequent studies on the TAN-XAD-4 resin prepared by adding water to the supernatent showed that the resins had copper capacities of 11-14 mg g^{-1} (0.17-0.22 mmol g^{-1}) resin. This value compares favorably to the PAN-XAD-4 resin prepared by Chwastowska and Mozer [197]. As previously discussed, this resin, synthesized in methanol, contains 0.054 mmol PAN g^{-1} resin, but has a copper capacity of only 127 μg g^{-1} resin (0.002 mmol Cu g^{-1}). The exchange capacity of the TAN-XAD-4 resin prepared here is similar to the values reported for other RPEC reagents. Silica gel loaded with PAN or 2-(2-thiazolylazo)-*p*-cresol has been shown to have an exchange capacity for uranyl ion of approximately 70 mg g^{-1} (0.26 mmol g^{-1}) [59]. An oxine-XAD-2 resin prepared in this laboratory [14] exhibits a copper capacity in excess of 40 mg g^{-1} (0.65 mmol g^{-1}) resin. Polystyrene-immobilized 1-nitroso-2-naphthol has an exchange capacity for copper of approximately 0.6 mmol g^{-1} [166]. For the sake of comparison, the widely-used I-8-HOQ has been shown to collect only 0.05-0.06 mmol Cu g^{-1} [48,138].

The results of the present work indicate that the capacity of the TAN-loaded XAD-4 resin was suitable for the preconcentration of trace elements from water samples.

The retention capacity of the resin was of the order of mg Cu g^{-1} resin, while trace elements in potable and natural water samples are typically of the order of μg L^{-1}. Correspondingly, the saturation of the resin by trace elements present in these samples is not expected.

4.7 Optimized Procedure for the Preparation of TAN-XAD-4 Resin

Based on the results of the preliminary experiments, the following optimized procedure was developed for the synthesis of TAN-impregnated XAD-4 resin. A 200-mL solution of TAN (*ca.* 0.01-0.02 M) was prepared in methanol. The solution was split into two 100-mL portions and each was equilibrated with 3.00 g precleaned XAD-4 resin for at least 2 h in a 125-mL screw-cap Nalgene FEP bottle. Twenty mL of TAN solution was removed from each bottle and replaced with 20 mL DDW, and the contents of each bottle equilibrated for an additional 2 h. The TAN-XAD-4 resin was recovered by filtration and rinsed with several portions of DDW until the washings appeared colorless. Before a batch of TAN-loaded resin was used in trace element studies, a sample was taken from each bottle and analyzed by INAA in order to confirm the absence of elemental contaminants. In the event resin samples found to contain undesirable trace elements, they were washed with 0.1 M ultrapure HNO_3 in order to remove those elements. Resins found to be still contaminated after the acid-washing step were used for routine cleanup columns (columns of TAN-XAD-4 used to scavenge trace elements from buffer solutions) but not in experiments dealing with PNAA.

The two resin samples were combined and stored in DDW in a screw-cap glass bottle. The washing and storage of the TAN-XAD-4 resin in DDW proved to be extremely important. In preliminary syntheses, TAN-loaded resins prepared in acetone or methanol were suction-filtered, air-dried at room temperature, and stored dry. The resins thus prepared displayed inferior trace element chelation properties and very low copper capacities (typically less than 0.05 mg Cu g^{-1} resin).

Further, these resins were difficult to handle from a physical standpoint. The dried resin beads floated in water, precluding the packing of the columns using a slurry. The coated XAD-4 resin also tended to adhere to plastic and glass, making it difficult to transfer the beads to the columns for packing and to sample vials for irradiation. An immediate wash of the filtered resin with DDW and its storage in water eliminated these problems. The resin beads, which were swollen by soaking in organic solvent, remained in the swelled state after the organic solvent was flushed out and replaced with water. As a result, the beads sank in water and could be slurry-packed into columns. Resins stored in DDW also displayed much higher copper capacities (as evidenced in Section 4.6 and Fig. 4.7) and were far more effective in the extraction of trace elements from aqueous solutions than resins which had been dried prior to use.

The resins synthesized in this manner exhibited an uptake of TAN by the resin of 0.2 to 0.4 mmol g^{-1} resin and copper capacities of 7-14 mg Cu adsorbed g^{-1} resin. All further experiments utilizing TAN-loaded XAD-4 were performed using resin samples synthesized by this method.

4.8 Effect of pH on RPEC of Trace Elements by TAN-XAD-4 Resin

The effect of pH on the retention characteristics of the TAN-impregnated XAD-4 resin was investigated. The general RPEC procedure has been described in detail in Section 3.8. In short, a 100-mL sample of 0.05 M buffer solutionwas spiked with a known volume of the multielement stock solution (typically 0.1-1.0 mL). The pH of the spiked solution was adjusted to the desired value with ultrapure nitric acid or aqueous ammonia. This solution was passed through a column of TAN-XAD-4 (50 mm x 7 mm i.d.) preconditioned at the same pH. Between three and six trials were performed at each pH value. The elements retained by the resin were quantified at each pH by NAA.

In general, most elements were poorly recovered from weakly acidic buffer solution and were more efficiently extracted onto the resin as the pH was increased. This can be attributed to the effect of pH on the formation of the metal chelate. Assuming the absence of side-reactions, the formation of a metal-TAN chelate may be depicted by the equilibrium reaction:

$$M^{n+}_{(aq)} + HA_{(r)} \rightleftharpoons MA^{(n-1)+}_{(r)} + H^{+}_{(aq)} \qquad [4.5]$$

where *aq* and *r* denote the aqueous and resin phases, respectively, and HA represents the neutral TAN molecule with the proton on the naphthol oxygen. The equilibrium constant, K_{eq}, for this reaction is given by

$$K_{eq} = \frac{[H^+]_{aq}[MA^{(n-1)+}]_r}{[M^{n+}]_{aq}[HA]_r} \qquad [4.6]$$

For a given element, the distribution coefficient, K_D, is defined by

$$K_D = [MA^{(n-1)+}]_r \,/\, [M^{n+}]_{aq} \qquad [4.7]$$

therefore,

$$K_D = K_{eq}\,[HA]_r \,/\, [H^+]_{aq} \qquad [4.8]$$

Taking the logarithm of both sides yields:

$$\log K_D = \log K_{eq} + \log\,[HA]_r + pH \qquad [4.9]$$

It can therefore be concluded that for a system with no competing reactions, the distribution coefficient, and hence the degree to which the metal is complexed on the solid resin phase, increases with increasing pH.

The pH effect may also be viewed in light of the fact that the metal forms a chelate with the TAN anion, which is produced upon deprotonation of the naphthol group. The deprotonation step, and hence the propensity of the TAN molecule to form chelates, is favored as the pH is increased.

According to Torré and Marina [19], the discussion of the mechanism of metal-ion retention by reversed-phase resins generally begins with the assumption that the ligand displays the same complexing properties whether loaded on a solid support or in solution. This implies that the complexing behavior of the ligand-loaded resin should be predictable given the appropriate formation constants for metal complexes in solution. For example, Brajter and co-workers [176] and Akaiwa *et al.* [25,190] discussed the similarities between the extraction of trace metals by RPEC methods and the stability constants for the appropriate metal chelates in solution. On that basis, the behavior of TAN as a chelating agent in solution (particularly as a reagent for solvent extration or spectrophotometry) would be expected to be comparable to that displayed as a reagent for RPEC. As an analytical reagent, TAN has been fruitfully employed in spectrophotometry and solvent extraction studies. Where appropriate, the results of the pH study have been compared to literature reports in which TAN, and in some cases PAN, in solution have been used to complex trace elements. Such comparisons should be made with caution, however. As discussed by Pesavento *et al.* [182,295] attempts to correlate the behavior of a ligand-impregnated resin with the solution complexation characteristics were generally not entirely successful.

Seven of the elements investigated (namely, cadmium, cobalt, copper, manganese, mercury, nickel, and zinc) were completely retained by the resin and exhibited similar general behavior. This result is not surprising, as several researchers have reported the solvent extraction of these elements using TAN. The recovery of these elements was low at low pH, increased to approximately 100% as the pH was raised, and remained quantitative as the pH was increased further. As all seven elements were nearly quantitatively extracted (>90%) from buffer solutions of pH 7.5, their simultaneous extraction by the TAN-XAD-4 resin should be possible under these conditions.

The TAN-XAD-4 column displayed no affinity for cadmium (Fig. 4.8) at pH < 5, but the cadmium uptake was > 95% for pH ≥ 6.3. The metal is prone to formation of hydrolysis products such as $CdOH^+$ and $Cd(OH)_2$ at pH 8 [296], but there is no evidence that formation of these species hindered the cadmium uptake by the column. The recovery was reproducible and quantitative at pH > 8. These results are consistent with reports of the extraction of neutral Cd-TAN complexes into benzene at pH > 7 [221] and into MIBK at pH > 7.3 [297]. The plot of cadmium recovery *vs.* pH presented in the latter study resembled the results in Fig. 4.8 in that no cadmium was extracted at pH < 5.7 and the recovery remained quantitative even at pH 8.5.

Cobalt (Fig. 4.9) was quantitatively (≥ 95%) extracted at pH > 5, with incomplete recoveries in more acidic solution. The solvent extraction behaviour of cobalt has been extensively studied, as the $Co(TAN)_2$ chelate can be recovered over a wide range of pH. Cobalt has been extracted into benzene at pH > 7 [221], into chloroform over the pH ranges 5-9 [218] and 4-10 [226] and into MIBK at pH > 4.5 [297]. Cobalt(II), like cadmium(II), is susceptible to hydrolysis to $Co(OH)^+$ at pH 8. This did not appear to inhibit the uptake of cobalt by the TAN-XAD-4 column at pH > 8.

The recovery of copper (Fig. 4.10) was at least 90% for pH ≥ 4.10. This result is to be expected, given the numerous studies on the formation of Cu-TAN chelates which appear in the literature. Copper was among the first metals used to investigate the complex formation properties of TAN. The solvent extraction of copper has been extensively investigated, and formation constants for chelates of Cu(II) with TAN have been reported to

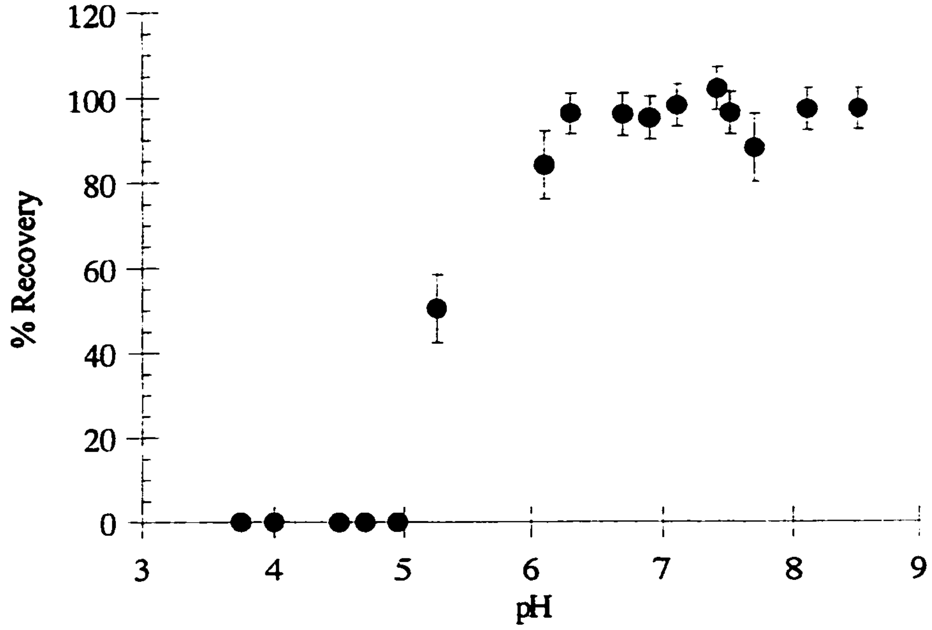


Figure 4.8. Recovery of Cd by TAN-XAD-4 resin as a function of pH.

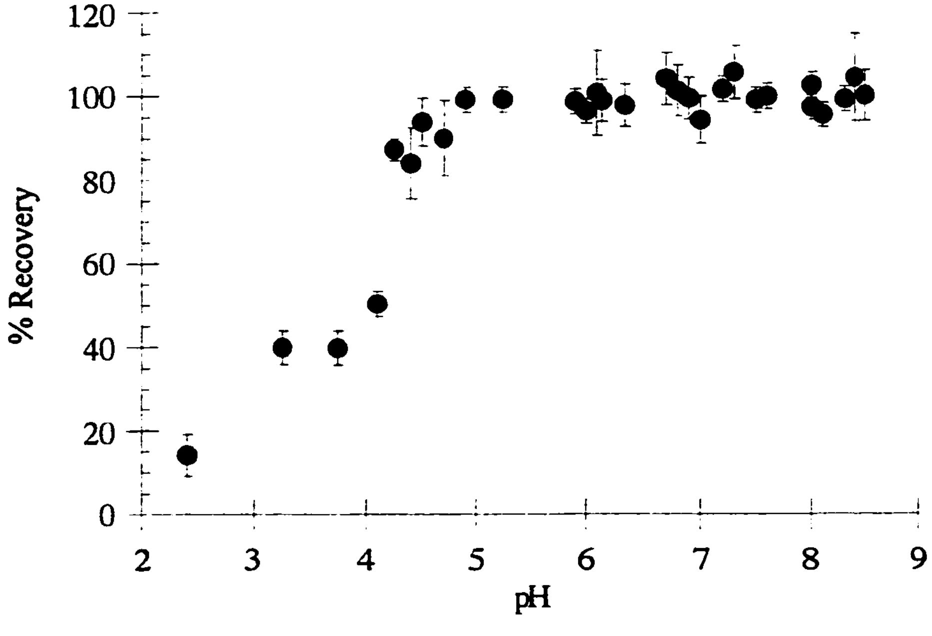


Figure 4.9. Recovery of Co by TAN-XAD-4 resin as a function of pH.

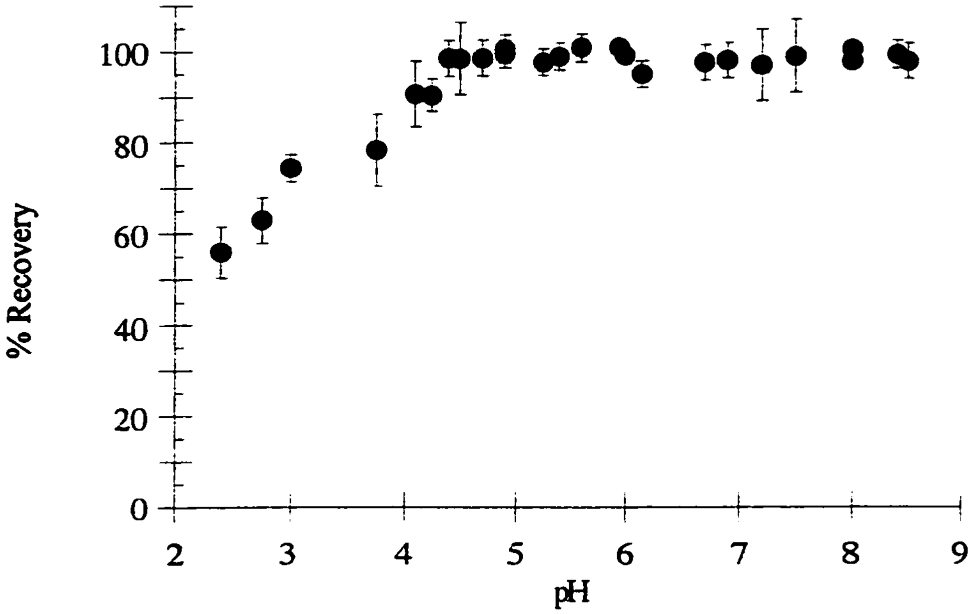


Figure 4.10. Recovery of Cu by TAN-XAD-4 resin as a function of pH.

be $K_1 = 10^{10.92}$ and $\beta_2 = 10^{22.52}$ at 20°C [55]. According to Komárek *et al.* [297], the Cu(II)-TAN chelate is extracted into MIBK at pH > 4. Navratil [221] reported the extraction of several TAN-metal chelates; of those investigated, the copper chelate is the only one formed at pH < 5.

Mercury (Fig. 4.11) was nearly quantitatively (≥ 90%) recovered at pH > 6.0 and > 80% for pH ≥ 4. The results obtained in this work are consistent with literature reports of solvent extraction studies on Hg-TAN chelates. Kolosova [298] reported the extraction of Hg(II) as the $Hg(TAN)_2$ chelate into chloroform at pH 5.5-8.0. Mercury can exist in aqueous solution in the 1+ and 2+ oxidation states, although the trace mercury present in solution is most likely in the divalent form. Navratil [221] reported TAN forms chelates with both mercury species. The chelates of TAN with Hg(I) and Hg(II) are extracted into benzene at pH > 7.

Manganese (Fig. 4.12) was not retained at all below pH 6.5 but was quantitatively (> 95%) extracted by the TAN-XAD-4 column at pH > 7.5. This behavior has been observed in extraction studies in which manganese is extracted as the neutral chelate of PAN or TAN. According to Rao and Rangamannar [299], the extraction of the Mn(II) chelate with PAN into chloroform is quantitative only at pH > 8.5. Goto *et al.* [300] determined manganese spectrophotometrically using PAN, and noted that the formation of the $Mn(PAN)_2$ chelate in the presence of Triton X-100 is complete at pH > 8.8. Miao and co-workers [301] loaded polyurethane foams with PAN for the extraction of manganese at pH 9.5. Grzegrzólka [302] reported the extraction of the $Mn(TAN)_2$ chelate into chloroform for the determination of manganese in water. The optimum pH for the extraction is 9.2-9.8.

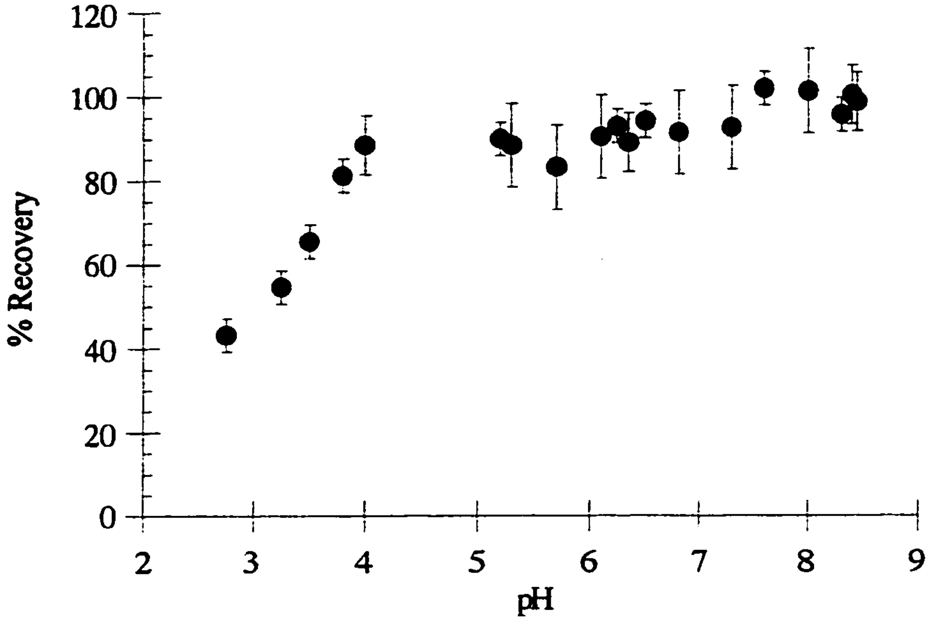


Figure 4.11. Recovery of Hg by TAN-XAD-4 as a function of pH.

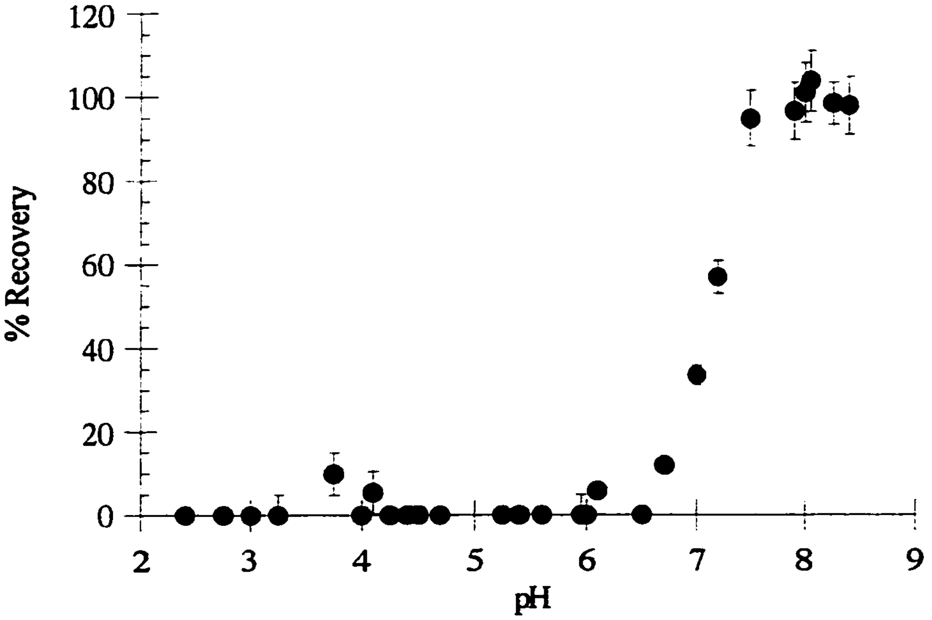


Figure 4.12. Recovery of Mn by TAN-XAD-4 as a function of pH.

The plot shown in Fig. 4.12 was unique in that trace manganese in solution was not retained at all by the column at $pH < 6.5$. The other elements which were quantitatively recovered over particular pH ranges were at least partially retained at other pH levels. These results suggest the possibility of separating manganese from other trace elements in solution, as manganese passes through the column at pH levels at which other elements, such as cobalt, copper, and nickel, are quantitatively retained.

At least 90% of trace nickel (Fig. 4.13) was extracted by TAN-XAD-4 from solutions of $pH > 5.2$. Nickel is similar to cobalt and copper, in that it has been extensively investigated in solvent extraction studies, primarily as the $Ni(TAN)_2$ complex, over a wide pH range for quantitative recovery. The solvent extraction of the Ni(II)-TAN chelate has been reported to be quantitative into benzene at $pH > 8$ [221], into chloroform at pH 3-11 [226] and at pH 7 [218], and into MIBK at $pH > 4.5$ [297]. Nickel has also been determined spectrophotometrically using TAN by solubilizing the chelate in surfactant. Optimum pH values for formation of the Ni(II)-TAN chelate of 4.7-10 [303] and 7.0 [237] have been reported.

Nickel(II) can form hydrolysis products such as $NiOH^+$, $Ni(OH)_2$, $Ni(OH)_3^-$, and $Ni(OH)_4^{2-}$ in basic media [296]. While a value for the stability constant for the formation of the nickel-TAN chelate was not found, it would be expected to be of the same order as that for cobalt, copper, and zinc (*i.e.* $\log K_1 \approx 10$). This value is significantly higher than the formation constant for $NiOH^+$ ($\log K_1 = 4.6$ [57]). Consequently, the recovery of nickel was reproducible and quantitative.

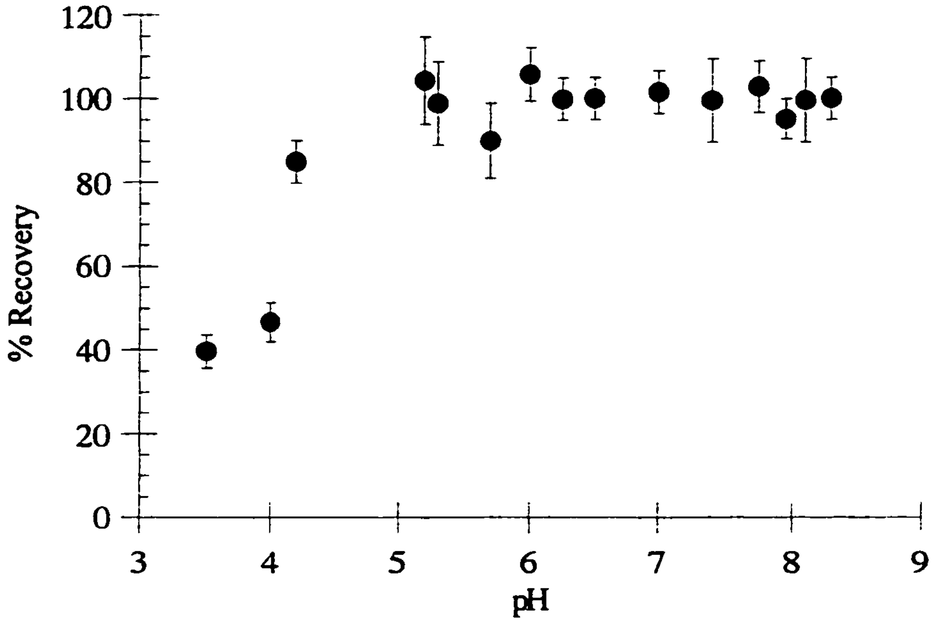


Figure 4.13. Recovery of Ni by TAN-XAD-4 as a function of pH.

Zinc (Fig. 4.14) was not retained by the column at $pH < 3.25$, but the recovery of this element was quantitative at $pH > 5.2$. In this manner, the plot of recovery *vs.* pH for zinc resembles that for cadmium, with the zinc recovery displaying lower pH threshold values for recoveries greater than a few percent (pH 3.25 compared to pH 5 for cadmium) as well as for complete uptake (pH 5.2 compared to 6.2 for cadmium). These results are consistent with the fact that the reported stability constants for Zn-TAN chelates are approximately a full order of magnitude higher than for cadmium (at 20°C, for zinc, $K_1 = K_2 = 10^{9.87}$; for cadmium, $K_1 = 10^{9.18}$, $K_2 = 10^{8.70}$ [55]). In solvent extraction studies, the Zn-TAN chelate has been quantitatively extracted into benzene at $pH > 7$ [221] and into MIBK at $pH > 6$ [297].

Two other elements investigated in this work, silver and uranium, were also quantitatively recovered by the TAN-XAD-4 column at the respective appropriate pH values. The plots of recovery *vs.* pH for silver and uranium followed a pattern of low recovery at low pH rising to approximately 100% as the pH increased. As the pH was raised further, however, the recoveries of these two elements decreased; it is in this respect that silver and uranium differed from the other seven elements which were completely recovered on the column.

The recovery of silver (Fig. 4.15) was particularly low in both weakly acidic (pH 3.0-5.0) and slightly alkaline (pH 8.0-8.5) solutions, but was quantitative (> 95%) over the pH range of 6.1-7.3. This is in good agreement with the quantitative extraction of Ag-TAN complexes into benzene at pH 7 as reported by Navratil [221]. The pattern of diminishing silver recovery as the pH is increased has been observed by Chung and Barnes

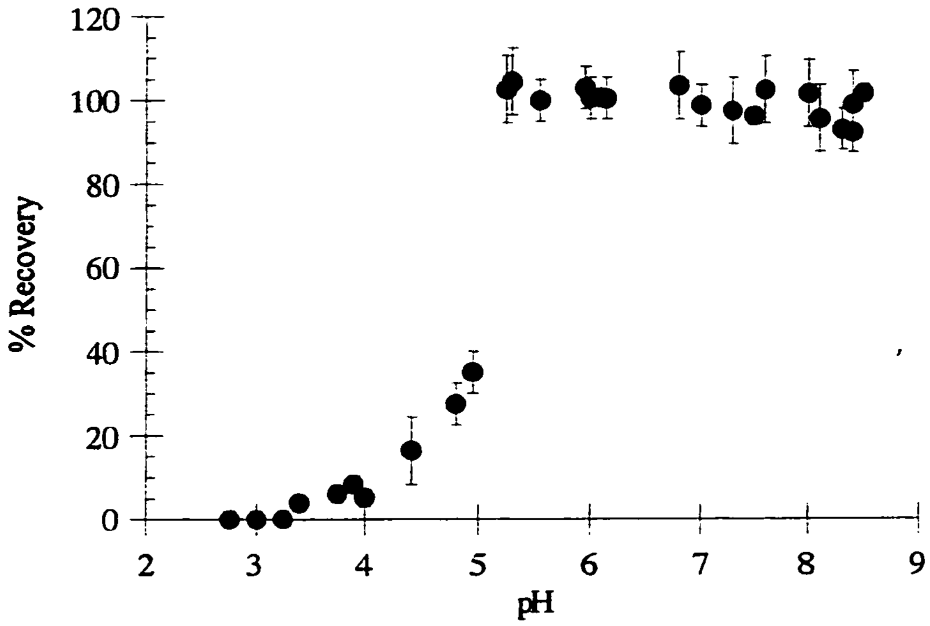


Figure 4.14. Recovery of Zn by TAN-XAD-4 as a function of pH.

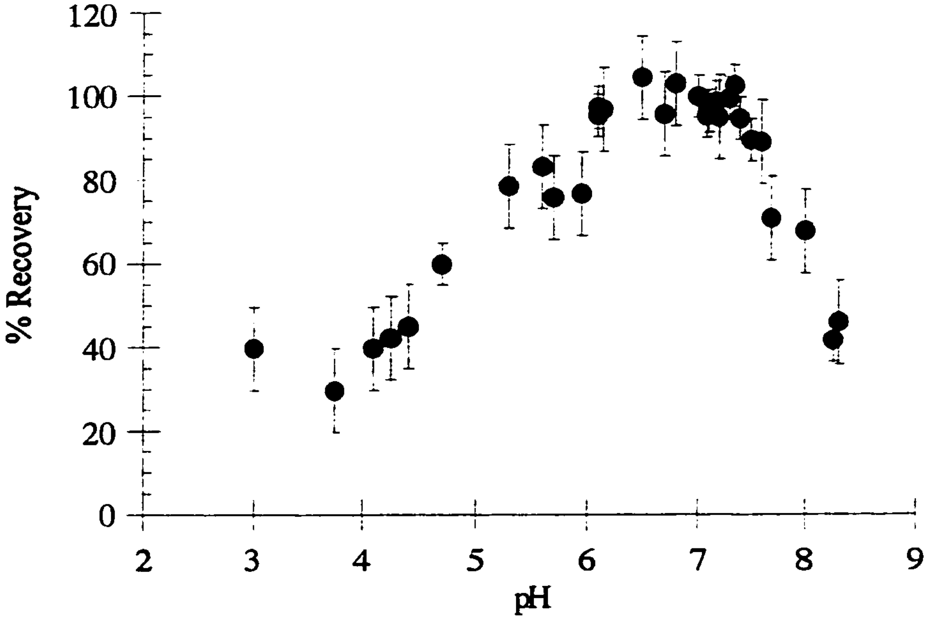


Figure 4.15. Recovery of Ag by TAN-XAD-4 as a function of pH.

[73], who collected silver on a column of PAN-loaded XAD-4 resin. The uptake of silver is nearly quantitative at pH 4, but drops off to approximately 20% at pH 6 and to less than 10% at pH 8.

It is possible that the poorer retention of silver by the TAN-XAD-4 resin is due to a competing side-reaction which precludes its collection on the column. Loss of silver due to the formation of hydrolysis products would not be expected, as silver (I) ion shows little propensity for hydrolysis in aqueous solution [304]. A more likely explanation is the presence of another complexing agent which competes with TAN.

The role of two buffers used in the experimental work, PIPES and TRIS, in the recovery of silver by the TAN-XAD-4 resin was evaluated using a tracer method. A sample of silver wire was subjected to a 7-h irradiation. The activated silver was dissolved in nitric acid and the resulting solution diluted with DDW to produce a solution containing 30.4 μg of silver in a 200-μL aliquot. The recovery of silver by the column was investigated using PIPES and acetate buffers. The tracer method permitted the use of sodium acetate, which would not have been feasible for the PNAA procedure. For solutions of elevated pH, a small amount of ammonia was added to the acetate solution to achieve the desired pH. The acetate buffer was chosen because of its ready availability and because the formation constants of the silver-acetate complexes are very low ($K_1 = 10^{0.4}$, $K_2 = 10^{-0.2}$ [305]).

The silver recovery in each buffer was determined following the procedure outlined previously. After passage of the sample solution through the column, the resin was rinsed into a medium vial with a small portion of the buffer solution and counted. As the acetate buffer was used at pH values well outside its useful buffering range, the pH of the effluent was measured in order to evaluate its stability. For the dilute silver solutions used, the acetate buffer could be used at pH as high as 7.35. The recoveries of silver from both acetate and PIPES are shown in Fig. 4.16.

In general, the recovery of silver from acetate buffer was at least 90% over the pH range 5.8-7.3, and was significantly higher than from PIPES buffer. The recovery of silver from PIPES buffer was nearly quantitative at pH 7.3, but was poorer in weakly acidic solution (< 60%) and at pH > 7.5. These inferior recoveries are most likely attributable to complexation of the silver ions in solution by some species present in the buffer. The PIPES buffer itself is comprised of a piperazine unit bearing two ethanesulfonic acid groups. Piperazine has some affinity for silver ($K_1 = 10^{3.40}$, $K_2 = 10^{2.64}$) [306] and these stability constants, coupled with the fact that the PIPES is present in very large excess (typically 0.05 M) suggest that the PIPES buffer may compete with the impregnated TAN for the silver ions.

The useful pH range for the PIPES buffer extends only as high as pH 7.5, so for more basic solutions, the desired solution pH was attained using tris(hydroxymethyl)-aminomethane (THAM, or "TRIS" buffer) and nitric acid. The trend of decreasing silver recovery with increasing pH continued as the pH was raised from 7.5 to 8.5. The THAM ligand also exhibits affinity for silver ion ($K_1 = 10^{3.14}$, $K_2 = 10^{3.43}$ [307]); it is presumably the presence of THAM which was responsible for the incomplete recovery of silver in this pH range.

The recovery of uranium (Fig. 4.17) was quantitative (> 95%) over the narrow pH range of 4.25-5.50. The recovery of uranium tailed off quite sharply on either side of this range, to less than 50% within 0.5 pH unit of the optimal range. As the pH increased, the

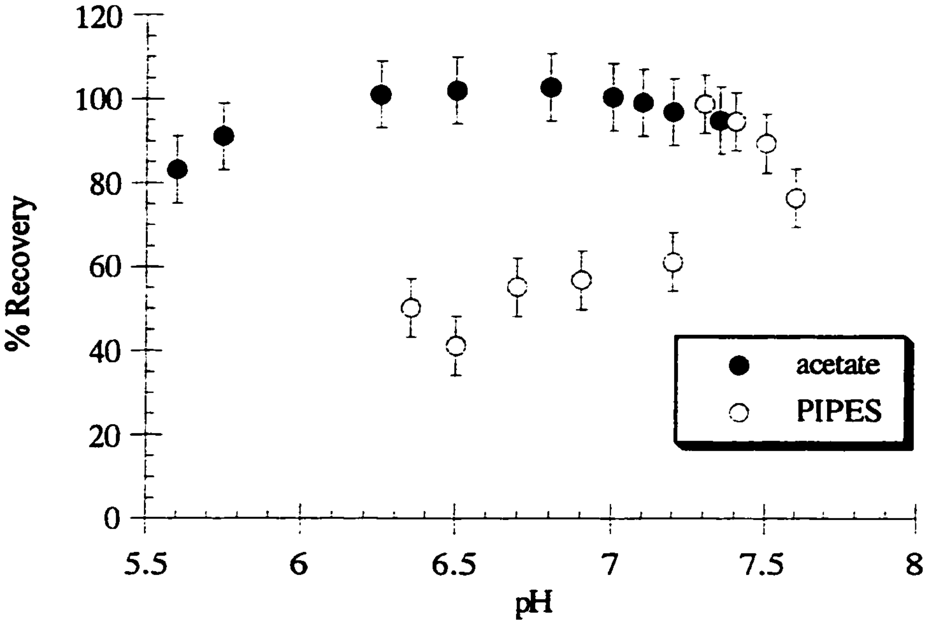


Figure 4.16. Recovery of Ag tracer by TAN-XAD-4 resin from acetate and PIPES buffers.

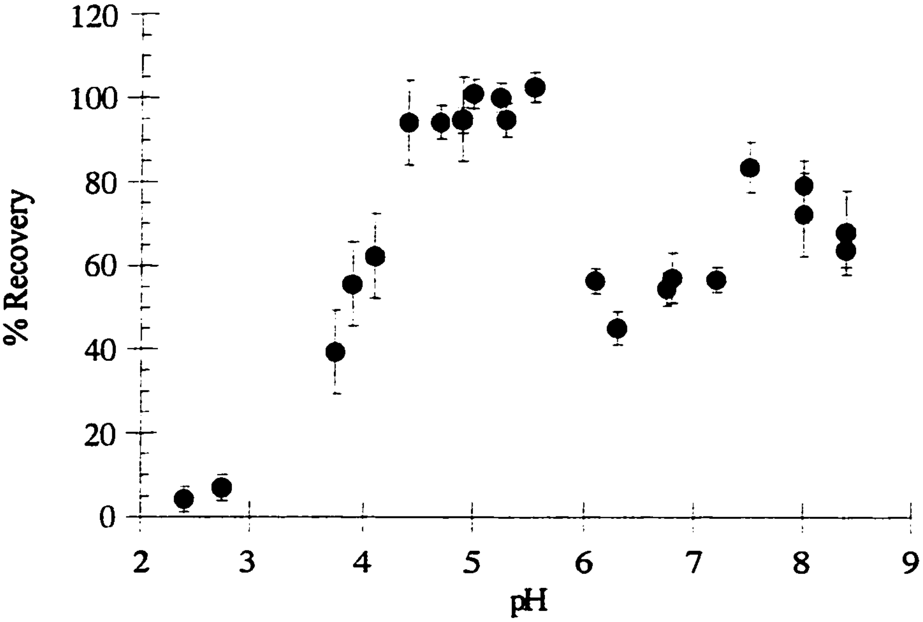


Figure 4.17. Recovery of U by TAN-XAD-4 resin as a function of pH.

uranium uptake increased again, to a local maximum of approximately 85% uranium recovery at pH 7.25.

In aqueous solution, uranium can exist in the 3+, 4+, 5+, and 6+ oxidation states. Of these, only U(IV) and U(VI) display any appreciable stability [308]. Hexavalent uranium is expected to predominate, given that the uranium standard was prepared in dilute nitric acid and taking into account the fact that U(VI) is very difficult to reduce.

Uranium(VI) reacts with TAN to form a 1:2 chelate which, when solubilized with surfactant, can be used for the spectrophotometric determination of uranium [58]. The optimum pH range for chelate formation and determination is 4.0-6.5, which is in good agreement with the results obtained in this study. The adsorption of uranyl ion on supports loaded with azo dyes has been studied previously. Vácha and Sommer [60] reported the quantitative recovery of uranium on XAD-4 resin loaded with PAN or TAN. The uptake of uranium is quantitative on the PAN-XAD-4 resin at pH 5.1 and on the TAN-XAD-4 resin over the pH range 5.0-8.5. Ueda *et al.* [59] prepared nine reversed-phase resins by loading azo dyes on silica gel. The column recovery of trace uranyl ion, as reported for solution of pH 6, is 100% for PAN-loaded silica gel and 93% using TAN as the active component.

Uranium(VI) is present in solution as the highly stable uranyl ion, UO_2^{2+}, at pH $\leq$ 2.5. At higher pH, hydrolysis products are formed, although the exact composition of a solution of U(VI) in neutral and alkaline media is not clear. Several hydrolyzed forms, including $UO_2(OH)^+$, $U_2O_5^{2+}$, $U_3O_8^{2+}$, and $U_3O_8(OH)^+$ are assumed to be present [309]. Some of these species may account for the increased recovery of uranium from pH 7.5 to 8.5. It is also possible that U(VI) forms complexes with the buffer at this pH range.

None of the other elements investigated in this study were quantitatively retained by the TAN-XAD-4 resin as any pH value. Arsenic (Fig. 4.18) was poorly retained by the TAN-XAD-4 resin; approximately 50% of trace arsenic was retained at pH 5.8-7.2. The resin also showed little tendency to chelate antimony, as its recovery was essentially negligible over the entire pH range studied.

Gold (Fig. 4.19) was favorably recovered in acidic media (approximately 80% recovery at pH 5) but poorly retained from neutral and weakly alkaline solutions. Although the recovery of gold by the resin was essentially negligible at pH 8.0, there appeared to be a trend of increasing recovery as the pH was increased from 8.0 to 8.5. The quantitative extraction of an Au(III)-TAN complex into benzene from aqueous solution of pH > 10 has been reported [221], so it is possible that the efficiency of the TAN-XAD-4 resin for gold could be improved by increasing the pH further.

In mildly alkaline media, Au(III) is susceptible to hydrolysis which may explain the poor recovery of gold at pH 7-8. At still higher pH, the addition of ammonia yields the stable complex ion $[Au(NH_3)]^{3+}$. Predominance of this cationic species could lead to more efficient recovery of gold by the ligand-impregnated resin as the pH is increased.

The plot of recovery of chromium as a function of pH is shown in Fig. 4.20. The column extracts a maximum of 60% trace chromium at pH 5.8. The metal is not retained at pH < 4, and is only partially retained (40-60%) at pH > 5.

In aqueous solution, chromium mainly exists in two stable oxidation states, namely Cr(III) and Cr(VI). At low pH, Cr(VI) is a powerful oxidant and Cr(III) predominates. In weakly acidic, neutral, and alkaline solution, both oxidation states are stable.

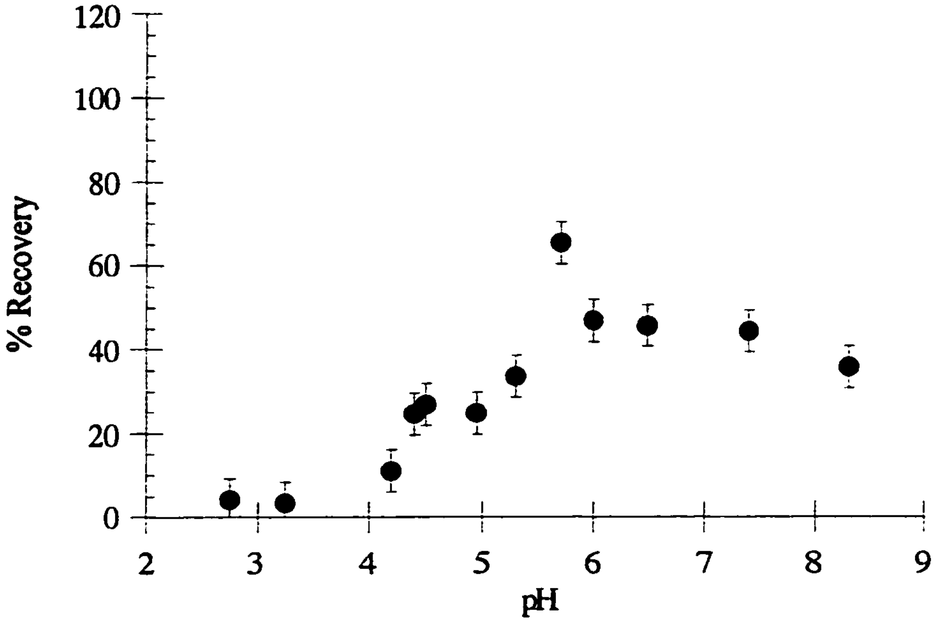


Figure 4.18. Recovery of As by TAN-XAD-4 resin as a function of pH.

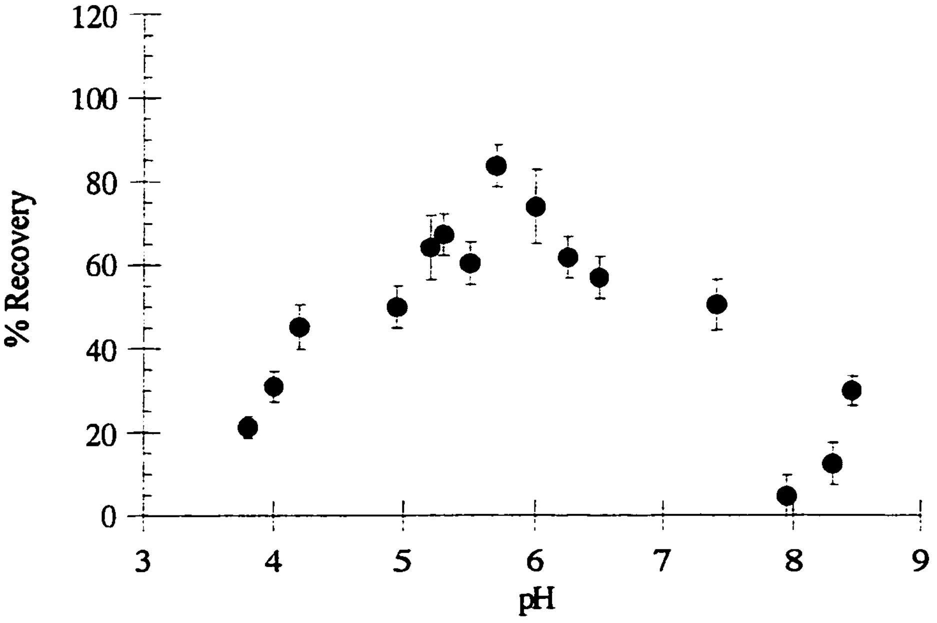


Figure 4.19. Recovery of Au by TAN-XAD-4 resin as a function of pH.

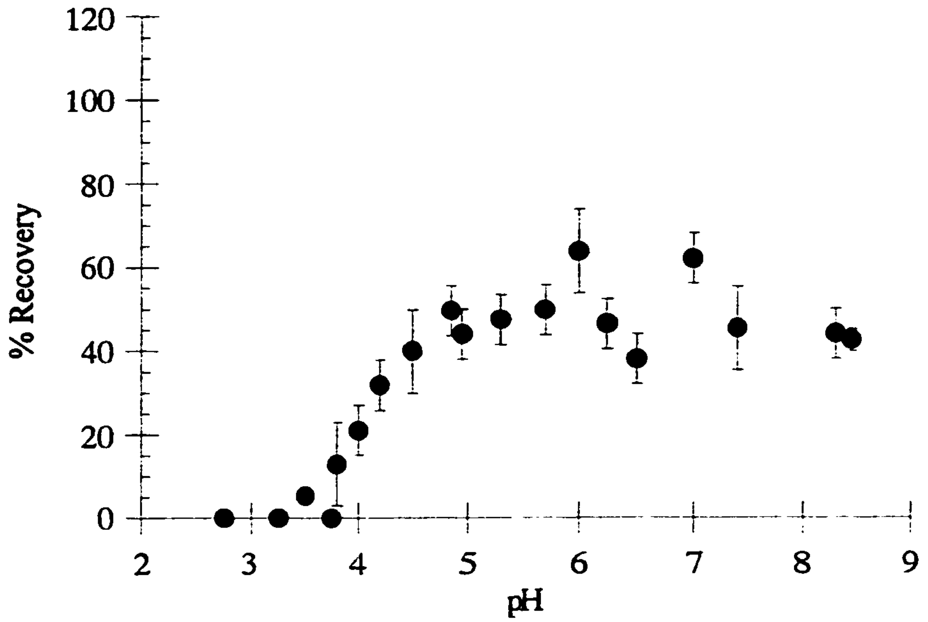


Figure 4.20. Recovery of Cr by TAN-XAD-4 resin as a function of pH.

Schroeder and Lee [310] reported that in buffer solutions of pH 5.9 or greater containing Cr(III), some of the Cr(III) was slowly oxidized to Cr(VI).

Over the pH range of 3.5-8.5 studied in this work, Cr(VI) can exist as either CrO_4^{2-} or $HCrO_4^-$ ions. Chromate ion, CrO_4^{2-}, is expected to predominate in neutral and alkaline solution, while $HCrO_4^-$ is the major species at pH < 5 [311,312]. Neither of these anionic species should exhibit any tendency to form complexes with TAN-XAD-4.

The major impediment to the extraction of Cr(III) by the TAN-loaded resin is the fact that aquo-complexes of Cr(III) are characterized by their inertness [154,313] and are correspondingly resistant to formation of chelates. Chromium(III) reacts with PAN at pH 3.2-3.7 [314] and with TAN at pH 5.7 [250], and these reactions have been exploited in the spectrophotometric determination of Cr(III) in water. In both cases, however, the reactions were carried out at temperatures greater than 80°C in order to overcome the inertness of Cr(III) at room temperature. It would therefore be expected that under normal experimental conditions that the TAN-XAD-4 column would not completely extract Cr(III), as the Cr(III)-TAN chelate would not form at room temperature.

Under the assumption that the TAN-loaded resin will not collect Cr(VI), it follows that the partial recovery of chromium by the RPEC method is a result of collection of Cr(III) by the column. Since it not probable that a Cr(III)-TAN complex will form at room temperature, it remains to be explained why any chromium was collected on the resin. The simplest explanation could be that Cr(III) was simply sorbed onto the column rather than chelated by the ligand. Schroeder and Lee [310] noted that the rate of sorption of Cr(III) onto solids was much faster than the rate of oxidation of Cr(III) to Cr(VI).

Another possibility involves the role of the buffer or complexing agents in the recovery of chromium by the resin. For example, Pasuellan and co-workers [154] investigated the retention of chromium on solid supports bearing immobilized iminodiacetate groups or oxine. The recovery of Cr(III) on the columns is negligible in the absence of auxiliary complexing agents, but quantitative over narrow ranges of pH when 0.1 M acetate was added.

The mechanism of retention notwithstanding, the quantitative uptake of chromium by the TAN-XAD-4 column does not appear to be possible, and certainly not without a reduction step to convert all chromium to the trivalent state, so analysis of chromium in water by this method is probably not feasible. Furthermore, the sensitivity of NAA for chromium is rather poor (approximately 400 counts μg^{-1} for a 7-h irradiation and 2-h count), so even if quantitative recovery of chromium by the resin were achieved, it is unlikely that the RPEC method would yield worthwhile results in the analysis of trace chromium in real water samples. As a result, the optimization of the preconcentration method for chromium was not pursued further.

The recovery of thorium (Fig. 4.21) was low at pH < 4, rose steadily as pH increased to a maximum value of 70% at pH 6.25, and fell as the solution became more basic. Thorium was not collected at all at pH ≥ 8.

Sharma and Eshwar [57] reported a method for the spectrophotometric determination of thorium in water. At pH 2.4 - 2.8, Th(IV) has been reported to form a chelate with TAN which is soluble in a methanol-water mixture. The metal to ligand ratio is 1:2 under these conditions. The results obtained in this thesis, however, indicate that the

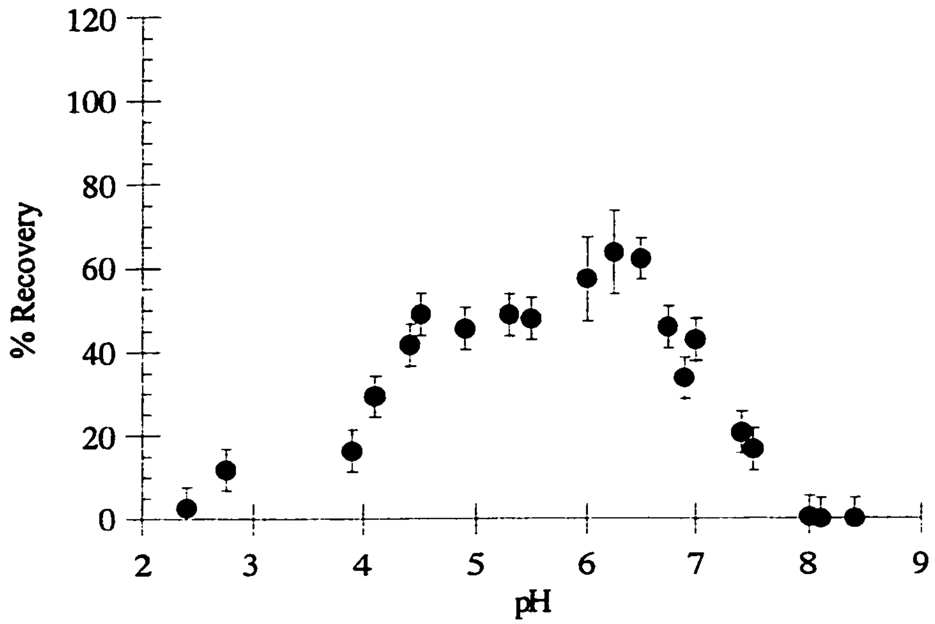


Figure 4.21. Recovery of Th by TAN-XAD-4 resin as a function of pH.

TAN-XAD-4 column displayed little affinity for thorium at pH < 4.

Vanadium (Fig. 4.22) was poorly retained over the entire pH range studied. The recovery of vanadium was very poor at pH < 3 and pH >7.5, and attained a peak value of only 45% around pH 5. Vanadium may exist in all of the oxidation states from 1- to 5+ [315] of which V(IV) and V(V) are stable in aqueous solution [316]. In aerated water, vanadium is most likely present in the pentavalent form [317], although Cole *et al.* [318] noted that a standard solution prepared by dissolving high-purity vanadium in nitric acid contains both V(IV) and V(V), with the composition of the mixture changing with time. In the present work, since the spiked buffer solutions were prepared (by adding an aliquot of acidified multielement solution to the buffer) and subjected to the column separation procedure the same day, it is assumed that the vanadium present in the spiked buffer solutions was primarily V(V).

Vanadium(V) exists as the dioxovanadium(V) ion (VO_2^+) in acidic media and as the vanadate ion (VO_4^{3-}) in strongly basic solution [312]. In neutral and mildly basic media, trace vanadium likely exists as protonated vanadates (HVO_4^{2-} or $H_2VO_4^-$) [319] or as VO_3^- [312]. It would not be expected that these anionic species would react with a complexing agent such as TAN.

Chelating agents should display a greater affinity for VO_2^+, which is stable in more acidic media. This behavior has been observed in the formation of a V-TAN complex in solution. Eshwar and Sharma [245] reported a method for the spectrophotometric determination of vanadium using TAN. At pH 2.0-2.5, V(V) forms a 1:1 complex with TAN which is insoluble in water but soluble in a methanol-water solvent. Bermejo-Berrera and co-

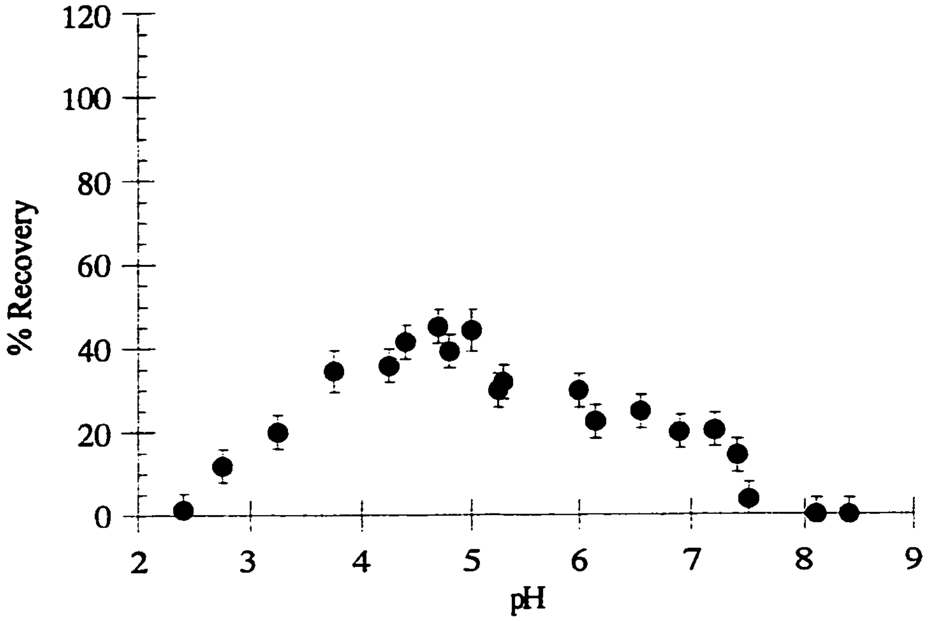


Figure 4.22. Recovery of V by TAN-XAD-4 resin as a function of pH.

workers [320] reported similar findings in the extraction of V(V) using oxine. The optimum pH for the extraction of chelate is 2.8-3.3, with the efficiency of the extraction falling off dramatically at pH > 3.5. Contrary to these reports, the TAN-XAD-4 column, while exhibiting poor recovery for vanadium at any pH, displayed little affinity for vanadium at pH < 3 (recovery was less than 20%).

The pH behavior of the elements investigated in this work is summarized in Fig. 4.23. There are two regions which merit consideration. Ranges of pH in which the recovery of a particular element is quantitative (*i.e.* 90% or greater) provide information regarding the elements could be successfully preconcentrated and the conditions required for this to take place. Regions of pH in which a given element is not retained by the resin (*i.e.* recovery is < 10%) are useful if separations of elements are to be considered.

The purpose of this project was to develop a preconcentration method for the simultaneous multielement analysis of water samples. It has been shown that at an optimum pH range of 8.0-8.5, cadmium, cobalt, copper, mercury, manganese, nickel, and zinc were completely retained by the column. Silver and uranium could also be quantitatively recovered on the TAN-XAD-4 column at the appropriate pH.

Other factors influencing the recovery of trace elements from solution, such as flow rate and column height, were also investigated. These optimization studies are described in the following four sections. Preliminary studies involving only a few elements had ascertained that cobalt, copper, and zinc were completely extracted at pH > 5.5. When only those elements were under investigation, the optimization experiments were performed in the pH range 6.0-7.0. Otherwise, optimization experiments were carried out at pH ≥ 8.0

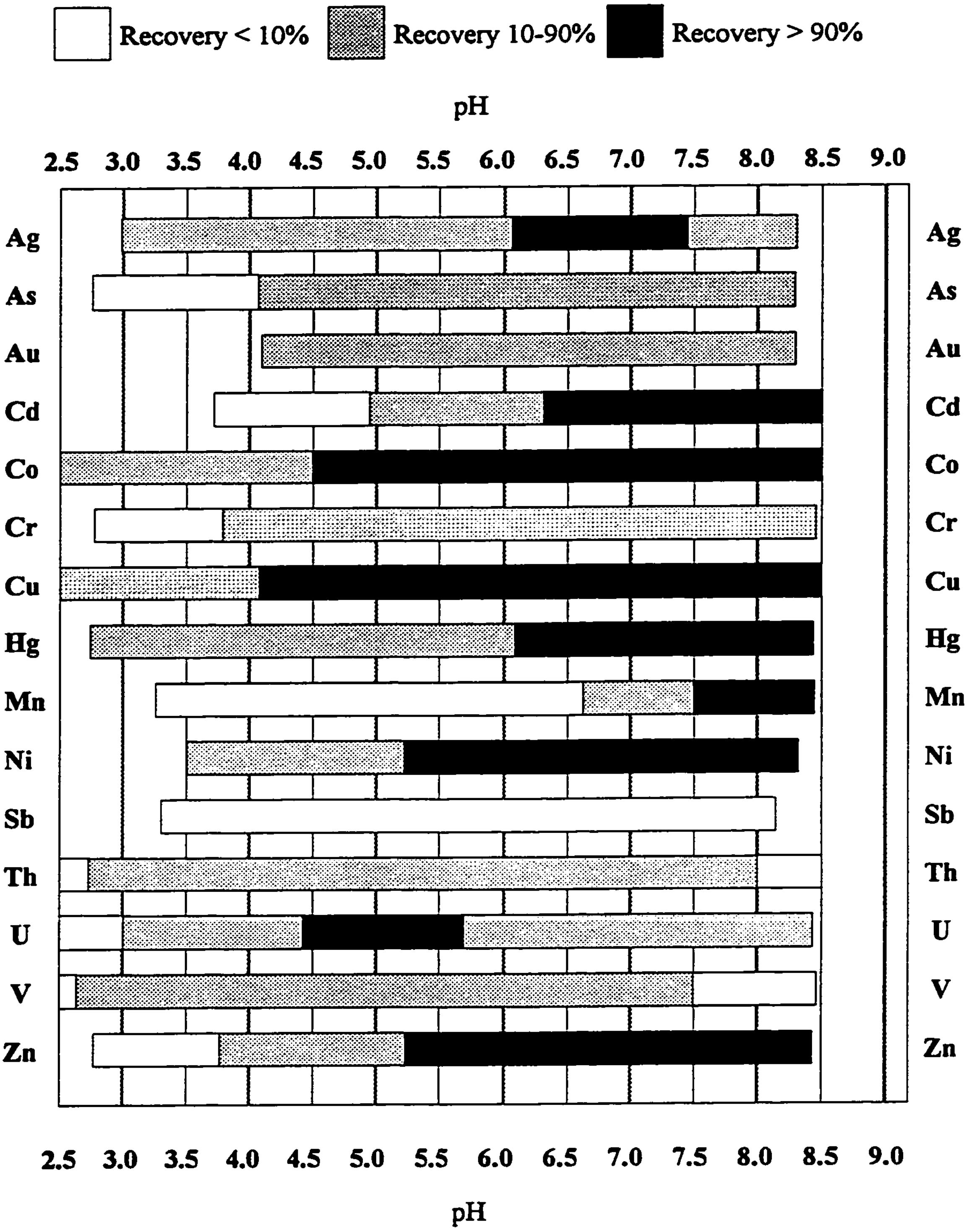


Figure 4.23. Summary of trace element retention by TAN-XAD-4 resin.

in an attempt to maximize the number of elements to be investigated.

4.9. Effect of Flow Rate

The effect of flow rate on the extraction of trace elements from spiked buffer solutions was investigated over the range of 0.3-10.0 mL min^{-1}. Three elements, namely cobalt, copper, and zinc, were tested to select the optimal flow rate. The general procedure is as follows. A 200-μL aliquot of stock multielement solution containing cobalt, copper, and zinc was added to 100 mL 0.05 M MES buffer and adjusted to pH 6.00. The recovery of each element was evaluated in triplicate at each flow rate, and the results are presented in Table 4.10.

The resin proved to be effective in the removal of trace elements at flow rates as high as 10.0 mL min^{-1}. The uptake of cobalt, copper, and zinc was quantitative over the range of flow rates investigated. These results are consistent with those reported earlier for TAN-XAD-4. Vácha and Sommer [60], for example, collected trace uranium from aqueous solution on TAN-impregnated XAD-4 resin, and reported quantitative recovery for uranium at flow rates from 15 to 18 mL min^{-1}. Porta and co-workers [66] described the preconcentration of six trace metals from river water on a microcolumn of TAN-XAD-2 at a flow rate of 10 mL min^{-1}.

The presence of TAN in the effluent was checked spectrophotometrically to estimate the amount of TAN bleeding off the column. It was confirmed that there was no loss of the chelating agent into the mobile phase even at the elevated flow rates of up to 10 mL

Table 4.10. Recovery of Co, Cu, and Zn as a function of flow rate. Conditions: pH 6.00, column dimensions = 50 mm x 7 mm i.d.

Flow Rate	Percent Recoveries of Elements		
(mL / min)	Co	Cu	Zn
0.3	97 ± 4	98 ± 4	96 ± 6
0.4	101 ± 6	102 ± 3	96 ± 7
0.5	100 ± 4	103 ± 3	95 ± 5
1.0	101 ± 4	100 ± 4	97 ± 6
1.4	102 ± 4	104 ± 5	95 ± 5
1.8	100 ± 5	101 ± 5	99 ± 6
3.0	99 ± 5	100 ± 3	100 ± 6
4.4	94 ± 8	105 ± 5	96 ± 7
5.0	102 ± 5	98 ± 4	94 ± 5
10.0	93 ± 8	96 ± 6	97 ± 5

$\min^{-1}$. Therefore, a high flow rate can be recommended when large-volume samples are to be processed.

4.10 Effect of Column Height

The minimum quantity of resin required to ensure quantitative extraction of trace elements was determined in three separate experiments. In the first study, a 200-μL aliquot of stock copper solution (containing 10.0 μg Cu) was added to 100 mL of 0.05 MES buffer and adjusted to pH 6.0. The buffered copper solution was passed through a column of TAN-XAD-4 resin, packed to variable height in the Bio-Rad Econo-Column of 7 mm i.d. The resin was then washed with pH 6.0 buffer and dried by passage of air through the column. To ensure uniform counting geometry, the height of the column was normalized by adding clean and dry XAD-4 resin to the column so that the column height of each sample was 59 to 61 mm. The resin was then transferred to a medium-size polyethylene vial, mixed thoroughly, and irradiated. The copper uptake was evaluated using a timing scheme of t_i:t_d:t_c = 10:1:10 min and the 1039.2-keV signal of ^{66}Cu. The results of this work are shown in Fig. 4.24.

The experiment was repeated using cobalt (a 200-μL aliquot containing 0.4 μg Co). The solution was adjusted to pH 8.4 with TRIS buffer and 1M NH_3 prior to passage through the column. The cobalt retention was determined using the same timing parameters as for the copper experiment and the 58.6-keV photopeak of ^{60m}Co. The results of this work are shown in Fig. 4.25.

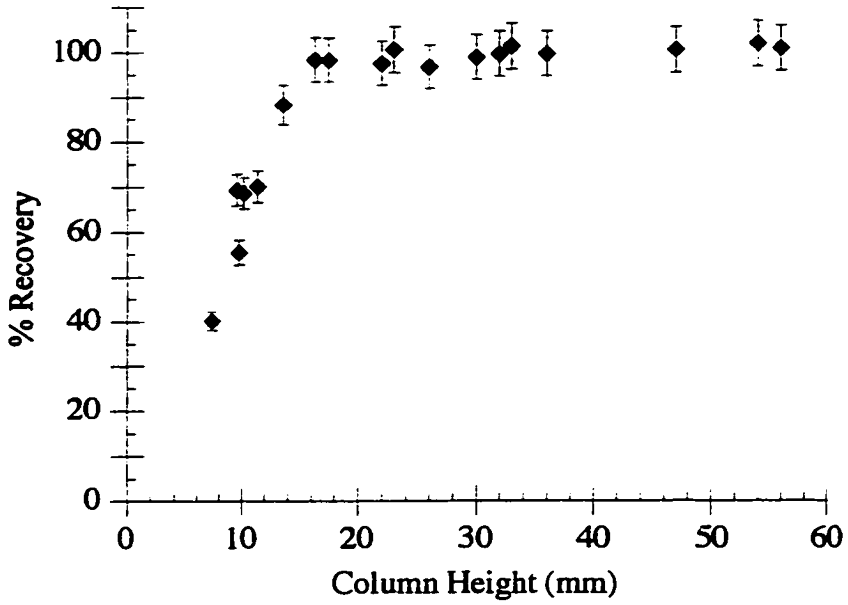


Figure 4.24. Cu recovery by TAN-XAD-4 resin column as a function of column height.

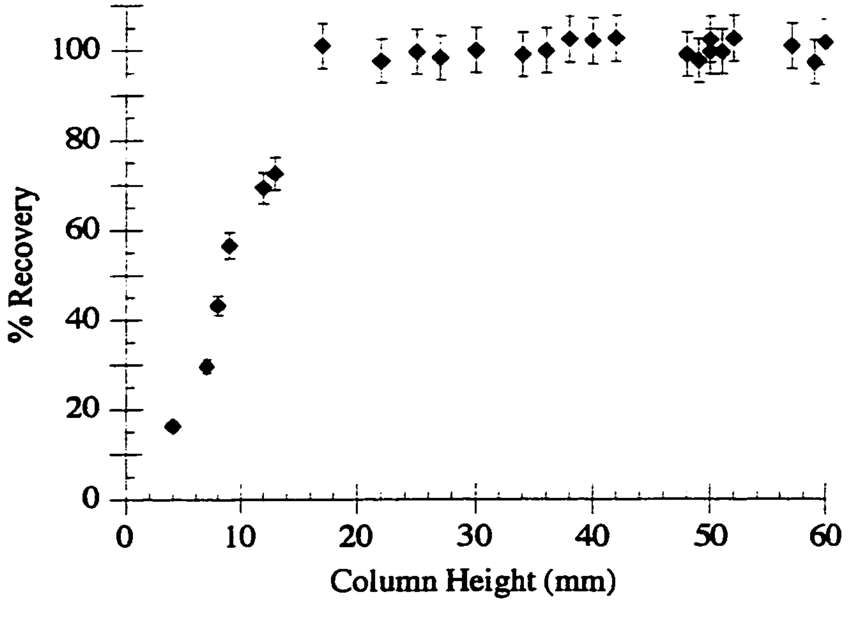


Figure 4.25. Co recovery by TAN-XAD-4 resin column as a function of column height.

For each experiment, the recovery of the element of interest was quantitative for a column height greater than 20 mm. The relative retention of each element tailed off sharply as the quantity of coated resin fell below 15 mm. For most further experiments, a column height of 50 mm was utilized to ensure that all elements can be retained even if they were present at significantly higher concentrations. For some experiments in which elements with long-lived nuclides were investigated, a 34-mm resin column was used; this smaller quantity represents the upper limit of resin which can be contained in a small irradiation vial. Since two small vials can be housed and irradiated in a medium vial, this is desirable for long irradiations in order to maximize the number of samples irradiated at one time.

A third experiment was performed using a multielement stock solution containing cobalt, copper, and zinc. The spiked solution was buffered to pH 6.00 and passed through the column of TAN-XAD-4. The column used in this experiment was a polyethylene irradiation vial (i.d. = 14 mm) with the bottom cut out. This column was fitted with a glass frit and connected to the sample reservoir with plastic fittings, as shown in Fig. 4.26. The fittings were made in-house, and designed to allow this column to be interchangeable with the Bio-Rad column depicted in Fig. 3.2. The quantity of the three trace elements was evaluated using two irradiation schemes, namely t_i:t_d:t_c = 10:1:10 min for the short-lived nuclides of cobalt and copper and t_i:t_d:t_c = 7:24:1 h for the analysis of zinc by the ^{69m}Zn nuclide. The uptake of these elements was evaluated for columns ranging in height from 10 to 50 mm.

The results, presented in Table 4.11, indicate that the trace metal uptake was quantitative for columns of height as low as 10 mm. This height in the polyethylene vial column (Fig. 4.26) corresponds to a 40-mm height using the Bio-Rad column of 7 mm i.d.

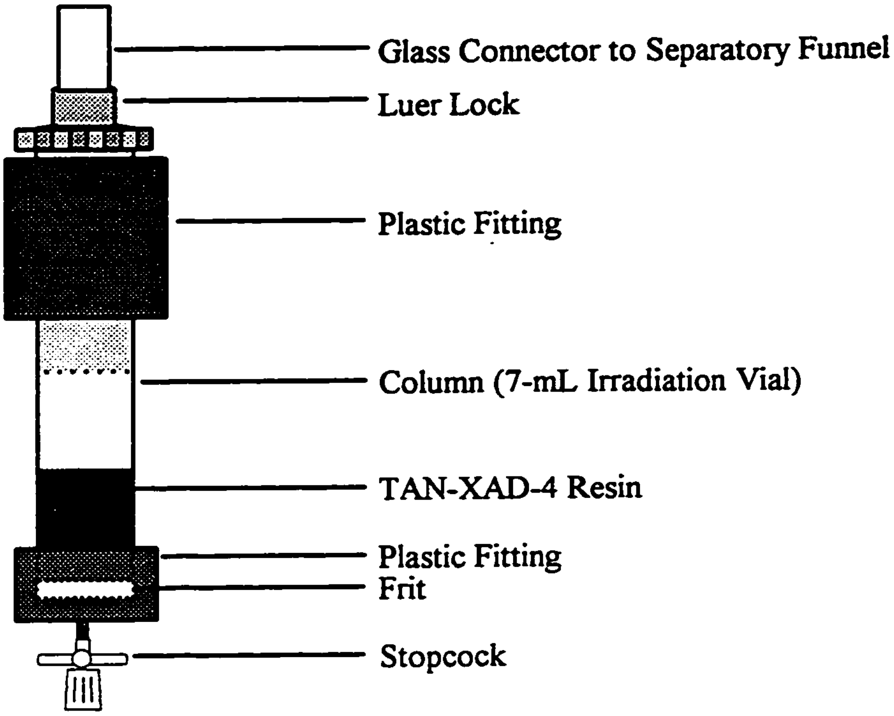


Figure 4.26. Column apparatus incorporating an irradiation vial as the column.

Table 4.11. Recovery of Co, Cu, and Zn as a function of column height. Conditions: pH 6.00, flow rate = 1.0 mL min^{-1}, column diameter = 14 mm

Column Height (mm)	Percent Recoveries of Elements Co	Cu	Zn
10	94 ± 8	101 ± 7	102 ± 7
15	99 ± 5	96 ± 4	100 ± 6
20	98 ± 5	99 ± 2	97 ± 5
25	94 ± 4	97 ± 8	97 ± 7
30	103 ± 5	98 ± 6	94 ± 5
40	97 ± 6	99 ± 5	102 ± 4
50	101 ± 4	100 ± 4	95 ± 6

(Fig. 3.2), and is thus consistent with the results of the single-element experiments described previously.

4.11 Effect of Particle Size

Resins of three different particle size ranges, namely 20-60, 60-100, and 100-200 mesh, were evaluated. Attempts to use resins of 100-200 mesh were not successful as the powder did not sink in water and proved difficult to handle due to its adherence to the glassware; this resin was not used in further experiments. A resin sample using 60-100 mesh grains could be used, although only after the finer particles were removed by flotation.

The effect of resin grain size on the extraction efficiency of TAN-XAD-4 was investigated at pH 6.10. A multielement solution was prepared and passed through the columns as previously described. Three replicates were run for each of the 20-60 mesh and 60-100 mesh resins. The recoveries for the elements studied are shown in Table 5.12.

The uptake of cobalt, copper, and silver was quantitative for both resins investigated. A comparison of the performance of the resins with respect to uranium and vanadium shows that while not consistent, the elemental recoveries were reproducible from one resin sample to the next. In contrast, the recovery of thorium was significantly improved when the elements were collected on the finer resin particles. The thorium recovery improved from 59% to 83% with the implementation of the finer resin particles. The latter figure represents a higher recovery of thorium than had been observed over the entire pH range investigated for the 20-60 mesh TAN-XAD-4 resin.

Table 4.12. Elemental recovery as a function of particle size. Conditions: pH 6.10, column dimensions = 50 mm x 7 mm i.d. (20-60 mesh), 20 x 14 mm i.d. (60-100 mesh), flow rate = 1.0 mL min^{-1}.

	Percent Recoveries of Elements	
Element	20-60 mesh	60-100 mesh
Ag	97 ± 4	103 ± 5
Cd	92 ± 6	88 ± 7
Co	95 ± 6	101 ± 8
Cu	102 ± 4	93 ± 5
Th	59 ± 5	83 ± 7
U	39 ± 7	36 ± 8
V	23 ± 6	28 ± 7
Zn	102 ± 6	95 ± 9

The use of the 60-100 mesh resin suffered from a major drawback. Initial attempts to evaluate the uptake of trace elements by the 60-100 mesh TAN-XAD-4 resin failed because the powder could not be quantitatively transferred into an irradiation vial. The powder adhered to the glass column, the frit, and stirring rods and spatulas used for removal from the column. Once transferred to a polyethylene vial, the powder adhered to the walls of the vial, making reproducible sample geometry impossible.

In order to avoid these problems, samples were run using the medium vial column apparatus as shown in Fig. 4.22. After sample passage and washing of the resin, the vial was capped at both ends, heat-sealed, and placed in a large vial for outer-site irradiation. While this modification was an improvement over the earlier attempt to transfer the powder from column to vial, the sample geometry was not as reproducible as was the case when samples were placed in a regular (*i.e.* uncut) vial. Furthermore, when the double-capped vial was used, the sample sat a few mm further away from the detector than when a regular vial was used, thereby lowering the observed count rates.

Because of the problems encountered in handling the 60-100 mesh resin, its use was not continued. The major difficulties, however, lay in the steps following passage of the sample and washings through the column, such as drying of the resin and its transfer to a vial for irradiation. These problems could be avoided by eluting the elements from the column prior to analysis, thereby eliminating the sample transfer step. The use of resin samples of smaller particle size merits further study, especially when the preconcentration step is to be coupled with an instrumental method such as AAS or ICP-MS in which the elements of interest are eluted from the column. However, as it has been pointed out earlier, elution can increase the possibility of contamination and may lead to an irreproducible recovery. Analysis of the elements while still on the resin is preferable.

4.12 Recovery of Trace Elements from Solutions of High Salinity

It has been previously established that aside from concentrating the elements of interest, the most important function of the preconcentration step is the removal of elements which may interfere in the analysis. To this point, the trace elements concentrated by the RPEC method have been removed from spiked buffer solutions prepared in DDW; these samples contained substantially lower quantities of potentially interfering elements than seawater. Even non-saline water samples (such as lake, ground, and tap water) contain much higher levels of sodium, magnesium, and other interfering elements than the spiked buffer solutions used in this work.

It is therefore necessary to evaluate the performance of the RPEC method when interfering elements are present. Sample solutions were prepared as previously described for the optimization of pH. The solutions were buffered to pH 8.4 with TRIS buffer. To each sample was added a 10-mL aliquot of a multielement solution containing sodium, magnesium, chlorine, and bromine. This multielement solution was prepared so that the 100-mL sample solution contained these four elements in concentrations similar to that found in seawater. Three sets of samples were processed; each set consisted of three spiked samples and one sample blank.

The first factor to consider in evaluating the utility of the RPEC method was the minimum number of aliquots of fresh buffer required to reduce the concentration of the interfering elements to manageable levels. After passage of the sample, the column was washed with seven 10-mL portions of fresh pH 8.4 buffer. The effluent was collected in 10-mL fractions, and a 1-mL sample was drawn from each and put in a small polyethylene vial for irradiation. The 1-mL liquid samples were analyzed by INAA, in order to determine the concentration of sodium, magnesium, bromine, and chlorine in each fraction.

The concentrations of sodium, chlorine, magnesium, and bromine were determined for each of the seven fractions of effluent, and the results are presented in Figs. 4.27 to 4.30, respectively. The results show similar trends for all four elements. Sodium and chlorine were present at mg mL^{-1} levels in the first fraction. Bromine and magnesium were present at lower concentrations (62 and 122 ppm, respectively), which is consistent with the fact that the initial concentrations of these elements were one to two orders of magnitude lower than sodium and chlorine. The second fraction contained significantly less sodium and chlorine than the first, with concentrations in the ppm range; the concentration of magnesium and bromine was reduced to below 3 ppm. The third fraction contained approximately 20% of sodium and chlorine as was present in the second fraction, and the levels of bromine and magnesium were reduced below 1 ppm. For the fourth and subsequent fractions of effluent, the concentrations of all four elements were approximately constant, although the trend of decreasing elemental content with successive portions of buffer continued.

Based on these results, it is recommended that at least four 10-mL portions of fresh buffer should be used in order to ensure that the levels of interfering elements on the column are sufficiently low. As a precaution, when utilizing the RPEC method coupled with

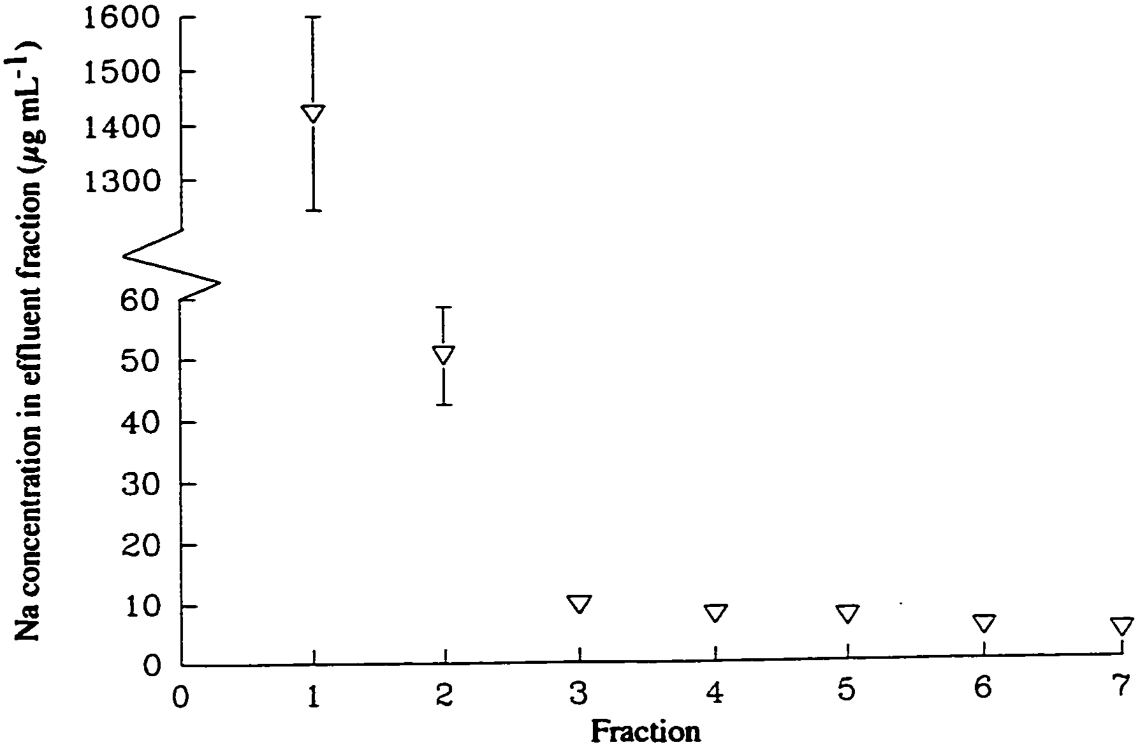


Figure 4.27. Sodium content of effluent fractions.

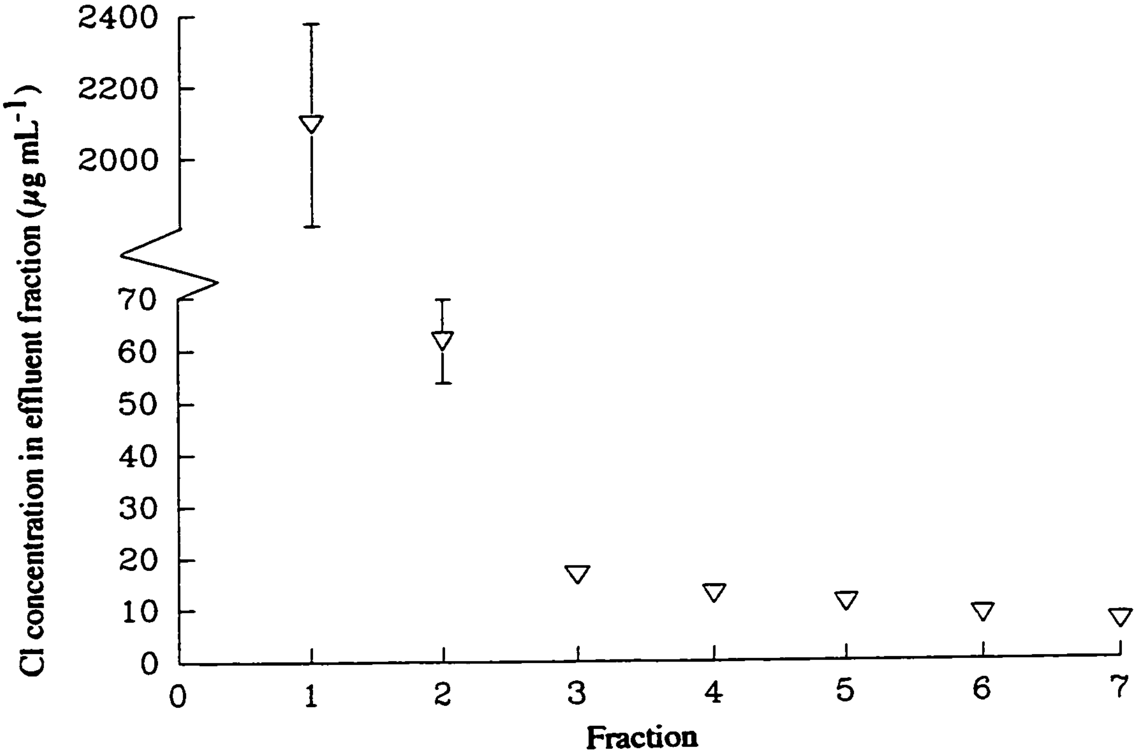


Figure 4.28. Chlorine content of effluent fractions.

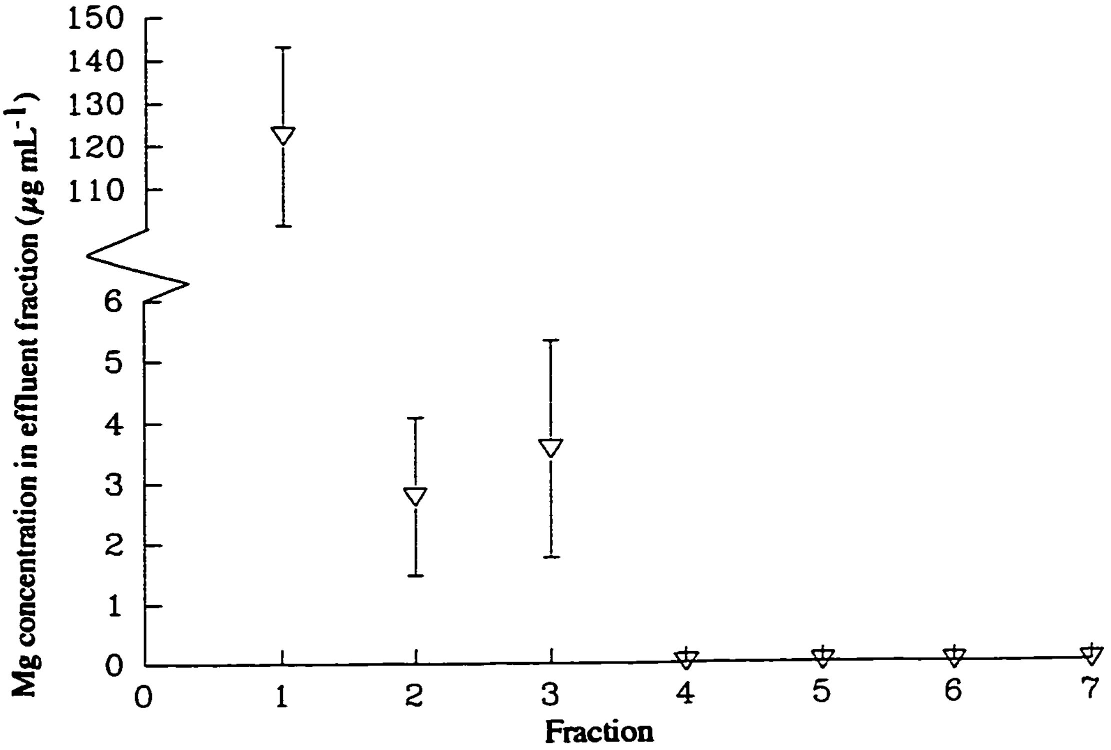


Figure 4.29. Magnesium content of effluent fractions.

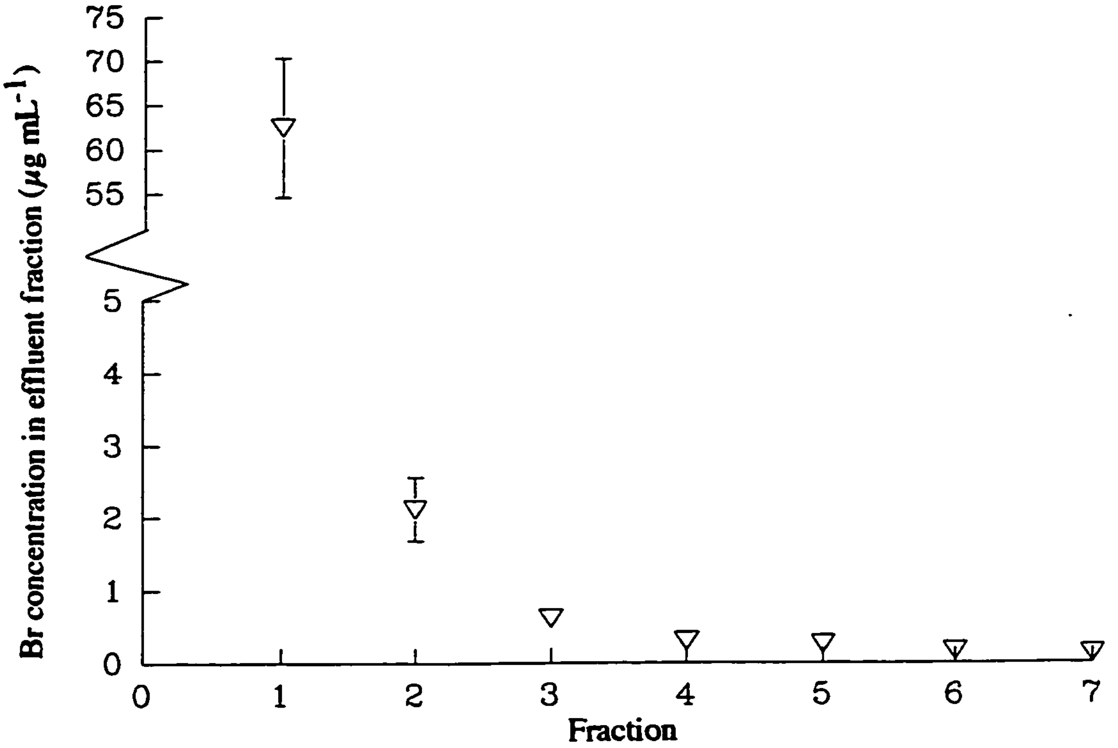


Figure 4.30. Bromine content of effluent fractions.

NAA for the analysis of saline samples, a 1-mL aliquot of effluent was analyzed prior to drying the column and transferring the resin beads to an irradiation vial. The absence of elevated levels of sodium and chlorine in the effluent signalled that the column had been effectively stripped of these elements.

Once the levels of elemental contamination in the effluent had been minimized, the levels of these elements still present on the resin were evaluated by NAA. It is of utmost importance that the levels of these elements, particularly sodium, be low enough that the analysis of the elements of interest is not impeded. The resin samples were subjected to a 10-min irradiation; elements of interest were quantified after 1-min decay and 10-min counting periods. The results of the analysis for bromine, chlorine, magnesium, and sodium are given in Table 4.13, in terms of the number of counts and the mass of the element found on the resin. Magnesium was not detected (*i.e.* there was no gamma-ray of either at 843.8 keV or 1014.4 keV of ^{27}Mg), and the quantities of the other three elements were found to be acceptably low.

The final and most important consideration in the evaluation of the RPEC method is the efficiency of the TAN-XAD-4 column in the extraction of trace elements of interest from solutions of high ionic strength. Based on the pH optimization studies, it would be expected that cadmium, cobalt, copper, manganese, nickel, and zinc would be extracted from the column at pH 8.4. The percentage recoveries of these elements are given in Table 4.14. The results show that all six elements were quantitatively retained on the column. This proves that the preconcentration method was effective in the very important application of separating trace elements of interest from the majority elements present in saline samples.

Table 4.13. Levels of potentially interfering elements on TAN-XAD-4 resin after passage of spiked artificial seawater.
N= 10; pH = 8.4; Flow Rate = 1.0 mL min-1; column 50 mm x 7 mm i.d.

Element	Counts	Mass Element (µg)
Br	1466 ± 132	1.12 ± 0.13
Cl	3410 ± 335	1.85 ± 0.22
Mg	ND	ND
Na	396 ± 57	2.69 ± 0.43

Table 4.14. Recovery of trace elements of interest from artificial seawater on TAN-XAD-4 resin.
N= 10; pH = 8.4; Flow Rate = 1.0 mL min-1; column 50 mm x 7 mm i.d.

Element	Percent Recovery
Cd	95 ± 5
Co	101 ± 5
Cu	96 ± 6
Mn	94 ± 7
Ni	96 ± 8
Zn	97 ± 6

4.13 Internal Quality Assessment

In the analysis of a sample of unknown composition, the validity of a reported value is dependent on many steps that are involved in the analysis, from experimental planning through sampling and sample handling, measurement, standardization and calibration, to reporting of results [321]. The uncertainty of the final reported result is dependent on the uncertainties in each analysis step. For the purpose of this work, discussion will be limited to sample pretreatment and subsequent analysis.

The ability of an analytical laboratory to generate valid results is based upon the implementation of a quality assurance program, the importance of which has been stressed by several authors [321-323]. The discussion of quality assurance incorporates two concepts: quality control, the experimental procedures undertaken in order to keep errors under control [323,324], and quality assessment, the means of expressing or displaying that the quality control procedures have been carried out effectively [325]. Quality assessment can be further subdivided into internal quality assessment, pertaining to the precision of measurements of an analyte within a single laboratory, and external quality assessment, which deals with the accuracy of the results. Both internal and external quality assessments of trace element measurements in water samples by preconcentration neutron activation analysis (PNAA) are described here.

It is understood that for any analytical procedure, replicate analysis will inevitably yield some variation in results. The variations may be due to random errors which are inherent in any measurement system; these tend to be relatively small and produce a spread of data which is governed by statistical laws. The variations may also be due to larger errors associated with some defect in the analytical procedure. The presence of these larger errors may be evidenced by the failure of the data to conform to the statistical model (by the presence of outliers, for example).

The purpose of internal quality assessment (IQA) undertaken here is to identify the uncertainties associated with each analysis step, and to evaluate the contribution of each to the uncertainty of the final result. Small, random uncertainties will manifest themselves in the variation of the results, which should fall within a specified range based on statistical data. In the event that large indeterminate errors exist, IQA may be used to identify such errors for the purpose of removing them from the system. The presence of bias, or unidirectional error, may also be detected using the IQA procedure. Identification of bias necessitates either an amended procedure, or the implementation of a correction factor, to remove its effect. As the focus of this thesis has been on method development, consideration will be given to the irradiation, counting, and standard preparation steps, rather than those associated with the analysis of field samples, such as sample acquisition, storage, transport, and handling.

Internal quality assessment was carried out using a number of steps. The samples were irradiated in the inner sites of the Dalhousie University SLOWPOKE-2 Reactor at a total flux of 5 or 10 x 10^{11} n cm^{-2} s^{-1}. The homogeneity, stability, reproducibility and mapping of the neutron flux were carried out in each of the sites [285,326]and discussed in section 3.1.

Elemental comparator standards were prepared by directly pipetting a known aliquot of ultrapure atomic absorption standard solution by a calibrated Eppendorf pipette onto a resin. The calibration was carried out by pipetting distilled water into a small beaker and weighing. The uncertainty associated with the various pipets used in this work ranged from 2 to 11 parts per thousand.

The steps in the IQA procedure will be numerically designated, in order to facilitate comparisons of one set of replicates to the other. For Steps 1-3, long-lived nuclides (that is, those with $t_{1/2} > 21$ d) were evaluated in multielement comparator standards spiked on XAD-4 resin. In Step 1, a single sample was irradiated for 7 h, and after a decay period of 20 days was counted ($t_d = 2$ h) 15 times over a period of 48 h without removing the sample from the detector or changing its position. In Step 2, a sample subjected to a 7-h irradiation was counted for 2 hours, an average of once per day for three weeks, covering a period of decay times spanning from 14 to 35 days. In Step 3, individual standards were prepared, irradiated and counted.

In Steps 4 through 6, medium-lived nuclides were evaluated using the timing scheme t_i:t_d:t_c = 10:1:10 min. In Step 4, a manganese standard was irradiated for 10 min, then subjected to repeat counts of 10 min duration without changing the position of the sample on the detector. In Step 5, a single sample (multielement stock solution spiked onto XAD-4 resin) was irradiated and counted 25 times over a period of four months. In Step 6, a liquid multielement standard was irradiated and counted 15 times. In Step 7, individually prepared standards were prepared and irradiated. The timing scheme t_i:t_d:t_c = 7:24:1 h was introduced for the analysis of ^{69m}Zn and ^{115}Cd.

The precision of the sets of replicate samples has been evaluated in two ways, by comparing the values of the coefficient of variation (CV) for each set, and with quality control (QC) charts. The CV provides a value upon which comparisons can be made regarding uncertainties introduced in each step of the analysis. The QC chart, a plot of the measured value (such as the number of counts) *vs.* the sample number, identifies individual measurements which may be in question (namely, those measurements falling outside a specified range) and provides insight into general trends.

In Step 1, a single sample was irradiated for 7 h and allowed to decay for 20 d. The peaks generated by the following long-lived nuclides were monitored (half-lives and γ-ray energies are given in parentheses): ^{203}Hg ($t_{1/2}$ = 46.59 d, γ-ray = 279.2 keV), ^{51}Cr ($t_{1/2}$ = 27.7 d, γ-ray = 320.1 keV), ^{110m}Ag ($t_{1/2}$ = 249.9 d, γ-ray = 657.8 keV), ^{65}Zn ($t_{1/2}$ = 243.8 d, γ-ray = 1115.5 keV), and ^{60}Co ($t_{1/2}$ = 5.2721 a, γ-ray = 1173.5 keV). Nickel was also evaluated, based on the decay of ^{58}Co ($t_{1/2}$ = 70.78 d, γ-ray = 810.8 keV), produced by the reaction ^{58}Ni(n,p)^{58}Co. This reaction proceeds sufficiently in the total neutron flux of the inner site to produce a detectable photopeak.

The experimental parameters utilized in Step 1 served to eliminate several potential sources of error. Since only one sample was prepared, and subjected to one 7-h irradiation, uncertainties associated with sample preparation and the irradiation are avoided. With the use of long decay and counting times (20-22 d and 2 h, respectively) the relative uncertainties in the determination of these timing parameters becomes negligible. Furthermore, the counting time is susceptible to influence by dead time losses, the effect of which becomes less pronounced for long decay times due to the lower overall activity of the sample.

The irradiated sample, having decayed for 20 d, was subjected to counts of 2 h duration, carried out 15 times over a period of 48 h without removing the sample from the detector or changing its position. Because the sample was not disturbed during the 48-h period, potential errors with respect to variances in sample geometry were eliminated. The one major source of error of uncertainty which could not be removed was the counting statistics, and the results of this experiment, as shown in Figs. 4.31-4.36, should provide a reasonable estimate of the contribution of the counting statistics to the overall uncertainty of the method. All sample counts were corrected to $t_d = 21$ d, although it should be noted that the implemented correction factors were slight.

Since the quality control charts in Figs. 4.31 through 4.36 are based on a single sample, the number of counts can be used rather than the sensitivities, which are necessary when comparing samples with different quantities of the elements of interest. In general, the precision of the results, expressed in terms of the CV was very good, with values ranging from 1.8% for mercury to 3.0% for chromium.

In Step 2, a second sample was irradiated for 7 h and subjected to 2-h counts to evaluate the count rates of the same six nuclides as for Step 1. The experiment was modified by counting the sample for the first time after a decay of approximately 14 days, then repeating the count an average of once per day over a period of 3 weeks. This modification introduced the uncertainty associated with variation in sample geometry, including the position of the sample on the detector and the perturbation of the contents of the vial. The results of this experiment are given in Figs. 4.37-4.42, with the number of counts corrected to $t_d = 21$ d.

In Table 4.15, a comparison of the values of the CV for the six elements for

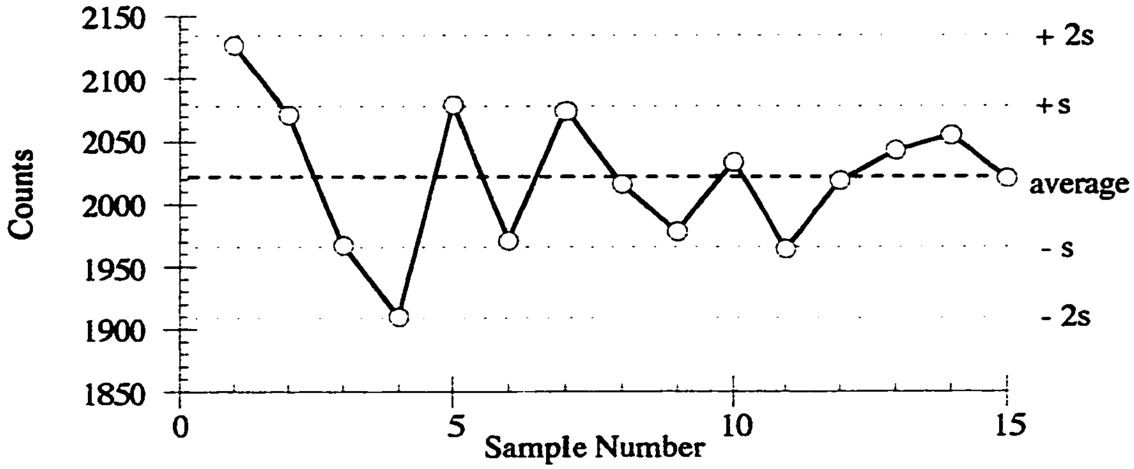


Figure 4.31. QC chart for repeat count of Ag standard (Step 1).

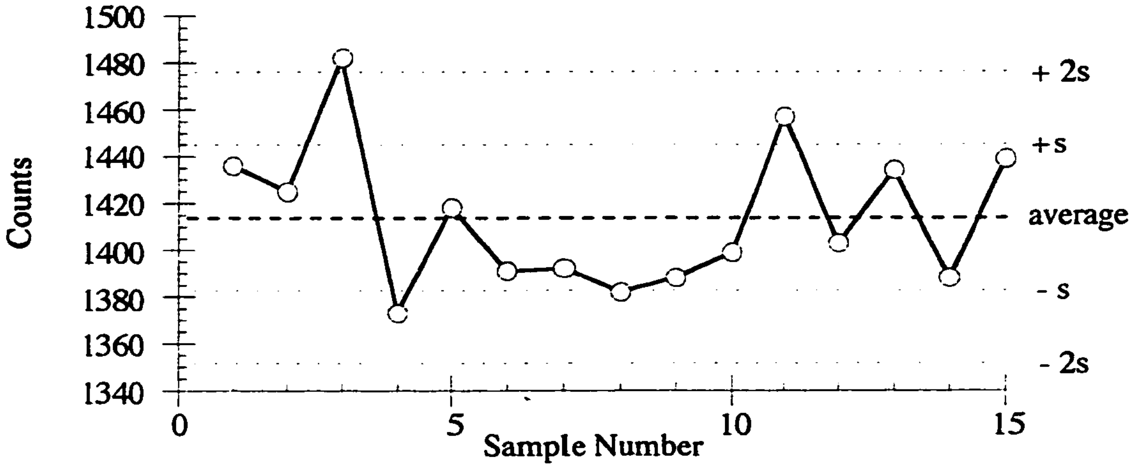


Figure 4.32. QC chart for repeat count of Co standard (Step 1).

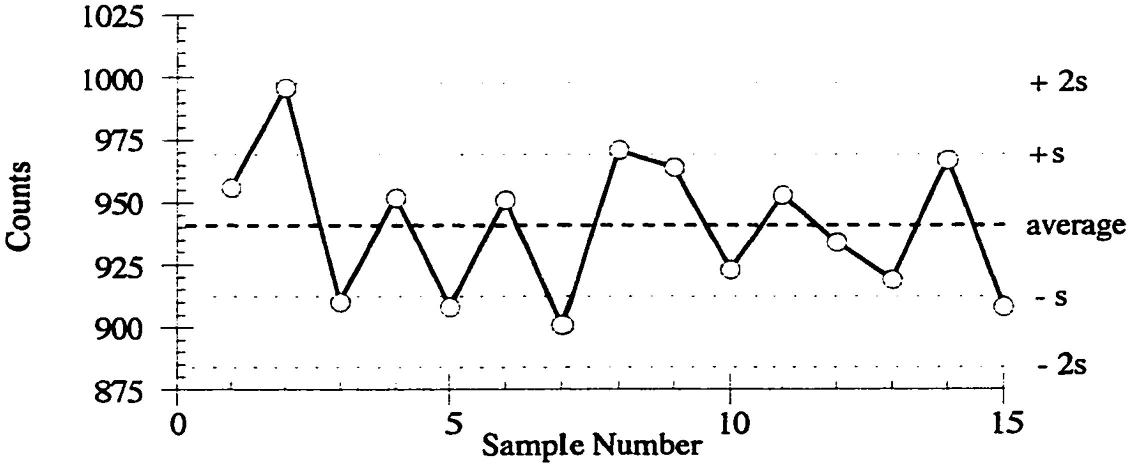


Figure 4.33. QC chart for repeat count of Cr standard (Step 1).

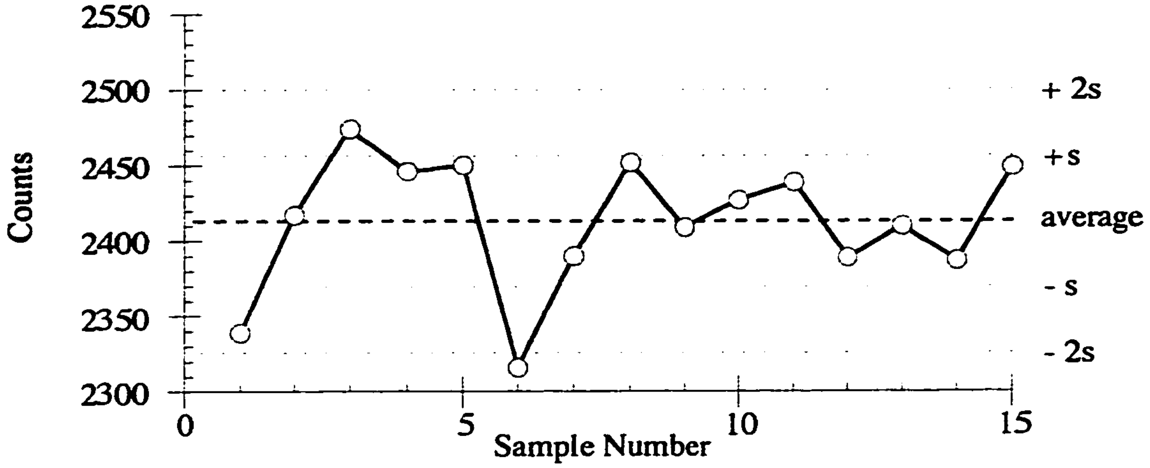


Figure 4.34. QC chart for repeat count of Hg standard (Step 1).

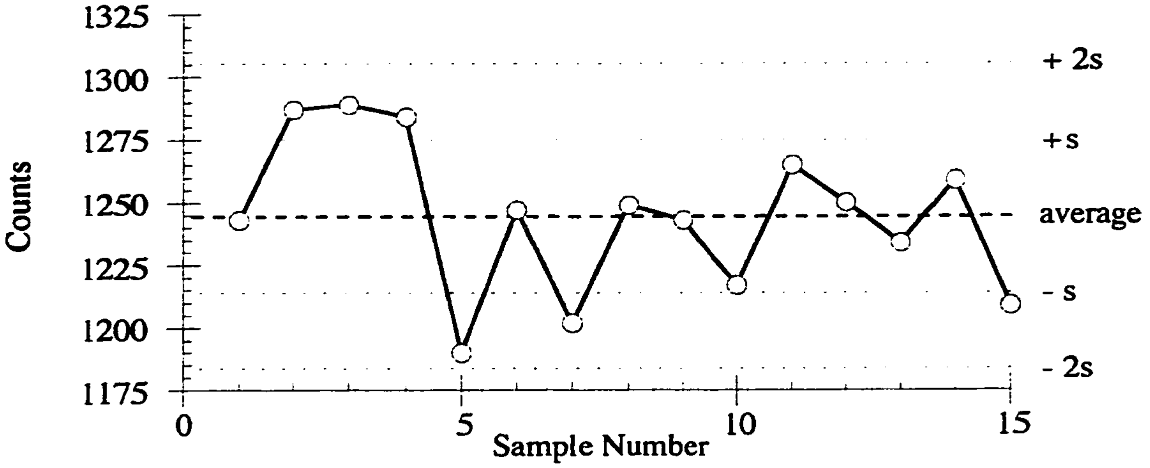


Figure 4.35. QC chart for repeat count of Ni standard (Step 1).

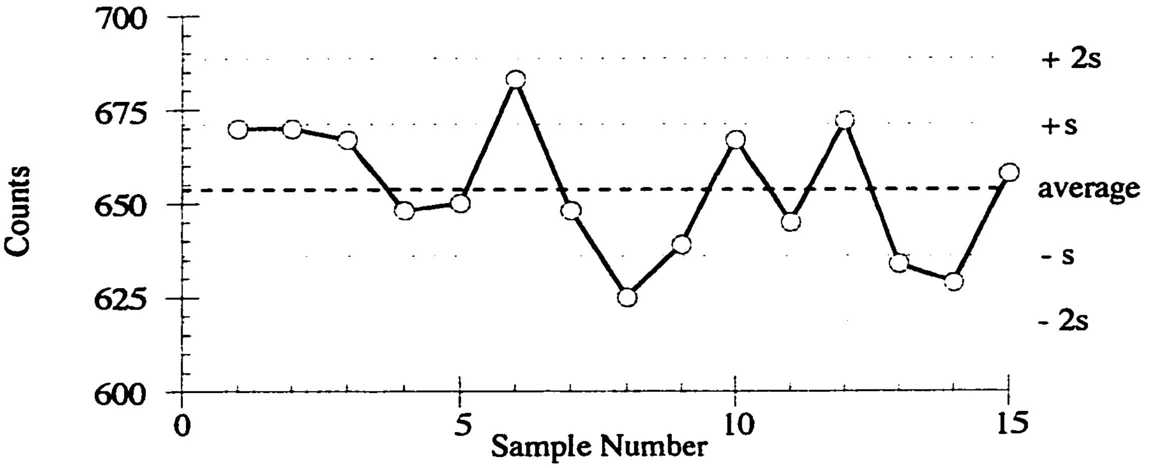


Figure 4.36. QC chart for repeat count of Zn standard (Step 1).

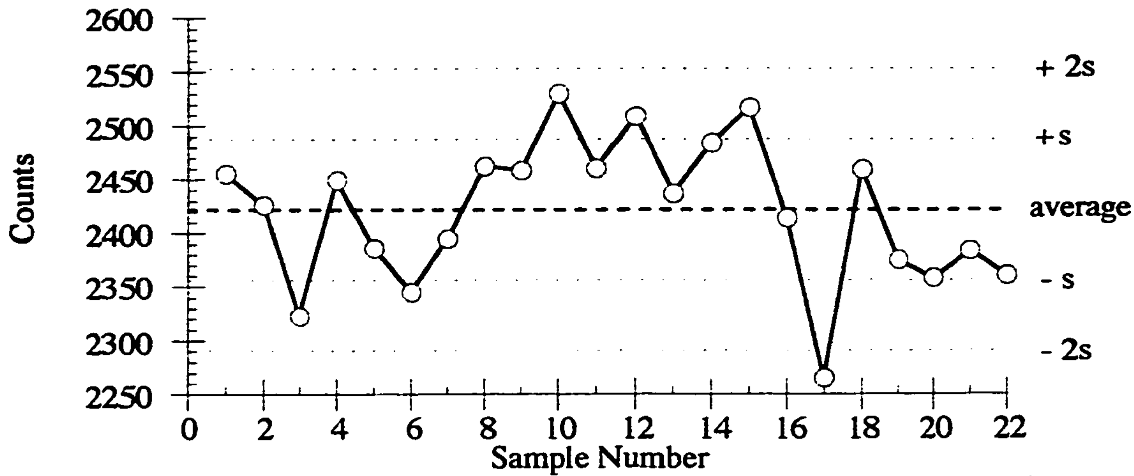


Figure 4.37. QC chart for repeat count of Ag standard (Step 2).

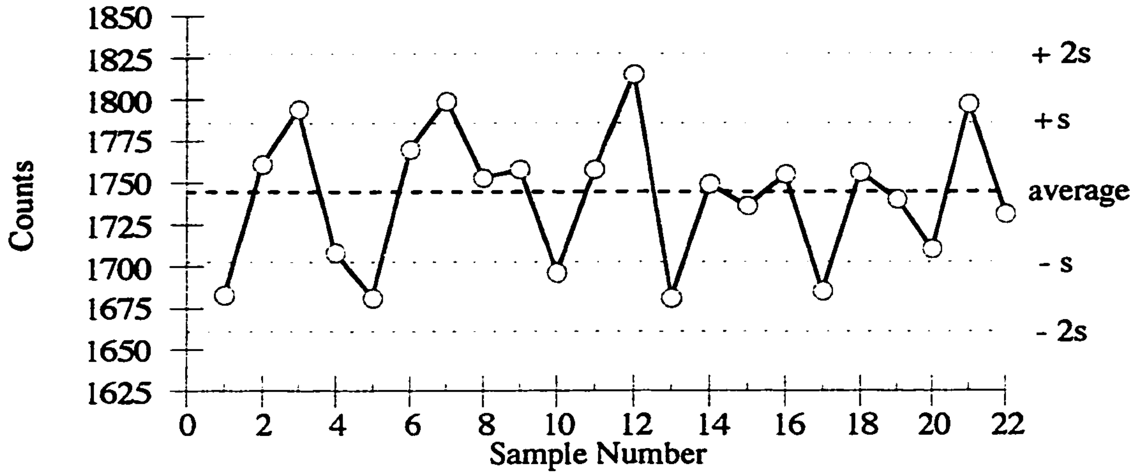


Figure 4.38. QC chart for repeat count of Co standard (Step 2).

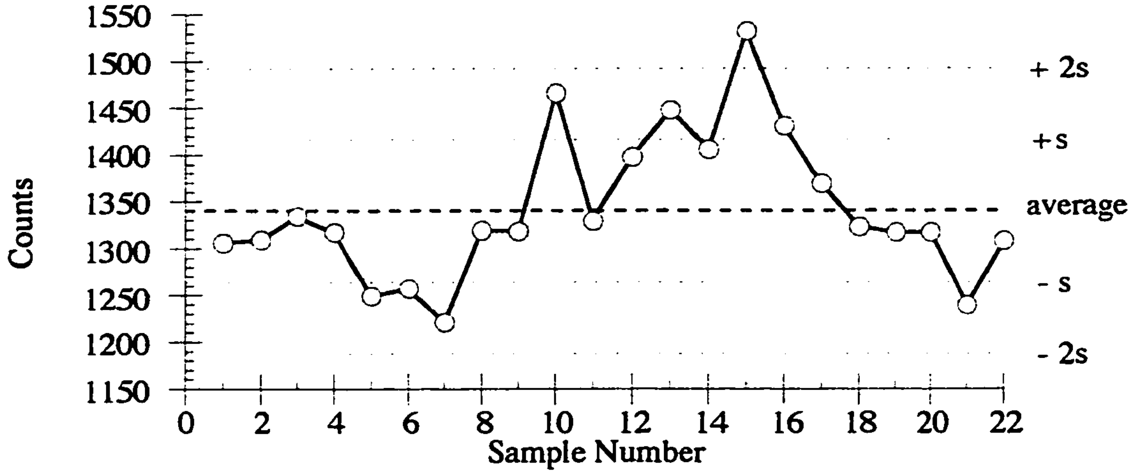


Figure 4.39. QC chart for repeat count of Cr standard (Step 2).

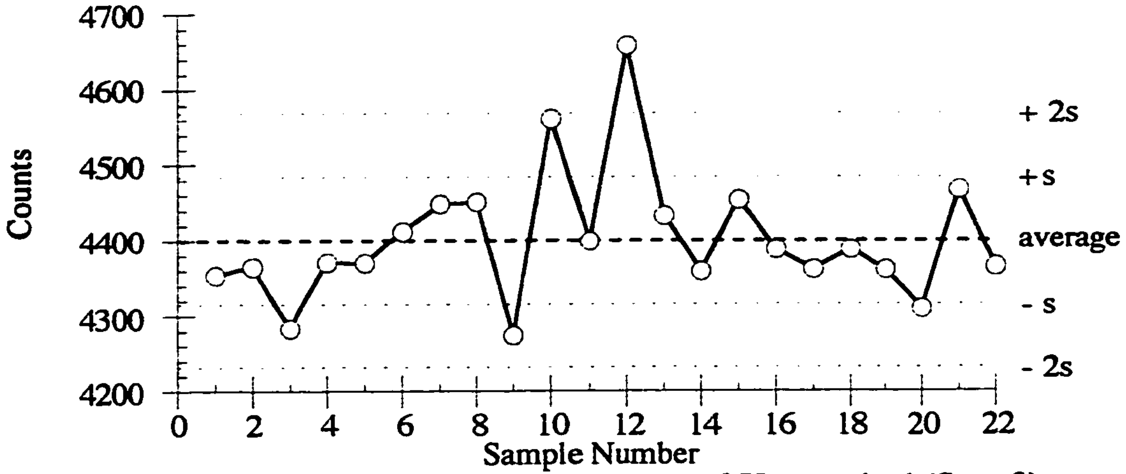


Figure 4.40. QC chart for repeat count of Hg standard (Step 2).

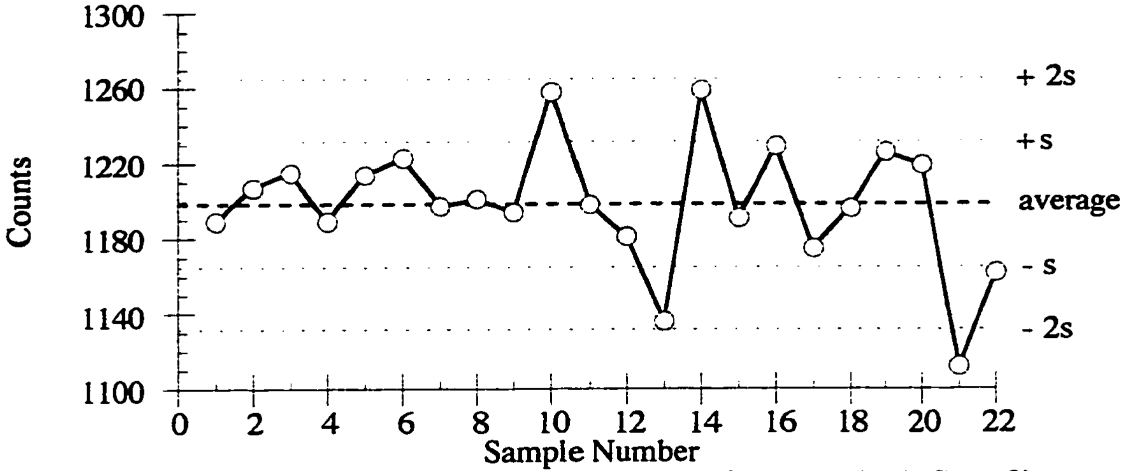


Figure 4.41. QC chart for repeat count of Ni standard (Step 2).

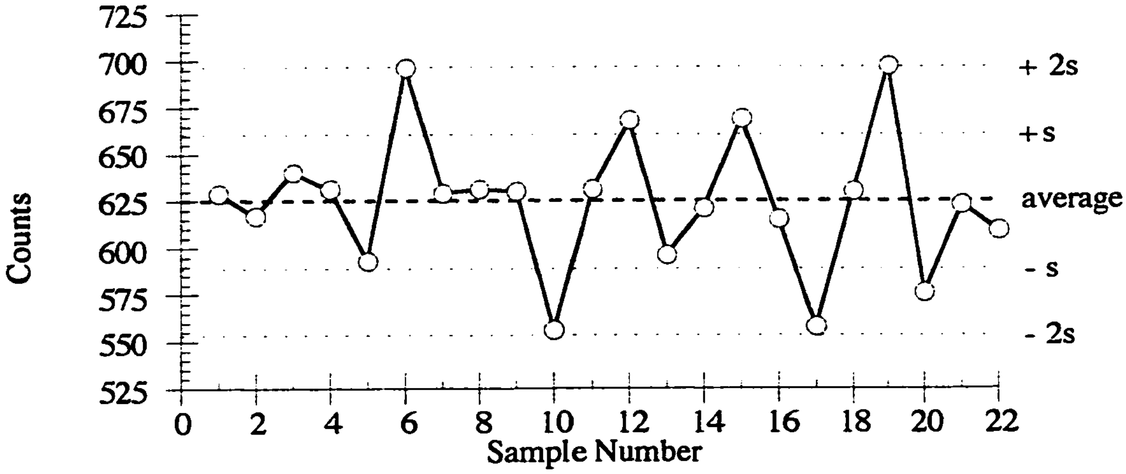


Figure 4.42. QC chart for repeat count of Zn standard (Step 2).

Table 4.15. Comparison of precision of replicate counts of standard samples using long-lived nuclides.

	Relative Standard Deviation (%)		
Element	Step 1	Step 2	Step 3
Ag	2.8	2.7	5.0
Co	2.2	2.4	4.7
Cr	3.0	5.7	7.4
Hg	1.8	1.9	3.2
Ni	2.4	2.8	5.4
Zn	2.7	5.7	8.4

Experimental conditions: $t_i = 7$ h; $t_c = 2$ h; t_d corrected to 21.00 d

Step 1: Single sample; single irradiation; sample counted 15 times over a period of 48 h without changing its detector position.

Step 2: Same as for Step 1, except that the sample was counted approximately once per day for 3 weeks; the sample was removed from the detector between counts.

Step 3: Individually prepared and irradiated samples.

the two steps is given. The RSD in Step 2 ranged between 1.9% for mercury and 5.7% for zinc. The precision of the results was essentially the same for both trials for cobalt, mercury, nickel, and silver, indicating that under conditions of normal sample handling, no detectable error was caused in placing the sample on the surface of the detector (*i.e.* sample geometry).

From the Step 1 experiments to those of Step 2, The values of the CV for chromium and zinc increased from 3.0% to 5.7% and from 2.7% to 5.7%, respectively. The increase in the value of the CV for zinc was most likely due to the low count rate, as the zinc signal was the smallest of the six investigated. The chromium signal was also relatively small, although the size of the signal must not have been the only factor contributing to the poor reproducibility. The signal from ^{58}Co, which exhibited fewer counts than ^{51}Cr, displayed superior precision (CV = 2.8%). The poor statistics of the chromium signal were probably also due to the fact that the 320.1-keV photopeak of ^{51}Cr is present over a higher background than the 810.8-keV photopeak of ^{58}Co, and to the proximity of the chromium signal to a relatively large signal due to the decay of ^{233}Pa ($t_{1/2}$ = 27.4 d, γ-ray = 311.9 keV). This nuclide is a daughter product from the decay of ^{233}Th, which is produced by the reaction $^{232}\text{Th}(n,\gamma)^{233}\text{Th}$. Both factors combine to make it difficult to ascertain reproducible boundaries for the integration of the 320.1-keV photopeak.

In Step 3 of IQA, several standards for each element were prepared and irradiated for 7 h. This set of replicates introduced variations in sample preparation and irradiation which were not present in steps 1 and 2. The values of the relative standard deviations for the six elements of interest are included in Table 4.16 with those from the first two steps of the QA analysis. These values ranged from 3.2% for mercury to 8.4% for zinc.

The QC charts for Step 3 are presented in Figs. 4.43-4.48.

The difference in the CV from Step 2 to Step 3 represents the uncertainty introduced in the sample preparation and irradiation steps. Uncertainty in the irradiation step arises from the variation in the irradiation time and in the neutron flux. The irradiation time is controlled by a timer on the irradiation control unit; for a 7-h irradiation, the deviation in irradiation time would be expected to be negligible. The variation in the inner-site neutron flux generated by the SLOWPOKE-2 facility is generally within 1%. Variations resulting from the sample preparation step may be due to pipetting, sample height (*i.e.* the amount of resin upon which the multielement solution was spotted), and the heterogeneity of the sample. As previously discussed, the volumes delivered by the Eppendorf pipets were determined to be reproducible within the range 2-11 parts per thousand, depending on the volume of the pipet used. For most of the standards, a sample volume of 200 μL was used; the 200-μL pipet exhibited an uncertainty of not more than 8 parts per thousand.

The next factor to investigate was the reproducibility of the irradiation step. To do this, a single sample was irradiated several times and the generated signals were compared. Such an experiment could only be carried out through the analysis of short-lived nuclides. Nuclides with $t_{1/2} < 3$ h could be studied with just a 1-2 day interval between irradiations; reirradiation for the purpose of analyzing the longer-lived nuclides used in Steps 1, 2, and 3 would require a delay period of months or years to ensure complete decay of the nuclides of interest.

The short-lived nuclides were measured using timing parameters of t_i:t_d:t_c = 10:1:10 min. The nuclides under investigation were (half-lives and gamma-ray energies are given in

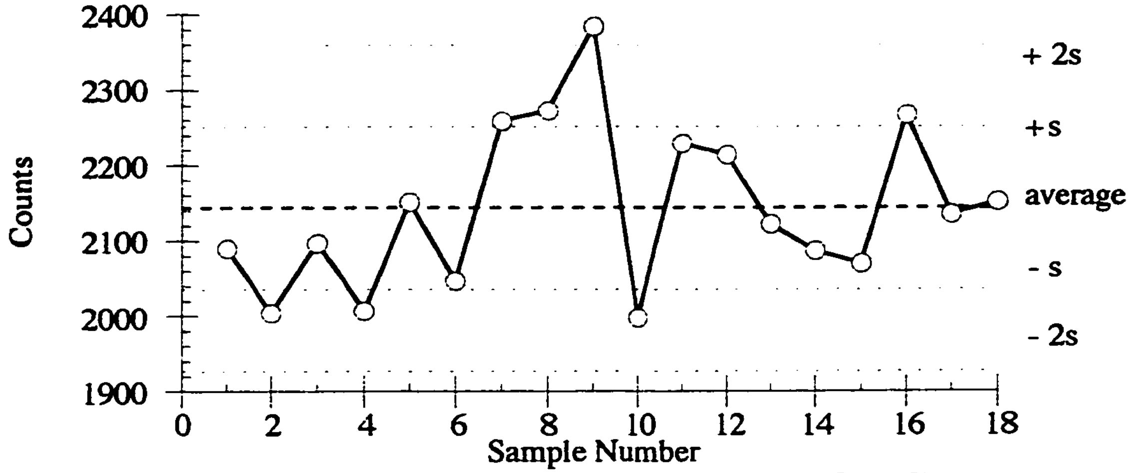


Figure 4.43. QC chart for Ag standards (Step 3).

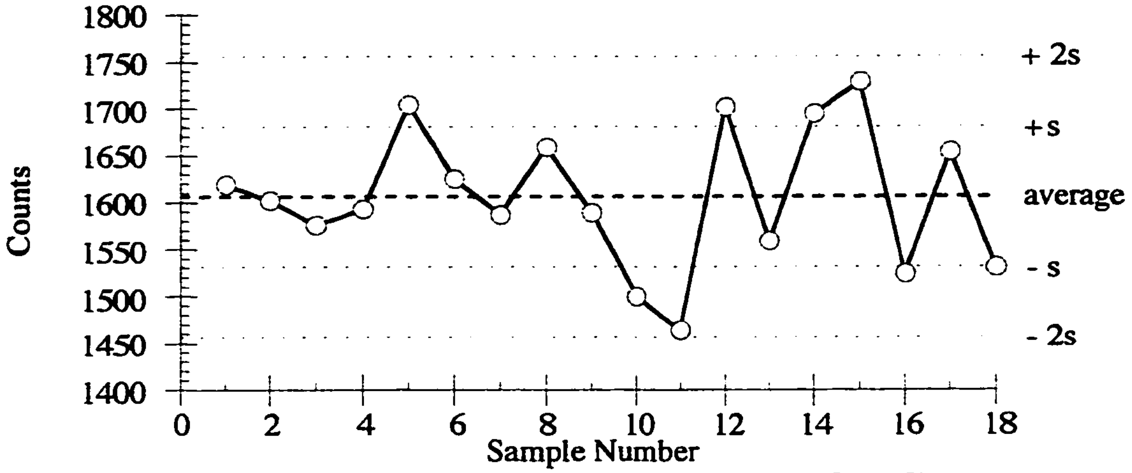


Figure 4.44. QC chart for Co standards (Step 3).

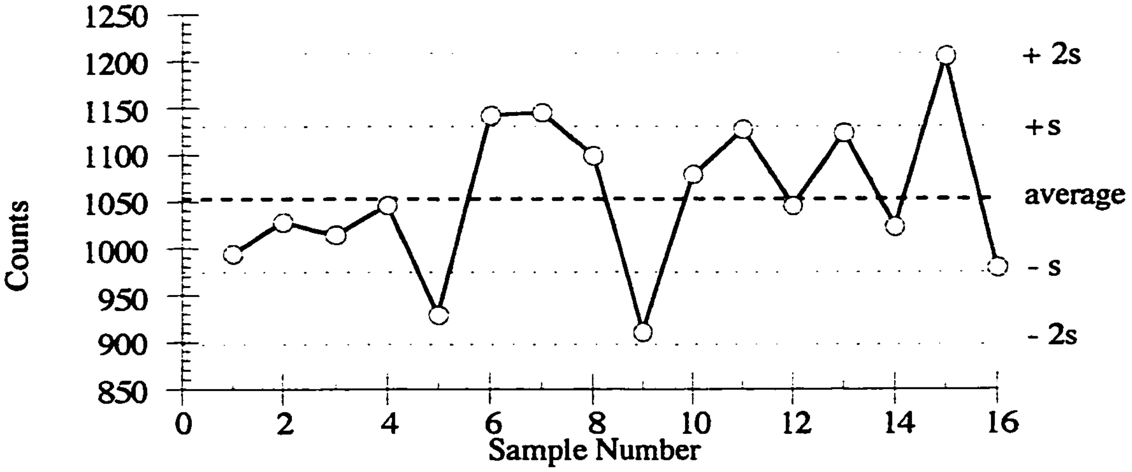


Figure 4.45. QC chart for Cr standards (Step 3).

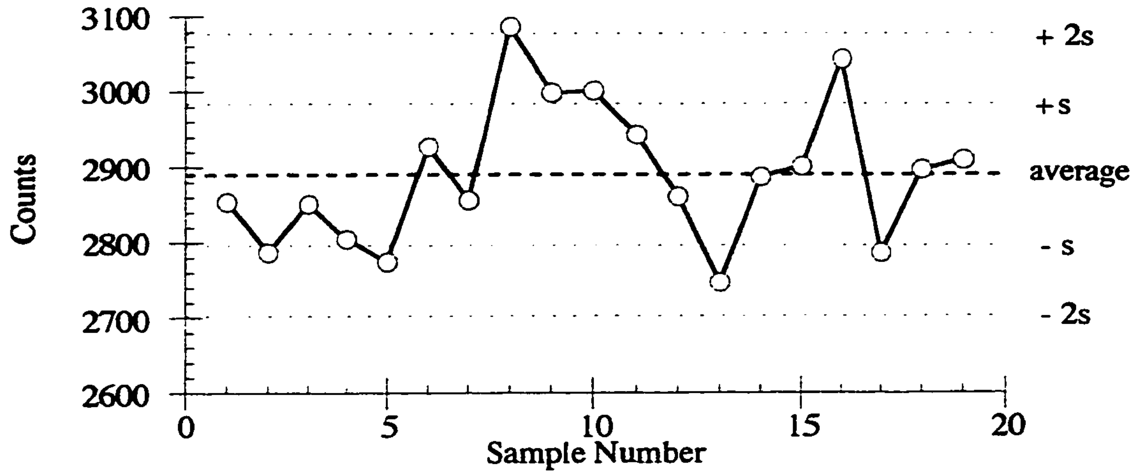


Figure 4.46. QC chart for Hg standards (Step 3).

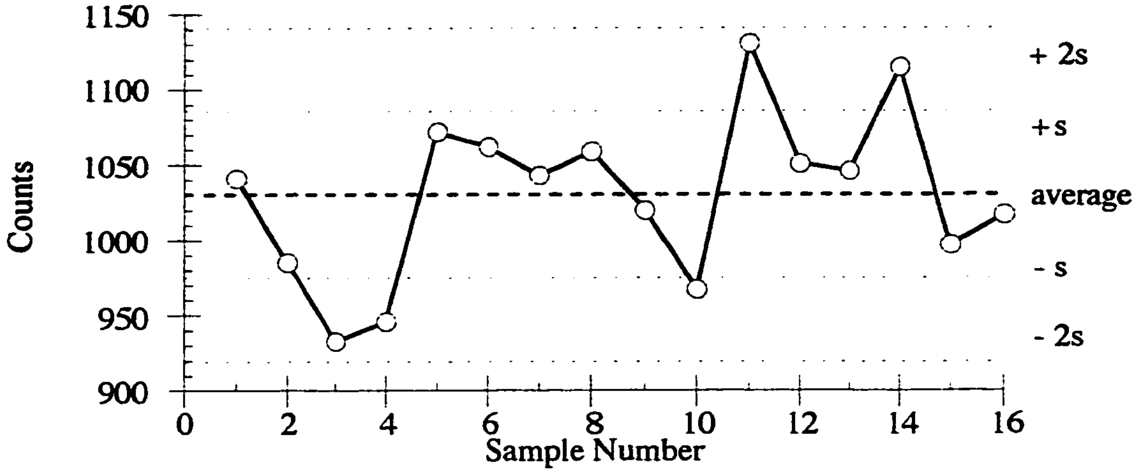


Figure 4.47. QC chart for Ni standards (Step 3).

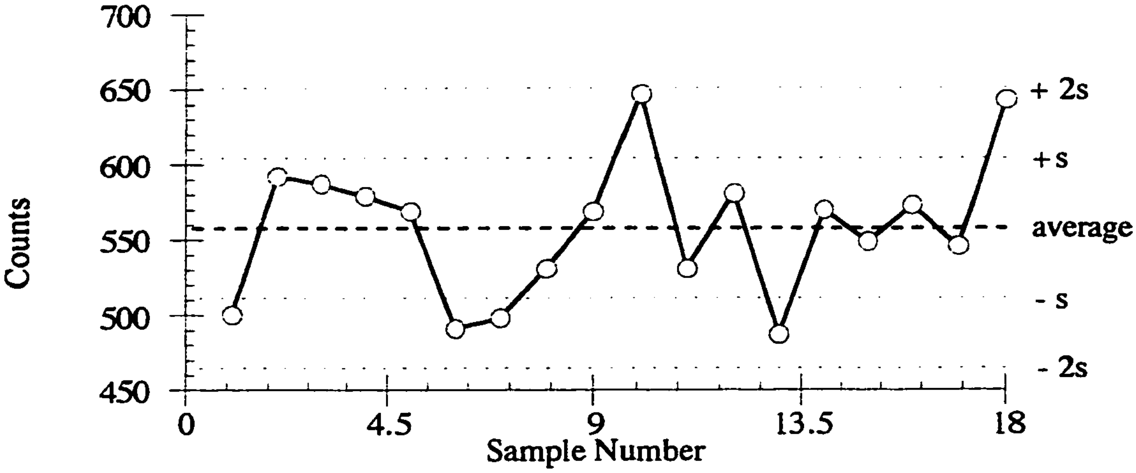


Figure 4.48. QC chart for Zn standards (Step 3).

parentheses): ^{60m}Co ($t_{1/2}$ = 10.47 min, = 58.6 keV), ^{239}U (23.45 min, 74.7 keV), ^{108}Ag (2.37 min, 633.0 keV), ^{56}Mn (2.579 h, 846.8 keV), ^{66}Cu (5.09 min, 1039.2 keV), and ^{52}V (3.743 min, 1434.1 keV). Cobalt and silver were previously evaluated using longer-lived nuclides, so a comparison may be drawn between the results obtained using the different nuclides.

In Step 4, an estimate of the contribution of the counting statistics to the uncertainty of the analysis of the short-lived nuclides was obtained by irradiating a single sample for 10 min and subjecting the sample to repeated 10-min counts without altering the sample position on the detector. Of the short-lived nuclides in question, only ^{56}Mn has a half-life long enough to produce sufficient activity to allow several recounts. The QC charts for manganese, with the number of counts corrected to t_d = 1 min, are given in Figs. 4.49 and 4.50, using the γ-rays at 846.8 keV and 1810.7 keV, respectively. The CV for 18 recounts using the 846.8-keV signal was 3.3%, in good agreement with values obtained for recounts using the longer-lived nuclides (Step 1). When the 1810.7-keV photopeak was used, the CV was 7.6%. This discrepancy is attributable to the higher count rate of the 846.8-keV peak (the average number of counts was 3345, compared to 414 for the 1810.7-keV peak). Since the 1810.7-keV peak sits on a very low background, the lower count rate must be the major contributing factor to the poor precision of the replicates. This result suggests that in order to maintain a minimum standard of precision, a threshold value for the size of the signal could be established. It should be noted that for this experiment, the spotted sample was placed in a small irradiation vial which did not contain any magnesium. Correspondingly, a correction due to the interference of magnesium to the quantitation of the manganese peak at 846.8 keV

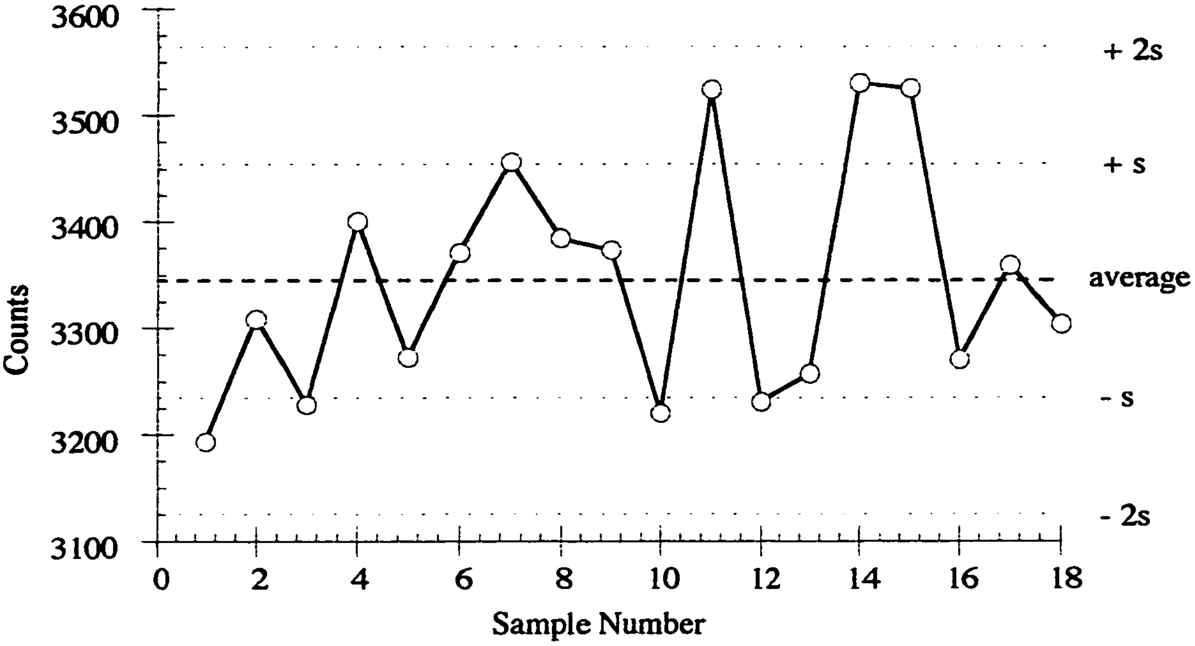


Figure 4.49. QC chart for repeat count of Mn standard at 846.8 keV (Step 4).

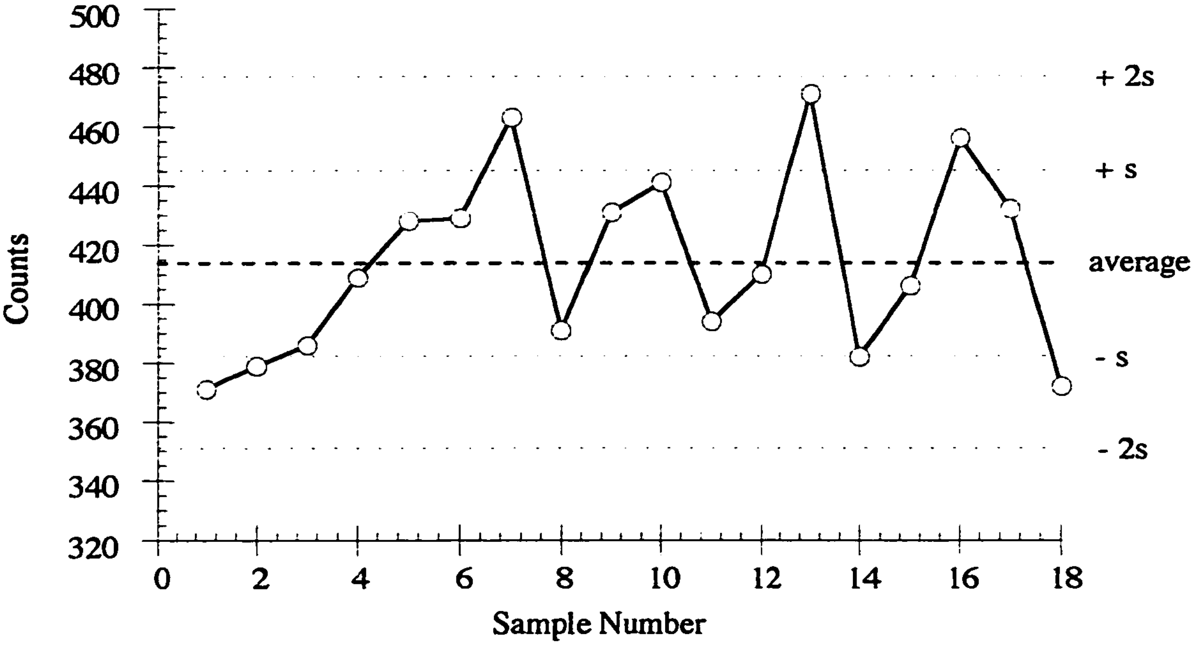


Figure 4.50. QC chart for repeat count of Mn standard at 1810.7 keV (Step 4).

was not necessary.

In Step 5, a single sample containing the elements of interest was irradiated 25 times; the irradiations were carried out no more than once per day and spread out over a period of 4 months. The results are depicted in Figs. 4.51-4.56. The CV results ranged from 3.0% for vanadium to 4.2% for manganese. Given that the counting statistics contribute approximately 3% to the overall uncertainty, the results of Step 5 indicate that the irradiation step contributes only insignificantly.

The samples analyzed to this point were standards spotted on XAD-4 resin. The resin, even when held down by a spacer, retains some mobility, so the distribution of the trace elements of interest may have changed from irradiation to irradiation, as the beads of resin moved about within the vial. This effect was evaluated in Step 6 of the QA analysis by running a liquid standard (a 200-μL spike of the stock multielement solution made up to 1 mL with DDW). This liquid standard was irradiated 15 times and counted under the same conditions as for the spotted standard. The liquid sample could not be subjected to long irradiations due to the possibility of radiolysis. The same six elements were analyzed by repeat irradiations and counts, and the results are given in Figs. 4.57-4.62. With the exception of uranium, the precision was generally superior to that observed for the reirradiated spotted standard used in Step 5. The degree of improvement, based on the difference in the CV, ranged from 1.1% for copper to 2.3% for silver. The latter figure was due in part to the fact that the multielement standard solution used in Step 6 contained approximately twice as much silver than was present in the solution used in Step 5.

A comparison of the values for the CV for each of Steps 4, 5, 6, and 7 (the

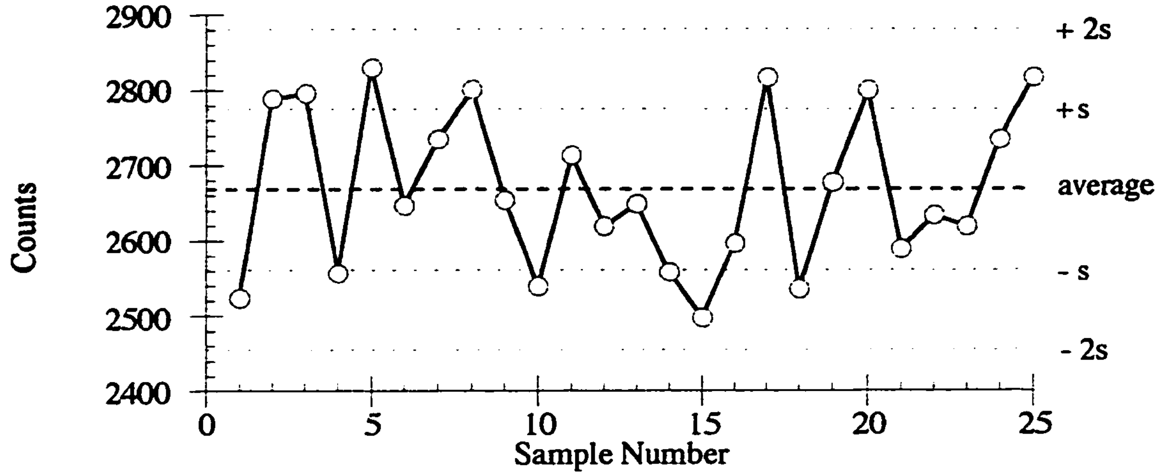


Figure 4.51. QC chart for repeat irradiation of Ag standard (Step 5).

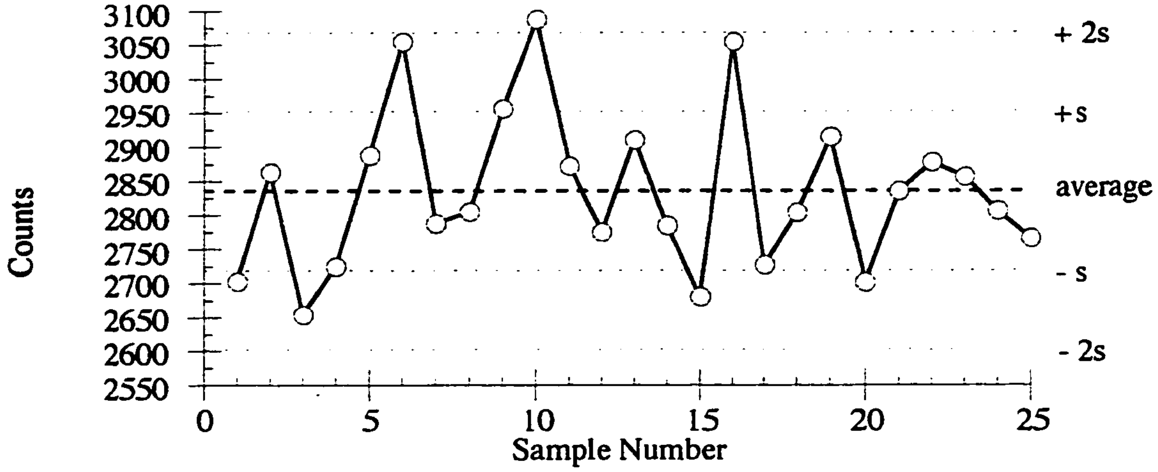


Figure 4.52. QC chart for repeat irradiation of Co standard (Step 5).

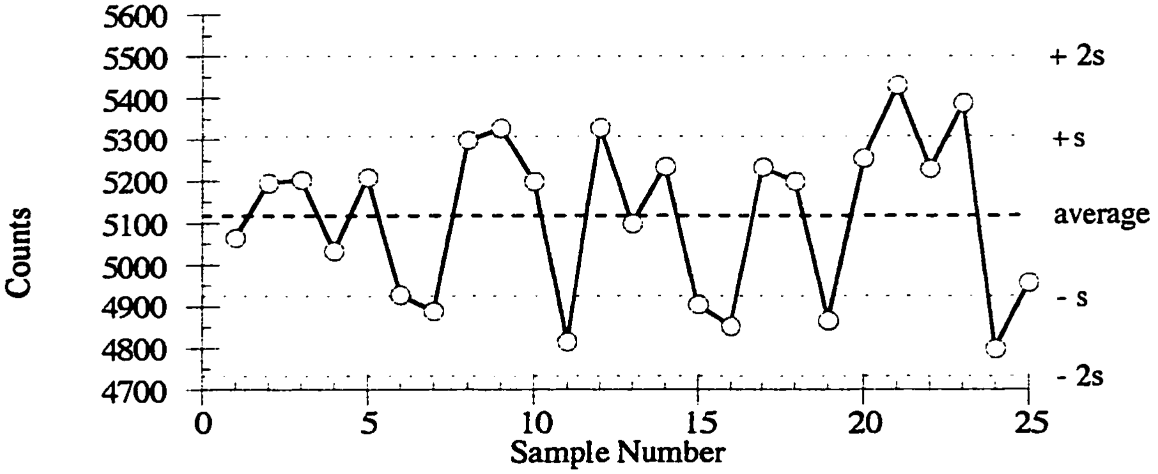


Figure 4.53. QC chart for repeat irradiation of Cu standard (Step 5).

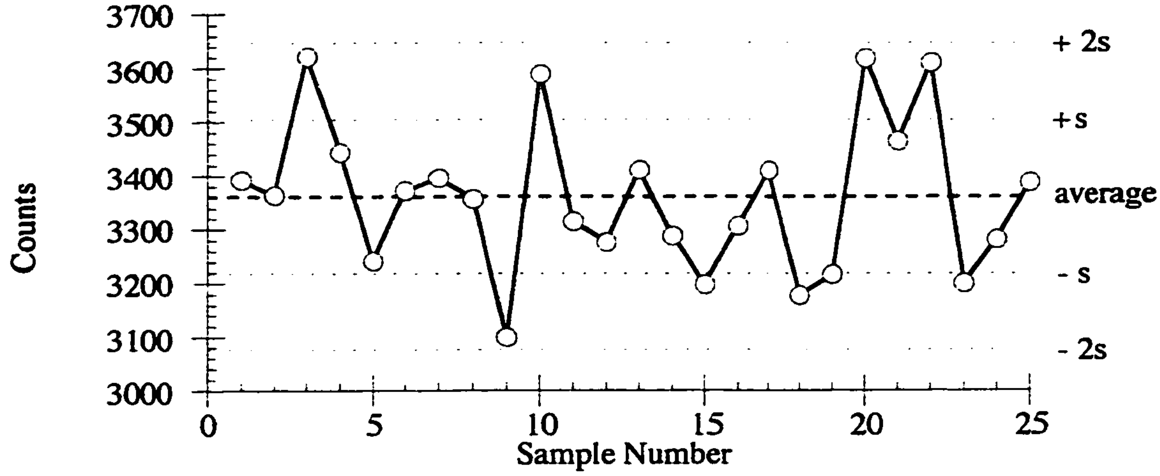


Figure 4.54. QC chart for repeat irradiation of Mn standard (Step 5).

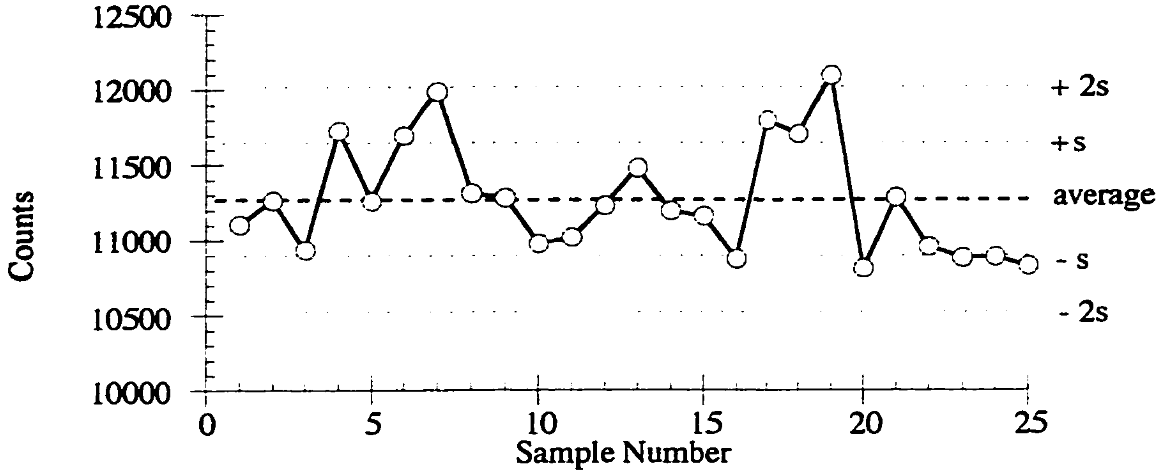


Figure 4.55. QC chart for repeat irradiation of U standard (Step 5).

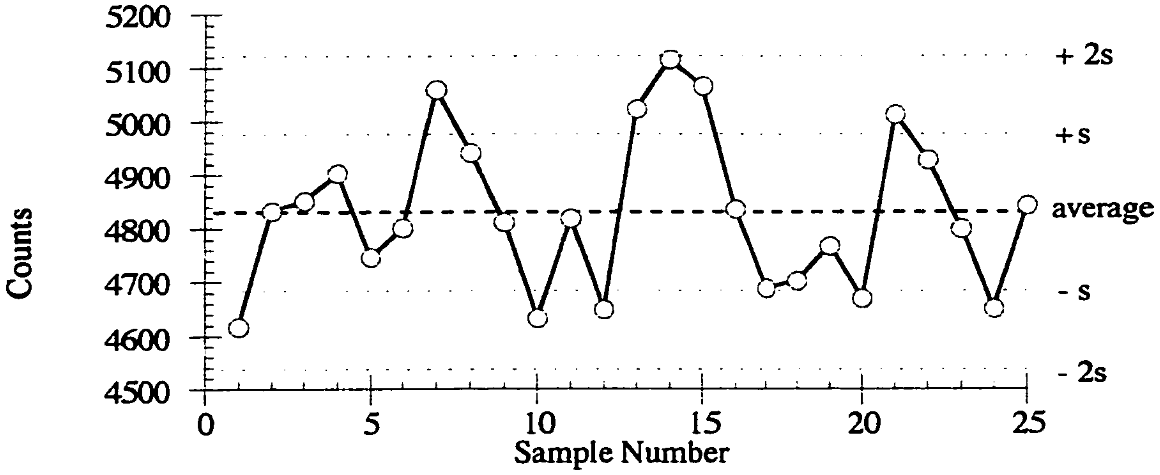


Figure 4.56. QC chart for repeat irradiation of V standard (Step 5).

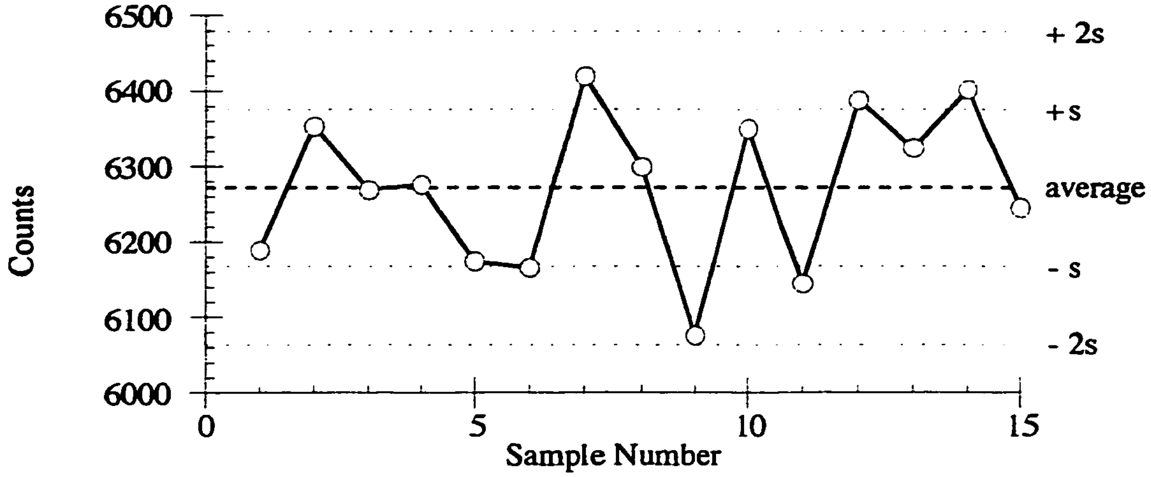


Figure 4.57. QC chart for repeat irradiation of liquid Ag standard (Step 6).

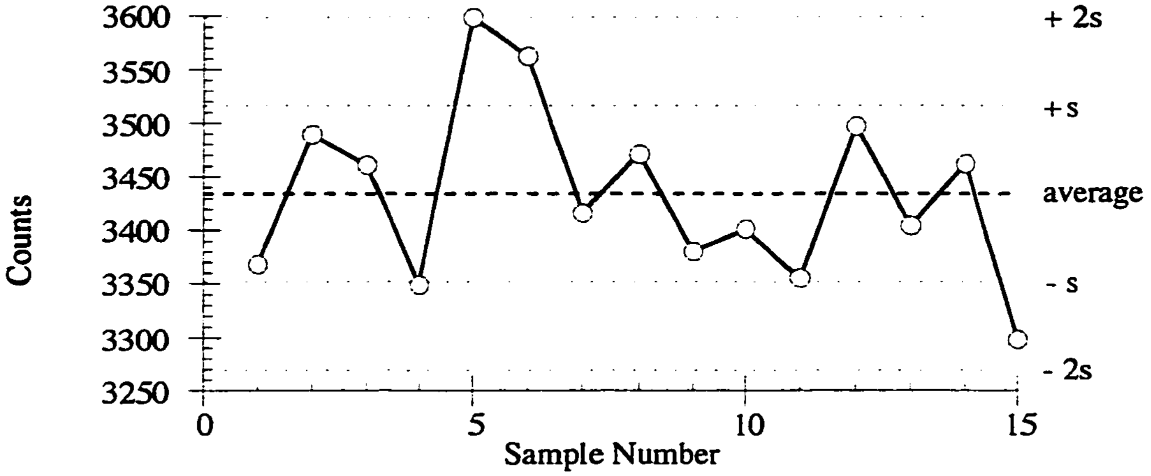


Figure 4.58. QC chart for repeat irradiation of liquid Co standard (Step 6).

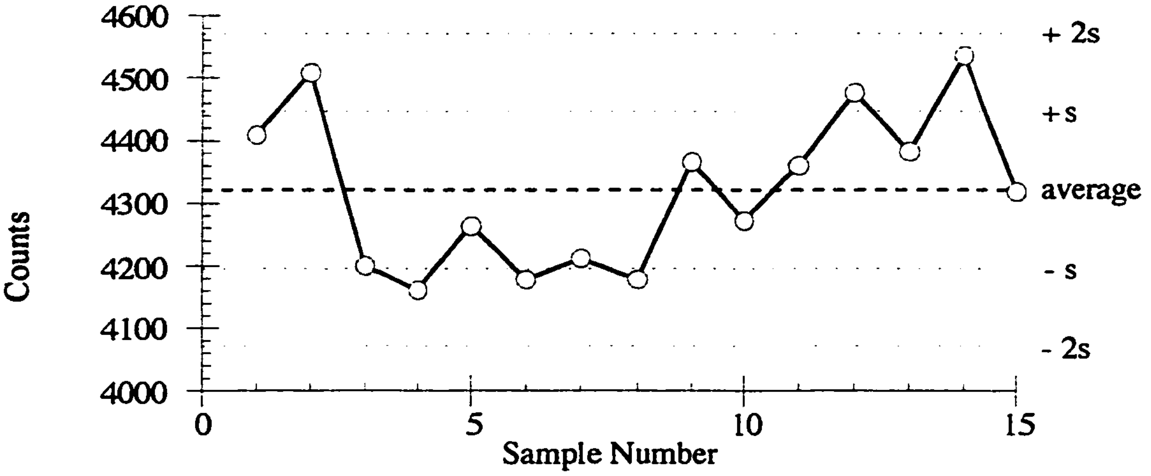


Figure 4.59. QC chart for repeat irradiation of liquid Cu standard (Step 6).

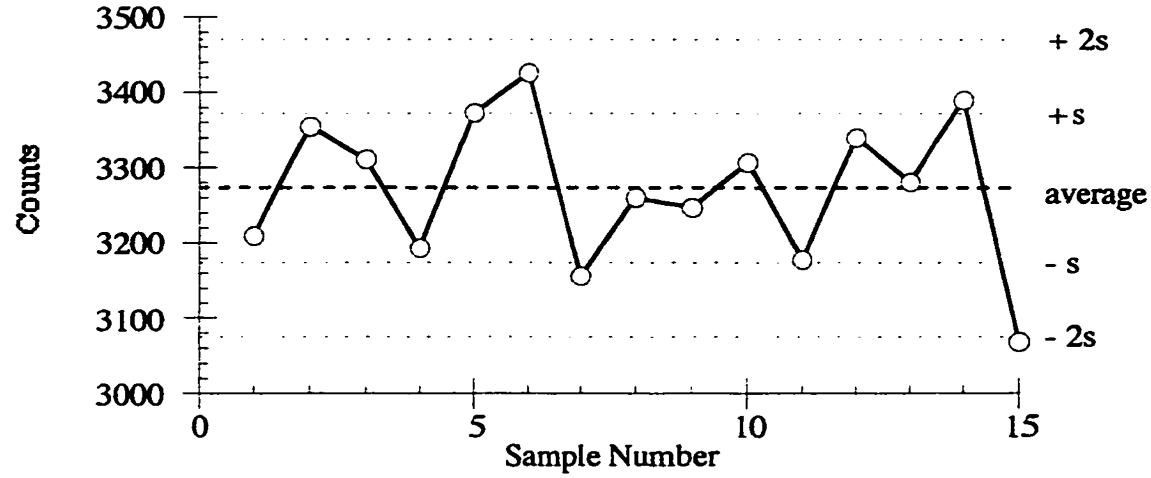


Figure 4.60. QC chart for repeat irradiation of liquid Mn standard (Step 6).

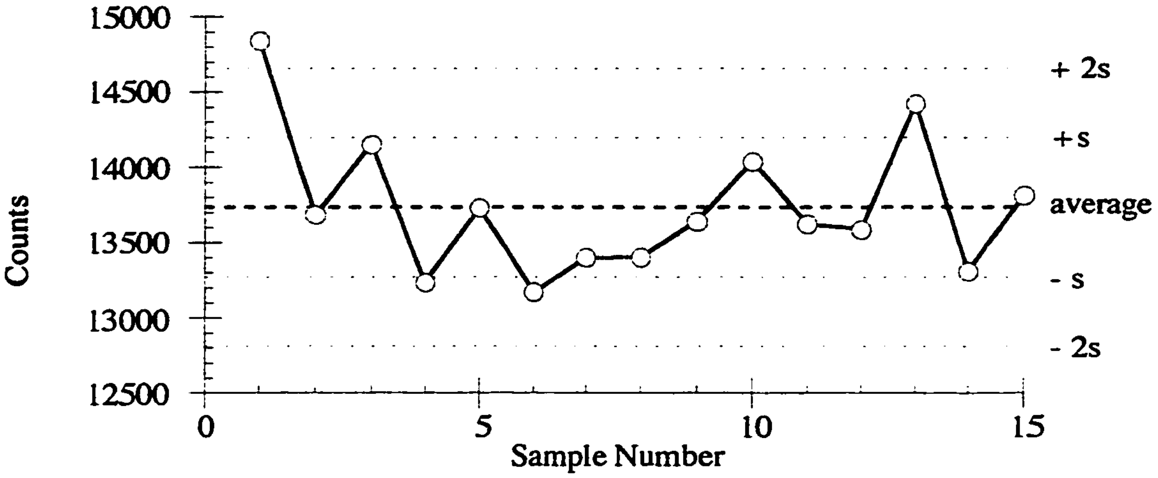


Figure 4.61. QC chart for repeat irradiation of liquid U standard (Step 6).

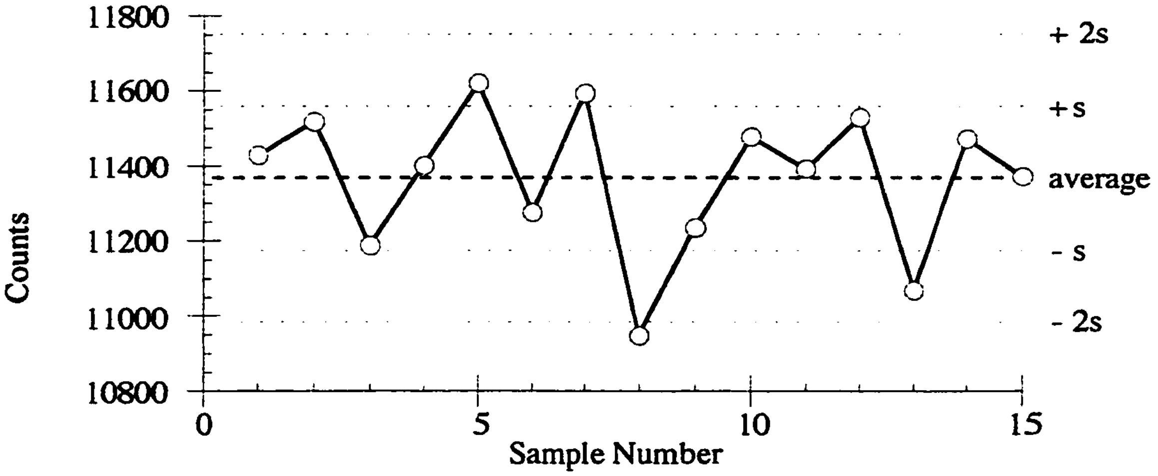


Figure 4.62. QC Chart for Repeat Irradiation of Liquid V Standard (Step 6).

latter of which is described below) is given in Table 4.17. The lower CV values for Step 6 indicate that the heterogeneity of the spotted sample results in a loss of precision. The irradiated sample is transported from the sample receiver to the reactor, and back again, at high speed. For the spike spotted on a sample of resin, this sample transfer may cause the contents of the sample vial to shift, so the distribution of the elements spiked on the resin may not be reproducible from one irradiation to the next. This problem is absent when the liquid sample is used.

As a further point of reference, the reproducibility observed for the manganese standard was only slightly improved compared to the single sample counted repeatedly without disturbing the sample geometry (Step 4). Since the sample used in the Step 4 analysis was subjected to only one irradiation, and was not equilibrated between counting periods, the distribution of the manganese in the vial should have been essentially unchanged from one count to the next. The manganese distribution should be reproducible in the equilibrated liquid sample, and it is unlikely that the sample transfer would disturb the equilibrium.

Step 7 in the quality assurance determination was the analysis of individually prepared standards. Generally, throughout the optimization studies, the parameter under investigation (pH, flow rate, etc.) was evaluated with three samples, which were coupled with one procedural blank and one standard. The blank and standard were prepared using the same geometry as that used for the samples. The standards were prepared and irradiated over an extended period of time, utilizing different multielement stock solutions and batches of precleaned vials and precleaned XAD-4 resin. The reproducibility of the standards was

Table 4.16. Comparison of precision of replicate counts of standard samples using medium-lived nuclides.

	Relative Standard Deviation (%)			
Element	Step 4	Step 5	Step 6	Step 7
Ag		4.0	1.7	4.3
Co		4.1	2.4	4.5
Cu		3.8	2.9	4.2
Mn	3.3	4.2	3.0	4.8
U		3.3	3.4	3.5
V		3.0	1.7	4.3

Experimental conditions: t_i:t_d:t_c = 10:1:10 min

Step 4: Single sample; single irradiation; sample counted 15 times over a period of 48 h without changing its detector position.

Step 5: Single sample, irradiated and counted 25 times.

Step 6: Liquid sample, irradiated and counted 15 times.

Step 7: Individually prepared and irradiated samples.

determined using 20 to 40 replicates. Since the measurements were carried out using different multielement stock solutions containing varying quantities of the elements of interest, the sensitivities (in counts μg^{-1}) were plotted against the sample number instead of the number of counts. The nuclides investigated were the six short-lived nuclides used in Steps 5 and 6, as well as nuclides of cadmium and zinc, ^{115}Cd ($t_{1/2}$ = 53.46 h, = 336.2 keV) and ^{69m}Zn (13.76 h, 438.6 keV). The results are shown in Figs. 4.63-4.70. In comparison to the values obtained in Step 3 for cobalt, silver, and zinc, the precision of the set of replicates was improved by using a shorter-lived nuclide instead of the longer-lived one.

As shown in Table 4.18, there was not a significant difference in the precision of the set of individual standards (Step 7) compared to the reirradiation of the single standard (Step 5) for the short-lived nuclides. For each of the six elements, the CV increased slightly when individual standards were used. The difference between the two sets of replicates was the introduction of sample preparation (*i.e.* pipetting, sample geometry) as a variable; the results indicate that this step did not make a significant contribution to the overall uncertainty.

Based on the 7 steps of the QA analysis for this experiment, several general trends can be observed. First, it generally follows that the precision for any set of replicate measurements is related to the size of the peak in question and the background upon which the peak is located. Larger peaks and lower backgrounds tend to improve the precision. For three of the elements studied (cobalt, silver, and zinc), the analysis was carried out using two nuclides with different half-lives; for each element, the precision is improved by using the shorter-lived nuclide, due to the higher count rate generated. The uncertainty due to the counting statistics, as established by repeat counts of a single sample, is generally of the order

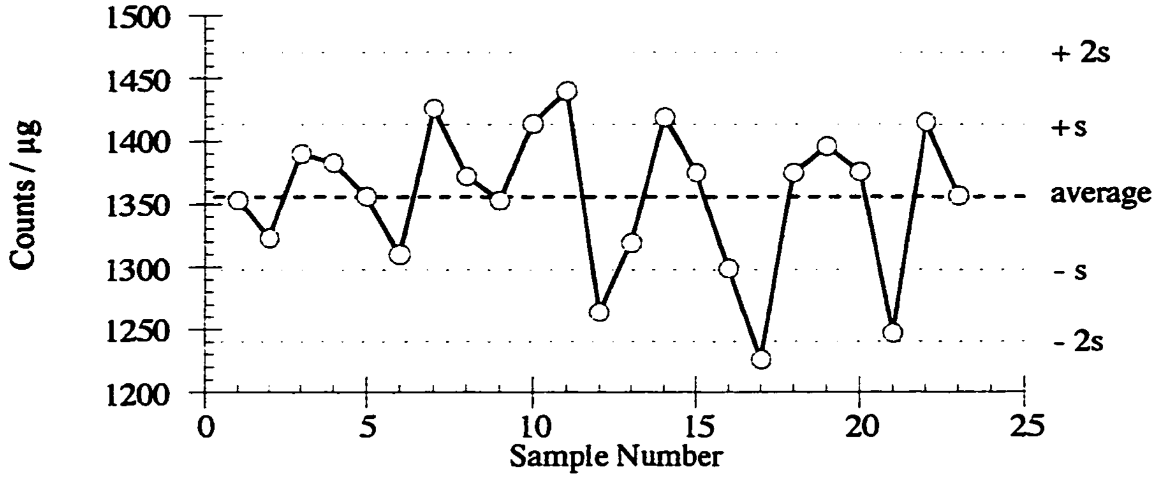


Figure 4.63. QC chart for Ag standards (Step 7).

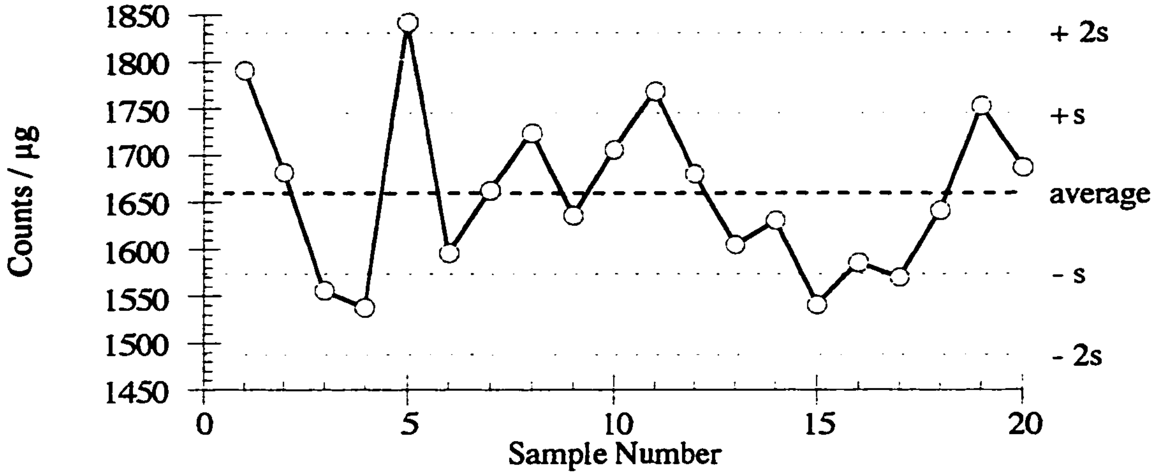


Figure 4.64. QC chart for Cd standards (Step 7).

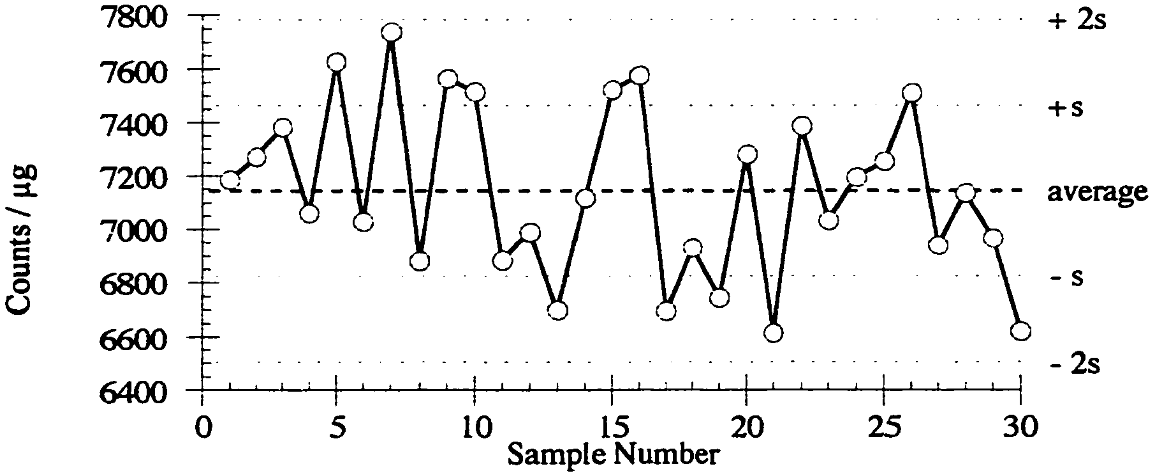


Figure 4.65. QC chart for Co standards (Step 7).

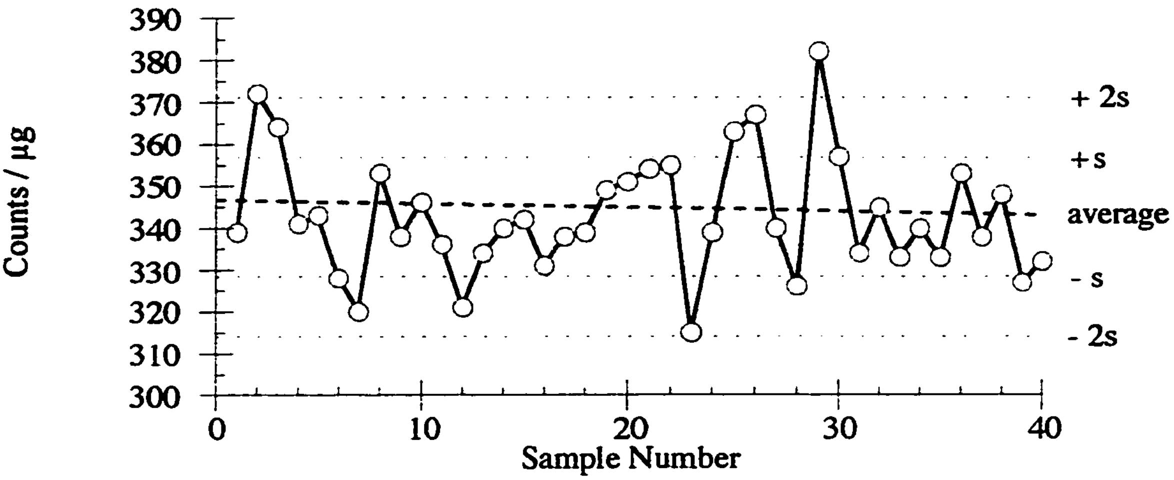


Figure 4.66. QC chart for Cu standards (Step 7).

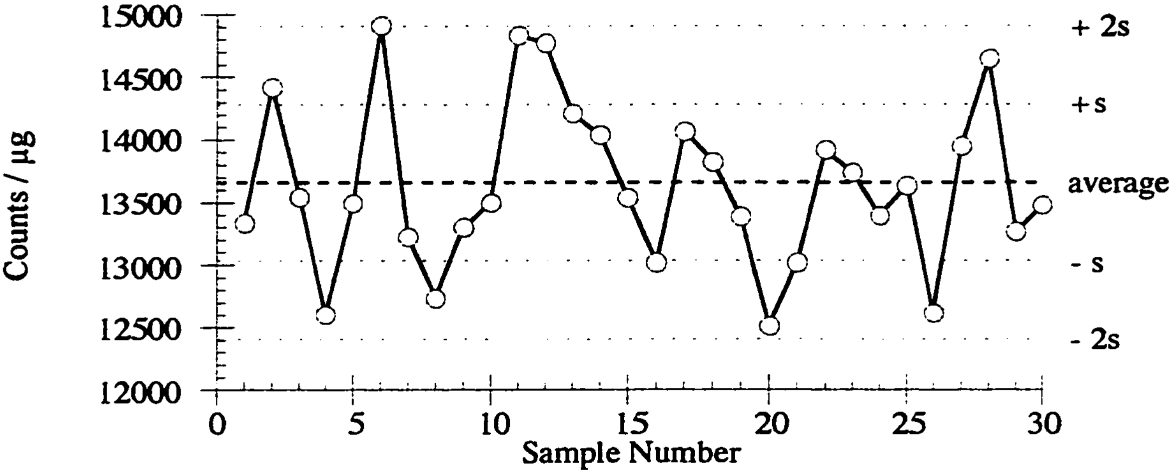


Figure 4.67. QC chart for Mn standards (Step 7).

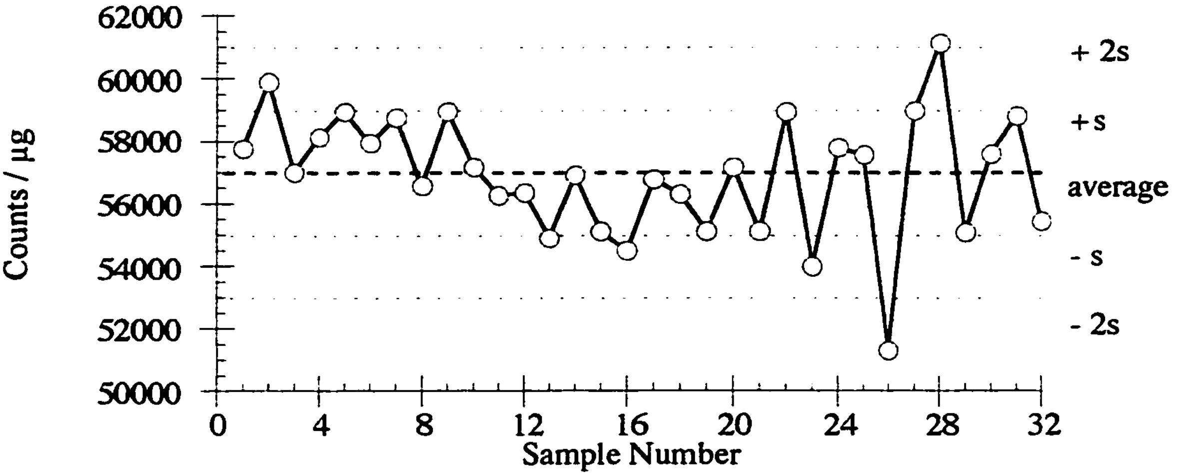


Figure 4.68. QC chart for U standards (Step 7).

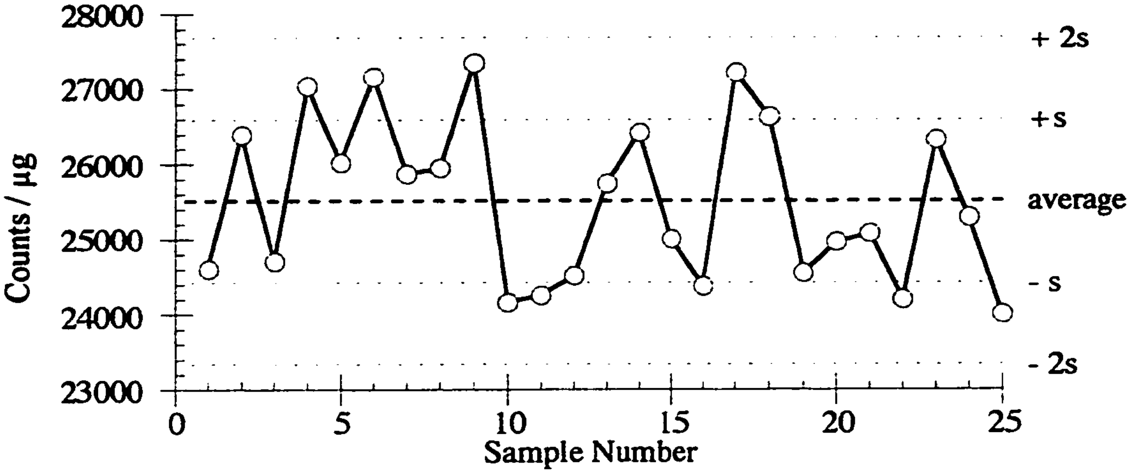


Figure 4.69. QC chart for V standards (Step 7).

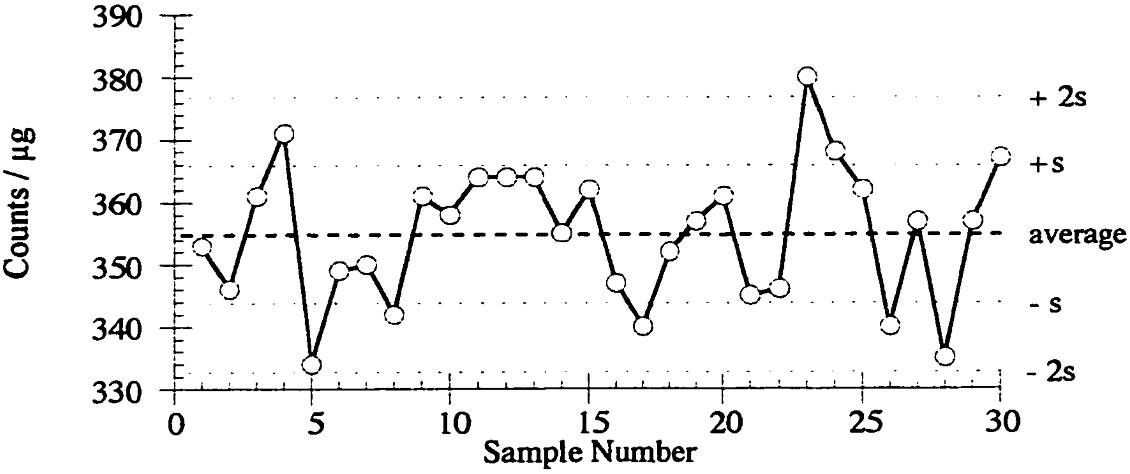


Figure 4.70. QC chart for Zn standards (Step 7).

of 2-3% RSD. With a couple of exceptions (involving small peaks with high or irreproducible backgrounds), the sample geometry, including the position of the sample on the detector, did not adversely affect the precision of the results, as long as some effort is expended to obtain reasonably reproducible conditions. Based on the repetition of 10-min irradiations of a single sample, the irradiation step appears to add approximately an extra 1% RSD to the overall uncertainty of the sample set (precision was generally 3-4% RSD for repeat irradiations of a single sample, compared to the 2-3% RSD attributed to counting statistics). For the short-lived nuclides used in Steps 5 and 7, the precision of the set of individual samples was not significantly worse than that displayed by the set of repeat irradiations of a single sample, suggesting that the sample preparation was quite reproducible.

The overall uncertainty in the set of standards ranged from 3.10% for ^{69m}Zn to 8.35% for ^{65}Zn. The set of chromium standards exhibited poor reproducibility (7.38% CV) but the remainder of the elements were much better (≤5.4% CV). As the standards were prepared under well-controlled conditions with no detectable loss of the elements of interest, their deviations are the lowest that could be expected for samples subjected to a preconcentration procedure.

4.14 Reproducibility of RPEC Procedure

The precision of the PNAA method was evaluated using three sets of replicate analyses. These were: ten spiked buffer, six tap water, and six spiked tap water samples. The details are given below.

In the first experiment, ten 100-mL buffer samples spiked with multielement stock solution were subjected to the RPEC separation at pH 8.3, and the elements collected on the resin were quantified by NAA. The elements determined in this experiment were cadmium, cobalt, copper, manganese, and zinc. Mercury and nickel, elements which were quantitatively retained by the resin under these conditions, were omitted in order to avoid long irradiation and decay periods. Zinc and cadmium were determined using 30-min irradiation and counting periods. The other elements were determined using the standard timing scheme of 10:1:10 min. The results given in Table 4.17 indicate that the precision of the RPEC method is good. For the ten replicates, the coefficient of variation ranged from 3.98% for cobalt to 6.93% for cadmium. The precision of the method for zinc was surprisingly low (4.52%), given the relatively low count rate (average number of counts = 631). By increasing the counting time to 60 minutes, the precision for zinc could possibly be improved even further.

The second set of replicate analyses was carried out using tap water samples taken from our laboratory. The cold water tap was run for twenty minutes, then a 20-L Nalgene jug was filled with water, and allowed to stand for 24 hours. Six 1000-mL aliquots were taken from the 20-L sample, and processed by the PNAA method. Copper, manganese, and zinc were analyzed. Cobalt and cadmium were not detected in the tap water samples. Zinc was determined using a timing scheme of 7:24:1 h, in order to obtain better counting statistics. The tap water sample contained a significant quantity of manganese (average number of counts for the photopeak at 846.8 keV was 82475, corresponding to a manganese concentration of 6.04 μg L^{-1}); consequently, the manganese analysis was carried out using the

Table 4.17. Precision of RPEC method.
Sample: Spiked buffer solution, pH 8.3.

	Number of Counts				
Trial	Cd	Co	Cu	Mn	Zn
1	2306	2538	2435	3301	644
2	1997	2459	2570	3219	650
3	1943	2765	2478	3079	606
4	2039	2753	2539	2978	639
5	2186	2670	2457	3327	637
6	2186	2789	2476	3345	598
7	1876	2715	2662	3140	590
8	2147	2655	2796	3278	625
9	2295	2616	2655	3192	688
10	2150	2738	2501	2968	634
Average	2116	2670	2557	3183	631
St. Dev.	147	106	115	138	29
CV (%)	6.93	3.98	4.50	4.35	4.52

1810.8-keV peak of ^{56}Mn, as this peak was easier to integrate than the 846.8-keV peak. The results of this work are presented in Table 4.18.

A comparison of Tables 4.17 and 4.18 indicates that the value of the CV is poorer for copper and zinc for the replicate analysis of the tap water sample than for the spiked buffer sample. This is to be expected, as the analysis of tap water requires an additional separation step which is not required in the analysis of spiked buffer solutions. The digestion step, followed by the removal of organic material on a column of XAD-7 resin, introduces additional reagents as well as the added work-up of the sample, which can lead to the greater variation of results. The improvement in the value of the CV for manganese is attributable to the higher manganese content in the tap water samples.

The third set of samples consisted of 500-mL tap water spiked with elements which were not detected in the tap water but which could be retained by the resin, namely cadmium, cobalt, mercury, and nickel. A 200-μL aliquot of a multielement stock solution containing these elements was added to the tap water samples which were allowed to equilibrate overnight, then digested and subjected to the PNAA method. The results are shown in Table 4.19. The CV ranged from 5.76% for cadmium to 7.12% for mercury. These values are somewhat higher than the values calculated for spiked buffer solution (Table 4.17). Again, the poorer precision may be attributed to the extra step involved in the PNAA procedure.

4.15 External Quality Assessment

The external quality assessment of the RPEC method using TAN-XAD-4 resin

Table 4.18. Precision of RPEC method.
Sample: Laboratory Tap Water, 1000 mL, Buffered to pH 8.3.

	Number of Counts		
Trial	Cu	Mn	Zn
1	4965	8999	8121
2	4648	8513	7072
3	4870	9320	7284
4	5235	8973	8028
5	4738	9248	7425
6	4505	8500	7987
Average	4827	8925	7653
St. Dev.	257	352	447
CV (%)	5.33	3.94	5.83

Table 4.19. Precision of RPEC method.
Sample: Spiked Laboratory Tap Water, 1000 mL, Buffered to pH 8.3.

	Number of Counts			
Trial	Cd	Co	Hg	Ni
1	7314	2918	2890	914
2	6319	2577	2744	856
3	7194	2869	2793	1002
4	6733	3055	2631	935
5	6478	2687	3189	979
6	6937	2805	3044	870
Average	6829	2819	2882	926
St. Dev.	393	170	205	58
CV (%)	5.76	6.02	7.12	6.27

was evaluated by analyzing two water standard reference materials (SRM) and three water reference materials (RM). These were NIST SRM 1643a and 1643b (Trace Elements in Water) and NRC RM SLRS-1 (Riverine Water), NASS-2 (Seawater), and SLEW-1 (Estuarine Water).

The reference materials were adjusted to pH 8.25 with TRIS buffer and ammonia solution, in order to maximize the number of elements that can be retained on the resin. Typically, three or four trials were performed for each material using different sample volumes. Each set of trials was coupled with a blank run and a multielement comparator standard. A 30-mm resin column was used; this quantity of resin can be contained in a small vial and, as previously noted, maximizes the number of samples which can be irradiated simultaneously. These samples were passed through the column at a flow rate of 1-3 mL min^{-1}. Following passage of a sample, the resin was rinsed with four 10-mL portions of a fresh buffer solution, dried by passage of forced air, then transferred to a vial for irradiation. The three standard irradiation schemes described earlier for the determination of trace elements were also used here. The results are presented in Tables 4.20 through 4.23. It is evident that there is good agreement between the measured and certified values.

The determination of uranium in two reference materials (NRC SLRS-1 and NIST NASS-2) was carried out. Uranium was preconcentrated separately at pH 5.0 as the range for quantitative retention did not fall within the range for the other elements studied, namely > 8.0. The uranium results are given in Table 4.24. Again, the experimental results are in acceptable agreement with the certified values.

Table 4.20. Analysis of NIST SRM 1643a (Trace Elements in Water) by PNAA. Experimental Conditions: Three 250-mL samples; pH = 6.0; Flow Rate = 2.0 mL min^{-1}

	Concentration ($\mu g\ L^{-1}$)	
Element	This Work	Certified Value
Co	19.7 ± 0.5	19 ± 2
Cu	19 ± 1	18 ± 2
Zn	69 ± 5	72 ± 4

Table 4.21. Analysis of NIST SRM 1643b (Trace Elements in Water) by PNAA.

Experimental Conditions: Four 100-mL samples; pH = 8.4; Flow Rate = 1.0 mL min^{-1}

	Concentration ($\mu g\ L^{-1}$)	
Element	This Work	NIST Value
Cd	19 ± 1	20
Co	28 ± 1	26
Cu	20.8 ± 0.9	21.9
Mn	26 ± 1	28
Zn	63 ± 2	66

Table 4.22. Analysis of NRC RM SLRS-1 (Riverine Water) by PNAA.

Experimental Conditions: Three samples (250 mL, 250 mL, 500 mL);
pH = 8.4; Flow Rate = 1.0-3.0 mL min^{-1}

	Concentration (μg L^{-1})	
Element	This Work	Certified Value
Cu	3.3 ± 0.2	3.58 ± 0.30
Mn	1.8 ± 0.2	1.77 ± 0.23
Zn	1.7 ± 0.3	1.34 ± 0.20

Table 4.23. Analysis of NRC RM SLEW-1 (Estuarine Water) by PNAA.

Experimental Conditions: Three samples (250 mL, 250 mL, 500 mL);
pH = 8.4; Flow Rate = 1.0-3.0 mL min^{-1}

	Concentration (μg L^{-1})	
Element	This Work	Certified Value
Cu	1.8 ± 0.2	1.76 ± 0.09
Mn	13.3 ± 0.7	13.1 ± 0.8

Table 4.24. Uranium Analysis of NRC RM SLRS-1 (Riverine Water) and NASS-2 (Seawater).

pH = 5.00; Flow Rate = 1.0-2.0 mL min^{-1}

	Concentration ($\mu g\ L^{-1}$)	
Sample	This Work	Certified Value
SLRS-1	0.36 ± 0.06	0.28 ± 0.03
NASS-2	2.8 ± 0.2	3.00 ± 0.15

4.16 Analysis of Water Samples

The preconcentration RPEC method developed in this work was applied to the analysis of natural water samples and tap water. Potable water samples were collected in acid-washed polyethylene containers. These samples were acidified to pH 1.0-1.5 with nitric acid and digested at 80°C for 20 minutes to break up humic and fulvic complexes that might exist. After cooling to room temperature, the samples were passed through a column of Amberlite XAD-7 to remove dissolved organic material. The effluent was adjusted to the desired pH with ammonia and organic buffer and passed through a column of TAN-XAD-4 at a flow rate of 3-5 mL min^{-1}. The quantity of elements collected on the resin were evaluated by NAA. River water samples were filtered first to remove particulate matter, then subjected to the same sample handling steps as those employed for the tap water samples.

The first set of tap water samples were collected from sites around Halifax. After digestion, the acidified samples (500.0 or 1000.0 mL) were adjusted to pH 6.0 with ammonia and 5 g ME buffer and subjected to the RPEC procedure for the determination of cobalt, copper, and zinc. The results are given in Table 4.25. The precision of the results was generally good, typically between ± 5 and 8%.

A second set of tap water samples were analyzed, as well as river water collected near Port Elgin, New Brunswick. A similar procedure was followed, except that the preconcentration step was carried out at pH 8.4. This modification made possible the determination of cadmium, manganese, and mercury, as well as the three elements determined in the first study. While nickel was quantitatively retained by the resin, the element could not

Table 4.25. Analysis of Halifax Tap Water Samples.

Experimental Conditions: Sample volumes 500.0 and 1000.0 mL;
pH = 6.00; Flow Rate = 3.0-5.0 mL min^{-1}

		Concentration (μg L^{-1})		
Sample	N	Co	Cu	Zn
Site #1	4	0.34 ± 0.05	27 ± 1	25.5 ± 0.8
Site #2	4	0.78 ± 0.09	67 ± 4	17 ± 1
Site #3	4	0.41 ± 0.06	14.3 ± 0.8	10.8 ± 0.5
Site #4	4	0.22 ± 0.04	39 ± 2	11.1 ± 0.6
Site #5	5	0.66 ± 0.05	11.5 ± 0.6	17 ± 1

be determined in tap water samples owing to the insensitivity of NAA.

The results are given in Table 4.26. Cadmium, cobalt, mercury, and nickel were not detected in the water samples investigated. The precision was of the same order as that observed for the water samples analyzed previously. The salinity of the river water did not interfere with the analysis.

4.17 Detection Limits

The detection limits for the elements of interest have been calculated according to the definitions of Currie [327]. Three "limiting levels" have been defined; these definitions are specific to radioactivity and are all related to the number of counts in the blank, μ_B. The critical level, L_C, is the number of counts required to recognize a signal as having been detected, and is given by

$$L_C = 2.33\sqrt{\mu_B} \qquad [4.10]$$

The detection limit, L_D, is the number of counts required in order to reliably claim detection and is given by

$$L_D = 2.71 + 4.65\sqrt{\mu_B} \qquad [4.11]$$

The determination limit, L_Q, is the number of counts required to ensure satisfactory precision ($RSD \leq 10\%$) for quantitative determination, and is given by

Table 4.26. Analysis of River and Tap Water Samples.
Experimental Conditions: Sample volumes 500.0 and 1000.0 mL;
pH = 8.3; Flow Rate = 3.0-5.0 mL min^{-1}

		Concentration ($\mu g\ L^{-1}$)		
Sample	N	Cu	Mn	Zn
Gaspereau River	6	7.6 ± 0.5	1.7 ± 0.2	5.3 ± 0.4
Port Elgin Tap #1	5	7.9 ± 0.6	0.72 ± 0.04	18 ± 3
Port Elgin Tap #2	4	6.5 ± 0.6	0.57 ± 0.05	13.1 ± 0.9
Port Elgin Tap #3	4	8.4 ± 0.3	1.0 ± 0.1	22 ± 1

$$L_Q = 50\ (1 + \sqrt{1 + \frac{\mu_B}{12.5}}\ ) \qquad [4.12]$$

These three limits have been evaluated for the nine elements which were recovered quantitatively by the TAN-XAD-4 resin (namely, cadmium, cobalt, copper, manganese, mercury, nickel, silver, uranium, and zinc). According to Currie, the number of counts attributable to the blank should be evaluated for a sample in which the element of interest is absent, or present at such low levels as to be undetected. The blank should be of a form as similar as possible to the samples which are to be quantified.

It must therefore be determined what actually constitutes the "blank". Since the samples to be analyzed consist of the elements of interest collected on the TAN-XAD-4 resin, a suitable blank might be simply a sample of TAN-XAD-4 resin, or a sample of the resin which has been used for a procedural blank run (*i.e.* a buffer sample with no multielement spike added). However, since the background in a real water sample would be expected to be higher due to the presence of other elements which may not be present in the buffer, the blank for these purposes will be considered to be columns of TAN-XAD-4 which have been used to extract trace elements from real samples (tap water or river water).

Because cadmium, cobalt, mercury, nickel, and silver were not detected in the tap water samples collected near Port Elgin, these samples shall be used to define the blank. Uranium and manganese were not detected in the Halifax tap water samples preconcentrated at pH 6, so the blank values for these two elements will be derived from the Halifax samples.

All of the real water samples investigated contained measurable quantities of copper and zinc, so a true blank sample cannot be obtained. In such instances, a so-called "synthetic blank" is an acceptable alternative [324]. The determination of the blank for copper and zinc has been carried out using the blank samples for the analysis of artificial seawater (that is, a buffer solution containing bromine, chlorine, magnesium, and sodium, but not a multielement spike).

The values for the Currie detection limits are given in Table 4.27. The values for the absolute detection limits L_D range from 0.014 μg for uranium to 7.57 μg for nickel. These values are consistent with the sensitivities of NAA for these elements. As cobalt and silver were quantified using both the 10-min and 7-h irradiation periods, two sets of values appear for these elements. It is interesting to note that the detection limits for cobalt and silver are only slightly higher when the longer-lived nuclides are used. For these two elements, the longer-lived nuclides have poorer sensitivities, but this is offset by the fact that the respective photopeaks sit on a much lower blank than for the shorter-lived nuclides. The detection limits for zinc are approximately three times higher using the longer-lived ^{65}Zn nuclide and a timing scheme of 7 h:21 d:2 h than the ^{69m}Zn nuclide and timing parameters of 7:24:1 h.

4.18 Elution of Trace Elements from TAN-XAD-4 Column

One of the major advantages of ligand-impregnated resins is their stability to mineral acids and bases. Owing to this stability, RPEC may be coupled with other analytical techniques such as AAS in which a liquid sample is required. The metals collected on the

Table 4.27. Detection limits for environmental water samples.

Element	Nuclide	Timing Parameters, t_i:t_d:t_c	L_C (μg)	L_D (μg)	L_Q (μg)
Ag	^{108}Ag	10:1:10 min	0.12	0.24	0.77
Ag	^{110m}Ag	7h:21d:2h	0.14	0.28	0.96
Cd	^{115}Cd	7:24:1 h	0.11	0.22	0.69
Co	^{60m}Co	10:1:10 min	0.041	0.083	0.26
Co	^{60}Co	7h:21d:2h	0.046	0.095	0.36
Cu	^{66}Cu	10:1:10 min	0.53	1.06	3.36
Hg	^{203}Hg	7h:21d:2h	0.075	0.15	0.50
Mn	^{56}Mn	10:1:10 min	0.016	0.031	0.098
Ni	^{58}Co	7h:21d:2h	3.7	7.6	27
U	^{239}U	10:1:10 min	0.0068	0.014	0.042
Zn	^{69m}Zn	7:24:1 h	0.41	0.83	2.66
Zn	^{65}Zn	7h:21d:2h	1.3	2.6	9.3

resin can be eluted with acid for analysis. The ability to remove metals by acidic eluents without degrading the resin also raises the possibility that the resin can be reused. The stability of the TAN-XAD-4 resin to successive column extractions and acidic stripping was evaluated by a tracer method.

A tracer solution containing ^{203}Hg, ^{65}Zn, and ^{60}Co was passed through a column of TAN-XAD-4 using the column apparatus shown in Fig. 4.26 (that is, with a polyethylene vial serving as the "column"). The 70-mL solution, containing 28.0 μg of cobalt, 3.5 μg mercury, and 75.5 μg of zinc, was passed through the column at pH 8.0. The column effluent was collected in a 100-mL volumetric flask. After passage of the sample solution, the column was treated with 20 mL of eluent to attempt to remove the radionuclides collected on the resin. The acidic eluate was collected in a 25-mL volumetric flask, which was made up to the mark with DDW.

After the passage of eluent through the column, the tracers present in the original 100-mL sample were assumed to exhibit one of three types of behavior. A fraction of a given element might be unretained by the column, in which case some activity will be present in the solution collected in the 100-mL flask. The remainder of the elements of interest will then be collected on the column. The elements present on the column may be stripped with the eluent; consequently, these elements will be present in the 25-mL volumetric flask. If the elements resist removal, the tracers will then be left on the column at the end of the experiment. By counting the contents of the two volumetric flasks, the amount of tracer present on the resin can be inferred by difference, obviating the need to remove the resin from the column apparatus and count the resin directly.

The column was washed with 4 M nitric acid and DDW, then readjusted to pH 8.0 and the experiment was repeated; the sample solution was the 25-mL acidic effluent from the previous experiment, also readjusted to pH 8.0 and diluted to 70 mL. A variety of eluting agents were investigated. The procedure was repeated several times, in order to determine whether or not the elements in question could be loaded on the column and removed reproducibly and quantitatively, as well as to determine the number of times the column could be reused without suffering a significant loss of performance. This consideration is not important when the RPEC method is coupled with NAA (since the resin is not reused after irradiation), but has significance in other instances. The number of times the resin could be reused can be important if the column method is to be coupled with an instrumental step in which a liquid sample is required, or if the column is to be used simply as a scavenger for trace elements.

The results are presented in Table 4.28. Three measurements were required for each trial. The initial tracer solution was counted in a 25-mL flask and was taken to represent the total quantity of tracers present. During the loading step, the column effluent was collected in a 100-mL flask; the tracer content in this flask was indication that some of the elements of interest were unretained by the resin. The acidic effluent was collected in the original 25-mL flasks and recounted to determine the amount of tracer which was recovered; that is, the amount of tracer which was successfully loaded on the resin and subsequently stripped.

The results show that the resin can be reused several times before suffering a

Table 4.28. Tracer studies for the elution of trace elements from the resin. Flow rate = 1 mL min^{-1} for both steps.

		% tracer collected on the resin			% tracer recovered from the resin by elution		
Trial	Eluent	Co	Hg	Zn	Co	Hg	Zn
1	2 M HNO_3	98.9	97.5	96.4	97.1	96.4	95.0
2	2 M HNO_3	96.4	93.6	93.4	94.2	91.5	90.8
3	2 M HNO_3	98.0	99.1	95.3	96.3	96.8	93.2
4	3 M HNO_3	100.0	96.9	93.5	95.8	96.0	89.5
5	3 M HNO_3	96.7	97.3	95.6	94.3	95.4	93.9
6	2 M HCl	94.1	92.5	93.4	88.7	90.1	85.7
7	1 M HCl/ 1M HNO_3	97.2	96.0	97.3	92.4	94.0	93.5
8	2 M HNO_3	95.7	93.8	100.0	94.1	92.0	98.4
9	2 M HNO_3	64.8	50.4	75.7	56.7	39.5	71.6

noticeable deterioration in performance. As the resin was stripped with acidic eluent following the eighth trial, the effluent appeared yellow, indicating the loss of TAN from the column. The performance of the resin for the ninth trial showed a sharp deterioration, presumably owing to the removal of some of the chelating agent from the column.

4.19 Calibration Curves for Uptake of Trace Elements

The linear range of the RPEC method was evaluated for a series of spiked buffer samples using either PNAA or radiotracers. Samples containing a wide range of masses of the elements of interest (specifically, cobalt, copper, manganese, mercury, nickel, and zinc) were prepared and passed through the column. The uptake of each element of interest was evaluated over a mass range of 1 mg down to the detection limits L_D, as given in Table 4.27. Multielement stock solutions were used for samples containing less than 200 μg of each element of interest. Samples containing more than 200 μg of the element of interest were processed using single-element stock solutions, in part to avoid competition for chelating sites or saturation of the column, but also to allow more flexibility in the choice of timing parameters for NAA. Generally, shorter irradiation times were necessary for larger quantities of the elements of interest in order to minimize the overall activity of the irradiated sample.

The calibration plots, as shown in Figs. 4.71-4.76, indicate that the preconcentration method is effective for the quantitative extraction of microgram to milligram quantities of the elements of interest.

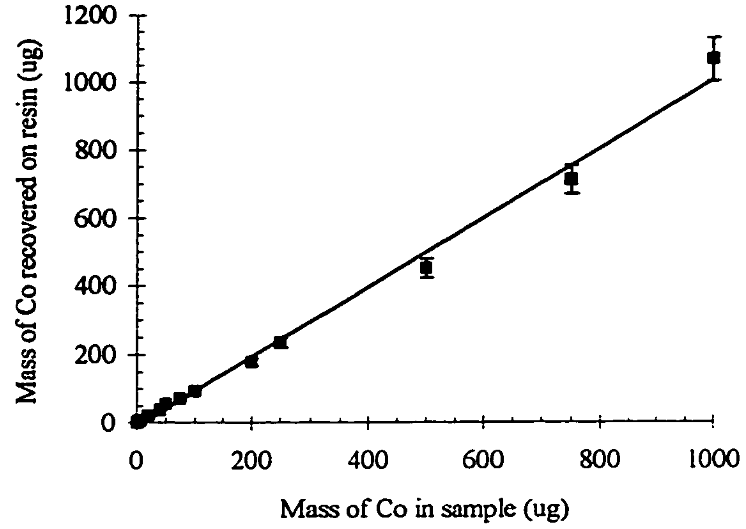


Figure 4.71. Calibration plot for the uptake of Co by the RPEC method.

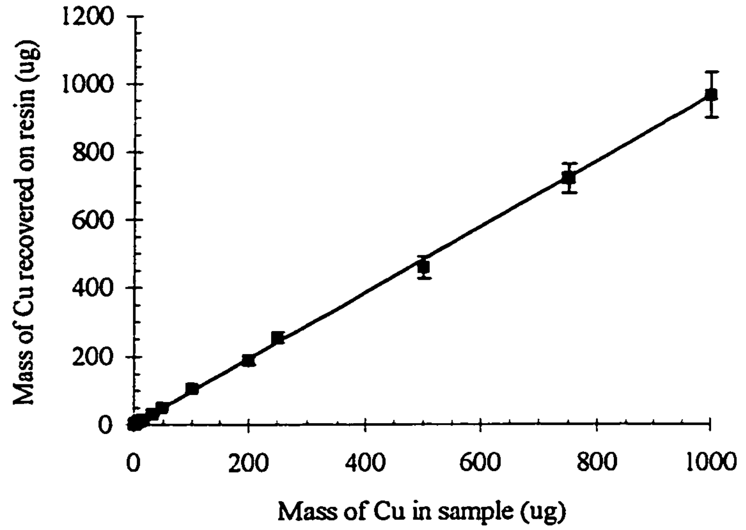


Figure 4.72. Calibration plot for uptake of Cu by the PNAA method.

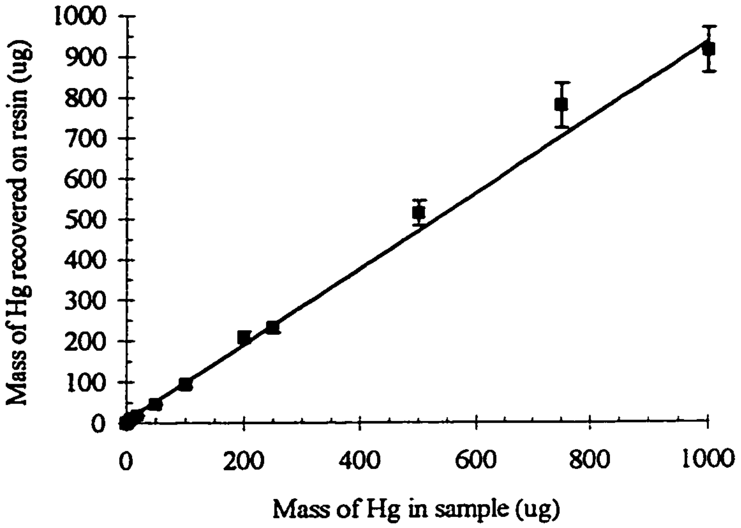


Figure 4.73. Calibration plot for uptake of Hg by the PNAA method.

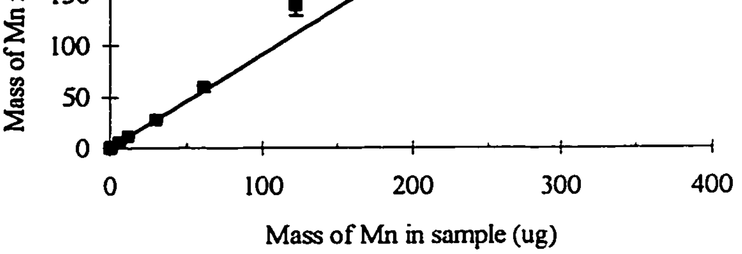


Figure 4.74. Calibration plot for uptake of Mn by the PNAA method.

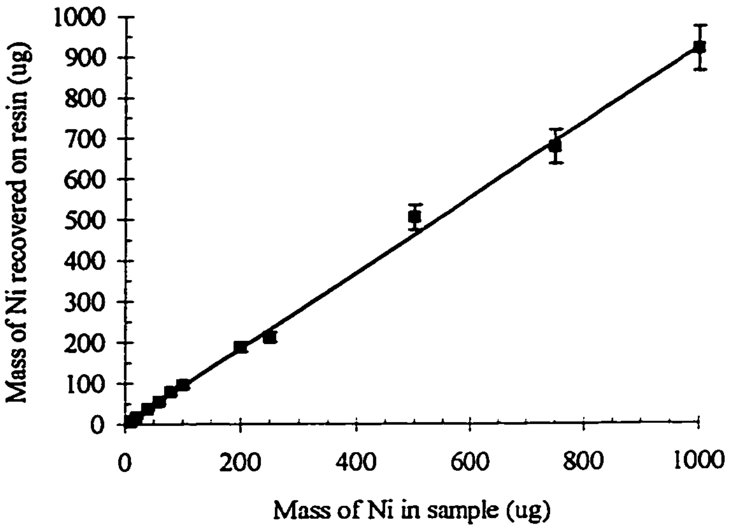


Figure 4.75. Calibration plot for uptake of Ni by the PNAA method.

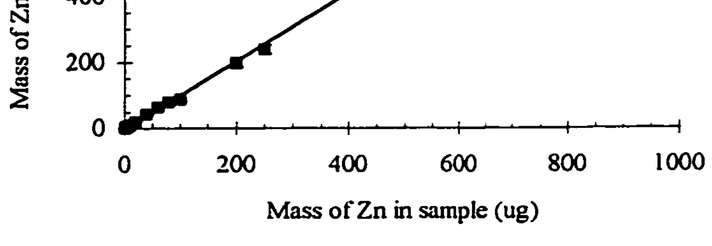


Figure 4.76. Calibration plot for uptake of Zn by the PNAA method.

4.20 Enrichment and Decontamination Factors

The enrichment factor of the RPEC is method is essentially the ratio of the volume of the original water sample to the volume of the preconcentrated sample. For the RPEC method developed here, trace elements present in a water sample of 1-L volume or more can be preconcentrated onto a 0.5-1.0-g sample of resin which occupies a volume of not more than 2 mL. An enrichment factor of at least 500 is therefore attainable, and larger values could be obtained with larger sample volumes. The enrichment factor of the method is enhanced by the fact that analysis is carried out on a solid sample. Typically, elution of the elements from the column requires several bed volumes of eluent, so the elution step tends to lower the degree to which the trace elements are concentrated.

The decontamination factor has been calculated using the artificial seawater samples described in Section 4.12, and is given by the ratio of mass of interfering elements present in the original sample to the mass of these elements in the final, preconcentrated sample. The decontamination factors of the RPEC method for bromine, chlorine, and sodium were calculated to be 5.4×10^4, 1.1×10^7, and 3.7×10^5, respectively. As magnesium was not detected on the resin after passage of the artificial seawater solution, no decontamination factor was calculated.

4.21 Preparation and Characterization of Dithizone-XAD-4 Resin

A reversed-phase resin comprised of dithizone (Dz) loaded on XAD-4 resin was prepared in batch mode in a manner similar to that utilized for the synthesis of TAN-XAD-4 resin. This resin was studied for two reasons. The more important of these was to identify trace elements of interest which were not concentrated on TAN-XAD-4 resin but which could be quantitatively retained by the Dz-loaded resin. Dithizone is a well-characterized chelating agent which is known to form complexes with numerous elements, so it would be expected that a Dz-loaded resin would be applicable to the simultaneous preconcentration of several elements. Furthermore, an advantage of ligand-impregnated resins is the ease with which the chelating group can be changed. The second reason for preparing Dz-XAD-4 is to demonstrate this point.

Attempts to synthesize Dz-XAD-4 using acetone or methanol as solvent produced resins which displayed inferior metal-complexing behavior. This was attributed to the fact that Dz is sparingly soluble in these solvents. Consequently, the loading of Dz on the resin phase was insufficient to provide an adequate number of complexing sites for the trace metals in solution.

The resin was instead prepared using dimethyl sulfoxide (DMSO) as the solvent. This solvent was chosen because it is miscible with water and satisfied the requirement of moderate solubility of Dz. The use of DMSO is disadvantageous in that the uptake of Dz on the resin cannot be evaluated directly by NAA of the resin, due to the fact that sulfur is present in the solvent, making accurate analysis of the sulfur content of the resin (and thus the determination of the Dz uptake by the resin) impossible. The quantity of Dz adsorbed on the resin was estimated by spectrophotometric analysis of the solvent before and after equilibration with the resin.

Dithizone has two potentially dissociable protons, so a distinction is drawn between two types of complexes. A primary dithizonate is formed when the metal ion reacts with the singly-charged anion, while complexes derived from the metal ion and the doubly-charged anion are termed secondary dithizonates [328]. Some metal ions, such as cobalt(II), copper(II), and mercury(II), are able to form both primary and secondary dithizonates. Secondary dithizonates are generally formed under conditions in which the quantity of chelating agent is insufficient. For most analytical applications (namely, in which the elements of interest are present at trace levels), this situation does not arise, so the use of dithizone as an analytical reagent invariably involves the formation of primary dithizonates.

The resin prepared by equilibrating 100 mL of a saturated solution of Dz in DMSO with 3.00 g XAD-4 resin contained 5.0×10^{-2} mmol Dz per gram of resin and had a copper exchange capacity of 2.9 mg Cu g^{-1} resin. The recovery of several trace elements as a function of pH was evaluated using this resin, following the RPEC method used with the TAN-XAD-4 resin.

Silver (Fig. 4.77) was essentially quantitatively retained ($\geq$ 90%) by the Dz-XAD-4 resin over the pH range 3-8. Silver was one of two elements (mercury being the other) to display a distinctly superior recovery on the Dz-XAD-4 resin than on TAN-XAD-4. While TAN-XAD-4 failed to quantitatively extract silver from buffer solutions of pH > 7.3 (Fig. 4.15), this behavior was not in evidence for the Dz-loaded resin. That silver would display such favorable recovery characteristics is to be expected, given that a highly stable silver dithizonate can be extracted from acidic solutions such as 4M sulfuric acid [329], permitting the separation of silver from other metals. The high affinity of dithizone for silver

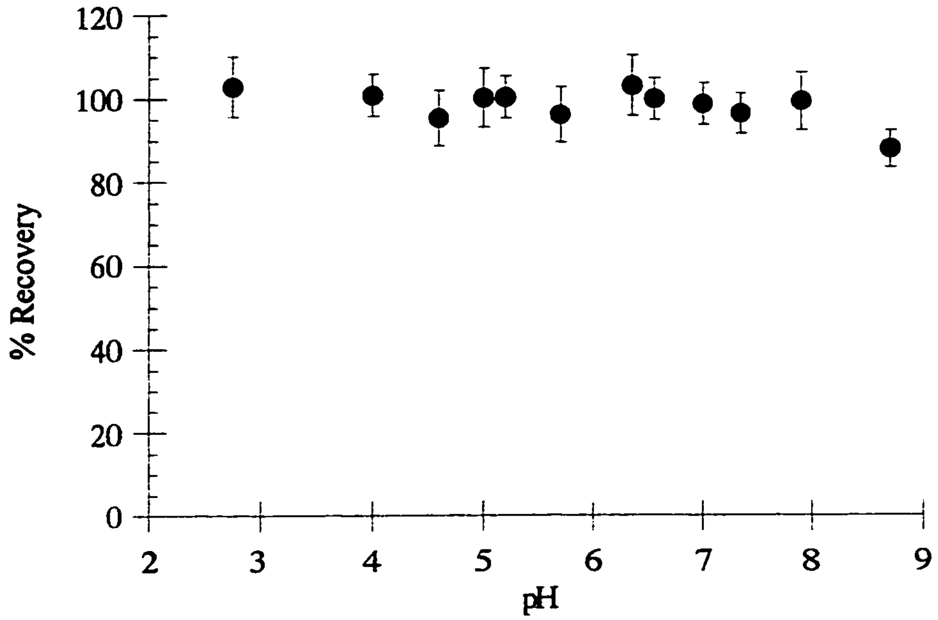


Figure 4.77. Recovery of Ag by Dz-XAD-4 resin as a function of pH.

has been exploited in the separation of silver and copper from cobalt by extracting the silver and copper dithizonates into carbon tetrachloride at pH 3 [330].

As shown in Fig. 4.78, mercury was completely recovered from solution at pH > 2.4. The mercury uptake did not drop off at elevated pH, in contrast to most of the other elements which were quantitatively retained by this resin. The use of dithizone as an analytical reagent for mercury is well documented. This is most likely due to the fact that mercury is extracted over a such a wide pH range that the separation of mercury from most other metals is feasible. Not surprisingly, the stability constant for the formation constant of mercury(II) dithizonate is quite high ($\log \beta_2 = 26.85$ [331]).

The extraction of mercury(II) has been reported from solutions as acidic as 6M H_2SO_4 [329]. Singh *et al.* [332] reported the formation of the mercury-dithizone complex at pH 2.4, and applied a spectrophotometric technique to the determination of mercury in tap water and in a pesticide solution. The high affinity of dithizone for mercury has been exploited in column separation procedures. Lee *et al.* [333] impregnated a styrene-divinylbenzene copolymer with dithizone and applied the resulting dithizone gel to the concentration of trace mercury from aqueous solutions acidified to pH 1. The method was used to determine mercury in river water, seawater, and industrial effluent.

Four other elements investigated in this work, cadmium, cobalt, copper, and zinc, were quantitatively retained by the resin at optimum pH, although in general, the retention characteristics of cadmium, cobalt, and zinc on the Dz-XAD-4 resin were less favorable than those exhibited in the TAN-XAD-4 studies.

Cadmium (Fig. 4.79) was quantitatively recovered by the resin over the pH

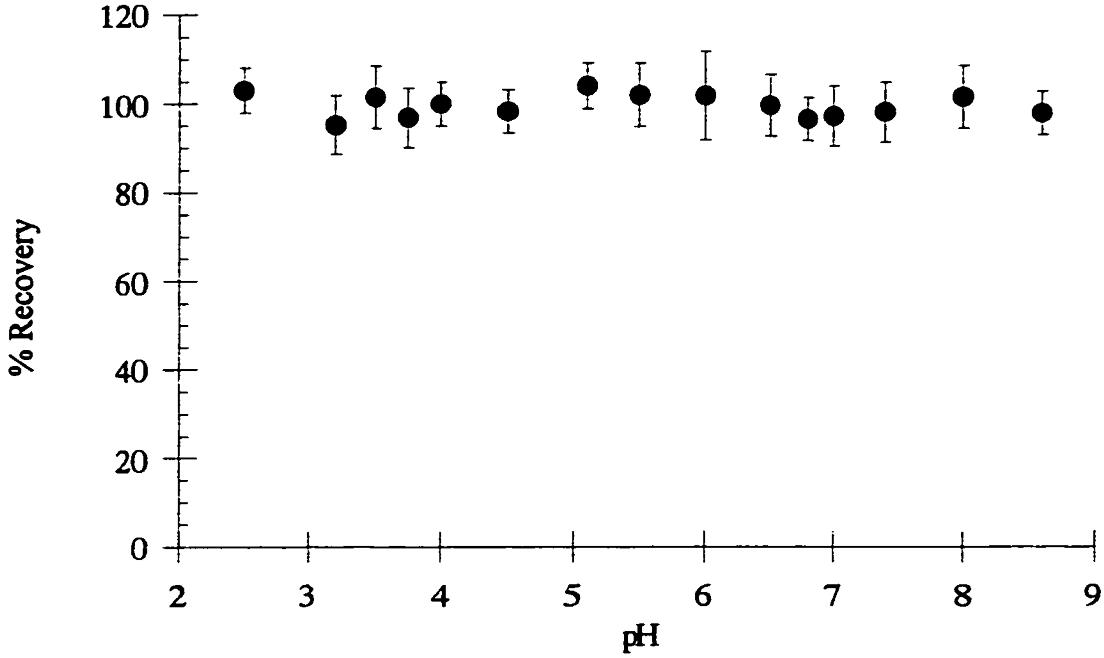


Figure 4.78. Recovery of Hg by Dz-XAD-4 as a function of pH.

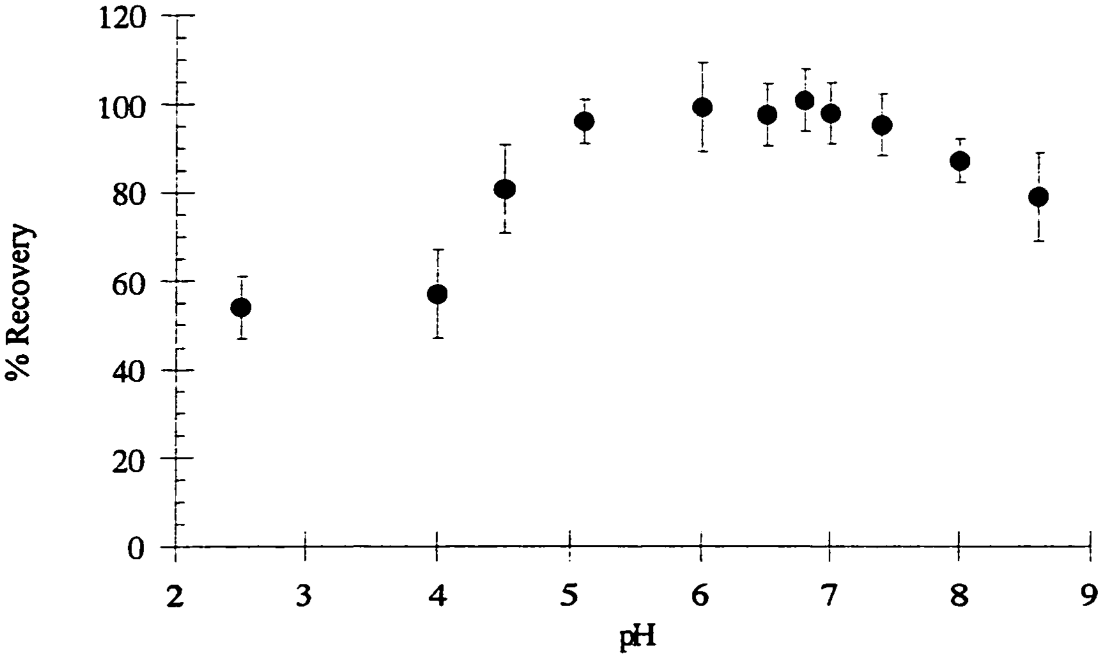


Figure 4.79. Recovery of Cd by Dz-XAD-4 as a function of pH.

range 5-7. In contrast to the recovery of cadmium on the TAN-XAD-4 resin, the uptake of cadmium on the dithizone resin was non-quantitative at higher pH (approximately 80% at pH 8.6). The cadmium-dithizone complex has been reported to be completely extracted at pH 7-14 [334], so the inability of the resin to completely retain cadmium at higher pH would not have been expected.

As shown in Fig. 4.80, the recovery of cobalt was > 95% at pH > 6. This is in good agreement with extraction studies; cobalt is quantitatively retained from aqueous solution at pH ≥ 6.5 [334]. While the Dz-loaded resin exhibited favorable recovery of cobalt at higher pH (*i.e.* the retention did not fall below 90%) the overall performance for cobalt was slightly inferior to that displayed by TAN-XAD-4. The minimum pH for quantitative uptake of cobalt on the TAN-XAD-4 resin was about 5 (Fig. 4.9) and the cobalt recovery in the pH range 3-5 was superior for the TAN-impregnated support. These observations are consistent with the fact that the reported stability constants for the Co(II)-TAN complex ($\log K_1 = 9.50$, $\log \beta_2 = 19.00$, Table 1.1) are higher than for the Co(II)-Dz complex ($\log \beta_2 = 13$ [331]).

The recovery of zinc (Fig. 4.81) was quantitative over the pH range 5-7.2. The recovery tailed off at pH values outside of this range. This behavior is unusual compared to that exhibited for many of the elements quantitatively retained on the dithizone or TAN-loaded resins. Generally, elements which were quantitatively recovered on a given resin followed a trend of increasing recovery with increasing pH, and constant and complete retention as the pH was increased further. It is difficult to account for the failure of the Dz-XAD-4 column to extract zinc at elevated pH, given the formation constants for the zinc-dithizone complex ($\log K_1 = 7.75$, $\log \beta_2 = 15.05$ [331]). While these values are several

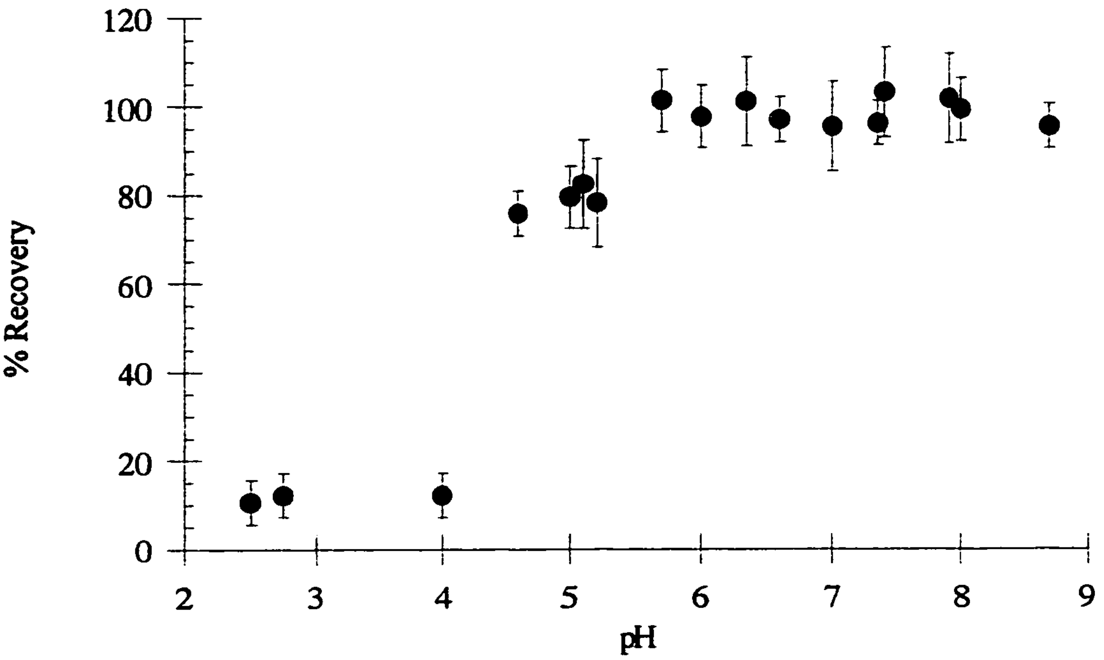


Figure 4.80. Recovery of Co by Dz-XAD-4 as a function of pH.

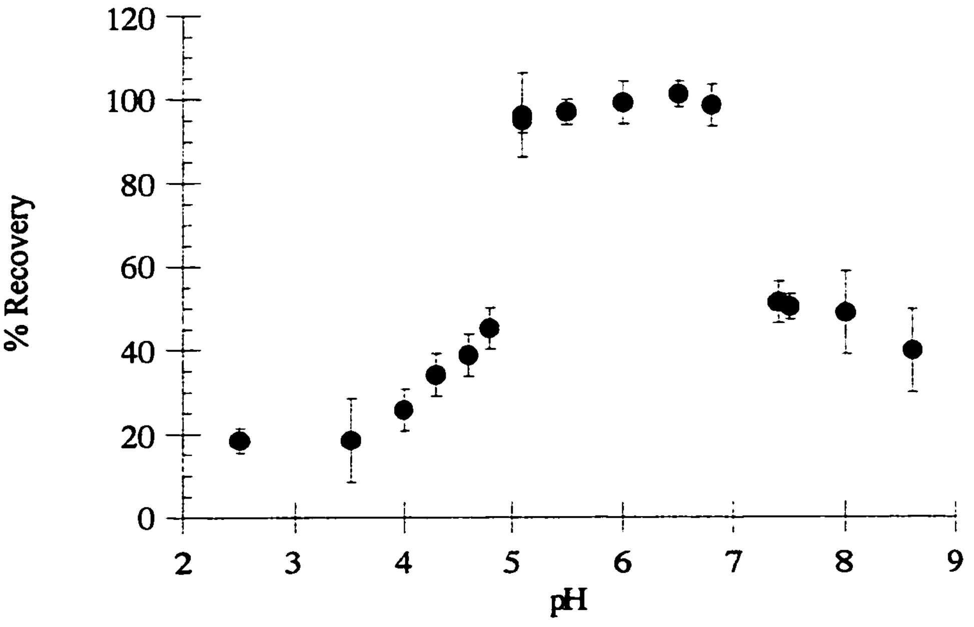


Figure 4.81. Recovery of Zn by Dz-XAD-4 as a function of pH.

orders of magnitude lower than those corresponding to TAN, (log K_1 = 9.87, log β_2 = 19.74, Table 1.1) they appear to be large enough to overcome the effects of hydrolysis or the possible formation of other zinc species at the higher pH values.

The recovery of copper (Fig. 4.82) is at least 90% at pH 4-9. The stability constant for the formation of copper(II) dithizonate is quite high (log β_2 =22.3 [331]) and almost as large as that for the Cu(II)-TAN complex (log β_2 = 22.52, Table 1.1). Correspondingly, the extraction of copper of resins loaded with either dithizone or TAN would be expected to be quantitative over wide ranges of pH. The extraction of copper dithizonate has been reported to be quantitative at pH > 2 [337] and copper is one of only a few elements which can be extracted as the dithizonate from dilute acid solution (*ca.* 0.5-1.0 M) [329].

No other elements investigated in this work were collected to any significant degree by the Dz-loaded resin. Arsenic and antimony passed completely through the resin over the entire pH range studied. In extraction studies, dithizone exhibits no affinity for the pentavalent species, although complexes with Sb(III) and As(III) are known to form [328].

Chromium (Fig. 4.83) was poorly retained over the entire pH range studied. The element passed completely through the resin at pH < 5.2, and the best recovery achieved by the resin was approximately 20% at pH 6.8-7.9.

The recovery of manganese by the dithizone-impregnated resin is shown in Fig. 4.84. The element was not retained at all at pH ≤ 5, with a general trend toward increasing recovery as the pH was increased. The recovery was only about 40% at pH 8.7. The extraction of manganese dithizonate has been reported, but generally at elevated pH.

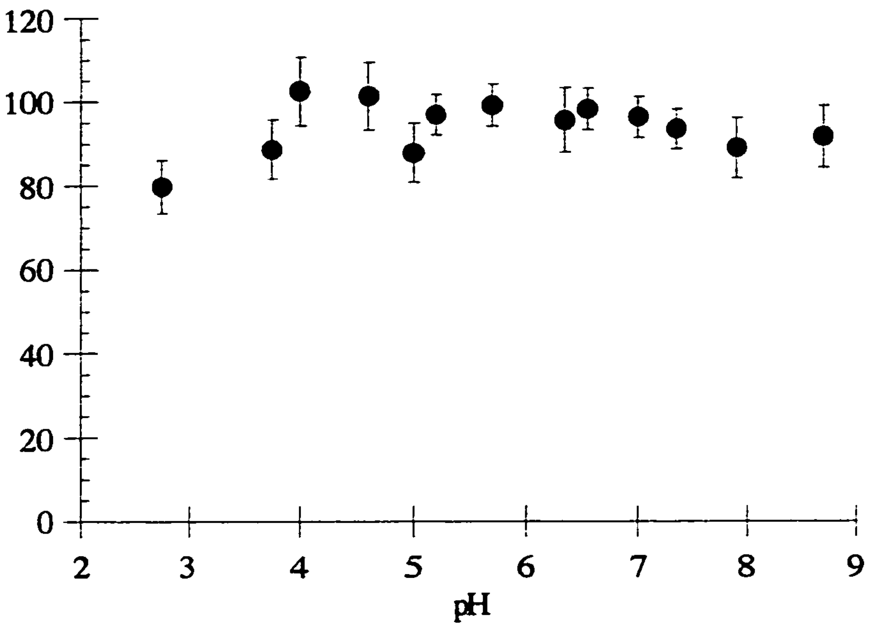


Figure 4.82. Recovery of Cu by Dz-XAD-4 as a function of pH.

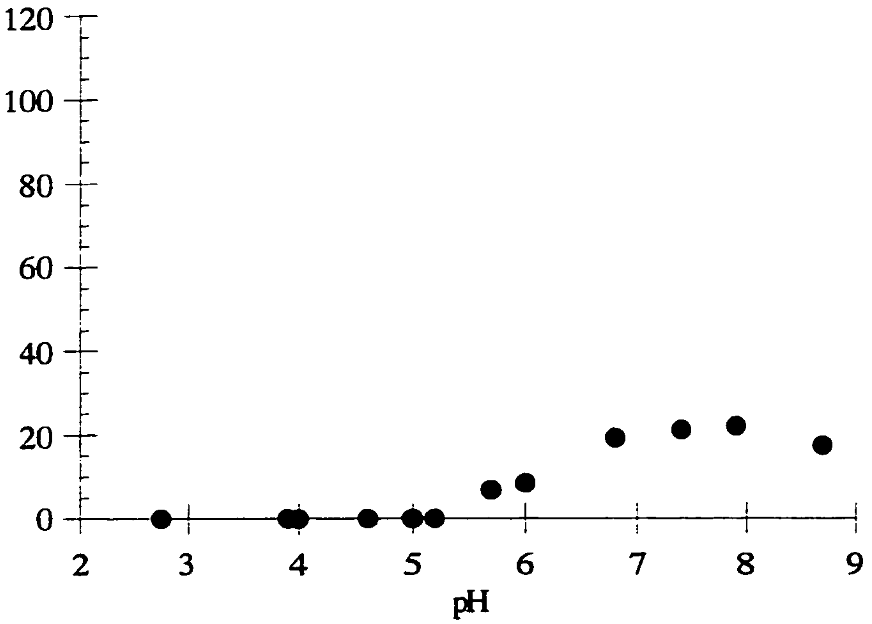


Figure 4.83. Recovery of Cr by Dz-XAD-4 as a function of pH.

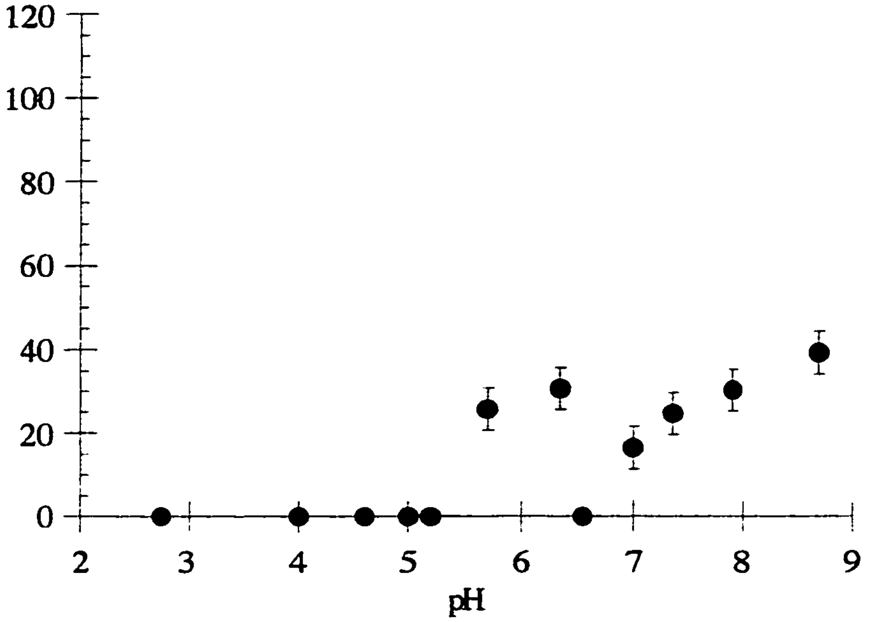


Figure 4.84. Recovery of Mn by Dz-XAD-4 as a function of pH.

Akaiwa and Kawamoto [335] reported the optimum pH extraction for manganese as 9.7, but also noted that the extraction was not quantitative even at this optimum pH. The results of manganese extraction studies using dithizone suggest that the performance of the Dz-XAD-4 resin could be improved by increasing the pH above 9, although it is uncertain whether the resin will recover all of the trace manganese under any conditions.

Thorium (Fig. 4.85) was poorly recovered by the dithizone-loaded resin. The recovery was generally less than 30% over the entire pH range investigated. The retention of uranium (Fig. 4.86) was inferior to that exhibited by the TAN-XAD-4 resin. The recovery was maximized (between 45-65%) in the pH range 5.2-8.0 but was negligible at pH values outside this range. Malik and Sharma [336] reported the colorimetric determination of 1:2 dithizone complexes of Th(IV) and U(VI), but the quantitation of trace quantities of these elements using dithizone has not been extensively investigated.

Vanadium (Fig. 4.87) was also poorly retained by the dithizone resin. The element was quantitatively eluted at pH < 3 and pH > 5. At the pH of maximum retention (pH 4.0), only 34% of vanadium was collected on the resin.

The results of the pH study indicate that in comparison to the TAN-XAD-4 resin, the Dz-XAD-4 column displayed superior performance in the extraction of silver and mercury from aqueous solution. Of the other elements investigated, the two resins were of comparable utility in the extraction of cadmium, cobalt, and copper, but the dithizone-loaded resin was inferior to the TAN-impregnated support in the collection of manganese, uranium, and zinc. The Dz-XAD-4 resin should have some utility as a reagent for the RPEC separation of silver and mercury from other trace metals, although its research potential is probably low,

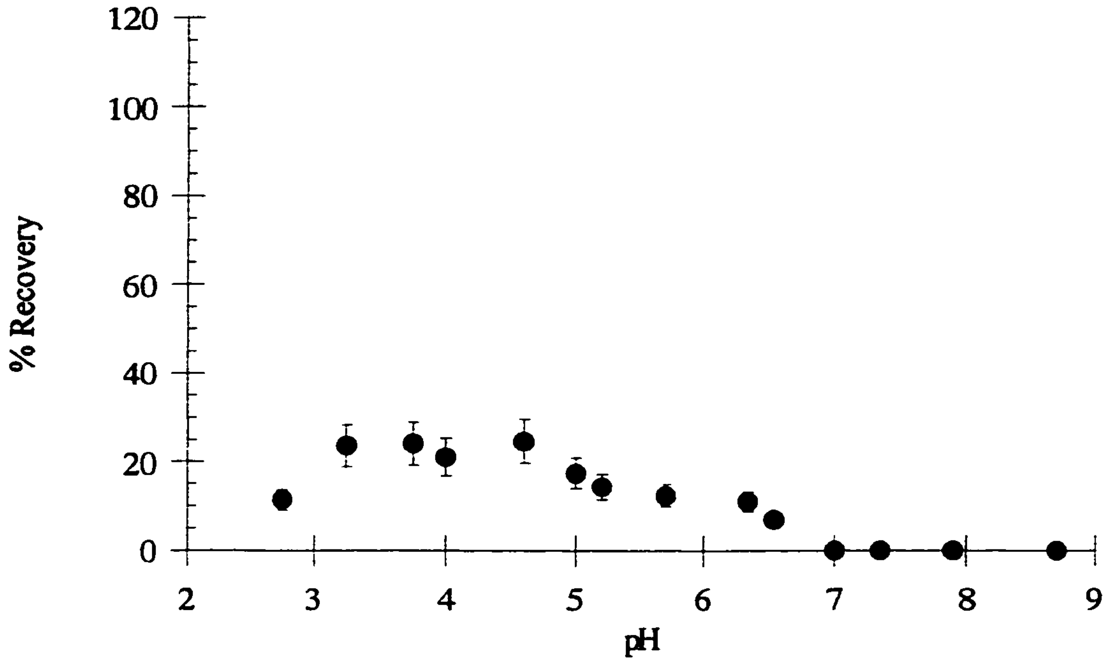


Figure 4.85. Recovery of Th by Dz-XAD-4 as a function of pH.

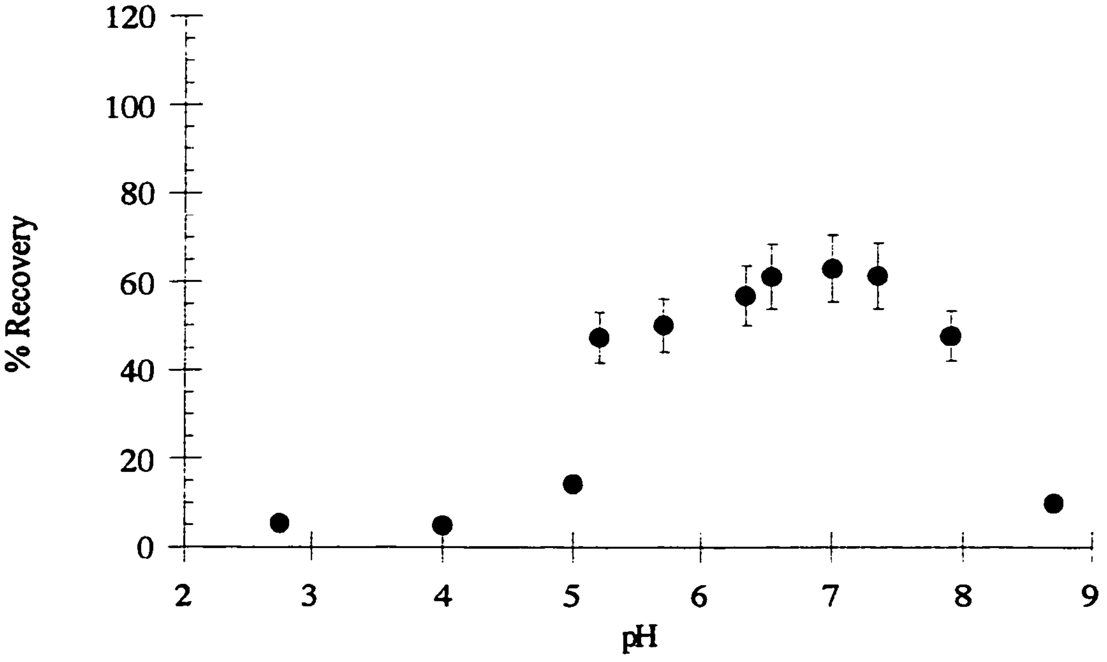


Figure 4.86. Recovery of U by Dz-XAD-4 as a function of pH.

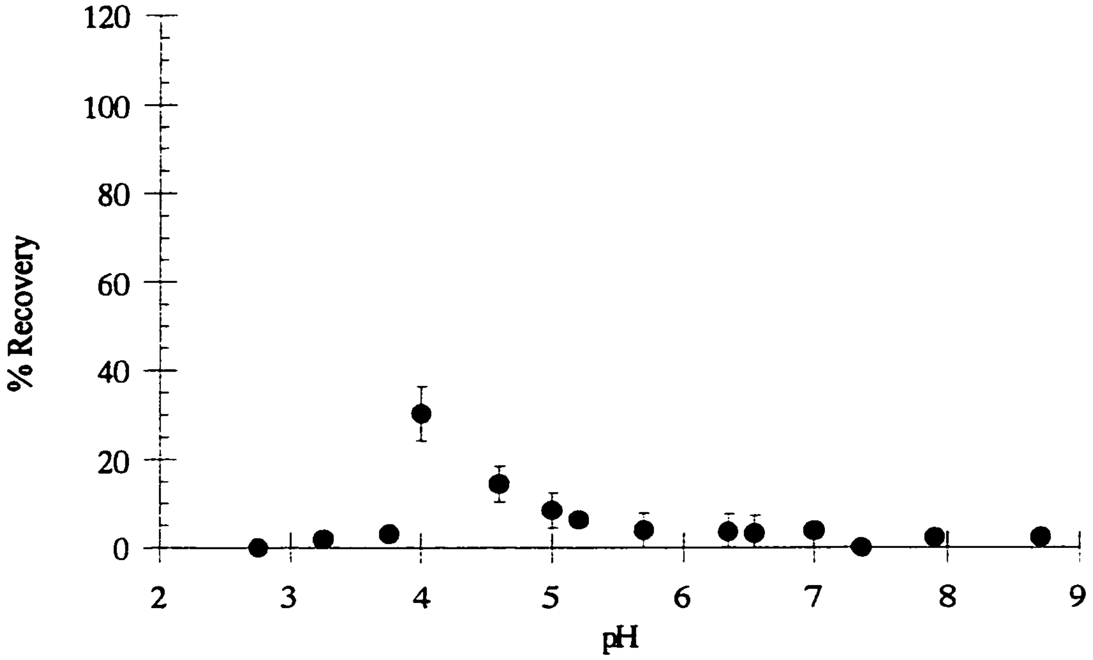


Figure 4.87. Recovery of V by Dz-XAD-4 as a function of pH.

given the large body of work devoted to the characterization of dithizone as an analytical reagent.

4.22 Loading of XAD-4 Resin with Trioctylphosphine Oxide

Trioctylphosphine oxide (TOPO) was also applied as a reagent for RPEC. The resin was prepared using the method developed in this thesis. The solvent used was 9:1 (v/v) methanol:DDW; the precleaned resin was equilibrated for 2 h with the solution of TOPO, then washed, filtered, and stored in DDW.

Two preparations were undertaken. For one set of experiments, the concentration of TOPO in the solution was initially 1.0×10^{-3} M; for the second, the concentration of TOPO was increased to 1.0×10^{-2} M. The amount of TOPO on the resin at the end of the equilibration was estimated by NAA, using the decay of ^{28}Al, produced in the reaction ^{31}P(n,α)^{28}Al. As ^{28}Al is also produced by the absorption of a neutron by ^{27}Al, corrections were made to account for the contribution of aluminum to the detected photopeak. The resin prepared in a solution with $[\mathrm{TOPO}]_0 = 1.0 \times 10^{-3}$ M contained approximately 40 mg TOPO per gram of resin (0.10 mmol g^{-1}), while for the preparation using $[\mathrm{TOPO}]_0 = 1.0 \times 10^{-2}$ M, the loading of TOPO on the resin was 160 mg g^{-1} (0.41 mmol g^{-1}).

The retention of seven elements (cobalt, copper, manganese, silver, thorium, uranium, and vanadium) was evaluated for the two TOPO-loaded resins. Not surprisingly, the resin containing the higher quantity of TOPO displayed superior performance of the two.

Three of the elements, cobalt (Fig. 4.88), copper (Fig. 4.89), and uranium (Fig. 4.90) were quantitatively ($>$ 90%) retained. The uranium results were interesting in that the recovery was at least 90% for pH 3.5-5.0 and fell to 40% as the pH was increased above 6.0. Thorium (Fig. 4.91) followed a similar pattern to uranium in that the recovery was maximized at lower pH (60-70% at pH 4.0-6.0) and dropped off as the pH was increased (about 30% recovery at pH 7).

The plots shown in Figs. 4.88 through 4.91 are presented with the recoveries of each element plotted for both resins on the same set of axes. It is evident that, with a couple of exceptions (cobalt at pH $<$ 6 and thorium at pH 6.0-6.5), the uptake of these four elements was essentially similar for both resins, despite the disparity in the amount of TOPO present.

In contrast, the recoveries of silver (Fig. 4.92) and vanadium (Fig. 4.93) exhibited a dependence on the amount of TOPO loaded on the resin. On the resin with 0.41 mmol g^{-1} TOPO, the uptake of silver rose steadily as the pH was increased, to a maximum of 80% at pH 6.0. The highest vanadium recovery was only 42% at pH 5.0 and the uptake of the element was less than 20% at pH $>$ 6.3. For both of these elements, the recovery on the resin containing 0.10 mmol g^{-1} TOPO was essentially negligible ($\leq$ 10%) over the entire pH range studied.

Manganese was not retained at all by either resin at pH $<$ 7.5, but approximately 50% of the trace element was collected at pH 8.0 on the resin with the higher concentration of TOPO. The uptake of manganese on the other, less concentrated TOPO resin was negligible at pH 8.0.

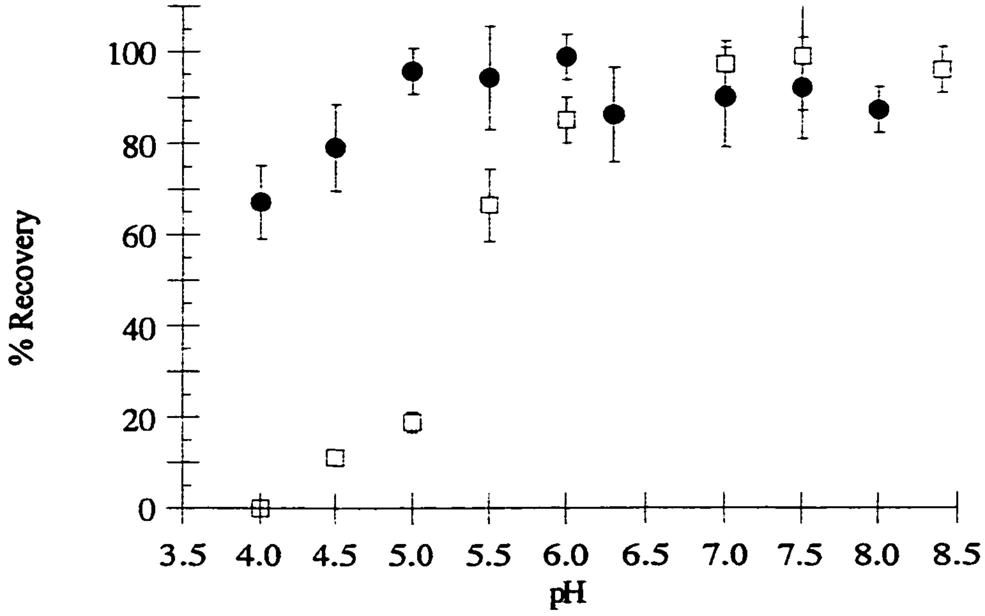


Figure 4.88. Recovery of Co on TOPO-XAD-4 resin as a function of pH. (□) $[TOPO]_r = 0.10$ mmol g^{-1} ; (●) $[TOPO]_r = 0.41$ mmol g^{-1}

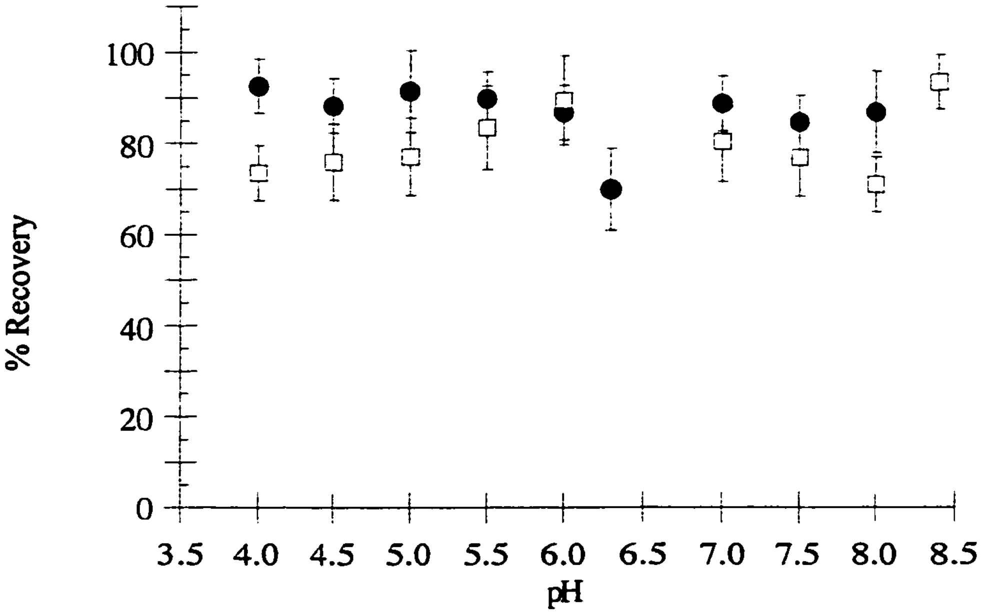


Figure 4.89. Recovery of Cu on TOPO-XAD-4 resin as a function of pH. (□) $[TOPO]_r = 0.10$ mmol g^{-1} ; (●) $[TOPO]_r = 0.41$ mmol g^{-1}

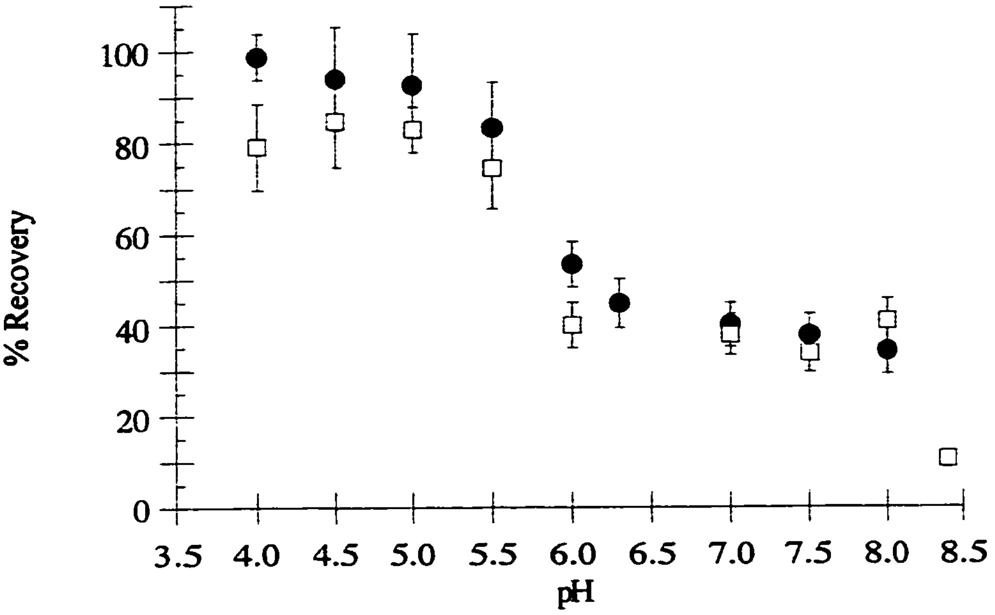


Figure 4.90. Recovery of U on TOPO-XAD-4 resin as a function of pH.
(□) $[TOPO]_r = 0.10$ mmol g^{-1} ; (●) $[TOPO]_r = 0.41$ mmol g^{-1}

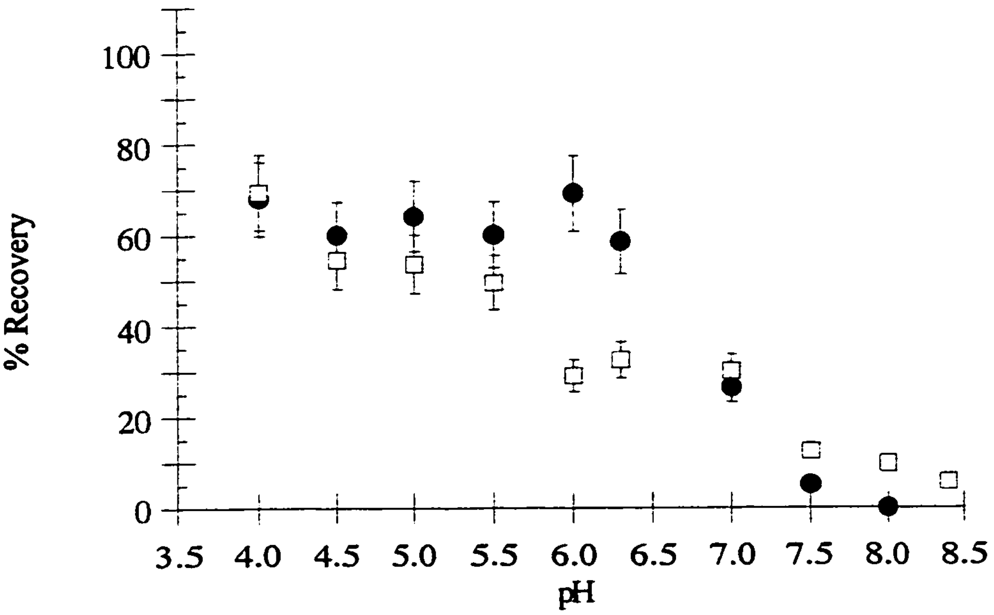


Figure 4.91. Recovery of Th on TOPO-XAD-4 resin as a function of pH.
(□) $[TOPO]_r = 0.10$ mmol g^{-1} ; (●) $[TOPO]_r = 0.41$ mmol g^{-1}

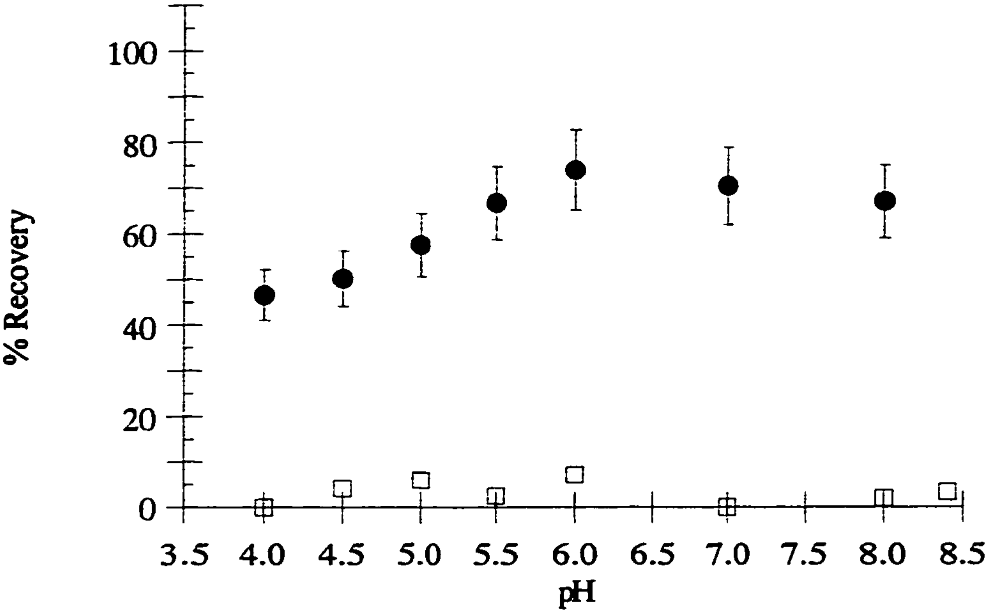


Figure 4.92. Recovery of Ag on TOPO-XAD-4 resin as a function of pH.
(□) $[TOPO]_r = 0.10$ mmol g^{-1} ; (●) $[TOPO]_r = 0.41$ mmol g^{-1}

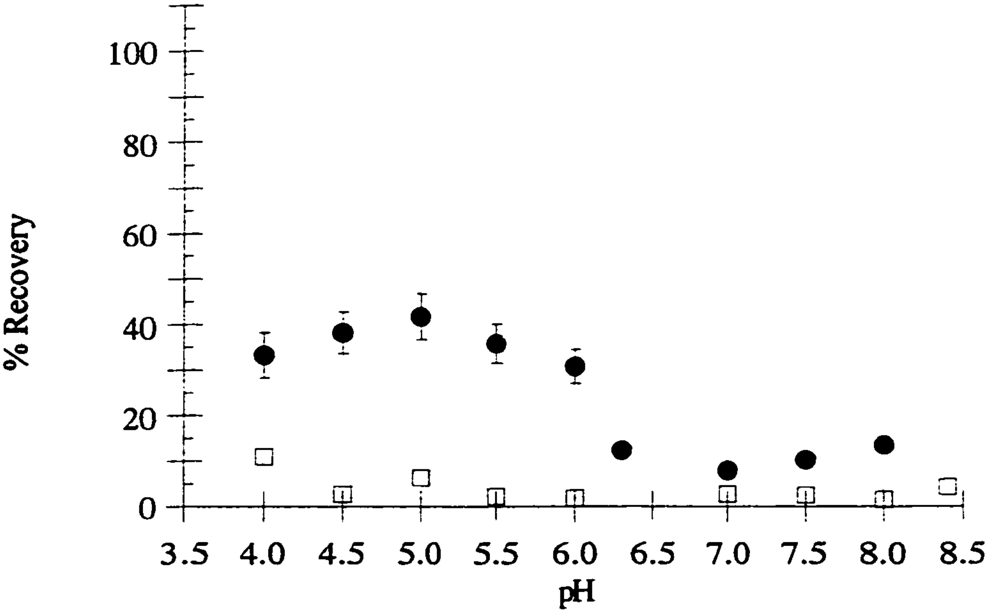


Figure 4.93. Recovery of V on TOPO-XAD-4 resin as a function of pH.
(□) $[TOPO]_r = 0.10$ mmol g^{-1} ; (●) $[TOPO]_r = 0.41$ mmol g^{-1}

These seven elements were chosen for this work in order to exploit their medium-lived nuclides. This allowed the metal retention characteristics of the TOPO resins to be evaluated in a shorter period of time than would be required if longer-lived nuclides (for example, those used to quantify nickel and zinc) were used. As the results of this preliminary study were not particularly encouraging, the investigation of TOPO was not carried further.

5. CONCLUSIONS AND RECOMMENDATIONS

A preconcentration neutron activation analysis (NAA) method for the simultaneous determination of several trace elements in water has been developed. The trace elements have been concentrated prior to irradiation by reversed-phase extraction chromatography (RPEC), using Amberlite XAD-4 resin impregnated with 1-(2-thiazolylazo)-2-naphthol (TAN). Subsequently, the elements were quantified by irradiating the resin directly; the use of NAA as the instrumental technique makes an elution step unnecessary. This is advantageous as the trace elements collected on the resin may be irreproducibly or incompletely eluted. The elimination of this extra step also has benefits related to the lowering of the analytical blank. The multielement capability of NAA has been exploited in that numerous elements can be determined using two irradiations and three decay and counting schemes (namely, t_i:t_d:t_c = 10:1:10 min, 7:24:1 h, or 7 h:21 d:2 h). Physical isolation of the elements retained on the resin is not necessary.

The synthesis of the TAN-loaded resin is relatively simple. In general, a sample of clean XAD-4 resin was equilibrated with a solution of TAN in acetone, methanol, ethanol, or a mixed solvent containing methanol and water. The factors which influence the uptake of TAN on Amberlite XAD-4 have been studied in order to maximize the loading of the chelating agent on the resin. It has been shown that a shaking time of two hours is sufficient to bring the system to equilibrium; longer shaking times did not effect a significantly higher value of $[TAN]_r$, the concentration of TAN on the resin.. Two experimental variables displayed the greatest effect on the amount of TAN loaded onto the resin. Not surprisingly, the value of $[TAN]_r$ rose as the concentration of TAN in solution was increased. It was also shown that as the solvent polarity was raised, the distribution of TAN shifted from the solution to the resin phase.

Both factors must be taken into consideration when devising a synthetic procedure for TAN-XAD-4. A solvent which is too polar does not yield the best results, as the solubility of TAN decreases with increasing solvent polarity. The method developed in this work involves an initial equilibration of XAD-4 resin with a solution of TAN in methanol (*ca.* 0.02 M) for two hours, followed by the addition of water to the system and a second two-hour shaking time. This optimized procedure for the preparation of TAN-XAD-4 resin can be completed in approximately four hours and requires only four reagents (XAD-4 resin, TAN, methanol, and deionized distilled water), and the two equilibration steps. The resin prepared in this manner contained approximately 0.2-0.4 mmol TAN per gram of XAD-4 and had an exchange capacity for copper of 7-14 mg (*ca.* 0.1-0.2 mmol) g^{-1}. Given that trace elements in natural water samples are typically present at ppm levels, the TAN-loaded resin should therefore be suitable for the preconcentration of these elements from real samples without the potential of saturation.

The factors influencing the extraction of trace elements from solution, including pH, flow rate, and column height, have been studied. Under appropriate conditions, the resin quantitatively retained nine elements (Ag, Cd, Co, Cu, Hg, Mn, Ni, U, and Zn). Seven of these elements (all except silver and uranium) could be simultaneously collected from solutions of pH ≥ 8.0 on a column of dimensions 50 mm x 7 mm i.d., at flow rates as high as 5 mL min^{-1}. The preconcentration procedure is rapid and relatively simple to execute.

Sample handling is minimized due to the elimination of the elution step. The enrichment factor of the method is at least 500, given a 1.0-L sample volume. This figure is derived from the fact that the trace elements present in the original sample are concentrated on a resin phase which is typically less than 1 g and occupies a volume of less than 2 mL. The high enrichment factor is attainable because the resin is analyzed directly. Elution studies suggest that removal of the trace elements from the column with acidic or organic eluent would require a larger volume of eluent than 2 mL.

The method is suitable for the quantitation of trace elements in saline samples such as seawater, as potentially interfering elements such as Br, Cl, Mg, and Na are not retained by the TAN-XAD-4 resin. The decontamination factors exhibited by the resin are very good; after passage of an artificial seawater sample and subsequent rinsing of the column with fresh buffer solution, magnesium was not detected, and only microgram quantities of the other three elements remained on the resin.

The precision of the RPEC method has been evaluated by replicate analysis of laboratory tap water and spiked samples. The precision of the method was generally within 6%. Internal quality assessment was carried out using spiked comparator standards, and external quality assessment was performed using reference materials. The accuracy of the method was shown to be good. Detection limits of the method were found to range from 0.014 μg for uranium to 7.6 μg for nickel. The latter figure is directly related to the relative insensitivity of NAA for nickel, but could be improved with different timing parameters (specifically, with a longer counting time), or by utilizing the shorter-lived nuclide of ^{65}Ni ($t_{1/2}$ = 2.52 h) and an intermediate irradiation time (1 to 4 hours, for example) not employed in this research work.

The detection limits of the PNAA method have been compared to the detection limits reported for ICP-MS and ICP-AES. These values are given in Table 5.1. These values suggest that for the determination of trace elements in non-interfering matrices such as ultrapure standards in acid solution, direct determination by ICP-MS or ICP-AES might be more suitable. However, the PNAA method still has significant application to the analysis of trace elements environmental samples such as seawater which contain large excess of potentially interfering elements.

Another potential application of the method is the analysis of solid samples such as biological materials or soil and rock samples which cannot be readily analyzed by INAA. The sample can be processed in a manner similar to a seawater sample following a digestion step. As for aqueous samples, the PNAA method would be useful for samples containing low concentrations of the elements of interest or high concentrations of potentially interfering elements. Elements which are quantified using short and medium-lived nuclides would be particularly amenable to the preconcentration procedure. As previously discussed, such elements are more difficult to determine using RNAA because their nuclides decay to a significant extent in the time required to carry out the post-irradiation separation step.

The PNAA method developed here was suitable for the simultaneous extraction of seven trace elements from solution at pH ≥ 8.0. The work presented in this thesis provides some indication of the potential application of ligand-impregnated resins in general, for trace element preconcentration by RPEC.

However, other column procedures, most notably those employing silica-

Table 5.1. Comparison of detection limits for ICP-MS, ICP-AES, and the PNAA method described in this work.

	Detection Limits (ppb)				
Element	ICP-MS	[ref.]	ICP-AES	[ref.]	PNAA
Ag	0.07	[5]	0.2	[337]	0.2
Cd	0.001	[338]	2	[339]	0.2
Co	0.0003	[338]	0.1	[337]	0.08
Cu	0.03	[338]	0.1	[339]	1
Hg	0.00008	[340]	0.05	[340]	0.1
Mn	0.0005	[338]	0.06	[339]	0.03
Ni	0.008	[338]	0.4	[339]	8
U	0.0015	[341]	1.5	[337]	0.01
Zn	0.007	[338]	2	[339]	3

immobilized 8-hydroxyquinoline or the chelating resin Chelex-100, have been shown to be superior in terms of the number of elements which can be collected. As it is unlikely that novel ligand-immobilized resins will supplant these well-characterized reagents, future effort should focus on the development of more selective ligand-loaded supports. Advantage can be taken of the fact that these can be produced fairly easily; once a general synthetic procedure has been developed, a variety of reversed-phase resins can be prepared simply by changing the complexing agent to be loaded. It should be possible to prepare ligand-impregnated resins of reproducible performance with respect to trace element preconcentration characteristics. With the appropriate choice of chelating agents, it should be possible to devise preconcentration schemes tailored either to collect as few or as many elements as possible. The latter could be achieved with the use of a mixed-bed column. With the proper choice of chelating agent-loaded resins, the performance of this mixed bed column might be superior to Chelex-100 or silica-immobilized 8-hydroxyquinoline with respect to physical limitations and the tendency of these reagents to collect elements such as calcium and magnesium. The preconcentration of only one or two elements might be possible by examining more selective chelating reagents as ligands for RPEC, or through the use of sequential column systems.

Advantage may be taken of the relative simplicity and ease of the RPEC separation in order to develop on-site preconcentration procedures. The analysis of tap and natural water samples almost always requires transport from the sampling site to the laboratory. Large volumes of water are generally required due to the low concentrations of the elements of interest, and to obtain a more representative sample. The development of an on-site method would obviate the often-times cumbersome and expensive transport of samples to the laboratory. Two possible applications of on-site separations could be found in seawater analysis, for the development of shipboard preconcentration procedures, or for the routine analysis of tap water samples for a community, in which large numbers of samples would have to be processed.

REFERENCES

1. Y. Oki, E. Tashiro, M. Maeda, C. Honda, Y. Hasegawa, H. Futami, J. Izumi, K. Matsuda. *Anal. Chem.*, **65**, 2096-2101 (1993).

2. K.R. Lum, M. Callaghan. *Anal. Chim. Acta*, **187**, 157-162 (1986).

3. G. Bozsai, G. Schlemmer, Z. Grobenski. *Talanta*, **37**, 545-553 (1990).

4. P.N. Keliher, H. Ibrahim, D.J. Gerth. *Anal. Chem.*, **62**, 184R-212R (1990).

5. V. Balaram. *At. Spectrosc.*, **14**, 174-179 (1993).

6. I.B. Brenner, H.E. Taylor. *CRC Crit. Rev. Anal. Chem.*, **23**, 355-367 (1992).

7. E.R. Collantes, W.J. Dunn III. *Appl. Spectrosc.*, **45**, 1537-1546 (1991).

8. B. Salbu, E. Steinnes, A.C. Pappas. *Anal. Chem.*, **47**, 1011-1016 (1975).

9. A. Chattopadhyay. *Trans. Am. Nucl. Soc.*, **32**, 200-202 (1979).

10. J.R. Donat, K.W. Bruland. *Anal. Chem.*, **60**, 240-244 (1988).

11. A.C. Almon. *Anal. Chim. Acta*, **249**, 447-450 (1991).

12. R.E. Sturgeon, S.S. Berman, A. Desaulniers, D.S. Russell. *Anal. Chem.*, **51**, 2364-2369 (1979).

13. R.E. Sturgeon, S.S. Berman, J.A.H. Desaulniers, A.P. Mykytiuk, J.W. McLaren, D.S. Russell. *Anal. Chem.*, **52**, 1585-1588 (1980).

14. R.R. Rao, D.G. Goski, A. Chatt. *J. Radioanal. Nucl. Chem., Art.*, **161**, 89-99 (1992).

15. R. Van Grieken. *Anal. Chim. Acta*, **143**, 3-34 (1982).

16. D.E. Leyden, W. Wegschieder. *Anal. Chem.*, **53**, 1059A-1065A (1981).

17. D.A. Skoog, D.M. West, F.J. Holler. *Fundamentals of Analytical Chemistry*, 6th ed., Saunders College Publishing, Montréal, p. 721, 1992.

18. J.P. Riley, D. Taylor. *Anal. Chim. Acta*, **40**, 479-485 (1968).

19. M. Torre, M.L. Marina. *CRC Crit. Rev. Anal. Chem.*, **24**, 327-361 (1994).

20. Bio-Rad Laboratories, Product Information 2020, July, 1978.

21. S. Blain, P. Appriou, H. Handel. *Anal. Chim. Acta*, **272**, 91-97 (1993).

22. S. Olsen, L.C.R. Pessenda, J. Ruzicka, E.H. Hansen. *Analyst*, **108**, 905-917 (1983).

23. K. Isshiki, F. Tsuji, T. Kuwamoto, E. Nakayama. *Anal. Chem.*, **59**, 2491-2495 (1987).

24. D.W. Lee, C.H. Eum, I.H. Lee, S.J. Jeon. *Anal. Sci.*, **4**, 505-510 (1988).

25. H. Akaiwa, H. Kawamoto, N. Nakata, Y. Ozeki. *Chem. Lett.*, 1049-1050 (1975).

26. F. Vernon, H. Eccles. *Anal. Chim. Acta*, **63**, 403-414 (1973).

27. L.D. Pennington, M.B. Williams. *Ind. Eng. Chem.*, **51**, 759-762 (1959); *Chem. Abstr.*, **53**:18335d (1959).

28. J.R. Parrish, R. Stevenson. *Anal. Chim. Acta*, **70**, 189-198 (1974).

29. F. Vernon, K.M. Nyo. *Anal. Chim. Acta*, **93**, 203-210 (1977).

30. R.E. Sturgeon, S.S. Berman, S.N. Willie. *Talanta*, **29**, 167-171 (1982).

31. C. Sarzanini, E. Mentasti, V. Porta, M.C. Gennaro. *Anal. Chem.*, **59**, 484-486 (1987).

32. W.A. de Oliviera, R. Narayanaswamy. *Talanta*, **39**, 1499-1503 (1992).

33. K. Brajter, E. Olbrych-Slęszynska, M. Staskiewicz. *Talanta*, **35**, 65-67 (1988).

34. G.A. Howard, A.J.P. Martin. *Biochem. J.*, **46**, 532-538 (1950).

35. R. Morabito. *Fresenius' J. Anal. Chem.*, **351**, 378-385 (1995).

36. M. Satake, K. Ishida, B.K. Puri, S. Usami. *Anal. Chem.*, **58**, 2502-2504 (1986).

37. M.M. Guedes da Mota, F.G. Römer, B. Griepink. *Fresenius' Z. Anal. Chem.*, **287**, 19-22 (1977).

38. H. Obata, H. Karatini, E. Nakayama. *Anal. Chem.*, **65**, 1524-1528 (1993).

39. W. Wegschieder, G. Knapp. *CRC Crit. Rev. Anal. Chem.*, **11**, 79-102 (1981).

40. R.S.S. Murthy, J. Holzbecher, D.E. Ryan. *Rev. Anal. Chem.*, **6**, 113-150 (1982).

41. M.L. Marina, V. Gonzalez, A.R. Rodriguez. *Microchem. J.*, **33**, 275-294 (1986).

42. G.V. Myasoedova, S.B. Savvin. *CRC Crit. Rev. Anal. Chem.*, **17**, 1-63 (1987).

43. C. Kantipuly, S. Katragadda, A. Chow, H.D. Gesser. *Talanta*, **37**, 491-517 (1990).

44. E.M. Basova, T.A. Bol'shova, O.A. Shpigun, V.M. Ivanov. *J. Anal. Chem.*, **48**, 757-774 (1993).

45. M. Chikuma, M. Nakayama, T. Itoh, H. Tanaka, K. Itoh. *Talanta*, **27**, 807-810 (1980).

46. K. Terada, K. Nakamura. *Talanta*, **28**, 123-125 (1981).

47. J.L. Lundgren, A.A. Schilt. *Anal. Chem.*, **49**, 974-980 (1977).

48. R.E. Sturgeon, S.S. Berman, S.N. Willie, J.A.H. Desaulniers. *Anal. Chem.*, **53**, 2337-2340 (1981).

49. A. Sugii, N. Ogawa, M. Hisamitsu. *Chem. Pharm. Bull.* **26**, 798-802 (1978); *Chem. Abstr.*, **88**:191839e (1978).

50. A.M. Naghmush, M. Trojanowicz, E. Olbrych-Sleszynska. *J. Anal. At. Spectrom.*, **7**, 323-328 (1992).

51. I.E. Boni, A. Hemmeler. *Chimica*, **34**, 443-444 (1958).

52. M. Kurahashi. *Bull. Chem. Soc. Jpn.*, **49**, 2927-2933 (1976).

53. G.D. Brykina, N.I. Stepanova, T.A. Belyavskaya. *Zh. Anal. Khim.*, **37**, 208-212 (1982); *Chem. Abstr.*, **96**:173546t (1982).

54. G.D. Brykina, N.I. Stepanova, A.V. Stefanov, L.S. Krysina, T.A. Belyavskaya. *Zh. Anal. Khim.*, **38**, 33-37 (1983); *Chem. Abstr.*, **98**:118760z (1983).

55. A.E. Martell. *Stability Constants of Metal-Ion Complexes*, The Chemical Society, Burlington House, London, , p.714, 1971.

56. O. Navratil. *Coll. Czech. Chem. Commun.*, **32** 2004-2010 (1967); *Chem. Abstr.*, **67**:82931z (1967).

57. C.D. Sharma, M.C. Eshwar. *J. Radioanal. Nucl. Chem.*, **91**, 323-328 (1985).

58. G.V. Rathaiah, J. Krishnama Charyulu, M.C. Eshwar. *J. Radioanal. Nucl. Chem.*, **99**, 337-344 (1986).

59. K. Ueda, Y. Koshino, Y. Yamamoto. *Anal. Lett.*, **18**, 2345-2359 (1985).

60. J. Vácha, L. Sommer. *Coll. Czech. Chem. Commun.*, **58**, 1813-1820 (1993).

61. V.M. Ivanov, N.A. Beketova, E.M. Basova, T.A. Bol'shova. *Zh. Anal. Khim.*, **46**, 1512-1519 (1991); *Chem. Abstr.*, **115**:222109z (1991).

62. N.A. Babkova, V.M. Ivanov, E.M. Basova, T.A. Bol'shova. *Otkrytiya. Izobret.*, **45**, 214-215 (1989); *Chem. Abstr.*, **112**:131559t (1990).

63. E.M. Basova, T.A. Bol'shova, V.M. Ivanov, O.A. Shpigun. *Zh. Anal. Khim.*, **48**, 284-296 (1993); *Chem. Abstr.*, **119**:19385b (1993).

64. N.A. Beketova, E.M. Basova, V.M. Ivanov, T.A. Bol'shova. *Zh. Anal. Khim.*, **45**, 2178-2185 (1990); *Chem. Abstr.*, **114**:114219f (1991).

65. C. Sarzanini, V. Porta, E. Mentasti. *New J. Chem.*, **13**, 463-471 (1989); *Chem. Abstr.*, **112**, 159539k (1990).

66. V. Porta, C. Sarzanini, O. Abollino, E. Mentasti, E. Carlini. *J. Anal. At. Spectrom.*, 7, 19-22 (1992).

67. S. Ide, M. Takagi, K. Ueno. *Bunseki Kagaku*, **31**, 651-656 (1982); *Chem. Abstr.*, **98**:46019q (1983).

68. V.P. Guinn. *Nuclear Analytical Methods in the Life Sciences*, R. Zeisler and V.P. Guinn, eds., Humana Press, Clifton, NJ, pp. 1-7, 1990.

69. W.D. Ehmann, D.E. Vance. *Radiochemistry and Nuclear Methods of Analysis*, Wiley, Toronto, pp. 271-272, 1991.

70. D. DeSoete, R. Gijbels, J. Hoste. *Neutron Activation Analysis*, Wiley-Interscience, Toronto, pp. 445-447, 1972.

71. G. Friedlander, J.W. Kennedy, E.S. Macias, J.M. Miller. *Nuclear And Radiochemistry*, 3rd ed., Wiley, Toronto, pp. 424-427, 1981.

72. W.D. Ehmann, D.E. Vance. *Radiochemistry and Nuclear Methods of Analysis*, Wiley, Toronto, p. 257, 1991.

73. Y.S. Chung, R.M. Barnes. *J. Anal. At. Spectrom.*, **3**, 1079-1082 (1988).

74. A.K. Singh, S.K. Dhingra. *Analyst*, **117**, 889-891 (1992).

75. D. Beauchemin, S.S. Berman. *Anal. Chem.*, **61**, 1857-1862 (1989).

76. A. Martín-Esteban, P. Fernández, C. Pérez-Conde, A. Gutiérrez, C. Cámara. *Anal. Chim. Acta*, **304**, 121-126 (1995).

77. H. Tanaka, M. Chikuma, A. Harada, T. Ueda, S. Yube. *Talanta*, **23**, 489-491 (1976).

78. H.A. Van der Sloot. *J. Radioanal. Chem.*, **37**, 727-739 (1977).

79. H.A. Van der Sloot, J.B. Luten. *Meas. Detect. Control Environ. Pollut., Proc. Int. Symp.*, 435-48 (1976); *Chem. Abstr.*, **87**:28753t (1977).

80. H.A. Van der Sloot. *ECN, ECN-1*, 215 pp., 1976; *Chem. Abstr.*, **86**:78473b (1977).

81. R.R. Greenberg, R. Zeisler, H.M. Kingston, T.M. Sullivan. *Fresenius' Z. Anal. Chem.*, **332**, 652-656 (1988).

82. R.R. Greenberg, H.M. Kingston, R. Zeisler, J. Woittiez. *Nuclear Analytical Methods in the Life Sciences*, R. Zeisler and V.P. Guinn, eds., Humana Press, Clifton, NJ, pp. 17-25, 1990.

83. J.E. Milley, A. Chatt. *J. Radioanal. Nucl. Chem.*, **110**, 345-363 (1987).

84. A.J. Blotcky, D. Hobson, J.A. Leffler, E.P. Rack, R.R. Recker. *Anal. Chem.*, **48**, 1084-1088 (1976).

85. P.R. Devi, G.R.K. Naidu. *J. Radioanal. Nucl. Chem., Lett.*, **146**, 267-272 (1990).

86. P.R. Devi, G.R.K. Naidu. *Analyst*, **115**, 1469-1471 (1990).

87. N.K. Shah, C.M. Wai. *J. Radioanal. Nucl. Chem., Art.*, **130**, 451-459 (1989).

88. H. Akaiwa. *J. Radioanal. Nucl. Chem., Art.*, **84**, 165-175 (1984).

89. H. Erlenmeyer, H. Dahn. *Helv. Chim. Acta*, **22**, 1369-1371 (1939); *Chem. Abstr.*, **30**:1269^7 (1940).

90. F. Burriel-Marti, F.P. Perez. *Anal. Chim. Acta*, **3**, 468-475 (1949).

91. F. Sebesta. *Extraction Chromatography*, T. Braun and G. Ghersini eds., Elsevier, New York, 1975.

92. Chemical Research Laboratory, Teddington. *Nature*, **170**, 648-650 (1952).

93. D.E. Carritt. *Anal. Chem.*, **25**, 1927-1928 (1953).

94. T.B. Pierce, P.F. Peck. *Analyst*, **86**, 580-584 (1961).

95. D. Mapper, J.R. Fryer. *Analyst*, **87**, 297 (1962).

96. T.B. Pierce, P.F. Peck. *J. Chromatog.*, **6**, 248-251 (1961).

97. T.B. Pierce. *Anal. Chim. Acta*, **24**, 146-152 (1961).

98. T.B. Pierce, P.F. Peck. *Anal. Chim. Acta*, **26**, 557-567 (1962).

99. H.P. Gregor, M. Taifer, L. Citarel, E.I. Becker. *Ind. Eng. Chem.*, **44**, 2834-2839 (1952); *Chem. Abstr.*, **47**:3493e (1953).

100. S.K. Sahni, J. Reedijk. *Coord. Chem. Rev.*, **59**, 1-139 (1984); refer especially to pp.2-13.

101. J.R. Parrish. *Chem. Ind.*, 386-7 (1955); *Chem. Abstr.*, **49**:11315h (1955).

102. J.R. Parrish. *Chem. Ind.*, 137 (1956); *Chem. Abstr.*, **50**:11561b (1956).

103. J.R. Parrish. *Anal. Chem.*, **54**, 1890-1892 (1982).

104. R.V. Davies, J. Kennedy, E.S. Lane, J.L. Williams. *J. Appl. Chem.*, **9**, 368-371 (1959); *Chem. Abstr.*, **53**:19447e (1959).

105. D.E. Leyden, A.L. Underwood. *J. Phys. Chem.*, **68**, 2093-2097 (1964).

106. J.P. Riley, D. Taylor. *Deep Sea Res.*, **19**, 307-317 (1972).

107. A.J. Paulson. *Anal. Chem.*, **58**, 183-187 (1986).

108. T.M. Florence, G.E. Batley. *Talanta,* **23,** 179-186 (1976).

109. L. Rasmussen. *Anal. Chim. Acta,* **125**, 117-130 (1981).

110. A.P. Mykytiuk, D.S. Russell, R.E. Sturgeon. *Anal. Chem.*, **52**, 1281-1283 (1980).

111. S.-C. Pai, T.-H. Fang, C.-T. A. Chen, K.-L. Jeng. *Mar. Chem.*, **29**, 295-306 (1990).

112. E. Cerrai, G. Ghersini. *Analyst*, **94**, 599-604 (1969).

113. J.S. Fritz, D.R. Beuerman, J.J. Richard. *Talanta*, **18**, 1095-1102 (1971).

114. J.S. Fritz, D.R. Beuerman. *Anal. Chem.*, **44**, 692-694 (1972).

115. A. Warshawsky. *Talanta*, **21**, 962-965 (1974).

116. R. Malvano, P. Grosso, M. Zanardi. *Anal. Chim. Acta*, **41**, 251-258 (1968).

117. S. Kawamura, T. Fujimoto, M. Izawa. *J. Chromatog.*, **34**, 72-76 (1968).

118. H. Wehner, S. Al-Murab, M. Stoeppler. *Radiochem. Radioanal. Lett.*, **13**, 1-6 (1973).

119. A. Delle Site. *J. Radioanal. Chem.*, **14**, 45-51 (1973).

120. W. Kemula, K. Brajter. *Chem. Anal. (Warsaw)*, **15**, 331-344 (1970).

121. K. Brajter. *Chem. Anal. (Warsaw)*, **18**, 125-135 (1973).

122. K. Brajter. *J. Chromatog.*, **102**, 385-390 (1974).

123. J.M. Hill. *J. Chromatog.*, **76**, 455-458 (1973).

124. T. Fujinaga, M. Satake, J. Miura. *Talanta*, **26**, 964 (1979).

125. S. Srivastava, G.N. Rao. *Analyst*, **115**, 1607-1609 (1990).

126. T. Fujinaga, T. Kuwamoto, E. Nakayama. *Talanta*, **16**, 1225-1226 (1969).

127. S. Majee, J. Das. *Chem. Anal.*, **32**, 985-989 (1987).

128. R. Saxena, A.K. Singh, S.S. Sambi. *Anal. Chim. Acta*, **295**, 199-204 (1994).

129. M.C. Yebra-Biurrun, A. Bermejo-Barrera, M.P. Bermejo-Barrera. *Anal. Chim. Acta*, **264**, 53-58 (1992).

130. M.C. Yebra-Biurrun, A. Bermejo-Barrera, M.P. Bermejo-Barrera, M.C. Barciela-Alonso. *Anal. Chim. Acta*, **303**, 341-345 (1995).

131. K. Dev, G.N. Rao. *Talanta*, **42**, 591-596 (1995).

132. A. Sugii, N. Ogawa, H. Hashizume. *Talanta*, **26**, 189-192 (1979).

133. A. Miyazaki, R.M. Barnes. *Anal. Chem.*, **53**, 299-304 (1981).

134. M. Grote, A. Kettrup. *Anal. Chim. Acta*, **172**, 223-239 (1985).

135. R. Shah, S. Devi. *Analyst*, **121**, 807-811 (1996).

136. J. Chwastowska, E. Kosiarka. *Talanta*, **35**, 439-442 (1988).

137. M.C. Gennaro, E. Mentasti, C. Sarzanini. *Talanta*, **33**, 620-622 (1986).

138. J.R. Jezorek, H. Freiser. *Anal. Chem.*, **51**, 366-373 (1979).

139. S.N. Willie, R.E. Sturgeon, S.S. Berman. *Anal. Chim. Acta*, **149**, 59-66 (1983).

140. J.W. McLaren, A.P. Mykytiuk, S.N. Willie, S.S. Berman. *Anal. Chem.*, **57**, 2907-2911 (1985).

141. M.A. Marshall, H.A. Mottola. *Anal. Chem.*, **57**, 729-733 (1985).

142. M.A. Marshall, H.A. Mottola. *Anal. Chem.*, **55**, 2089-2093 (1983).

143. S. Nakashima, R.E. Sturgeon, S.N. Willie, S.S. Berman. *Fresenius' Z. Anal. Chem.*, **330**, 592-595 (1988).

144. D. Beauchemin, J.W. McLaren, A.P. Mykytiuk, S.S. Berman. *J. Anal. At. Spectrom.*, **3**, 305-308 (1988).

145. T. Honjo, H. Kitayama, K. Terada, T. Kiba. *Fresenius' Z. Anal. Chem.*, **330**, 159-160 (1988).

146. S.R. Bysouth, J.F. Tyson, P.B. Stockwell. *Analyst*, **115**, 571-573 (1990).

147. B.-J. Daih, H.-J. Huang. *Anal. Chim. Acta*, **258**, 245-252 (1992).

148. K. Akatsuka, J.W. McLaren, J.W. Lam, S.S. Berman. *J. Anal. At. Spectrom.*, **7**, 889-894 (1992).

149. J.W. McLaren, J.W.H. Lam, S.S. Berman, K. Akatsuka, M.A. Azeredo. *J. Anal. At. Spectrom.*, **8**, 279-286 (1993).

150. C.-R. Lan, M.-H. Yang. *Anal. Chim. Acta*, **287**, 111-117 (1994).

151. C.-R. Lan, M.-H. Yang. *Anal. Chim. Acta*, **287**, 101-109 (1994).

152. B. Mohammad, A.M. Ure, D. Littlejohn. *J. Anal. At. Spectrom.*, **8**, 325-331 (1993).

153. E. Beinrohr, M. Cakrt, J. Garaj, M. Rapta. *Anal. Chim. Acta*, **230**, 163-170 (1990).

154. B. Pasullean, C.M. Davidson, D. Littlejohn. *J. Anal. At. Spectrom.*, **10**, 241-246 (1995).

155. R. Purohit, S. Devi. *Talanta*, **38**, 753-759 (1991).

156. R. Purohit, S. Devi. *Analyst*, **120**, 555-559 (1995).

157. R. Purohit, S. Devi. *Analyst*, **116**, 825-830 (1991).

158. U. Pyell, G. Stork. *Fresenius' J. Anal. Chem.*, **342**, 281-286 (1992).

159. B.K. Esser, A. Volpe, J.M. Kenneally, D.K. Smith. *Anal. Chem.*, **66**, 1736-1742 (1994).

160. G. Persaud, F.F. Cantwell. *Anal. Chem.*, **64**, 89-94 (1992).

161. J.A. Resing, M.J. Mottl. *Anal. Chem.*, **64**, 2682-2687 (1992).

162. W.M. Landing, C. Haraldsson, N. Paxéus. *Anal. Chem.*, **58**, 3031-3035 (1986).

163. Y. Inoue, H. Kumagai, Y. Shimomura, T. Yokoyama, T.M. Suzuki. *Anal. Chem.*, **68**, 1517-1520 (1996).

164. A.G. Howard, M. Volkan, D.Y. Ataman. *Analyst*, **112**, 159-162 (1987).

165. E. Mentasti, C. Sarzanini, M.C. Gennaro, V. Porta. *Polyhedron*, **6**, 1197-1202 (1987).

166. J. Ghosh, H.R. Das. *Talanta*, **28**, 274-276 (1981).

167. M.C. Gennaro, E. Mentasti, C. Sarzanini. *Polyhedron*, **5**, 1013-1015 (1986).

168. N. Simonzadeh, A.A. Schilt. *Talanta*, **35**, 187-190 (1988).

169. R. Saxena, A.K. Singh, D.P.S. Rathore. *Analyst*, **120**, 403-405 (1995).

170. A.G. Howard, R. Danilona-Mirzaians. *Anal. Lett.*, **22**, 257-267 (1989).

171. R.J. Phillips, J.S. Fritz. *Anal. Chem.*, **50**, 1504-1508 (1978).

172. T. Fujinaga, M. Satake, T. Yonekubo. *Talanta*, **19**, 689-692 (1972).

173. K.F. Sugawara, H.H. Weetall, G.D. Schucker. *Anal. Chem.*, **46**, 489-492 (1974).

174. J.W. McLaren, K.W.M. Siu, J.W. Lam, S.N. Willie, P.S. Maxwell, A. Palepu, M. Koether, S.S. Berman. *Fresenius' J. Anal. Chem.*, **337**, 721-728 (1990).

175. S. Watanesk, A.A. Schilt. *Talanta*, **33**, 895-899 (1986).

176. K. Brajter, E. Dabek-Zlotorzynska. *Talanta*, **27**, 19-24 (1980).

177. K. Brajter, E. Dabek-Zlotorzynska. *Fresenius' Z. Anal. Chem.*, **326**, 763-765 (1987).

178. M. Nakayama, M. Chikuma, H. Tanaka, T. Tanaka. *Talanta*, **29**, 503-506 (1982).

179. M. Nakayama, K. Itoh, M. Chikuma, H. Sakurai, H. Tanaka. *Talanta*, **31**, 269-274 (1984).

180. P. Jones, O.J. Challenger, S.J. Hill, N.W. Barnett. *Analyst*, **117**, 1447-1450 (1992).

181. O.J. Challenger, S.J. Hill, P. Jones, N.W. Barnett. *Anal. Proc.*, **29**, 91-93 (1992).

182. M. Pesavento, A. Profumo, C. Rioli, T. Soldi. *Analyst*, **114**, 623-626 (1989).

183. P. Fernández, C. Pérez-Conde, A. Gutiérrez, C. Cámara. *Talanta*, **38**, 1387-1392 (1991).

184. K.S. Lee, W. Lee, D.W. Lee. *Anal. Chem.*, **50**, 255-258 (1978).

185. A.G. Howard, M.H. Arbab-Zavar. *Talanta*, **26**, 895-897 (1979).

186. C. Samara, T.A. Kouimtzis. *Anal. Chim. Acta*, **174**, 305-311 (1985).

187. M. Chikuma, H. Aoki. *J. Anal. At. Spectrom.*, **8**, 415-417 (1993).

188. E. Olbrych-Sleszynska, K. Brajter, W. Matuszewski, M. Trojanowicz, W. Frenzel. *Talanta*, **39**, 779-787 (1992).

189. C. Németh, J. Somlai, J. Tóth. *J. Radioanal. Nucl. Chem., Art.*, **204**, 285-293 (1996).

190. H. Akaiwa, H. Kawamoto, N. Nakata. *J. Radioanal. Chem.*, **36**, 59-64 (1977).

191. H. Akaiwa, H. Kawamoto, K. Ogura. *Talanta*, **24**, 394-395 (1977).

192. H. Akaiwa, H. Kawamoto, K. Ogura. *Talanta*, **28**, 337-339 (1981).

193. K. Brajter, E. Dabek-Zlotorzynska. *Talanta*, **37**, 613-618 (1990).

194. M. Trojanowicz, K. Pyrzynska. *Anal. Chim. Acta*, **287**, 247-252 (1994).

195. K. Brajter, E. Dabek-Zlotorzynska. *Talanta*, **33**, 149-154 (1986).

196. T. Braun, M.N. Abbas. *Anal. Chim. Acta*, **119**, 113-119 (1980).

197. J. Chwastowska, E. Mozer. *Talanta*, **32**, 574-576 (1985).

198. F. Lázaro, M.D. Luque de Castro, M. Valcárcel. *Anal. Chim. Acta*, **214**, 217-227 (1988).

199. K. Brajter, E. Dabek-Zlotorzynska. *Analyst*, **113**, 1571-1574 (1988).

200. A.M. Naghmush, K. Pyrzynska, M. Trojanowicz. *Talanta*, **42**, 851-860 (1995).

201. L. Joseph, V.N.S. Pillai. *Analyst*, **114**, 439-443 (1989).

202. B.B. Prasad, S. Sundd. *Chromatographia*, **40**, 571-576 (1995).

203. M. Pesavento, T. Soldi, A. Profumo. *Talanta*, **39**, 943-951 (1992).

204. K. Brajter, E. Olbrych-Sleszynska. *Analyst*, **111**, 1023-1027 (1986).

205. H.W. Handley, P. Jones, L. Ebdon, N.W. Barnett. *Anal. Proc.*, **28**, 37-38 (1991).

206. K. Brajter, E. Olbrych-Sleszynska. *Talanta*, **30**, 355-358 (1983).

207. B. Paull, M. Foulkes, P.Jones. *Analyst*, **119**, 937-941 (1994).

208. M. Chikuma, M. Nakayama, T. Tanaka, H. Tanaka. *Talanta*, **26**, 911-912 (1979).

209. S. Ide, T. Haraguchi. *Sekiyu Gakkaishi*, **34**, 427-431 (1991); *Chem. Abstr.*, **115**:269391a (1991).

210. I.M. Maksimova, E.I. Morosanova. *Zh. Anal. Khim.*, **49**, 602-606 (1994); *Chem. Abstr.*, **121**:98578j (1994).

211. I.E. Boni, A. Hemmeler. *Chimica*, **34**, 445-446 (1958).

212. N. Kaneniwa. *Kanazawa Daigaku, Yakugakubu Kenkyu Nempo*, **9**, 27-34 (1959); *Chem. Abstr.*, **54**:4541g (1960).

213. B.S. Jensen. *Acta Chem. Scand.*, **14**, 927-932 (1960).

214. V. Chromy, J. Vrestal. *Chem. Listy*, **60**, 1537-1542 (1966); *Chem. Abstr.*, **66**:34648v (1967).

215. H. Wada, G. Nakagawa. *Bunseki Kagaku*, **14**, 28-33 (1965); *Chem. Abstr.*, **62**:12419c (1965).

216. A. Kawase. *Bunseki Kagaku*, **11**, 621-634 (1962); *Chem. Abstr.*, **57**:7878d (1962).

217. A. Kawase. *Bunseki Kagaku*, **12**, 904-910 (1963); *Chem. Abstr.*, **60**:4777e (1964).

218. A. Kawase. *Bunseki Kagaku*, **12**, 810-821 (1963); *Chem. Abstr.*, **60**:6208f (1964).

219. A. Kawase. *Bunseki Kagaku*, **13**, 609-614 (1964); *Chem. Abstr.*, **61**:11325d (1964).

220. A. Kawase. *Talanta*, **12**, 195-210 (1965).

221. O. Navratil. *Coll. Czech. Chem. Commun.*, **29**, 2490-2506 (1964); *Chem. Abstr.*, **62**:8365f (1965).

222. O. Navratil. *Sb. Ref. Celostatni Radiochem. Konf.*, **3**, Liblice, Czech., 112-118 (1964); *Chem. Abstr.*, **64**:16712h (1966).

223. O. Navratil. *Coll. Czech. Chem. Commun.*, **31**, 2492-2500 (1966); *Chem. Abstr.*, **65**:8072e (1966).

224. O. Navratil, R.W. Frei. *Anal. Chim. Acta*, **52**, 221-227 (1970).

225. G. Nakagawa, H. Wada. *Nippon Kakagu Zasshi*, **83**, 1185-1189; *Chem. Abstr.*, **59**:9289d (1963).

226. H. Wada, G. Nakagawa. *Anal. Lett.*, **1**, 687-695 (1968).

227. A.I. Busev, V.M. Ivanov, L.S. Krysina. *Vestn. Mosk. Univ., Ser. II*, **23**, 80-84 (1968); *Chem. Abstr.*, **69**:8183g (1968).

228. A.I. Busev, V.M. Ivanov, L.I. Bogdanovich. *Zh. Anal. Khim.*, **24**, 1273-1276 (1969); *Chem. Abstr.*, **72**:8964z (1970).

229. V.M. Ivanov, A.I. Busev, V.G. Gresl, A.N. Zagruzina. *Zh. Anal. Khim.*, **26**, 1553-1560 (1971); *Chem. Abstr.*, **75**:147500v (1971).

230. N.S. Ershova, V.M. Ivanov, A.I. Busev. *Zh. Anal. Khim.*, **28**, 2220-2226 (1969); *Chem. Abstr.*, **80**:77994m (1974).

231. M. Kurahashi. *Bull. Chem. Soc. Jpn.*, **47**, 2067-2068 (1974).

232. M. Kurahashi. *Bull. Chem. Soc. Jpn.*, **49**, 3053-3059 (1976).

233. M. Kurahashi, A. Kawase, K. Hirotsu, M. Fukuyo, A. Shimada. *Bull. Chem. Soc. Jpn.*, **45**, 1940 (1972).

234. M. Kurahashi, A. Kawase. *Bull. Chem. Soc. Jpn.*, **49**, 1419-1420 (1976).

235. M. Kurahashi, A. Kawase. *Bull. Chem. Soc. Jpn.*, **49**, 127-130 (1976).

236. H. Watanabe, J. Miura. *Bunseki Kagaku*, **25**, 667-670 (1976); *Chem. Abstr.*, **86**:132885c (1977).

237. J. Miura, H. Ishii, H. Watanabe. *Bunseki Kagaku*, **25**, 808-809 (1976); *Chem. Abstr.*, **86**:182452e (1977).

238. H. Ishii, J. Miura, H. Watanabe. *Bunseki Kagaku*, **26**, 252-256 (1977); *Chem. Abstr.*, **87**:193115u (1977).

239. J. Miura, M. Satake. *Fukui Daigaku Kogakubu Kenkyu*, **26**, 259-264 (1978); *Chem. Abstr.*, **90**:47899y (1979).

240. T. Tanaka, K. Hiro, A. Kawahara. *Osaka Kogyo Gijutsu Shikensho Kiho*, **31**, 251-254 (1980); *Chem. Abstr.*, **94**:149626g (1981).

241. G.D. Brykina, N.Filippova, L.S. Krysina, T.A. Belyavskaya. *Zh. Fiz. Khim.*, **53**, 2075-2078 (1979); *Chem. Abstr.*, **91**:181941e (1979).

242. K. Isshiki, E. Nakayama. *Anal. Chem.*, **59**, 291-295 (1987).

243. K. Li, F. Liu, C. Li, S. Tong. *Lizi Jiaohuan Yu Xifu*, **4**, 353-357 (1988); *Chem. Abstr.*, **112**:110931t (1990).

244. U.G. Goakar, M.C. Eshwar. *Analyst*, **111**, 1393-1395 (1986).

245. M.C. Eshwar, C.D. Sharma. *Microchem. J.*, **35**, 27-29 (1987); *Chem. Abstr.*, **106**:168005m (1987).

246. M.C. Eshwar, C.D. Sharma. *Zh. Anal. Khim.*, **42**, 874-878 (1987); *Chem. Abstr.*, **107**:189787d (1987).

247. M.C. Eshwar, J.K. Charyulu. *Sci. Cult.*, **53**, 83-84 (1987); *Chem. Abstr.*, **108**:15443u (1988).

248. G.V. Rathaiah, M.C. Eshwar. *Indian J. Technol.*, **23**, 157-158 (1985); *Chem. Abstr.*, **103**:226543m (1985).

249. C.D. Sharma, S.G. Nagarkar, M.C. Eshwar. *Bull. Chem. Soc. Jpn.*, **59**, 1662-1664 (1986); *Chem. Abstr.*, **105**:53735m (1986).

250. G.V. Rathaiah, M.C. Eshwar. *Bull. Chem. Soc. Jpn.*, **58**, 2447-2448 (1985); *Chem. Abstr.*, **103**:226552p (1985).

251. M.C. Eshwar, G.V. Rathaiah. *Curr. Sci.*, **55**, 1024-1024 (1986); *Chem. Abstr.*, **105**:237606m (1986).

252. S.L.C. Ferreira, R.M.W. Nano. *Talanta*, **41**, 1937-1941 (1994).

253. S. Kalyanaraman, A. Sugiyama, T. Fukasawa. *Analyst*, **110**, 213-214 (1985).

254. E. Malinowska, K. Kasiura. *Chem. Anal.*, **31**, 797-809 (1986); *Chem. Abstr.*, **107**:69825t (1987).

255. R.R. Rao, A. Chatt. *J. Radioanal. Nucl. Chem., Art.*, **168**, 439-448 (1993).

256. E.P. Hamilton, A. Chatt. *J. Radioanal. Chem.*, **71**, 29-45 (1982).

257. H.K. Sharma, B. Singh, V.K. Mittal, H.S. Sahota. *Nucl. Geophys.*, **3**, 289-295 (1989).

258. D.Z. Piper, G.G. Goles. *Anal. Chim. Acta*, **47**, 560-563 (1969).

259. F. Girardi, E. Sabbioni. *J. Radioanal. Chem.*, **1**, 169-178 (1968).

260. R. Dybczyński. *J. Chromatogr.*, **600**, 17-36 (1992).

261. A. Bilewicz, B. Bartos, J. Narbutt, H. Polkowska-Motrenko. *Anal. Chem.*, **59**, 1737-1738 (1987).

262. H. Polkowska-Motrenko, W. Zmijewska, B. Bartos, A. Bilewicz, J. Narbutt. *J. Radioanal. Nucl. Chem., Lett.*, **164**, 115-122 (1992).

263. K. Samsahl. *Anal. Chem.*, **39**, 1480-1483 (1967).

264. K. Samsahl. *Sci. Total Environ.*, **1**, 65-74 (1972).

265. G.V. Iyengar. *J. Radioanal. Nucl. Chem., Art.*, **110**, 503-517 (1987).

266. J.R.W. Woittiez, M. De La Cruz Tangonan. *J. Radioanal. Nucl. Chem., Art.*, **158**, 313-321 (1992).

267. I. Büttner, V. Hamm, A Knöchel, R. Sen Gupta. *Fresenius' J. Anal. Chem.*, **346**, 446-452 (1993).

268. M. Gallorini, R.R. Greenberg, T.E. Gills. *Anal. Chem.*, **50**, 1479-1481 (1978).

269. R.R. Greenberg. *Anal. Chem.*, **58**, 2511-2516 (1986).

270. R. Pietra, S. Fortaner, E. Sabbioni, M. Gallorini. *J. Tr. Microprobe Tech.*, **11**, 235-250 (1993).

271. R.R. Greenberg, H.M. Kingston. *Anal. Chem.*, **55**, 1160-1165 (1983).

272. C. Lee, N.B. Kim, I.C. Lee, K.S. Chung. *Talanta*, **24**, 241-245 (1977).

273. A. Hirose, K. Kobori, D. Ishii. *Anal. Chim. Acta*, **97**, 303-310 (1978).

274. A. Hirose, D. Ishii. *J. Radioanal. Chem.*, **46**, 211-215 (1978).

275. J. Arunachalam, S. Gangadharan. *J. Radioanal. Nucl. Chem., Art.*, **168**, 471-476 (1993).

276. L. Xilei, M. Speziali, E. Orvini. *J. Radioanal. Nucl. Chem., Art.*, **157**, 265-272 (1992).

277. Y. Sasaki, H. Takeishi, T. Adachi, K. Izawa. *J. Radioanal. Nucl. Chem., Art.*, **139**, 143-151 (1990).

278. A.J. Blotcky, J.P. Claassen, F.R.Roman, E.P. Rack, S. Badakhsh. *Anal. Chem.*, **64**, 2910-2913 (1992).

279. A.J. Blotcky, C. Falcone, V.A. Medina, E.P. Rack, D.W. Hobson. *Anal. Chem.*, **51**, 178-182 (1979).

280. A.J. Blotcky, W.C. Duckworth, A. Ebrahim, F.K. Hamel, E.P. Rack, R.B. Sharma. *J. Radioanal. Nucl. Chem., Art.*, **134**, 151-160 (1989).

281. S.K. Nyarku, A. Chatt. *J. Radioanal. Chem.*, **71**, 129-145 (1982).

282. P.R. Devi, T. Gangaiah, G.R.K. Naidu. *Anal. Chim. Acta*, **249**, 533-537 (1991).

283. H.M. Kingston, I.L. Barnes, T.J. Brady, T.C. Rains, M.A. Champ. *Anal. Chem.*, **50**, 2064-2070 (1978).

284. W. Xiaolin, C. Yinliang, W. Xiuyuan, S. Ying, F. Yibei, G. Gaopin. *J. Radioanal. Nucl. Chem., Art.*, **147**, 377-384 (1991).

285. D.E. Ryan, A. Chatt, J. Holzbecher. *Anal. Chim. Acta*, **200**, 89-100 (1987).

286. G. Erdtmann. *Neutron Activation Tables*, K.H. Leiser, ed., Verlag Chemie, New York, 1976.

287. R.L. Heath. *Gamma-Ray Spectrum Catalogue*, 3rd. Ed. on CD-ROM, 1997.

288. J.J. Kipling. "*Adsorption from Solutions of Non-Electrolytes*", Academic Press, New York, p. 91, 1965.

289. C.L. Mantell. "Ads*orption*", McGraw-Hill, New York, p. 25, 1951.

290. R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden. "*Environmental Organic Chemistry*", Wiley-Interscience, Toronto, p. 258, 1993.

291. J.J. Kipling. "*Adsorption from Solutions of Non-Electrolytes*", Academic Press, New York, p. 25, 1965.

292. D.J. Mackey. *J. Chromatogr.*, **237**, 79-88 (1982).

293. D.J. Mackey. *J. Chromatogr.*, **242**, 275-287 (1982).

294. H. Koshima. *Anal. Sci.*, **1**, 289-90 (1985); *Chem. Abstr.*, **104**:75729u (1986).

295. M. Pesavento, A. Profumo, R. Biesuz. *Talanta*, **35**, 431-437 (1988).

296. B.A. Eichenberger, K.Y. Chen. "*Origin and Nature of Selected Inorganic Constituents in Natural Waters*", in *Water Analysis*, v.1, R.A. Minear, L.H. Keith, eds.,Academic Press, Montreal, p.1-54, 1982.

297. J. Komárek, J. Havel, L. Sommer. *Coll. Czech. Chem. Commun.*, **44**, 3241-3255 (1979).

298. I.V. Kolosova. *Tr. Perm. Gos. Med. Inst.*, **99**, 446-450 (1970); *Chem. Abstr.*, **78**:37601h (1973).

299. K.A. Rao and B. Rangamannar. *J. Radioanl. Nucl. Chem., Lett.*, **93**, 319-326 (1985).

300. K. Goto, S. Taguchi, Y. Fukue, K. Ohta, H. Watanabe. *Talanta*, **24**, 752-753 (1977).

301. F. Miao, J. Liu, Y. Zhang, H. Li. *Beijing Huagong Xueyuan Zuebao, Ziran Kexueban*, 17, 84-88 (1990); *Chem. Abstr.*, **115**:173646m (1991).

302. E. Grzegrzólka. *Chem. Anal.* **22**, 303-339 (1977).

303. H. Watanabe, H. Matsunaga. *Bunseki Kagaku*, **25**, 35-39 (1976); *Chem. Abstr.* **85**:136632v (1976).

304. I.C. Smith, B.L. Carson. "*Trace Metals in the Environment*", Vol. 2, Ann Arbor Science, Ann Arbor, p.418, 1977.

305. D.A. Skoog, D.M. West, F.J. Holler. *Fundamentals of Analytical Chemistry*, 6th ed., Saunders College Publishing, Montréal, p.A.11, 1992.

306. A.E. Martell, R.M. Smith. *Critical Stability Constants*, Vol. 2, Plenum Publishing, New York, p. 91, 1977.

307. *Ibid.*, p. 20.

308. F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 5th ed., John Wiley and Sons, Toronto, pp. 988-989, 1988.

309. P.N. Palei. *Analytical Chemistry of Uranium*, Ann Arbor-Humphrey Scence, Ann Arbor, pp. 20-27, 1970.

310. D.C. Schroeder, G.F. Lee. *Water, Air, Soil Pollut.*, **4**, 355-365 (1965).

311. M. Sperling, S. Xu, B. Welz. *Anal. Chem.*, **64**, 3101-3108 (1992).

312. F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 5th ed., John Wiley and Sons, Toronto, p. 693, 1988.

313. V.M. Rao, M.N. Sastri. *Talanta*, **27**, 771-777 (1980).

314. B. Subramanyam, M.C. Eshwar. *Bull. Chem. Soc. Jpn.*, **49**, 347-348 (1976).

315. R.J.H. Clark. *The Chemistry of Titanium and Vanadium*, Elsevier Publishing Company, New York, p.15, 1968.

316. K. Hirayama, D.E. Leyden. *Anal Chim. Acta*, **188**, 1-7 (1986).

317. H.A. Van der Sloot, H.A. Das. *J. Radioanal. Chem.*, **35**, 139-146.

318. P.C. Cole, J.M. Eckert, K.L. Williams. *Anal. Chim. Acta*, **153**, 61-67 (1983).

319. B. Markert. *Fresenius' J. Anal. Chem.*, **349**, 697-702 (1994).

320. P. Bermejo-Barrera, E. Beceiro-Gonzalez, A. Bermejo-Barrera, F. Bermejo-Martinez. *Analyst*, **115**, 545-547 (1990).

321. ACS Committee on Environmental Improvement. *Anal. Chem.*, **52**, 2242-2249 (1980).

322. K. Heydorn. *J. Radioanal. Nucl. Chem., Art.*, **151**, 139-148 (1991).

323. J.K. Taylor. *Anal. Chem.*, **53**, 1588A-1596A (1981).

324. J.K. Taylor. *Quality Assurance of Chemical Measurements.* Lewis Publishing, Chelsea, MI, p.111, 1989.

325. J.K. Taylor. *Quality Assurance of Chemical Measurements.* Lewis Publishing, Chelsea, MI, p.2, 1989.

326. J. Holzbecher, A. Chatt, D.E. Ryan. *Cdn. J. Spectrosc.*, **30**, 67-79 (1985).

327. L.A. Currie. *Anal. Chem.*, **40**, 586-593 (1968).

328. H.M.N.H. Irving. *CRC Crit. Rev. Anal. Chem.* **8**, 321-366 (1980).

329. J. Starý. *The Solvent Extraction of Metal Chelates.* Pergammon Press, New York, pp. 138-150, 1964.

330. A. Elek, J. Bogáncs, E. Szabo. *J. Radioanal. Chem.*, **4**, 281-288 (1970).

331. A.E. Martell. *Stability Constants of Metal-Ion Complexes*, The Chemical Society, Burlington House, London, , pp. 680-681, 1971.

332. H.B. Singh, B. Kumar, R.L. Sharma, M. Katyal. *Analyst*, **114**, 853-855 (1994).

333. Y.K. Lee, K.J. Whang, K. Ueno. *Talanta*, **22**, 535-538 (1975).

334. J. Fries, H. Getrost. *Organic Reagents for Trace Analysis*, Merck Darmstadt, p.209, 1977.

335. H. Akaiwa, H. Kawamoto. *Anal. Chim. Acta*, **40**, 407-412 (1968).

336. W.U. Malik, T.C. Sharma. *Fresenius' Z. Anal. Chem.*, **258**, 124-125 (1972).

337. H.H. Willard, L.L. Merritt, Jr., J.A. Dean, F.A. Settle, Jr. *Instrumental Methods of Analysis*, 7th ed., Wadsworth Publishing Company, Belmont, CA, pp. 876-877, 1988.

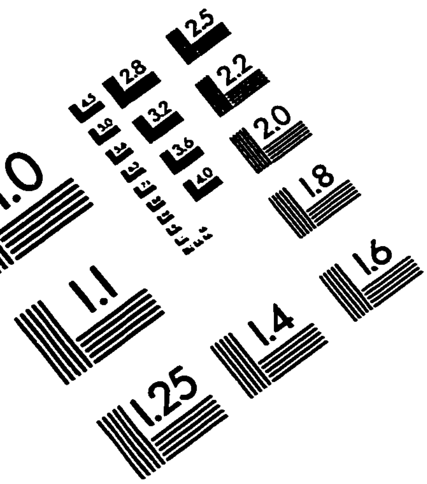
338. A. Alimonti, F. Petrucci, S. Fioravanti, F. Laurenti, S. Caroli. *Anal. Chim. Acta*, **342**, 75-81 (1997).

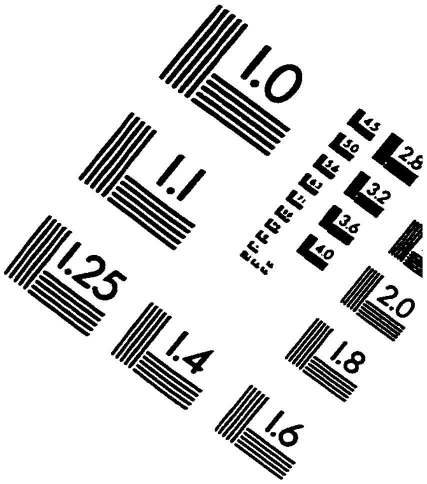
339. D.A. Skoog, J.J. Leary. *Principles of Instrumental Analysis*, 4th ed., Saunders College Publishing, Montréal, p.223, 1992.

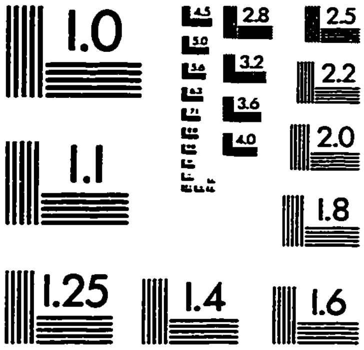
340. W.L. Clevenger, B.W. Smith, J.D. Wineforder. *Crit. Rev. Anal. Chem.*, **27**, 1-26 (1997).

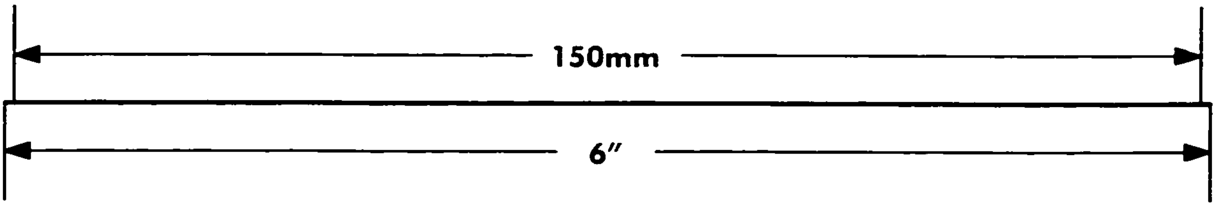
341. A. Lorber, Z. Karpas, L. Halicz. *Anal. Chim. Acta*, **334**, 295-301 (1996).

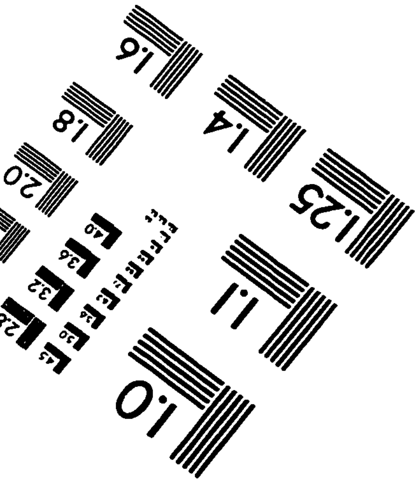
IMAGE EVALUATION TEST TARGET (QA-3)

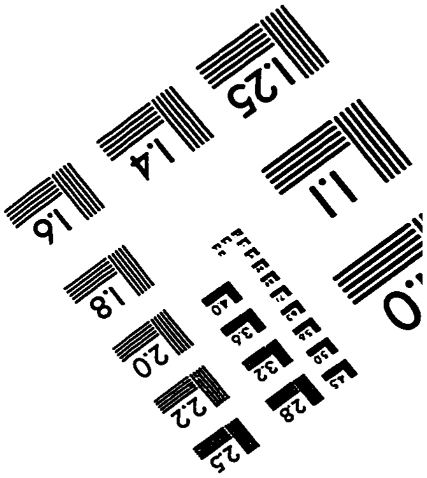












APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989