# PRECONCENTRATION AND INSTRUMENTAL METHODS FOR TRACE ELEMENTS IN MARINE SAMPLES BY NEUTRON ACTIVATION

BY

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# ABSTRACT

Neutron activation analysis (NAA) methods have been developed in this study for the determination of trace elements in marine samples. An instrumental NAA (INAA) method has been used for measuring concentrations of up to 21 elements in microgram quantities of marine suspended particulate matter (SPM) while preconcentration methods followed by NAA have been developed for determining Mo, Co, Zn, Mn and V in sea water.

The INAA method for marine SPM consists of two irradiation and four decay periods. Concentrations of Al, Ba, Br, Ca, Cl, I, Mg, Mn, Na, Sr, Ti and V have been measured using their short-lived thermal neutron activation products while long-lived nuclides have been utilized for determining Au, Ce, Fe, Hg, K, La, Sc, Sm and Zn content. The major problems associated with multielement analysis in microgram amounts of marine SPM and procedures developed to minimize their effects are described here. The precision of the INAA method varied between 3 and 22%. The accuracy of measurements has been observed to be ± 10% in general. The limits of detection and determination are also reported here. The nature and origin of SPM have been studied using interelement concentration correlationships.

Molybdenum has been selectively and quantitatively preconcentrated from sea water by cocrystallization with $\beta$-naphthoin oxime. Factors affecting the recovery of Mo have been investigated in detail using a radioactive tracer and reported here. The method developed has been applied to determine Mo concentrations in marine and estuarine water samples. The precision and the accuracy (better than ± 10%) of the method and the limits of detection (0.30 µg Mo $L^{-1}$) and determination (1.00 µg Mo $L^{-1}$) have been evaluated.

Cobalt, Zinc and Manganese have been preconcentrated using chitosan. Conditions have first been established using radioactive tracers to obtain maximum possible recoveries for each element. Details of the methods developed are reported here. The applicability of the methods have been evaluated by analyzing a few sea water samples. Detection limits of 0.034 µg Co $L^{-1}$, 1.22 µg Zn $L^{-1}$ and 0.22 µg Mn $L^{-1}$, and determination limits of 0.11 µg Co $L^{-1}$, 4.13 µg Zn $L^{-1}$ and 1.17 µg Mn $L^{-1}$ have been obtained.

An analytical method has been developed for preconcentrating vanadium from sea water with $Mg(OH)_2$ which is formed by adding ammonium hydroxide to sea water. The method has been found to be quantitative and specific for concentrating V under the experimental conditions used. The method has been applied to determine V concentrations in a few sea water samples. A detection limit of 0.38 µg V $L^{-1}$ and a determination limit of 1.50 µg V $L^{-1}$ have been achieved.

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# LIST OF ABBREVIATIONS

a - annum

b - barn

°C - degree Celcius

cm - centimetre

d - day

g - gram

h - hour

keV - kiloelectron volt

L - litre

mg - milligram

mL - millilitre

min - minute

MeV - Million electron volt

μg - microgram

ng - nanogram

ppb - parts per billion

ppm - parts per million

% - percent

$^{o}$/oo - parts per thousand

s - second

# 1. INTRODUCTION

## 1.1 General

The ocean is an extremely complex chemical system containing all the elements of the earth's crust in either dissolved or particulate fractions of water. It contains approximately 3 to 3.5% of dissolved solids - primarily halides, sulphates and carbonates of sodium, magnesium, calcium, potassium and strontium. The concentrations of these substances vary so little that they have been classed as conservative properties of the sea. In addition to these constituents, traces of at least fifty other elements have been detected. Elements present in concentrations below 1 mg $kg^{-1}$ are generally referred to as trace elements. The concentrations of toxic and nutrient trace elements in sea water are of considerable interest, and great effort has been devoted to the elucidation of their roles in geochemical and biological cycles of the oceans (RIL65, RIL71).

The present study involves determination of multielement content in oceanic suspended particulate matter and concentrations of some selected trace elements in water samples collected from the Atlantic Ocean.

The classification of substances present in water as dissolved, colloidal and particulate is fairly arbitrary (HOR69). Substances having particle diameters $<10^{-4}$ µm are considered as soluble (i.e. dissolved fraction), those with diameters between $10^{-4}$ µm and $10^{-2}$ µm as colloidal and the remainder (i.e. those with diameters $>10^{-2}$ µm) as particulate. Fraction that is collected on a 0.4 µm Nuclepore membrane filter is considered in this work as suspended particulate matter (SPM) and that passed through it as the soluble fraction.

## 1.2 Sample Collection and Storage

Sample collection and storage are two very important steps in trace element analysis of aquatic samples. It is, therefore, essential that these steps be performed with an awareness of all possible sources of contamination.

A variety of sampling devices, from plastic buckets to discrete depth samplers have been used (IAEA70). Samplers are best constructed of polyethylene, polypropylene, polycarbonate or Teflon. Sampling procedures are discussed in detail in the above reference. Linear polyethylene sample containers have been used in the present work.

It has been reported by several workers (MUR72, DUK68, GAR74) that the equilibrium times for adsorption and desorption of heavy metals in particulate-water mixtures are rapid and less than 72 h. Maximum adsorption occurs at pH values above 7.5. With any change in solution equilibrium after collection, adsorption sites of particulate matter provide a path for removal of metal species, while under some conditions desorption of adsorbed metals is possible. Because of the unpredictable nature of bacterial growth in stored samples (MOE72) which may result in changes in the carbon dioxide content and thus the pH of water, it is advisable that particulate matter be separated from water as soon as possible after sample collection. Changes in pH may result in precipitation, changes in the degree of complexation and adsorption behaviour, and in the rate of redox reactions involving heavy metal species in solution. Carpenter et. al. (CAR75) have recommended that the samples should be chilled to near 4°C to retard the bacterial growth, if the time between sample collection and filtration is in excess of a few hours.

Teflon or high purity polyethylene or polypropylene are preferred materials for storage containers (IAEA70). Heavy metal impurities in these polymer materials, which generally result from catalysts, promoters or metal dies used in the manufacturing processes, may contaminate the sample. The surface metal impurities may be readily leached out with dilute hydrochloric or nitric acid. Although these acid-leaching treatments are necessary to remove surface contamination from container materials, such treatments can activate adsorption sites capable of removing trace metals from solution. For this reason, it is necessary that after acid treatment the containers be well-rinsed with distilled water and portions of sample (BAT77a). Such treatments have been carried out in the work reported here.

Where only a total metal analysis is required, adsorptive losses are generally minimized by acidifying sample after filtration to 0.05 M $[H^+]$ with either hydrochloric or nitric acid (ASTM75). Acidification before filtration, however, will release metals from particulate matter and is not advisable. In metal speciation studies, storage at 4°C (CAR75, FUK75) and freeze drying (HOL76) of filtered water samples have been used to reduce bacterial growth, which is responsible for losses and transformation of metal species.

In this study, water samples collected in 20-L specially prepared Niskin water samplers were filtered through 0.4 μm Nuclepore polycarbonate membrane filters on board ship within 30 min of collection. Water samples were stored in 2-L precleaned polyethylene bottles. These bottles were soaked for 16 h in 2M HCl and rinsed thoroughly with deionized water. The bottles were then filled with deionized water to which 2 mL of concentrated ULTREX HCl were added. The bottles were emptied first and then washed with a portion of filtered sea water just before storing the samples.

## 1.3 Analytical Methodologies

A brief introduction to the trace element analysis of marine SPM and the different types of preconcentration techniques applicable to sea water analysis are presented here.

### 1.3.1 Suspended Particulate Matter (SPM)

Determination of trace elements in marine suspended matter is difficult for several reasons:

(a) small sample weights available for trace element analysis because of the low suspended matter load in these waters;

(b) presence of large amounts of major elements may cause severe interferences in trace element determination; and

(c) blank values may be comparable to or even greater than the concentrations of certain elements present in suspended matter.

Instrumental methods are best suited for determining the concentrations of a number of elements in samples of low weights. Two instrumental techniques, namely x-ray fluorescence and neutron activation analysis (NAA) have previously been used for analysing SPM. Atomic absorption spectrometry has also been used widely, after a preliminary sample dissolution step. An instrumental neutron activation analysis (INAA) method has been developed in the work reported to determine concentrations of 21 elements in SPM collected from the Atlantic Ocean.

### 1.3.2 Soluble Fraction

The concentrations of the dissolved trace elements in sea water are generally very low, frequently in the parts per billion (ppb) range or lower. Due to severe interferences from major elements in the matrix, the low levels of elements in sea water are below the sensitivity limits of most analytical methods. In addition, when good precision and accuracy are required, the number of useful methods for analysis of trace metals in sea water is greatly reduced. With the possible exception of anodic stripping voltammetry and neutron activation analysis, multielement analytical techniques usually require a prior concentration step which ideally enriches the metal ions of interest while removing the abundant and interfering alkali and alkaline earth ions. For multielement analysis of sea water, however, these two methods also suffer from disadvantages which significantly reduce their applicability.

Anodic stripping voltammetry is a convenient and highly sensitive technique for analysis of heavy metals at the ppb or lower levels. Applications of this technique to sea water and other samples of marine origin employing different types of electrodes have been reported (FLO72, LUN75, ZIR72). The chief limitation of the technique, however, is that only a few elements present in an electroactive form, e.g., Zn, Cd, Pb and Cu can be determined.

A drying step is generally applied to remove water when instrumental neutron activation analysis (INAA) is used. The high content of salts, particularly sodium chloride, in sea water considerably reduces the number of elements which can be determined by INAA. Reports concerning determinations of a few selected elements have been published (PIP69, BOL64) showing that the high amounts of $^{24}Na(t_{\frac{1}{2}} = 15\ h)$ and $^{38}Cl(t_{\frac{1}{2}} = 37\ min)$ prevent the measurement of medium- and short-lived nuclides. However, by introducing radiochemical separations, a few more elements can be determined (SCH65).

Development of a radiochemical neutron activation analysis (RNAA) method was not attempted in the present work because (i) of the need for using remote controlled handling of irradiated samples in a well-shielded fume hood, which is not available in this laboratory; and (ii) this method is suitable only for elements which produce long-lived nuclides.

One of the main objectives of this work is to develop methods to preconcentrate a selected number of elements from sea water. It is also our intention to obtain the final concentrate in solid form so that NAA can be readily applied for elemental determinations.

### 1.3.2.1 Preconcentration Techniques

In trace element analysis, suitable preconcentration methods can improve the detection limit and sensitivity of determination, and can simplify the overall treatment of a sample. Preconcentration becomes essential when the detection limit of the analytical technique used for a desired element is lower than the concentration of that element in a given sample. Since the relative concentration of trace elements in the prepared concentrate is usually higher than that in the original sample, use of large volumes of the original sample for preconcentration purposes can essentially increase the absolute amount of the trace element to be measured, thereby decreasing the limit for detection. Preconcentration procedures can drastically reduce the final volume of the sample to be analyzed - a factor which is important in the trace element analysis of sea water by NAA. Methods can also be developed not only to preconcentrate the elements of interest but also to minimize, if not completely eliminate, the matrix elements which interfere seriously in the final step of measurement using a given analytical technique.

On the other hand, preconcentration has several disadvantages. Since preconcentration is a technique which is done before the final determination step, it is subjected to 'reagent blanks' and other contaminations. Consequently, ultrapure reagents and ultraclean equipment will have to be used, and proper blank subtractions, if necessary, will have to be made. Preconcentration may lead to the loss of volatile elements under certain experimental conditions. Methods involving preconcentration steps generally increase the overall time for analysis. In any preconcentration scheme, careful consideration must be given to the efficiency of recovery and purity of the elements of interest. Elements with similar chemical properties may preconcentrate together and interfere in their determinations. This is particularly true with methods which are not very selective for individual elements. However, multielement specific techniques such as NAA, which is the technique of choice for the present work, can be used under such circumstances.

Many different methods of varying importance are used in analytical preconcentration. Evaporation, lyophilization, coprecipitation, solvent-extraction and ion-exchange methods are most frequently used.

In the analysis of sea water, the simplest way of preconcentration would be to dry the sample, by either evaporation or lyophilization. Removal of water will provide a concentrate with many trace elements at levels sufficient for determination by NAA. However, the high activities of $^{24}$Na and $^{38}$Cl produced on thermal neutron irradiation of the dried samples would necessitate separation before analysis, particularly for elements with short and medium half-lives.

Cocrystallization and coprecipitation have been used in the preconcentration of trace elements from sea water. In cocrystallization, the organic reagent, which combines with the trace element of interest, is directly crystallized from aqueous solution. The system does not require an additional carrier which is normally used in coprecipitation of an element. Cocrystallization is based on the fact that if a trace element and an organic reagent combine to form a compound less soluble than the reagent, the crystallized product should be enriched with the element. The organic reagents are usually added to sea water as solutions of water miscible organic solvent, after which the mixture is reduced in volume. The crystals are then collected by filtration. The consumption of the organic reagent in this case may be very small compared to that in solvent extraction. The use of organic reagents for preconcentration would be much more favourable especially in thermal neutron activation analysis; because in addition to their selectivity for separation, the organic compounds composed of H, C, O and N are essentially non-interfering for all nuclides except the very short-lived ones. Present study involves a preconcentration of Mo using cocrystallization with $\beta$-naphthoin oxime.

Inorganic carriers are used in the preconcentration of trace elements from dilute solutions by coprecipitation. In order to coprecipitate trace elements, amorphous precipitates of high surface activity (hydroxides, sulphides and others) are most frequently used. Preconcentration of vanadium with $Mg(OH)_2$, investigated in the present study, involves a coprecipitation mechanism. Kolthoff (KOL32) has classified the mechanisms of coprecipitation as adsorption, occlusion and mixed crystal formation.

(i) Surface adsorption of a trace element occurs as a result of the attractive forces between opposite electrical charges of the carrier precipitate and the tracer ion. Carrying of elements by this mechanism is favoured by large surface area of the precipitate and the sparingly or low dissociability of the compound formed by the trace ion and the oppositely charged lattice ion.

(ii) Occlusion or internal adsorption is due to the adsorption of trace ions on surfaces of growing crystals, where the trace ions are entrapped by the newly formed succeeding crystal layers. The extent of occlusion depends upon the speed of precipitation and the degree of supersaturation of the reagent during precipitation.

(iii) In mixed crystal formation, tracer ion is incorporated into the crystal lattice of the reagent precipitate. In this case, tracer ions may replace some of the carrier ions of like charge in the crystal lattice, and are thus carried. The extent of mixed crystal formation is determined by the relative insolubilities of the micro and the macro components of the precipitate and the ability of the host precipitate to incorporate impurities.

It is not always necessary to introduce a collector into the solution; sometimes the matrix may be used instead. This approach is particularly suitable for hydroxides. It is sometimes necessary to control the charge of the trace elements e.g. by transforming them into complex anions, because in the separation of part of the matrix as a slightly soluble crystalline compound, the precipitate surface develops a positive charge. However, hydroxides adsorb hydroxyl ions and, hence, this rule does not apply to them.

Solvent extraction methods may be used for separating (selective or group) trace elements. Simplicity and rapidity are important advantages of these methods. Various systems are used in the extraction of trace elements; chelating systems are most frequently used. Dithizone, dithiocarbamates, 8-hydroxyquinoline, diethyl- and pyrrolidine-dithiocarbamates are conventional reagents for group separation.

Ion-exchange, which often involves complex formation, are of particular interest among the preconcentration methods. These methods are used to mask elements which are not to be sorbed and to transform the elements of interest into a well-sorbed form. Numerous chelate-forming organic reagents may be used for this purpose, besides the usual inorganic exchangers. Chelating resins have also been used in preconcentrating trace elements from sea water (RIL68a, WIN72, HOL74).

Complexes of trace elements are adsorbed well by active charcoal under certain conditions. This adsorbent behaves as an anion-exchanger in aqueous solution, e.g. it selectively adsorbs anionic complexes of noble metals. On the other hand, oxidized charcoal (treated with nitric acid, for example) is a cation exchanger and adsorbs multi-charged cations as well. Active charcoal can also concentrate metal chelates, e.g. diethyldithiocarbamates of transition elements. In the present study the natural chelating polymer chitosan was found to act as an efficient adsorbent for manganese hydroxide.

In natural waters the presence of organically bound metals are well known (SLO67). Especially, humic substances are held responsible for complexation of Co, Zn, Cu and Cd. In this study, elemental concentrations of the filtered, acidified and UV-irradiated (except for Mo) sea water samples have been determined. Hence, the concentrations measured include, 'free', 'acid exchangeable' (adsorbed onto colloidal material in the solution) and 'organically bound and UV oxidizable' metal ions. Still a possibility of metal ions being bound to organic compounds not destroyed by UV-irradiation may exist, e.g. for zinc (BLU78).

### 1.3.2.2 Analytical Techniques

A variety of techniques has been used to determine concentrations of trace elements in sea water, with or without a preconcentration step. These include atomic absorption spectrometry, emission spectrography, x-ray spectrometry, anodic stripping voltammetry and neutron activation analysis (NAA). The applications of these techniques with reference to the elements determined in the present work have been reviewed in the corresponding chapters. Since NAA has been used in this work, the theory of it is presented below.

## 1.4 Neutron Activation Analysis

### 1.4.1 General Principles

Neutron activation analysis (NAA) has become a powerful analytical tool in trace element determination as a result of its high sensitivity, simplicity and selectivity.

The basic principle of NAA is that a stable isotope when irradiated by neutrons can undergo a nuclear transformation to produce a radioactive nuclide, which decays with the emission of gamma-, beta- or alpha-rays which are then detected by suitable radiation detection equipment. The detection of radiation of the appropriate energy permits identification, and net area of the photopeak allows estimation of the amount of a particular element present in the sample before irradiation. The actual magnitude of response at the particular energy involved is a direct measure of the amount of that element present in the sample.

When an element is bombarded with neutrons, the resulting initial activity, $A_o$, is given by

$$A_o = \frac{WN\sigma\epsilon\Theta\Phi}{A}\left[1 - \exp\left(-\lambda t_i\right)\right] \tag{1}$$

i.e.
$$A_o = \frac{WN\sigma\epsilon\Theta\Phi}{A}\left[1 - \exp\left(- \frac{\ln 2}{t_{\frac{1}{2}}} t_i\right)\right] \tag{2}$$

where, $A$ = atomic weight of the element

$N$ = Avogadro's number

$t_i$ = irradiation time

$t_{\frac{1}{2}}$ = half-life of the nuclide formed

$W$ = weight of the element in question, g

$\Phi$ = neutron flux, n cm$^{-2}$ s$^{-1}$

$\sigma$ = cross section of reaction, cm$^2$

$\epsilon$ = efficiency of the detector

$\Theta$ = percentage isotopic abundance of the element

$\lambda$ = decay constant of the nuclide formed

If $t_d$ is the decay time between the end of irradiation and the beginning of counting, the activity, $A_t$, at the start of counting is given by

$$A_t = A_o e^{-\lambda t_d} \tag{3}$$

If the activation equation alone is used, it is possible to calculate the concentration of a given element. This type of absolute determination is, however, not very accurate due to several reasons such as: (i) the cross sections of most nuclides are probably known no better than 5-15%; (ii) there are discrepancies in isotopic abundances and half-lives; (iii) the flux is not in general accurately known; (iv) all timing parameters must be reliably reproduced; and (vi) the detector must be properly calibrated for efficiency values. It is difficult to obtain accuracy of better than ± 20% without extreme care and effort in absolute determinations with most samples. The majority of activation analyses done today utilize the comparator technique. In this method a known weight of the element sought (called "standard") and unknown sample are irradiated simultaneously for the same time in the same flux. Under ideal conditions, the specific activities (disintegration rate/weight of the element) of both standard and unknown are the same. If the unknown and the standard are counted under identical conditions (counting efficiencies, $\epsilon_s$ and $\epsilon_x$ equal), one can use the following relation to calculate the amount of the unknown:

$$W_x = \frac{W_s A_x}{A_s} \qquad (4)$$

or, since $R_x = A_x \epsilon_x$ and

$$R_s = A_s \epsilon_s$$

$$W_x = \frac{W_s R_x}{R_s} \qquad (5)$$

where $W_x$ = weight of the element x in unknown

$W_s$ = weight of the element x in standard

$A_x$ = disintegration rate of unknown

$A_s$ = disintegration rate of standard

$R_x$ = count rate of unknown

$R_s$ = count rate of standard

$\epsilon_x$ = counting efficiency of unknown

$\epsilon_s$ = counting efficiency of standard

The comparator technique eliminates many of the uncertainties generally encountered in the absolute procedure.

It can be seen from equation (2), that the sensitivity of an analysis depends upon the flux of bombarding particles, the cross section for the reaction involved, the half-life of the nuclide measured, the duration of the irradiation and the efficiency of the detector. The specificity of NAA is usually excellent since the purity of radionuclide measured may be checked by measuring its characteristic half-life.

Use of high-resolution detectors in NAA permits simultaneous determinations for a number of elements. In cases, for instance, where the matrix is not activated or only mildly activated or has a short half-life, non-destructive analysis can be applied. In some complex samples, however, the number and intensity of major radioactive products may be so large that activity measurement of a desired component can be rather difficult. For this reason and for the fact that the ultimate sensitivity and accuracy are obtained only after isolation of elements of interest from the matrix, either pre- or post irradiation chemical separation techniques are routinely employed in many practical activation analysis problems.

The neutron flux in a reactor is composed of thermal (energy about 0.025 eV), epithermal or resonance (energies 0.4 eV - 1 MeV) and fast (energies greater than 1 MeV) neutrons. Epithermal and fast neutron fluxes are relatively low compared to the thermal flux. When an irradiation is done without shielding for any type of neutrons, it is generally designated as thermal NAA. Thermal neutron activation has been used throughout the present study.

The applicability of epithermal and cyclic instrumental neutron activation techniques has also been investigated here, for analyzing SPM. Some important features of these two techniques are briefly discussed in the following sections.

### 1.4.2 Epithermal Instrumental Neutron Activation Analysis

Epithermal INAA (EINAA) is based on the suppression of the activity of nuclides having low $I/\sigma$ values, i.e. namely nuclides following the $1/v$ law (v - velocity of neutrons) in the epithermal neutron energy region, in favour of nuclides having high $I/\sigma$ values ($I$, $\sigma$ are resonance integral and neutron activation cross section for epithermal and thermal neutrons, respectively). Cadmium and boron shields which have very high cross sections for thermal neutrons, are generally used to screen out the thermal neutrons. Activation occurs with both thermal and epithermal neutrons for example without a Cd cover, whereas with a Cd cover the $(n,\gamma)$ reactions are possible only with epicadmium neutrons. The measured ratio of the two activities for a given irradiation position is called the cadmium ratio ($R_{cd}$) of the nuclide of interest (SOE72). Cadmium ratios for nuclides are often expressed in terms of Cd ratio for gold.

$$R_{cd} = \frac{\text{Activity without Cd foil}}{\text{Activity with Cd foil}} = \frac{\Phi_{th}\sigma + \Phi_e I}{\Phi_e I}$$

where $\Phi_{th}$, $\Phi_e$ = thermal and epithermal fluxes respectively.

Another important parameter in ENAA is the advantage factor, $F_a$, defined by the following equation.

$$F_a = \frac{R_{cd,I}}{R_{cd,i}}$$

I = intensity of gamma-ray of interest

$T = t_i + t_w + t_c + t_{w'}$

where, $t_i$ = time of irradiation

$t_w$ = time between end of irradiation and start of counting

$t_c$ = time of counting

$t_{w'}$ = time between end of counting and start of irradiation

A knowledge of other elements present in the sample matrix is important in choosing the best timing parameters in CINAA, especially those producing nuclides likely to contribute radiation to the background underlying the signal of interest.

### 1.4.4 Dead Time Corrections

An analyzer system requires a certain time to process and register a signal. During this time, the system is not able to analyze another signal. This time loss is referred to as the dead time. Correction for the dead time can be automatically done by counting in the live time mode, where the sample is counted for an additional time equal to the dead time. However, this correction is inadequate for counting short-lived nuclides which decay during counting. In addition, if the activity of a standard differs considerably from that of a sample significant errors can arise. Dead time corrections have been applied in the present study during analysis of SPM for short-lived nuclides and also of the soluble fraction for vanadium (SOE72).

### 1.4.5 Interfering Nuclear Reactions

In NAA, there is a possibility that a nuclide of interest may be formed by reactions other than normal (n, $\gamma$) type from isotopes of other elements. These interfering nuclear reactions are caused by fast and epithermal neutrons and are generally of (n, p) or (n,$\alpha$) type. Depending on the matrix composition, it may be necessary to correct for these contributions to a nuclide of interest, although these are insignificant in most cases as a result of low fluxes and cross sections of epithermal and fast neutrons. Corrections for the interfering reactions can be made using the following equation,

$$A_{int}/A = 0.22 \times \frac{\Theta_{int} \sigma_{int} W_{int} M}{\Theta \sigma W M_{int}}$$

where, 'int' refers to interfering reaction

$A_{int}$, $A$ = activities of the nuclides due to interfering reaction and reaction of interest, respectively

$W_{int}$, $W$ = weights of the corresponding elements

$M_{int}$, $M$ = atomic weights of the corresponding elements

0.22 = the ratio of fast to thermal neutron fluxes in DUSR

Possible interfering reactions have been taken into account in the present study.

## 1.5 Summary of Objectives

The principal objective of this research is to develop nuclear analytical methods for the determination of trace elements in marine samples. An INAA method has been developed to determine elemental concentrations in marine SPM. Concentrations of 21 elements have been determined using different irradiation, decay and counting conditions. Several different preconcentration methods have been developed for separating selected trace metals from sea water. A selective method based on co-crystallization with $\beta$-napthoin oxime has been used to concentrate molybdenum. Cobalt, zinc and manganese have been preconcentrated using a natural chelating polymer, chitosan. Vanadium has been preconcentrated with magnesium hydroxide formed by adding ultrapure alkali to sea water. The detailed objectives are described in individual chapters.

# 2. MULTIELEMENT DETERMINATION OF MARINE SUSPENDED PARTICULATE MATTER

An instrumental neutron activation analysis (INAA) method has been developed for the determination of elemental concentrations in marine suspended particulate matter (SPM). Concentrations of up to 21 elements have been determined using two irradiation and four decay periods. The precision, accuracy, and the detection and determination limits of the method have been evaluated. The distribution of trace elements among different fractions in SPM have been investigated through interelement correlations. The details of the method developed and the problems associated in analyzing microsamples of SPM are described in this chapter.

## 2.1 INTRODUCTION

Suspended particulate matter (SPM) in sea water is frequently conglomerates of various components. Sizes of individual components vary from less than one micrometre up to several millimetres; the majority by number of particles in the sea have sizes less than 10 μm (GOL72). In practice, SPM is commonly defined with reference to a minimum diameter, depending on the pore size of the filter being used for collecting them (LOR77). Fraction retained on a Nuclepore polycarbonate membrane filter with a pore size of 0.4 μm was considered as SPM in the work reported here. Similar definitions have been adapted by other researchers (RIL75).

Both the nature and load of suspended material in the sea can be highly variable. The range and the mean SPM concentrations for the whole water column in the major oceans are summarized in Table 2.1.

Table 2.1 Summary of SPM Load in Major Oceans[a]

| Water Body | Range, μg $L^{-1}$ | Mean, μg $L^{-1}$ |
|---|---|---|
| N. Atlantic | 0.5 - 247 | 49 |
| S. Atlantic | 1.5 - 197 | 51 |
| N. Pacific | 0.5 - 152 | 37 |
| S. Pacific | 4.5 - 86 | 30 |
| Indian | 9 - 177 | 72 |
| Caribbean | 0.5 - 139 | 40 |
| Gulf of Mexico | 12.5 - 193 | 66 |

a - Ref. JAC69

The total amounts of dissolved substances in sea water are, of course, very much greater than that of the suspended material.

The particulate material is carried to the sea mainly by rivers and estuaries. In addition to this transport, rapidly growing amounts of solid wastes are brought into the sea by pipeline or dumped from barges. It may also come from airborne dust settling on the sea surface. Very fine-grained material is carried away into the open sea and slowly settles into deep waters.

Natural marine SPM consists of a large number of components: inorganic material (sand, clay and minerals), living organisms (phytoplankton, zooplankton, bacteria and fungi), and organic detritus. The chemical composition of inorganic suspended material in the sea resembles that of the marine bottom sediment. Suspended material of large size may settle down on bottom sediment. In addition, water movement may stir up the bottom so that fine sediment may find itself suspended again. The quantity of organic matter suspended in seawater can be comparable to and sometimes present even in excess of the quantity of inorganic particulate material.

An INAA method has been developed here to determine elemental concentrations in marine SPM. Instrumental methods eliminate the possible contaminations from the reagents and equipments, and also losses by volatilization and adsorption onto container walls. Multielement capability of the INAA technique reduces the total analysis time, and the high sensitivities obtainable make it possible to determine very low concentrations of trace elements in the presence of relatively high concentrations of major elements. However, contribution from the blank filters used to collect SPM may be large for some elements. It is, therefore, necessary to use filters with low trace element contents. In this study Nuclepore filters have been used.

## 2.2 OBJECTIVES

The principal objective of the present study was to develop an instrumental neutron activation analysis (INAA) method to determine the elemental concentrations in microgram quantities of marine suspended particulate matter. Different irradiation, decay and counting times were used to obtain good sensitivities and precisions.

The sample weights available for this study were in the range of 60-600 µg collected from the Atlantic Ocean. These weights were too small to be subjected to fractionation procedures of trace metals to study the distribution of trace metals among different fractions in SPM, because of the possible serious losses and contaminations. Instead, the nature of SPM has been investigated by studying the inter-element relationships, after determining the elemental concentrations by INAA. Contributions from the blank Nuclepore filters for trace elements have been estimated and corrections have been made whenever necessary. The precision of the INAA method has been evaluated by repeated analysis of two samples having different total suspended matter weights and different trace element contents, using short-lived nuclides. The accuracy of the method has been estimated by analyzing some NBS Standard Reference Materials. The detection and determination limits for the trace elements studied have been calculated.

## 2.3 LITERATURE SURVEY

Methods for collecting SPM from water and the techniques presently being used in the determination of major, minor and trace elements in this matrix are discussed here. Some reported values for the elemental concentrations in suspended matter in the literature are also presented here.

### 2.3.1 Methods of Collecting Suspended Matter

In general, particulate matter is separated from water by filtration or centrifugation.

### 2.3.1.1 Filtration

The fraction which is collected from water on a 0.4 (also 0.45) µm pore size filter is now accepted as suspended particulate matter (SPM) (RIL75). In the selection of a filtering medium, there are several pertinent properties that should be considered. They can be summarized as follows:

(1) The filter should have a reproducible and uniform pore size. The most commonly used pore size is 0.4 µm; this will retain all phytoplankton and most marine bacteria, in addition to inorganic material.

(2) The rate of filtration should be high, and the filter should not be clogged easily.

(3) It should be easily brought to constant weight, so that the mass of total particulate material can be determined gravimetrically.

(4) Chemical interaction among the filter, particulates, and solution, such as adsorption, dissolution, ion exchange and precipitation should not take place.

(5) It should have reasonable mechanical strength.

Filtration by membrane filtering apparatus has proven to be most satisfactory and is the generally accepted procedure (MAR68). Sheldon (SHE72) has investigated the properties of various membrane filters. All cellulose ester membrane filters (such as Millipore) have been found to retain particles much smaller than the stated pore size, even from samples with low particle concentrations; the total range of effective pore size was below 1 μm for filters with different stated pore sizes. He considered that these are probably the best filters for total particle retention. The average minimum size of particles retained (median retention) by perforated polycarbonate membranes (such as Nuclepore) has been found to be similar to the stated pore size when relatively small sea water samples with moderate concentrations of the particles were filtered. These membranes can filter to the point of overloading without changing their effective pore size. In addition, Spencer et al. (SPE72) found that Millipore filters lose weight as water passes through them due to the washing out of the protective detergent materials coated on the surface of filters. No such loss has been reported with Nuclepore filters (BIS74).

Cranston et al. (CRA72) found the Nuclepore filter to be superior in terms of interaction of the filter with suspended particles and the solution. Lower weight of Nuclepore filters compared to Millipore filters (20 mg vs 80 mg) makes them preferable especially in the case of small sample weights, because of the less possible weighing errors. Filters of the same nominal pore size have been shown to vary with the speed of filtration and particulate retention (WAN75) and in trace element contamination (BET75). Nuclepore filters have all the above mentioned advantages over Millipore membranes and hence were used in this study. It is also important that the filters used to collect suspended matter for trace element analysis contain low elemental levels. It has been observed in this study that Nuclepore membranes have low concentrations of most of the elements detected in suspended matter, and except for a few, blank corrections are not necessary.

Pressure filtration (SPE69, SEG75) offers advantages in terms of speed of filtration over the standard vacuum or gravity filtration. This decreased filtration time lessens the possibility of differential particle settling creating a non-representative sample of particles in cases where the entire water sample cannot be filtered. Water sample may also be stirred to prevent the concentration gradients. To avoid contamination during filtration, it is preferable that this operation be performed in a dust-free condition. This is especially true for sea water samples where the trace metal concentrations are low (c.f. ppb level). Spencer et. al. (SPE72) have stated an additional advantage of using a filter apparatus, where the water sample was completely out of contact with the atmosphere thereby preventing the oxidation of sulphide-containing waters which may give high particulate matter concentrations from the precipitation of manganese and iron oxide and elemental sulphur. A nitrogen pressure of 14 p.s.i. has been used by them. Suspended matter collected on filters is generally washed repeatedly with small amounts of deionized water to remove the adsorbed sea salts (SPE72, PRI75, PRI73), and dried in an oven at about 60°C, to a constant weight.

### 2.3.1.2 Centrifugation

In cases where filtration is difficult, centrifugation can be a useful alternative (IAEA70). It may be essential in the determination of elements where the adsorption onto the filter is considerably high. Insignificant mercury losses have been observed when centrifugation was used (GAR73, VAN76a). The effectiveness of centrifugation in separating particulates is a function of centrifuge speed, time and particle density. To avoid contamination, it is necessary to use Teflon or polyethylene liners for continuous centrifugation. However, this method needs expensive equipment in comparison to a filtering system, and is not applicable everywhere. In this study, SPM samples have been collected by pressure filtration.

### 2.3.2 Methods of Determination

Techniques used in the past for the determination of elements in SPM collected from different bodies of waters include x-ray fluorescence, x-ray emission, neutron activation, atomic absorption and in very few cases colorimetry and kinetic determinations. The last three techniques generally require the elements to be determined in the solution phase and they are essentially single element techniques, whereas multielement analysis can be performed on solid samples using the first three techniques.

Decomposition of suspended matter samples is generally carried out using hydrochloric, nitric and hydrofluoric acids at temperatures of about 90-100°C (LOR77, EGG76). In order to minimize possible contaminations during this dissolution step, ULTREX acids and Teflon digestion bombs are used. By this procedure, Nuclepore filters are not completely decomposed (LOR77). After the dissolution step, samples are transferred to volumetric flasks and diluted to a constant volume with either water (EGG76) or with a solution of boric acid in water (LOR77). Analysis is carried out using this solution. A mixture of nitric and sulphuric acids has also been used (YEM71), where the dissolution of both the filter and suspended matter is desired.

However, dissolution of only the suspended matter is preferable, because of the possibility of excluding the contributions to the elemental concentrations from the blank filter.

Flame atomic absorption methods have been used to determine elemental concentrations of relatively large samples of marine and river suspended matter. Rantala and Loring (RAN77) have determined Si, Al, Fe, Mn, Ca, K, Na, Mg, Cu and Zn in suspended matter of marine waters. Sample weights ranged from 0.5 to 20 mg, and Cu and Zn have been determined only in samples larger than 3 mg in weight. Concentrations of Cd, Co, Cu, Ni,Pb, Fe and Mn in suspended matter from river waters have been determined by Tessier et. al. (TES80) after being subjected to a sequential extraction procedure designed to partition the particulate matter into five fractions. Flameless atomic absorption spectrometry with a graphite furnace (COS78, EGG76, HIR75) or an arc atomizer (BEL72) is very sensitive and therefore preferable, especially when small sample weights are available.

Colorimetric and kinetic (YEM71, YEM75) methods have been applied to determine the concentrations of Fe, Al, Ti, Co and Mn in suspended matter from ocean waters.

Contaminations from the reagents and apparatus, the possible losses of the certain elements by volatilization, the relatively long time necessary for the total analysis, and the poor sensitivity when small samples are available (since determinations are carried out on portions of the determined the concentrations of Mn, Fe, Co, Hg, Zn, Sc, La and Sb. In order to prevent the neutron damage of Millipore filters, samples on the filters have been transformed to a hard woody pellet using a stainless steel pellet press. They have used three different decay and counting times; irradiation times and the neutron flux have not been specified. A decay of a few hours and a counting time of 400-1000 s to determine Mn, a decay of 4 d and a counting time of 1000-2000 s to determine La and Au, and a decay of 21-28 d and a counting time of 8,000-20,000 s to determine Hg, Sc, Cr, Sb, Fe, Zn and Co have been used. Since most of their samples had Cr and Au quantities within the blank error, concentrations for these elements have not been reported. The detection limits have been calculated on the basis of variability in the blank filters. The study by Ellis et. al. (ELL79) is the most complete report so far about application of INAA to suspended matter. They determined concentrations of Al, As, Ba, Br, Ca, Ce, Cl, Co, Eu, Fe, Gd, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Rb, Sc, Sm, Th, Ti, V, Yb, and Zn in estuarine suspended matter with sample weights ranging from 0.75 mg to 7.5 mg using four different irradiation and decay periods and two different fluxes. The average precision was between ±10 and ±16% for most of the elements and the accuracy was within ± 10%. The detection limits have been found to range between 0.37 ng and 1.0 μg.

A few selected examples of methods used for analyzing suspended matter are summarized in Table 2.2. Concentration ranges for some elements determined in marine suspended matter are given in Table 2.3.

Table 2.2 Survey of Methods used for Analyzing Suspended Matter

| Method of Determination | Type of Suspended Matter | Elements Determined | References |
|---|---|---|---|
| Flame Atomic Absorption | Coastal | Si, Al, Ti, Fe, Mn, Ca, K, Na, Mg, Cu, Zn | LOR77, RAN77 |
| | Open Ocean | Mg, Ca | EGG76 |
| | Coastal | Mn, K, Mg, Ca | HIR75 |
| | River | Cd, Co, Cu, Ni, Pb, Zn, Fe, Mn | TES80 |
| Flameless Atomic Absorption | | | |
| (i) Heated Graphite Furnace | Coastal and Estuary | Mn, Zn, Pb, Cd | COS78 |
| | Coastal | Fe, Mn | HIR75 |
| | Open Ocean | Al, Fe, Mn | EGG76 |
| (ii) DC Arc Atomizer | Open Ocean | Mn, Pb, Ag, Cd | BEL72 |
| Colorimetric and Kinetic | Open Ocean | Fe, Ti, Al<br>Co, Mn | YEM71,YEM75<br>YEM71,YEM75 |
| X-ray Fluorescence | Ocean | Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe | BAK76 |
| | Ocean | K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, Rb, Sr | VAN76b |

Table 2.2 Survey of Methods used for Analyzing Suspended Matter (cont'd.)

| Method of Determination | Type of Suspended Matter | Elements Determined | References |
|---|---|---|---|
| X-ray Emission | Coastal and Estuary | Si, Al, Ti, Fe, K, Ca, Mg, P, Mn, S, Zn, Pb | PR173,PRI75 |
| Instrumental Neutron Activation | Estuary | Al, Ba, Ca, Cl, I, Mg, Ti, V, Eu, K, Mn, Na, As, Br, Sb, Ce, Co, Cr, Fe, Gd, Hf, Hg, La, Lu, Nd, Rb, Sc, Sm, Th, Yb, Zn | ELL79 |
| | Open Ocean | I | WON76 |
| | Coastal | Hg | VAN76a |
| | River | K, Cs, Ag, Au, La, Ce, Sm, Cr, Br, Mn, Fe, Co, Zn, Sb | UKE77 |
| | Coastal | Mn, Fe, Co, Hg, Zn, Sc, La, Sb | SPE72 |
| | Coastal | Co, Cr, Fe | PIP69 |

Table 2.3 Literature Values for Elemental Concentrations in Suspended Matter (in ppm vs sea water)

| Element | Open Ocean Water[a] | Coastal Water | References |
|---|---|---|---|
| Ag | 0.0035-0.018 | | BEL72 |
| Al | 0.005-155 | 0.03-300 | EGG76,PRI75, PRI73,SPE70 |
| Ca | 0.02-0.775 | 0.31-16.05 | EGG76,PRI75 |
| Cd | 0.001-0.016 | | BEL72 |
| Co | | 0.8-41[a] | SPE72,PIP69 |
| Cr | | 0.18-0.26 | PIP69 |
| Cu | | 0.051-0.253 | SPE70 |
| Fe | 0.02-1.155 | 0.5-192 | EGG76,SPE72, PRI75,SPE70 |
| Hg | | 0.0012-0.156 | SPE72 |
| I | 0.001-0.127 | | WON76 |
| K | | 0.17-35.50 | PRI75,PRI73 |
| La | | 0.05-14.24[a] | SPE72 |
| Mg | 0.01-0.32 | 0.31-29.7 | EGG76,PRI75, PRI73 |
| Mn | 0.0001-0.54 | 0.012-57.87 | EGG76,BEL72, SPE72,PRI75 |
| Pb | 0.003-2.5 | | BEL72 |
| Sb | | 0.09-32.3[a] | SPE72 |
| Sc | | 0.025-6.823[a] | SPE72 |
| Si | 0.24-5.9 | 1.16-442.78 | EGG76,PRI75 |
| Ti | | 0.02-4.70 | PRI75,PRI73 |
| Zn | | 0.031-2.322 | SPE72 |
| Ni | | 0.0025-0.131 | SPE70 |

a = ppb

## 2.4 EXPERIMENTAL

### 2.4.1 Sample Collection

Suspended matter samples were collected from Cabot Strait and the Gulf of St. Lawrence in the Atlantic Ocean, during a cruise organized by the Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, N.S., Canada. Twenty-two samples of suspended matter were collected from five different stations (see Figure 2.1) and from up to six depths. Sample descriptions are presented in Appendix A. Water samples collected in 20-L modified (inside and joints coated with Teflon) Niskin water samplers were filtered through preweighed Nuclepore filters (47 mm diameter and 0.4 μm pore size) under a pressure of 5 p.s.i. of gaseous nitrogen. Water samplers were fitted to Millipore filter holders so that the samples were out of contact with atmosphere during filtration. Disposable filter holders of Millipore design were used to hold weighed Nuclepore filters preloaded before the cruise. Suspended matter samples with weights ranging from 60 to 600 μg were collected by filtering 1.75 L to 11.71 L water samples. Samples were transferred to the chemical laboratory at Bedford Institute, within about two weeks after sample collection; they were washed with 50 mL of distilled deionized water to remove sea salts.

### 2.4.2 Sample Preparation

The washed suspended matter samples were then transferred to our laboratory. Filters with suspended matter were

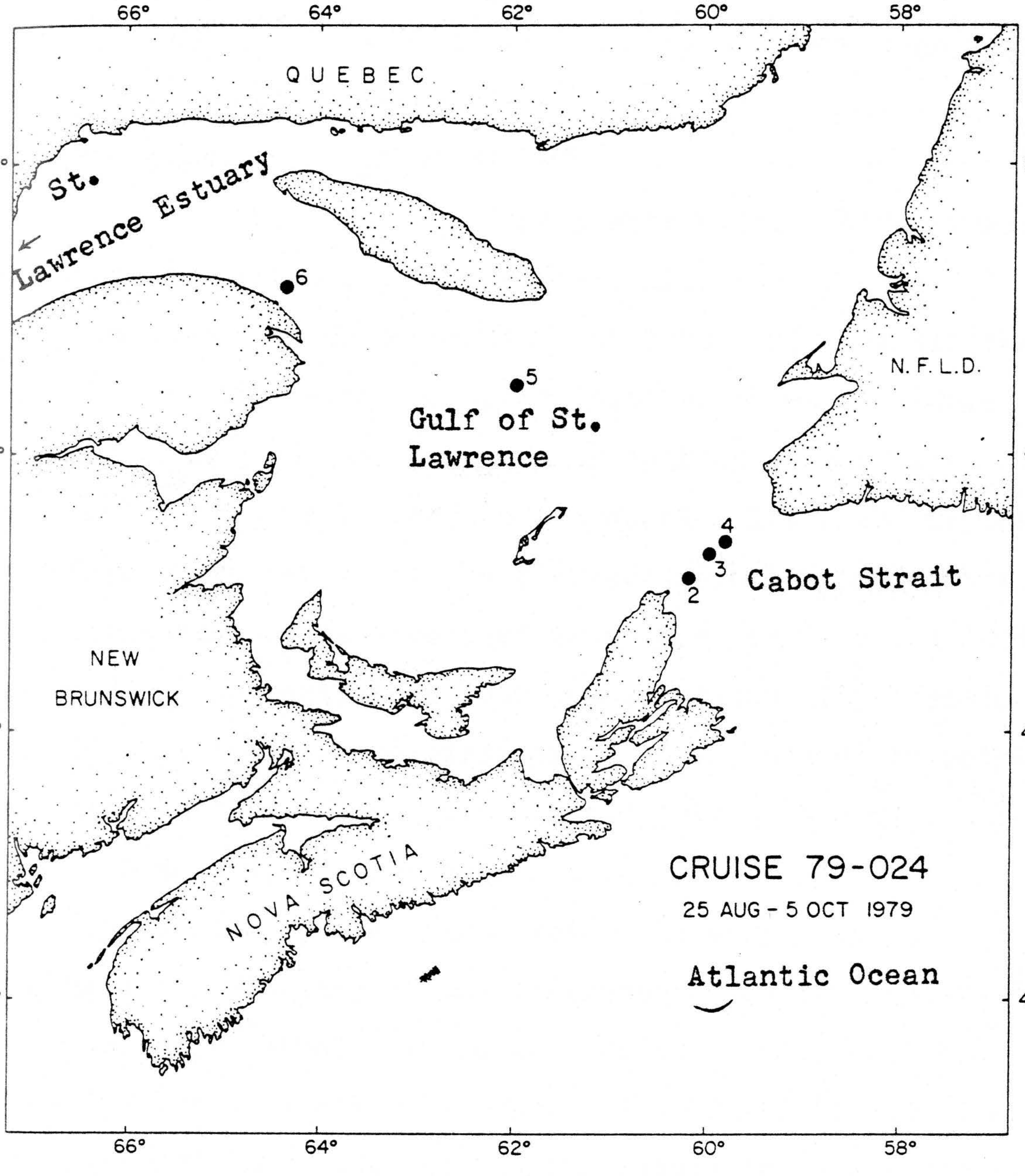


Fig. 2.1 Sample Stations in the Atlantic Ocean

carefully removed from the filter holders, dried in an oven at 60°C for 2 h and cooled in a desiccator. The samples were transferred into precleaned (with deionized water) and preweighed polyethylene bags (about 1 mm x 1 mm in size). The suspended matter samples in polyethylene bags were then weighed and heat-sealed.

### 2.4.3 Comparator Standards

Most of the standards were prepared using Alfa-Atomic Absorption Spectroscopy Standards. Aliquots of stock solutions, having concentrations of 1000 ppm, were diluted as desired with deionized water just before use. Single element standards were prepared by spiking appropriate amounts of these solutions on Nuclepore filters and drying under an Infra Red lamp. Reagent grade potassium bromide and potassium iodide were used to prepare bromide and iodide standards. Approximately 1000 ppm solutions of potassium bromide and iodide were first prepared and stored in polyethylene bottles. They were diluted just before use.

### 2.4.4 Standard Reference Materials

Three standard reference materials were used to evaluate the accuracy of the instrumental neutron activation analysis method. These were Subbituminous Coal NBS SRM-1635, Urban Particulate Matter NBS SRM-1648, and River Sediment NBS SRM-1645. It was impossible to find a standard reference material having roughly the same elemental composition as that of the suspended matter samples studied. Due to large concentrations of Al and Mn, the last two of the above reference materials could not be used for the short-lived nuclides. These gave high dead times, after a 10-min irradiation. Long decay times were therefore necessary before the samples could be counted, during which time the short-lived nuclides of interest were almost completely decayed. Coal 1635 appeared to be the best suited standard reference material for short-lived nuclides of interest in this study. Main activities of this standard after a 10-min irradiation were due to $^{28}$Al and $^{24}$Na. Same irradiation, decay and counting conditions as for the suspended matter samples (see section 2.5.6) were used; however, samples had to be counted at a greater distance from the detector to have a dead time below about 20%. Dead time corrections were made whenever necessary, to correct for the decay of the nuclides during counting time. Contribution from $^{27}$Al to $^{27}$Mg peak through the reaction $^{27}$Al (n,p) $^{27}$Mg was found to be important here, and the necessary corrections were made in calculating Mg concentrations. Contribution to $^{24}$Na peak via the reaction $^{27}$Al(n, $\alpha$) $^{24}$Na was found to be insignificant. The other two standards were irradiated for 16 h and evaluated for the elements which produce long-lived nuclides.

### 2.4.5 Irradiations

All irradiations were done in the Dalhousie University SLOWPOKE-2 Reactor (DUSR) at a flux of $5 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$ for varying lengths of time.

### 2.4.6 Gamma-ray Spectrometry

The activities of irradiated samples and standards (and the tracers used in water studies) were measured by gamma-ray spectrometry. Three different systems were used in this study.

A 60 $cm^3$ coaxial Ge(Li) detector with a resolution of 1.9 keV at the 1332 keV gamma-ray of $^{60}Co$, connected to a TN-11 model 4096-channel pulse height analyzer was used during all thermal and epithermal NAA studies, with irradiation times varying from 5 min to 16 h. The efficiency of the Ge(Li) detector was 9.4% compared to a standard NaI(Tl) detector.

A low energy photon detector (LEPD) with an active area of 500 $mm^2$ and a sensitive depth of 10 mm having a resolution of 0.580 keV at 122 keV gamma-ray of $^{57}Co$, connected to TN-1700 model 4096-channel pulse height analyzer was used during the attempted cyclic instrumental neutron activation analysis.

For the measurement of activities during tracer experiments, a 7.5 cm x 7.5 cm well-type NaI(Tl) detector connected to a Canberra 8100/e model 4096-channel pulse height analyzer was used.

### 2.4.7 Cadmium Shields

For epithermal irradiations Cd shields were prepared from 0.5 mm thick, 3 x 4 cm pieces of cadmium foil. They were shaped into cylinders which fit into the medium size irradiation vials; 1.3 cm diameter circles of Cd sheets were used to cover the ends of the cylinder. Suspended matter samples were sealed with an extra polyethylene bag to prevent contamination by cadmium when irradiations were done with epithermal neutrons.

### 2.4.8 Development of Instrumental Neutron Activation Analysis Methods

Concentrations of twenty-one elements in marine SPM were determined by INAA, and the different methods developed are described here.

#### 2.4.8.1 Trace Element Determination Through Short-Lived Nuclides

An attempt was first made to investigate the possibility of determining any trace elements with nuclides having very short half-lives ($t_{\frac{1}{2}} < 65$s), by cyclic instrumental neutron activation analysis (CINAA). Nuclear data for the nuclides of interest are given in Table 2.4. In this study a LEPD was used, to obtain a higher resolution and a low Compton background from the high energy gamma-rays of the main activities due to $^{24}$Na, $^{38}$Cl, $^{28}$Al and $^{56}$Mn. The energy calibration was 0.15 keV per channel. Optimized irradiation and counting times developed by Tout (TOU80) were used in this study. Considering the half-lives of the nuclides, a 20 s irradiation time and a 20 s counting time were selected. The decay time ($t_d$) and the delay between the end of counting of one cycle and the beginning of irradiation of the next cycle were both 2 s each. The total counting time was 200 s. In a few suspended matter samples, the $^{46m}$Sc peak could barely be detected. However, the calculated net peak areas were the same as or less than the detection limits calculated by Currie's method (CUR68). Moreover, it was found that the concentration of Sc obtained in this study by comparing the peak areas of the samples with that of a standard irradiated and counted under the same conditions did not agree with the values obtained through the long-lived nuclide ($^{46}$Sc) obtained after 16 h irradiation. In spite of the disadvantage of requiring a longer total analysis time, determinations based on $^{46}$Sc ( cf. section 2.4.8.2) were more reliable due to (a) higher peak-to-background ratio of 1120 keV gamma-ray of $^{46}$Sc compared to 142 keV gamma-ray of $^{46m}$Sc and (b) greater cross section for $^{45}$Sc(n, $\gamma$ ) $^{46}$Sc reaction compared to that for $^{45}$Sc(n, $\gamma$ )$^{46m}$Sc ( cf. 23b vs 11b) which becomes very important at this very low concentration level. Detailed dead time corrections are also necessary for reliable determinations through $^{46m}$Sc. For comparison, Sc concentrations determined by the two methods are presented in Table 2.5 for a few samples. At this low concentration found in marine SPM cyclic instrumental neutron activation analysis method was not found to give any advantages over the conventional method.

Following CINAA, elements which produce short-lived nuclides ($t_{\frac{1}{2}}$ = 2.3 min - 2.8 h) were studied. The irradiation, decay and counting times were selected by a trial and error method to obtain favourable peak-to-background ratios for the minor elements detected. The nuclear data for these elements are given in Table 2.6. Considering the half-lives of both minor and major interfering nuclides, their relative concentrations and the analyzer dead time, irradiation, decay and counting times of 10 min, 3 min and 10 min respectively were finally selected. Samples were counted at two different distances from the detector, depending on the analyzer dead time. The dead time was always kept below 20%; it was less than 15% for more than 75% of the samples. The main activities of the suspended matter samples were found to be due to $^{28}$Al, $^{38}$Cl, $^{24}$Na and in some cases $^{56}$Mn, after the 10 min irradiation. A typical gamma-ray spectrum obtained under these conditions is given in Fig. 2.2. In calculating the concentrations of trace elements, dead time corrections were made for the nuclides, $^{52}$V, $^{28}$Al and $^{51}$Ti whose decay during the counting time of 10 min is important. Contribution from $^{27}$Al to $^{27}$Mg peak through the fast neutron reaction $^{27}$Al(n, p) $^{27}$Mg was found to be important here and the necessary corrections were made.

Interferences from the major activities found for SPM samples, namely $^{24}$Na, $^{28}$Al and $^{56}$Mn produced by thermal neutrons could be reduced considerably by irradiating the samples with epithermal neutrons. The possibility of determining elements with short-lived nuclides having relatively high advantage factors for epithermal neutrons (e.g. $^{116}$In, $^{101}$Mo, $^{87m}$Sr) were investigated. Three suspended matter samples were shielded with Cd foils and irradiated for 15 min. They were counted for 10 min after a 5 min

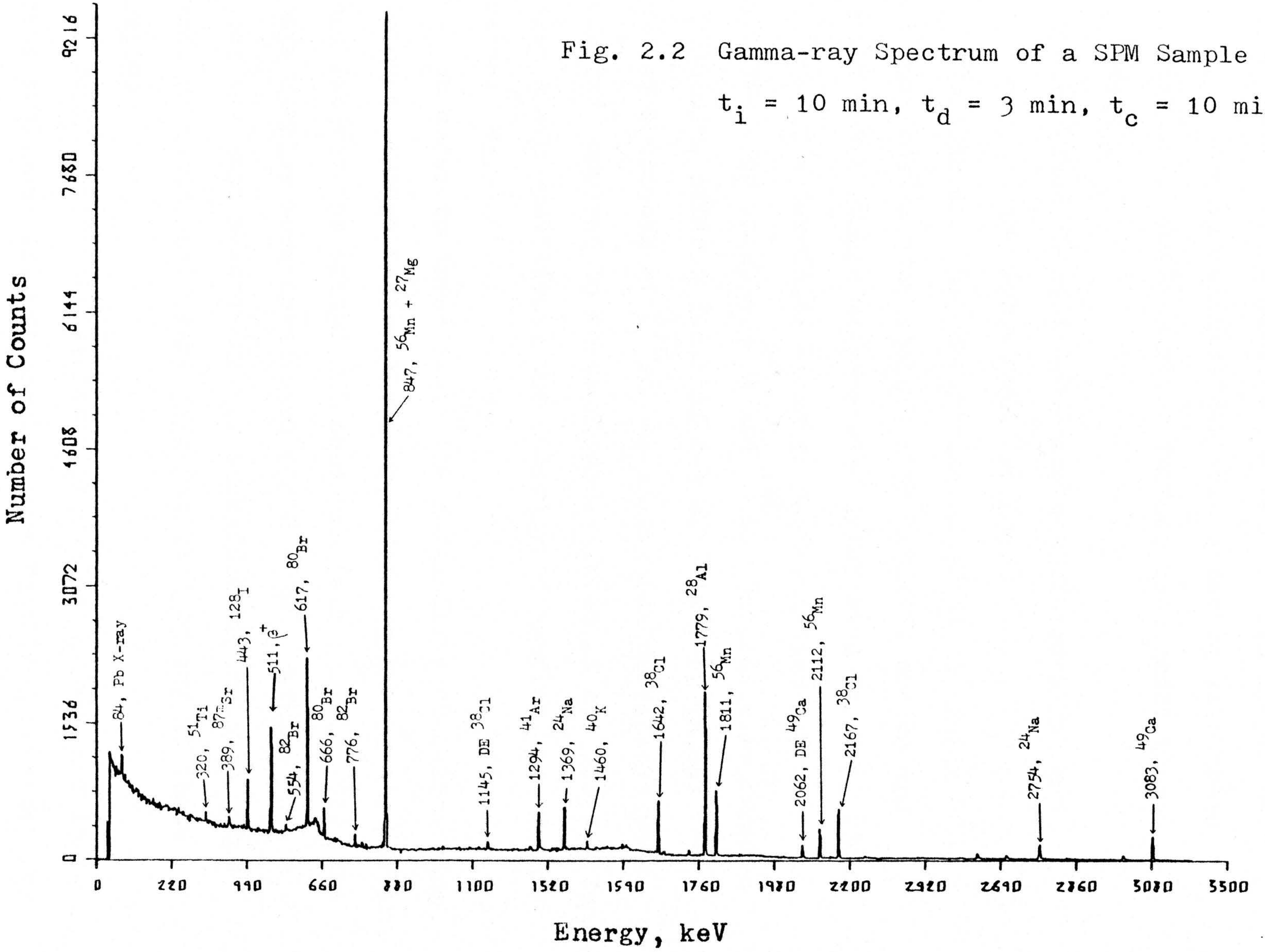


Fig. 2.2 Gamma-ray Spectrum of a SPM Sample - $t_i$ = 10 min, $t_d$ = 3 min, $t_c$ = 10 min

decay. Except for the improvements of the $^{128}$I and $^{80}$Br peaks which have high advantage factors for epithermal neutrons, no additional nuclides were detected with these irradiations. EINAA was not further used under these conditions.

### 2.4.8.2 Trace Element Determinations Through Medium- and Long-Lived Nuclides

Considering the concentrations of Na and Mn in SPM, six suspended matter samples with highest, medium and lowest total sample weights were irradiated for 1 h, with the aim of determining elements having medium-lived nuclides, for example, $^{42}$K and $^{140}$La. Samples were counted for 30 min, after a decay of 2-3 h. However, except for 103 keV photopeak of $^{153}$Sm, no additional photopeaks were detected compared to those observed after 10 min irradiation. Under these conditions, the activity of samples was mainly due to $^{24}$Na.

In order to investigate the possibility of determining elements through medium-lived nuclides and having high advantage factors for epithermal neutrons (e.g. $^{76}$As, $^{72}$Ga), the above samples were irradiated for 2 h in a cadmium shield, after the sodium activity was significantly decayed. However, no additional peaks were detected in any of these samples.

To determine the elements producing medium- and long-lived nuclides, all the samples were finally irradiated for 16 h. They were then counted after three different decay times. After a decay of 1-2 d, the nuclides $^{198}$Au, $^{82}$Br, $^{60}$Co, $^{51}$Cr, $^{42}$K, $^{140}$La, $^{24}$Na and $^{153}$Sm; after a decay of 1 w, the nuclides $^{198}$Au, $^{82}$Br, $^{60}$Co, $^{51}$Cr, $^{140}$La, $^{24}$Na and $^{153}$Sm and after a decay of 3-4 w, the nuclides $^{82}$Br, $^{60}$Co, $^{141}$Ce, $^{51}$Cr, $^{59}$Fe, $^{203}$Hg, $^{47}$Sc and $^{65}$Zn were detected. Counting times were 30 min or 1 h after the first, 2 h after the second and 8 h after the third decay time. The nuclear data for these nuclides are presented in Table 2.7. The gamma-ray spectra obtained for a suspended matter sample after the above mentioned decay times are presented in Fig. 2.3 and 2.4.

Table 2.4 Nuclear Data for Elements of Interest in Cyclic Instrumental Neutron Activation Analysis (CINAA)

| Element | Target Isotope | Isotopic Abundance,% | Cross Section,b | Nuclide | Half-Life | Gamma-Ray Energy, keV |
|---|---|---|---|---|---|---|
| Ag | $^{109}$Ag | 48.7 | 89 | $^{110}$Ag | 24.6 s | 658 |
| Rb | $^{85}$Rb | 72.2 | 0.1 | $^{86m}$Rb | 1.04 m | 556 |
| Sc | $^{45}$Sc | 100 | 11 | $^{46m}$Sc | 20 s | 143 |
| Se | $^{76}$Se | 9.02 | 21 | $^{77m}$Se | 17.5 s | 162 |

Table 2.5 Comparison of Sc Concentrations ($\mu g\ g^{-1}$) Determined by Cyclic INAA and Conventional INAA

| Method | Sample Number | | | | | |
|---|---|---|---|---|---|---|
| | 4506 | 4557 | 4560 | 4577 | 4591 | 4617 |
| CINAA ($^{46m}Sc$) | 0.83 | 2.58 | 1.34 | 9.06 | 2.09 | 2.08 |
| TINNA ($^{46}Sc$) | 2.31 | 3.24 | 4.35 | 13.0 | 4.32 | 5.73 |

Table 2.6 Nuclear Data for Elements Detected in Suspended Particulate Matter by INAA with 10 min Irradiation

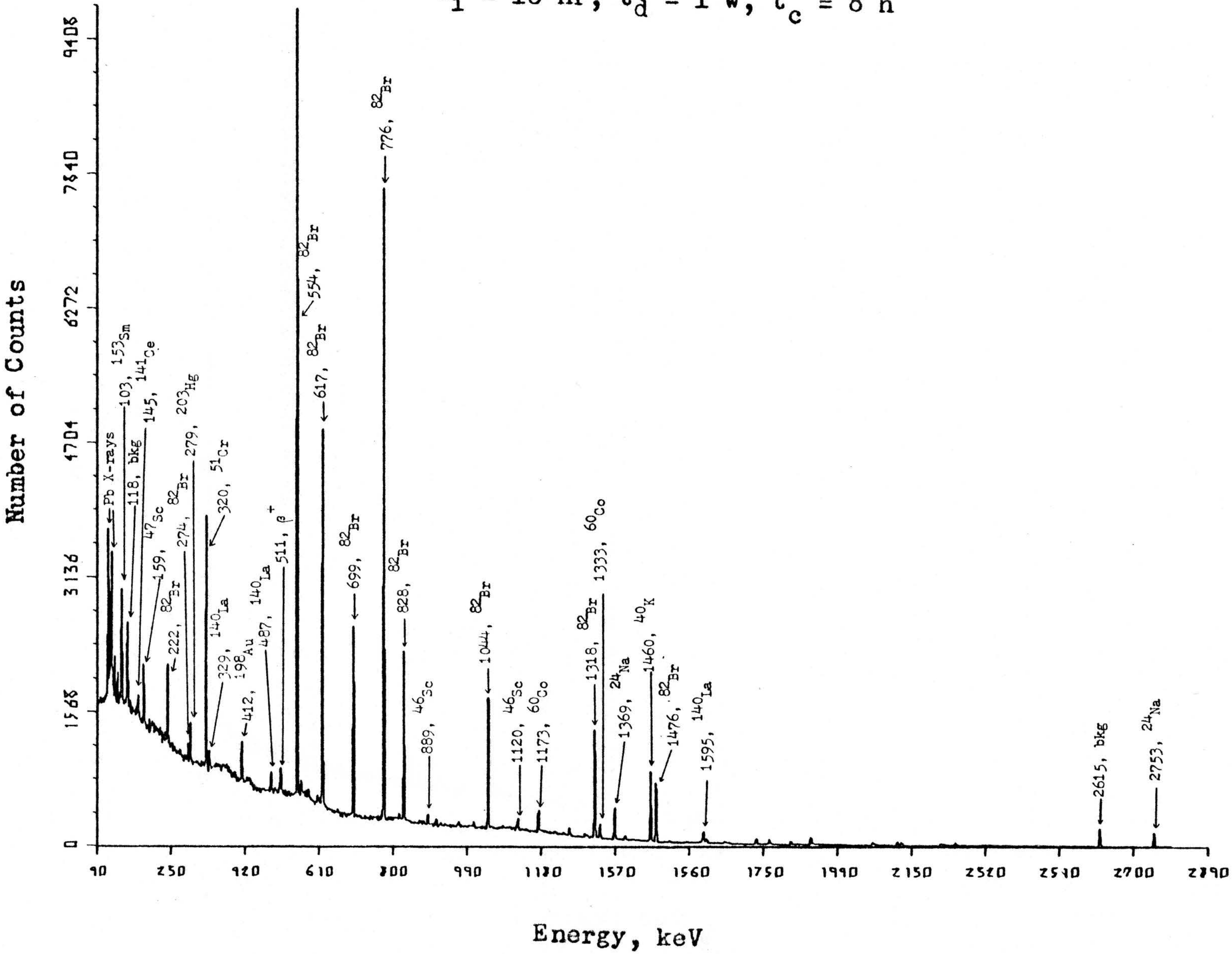
| Element | Target Isotope | Isotopic Abundance,% | Cross Section,b | Nuclide | Prod. Half-Life | Gamma-Ray Energy Used, keV |
|---|---|---|---|---|---|---|
| Al | $^{27}Al$ | 100 | 0.23 | $^{28}Al$ | 2.3 min | 1779 |
| Ba | $^{138}Ba$ | 71.7 | 0.35 | $^{139}Ba$ | 1.38 h | 166 |
| Br | $^{79}Br$ | 50.5 | 8.5 | $^{80}Br$ | 18 min | 617 |
| Ca | $^{48}Ca$ | 0.185 | 11 | $^{49}Ca$ | 8.5 min | 3083 |
| Cl | $^{37}Cl$ | 24.5 | 0.43 | $^{38}Cl$ | 37.3 min | 1642 |
| I | $^{127}I$ | 100 | 6.2 | $^{128}I$ | 25 min | 443 |
| Mg | $^{26}Mg$ | 11.2 | 0.03 | $^{27}Mg$ | 9.5 min | 1014 |
| Mn | $^{55}Mn$ | 100 | 1.3 | $^{56}Mn$ | 2.58 h | 1811 |
| Na | $^{23}Na$ | 100 | 0.53 | $^{24}Na$ | 15 h | 1368 |
| Sr | $^{86}Sr$ | 9.96 | 0.80 | $^{87m}Sr$ | 2.8 h | 389 |
| Ti | $^{50}Ti$ | 5.34 | 0.14 | $^{51}Ti$ | 5.8 min | 320 |
| V | $^{51}V$ | 99.8 | 4.8 | $^{52}V$ | 3.8 min | 1434 |

Table 2.7 Nuclear Data for Elements Detected in Suspended Particulate Matter by INAA with 16 h Irradiations

| Element | Target Isotope | Isotopic Abundance,% | Cross Section,b | Nuclide | Prod. Half-Life | Gamma-Ray Energy Used, keV |
|---|---|---|---|---|---|---|
| Au | $^{197}$Au | 100 | 98.8 | $^{198}$Au | 2.69 d | 412 |
| Ce | $^{140}$Ce | 88.5 | 0.54 | $^{141}$Ce | 33 d | 145 |
| Co | $^{59}$Co | 100 | 37 | $^{60}$Co | 5.25 a | 1173 |
| Cr | $^{50}$Cr | 4.31 | 16 | $^{51}$Cr | 27.8 d | 320 |
| Fe | $^{59}$Fe | 0.33 | 123 | $^{59}$Fe | 45 d | 1099 |
| Hg | $^{202}$Hg | 29.8 | 4.9 | $^{203}$Hg | 46.6 d | 279 |
| K | $^{41}$K | 6.88 | 1.3 | $^{42}$K | 12.5 h | 1525 |
| La | $^{139}$La | 99.9 | 9.56 | $^{140}$La | 40.2 h | 1596 |
| Sc | $^{46}$Sc | 100 | 23 | $^{47}$Sc | 84 d | 1120 |
| Sm | $^{152}$Sm | 26.7 | 210 | $^{153}$Sm | 47 h | 103 |
| Zn | $^{64}$Zn | 48.9 | 0.82 | $^{65}$Zn | 243.8 d | 1115 |

Fig. 2.3 Gamma-ray Spectrum of a SPM Sample -

$t_i$ = 16 hr, $t_d$ = 1 w, $t_c$ = 8 h



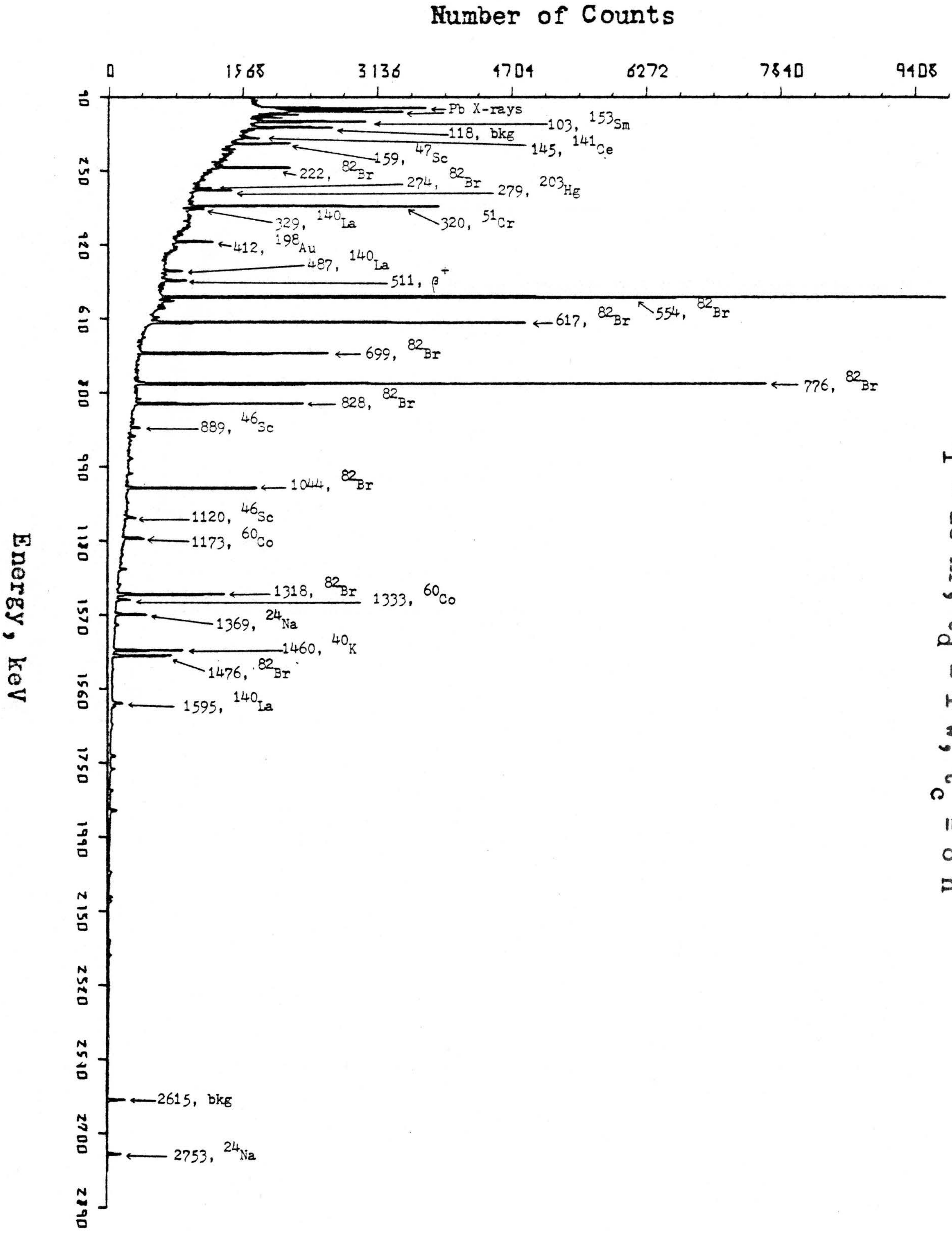


Fig. 2.3 Gamma-ray Spectrum of a SPM Sample -
$t_i$ = 16 hr, $t_d$ = 1 w, $t_c$ = 8 h

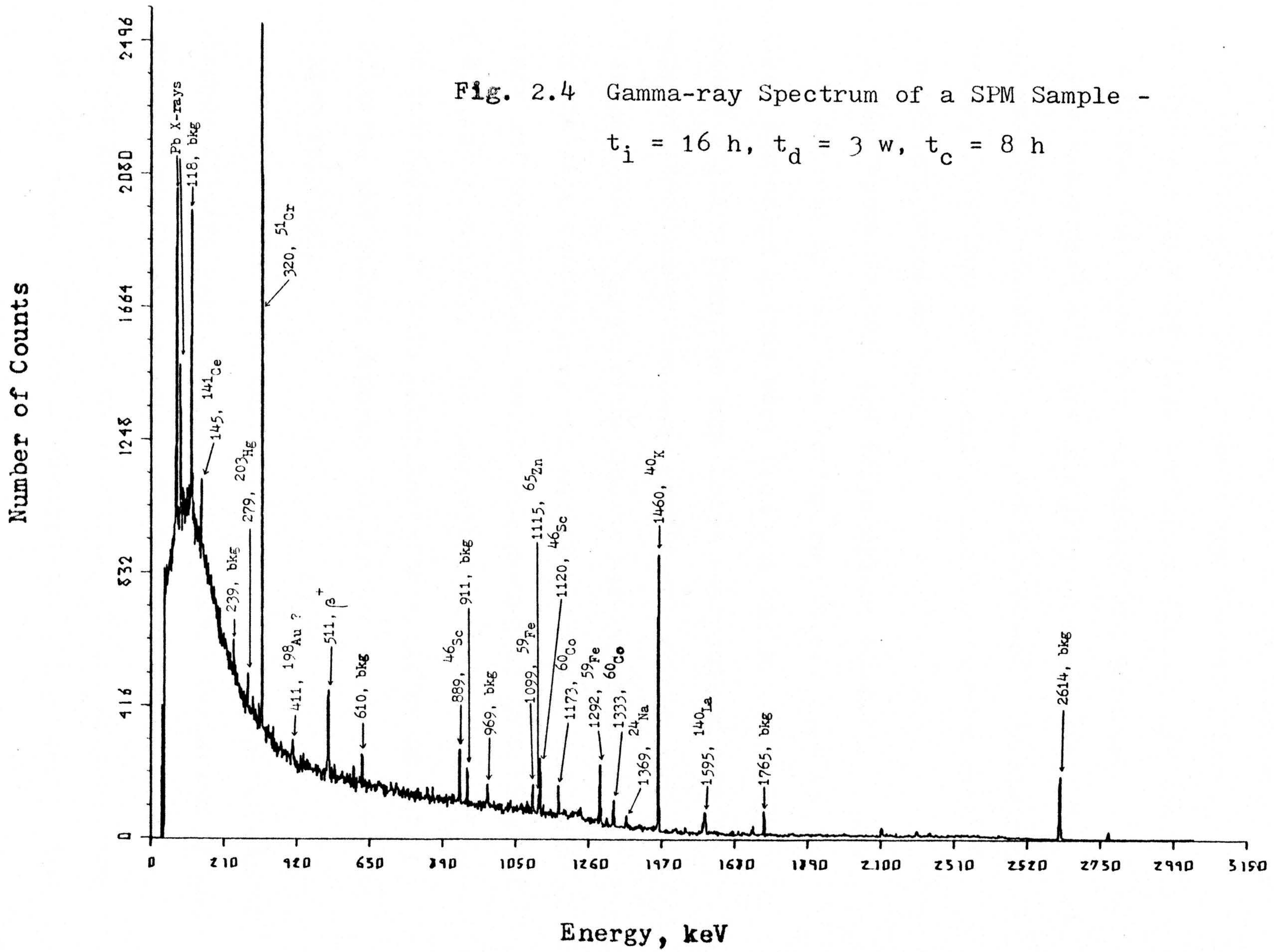


Fig. 2.4 Gamma-ray Spectrum of a SPM Sample - $t_i$ = 16 h, $t_d$ = 3 w, $t_c$ = 8 h

## 2.5 RESULTS AND DISCUSSION

Trace element concentrations of marine suspended matter determined by INAA methods are presented here. Contributions from the blank Nuclepore filters and blank polyethylene bags have been calculated and reported. Problems associated with the analysis of samples of very small weights, c.f. 60-600 µg, are discussed. Precision, accuracy, detection and determination limits have been evaluated and reported here.

### 2.5.1 Nuclepore Filters and Polyethylene Sheets

In this study, all the Nuclepore filters used to collect suspended matter were from one batch. Randomly selected filters from the same batch were analyzed in groups of three under the same conditions as the suspended matter samples. Polyethylene sheets were also analyzed under the same conditions. Elemental content of Nuclepore filters and polyethylene sheets are presented in Tables 2.8 and 2.9, respectively. For comparison purposes concentrations determined in this laboratory for a different batch of filters, and values reported by the Nuclepore corporation are also reported.

These data indicate that the elemental concentrations of Nuclepore filters vary from batch to batch. Variation of the elemental concentrations found within the batch used in this study was generally found to be within ±10%. However, for Cr, it was ±20%. All the concentrations are generally low.

Table 2.8 Elemental Concentrations in Nuclepore Filters, (μg/filter)

| Element | This Work[c] | Ellis[d] | Nuclepore Corporation[e] |
|---|---|---|---|
| Al | 14.7[a] | 0.30 | 0.865 |
| Au | 1.12[b] | - | - |
| Ba | N.D. | - | - |
| Br | 0.327 | 0.01 | - |
| Ca | N.D. | 0.30 | 1.70[a] |
| Ce | N.D. | - | - |
| Cl | 0.948 | 0.07 | - |
| Co | 87.8[a] | 13.0[a] | - |
| Cr | 0.542 | - | 0.208 |
| Fe | N.D. | 1.2 | 1.56 |
| Hg | 4.00[a] | - | - |
| I | 2.49[a] | - | - |
| K | N.D. | 0.3 | 0.294 |
| La | 0.235[a] | - | - |
| Mg | N.D. | 0.3 | 0.104 |
| Mn | 2.46[a] | 2.6[a] | 52.0[a] |
| Na | 0.131 | 0.32 | 1.14 |
| Sc | 0.0611[a] | 0.12[a] | - |
| Sm | N.D. | - | - |
| Sr | N.D. | - | - |
| Ti | N.D. | 1.1[a] | 0.208 |
| V | 0.111[a] | 2.3[a] | - |
| Zn | N.D. | - | 0.104 |

N.D. - not detected
a - ng/filter
b - pg/filter
c - average of nine filters
d - Reference ELL76
e - Catalog Lab 50

Table 2.9 Elemental Concentrations of Polyethylene Sheets

| Element | Concentration, μg/Average Weight of a Bag | Concentration, μg/g |
|---|---|---|
| Al | 18.8$^{a}$ | 514$^{c}$ |
| Au | 20.8$^{b}$ | 569$^{d}$ |
| Ba | N.D. | N.D. |
| Br | 13.1$^{a}$ | 358$^{c}$ |
| Ca | N.D. | N.D. |
| Ce | N.D. | N.D. |
| Cl | 0.184 | 5.03 |
| Co | 2.84$^{a}$ | 77.7$^{c}$ |
| Cr | N.D. | N.D. |
| Fe | N.D. | N.D. |
| Hg | N.D. | N.D. |
| I | 0.756$^{a}$ | 20.7$^{c}$ |
| K | N.D. | N.D. |
| La | 0.130$^{a}$ | 3.56$^{c}$ |
| Mg | N.D. | N.D. |
| Mn | 0.746$^{a}$ | 20.4$^{c}$ |
| Na | 16.0$^{a}$ | 438$^{c}$ |
| Sc | 0.106$^{a}$ | 2.90$^{c}$ |
| Sm | N.D. | N.D. |
| Sr | N.D. | N.D. |
| Ti | N.D. | N.D. |
| V | 0.122$^{a}$ | 3.34$^{c}$ |
| Zn | N.D. | N.D. |

a - ng/0.03655g

c - ng/g

b - pg/0.03655g

d - pg/g

Average Weight of a Bag = 0.03655g

However, depending on the concentrations of elements in the samples collected on filters, contributions from the blank filters may be significant. In order to correct for the contributions from the blank filters to the elemental concentrations in samples, it is necessary to have low coefficients of variation of elemental concentrations in the blank filters. It is always important that blank filters are analyzed along with the samples.

### 2.5.2 Elemental Content of Suspended Particulate Matter

Concentrations of twenty-one elements in SPM were determined by INAA. These concentrations expressed as µg/filter, ng $L^{-1}$ and mg $g^{-1}$ are tabulated in Appendix B, C and D, respectively. Necessary corrections have been made for the elements Au, Br, Cl, Hg, Sc and La for the contributions from Nuclepore filters and polyethylene bags. Chromium concentration of the Nuclepore filters was high (about 0.5 µg/filter) with a coefficient of variation of more than ± 20%. Cobalt concentration in the blank filters was higher by about an order of magnitude than that found in the suspended matter. Consequently, the concentrations of these two elements could not be reliably determined in marine SPM samples.

The ranges and the averages found for the elemental concentrations are summarized in Tables 2.10 and 2.11, in units of mg $g^{-1}$ and ng $L^{-1}$ respectively. The units of mg $g^{-1}$ are useful when studying the composition of and interelement correlations in suspended matter, and when comparing these concentrations with concentrations in sediments. The units of ng $L^{-1}$ are more useful when comparing the elemental concentrations in suspended matter with those of surrounding water (soluble fraction).

Table 2.10 Elemental Concentrations of SPM
mg $g^{-1}$ [a]

| Element | Range | Average[b] |
|---|---|---|
| Al | 0.589-46.3 | 10.8 |
| Au | N.D.-1.24 | 0.604 |
| Br | 0.498-2.94 | 1.38 |
| Ca | N.D.-259 | 75.4 |
| Ce | N.D.-0.218 | 0.0723 |
| Cl | 6.16-700 | 147 |
| Fe | N.D.-48.3 | 14.7 |
| Hg | N.D.-0.168 | 0.0712 |
| I | 0.100-1.64 | 0.610 |
| K | N.D.-17.7 | 7.52 |
| La | N.D.-0.0525 | 0.0212 |
| Mg | N.D.-28.3 | 15.0 |
| Mn | 0.0272-6.19 | 2.71 |
| Na | 8.98-128 | 67.3 |
| Sc | 1.28-13.0 | 4.32 |
| Sm | N.D.-6.63 | 2.65 |
| V | N.D.-96.3 | 44.0 |
| Zn | N.D.-5.96 | 1.34 |

N.D. - not detected.

a - values for Ba, Sr and Ti are not reported here since they were detected only in two or three samples (individual values are given in Appendix D)

b - average of elements detected

Sodium and chlorine content found in SPM generally increased with increasing weight of total suspended matter. These two elements had the highest concentrations and the total sample activities were roughly proportional to these concentrations. However, the concentrations of Na and Cl found here are probably not the actual concentrations associated with suspended matter; incomplete removal of adsorbed elements (which are present in sea water at high concentrations) during washing with deionized water should partly account for these high concentrations.

Next to Na and Cl, the highest concentrations found in SPM were due to Ca. Aluminum, Fe, Mn, K and Mg were the rest of the main inorganic contributors to the weight of SPM samples.

### 2.5.3 Precision of the Method

The precision of the INAA methods developed here was studied by repeated analysis of suspended matter samples having different weights and elemental concentrations. Samples were analyzed three times for the elements determined after 10 min irradiation. Nuclides were allowed to decay completely between the analyses. Table 2.12 represents the reproducibilities obtained for these elements along with their concentrations, for two suspended matter samples (one of the lowest and the second highest weight).

Table 2.11 Elemental Concentrations of SPM ng $L^{-1}$[a]

| Element | Range | Average |
|---|---|---|
| Al | 9.67-1710 | 478 |
| Au | N.D.-93.0 | 23.5 |
| Br | 16.3-154 | 49.7 |
| Ca | N.D.-16,800 | 4054 |
| Ce | N.D.-9.08 | 3.40 |
| Cl | 439-20,200 | 4796 |
| Fe | N.D.-1700 | 549 |
| Hg | N.D.-11.9 | 3.02 |
| I | 1.65-117 | 22.5 |
| K | N.D.-620 | 279 |
| La | N.D.-3.32 | 0.954 |
| Mg | N.D.-2560 | 756 |
| Mn | 0.450-557 | 131 |
| Na | 383-11400 | 2509 |
| Sc | 27.3-650 | 162 |
| Sm | N.D.-447 | 117 |
| V | N.D.-2270 | 875 |
| Zn | N.D.-421 | 68.7 |

N.D. - not detected

a - Values for Ba, Sr and Ti are not reported here since they were detected only in two or three samples.

Table 2.12 Precision of the INAA Method

| Element | Sample Number and Weight 4535 (510 µg) | | 4577 (60 µg) | |
|---|---|---|---|---|
| | Concentration µg/filter | % RSD | Concentration µg/filter | % RSD |
| Al | 8.24 ± 0.21 | 2.6 | 2.68 ± 0.091 | 3.4 |
| Br | 0.449 ± 0.044 | 9.8 | 0.117 ± 0.020 | 17.0 |
| Ca | 30.5 ± 1.4 | 4.7 | 2.67 ± 0.52 | 19.9 |
| Cl | 82.1 ± 1.8 | 2.2 | 8.09 ± 0.36 | 4.5 |
| I | 106 ± 10[a] | 9.8 | 63.4 ± 1.8[a] | 2.9 |
| Mg | 10.4 ± 1.0 | 10.0 | 1.52 ± 0.34 | 22.2 |
| Mn | 0.699 ± 0.023 | 3.3 | 0.271 ± 0.014 | 5.1 |
| Na | 46.6 ± 0.50 | 1.1 | 4.49 ± 0.14 | 2.7 |
| Ti | 0.438 ± 0.14 | 31.3 | - | - |
| V | 12.1 ± 1.7[a] | 13.8 | 5.66 ± 0.68[a] | 12.0 |

a - ng

It can be concluded that higher concentrations of elements generally produce more reproducible results. However, when the nuclide of interest is at the low energy end of the gamma-ray spectra, high compton background can lead to lower precisions (higher % RSD value for I in sample 4535 compared to that of sample 4577).

### 2.5.4 Accuracy of the Method

It has been mentioned in section 2.4.4 that three different standard reference materials have been used to study the accuracy of the INAA method. Concentrations determined by this method along with the NBS certified values are presented in Table 2.13. Values reported by Germain et. al. (GER80) are given for comparison, whenever the NBS values are not available. The measured elemental concentrations agree within ± 10% of the certified values or those reported by Germain et al.

### 2.5.5 Limits of Detection and Determination

Detection limit is defined as the minimum concentration of an element at which a given analytical procedure may be relied upon to lead to its detection (CUR68). The determination limit is defined as the minimum concentration at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate (CUR68). In this study, the method described by Currie (CUR68), which takes into account the matrix composition and counting statistics, was used.

Table 2.13 Accuracy of the INAA Method

(Concentrations in $\mu g\ g^{-1}$)

| Element | Coal NBS-SRM-1635 | | Urban Particulate Matter NBS-SRM-1648 | | River Sediment NBS-SRM-1645 | |
|---|---|---|---|---|---|---|
| | This Work[c] | Literature Values | This Work[d] | Literature Values[a] | This Work[e] | Literature Values[a] |
| Al,% | 0.29 ± 0.005 | $0.32^a$, $0.30^b$ | | | | |
| Au | | | 0.056 ± 0.018 | | | |
| Ba | 73 ± 12 | 70 ± $9^b$ | | | | |
| Ca,% | 0.571 ± 0.021 | 0.57 ± $0.07^b$ | | | | |
| Ce | | | 51.0 ± 0.2 | 55 | | |
| Co | | | | | 8.0 ± 0.3 | 8 |
| Cr | | | 420 ± 4 | 403 ± 12 | | |
| Fe,% | | | 3.60 ± 0.03 | 3.91 ± 0.10 | 10.6 ± 0.21 | 11.3 ± 1.2 |
| Hg | | | 31.4 ± 3.7 | | | |
| I | 0.87 ± 0.18 | 0.6 ± $0.3^b$ | | | | |
| La | | | 35.7 ± 1.0 | 42 | 8.85 ± 0.64 | 9 |
| Mg,% | 0.092 ± 0.001 | 0.10 ± $0.02^b$ | | | | |
| Mn | 22.2 ± 0.40 | 21.4 ± $1.5^a$ | | | | |
| Na,% | 0.24 ± 0.005 | 0.24 ± $0.02^a$ | | | | |
| Sc | | | 7.35 ± 0.09 | 7 | 2.06 ± 0.03 | 2 |
| Sm | | | 4.37 ± 0.003 | 4.4 | 1.56 ± 0.12 | |
| Sr | 112 ± 11 | 129 ± $14^b$ | | | | |
| Ti,% | 0.02 ± 0.001 | $0.02^a$ | | | | |
| V | 4.55 ± 0.13 | 5.2 ± $0.5^a$ | | | | |
| Zn | | 4.5 ± $0.5^b$ | 4607 ± 24 | 4760 ± 140 | 1780 ± 64 | 1720 ± 169 |

a = NBS values
b = Ref. GER80
c = average of 6 determinations
d = average of 2 determinations
e = average of 2 determinations

The detection limits (in number of counts) were calculated using the equation

$$2.71 + 4.65 \sqrt{\mu_B}$$

where $\mu_B$ is the number of background counts under the gamma-ray peak of interest.

The determination limit, when a standard deviation of ± 10% is allowed, is given by the equation

$$50 \left[ 1 + \left( 1 + \frac{\mu_B}{12.5} \right)^{\frac{1}{2}} \right]$$

Detection and determination limits in number of counts/specific activity = limits in µg.

The detection and determination limits calculated using the above equations for two suspended matter samples, one with the lowest weight (60 µg) and another with a higher weight (510 µg) are presented in Tables 2.14 and 2.15. The values for Ba, Sr and Ti have been included only for information; they have been detected only in two or three samples. Detection and determination limits were found to vary with the particular sample. The following conclusions can be made by comparing these limits with the concentrations found in suspended matter. The concentrations of Al, Br, Cl, I, Mn and Na in both the samples, and those of Ca, Fe, Hg, Mg, Sc, V and Zn in the higher weight sample lie above their determination limits. The concentrations of Au, Fe, La and Sm in both the samples and those of Ca, Ce, Fe, Hg, Mg, Sc, V and Zn in the lower weight sample lie below their

Table 2.14 Detection Limits of INAA of SPM

| Element | Sample Number and Weight | | | |
|---|---|---|---|---|
| | 4521-60 µg | | 4535-510 µg | |
| | Detection Limits | | Detection Limits | |
| | µg | µg $g^{-1}$ | µg | µg $g^{-1}$ |
| Al | 0.0390 | 0.650 | 0.148 | 0.290 |
| Au | 0.639[a] | 10.7 | 1.35[a] | 2.65 |
| Ba | 0.179 | 2.99 | 0.515 | 1.01 |
| Br | 0.0194 | 0.323 | 0.0720 | 0.142 |
| Ca | 1.26 | 20.9 | 4.91 | 9.62 |
| Ce | 9.76[a] | 163 | 11.8[a] | 23.1 |
| Cl | 0.328 | 5.46 | 1.23 | 2.40 |
| Co | 4.14[a] | 69.0 | 5.80[a] | 11.4 |
| Cr | 44.4[a] | 740 | 28.3 | 55.5 |
| Fe | 1.71 | 28.5[b] | 2.37 | 4.65[b] |
| Hg | 10.1[a] | 168 | 10.1[a] | 19.8 |
| I | 6.10[a] | 0.102 | 18.0[a] | 0.0353 |
| K | 0.587 | 9.78[b] | 2.75 | 5.39[b] |
| La | 2.82[a] | 47.0 | 9.62[a] | 13.2 |
| Mg | 2.10 | 35.0 | 7.39 | 14.5 |
| Mn | 17.0[a] | 0.284 | 67.6[a] | 0.133 |
| Na | 0.260 | 4.33 | 1.02 | 2.00 |
| Sc | 0.352[a] | 5.87 | 0.259[a] | 0.508 |
| Sm | 0.179[a] | 2.98 | 0.342[a] | 0.671 |
| Sr | 0.344 | 5.74 | 1.05 | 2.06 |
| Ti | 0.231 | 3.86 | 0.664 | 1.30 |
| V | 1.82[a] | 0.0303 | 6.96[a] | 0.0137 |
| Zn | 0.138 | 2.30[b] | 0.148 | 0.290[b] |

a - ng

b - mg $g^{-1}$

Table 2.15 Determination Limits of INAA of SPM

| Element | Sample Number and Weight | | | |
|---|---|---|---|---|
| | 4521-60 μg | | 4535-510 μg | |
| | Determination Limits | | Determination Limits | |
| | μg | μg $g^{-1}$ | μg | μg $g^{-1}$ |
| Al | 0.155 | 2.59 | 0.481 | 0.944 |
| Au | 2.07[a] | 34.5 | 4.39[a] | 8.61 |
| Ba | 0.616 | 10.3 | 1.63 | 3.20 |
| Br | 0.0677 | 1.13 | 0.228 | 0.447 |
| Ca | 12.3 | 205 | 20.9 | 41.0 |
| Ce | 30.8[a] | 513 | 37.0[a] | 72.5 |
| Cl | 1.28 | 21.4 | 3.98 | 7.80 |
| Co | 15.3[a] | 255 | 20.7[a] | 40.6 |
| Cr | 0.145 | 2.42[b] | 91.5 | 0.179[b] |
| Fe | 5.92 | 98.7[b] | 8.03 | 15.8[b] |
| Hg | 33.6[a] | 560 | 32.3[a] | 63.3 |
| I | 21.9[a] | 0.364 | 57.8[a] | 0.113 |
| K | 1.96 | 32.7[b] | 8.60 | 16.9[b] |
| La | 6.74[a] | 160 | 21.2[a] | 41.6 |
| Mg | 8.13 | 136 | 24.0 | 47.1 |
| Mn | 69.3[a] | 1.16 | 0.221 | 0.434 |
| Na | 0.981 | 16.4 | 3.28 | 6.43 |
| Sc | 1.19[a] | 19.8 | 0.907[a] | 1.78 |
| Sm | 0.564[a] | 9.40 | 1.05[a] | 2.06 |
| Sr | 1.25 | 20.8 | 3.38 | 6.62 |
| Ti | 2.807 | 13.5 | 2.12 | 4.15 |
| V | 7.05[a] | 0.118 | 22.5[a] | 0.0442 |
| Zn | 0.463 | 7.72[b] | 0.493 | 0.967[b] |

a - ng
b - mg $g^{-1}$

detection limits. Concentrations of K in both the samples and Ce in the higherweight sample, lie between the detection and determination limits. These results show that depending on the sample weight and the concentrations of elements, the limits can vary significantly.

### 2.5.6 Nature of SPM

In order to investigate the nature of SPM, the relationship between salinity and total SPM load has been studied. The variation of total SPM load with salinity is presented in Fig. 2.5 for the samples analyzed. For some samples, the SPM load was found to decrease with increasing salinity, but for a few others it was not related to variations in salinity. The decrease in SPM load with salinity can be explained as due to flocculation and precipitation of clay and hydrous oxide particles. In cases where there are no relationships between the SPM load and salinity, SPM may consist mainly of biological materials. Sundby(SUN74) has reported the presence of high algae concentrations where no relationship between SPM load and salinity was observed.

Trace elements present in SPM can be associated with different fractions. A knowledge of distribution of various trace metals among solid phases is necessary for estimating its biological availability and physicochemical reactivity. Trace metals in SPM can be present (i) as adsorbed on solids where they are readily available, (ii) in carbonates, organic material or metallic hydroxides,

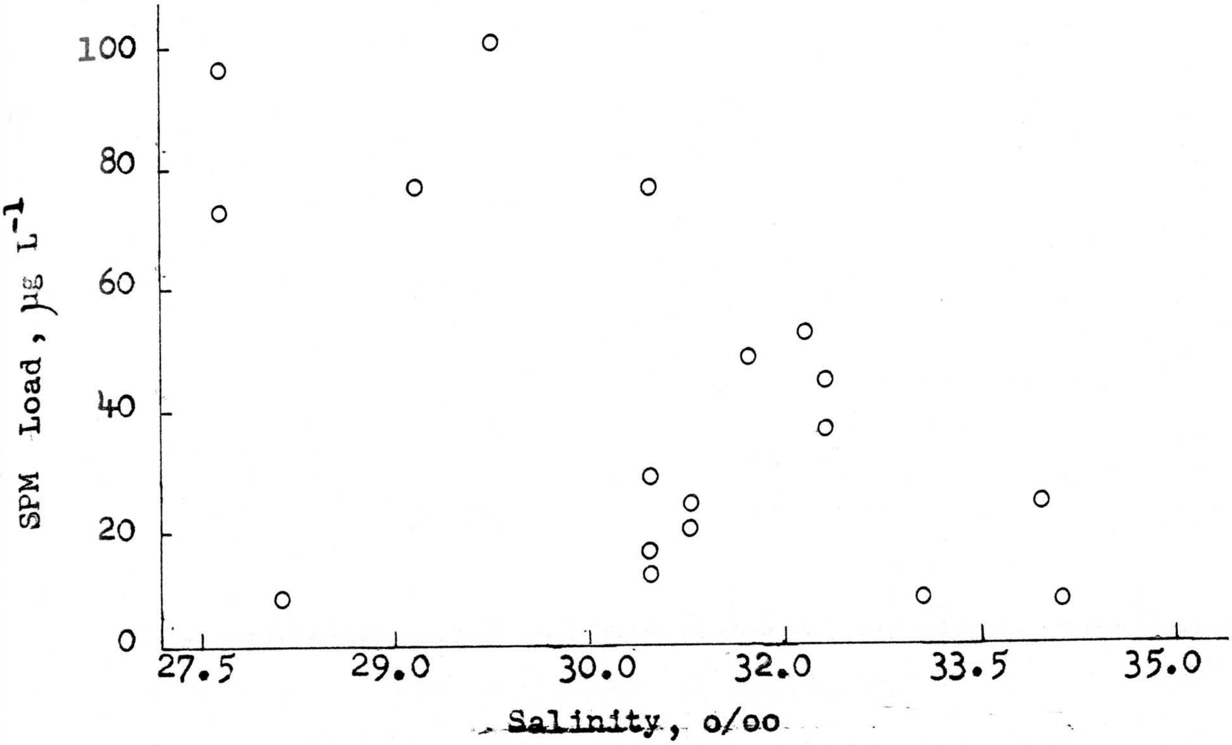


Fig. 2.5 Relationship between Salinity and Suspended Matter Load

where chemical changes are required before they are released, so they are less available; or (iii) in the crystal structure of suspended materials where they are chemically stable and unavailable to the aquatic species.

Trace metals associated with sedimentary carbonates can exist either as separate phases or in structural positions such as within Ca or Mg carbonates. The scavenging action of Fe and Mn oxides is generally thought to be the result of two complementary processes: adsorption and coprecipitation.

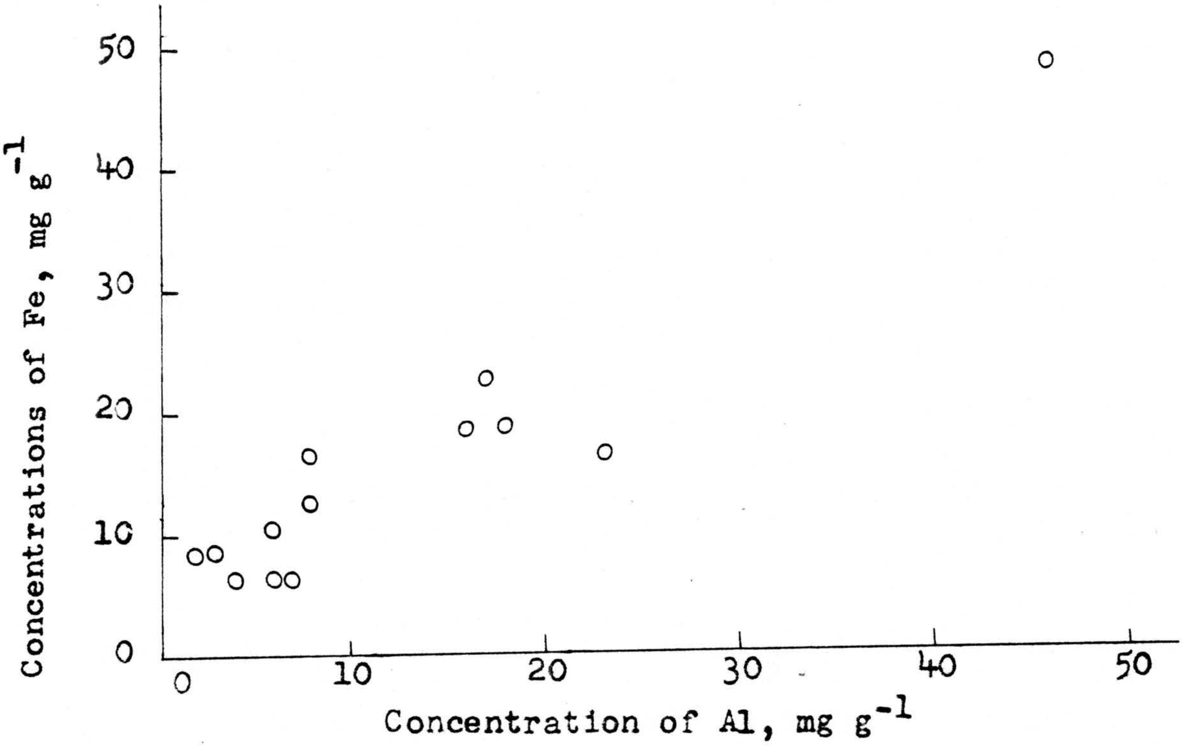


Fig. 2.6 Relationships between Concentrations of Fe and Al

In this study, an attempt has been made to study the distribution of trace metals in SPM by studying the inter-element correlations. Table 2.16 presents the linear regression correlation coefficients calculated for the elements detected in SPM and some selected values are presented in Table 2.17, which are important in interpreting the distribution of trace metals among various components. Most of the elements were found to be highly correlated to Al; these include Ce, Fe, K, La, Sc, Sm and V. Since the concentration of Al in SPM is mainly governed by the aluminosilicates (SPE70), concentrations of the above elements in

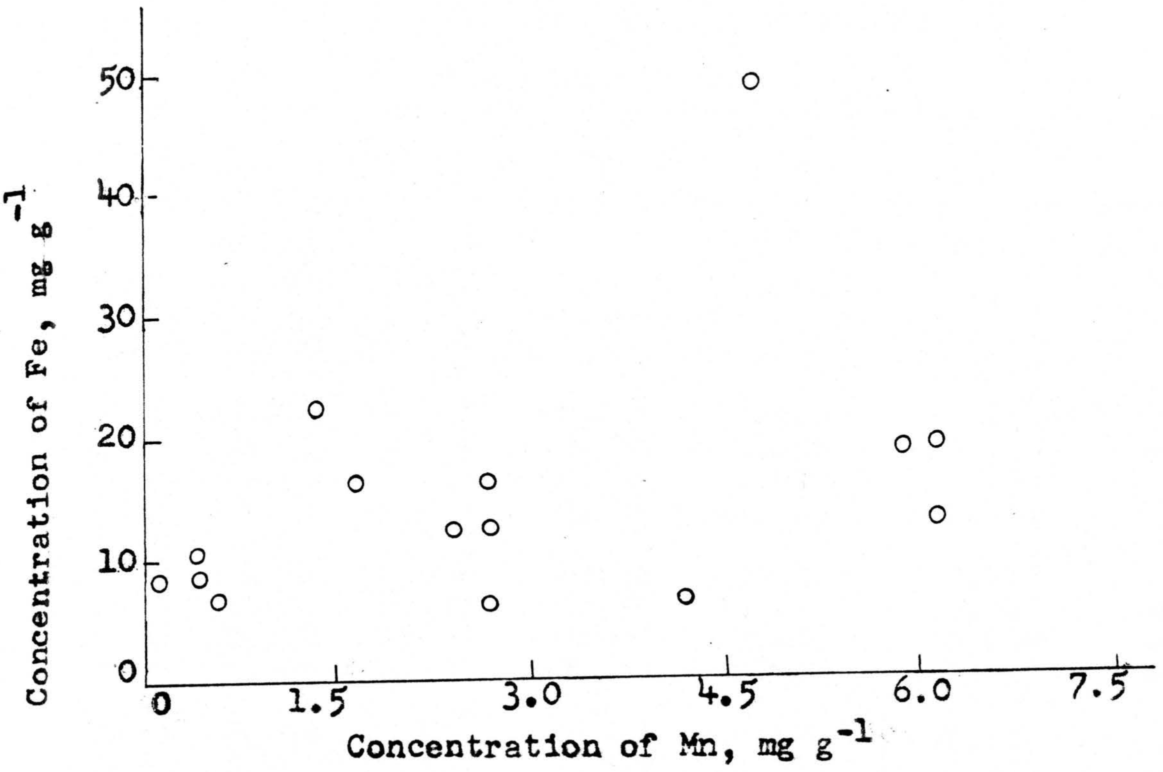


Fig. 2.7 Relationship between Concentrations of Fe and Mn

SPM are controlled by aluminosilicates. The linear relationship between the Al and Fe concentrations is presented in Figure 2.6. A similar linear relationship has been observed by Spencer and Sachs (SPE70).

Table 2.16 Linear Regression Correlation Coefficients for the Elements Determined in SPM

| Element | Al | Au | Br | Ca | Ce | Cl |
|---|---|---|---|---|---|---|
| Au | 0.269 | | | | | |
| Br | 0.114 | 0.411 | | | | |
| Ca | -0.215 | -0.281 | -0.194 | | | |
| Ce | 0.880 | 0.154 | 0.388 | -0.281 | | |
| Cl | -0.185 | -0.430 | -0.106 | 0.420 | -0.246 | |
| Fe | 0.955 | 0.348 | 0.374 | -0.196 | 0.834 | -0.215 |
| Hg | 0.208 | 0.013 | 0.341 | 0.136 | 0.234 | 0.035 |
| I | 0.002 | 0.263 | 0.746 | -0.189 | 0.441 | 0.096 |
| K | 0.751 | 0.048 | 0.236 | -0.383 | 0.713 | -0.115 |
| La | 0.801 | 0.111 | 0.353 | -0.124 | 0.927 | -0.236 |
| Mg | 0.478 | 0.077 | 0.597 | -0.496 | 0.294 | -0.026 |
| Mn | 0.506 | 0.191 | -0.008 | -0.304 | 0.423 | -0.320 |
| Na | 0.038 | -0.603 | -0.012 | -0.115 | -0.184 | 0.316 |
| Sc | 0.750 | 0.582 | 0.533 | -0.318 | 0.909 | -0.357 |
| Sm | 0.836 | 0.275 | 0.146 | 0.011 | 0.888 | -0.284 |
| V | 0.923 | 0.270 | 0.206 | -0.022 | 0.820 | -0.299 |
| Zn | 0.264 | 0.407 | -0.029 | -0.177 | -0.315 | -0.105 |

Table 2.16 (continued)

| Element | Fe | Hg | I | K | La | Mg |
|---|---|---|---|---|---|---|
| Hg | 0.341 | | | | | |
| I | 0.080 | 0.024 | | | | |
| K | 0.697 | 0.470 | -0.049 | | | |
| La | 0.819 | 0.460 | 0.272 | 0.740 | | |
| Mg | 0.535 | 0.427 | 0.050 | 0.911 | 0.331 | |
| Mn | 0.384 | -0.015 | -0.023 | 0.140 | 0.378 | -0.105 |
| Na | -0.027 | 0.164 | 0.217 | 0.495 | -0.113 | 0.702 |
| Sc | 0.822 | 0.328 | 0.276 | 0.661 | 0.842 | 0.405 |
| Sm | 0.792 | 0.142 | 0.077 | 0.598 | 0.913 | 0.159 |
| V | 0.861 | 0.291 | -0.033 | 0.769 | 0.877 | 0.375 |
| Zn | 0.572 | 0.079 | -0.092 | 0.098 | -0.409 | 0.264 |

Table 2.16 (continued)

| Element | Mn | Na | Sc | Sm | V |
|---|---|---|---|---|---|
| Na | -0.107 | | | | |
| Sc | 0.447 | -0.199 | | | |
| Sm | 0.566 | -0.207 | 0.804 | | |
| V | 0.455 | -0.074 | 0.877 | 0.906 | |
| Zn | -0.118 | 0.138 | 0.133 | -0.225 | -0.021 |

Manganese and Mg concentrations are also controlled to a lesser extent by aluminosilicates, indicating at least one phase other than silicates is an important control.

Zinc is not correlated to Al, but is significantly correlated to Fe, indicating the possibility of coprecipitation of Zn with hydrous iron oxide.

Mercury is not correlated to either Al or Fe. It is possible that Zn and Hg are associated with the organic matter present in SPM. Spencer and Sachs (SPE70) reported that Zn in surface waters are associated with organic matter in water of the Gulf of Mexico.

Iron and Mn are not correlated to each other indicating different concentrating mechanisms for these two elements in SPM. Figure 2.7 presents the relationship between Fe and Mn concentrations. Manganese is probably present as a separate oxide as well as in association with aluminosilicates.

Calcium and Mg in SPM are probably mainly present as their carbonates. Potassium and Na are highly correlated to Mg. Calcium, Mg, Na and K may be correlated with organic matter.

Table 2.17 Correlations Functions for Some Selected Pairs of Elements in SPM

| Pairs of Elements | Degrees of Freedom | Correlation (R) | Probability[a] | Level of Significance[b] |
|---|---|---|---|---|
| Al,Ce | 10 | 0.880 | < 0.001 | S** |
| Al,Fe | 13 | 0.955 | < 0.001 | S** |
| Al,Hg | 16 | 0.208 | > 0.1 | NS |
| Al,K | 14 | 0.751 | < 0.001 | S** |
| Al,La | 10 | 0.801 | 0.01-0.001 | S* |
| Al,Mg | 11 | 0.478 | 0.1-0.05 | PS |
| Al,Mn | 17 | 0.506 | 0.05-0.01 | S |
| Al,Sc | 17 | 0.750 | < 0.001 | S** |
| Al,Sm | 15 | 0.836 | < 0.001 | S** |
| Al,V | 14 | 0.923 | < 0.001 | S** |
| Al,Zn | 13 | 0.264 | > 0.1 | NS |
| Fe,Hg | 13 | 0.341 | > 0.1 | NS |
| Fe,K | 11 | 0.697 | 0.1-0.001 | S* |
| Fe,La | 8 | 0.819 | 0.01-0.001 | S* |
| Fe,Mg | 10 | 0.535 | 0.1-0.05 | PS |
| Fe,Mn | 13 | 0.384 | > 0.1 | NS |
| Fe,Sc | 13 | 0.822 | < 0.001 | S** |
| Fe,Sm | 12 | 0.792 | < 0.001 | S** |
| Fe,V | 12 | 0.861 | < 0.001 | S** |
| Fe,Zn | 11 | 0.572 | 0.05-0.01 | S |
| Hg,Mg | 11 | 0.427 | > 0.1 | NS |
| Hg,Zn | 13 | 0.079 | > 0.1 | NS |
| K,Mg | 10 | 0.911 | < 0.001 | S** |
| Mg,Na | 11 | 0.702 | 0.01-0.001 | S* |

a - Probability that a linear relationship does not exist.

b - The following scheme of classification (BR072) for various values of probability function has been adopted in this study: probability greater than 0.1, not significant (NS); between 0.10 and 0.05, possibly significant (PS); between 0.05 and 0.01, significant (S); between 0.01 and 0.001, highly significant (S*); probability less than 0.001, very highly significant. However, these classifications are arbitrary.

### 2.5.7 Variation of SPM Load with Depth

From the water circulation pattern it is evident that the surface waters (and up to a depth of about 50 m) of the Gulf of St. Lawrence and Cabot Strait represent low saline water of the St. Lawrence River (due to river runoff) whereas waters at greater depths (100-150 m) represent that of the Atlantic Ocean.

During the time of sample collection (1979 August), the river runoff was relatively small, hence the amount of inorganic matter carried to the ocean is also small. The amount of biological materials in water is relatively high during this season and thus SPM contains more biological materials than inorganic materials. Biological materials are generally concentrated in about the top 50 m and they are unevenly distributed. The SPM load is generally governed by the above two processes, except for depths of about 50 m above the bottom, where the inorganic fraction of SPM increases as a result of resuspension of the bottom sediment. Salinity, SPM load and temperature data of the samples are presented in Appendix A.

Variations of SPM load with depth generally agrees with what is expected according to the above mentioned control processes where the highest SPM load is observed in surface waters and a decrease is observed with increasing depth. The lower SPM load at the surface for station numbers 2 and 4, and the increase with depth up to 50 m (for station number 4) should be due to differences in biological activities. However, the highest SPM load obtained at 150 m for station number 4 cannot be explained, since even resuspension of bottom sediments is not important at this depth (bottom depth being 488 m). The slight increase in SPM load at a depth of 50 m (lowest temperature) for station numbers 3 and 5 can be explained as due to trapping and slow settling of biological materials at this depth due to increased density of the water column.

### 2.5.8 Conclusion

An analytical method has been developed to determine concentrations of twenty-one elements in marine SPM. For the analysis of SPM samples with very low weights, such as those used in this study, instrumental methods are most suitable since these methods avoid possible losses and contaminations which are generally encountered in destructive methods where samples have to be taken into solution. Different irradiation, decay and counting times have been selected in this study to obtain good sensitivities for the trace elements of interest, and to minimize the interference from major elements, namely Na, Cl, Al and Mn.

Two different irradiation times and four different decay times have been used. Concentrations of Al, Ba, Br, Ca, Cl, I, Mg, Mn, Na, Sr, Ti and V have been determined using a 10-min irradiation and a 3-min decay. Barium and Sr have been detected only in two or three samples. A longer decay time (20-25 min) was found to improve the peak-to-background ratios for the two peaks of $^{139}$Ba (at

166 keV) and $^{87m}Sr$ (at 389 keV). To reduce the interference from the Compton background, use of a longer decay time is recommended in the determination of these two elements.

Concentrations of other elements were determined using a 16-h irradiation. The decay times were 1-2 d for $^{42}K$ and $^{140}La$, 1 W for $^{153}Sm$ and $^{198}Au$ and 3-4 w for $^{141}Ce$, $^{59}Fe$, $^{203}Hg$, $^{46}Sc$ and $^{65}Zn$. In cases where the activity of the sample was low, the decay time of 1-2 d was suitable for $^{198}Au$ and $^{153}Sm$. Most of the samples were highly active after 16 h irradiation (due to $^{24}Na$); analyzer dead times of about 20% were found after a decay of 1-2 d. However, the concentrations of K and La were determined under these conditions since these could not be detected with a shorter irradiation (c.f. 1 h).

Attempts have also been made to use CINAA and EINAA methods, although these were not found to give any advantage over the conventional TINAA methods.

Extremely low weights of the samples available in this study is one of the major sources of error due to the possible inaccuracies in weighing the samples. This problem could be minimized if higher weights could be obtained by filtering larger volumes of sea water.

The INAA method can be extended to determine some other elements, if a higher neutron flux than that used in this study is available.

The precision of the INAA method has been evaluated by repeated analysis of SPM samples, and found that the precision depends on the weight of the samples, concentration of the individual elements and the background activities.

The accuracy of the method has been studied by analyzing three NBS-SRM samples. The results obtained have been found to agree within ± 10% of the certified values for most of the elements.

The data obtained (for SPM load, elemental concentrations in SPM etc.) have been explained with the author's limited knowledge of chemical oceanography, and it is hoped that chemical oceanographers will make more rigorous interpretation of the data.

# 3. DETERMINATION OF MOLYBDENUM IN SEA AND ESTUARINE WATER WITH $\beta$-NAPHTHOIN OXIME

An analytical method has been developed for the determination of microgram quantities of molybdenum in sea and estuarine water. The method consists of preconcentration of molybdenum using $\beta$-naphthoin oxime followed by the determination of the element employing neutron activation analysis. Various factors that can influence yield and selectivity of the preconcentration process have been investigated in detail. A comparison study between $\alpha$-benzoin oxime and $\beta$-naphthoin oxime for cocrystallizing molybdenum from sea water has been carried out. Interferences from Na, Cl and Br have virtually been eliminated by the cocrystallization process. Selectivity of $\beta$-naphthoin oxime in preconcentrating molybdenum has been studied using a standard steel sample. The method has been applied to determine molybdenum content of sea and estuarine water. A detection limit of 0.30 $\mu$g Mo $L^{-1}$ sea water has been achieved. Precision and accuracy of the method have been evaluated using an intercomparison fresh water and a biological standard reference material. Details of the method are described in this chapter.

## 3.1 INTRODUCTION

The average abundance of molybdenum in the earth's crust is $10^{-4}$%, i.e., 1 ppm; however, certain rocks may contain molybdenum ranging over three orders of magnitude (KOL32). The molybdenum content of plants can vary between less than 0.1 and 100 ppm; the general range is 1 to 3 ppm. Concentrations of molybdenum in sea water have been reported to vary between as little as 0.24 $\mu g\ L^{-1}$ and as much as 16 $\mu g\ L^{-1}$ (BRO65, BLA52). The principal form of molybdenum in sea water is $MoO_4^{2-}$ (RIL65). In order to determine molybdenum levels in a variety of complex sample matrices, it is therefore necessary to develop sensitive analytical methods which respond in a linear fashion to the molybdenum concentrations ranging over orders of magnitude.

In the past, gravimetric (WIS62), volumetric (NIC44), colorimetric (HOF40), polarographic (UHL37), atomic absorption spectrometric (DAV61), and neutron activation analysis (ABU74) methods have been used for the measurement of molybdenum content in biological materials, rocks, and industrial samples. However, these methods cannot directly be applied to sea water due to very low amounts of molybdenum in the presence of large quantities of interfering elements. Some of these methods have been critically evaluated by Fishman and Mallory (FIS68). Neutron activation analysis (NAA) has been shown to be a sensitive and specific technique for the determination of multielement concentrations in a wide variety of matrices. However, neither instrumental NAA (INAA) nor radiochemical NAA (RNAA) could be used for measuring molybdenum content of untreated sea water because of severe interferences from and possible radiation hazards of $^{24}$Na, $^{38}$Cl, and $^{82}$Br. Preconcentration of molybdenum from sea water prior to neutron activation is an attractive alternative to either INAA or RNAA.

Methods used during past several years to preconcentrate molybdenum from sea water include coprecipitation (CHA66a, KIM69, HEA70), ion-exchange (RIL 68a, RIL68b,KAW69), extraction (CHA69, FUJ73), and adsorption and chelation (RIL72, MUZ71 , MUZ73a, VAN77a, VAN77b ). Preconcentration methods involving coprecipitation and cocrystallization are considered to be useful in the analysis of sea water. Organic cocrystallizing reagents are generally more selective for a given element than inorganic coprecipitating reagents.

Historically, Knowles (KNO32) first reported the use of $\alpha$-benzoin oxime as a fairly selective reagent for cocrystallizing molybdenum in steel, ore and other commercial products. Out of 34 elements studied, only chromium, palladium, tantalum, vanadium and tungsten were found to cocrystallize with molybdenum under the experimental conditions used. Since then Weiss and Lai (WEI61) have used $\alpha$-benzoin oxime for preconcentrating molybdenum in sea water. Gravimetric and colorimetric methods have been used for determining molybdenum in the above matrices. Several researchers

NAD69, SAV74) have used α-benzoin oxime to isolate molybdenum after irradiation with neutrons and dissolution (RNAA) of solid samples, such as rocks, bovine liver and orchard leaves. Tungsten has been reported to be extracted along with molybdenum. No one has used a combination of α-benzoin oxime and NAA for the preconcentration and determination of molybdenum in sea water. Interferences from other elements present in sea water have not also been studied in detail. Another oxime, namely β-naphthoin oxime, can also be used to preconcentrate molybdenum, perhaps more efficiently than α-benzoin oxime.

## 3.2 OBJECTIVES

The principal objective of the present study is to develop an analytical method for the determination of trace quantities of molybdenum in sea and estuarine water employing NAA preceded by preconcentration of the element using β-naphthoin oxime. Various factors that can influence the yield of molybdenum have been investigated in detail using radioactive tracers. These factors include: (i) amount of β-naphthoin oxime; (ii) pH of the medium; (iii) temperature of the medium; (iv) stability of β-naphthoin oxime in acetone; (v) effect of aging the cocrystallized product; (vi) stirring time; (vii) sample volume; (viii) reagent recovery; (ix) linearity of cocrystallization; and (x) salinity.

Concentrations of sodium, chlorine and bromine in untreated sea water and cocrystallized product have been compared for evaluating the ability of β-naphthoin oxime to reduce interferences from these three elements. Selectivity of β-naphthoin oxime in preconcentrating molybdenum has been studied using two diverse matrices, viz. sea water and steel, which are known to contain several elements at drastically different concentration levels. Precision and accuracy of measurements have been evaluated. Limits of detection and determination have been calculated and reported here. A comparison study between α-benzoin oxime and β-naphthoin oxime for cocrystallizing molybdenum in sea water and steel has been done to show the advantages of using the latter reagent.

## 3.3 LITERATURE SURVEY

### 3.3.1 Biological Significance of Molybdenum

Since several analytical methods have been developed for determining molybdenum in biological matrices, it may not be inappropriate to briefly describe biological significance of the element.

The importance of molybdenum as a biologically functional trace element is primarily due to its presence in a number of enzymes in living systems. The two molybdenum containing enzymes, respiratory nitrate reductase and formate dehydrogenase are important in the metabolism of various microorganisms (JAE76).

In conjunction with iron and other cofactors, nature utilizes molybdenum in a number of oxidation reduction enzymes (SCH76). The two enzymes vital to nitrogen cycles on the earth, assimilatory nitrate reductase and nitrogenase are both molybdoenzymes. Soil bacteria and algae reduce molecular nitrogen into ammonia in the presence of nitrogenase.

Molybdenum is known to be a dietary essential trace element for many animals (EDG70). It has also been found to be essential for growth of higher plants (ARN39).

However, molybdenum induces toxic effects on humans, animals and plants when ingested in higher amounts. The role of molybdenum in animal nutrition has been focussed mainly on its interaction with copper and sulfate, particularly in ruminant nutrition. It has been proposed (DOW69) that copper could become unavailable in the rumen due to the formation of cupric molybdate, $CuMoO_4$. High dietary levels of molybdenum leads to copper deficiency. A study performed in four human subjects (MER76) measuring the effects of dietary molybdenum for humans on uric acid excretion has detected significant influence of molybdenum on copper metabolism. They have reported that in human subjects with a normal copper intake, a dietary molybdenum intake of 0.5 to 1 mg per day could be assumed as safe.

### 3.2.2 Methods for Determining Molybdenum

Coprecipitation with inorganic carriers have been widely used in literature in the preconcentration of molybdenum from various matrices. The methods which have been used in the earlier determinations of molybdenum in sea water are summarized in table 3.1.

As mentioned before almost all the inorganic coprecipitating agents act as scavenging agents for a number of elements and therefore although they have been reported to offer a good reproducibility, their selectivity in the determination of molybdenum is low.

Preconcentration by cocrystallization with organic reagents provides a more selective separation of molybdenum when compared to those by using inorganic coprecipitating agents.

Knowles (KNO32) in the determination of molybdenum in ores, steels and other commercial products used cocrystallization of the element with $\alpha$-benzoin oxime in acid solution.

A greater specificity has been reported to be achieved by coprecipitating molybdenum from natural waters with tanin and methyl violet (KUZ58).

A method based upon the concentration of molybdenum from sea water by cocrystallization with $\alpha$-benzoin oxime has been reported by Weiss et al. (WEI61). Following this separation, the oxime was eliminated by acid oxidation, molybdenum was purified by ion-exchange and quantitatively determined colorimetrically. Radiometric corrections for losses of molybdenum incurred during the analytical procedures were applied and concentration of molybdenum has

Table 3.1 Coprecipitation Methods with Inorganic Carriers used to Concentrate Molybdenum

| Method of Concentration | Method of Determination | References |
|---|---|---|
| Coprecipitated with ferric hydroxide | Spectrographic | KIM69 |
| Coprecipitated with ferric hydroxide | Photometric with thiocyanate or with dithiol | ISH58 |
| Coprecipitated with tanin + oxine + thionalide + $Fe^{3+}$ + $Al^{3+}$ | Spectrographic | BLA52 |
| Coprecipitated with manganese dioxide | Photometric with thiocyanate | BAC64 |
| Coprecipitated with manganese dioxide | Photometric with dithiol | CHA66a,<br>HEA70 |
| Coprecipitated with thorium hydroxide | Spectrometric | KIM70 |

been determined to be 12.2 ± 0.1 $\mu g\ L^{-1}$ in surface sea water collected 40 miles west of San Francisco.

Methods based on solvent extraction of molybdenum complexes have been extensively used in the determination of molybdenum in waters, geological, biological and industrial materials.

Chau and Lum-Shui-Chan (CHA69) investigated the use of atomic absorption in conjunction with solvent extraction using 1% oxime in methyl isobutyl ketone (MIBK) for the preconcentration of molybdenum from 100 mL samples of lake water. The detection limit was 3 $\mu g\ L^{-1}$ in which a preconcentration factor of 20 was achieved.

Kim, Alexander and Smythe (KIM76) used long chain alkyl amines for preconcentration and determination of tracers of molybdenum in soils, sediments and natural waters. Solvent extraction of molybdenum thiocyanate complex with long chain alkyl amine Aliquat 336 in chloroform, followed by evaporation of the solvent, dissolution in MIBK and the final determination by atomic absorption spectroscopy give detection limits of 0.1-1.0 ppm with a relative standard deviation better than 5% on 1 g samples for molybdenum in soils and sediments, and 0.0110-0.0014 ppm for sea water, fresh water and estuarine water using 100 mL samples.

Application of ion-exchange chromatography in conjunction with atomic absorption or spectrophotometry has been studied by a number of workers in the determinations of molybdenum in sea water (RIL68a, RIL68b, KAW69).

The use of a foam separation technique combined with a spectrophotometric determination for the determination of molybdenum in sea water has been reported (KIM71).

Hason, Szabo and Chasteen (HAN77) have used electron paramagnetic resonance spectroscopy for the determination of molybdenum in sea water, which was based on the extraction of paramagnetic $Mo(SCN)_5$ into isoamyl alcohol, with a detection limit of 0.46 $\mu g\ L^{-1}$ molybdenum and a relative precision of 4.7% at the 11 $\mu g\ L^{-1}$ level.

In addition to the above mentioned methods using preconcentration and final determination of molybdenum by gravimetry, colorimetry, spectrometry, photometry etc., radiochemical separation methods have also been widely used in a number of complex matrices.

In the determination of molybdenum and selenium in orchard leaves and bovine liver using neutron activation analysis by Abu-Samra et al. (ABU74), the samples were irradiated for 40 h with a thermal neutron flux of $8 \times 10^{13}$ n $cm^{-2}$ $s^{-1}$ and molybdenum was separated through a double precipitation, first as $\alpha$-benzoin oxime complex and then as the sulphide. Interference by phosphate ion was removed by the addition of phosphate carrier, $NH_4H_2PO_4$ and precipitation with Zr(IV).

Nadkarni and Halder (NAD69) determined traces of molybdenum in samples of alloy steel by neutron activation analysis, using selective extraction of molybdenum (VI) into chloroform with $\alpha$-benzoin oxime. Tungsten was found to be an interfering element.

Livingston and Smith (LIV67) used neutron activation analysis followed by chemical separation using cupferron for the determination of molybdenum in samples of human teeth, dry human tissues, dry vegetable tissues and dried powdered kale.

Weers et al. (WEE74) have used a combined extraction of $^{99}$Mo and its daughter product in the determination of molybdenum in standard kale powder and standard animal blood. They used either a chloroform solution of acetylacetone (1:1) or a 3% triaurylamine in kerosene as the extracting agent.

Stray et al. (STR63) used substoichiometric principle, which eliminates the necessity for determining the chemical yield in activation analysis, in the determination of traces of molybdenum in germanium dioxide. They used a solution of hydroxy quinoline (oxine) in chloroform to extract molybdenum substoichiometrically. The count rate on the chloroform extract of molybdenum oxinate was measured after the ratio $^{99m}Tc/^{99}Mo$ reached a constant value.

In a multielement radiochemical neutron activation analysis of standard reference samples, Bovine Liver and Orchard Leaves (NBS-SRM-1571) (GUZ76), molybdenum, tungsten and gallium have been separated from other elements by adsorption onto a Dowex 50 column. Molybdenum and tungsten were then eluted with a 0.5 M hydrochloric acid solution.

### 3.3.3 Molybdenum Content of Sea Water

Molybdenum content of sea water varies from ocean to ocean. The range is generally narrow, but exceptions are known. Some of the values reported in literature are summarized in Table 3.2.

## 3.4 EXPERIMENTAL

### 3.4.1 Preparation of β-Naphthoin Oxime

β-Naphthoin was prepared from β-naphthaldehyde by following a method prescribed by Robinson (FUL39). A mixture of β-naphthaldehyde (24 g), aqueous alcohol (200 ml of 80%), potassium cyanide (2.4 g) and water (24 ml)was refluxed for 30 min. The naphthoin product was recrystallized from alcohol, m.p. 125-126°C. β-Naphthoin oxime was prepared from β-naphthoin according to a procedure which is similar

Table 3.2 Molybdenum Content of Sea Water

| Origin | Range ( $\mu g\ L^{-1}$ ) | Mean ( $\mu g\ L^{-1}$ ) | Reference |
|---|---|---|---|
| Indian Ocean | 9.8-12.5 | 11.3 | SUG60 |
| Western North Pacific | 8.6-11.6 | 10.0 | SUG60 |
| Eastern China Sea | 8.6-11.8 | 9.9 | SUG60 |
| New Zealand coastal waters | 0.24-1.25 | 0.75 | BRO65 |
| Western North Atlantic coastal waters | 6.3-14.0 | 8.6 | YOU59 |
| Atlantic | - | 3.9 | ZHA63 |
| British in-shore waters | 12.0-16.0 | 14.0 | BLA52 |
| Irish Sea | 8.4-10.3 | 9.4 | RIL68a |
| Black Sea | - | 2.5 | ZHA63 |
| Northeast Atlantic | 8.8-13.0 | 10.7 | MOR75 |
| Northeast Atlantic | 2.1-20.3 | 11.6 | RIL72 |

to the one given for preparation of α-benzoin oxime from α-benzoin (WEL47). β-Naphthoin (7.4 g) was dissolved in a minimum amount of ethanol and added to an aqueous solution containing 4 g of hydroxylamine hydrochloride that had previously been neutralized with 2.2 g of sodium hydroxide. Mixture was refluxed for one and one-half hour and then β-naphthoin oxime was precipitated by treating with water.

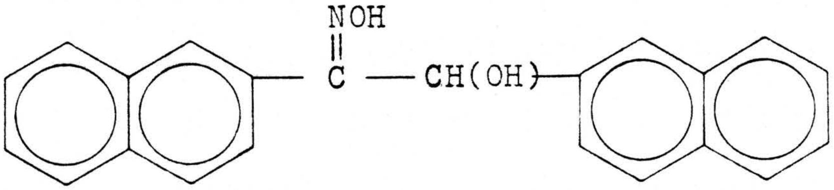
Precipitate was filtered, dried and recrystallized first from alcohol, then from benzene. The melting point of recrystallized β-naphthoin oxime was measured to be 171°C compared to the literature value of 172°C.

### 3.4.2 α-Benzoin Oxime, and Oxime Solutions

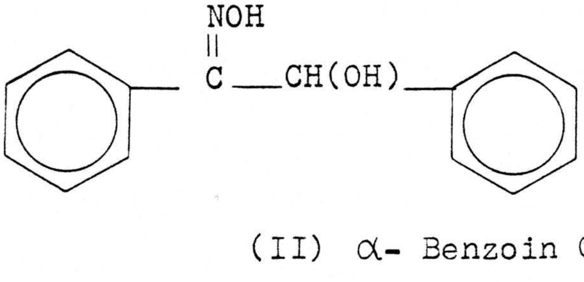
α-Benzoin oxime supplied by Fisher Scientific was purified by recrystallization from alcohol prior to use.

Both the oximes were redissolved in acetone several hours before use. The concentrations of the solutions used were 1 g β-naphthoin oxime per 50 mL acetone and 2 g α-benzoin oxime per 50 mL acetone.

The structures of β-naphthoin oxime and α-benzoin oxime are shown in Figure 3.1.



(I) β - Naphthoin Oxime



(II) α- Benzoin Oxime

Fig. 3.1 Structures of β-naphthoin and α-benzoin oximes

### 3.4.3 Samples of Sea and Estuarine Water

Samples of sea water from the North West Arm of the Atlantic Ocean in Halifax, Nova Scotia, were obtained from the chemical oceanography laboratory, Department of Oceanography, Dalhousie University. This water can essentially be considered as surface sea water for classification purposes. Samples of sea water were collected in precleaned polyethylene bottles. One, and one-half litre portions of the sea water were used in the preconcentration procedure which was carried out within 2-3 h of sample collection.

Samples of estuarine water were collected from the Saguenay Fjord, Quebec, during the C.S.S. Hudson Cruise #76-006 organized by the Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia. Details of sample collection were described elsewhere (ELL79). Water samples, collected from a depth of 5 m, were acidified to pH 2 with concentrated HCl and kept sealed in precleaned polyethylene bottles until the time of analysis.

### 3.4.4 Comparator Standard and Standard Reference Materials

Atomic absorption standard solution of molybdenum, present as $MoO_4^{2-}$ and containing 1000 μg molybdenum per mL, was used in all experiments designed to optimize conditions for cocrystallizing molybdenum with β-naphthoin oxime. Aliquot portions of this solution were diluted to desired concentrations prior to use.

A Standard Steel sample (B.C.S. NO. 322 = S.S. No. 52) containing high amounts of antimony, arsenic, chromium, manganese, molybdenum, nickel, titanium, tungsten and vanadium, was analyzed by both INAA and preconcentration methods to evaluate the selectivity of cocrystallization.

A Fresh Water Intercomparison sample (IAEA W-3) was provided by the International Atomic Energy Agency (IAEA). The U. S. National Bureau of Standards (NBS) supplied the Bovine Liver (NBS SRM-1577) standard reference material (SRM). Both of these samples were used for evaluating precision and accuracy of the method developed.

### 3.4.5 Irradiations

All irradiations were carried out in the Dalhousie University SLOWPOKE-2 Reactor (DUSR) at a flux of either $1 \times 10^{12}$ or $5 \times 10^{11}$ n $cm^{-2}s^{-1}$ for varying lengths of time. The details of composition, homogeneity, and reproducibility of the DUSR neutron flux have been reported elsewhere by Ryan et al. (RYA78).

### 3.4.6 Gamma-ray Spectrometry

The Ge(Li) detector connected to the TN-11 PHA and the NaI(Tl) detector connected to the Canberra 8100/e PHA (systems have been described in section 2.4.6) have been used in the molybdenum study.

### 3.4.7 Equilibrium between $^{99}$Mo and $^{99m}$Tc

Molybdenum can be determined by NAA using either of the following parent-daughter pairs: $^{99}$Mo-$^{99m}$Tc and $^{101}$Mo-$^{101}$Tc. The production modes of these nuclides are:

$$^{98}Mo(n,\gamma)\ ^{99}Mo \xrightarrow[67h]{} {}^{99m}Tc \xrightarrow[6h]{} {}^{99}Tc \xrightarrow[2.12 \times 10^{5}a]{} {}^{99}Ru(stable)$$

$$^{100}Mo(n,\gamma)\ ^{101}Mo \xrightarrow[14.6\ min.]{} {}^{101}Tc \xrightarrow[14.0\ min.]{} {}^{101}Ru(stable)$$

The natural abundance of $^{98}$Mo is 23.8% and the thermal neutron capture cross section is 0.12 barn. The equivalent figures for $^{100}$Mo are 9.6% and 0.02 barn. $^{99}$Mo is the more useful isotope in analysis of complex matrices as it gives greater sensitivity and more time for processing a batch of samples. It may be measured either by beta or gamma detection. The latter was used in this work. The nuclides $^{99}$Mo and its daughter $^{99m}$Tc with gamma-ray energies 140 keV and 142 keV, respectively, were counted together after they had reached equilibrium. The gamma-ray energies of 181 keV and 740 keV of $^{99}$Mo may also be used for calculations; however, the sensitivities of these two peaks for detecting $^{99}$Mo in the sample are considerably low when compared to that of 140 keV peak. If the activation to $^{101}$Mo is used for the analysis, the 191 keV gamma-ray of $^{101}$Mo or 307 keV gamma-ray of $^{101}$Tc may be used.

Equilibrium between $^{99}$Mo and $^{99m}$Tc was studied. Ten microgram amounts of atomic absorption molybdenum standard solution were added onto Nuclepore membrane filters which were dried under an infra-red lamp. These filters were irradiated for 5 h at a flux of 1 x $10^{12}$ n cm$^{-2}$ s$^{-1}$ in the DUSR facility. All gamma-rays emitted by $^{99}$Mo and

$^{99m}$Tc were assayed using a Ge(Li) detector for decay periods ranging between 1 h and 5 d. It was observed that at least a 2-3 d decay period should be allowed for the equilibrium between $^{99}$Mo and $^{99m}$Tc to be reached (Fig. 3.2) before the 140 keV gamma-ray of $^{99m}$Tc can be used for the determination of molybdenum.

### 3.4.8 General Methods for Tracer Studies

Ten millilitres of $^{99}$Mo-$^{99m}$Tc solution containing about 10 μg of molybdenum were transferred to a test tube, counted in the well-type NaI(Tl) detector, and the number of net counts under the area of 140 keV photopeak ( 5 x $10^3$ counts/μg Mo) was calculated. This tracer solution was added to 100 mL deionized water and mixed thoroughly. The pH of the mixture was then adjusted to a desired value and an appropriate buffer solution was added to it. β-Naphthoin oxime in acetone was added slowly while stirring the reaction mixture. The solution was stirred for an additional period. It was either kept at room temperature or boiled gently to remove acetone. The cocrystallized product was collected after 1-3 d on a Nuclepore membrane filter (47-mm diameter, 0.4 μm pore size), dried in air, dissolved in 10 mL of acetone in a test tube, and counted in the NaI(Tl) detector.

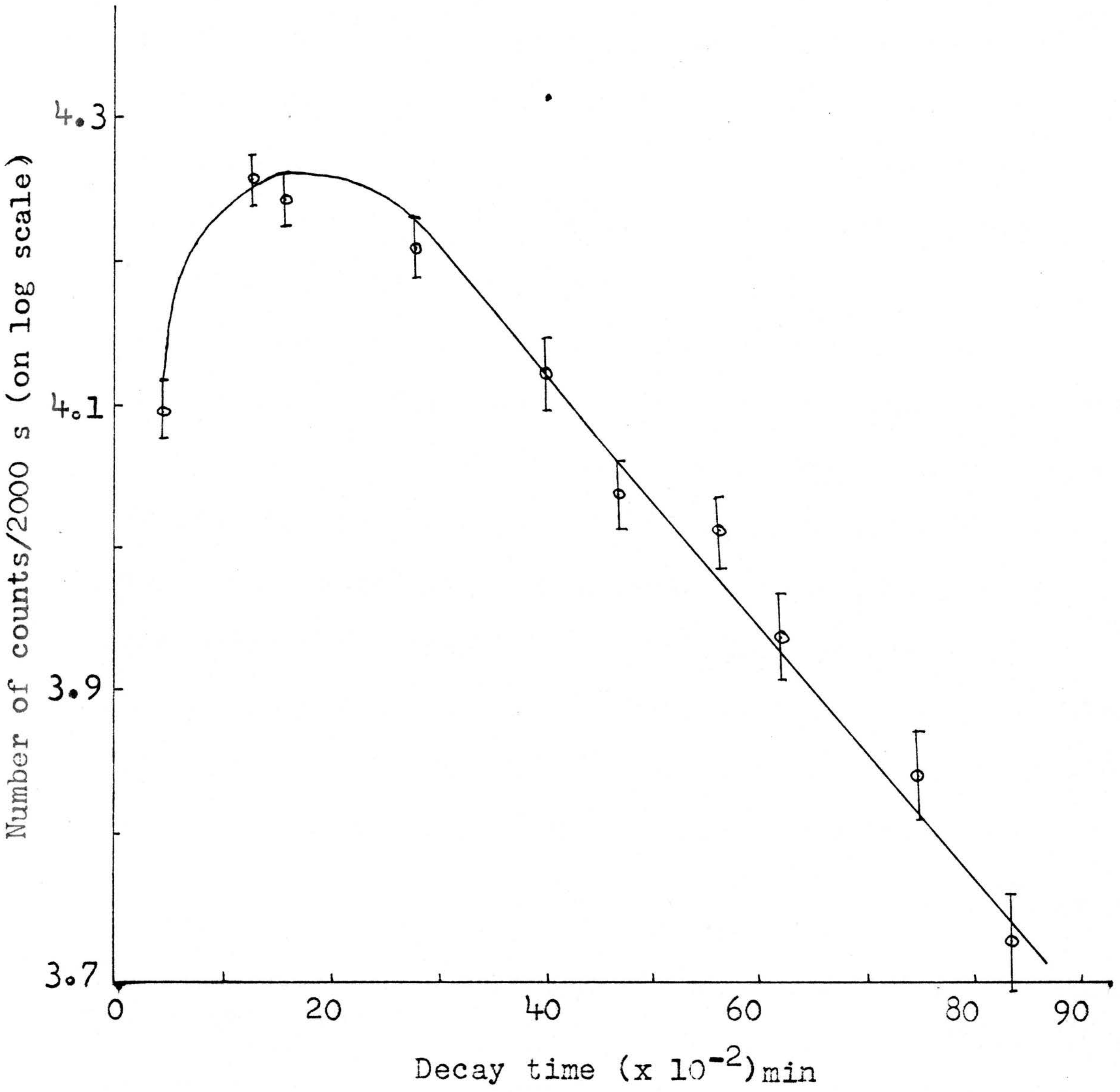


Fig. 3.2 Equilibrium between $^{99}$Mo and $^{99m}$Tc

## 3.5 METHODOLOGY

Before applying the cocrystallization procedure with β-naphthoin oxime to the real samples, it was necessary to establish the optimum conditions for a quantitative recovery of molybdenum from dilute solutions. For this purpose, several sets of experiments containing known amounts of $^{99}$Mo were carried out. In all these experiments, the general tracer method described in section 3.4.8 was followed. The results obtained from these studies are discussed below.

### 3.5.1 Amount of β-Naphthoin Oxime

The amount of β-naphthoin oxime was varied from 10 to 200 mg while the molybdenum content was kept constant at 10 μg. The pH was adjusted to 2 in this set of experiments because it had previously been reported (WEI61) that α-benzoin oxime, a compound similar to β-naphthoin oxime, gave quantitative recovery over a pH range of 1.8 to 5.5. The average of 3 determinations are shown in Table 3.3. These results indicate that the recovery of molybdenum is quantitative when 100-200 mg of β-naphthoin oxime per 10 μg of molybdenum are used.

Table 3.3 Effect of the Amount of β-Naphthoin Oxime on the Recovery of $^{99}$Mo

| mg β-naphthoin oxime/ 10 μg Mo | $^{99}$Mo recovered, % |
|---|---|
| 10 | 89.3 ± 1.8 |
| 20 | 90.2 ± 1.6 |
| 40 | 96.9 ± 1.5 |
| 100 | 98.1 ± 0.1 |
| 200 | 100. ± 0.1 |

### 3.5.2 pH of the Medium

Ten microgram quantities of $^{99}$Mo were cocrystallized with 200 mg of β-naphthoin oxime from 100 mL of water at pH varying between 0.50 and 10.0. The average of 3 measurements at each pH (Table 3.4) shows that the optimum pH for quantitative recovery of molybdenum is 2.

Table 3.4 Effect of the pH of Medium on the Recovery of $^{99}$Mo

| pH of the medium | $^{99}$Mo recovered, % |
|---|---|
| 0.50 | 93.2 ± 1.3 |
| 2.0 | 100 ± 0.1 |
| 5.0 | 75.0 ± 1.9 |
| 7.0 | 36.7 ± 3.0 |
| 10.0 | 0.90 ± 0.05 |

### 3.5.3 Temperature of the Medium

Quantitative recoveries of $^{99}$Mo were obtained using 100/200 mg β-naphthoin oxime per 10 μg of molybdenum (Table 3.3) at room temperature, 20°C. In order to observe the effect of temperature on the yield, water containing $^{99}$Mo tracer was heated to 90°C prior to the addition of β-naphthoin oxime. Only 88.1 ± 2.3% (average of 3 determinations) of the original $^{99}$Mo tracer were recovered. Henceforth, all cocrystallizations were carried out at room temperature.

### 3.5.4 Stability of β-Naphthoin Oxime in Acetone

In order to investigate the stability of the cocrystallizing reagent, solutions of β-naphthoin oxime in acetone were prepared from 1 h to 5 d prior to use. $^{99}$Mo tracer recoveries obtained using these reagent solutions (pH 2, room temperature) did not show any significant variations. In general, reagent solutions prepared 4-6 h before use were added in routine work.

### 3.5.5 Effect of Aging the Cocrystallized Product

Several experiments were carried out to observe the effect of aging the cocrystallized product at both elevated and room temperatures on the recovery of molybdenum. Aging was found to greatly influence the yield of $^{99}$Mo tracer. In the first set of experiments, 10 μg portions of $^{99}$Mo tracer in 100 mL of water were cocrystallized at pH 2 and room temperature with 200 mg of β-naphthoin oxime in acetone; the mixture was gently boiled for 15 min to remove acetone; the product was filtered after cooling to room temperature; and molybdenum recoveries varying between 70 and 83% were obtained. In the second set of experiments, after removing acetone by boiling as before, the mixture was cooled in an ice bath for about 4 h; recoveries of 80-90% of $^{99}$Mo were obtained indicating incomplete cocrystallization. Between 80-93% of $^{99}$Mo were collected in the third set of experiments where acetone was allowed to evaporate at room temperature for 12-15 h after precipitation. More than 98% of $^{99}$Mo were recovered (Tables 3.3 and

3.4) by allowing acetone to evaporate and the cocrystallized product to settle for 2 d at room temperature. Consequently, the last procedure was followed in routine determinations of molybdenum.

### 3.5.6 Stirring Time

The effect of stirring time on the recovery of molybdenum by β-naphthoin oxime was studied. Quantitative recoveries (>98%) of molybdenum were obtained under the following conditions: stirring for 10 min during the addition of β-naphthoin oxime in acetone to water, and a further stirring for 15 min.

### 3.5.7 Sample Volume

Volume of water was varied between 100 and 1000 mL while keeping the total amount molybdenum constant. In each case, molybdenum was quantitatively recovered.

### 3.5.8 Reagent Recovery

More than 98% of the 200 mg β-naphthoin oxime added to solutions was recovered when optimal procedure was followed.

### 3.5.9 Salinity

$^{99}$Mo tracer experiments carried out with waters of different salinity, viz. deionized and sea, gave quantitative recovery (>98%) with β-naphthoin oxime (Tables 3.3 and 3.7). It was, therefore, concluded that salinity had no detectable effect on the yield of molybdenum.

### 3.5.10 Linearity of Cocrystallization

To study the linearity of the cocrystallization procedure, tracer experiments were carried out with molybdenum concentrations varying between 1 and 10 µg in 10 mL of water, activity measured, and diluted to 100 mL. The cocrystallized product from each experiment was dissolved in 10 mL of acetone prior to measurement in the well-type NaI (Tl) detector. The number of counts (with standard deviation) at each molybdenum concentration is shown in Table 3.5. A plot of these data (Fig. 3.3) gives a straight line passing through the origin indicating that recovery is independent of molybdenum concentration, for the range studied.

Table 3.5 Linearity of Cocrystallization

| Mo content, µg | Number of Counts/2000 s |
|---|---|
| 1 | 6470 ± 520 |
| 2 | 13640 ± 960 |
| 5 | 34000 ± 2040 |
| 10 | 69300 ± 2770 |

### 3.5.11 Effect of an Oxidizing Agent

Weiss and Lai (WEI61) have reported that molybdenum is hexavalent in untreated sea water and is partially reduced in acidified sea water. They have used bromine to oxidize molybdenum to hexavalent state in the acidified sea water in their determination of molybdenum using cocrystallization with $\alpha$-benzoin oxime. However, in the present work bromine could not be used for this purpose,

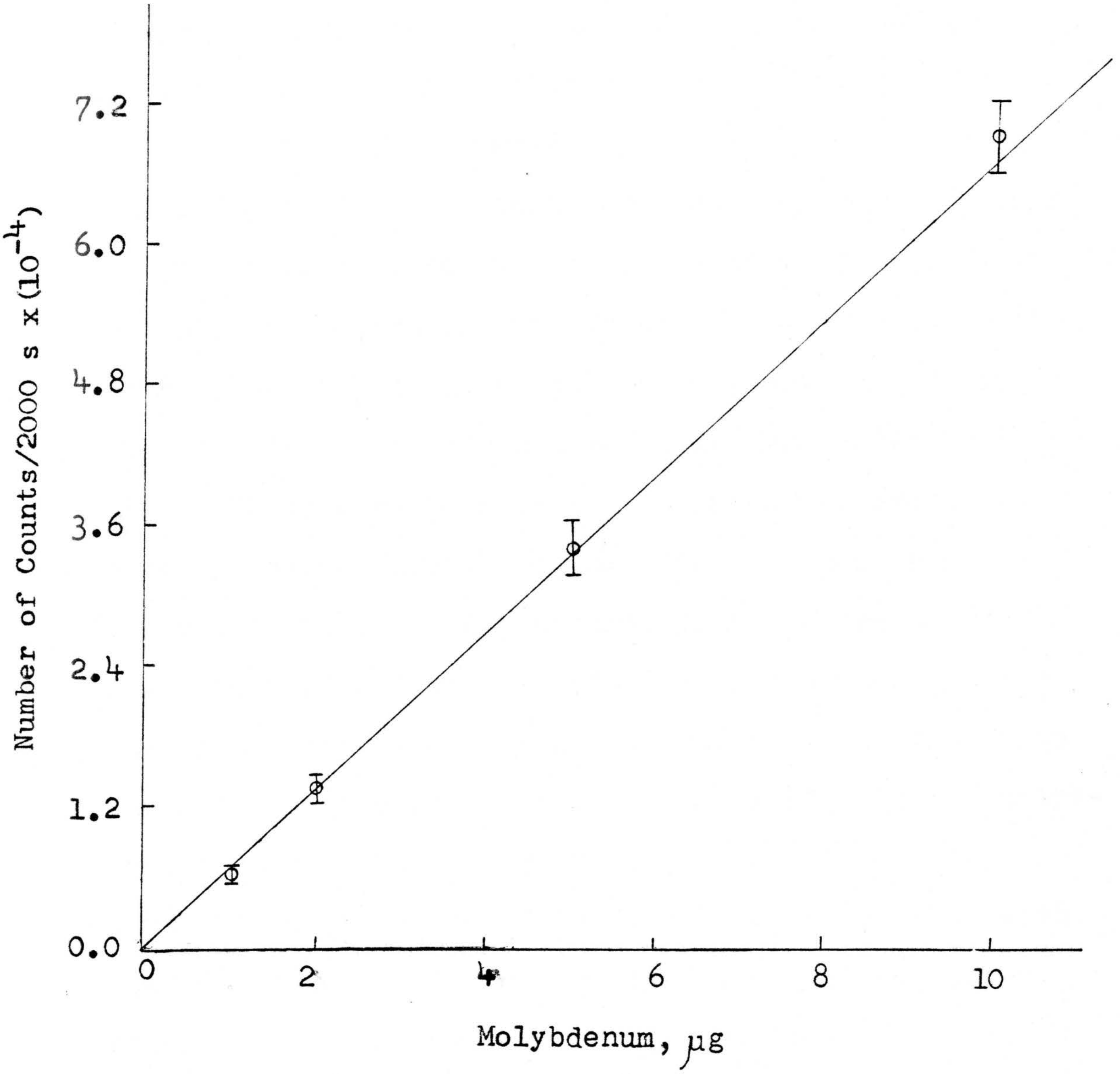


Fig. 3.3 Linearity of cocrystallizing molybdenum with β-naphthoin oxime.

as the final determination of molybdenum was carried by neutron activation analysis. High bromine activities produced ($^{80}$Br in 15 min irradiations, $^{82}$Br in 5 h irradiations) made it impossible to make gamma-ray measurements of the irradiated samples. These nuclides of bromine emit a number of gamma-rays with energies varying over a wide range and also exhibits a high dead time.

To investigate the necessity of using an oxidizing agent, two sets of experiments were carried out. To four one-litre samples of sea water, 10 μg(10 ml of the tracer solution) of $^{99}$Mo tracer were added. After adjusting the acidity of the solution to pH 2 with concentrated nitric acid, a few drops of hydrogen peroxide were added to two samples. These were then boiled to decompose excess hydrogen peroxide which could oxidize β-naphthoin oxime. After cooling to room temperature, samples were brought back to the original volumes with deionized water and the pH was again checked. Hydrogen peroxide was not added to the second set of experiments. Cocrystallization of molybdenum was carried out using 200 mg of β-naphthoin oxime. Precipitates were collected by filtration and washed with deionized water, air-dried and dissolved in 10 ml of acetone. Gamma-ray measurements of the liquid samples were made with the NaI(Tl) detector. $^{99}$Mo tracer recoveries obtained in these experiments are presented in Table 3.6. Quantitative recoveries obtained in the experiments, where no hydrogen peroxide was added indicate that there is no reduction of molybdenum (VI) at acidic pH and therefore it is not necessary to use an oxidizing agent.

The masking of the reaction between molybdenum and β-naphthoin oxime in the presence of hydrogen peroxide, is believed to be due to formation of paramolybdic acid; the $MoO_4^{2-}$ ions being then substituted by $MoO_5^{2-}$ ions. It has been reported (FE140) that certain reactions of $MoO_4^{2-}$ ions can be avoided by addition of $H_2O_2$.

Table 3.6 Effect of Hydrogen Peroxide on Cocrystallization of Molybdenum

| Experiment Number | $^{99}$Mo tracer recovered, % | |
|---|---|---|
| | $H_2O_2$ added | without $H_2O_2$ |
| 1 | 1.9 | |
| 2 | 0.3 | |
| 3 | | 100.0 |
| 4 | | 100.3 |

### 3.5.12 Reagent Blanks

Cocrystallized products from blank experiments were irradiated in the DUSR at a flux of 1 x $10^{12}$ n $cm^{-2}$ $s^{-1}$ for 15 min to assay 307 keV photopeak of $^{101}$Tc, and later on for 5 h to assay 140 keV gamma-ray of $^{99m}$Tc using both Ge(li) and NaI(Tl) detectors. No detectable amount of molybdenum was found in blank cocrystallized products under the experimental conditions described.

### 3.5.13 Optimal Procedure for Molybdenum in Sea Water

Various experimental parameters established above using deionized water were re-evaluated using sea water spiked with $^{99}$Mo tracer. Ten millilitres of $^{99}$Mo-$^{99m}$Tc solution of known activity and containing about 10 μg of molybdenum were added to each of 7 samples of sea water (0.5 - 1 L). The pH was adjusted to 2 with conc. nitric acid, and a 0.2M KCl-0.2M HCl buffer solution was added. A solution of 200 mg β-naphthoin oxime in acetone was added at room temperature while stirring for 10 min. The mixture was stirred for an additional 15 min. The cocrystallized product was allowed to settle for 2 d before filtering through Nuclepore membranes. The residue was washed several times with deionized water, dried at first in air and then in a desiccator to a constant weight. The cocrystallized product was redissolved in 10 mL of acetone, counted in the well-type NaI(Tl) detector, and appropriate decay corrections were made in calculating the yields through the 140 keV gamma-ray of $^{99m}$Tc. Quantitative recoveries were obtained as shown in Table 3.7.

Table 3.7 Recovery of $^{99}$Mo Tracer from Sea Water

| Sample No. | $^{99}$Mo recovered, % |
|---|---|
| 1 | 100.5 |
| 2 | 100.1 |
| 3 | 101.7 |
| 4 | 100.2 |
| 5 | 100.9 |
| 6 | 100.1 |
| 7 | 100.3 |

## 3.6 RESULTS AND DISCUSSION

### 3.6.1 Molybdenum Content of Sea Water

Ten samples of sea water collected from the Atlantic Ocean over a period of 6 months during 1977-78 were analyzed for molybdenum content. The pH of water sample was adjusted to 2 and subsequently molybdenum was cocrystallized with $\beta$-naphthoin oxime by the procedure described above. The dried product was heat-sealed in a precleaned polyethylene bag and irradiated simultaneously with molybdenum standards in the DUSR at a flux of $1 \times 10^{12}$ n $cm^{-2}s^{-1}$ for 5 h. The 140 keV gamma-ray of $^{99m}Tc$ was assayed using a Ge(Li) detector after a decay of 2-3 d. The results obtained for the 10 sea water samples are given in Table 3.8. Figure 3.4 represents a typical gamma-ray spectrum obtained under these conditions. Molybdenum content of coastal surface sea water was found to vary in this work within the small range of 7.31 to 7.95 $\mu g\ L^{-1}$. Molybdenum concentration ranges (in $\mu g\ L^{-1}$) reported in literature include: 0.24-1.25 in New Zealand coastal waters (BRO65), 0.8 and 1.4 in Rhine surface water (VAN77a, VAN76c), 2-12 around French coast (DAR76, GUE76), 6.3-14.0 in western North Atlantic coastal waters (YOU59), 8.4-10.3 in Irish Sea (RIL68a), 8.6-11.6 in western North Pacific (SUG60), 8.6-11.8 in eastern China Sea (SUG60), 9.8-13.3 in the Indian Ocean (SUG66), 12.0-16.0 in British in-shore waters (BLA52), and mean concentrations of 2.5 and 3.9 in the Black Sea and the Atlantic Ocean, respectively (ZHA63). It appears that the molybdenum content of coastal

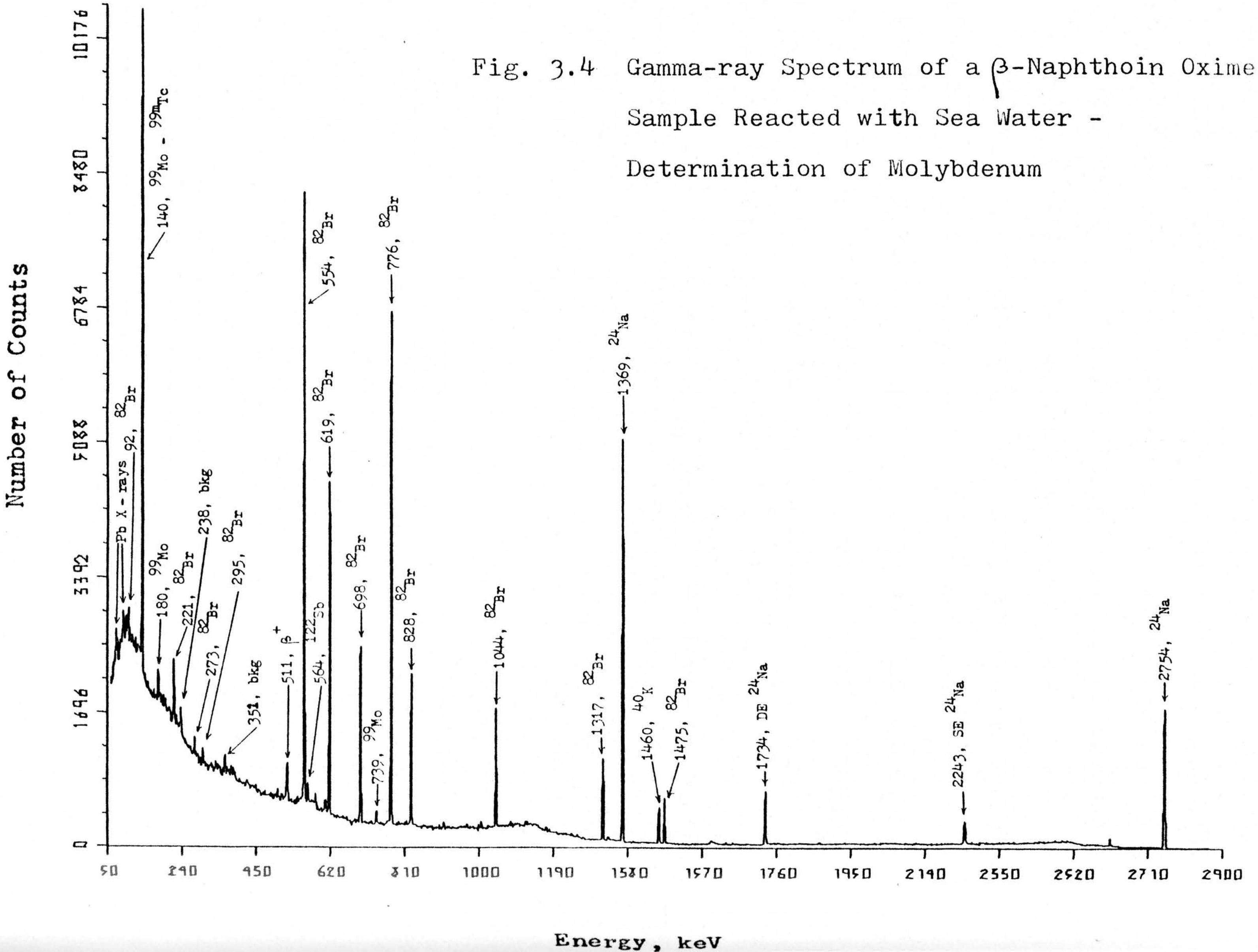


Fig. 3.4 Gamma-ray Spectrum of a β-Naphthoin Oxime Sample Reacted with Sea Water - Determination of Molybdenum

sea water is generally below 10 $\mu g\ L^{-1}$ which is in good agreement with our results (Table 3.8).

Table 3.8 Molybdenum Content of Sea Water

| Sample No. | Volume used, L | Mo Content, $\mu g\ L^{-1}$ |
|---|---|---|
| 77-11-01 | 1.0 | 7.84 |
| 78-02-01 | 1.0 | 7.76 |
| 78-02-02 | 1.0 | 7.61 |
| 78-04-01 | 1.0 | 7.95 |
| 78-04-02 | 1.0 | 7.55 |
| 78-05-01 | 0.5 | 7.31 |
| 78-05-02 | 1.0 | 7.69 |
| 78-05-03 | 0.5 | 7.37 |
| 78-05-04 | 1.0 | 7.32 |
| 78-05-05 | 0.5 | 7.54 |

### 3.6.2 Molybdenum Content of Estuarine Water

Seven samples of estuarine water collected from the Saguenay Fjord were analyzed for molybdenum levels by a method similar to that of sea water. One litre portions of water were used for analysis. The results obtained are presented in Table 3.9 and in Fig. 3.5. Molybdenum levels were found to vary with salinity in a linear fashion. The same trend was also observed by other researchers (HEA70, VAN77a, MOR75). This variation in estuarine water could be the result of the extent of dilution of sea water with high molybdenum content by river water of relatively low molybdenum levels (HEA70).

Table 3.9 Characteristics and Molybdenum Content of Estuarine Water Samples

| Sample Number | Depth (m) | Salinity (o/oo) | Mo Content ( µg L-1) |
|---|---|---|---|
| 3016 | 150 | 29.848 | 6.11 |
| 3019 | 5 | 19.050 | 3.83 |
| 3032 | 5 | 16.190 | 3.35 |
| 3053 | 5 | 11.328 | 2.07 |
| 3060 | 5 | 9.205 | 2.49 |
| 3074 | 5 | 2.229 | 0.40 |
| 3081 | 5 | 4.655 | 1.21 |

### 3.6.3 Reduction of Na, Cl, Br Content by Cocrystallization

In order to investigate the effectiveness of β-naphthoin oxime to reduce sodium, chlorine and bromine content, both untreated sea water and cocrystallized product were analyzed. One millilitre portions of untreated sea water and products of cocrystallization from 1-L samples of the same sea water were irradiated for 2 min at a flux of $5 \times 10^{11}$ n $cm^{-2}s^{-1}$. Gamma-ray measurements were made with the Ge(Li) detector after a decay period of 3 min. Net areas under the 1369 keV photopeak of $^{24}Na$, 2167 keV of $^{38}Cl$, and 617 keV of $^{80}Br$ were compared after appropriate corrections for volumes of water used. The results showed that the concentrations of sodium and chlorine in sea water were reduced by a factor of $3 \times 10^4$, and that of bromine by

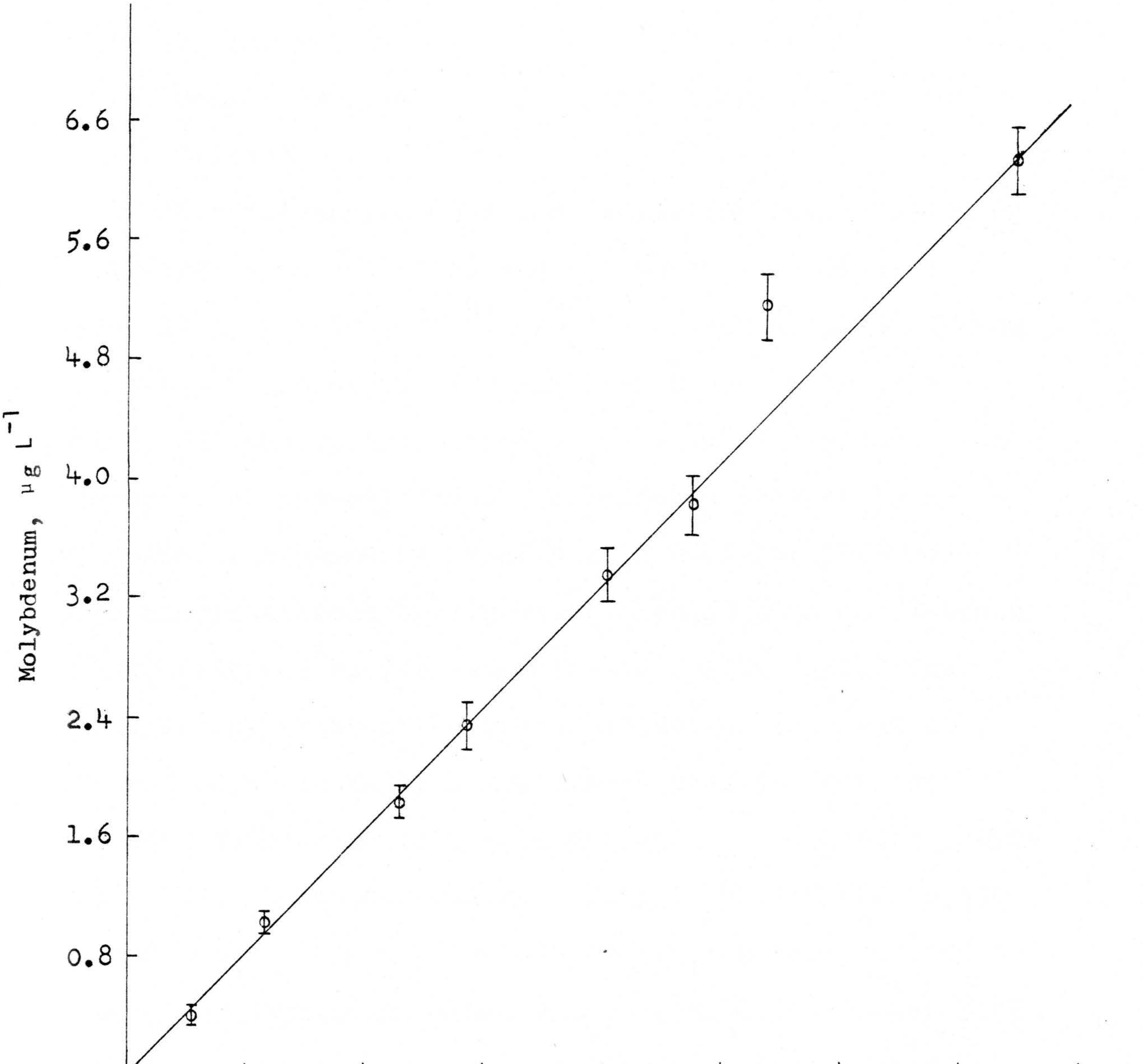


Fig. 3.5 Variation of molybdenum content in estuarine water with salinity.

$5 \times 10^3$ using the cocrystallization procedure, which enabled the determination of molybdenum in sea water possible without any spectral interference and risk of radiation hazard.

### 3.6.4 Comparison between β-Naphthoin and α-Benzoin Oximes

The efficiency of the two oximes for cocrystallizing molybdenum from deionized and sea water were studied using 10 μg portions of $^{99}Mo$-$^{99m}Tc$ tracer at pH 2, 200 mg of β-naphthoin oxime, 200 and 1500 mg of α-benzoin oxime, and the optimal procedure described earlier. Ten microgram of non-radioactive molybdenum present in a solution of a standard steel sample (BCS No. 322) were also cocrystallized by pH 2 using β-naphthoin and α-benzoin oximes followed by its determination using INAA. The average recoveries of 3 determinations of each sample are presented in Table 3.10. These results show that β-naphthoin oxime is more efficient in collecting molybdenum than α-benzoin oxime. This is mainly due to the higher solubility of α-benzoin oxime in water compared to that of β-naphthoin oxime, which results in a lower yield.

### 3.6.5 Selectivity of β-Naphthoin Oxime for Molybdenum

An attempt was made to study the selectivity of β-naphthoin oxime for cocrystallizing molybdenum from two different matrices, namely sea water and solution of the standard steel sample, containing several elements at widely varying concentration levels.

3.10 Comparison of β-Naphthoin and α-Benzoin Oximes for cocrystallizing Mo

| Sample | Total Volume | mg reagent/ 10 μg Mo | Recovery,% |
|---|---|---|---|
| Deionized water | 100 mL | 200, β-naphthoin oxime | 100 ± 0.1 |
| | 100 mL | 200, α-benzoin oxime | 25 ± 2 |
| | 100 mL | 1500, α-benzoin oxime | 100 ± 0.4 |
| Sea water | 1000 mL | 200, β-naphthoin oxime | 100 ± 0.5 |
| | 1000 mL | 1500, α-benzoin oxime | 69 ± 1 |
| Standard steel | 100 mL | 200, β-naphthoin oxime | 88 ± 1 |
| | 100 mL | 1500, α-benzoin oxime | 65 ± 2 |

Qualitative measurements were carried out to identify both short-and long-lived neutron activation products of the materials cocrystallized from sea water. Experimental conditions used were for (i) short-lived nuclides: 15-min irradiation, 7-min decay, and 10-min counting; and (ii) long-lived nuclides: 5-h irradiation, 2-d decay, and 1-h counting. All samples were irradiated at a flux of $1 \times 10^{12}$ n $cm^{-2}s^{-1}$ and counted in a Ge(Li) detector. The nuclides detected in samples cocrystallized at pH 2 are shown in Table 3.11. In general, levels of all elements were very low. The concentrations of V, I, Mn and Al were reduced by factors of $2 \times 10^2$, $2 \times 10^1$, $2 \times 10^1$ and 10, respectively

Table 3.11 Nuclides Detected in Sea Water Cocrystallized with β-Naphthoin Oxime at pH 2

| short-lived nuclides | | long-lived nuclides | |
|---|---|---|---|
| nuclide | γ-ray energy, keV | nuclide | γ-ray energy, keV |
| $^{28}$Al | 1779 | | |
| $^{80}$Br | 617, 640, 666, 704, 1257 | $^{82}$Br | 221, 554, 619, 698, 776, 838, 1044, 1317, 1475 |
| $^{49}$Ca | 3083 | | |
| $^{38}$Cl | 1642, 2167 | | |
| $^{128}$I | 443, 526, 743, 969 | | |
| $^{56}$Mn | 847, 1811 | | |
| $^{101}$Mo | 191, 591 | $^{99}$Mo-$^{99m}$Tc | 140, 181, 740, 778 |
| $^{24}$Na | 1369, 2754 | $^{24}$Na | 1369, 2754 |
| $^{101}$Tc | 307 | $^{122}$Sb | 564 |
| $^{52}$V | 1434 | | |

in cocrystallized products compared to those in sea water. The 140 keV gamma-ray of $^{99}$Mo-$^{99m}$Tc, used in this work, is free from interference by gamma-rays of $^{82}$Br.

Precipitations were also carried out at pH 0.5 and 5.0 with one-litre samples of sea water and 200 mg of β-naphthoin oxime to see whether any other elements present in sea water could be cocrystallized with β-naphthoin oxime by varying the acidity of the reaction medium. Recoveries of molybdenum were around 82% and 21% at pH 0.5 and 5.0 respectively. At these pH values, no additional peaks were observed in the gamma-ray spectra other than those obtained at pH 2. The selectivity of β-naphthoin oxime in cocrystallizing molybdenum from sea water at pH 2 is sufficiently high to enable its interference-free determination.

A sample of steel (BCS No. 322) containing Al (0.093%), As (0.012%), Cr (0.039%), Mn (0.28%), Mo (0.045%), Sb (0.004%), Sn (0.24%), Ti (0.042%), V (0.008%) and W (0.048%) (BCS66), in addition to several trace elements, was dissolved in aqua-regia. Several portions of this solution were treated with β-naphthoin oxime at pH2 and the cocrystallized products were analyzed for both short- and long-lived nuclides under the same conditions as those used for sea water. Figure 3.6 represents a gamma-ray spectra of the long-lived nuclides. Several nuclides were detected and are given in Table 3.12. Comparison of qualitative data (Tables 3.11 and 3.12) shows that chemically similar elements, such as Cr and W, are cocrystallized with molybdenum when all of them are present at high concentrations such as the steel sample analyzed here. No gamma-rays of $^{51}Cr$ and $^{187}W$ nuclides were detected in the product cocrystallized from sea water (Table 3.11), perhaps because of their very low levels.

Fig. 3.6 Gamma-ray Spectrum of a β-Naphthoin Oxime Sample Reacted with a Steel Solution

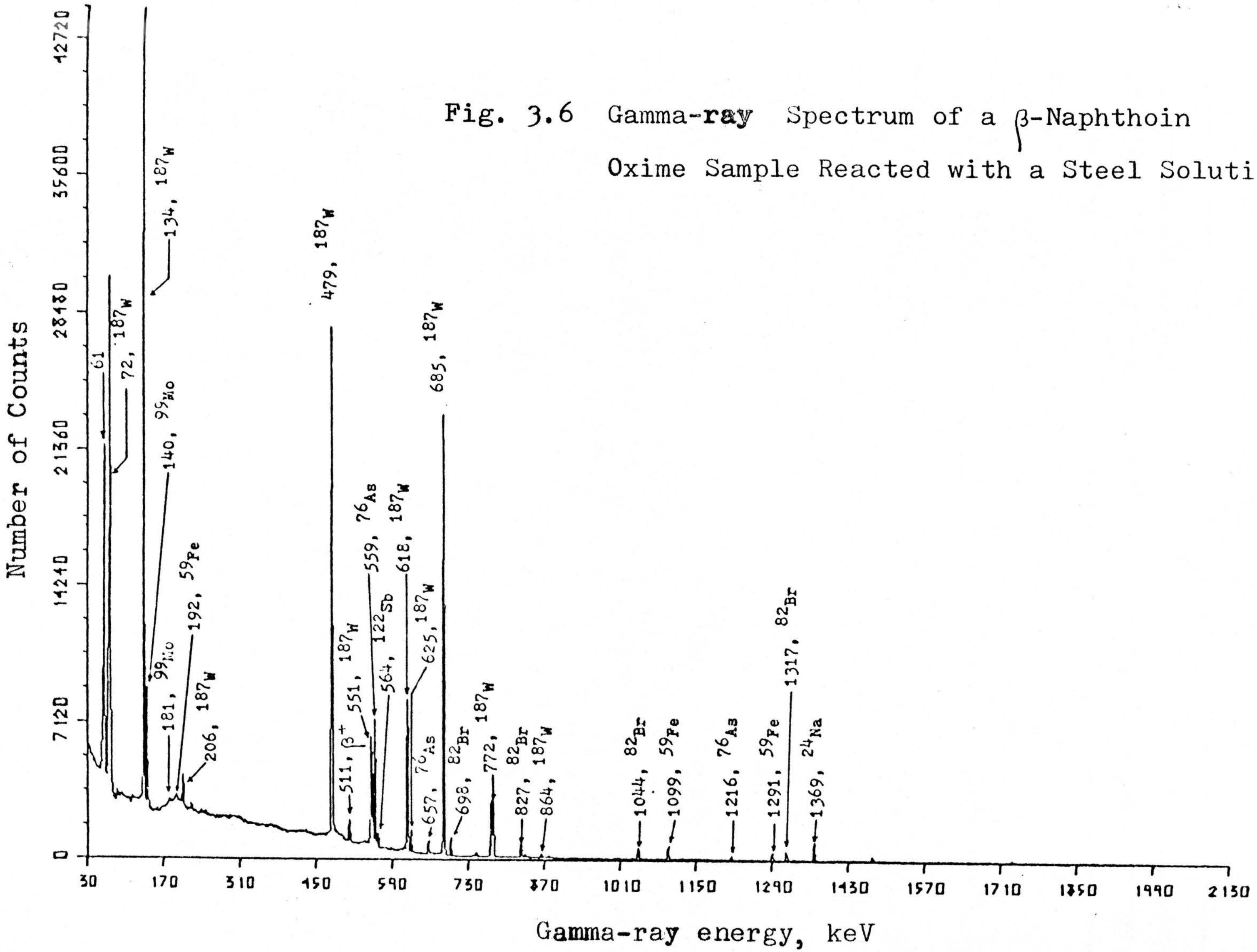


Table 3.12 Nuclides Detected in Steel Cocrystallized with β-Naphthoin Oxime at pH 2

| short-lived nuclides | | long-lived nuclides | |
|---|---|---|---|
| nuclide | γ-ray energy, keV | nuclide | γ-ray energy, keV |
| $^{28}$Al | 1779 | | |
| $^{76}$As | 559, 657 | $^{76}$As | $559^{*}$, 657, 1217 |
| $^{80}$Br | 617, 640, 666 | $^{82}$Br | 554, 619, 698, 776, 838, 1044, 1317, 1475 |
| $^{38}$Cl | 1642, 2167 | $^{51}$Cr | $320^{*}$ |
| $^{56}$Mn | 847, 1811 | $^{59}$Fe | 192, $1099^{*}$, 1292 |
| $^{101}$Mo | 191, 591 | $^{99}$Mo-$^{99m}$Tc | $140^{*}$, 181, 740, 778 |
| $^{24}$Na | 1369, 2754 | | |
| $^{122m}$Sb | 62 | $^{122}$Sb | $564^{*}$ |
| $^{123}$Sn | 160 | $^{117m}$Sn | $158^{*}$ |
| $^{125m}$Sn | 332 | | |
| $^{101}$Tc | 307 | | |
| $^{51}$Ti | 320 | | |
| $^{52}$V | 1434 | | |
| $^{187}$W | 72, 134, 479, 551, 618, 686, 773 | $^{187}$W | 72, 134, 479, 551, 618, $686^{*}$, 773 |

* Used for quantitative determinations.

In order to investigate the variation of selectivity for cocrystallizing molybdenum with β-naphthoin oxime from the steel solution, reactions were carried out at three different pH values, namely 0.5, 2.0 and 5.0 Concentrations of As, Cr, Fe, Mo, Sb, Sn and W in the cocrystallized products were measured using interference-free gamma-rays (indicated by * in Table 3.12) of their long-lived nuclides. Recoveries of these elements were then calculated by comparing the above concentrations with those obtained using INAA of the untreated steel sample. The results are presented in Table 3.13.

Table 3.13 Effect of pH on the Cocrystallization of Elements from a Steel Sample

| pH | Recoveries of the Elements, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | As | Cr | Fe | Mo | Sb | Sn | W |
| 0.5 | 0.5 | N.D. | 0.9 | 84.2 | 9.0 | N.D. | 87.9 |
| 2.0 | 53.6 | 8.8 | 11.2 | 88.5 | 46.0 | 25.8 | 91.3 |
| 5.0 | 96.8 | 83.4 | 93.6 | 94.5 | 86.7 | 43.6 | 97.8 |

N.D. - not detected

This study shows that the selectivity of β-naphthoin oxime to cocrystallize molybdenum in the steel sample can be increased by decreasing the pH below 2. In addition to molybdenum, tungsten is the only element which has a considerable recovery at pH 0.5. However, the gamma-rays emitted by $^{187}$W do not interfere with those emitted by $^{99}$Mo-$^{99m}$Tc if counted with a high-resolution Ge(Li) detector as used in the present work. At pH 5, hydrous oxides of the elements, such as Fe and Cr, are considered to be precipitated giving high recoveries. It is, therefore, recommended that samples containing high levels of As, Cr, Fe, Sb, Sn and W, cocrystallizations with $\beta$-naphthoin oxime for molybdenum be carried out at pH 0.5.

### 3.6.6 Nuclear Interference

The 140 keV gamma-ray of $^{99}$Mo-$^{99m}$Tc, used in this work, may be interfered with by the 142 keV gamma-ray of $^{59}$Fe. However, two highly populated gamma-rays, viz. 1099 and 1292 keV, of $^{59}$Fe were not detected in products cocrystallized from sea water (Table 3.11). Moreover, the half-life determined through the 140 keV gamma-ray of $^{99}$Mo-$^{99m}$Tc agreed very well with that reported in the literature. Consequently, any interference from the 142-keV photopeak of $^{59}$Fe was ignored.

Although less than 1% of iron was cocrystallized from the steel sample at pH 0.5 (Table 3.13), appropriate correction factors were applied to obtain reliable measurements of molybdenum.

The $^{99}$Mo and $^{99m}$Tc nuclides are also produced from the fission of $^{235}$U present in sea water. The fission process may contribute towards the total activity of the $^{99}$Mo and $^{99m}$Tc nuclides (VAN77a). However, none of the gamma-rays emitted by the neutron activation product of uranium, namely $^{239}$U and its daughter $^{239}$Np, were detected in the material cocrystallized from sea water at pH 2 (Table 3.11). Consequently, any contribution from fission of uranium towards the measured activity of $^{99}$Mo and $^{99m}$Tc was discarded in the present work.

The $^{99}$Mo nuclide can also be produced by the interfering reaction $^{102}$Ru $(n, \alpha)^{99}$Mo. However, the average ruthenium concentration of $7 \times 10^{-4}$ μg per kg of sea water was considered too low to produce any measurable quantity of $^{99}$Mo. Any interference from the above reaction was therefore discarded.

### 3.6.7 Precision and Accuracy

Since no sea water standard reference material (SRM) with certified molybdenum content was available, the precision and accuracy for determining molybdenum were evaluated by replicate analyses of a fresh water intercomparison sample and a biological SRM. The Fresh Water Intercomparison sample (IAEA W-3) provided by the International Atomic Energy Agency (IAEA) was diluted according to the method prescribed by the Agency (DYB76). Approximately 1 g of Bovine Liver (NBS SRM-1577) supplied by the U.S. National Bureau of Standards (NBS) was dissolved in a mixture of ultrapure nitric, hydrochloric and sulfuric acids, and was diluted to about 600 mL with deionized water. Molybdenum was cocrystallized from both the Fresh Water and the Bovine Liver solution with β-naphthoin oxime by a procedure identical to that of sea water. Results are presented in

Table 3.14. The precision of measurement was found to be better than ± 10%. Molybdenum levels of the Fresh Water and Bovine Liver determined in this study are in good agreement with those reported by others (DYB76, VAN79a, NBS77, VAN79b, NAD73, LIV77), as shown in Table 3.14.

Table 3.14 Molybdenum Content of an Intercomparison Sample and a Standard Reference Material

| matrix | this work | reported values |
|---|---|---|
| Intercomparison Water (IAEA W-3) | $7.07 \pm 0.13\ \mu g\ L^{-1}$ | 8.0[a], 7.2[b] $\mu g\ L^{-1}$ |
| Bovine Liver (NBS SRM-1577) | $3.1 \pm 0.3\ \mu g\ g^{-1}$ | (3.4)[c], $3.4 \pm 0.2$[d], 3.0[e], 3.19[f] $\mu g\ g^{-1}$ |

[a] IAEA value, Ref. DYB76; [b] Ref. VAN79a; [c] NBS noncertified value, Ref. NBS77; [d] Ref. VAN79b; [e] Ref. NAD73; [f] Ref. LIV77.

### 3.6.8 Limits of Detection

The limits of detection and determination for molybdenum cocrystallized with β-naphthoin oxime from various matrices were calculated according to the methods prescribed by Currie (CUR68). The results are shown in Table 3.15. These limits lie well below the observed concentrations of molybdenum in the materials studied.

Table 3.15 Detection and Determination Limits for Molybdenum

| Matrix | detection limit | determination limit |
|---|---|---|
| Intercomparison Water (IAEA, W-3) | 0.18 $\mu g\ L^{-1}$ | 0.57 $\mu g\ L^{-1}$ |
| Sea Water | 0.30 $\mu g\ L^{-1}$ | 1.00 $\mu g\ L^{-1}$ |
| Bovine Liver (NBS SRM-1577) | 0.32 $\mu g\ g^{-1}$ | 0.99 $\mu g\ g^{-1}$ |
| Steel (BCS No. 322) | 8.43 $\mu g\ g^{-1}$ | 26.3 $\mu g\ g^{-1}$ |

## 3.7 CONCLUSION

A method has been developed for preconcentrating molybdenum from sea water and estuarine water samples by cocrystallization with $\beta$-naphthoin oxime and finally determining by neutron activation. Cocrystallization procedure was carried out at pH 2, and 200 mg of $\beta$-naphthoin oxime were used for 1-L samples of sea and estuarine water. The preconcentration method for molybdenum from water is quantitative; and the final determination by neutron activation is interference-free. The preconcentration method reduced the sodium and chlorine content in sea water by a factor of $3 \times 10^4$, making accurate determination of molybdenum feasible with the samples irradiated for about 5 h and counted after 2-3 d. Tracer experiments carried out with sea water samples showed that the results are independent of sample volume for the same amount of molybdenum. Molybdenum content of sea water was estimated to be in the range of 7.31 to 7.95 $\mu g\ L^{-1}$. A linear relationship was found between the salinity and the molybdenum content for estuarine water.

Experiments carried out with steel, which contains high concentrations of other elements that cocrystallize with β-naphthoin oxime, show that molybdenum can still be recovered quantitatively around pH 2. Since none of the nuclides of other elements which cocrystallize with β-naphthoin oxime emit gamma-rays interfering with the 140 keV gamma-ray of $^{99}$Mo-$^{99m}$Tc, it is not necessary to separate these elements before the final determination, or to use masking agents before or during the cocrystallization procedure. This is one of the advantages of the present method for determining molybdenum. In the determination of molybdenum in sea water by preconcentration with α-benzoin oxime and spectrometry, Weiss and Lai (WEI61) have used a Dowex 2 column to separate molybdenum from other elements that cocrystallized with α-benzoin oxime. Such a step is not required while using NAA.

Since the settling of the precipitates takes a long time, the total time required for the analysis is also long. This is a disadvantage in routine analysis of samples by this method.

β-Naphthoin oxime was found to cocrystallize molybdenum quantitatively from water with a high degree of selectivity. It was found to be superior to α-benzoin oxime. No interferences from Na, Cl, Br, Fe, Cr, W, and U were observed in the determination of molybdenum levels of sea and estuarine water using β-naphthoin oxime and NAA. The detection limits were adequate for measuring small amounts of molybdenum in the presence of large quantities of interfering elements.

# 4. DETERMINATION OF COBALT, ZINC AND MANGANESE IN SEA WATER

Analytical methods have been developed for the determination of cobalt, zinc and manganese in sea water. The methods consist of preconcentration of the elements with chitosan at pre-determined pH values, followed by their determinations by neutron activation. For these three elements, maximum recoveries are obtained at three different pH values. Two different mechanisms of preconcentration have been postulated: cobalt and zinc are complexed by chitosan leading to the formation of corresponding chelates, whereas for manganese, the predominant mechanism of concentration is coprecipitation of hydrous manganese oxide and manganese hydroxide with chitosan. In the determinations of elemental concentrations of sea water samples, corrections have been made for the recoveries obtained by using radioactive tracers with each and every sample.

## 4.1 INTRODUCTION

Determination of cobalt, zinc and manganese in sea water are of much interest to chemical oceanographers. The principal forms of dissolved species in sea water are probably hydrated $Co^{2+}$, $CoCl^+$ and $CoOH^+$ for cobalt, hydrated $Zn^{2+}$, $ZnCl^+$, $Zn(OH)_2^o$ and $Zn(OH)^+$ for zinc, and hydrated $Mn^{2+}$, $MnCl^+$ and $Mn(OH)^+$ for manganese (RIL75, VAN76a).

Cobalt is the central metallic ligand of the tetrapyrole-structured cyanocobaltamin, $C_{63}H_{88}O_{14}N_{14}PCo$ (Vitamin $B_{12}$). It is well established that this vitamin, as a free metabolite in sea water, regulates phytoplankton fertility and that a number of microorganisms require it in their environment. The presence of artificial radioactive isotopes of Co in sea water as a result of nuclear waste disposal makes it desirable to acquire an accurate knowledge of the distribution and behaviour of stable Co in the marine environment.

Zinc concentrations in sea water vary over a wide range (see Table 4.2). These variations have been explained as due to different reasons. For example, Spencer and Brewer (SPE71) have reported that concentrations of Zn in summer in the Gulf of Maine were slightly higher than in winter because of the influence of terrestrial runoff and the reduced mixing in the stratified water column. Significantly low concentrations of Zn above depths of 125m have been explained as due to biological removal (ZIR71). Zinc serves as a cofactor of the enzyme carbonic anhydrase.

Measurement of the concentration of Mn in the overlying sea water may help to explain the source and origin of manganese in deep ocean sediments. Manganese is also an essential element which is required for the life and growth of aquatic living species. Determination of its levels are therefore of interest to oceanographers and biologists.

Extremely low concentrations of these metals make preconcentration essential both for separating them from major interfering elements and to have concentrations within the sensitivities of different analytical techniques. A number of preconcentration procedures have been used for this purpose, for example, chelation-solvent extraction (JAN70, DAN78), chelating ion exchange (FLO76, HOL74), co-precipitation and cocrystallization (GOM78, BOY75) and electrolytic preconcentration (BAT77b, LUN74). Cobalt, zinc and manganese are often preconcentrated with other elements using non-specific multielement preconcentration methods.

In this study, cobalt, zinc and manganese have been preconcentrated with a fairly good specificity from sea - water using chitosan, followed by their determination by neutron activation. The chelating ability of chitosan has been previously studied by Muzzarelli (MUZ73b, MUZ77).

Chitosan (obtained from the Food, Chemicals and Research Laboratories, Ltd., 4900, 9th Avenue N.W., Seattle, U.S.A.) is produced from the natural product chitin by deacetylation with alkali. Chitin occurs widely in lower animals, fungi, etc. The dry arthropod exo-skeletons of crabs and lobsters contain from 20 to 50% chitin. Chitin is a polysacharide consisting of $\beta(1 \rightarrow 4)$ 2-acetamido-2-deoxy-D-glucose units, some of which are deacetylated. This natural polymer, called poly-N-acetyl-D-glucosamine can be formally considered a derivative of cellulose where the C-2 hydroxyl groups have been completely replaced by acetamido groups (see Fig. 4.1).

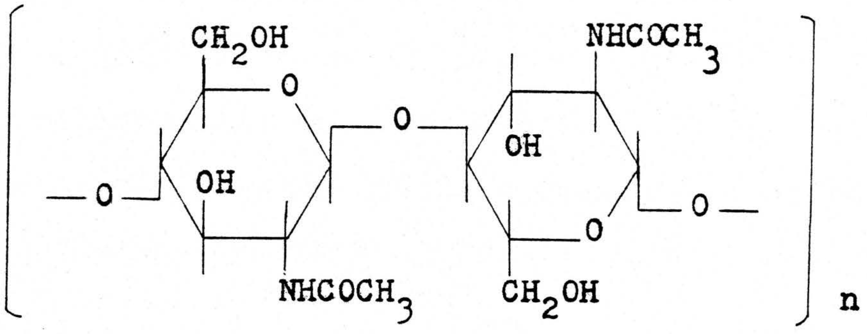


**Fig. 4.1 Structure of Chitin**

Chitosan was obtained as flakes. During the course of this study, three different batches of chitosan were used, and it was found that the elemental content and the collection efficiencies of trace elements vary significantly from batch to batch. These differences in collection efficiencies of trace elements, should mainly be due to the differences in available free amine groups (i.e. extent of **deacetylation) when complex formation is the mechanism of collection.**

## 4.2 OBJECTIVES

The main objective of this work is to develop analytical methods for preconcentrating cobalt, zinc and manganese from sea water using the deacetylated product of the naturally occurring polymer chitin, called chitosan. First, factors that could influence the recovery of the elements of interest have been investigated using radioactive tracers. These factors included, (i) pH of the solution, (ii) reaction time and (iii) the amount of chitosan. After establishing the conditions for best recoveries with tracer studies, the preconcentration methods have been applied to a few sea water samples collected from the Atlantic Ocean in order to demonstrate the applicability of the procedures to real samples.

## 4.3 LITERATURE SURVEY

### 4.3.1 Methods for Determining Cobalt, Zinc and Manganese in Sea Water

It has been stated earlier that manganese, cobalt and zinc are generally preconcentrated from sea water using multielement preconcentration schemes. For example, solvent extraction with pyrrolidine dithiocarbamate in methyl isobutyl ketone, followed by atomic absorption or x-ray fluorescence (PAU73, MOR68), chelating ion exchange with chelex-100 followed by atomic absorption or neutron activation analysis (RIL68a, HIR78), preconcentration on activated carbon followed by neutron activation analysis (VAN76a) or atomic absorption (KER73) have been used.

These preconcentration methods used in the past along with the methods of determination are summarized in Table 4.1. Some neutron activation analysis determinations are described below.

Lee <u>et al</u>. (LEE77) have used a column filled with a

1:1 mixture of chelex-100 resin (50-100 mesh) and Pyrex glass powder of the same mesh size, to concentrate, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Sc, U, V and Zn in sea water. Major interfering elements such as sodium, potassium, bromine and chlorine have been completely removed from the column with 100 ml of 0.01M nitric acid and the other elements with 50 ml of 4M nitric acid. Elemental concentrations have been determined by NAA in an aliquot of the concentrated eluate.

Fujinaga et. al. (FUJ73) have preconcentrated the trace metals V, Al, Cu, Mo, Zn and U in neutral waters by converting the dissolved trace metal ions into the oxine chelates at pH 5.2 and extracting the chelates with o-phenylphenol which is a liquid above 56°C and solidifies at room temperature. Concentrations have been determined by NAA of the precipitates obtained.

In a neutron activation analysis determination of Cu, Zn and Mn, Slowey and Hood (SLO71) have used diethyldithiocarbamate extraction to remove most of the interferences from the major elements. They have first oxidized the water samples with peroxydisulfuric acid.

A method based on preconcentration of manganese as the pyrrolidine-dithiocarbamate complex on a layer of active carbon and determination of the manganese in the carbon concentrate by neutron activation analysis has been reported by Wijkstra and van der Sloot (WIJ78). A similar procedure has been reported by van der Sloot (VAN76a) for Zn and Co.

Table 4.1 Survey of Methods used for Preconcentrating Cobalt, Zinc and Manganese

| Preconcentration Method | Determination Method | Elements | Reference |
|---|---|---|---|
| Sodium Diethyl Dithiocarbamate/Chloroform Extraction | NAA | Mn, Zn | SLO71 |
| Ammonium Pyrrolidine Dithiocarbamate(APDC)/ Methyl Isobutyl Ketone(MIBK) Extraction | AAS | Mn, Zn, Co | PAU73 |
| Ammonium Pyrrolidine Dithiocarbamate (APDC)/ Methyl Isobutyl Ketone (MIBK) Extraction | XRF | Mn, Zn, Co | MOR68 |
| MIBK - Nitric Acid successive Extraction | AAS | Zn | JAN78 |
| Oxine/o-Phenyl Phenol | NAA | Zn | FUJ73 |
| Coprecipitation with $MnO_2$ | POL | Co | HAR73 |
| Cocrystallization with 1-Nitroso-2-Naphthol | SPEC | Co | FOR66,<br>WEI60 |
| Coprecipitation with Iron(111) Hydroxide and Extraction with Diethyl Dithiocarbamate | NAA | Zn, Mn | RON62 |
| Chelating Ion Exchange with Chelex-100 | AAS | Mn, Zn, Co | RIL68a,<br>RIL68c |
| Chelating Ion Exchange with Chelex-100 | NAA | Mn, Zn | HIR78 |
| Ion Exchange with Tetraethylene Pentamine Resin | AAS | Co, Zn | ALB76 |
| Anion Exchange with Dowex 1 (AG1-X8) and Solvent Extraction with Tetrahydrofuran/ Monomethylether of Ethylene Glycol/HCl | AAS | Mn, Zn, Co | KOR75 |

Table 4.1 (continued)

| Preconcentration Method | Determination Method | Elements | Reference |
|---|---|---|---|
| APDC Extraction and Adsorption on Activated Carbon | NAA | Zn, Co | VAN76a |
| Photometric Determination Based on Catalytic Action of Mn on the Reaction of Oxidation of Leuco Base, Crystal Violet by Periodate Ion | | Mn | KES72 |
| Direct Determination by Graphite Furnace Atomic Absorption Spectroscopy-Matrix Modification and Selective Volatilization has been used | | Mn, Zn | STU79 |
| Direct Determination by Anodic Stripping Voltametry | | Zn, Co | SMI71,<br>ZIR72 |

NAA - Neutron Activation Analysis

AAS - Atomic Absorption Spectrometry

XRF - X-ray Fluorescence

POL - Polarography

SPEC - Spectrophotometry

### 4.3.2 Cobalt, Zinc and Manganese Concentrations in Sea Water

Some of the values reported in literature for the concentrations of cobalt, zinc and manganese are summarized in Table 4.2.

Table 4.2 Cobalt, Zinc and Manganese Concentrations in Sea Water

| Origin | Mn | Co | Zn | Reference |
|---|---|---|---|---|
| | Concentration, $\mu g\ L^{-1}$ | | | |
| Atlantic, Coastal | 1.2 | | 1.7 | STU79 |
| Northeast Atlantic | 1.0-5.0 | | 1.0-22.0 | RIL72 |
| North Indian Ocean and Arabian Sea | 0.69-1.29 | 0.005-0.092 | 3.9-48.4 | TOP69 |
| Menai Straits, U.K. | 1.86 | 0.07 | 25.2 | MOR68 |
| Botany Bay, Australia | | 0.25 | | BAT77b |
| North Central Pacific Ocean | | 0.24 | | ARM71 |
| North West Coast, USA | | 0.13 | | ARM71 |
| Gulf of Mexico,<br>- Coastal<br>- Open Sea | <br>0.18-19<br>0.05-0.88 | | <br>2.1-10<br>0.2-15 | SLO71 |
| North Western Atlantic Ocean | | 0.05-1.04 | 3.2-13.3 | ALB76 |
| North Eastern Atlantic | 0.12-1.0 | | 0.6-5.2 | CHE74 |
| Indian Ocean | 0.23 | | 1.4 | CHE74 |

These results show that the concentrations of Mn, Co and Zn in different oceans are relatively variable. Within one ocean they can be varied by one to two orders of magnitude at different depths.

## 4.4 EXPERIMENTAL

### 4.4.1 Purification of Chitosan

Chitosan flakes, dried in an oven for about two days at 60°C were powdered using a micromill, which has a blade rotating at a speed of 20,000 rpm. Cold water was passed through both the upper and lower chambers of the mill during operation. Capacity of the micromill was about 30-35 mL and about 1 h milling was needed to prepare 1 g of 100-200 mesh chitosan. Chitosan with different mesh sizes were obtained by sieving through nylon sieves. It was possible to remove sodium, calcium and potassium present in chitosan almost completely by washing with deionized water, about two times for 1 h periods using a mechanical shaker. Chitosan powder was purified by washing with a 0.1M EDTA solution at pH 10 for about 15 min, followed by two washings with deionized water. Zinc and copper could be completely removed by this process; however cobalt could only be removed partially. Elemental concentrations in chitosan are presented in Table 4.3. Attempts to remove manganese from chitosan were not successful. Acid washing of chitosan was not successful because it tends to dissolve and give a jelly even with mineral acids. However, the blank manganese value for chitosan was well below the concentrations determined in sea water.

Table 4.3 Elemental Concentrations in Chitosan

$\mu g\ g^{-1}$

| Element | Chitosan, Unwashed | Chitosan, EDTA Washed |
|---|---|---|
| Al | 6.87 | 2.76 |
| Br | 3.16 | 2.48 |
| Cl | 3.25 | 1.71 |
| Co | 0.257 | 0.191 |
| Cr | 4.44 | 3.89 |
| Cu | 3.15 | N.D. |
| Fe | 183 | 135 |
| I | 0.452 | 0.370 |
| Mg | 87.7 | 43.1 |
| Mn | 1.36 | 1.57 |
| Na | 1.63 | 0.829 |
| Sc | 6.97[a] | 5.65[a] |
| V | 14.1[a] | 8.19[a] |
| Zn | 5.30 | N.D. |

a - $ng\ g^{-1}$

N.D. - not detected

### 4.4.2 Selection of Radioactive Tracers

$^{56}$Co, $^{65}$Zn and $^{54}$Mn tracers were obtained from the Radiochemical Centre, Amersham, Buckinghamshire, England, as solutions in 1M HCl, at a concentration of 100 $\mu g\ mL^{-1}$. The reason for selecting non-neutron activation products, namely $^{56}$Co and $^{54}$Mn, was to use them in actual determinations of these elements in real samples and to make necessary yield corrections to improve accuracy. For zinc, $^{65}$Zn was the only available radio-tracer. However, since none of these tracers could be obtained in the carrier free state, it was necessary to calculate the amount of $^{59}$Co, $^{64}$Zn and $^{55}$Mn present in the above tracer solutions by irradiating and counting aliquots of them. Carrier-free tracers with high specific activities would be ideal for this purpose.

### 4.4.3 Reagent Blanks

The concentrationsof Co, Zn and Mn in the ultrex reagents used are presented in Table 4.4.

Table 4.4 Co, Zn and Mn Concentrations in Ultrex Reagents Used, ppb

| Element | Reagent<br>HCl | <br>$HNO_3$ | <br>$NH_4OH$ |
|---|---|---|---|
| Co | 1 | $<0.1$ | $<1$ |
| Zn | $<1$ | 2 | $<1$ |
| Mn | 0.3 | 0.5 | 0.2 |

Contribution from these reagents to the concentrations of the three elements determined in sea water were found to be insignificant.

### 4.4.4 Preparation of Sea Water Samples

Sea water samples were filtered through 0.4 µm Nuclepore Polycarbonate membranes, acidified with ULTREX hydrochloric acid to about pH 1.5-2 immediately after collection. The samples were transferred to our laboratory and irradiated with UV light for 3 h to destroy organic matter.

### 4.4.5 Gamma-ray Spectrometry

For tracer experiments, a NaI(Tl) detector connected to Canberra 8100 /e model 4096 channel pulse height analyzer (PHA) was used. Neutron activated samples were counted with the Ge(Li) detector connected to TN-11 multichannel PHA.

### 4.4.6 Different Procedures to Collect Trace Metals with Chitosan

Different procedures were tested for using chitosan to collect trace metals. These included ultrasonic shaking, magnetic stirring, mechanical shaking and co-precipitation with chitosan.

Mechanical shaking and magnetic stirring showed no difference in collection efficiencies, when used for the same length of time. When ultrasonic shaking was used, it was found that chitosan tended to swell even after about one-half hour making the filtration difficult and time consuming. This method was first thought to be more efficient because of the high penetration power of trace metals into the structure of chitosan. However, this method was not used due to the above mentioned reason.

Coprecipitation of trace elements were attempted by adding chitosan dissolved in acetic acid to sea water, while stirring the solution, and at the same time adding ammonium hydroxide to the solution to precipitate chitosan. However, this method was found to be very tedious and time consuming. Precipitate was collected by centrifugation, was dried under vacuum for 2-3 d to obtain a suitably dried product for irradiation. Moreover, it was found that a large amount of sodium is collected under these conditions; precipitates had to be washed with deionized water after freeze drying step to remove sodium.

### 4.4.7 Preliminary Experiments with Sea Water

The trace elements that could be concentrated with chitosan from sea water were first investigated by carrying out experiments with 1L samples of sea water, using 200 mg of 100-200 mesh purified chitosan(prewashed with 0.1M EDTA solution and deionized water). Reactions were carried out at pH 2.5, 5.5, 8 and 10, using a reaction time of 1 h. It was observed that in the experiment carried out at pH 2.5 chitosan had partially dissolved. Chitosan was collected on Whatman Number 1 filters, air dried and sealed in small polyethylene vials. Filtration was found to be very difficult and slow in the experiments at pH 2.5. Samples were first irradiated for 10 min and counted for 10 min after a decay of 3 min. However, samples from both the experiments carried out at pH 2.5 and pH 5.5 could not be counted for more than one hour because of the high activity produced by $^{38}$Cl. Nuclides observed with the experiments at pH 8 and 10 were, $^{128}$I, $^{80}$Br, $^{38}$Cl, $^{54}$Mn, $^{28}$Al, $^{52}$V and $^{24}$Na. At pH 8, an increase in I, Br, Cl, Mn, V, above the blank was observed. At pH 10, an increase was observed for all these except for V. In the other two experiments, an increase of concentrations of Br and Cl was observed.

Samples were then irradiated for 16 h, and counted after a decay of about 1 d and 8-10 d.

In the experiment at pH 2.5, an increase in concentration was observed for Br and Na.

At pH 5.5, peaks due to $^{239}$Np were observed in addition to those observed during short irradiations. This is due to concentration of uranium. A slight increase in Na concentration was also observed.

At pH 8, an increase in Zn (both the peaks, at 439 keV of $^{69m}$Zn after a 1 d decay and at 1115 keV of $^{65}$Zn after 8-10 d decay were used) Co, U($^{239}$Np peaks) and Ni($^{58}$Co peaks) were observed.

In the experiment at pH 10, Co concentration was found to be increased, but not the Zn concentration.

From the above experiments it was decided to investigate in detail the feasibility of using chitosan to concentrate cobalt, zinc, manganese and vanadium from sea water.

### 4.4.8 General Procedure for Tracer Studies

One millilitre of the tracer with a desired activity was added to 100 mL of sea water in a polyethylene beaker. After about 30 min, the pH of the solution was adjusted to a desired value with $HNO_3$ or $NH_4OH$. The solution was transferred into a 250 mL Erlenmeyer flask, preweighed amount of 200-400 mesh chitosan was added, the flask was stoppered and the solution was shaken for a desired time using the mechanical shaker. Chitosan was collected by filtration on a Whatman Number 1 filter and transferred to a medium size polyethylene vial for counting. Recoveries were calculated by comparing the photopeak areas of the samples with a 1 mL aliquot of the tracer solution.

## 4.5 PRECONCENTRATION OF COBALT

As has been mentioned before, the factors which can influence the recovery of cobalt from sea water samples were first investigated using radioactive tracer. The optimized conditions were then applied to determine the cobalt concentration in sea water.

### 4.5.1 The pH of the Medium

Experiments were carried out with 100 mL samples of sea water, into which 0.5 µg of $^{56}Co$ tracer solution was added. A shaking time of 1 h and 100 mg of chitosan were used. Results obtained in these experiments are presented in Table 4.5.

Table 4.5 Effect of pH on $^{56}$Co Tracer Recovery

| pH | Recovery, %* |
|---|---|
| 4 | 23 ± 0.6 |
| 6 | 30 ± 0.8 |
| 7 | 33 ± 0.7 |
| 8 | 68 ± 1.1 |
| 8.5 | 84 ± 1.8 |
| 9 | 86 ± 1.7 |
| 9.5 | 86 ± 1.7 |
| 10 | 70 ± 1.6 |

* - the given deviations are due to counting statistics

The increase in recovery up to 9.5 (constant from 8.5 - 9.5) should be due to the increased amount of free amino groups in chitosan and the increased stability of the complex formed. Decreased recovery at pH 10 could be due to the predominant existence of Co as its hydroxy complex, so that the collection of cobalt with chitosan depends on the **stability constants of hydroxy and chitosan** complexes of Co.

### 4.5.2 Amount of Chitosan

To investigate the effect of amount of chitosan on the recovery of cobalt, two experiments were carried out with 100 mg and 200 mg of chitosan for 0.5 µg of $^{56}$Co in 100 mL sea water. Reactions were carried out at pH 9 and the shaking time was 1 h; the results are presented in

Table 4.6.

Table 4.6 Variation of $^{56}$Co Tracer Recovery with Amount of Chitosan

| Amount of Chitosan, mg | Recovery, %* |
|---|---|
| 100 | 86 ± 1.6 |
| 200 | 88 ± 1.4 |

* - the given deviations are due to counting statistics

This increase in recovery of cobalt obtained when the amount of chitosan is doubled is not significant when the radioactive counting statistics are taken into consideration.

### 4.5.3 Reaction Time

Effect of shaking time on the recovery of cobalt was investigated using 0.1 μg cobalt per 100 mL of sea water samples. Experiments were carried out at pH 9 using 100 mg of chitosan and the results are presented in Table 4.7.

Table 4.7 Effect of Shaking Time on $^{56}$Co Tracer Recovery

| Shaking Time | Recovery, %* |
|---|---|
| 20 min | 86 ± 3.1 |
| 1 h | 86 ± 3.2 |
| 2 h | 86 ± 3.2 |

* - the given deviations are due to counting statistics

At this concentration of cobalt, the recovery is independent of shaking time. However, when the concentration was reduced to 0.01 µg per 100 mL, which is of the same order of concentration reported in literature for cobalt, the recovery was only 60%, which didn't increase with increasing shaking time of up to 6 h.

### 4.5.4 Determination of Cobalt in Sea Water

Three sea water samples collected from the Atlantic Ocean were analyzed for cobalt. To one litre of filtered and UV irradiated sea water, 0.05 µg of the $^{56}$Co tracer was added. After about one-half hour, pH of the solution was adjusted to 9 with ULTREX $NH_4OH$. The solution was transferred to two 1L Erlenmeyer flasks (500 mL of solution to each); 100 mg of 200-400 mesh, EDTA washed chitosan were added to each flask; the flasks were stoppered and shaken for 1 h in the mechanical shaker. Chitosan was collected on a Whatman Number 1 filter paper, dried in an oven at about 60°C for approximately 3 h. Dried chitosan was sealed in a polyethylene bag. Chitosan recovery was greater than 98%. Tracer recovery in each experiment was calculated by comparing the photopeak areas (counted with NaI(Tl) detector) of samples with that of a standard containing 0.05 µg of cobalt. Samples, 0.05 µg of $^{56}$Co tracer spiked on Nuclepore filter, and a cobalt standard prepared from atomic absorption standard and spiked on a Nuclepore filter, and a chitosan blank were irradiated for 16 h at a flux of $5 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$. Samples were counted after a decay of 2 - 3 w using the

Ge(Li) detector connected to TN-11 multichannel analyzer. Concentration of cobalt in sea water was calculated, after making corrections for the contributions from the blank chitosan and the added tracer which was not carrier free. Photopeaks at 1173 keV and 1332 keV of $^{60}Co$ were used in calculations. A typical gamma-ray spectra obtained under these conditions is presented in Figure 4.2.

The collection efficiency of cobalt under the conditions used varied from 50-58%, which agrees with the lowest concentration studied in the tracer experiments. Lower recoveries obtained at the concentration level of sea water would probably be due to decrease in reaction rate; diffusion of ion to the surface of chitosan being the rate determining step.

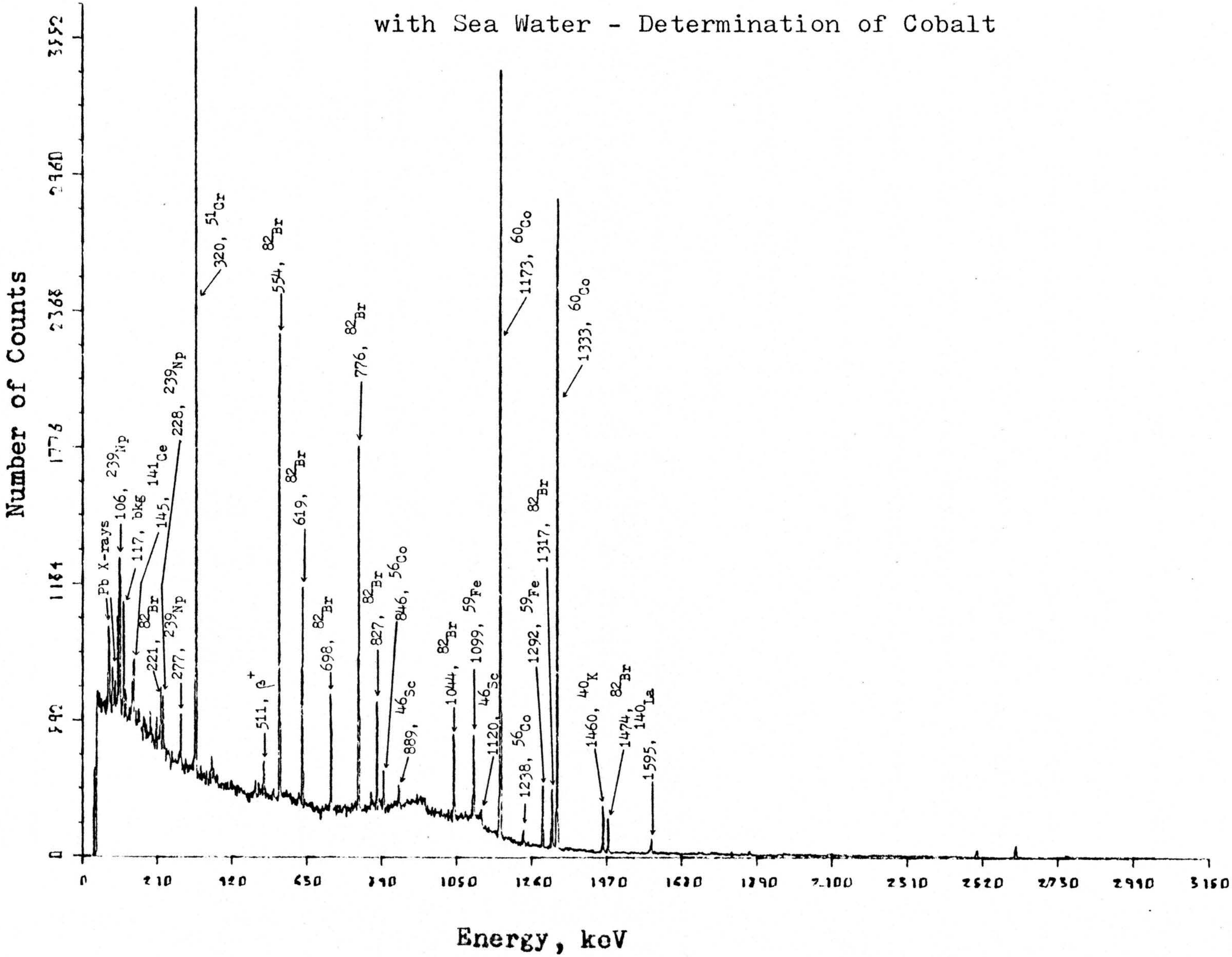
Necessary recovery corrections were made for each sample. Concentrations of cobalt for sea water samples collected from two different stations are given in Table 4.8.

Table 4.8 Cobalt Concentration in Sea Water

| Station Number* | Depth, m | Co Concentration, $\mu g\ L^{-1}$ |
|---|---|---|
| 2 | 1 | 2.11 |
| 5 | 1 | 0.229 |
| 5 | 20 | 1.25 |

* - see Fig. 2.1

Fig. 4.2 Gamma-ray Spectrum of a Chitosan Sample Reacted with Sea Water - Determination of Cobalt



Variation in the cobalt content of sea water is evident from the above table. Station 2 is close to shore, and its cobalt level may be influenced by increased input from nearby land. The concentration of Co in sea water collected at **1m** depth (station number 5) is typical of the values reported in literature. Cobalt content was found to increase with depth at the same station; more samples need to be collected and analyzed before oceanographic interpretations can be made.

## 4.6 PRECONCENTRATION OF ZINC

### 4.6.1 The pH of the Medium

Effect of varying pH of the medium on the recovery of zinc was studied using 1 µg of $^{65}$Zn tracer per 100 mL of sea water, and 100 mg of chitosan. A shaking time of 1 h was used. Results of these experiments are presented in Table 4.9.

Table 4.9 Effect of pH on $^{65}$Zn Tracer Recovery

| pH | Recovery, %* |
|---|---|
| 4 | 59 ± 0.7 |
| 6 | 61 ± 0.8 |
| 7 | 62 ± 0.8 |
| 7.5 | 60 ± 0.8 |
| 8 | 73 ± 0.7 |
| 8.5 | 66 ± 0.6 |
| 9 | 34 ± 1.1 |

* - the given deviations are due to counting statistics

From this set of experiments, it was decided to carry out the experiments at pH 8. Low recovery at pH 9 can be explained as due to predominant existence of zinc as $Zn(OH)_2^o$ at this pH.

### 4.6.2 Amount of Chitosan

Experiments were carried out with 1 µg of $^{65}Zn$ tracer per 100 mL of sea water and with varying amounts of chitosan. Reaction time was 1 h and the results obtained are given in Table 4.10.

Table 4.10 Variation of $^{65}Zn$ Recovery with the Amount of Chitosan

| Amount of Chitosan, mg | Recovery, %* |
|---|---|
| 25 | 51 ± 0.6 |
| 50 | 65 ± 0.8 |
| 100 | 73 ± 0.8 |
| 200 | 73 ± 0.8 |

* - the given deviations are due to counting statistics

These results show that the recovery drops significantly when the amount of chitosan used is 25 mg, and it remains constant when 100-200 mg of chitosan is used.

### 4.6.3 Reaction Time

**Table 4.11** gives the variation in $^{65}Zn$ tracer recoveries with the shaking time. These experiments were carried out with 100 mg chitosan and at a Zn concentration of 0.2 µg per 100 mL of sea water.

Table 4.11 Effect of Shaking Time on $^{65}$Zn Tracer Recovery

| Shaking Time | Recovery, %* |
|---|---|
| 20 min | 60 ± 1.8 |
| 1 h | 71 ± 2.3 |
| 5 h | 68 ± 2.1 |

* - the given deviations are due to counting statistics

Since only 60% recovery was obtained with a shaking time of 20 min, it was decided to use a 1 h shaking time. The slight variation in recovery with 5 h shaking time can be accounted as due to variation in counting statistics.

### 4.6.4 Determination of Zinc in Sea Water

**Five** sea water samples collected from the **Atlantic Ocean** were analyzed for zinc. To 500 mL of filtered, UV irradiated sea water 0.1 µg of $^{65}$Zn tracer solution was added and the pH was adjusted to 8 with ULTREX ammonium hydroxide. The solution was transferred to 1L Erlenmeyer flask, 200 mg of 200-400 mesh, EDTA-washed chitosan were added. The flask was stoppered and shaken for 1 h in the mechanical shaker. Chitosan was collected on a Whatman Number 1 filter, dried in an oven at about 60°C for 3 h and sealed in a polyethylene bag. Chitosan recovery was more than 98%. Recoveries of the $^{65}$Zn tracer were calculated by comparing the 1115 keV photopeak areas of the samples with an aliquot of the tracer solution containing 0.1 µg of zinc. Recoveries of the tracer in these experiments varied from 63% to 69%. Samples, an aliquot of the tracer solution spiked on a Nuclepore filter and a zinc standard spiked on Nuclepore filter, were irradiated for 16 h at a flux of $5 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$. In the calculations of zinc concentration, the 439 keV photopeak of $^{69m}$Zn could be used. However, because of the high Compton contribution from $^{82}$Br, this peak was not used. The 1115 keV photopeak of $^{65}$Zn after correcting for the contribution from the added tracer (for both the original activity and the activity after re-irradiation) was used to estimate the zinc concentration in sea water. Concentrations of zinc for sea water samples collected from five different stations (see Fig. 2.1) at a depth of 1 m are presented in Table 4.12. Figure 4.3 represents a gamma-ray spectrum obtained under the above mentioned conditions.

Table 4.12 Zinc Concentrations in Sea Water

| Station Number | Zinc Concentration μg L$^{-1}$ |
|---|---|
| 2 | 3.76 |
| 3 | 3.05 |
| 4 | 3.80 |
| 5 | 6.93 |
| 6 | 4.84 |

These results show that the Zn concentration of these surface waters are highly variable. The concentrations are lower in Cabot Strait, compared to that in the Gulf of St. Lawrence. They do not have any direct relationship with the salinity. The observed variations probably indicate the importance of biological organisms

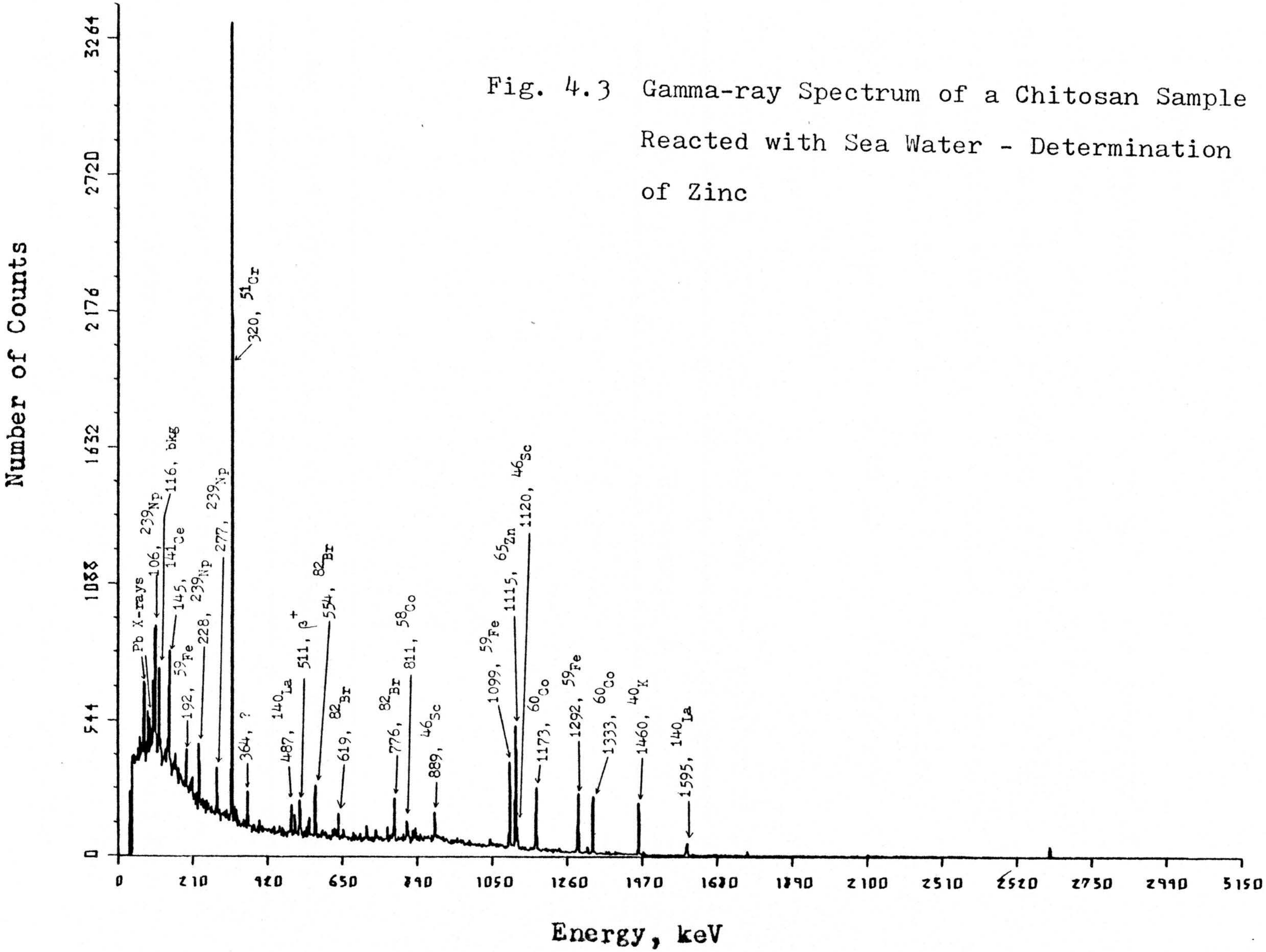


Fig. 4.3 Gamma-ray Spectrum of a Chitosan Sample Reacted with Sea Water - Determination of Zinc

(ZIR71) in controlling the Zn concentrations. However, it is important that more samples be analyzed to draw more definite conclusions.

## 4.7 PRECONCENTRATION OF MANGANESE

### 4.7.1 The pH of the Medium

To investigate the effect of pH on the recovery of manganese, experiments were carried out with 100 mL samples of sea water, into which 0.5 μg of the $^{54}Mn$ tracer solution was added. One hundred mg of chitosan and a shaking time of 1 h were used. The pH of the solution was varied from 4 to 10 and the results are presented in Table 4.13.

Table 4.13 Effect of pH on $^{54}Mn$ Tracer Recovery

| pH | Recovery, %* |
|---|---|
| 4 | 1 ± 0.3 |
| 6 | 1 ± 0.4 |
| 8 | 2 ± 0.5 |
| 9 | 7 ± 0.6 |
| 9.5 | 76 ± 1.2 |
| 10 | 79 ± 1.3 |

* - the given deviations are due to counting statistics

The high recoveries obtained at pH 9.5 and 10 are mainly due to coprecipitation of hydrous manganese oxide and $Mn(OH)_2$ with chitosan. Extremely low recoveries obtained in the pH range from 6 to 9 compared to those of cobalt and zinc indicate that the contribution from a complex formation mechanism with chitosan is very low for manganese. To investigate the precipitation of manganese hydroxide in the absence of chitosan, an experiment was carried out at pH 9.5 with no chitosan, and a recovery of only 14% was obtained. As will be mentioned later, manganese is also coprecipitated with magnesium hydroxide; however, magnesium hydroxide is not precipitated from sea water at this pH. This indicates that the collection of manganese at this pH is mainly due to coprecipitation with chitosan. It was found that at pH 10 less than 10 µg of magnesium was precipitated from 100 mL of sea water.

Two experiments were carried out at pH 10.2 with no chitosan, and at two different manganese concentrations, 0.02 µg and 0.5 µg Mn per 100 mL of sea water. Recoveries of 97% were obtained in each of these experiments. This is due to the coprecipitation of manganese with magnesium hydroxide. At pH 10.2 about 40 mg of magnesium was precipitated from 100 mL of sea water.

### 4.7.2 Amount of Chitosan

The amount of chitosan was varied from 100 mg to 400 mg in experiments carried out at pH 10, with 0.5 µg of Mn tracer per 100 mL of sea water. Results of these experiments are presented in Table 4.14.

Table 4.14 Variation of $^{54}$Mn Tracer Recovery with the Amount of Chitosan

| Amount of Chitosan, mg | Recovery, %* |
|---|---|
| 100 | 79 ± 0.9 |
| 200 | 86 ± 0.9 |
| 400 | 86 ± 0.9 |

* - the given deviations are due to counting statistics

This observed increase in Mn recovery **with increasing amount of chitosan is mainly due to the increase in total surface area of chitosan available for adsorption of** previously mentioned manganese compounds.

### 4.7.3 Reaction Time

The shaking time was varied from 1 h to 4 h, in a series of experiments carried out at pH 10, with 100 mg of chitosan and 0.5 µg of manganese tracer solution per 100 mL sea water. Results of these experiments are presented in Table 4.15.

Table 4.15 Effect of Shaking Time on $^{54}$Mn Tracer Recovery

| Shaking Time | Recovery, %* |
|---|---|
| 1 h | 79 ± 0.9 |
| 2 h | 80 ± 0.9 |
| 4 h | 81 ± 0.9 |

* - the given deviations are due to counting statistics

No significant changes in recovery with increasing shaking time were observed. From these results it was decided to use a 1 h shaking time in future experiments.

### 4.7.4 Determination of Manganese in Sea Water

Applicability of the method developed, was studied by analyzing two sea water samples collected from the Atlantic Ocean. To 500 mL of filtered, UV irradiated sea water sample in a 600 mL beaker 0.1 μg of Mn tracer was added. After about 30 min, the pH of the solution was adjusted to 10, using ULTREX $NH_4OH$. Water sample was transferred to a 1L Erlenmeyer flask and 100 mg of 200-400 mesh chitosan were added. The flask was stoppered and was shaken for 1 h using the mechanical shaker. Chitosan was collected on a Whatman Number 1 filter and washed with 2 x 20 mL of deionized water. Dried chitosan was sealed in a precleaned polyethylene bag. Chitosan recovery was more than 98%. Manganese recovery was calculated by comparing the 843 keV photopeak areas of the samples with that of a 0.1 μg $^{54}$Mn standard. Recoveries around 73% were obtained in these experiments. Samples were irradiated for 10 min and counted with the Ge(Li) detector for 10 min after a 3 min decay. An aliquot of $^{54}$Mn tracer solution spiked on Nuclepore filter, a manganese standard on Nuclepore filter and a chitosan blank were also irradiated and counted under the same conditions. Manganese concentration was calculated by comparing the areas of 1811 keV photopeak of the samples (corrected for the blank and the contribution from the tracer) with that of a manganese standard.

Two sea water samples were analyzed from station number 3, and the concentrations obtained were 1.21 and 1.03 $\mu$g $L^{-1}$. Figure 4.4 represents a gamma-ray spectrum obtained under the above mentioned conditions.

## 4.8 Detection and Determination Limits

The detection and determination limits for the elements Co, Zn and Mn in sea water, calculated using the Currie's method (CUR68) are given in Table 4.16.

Table 4.16 Detection and Determination Limits $\mu$g $L^{-1}$

| Element | Detection Limit | Determination Limit |
|---|---|---|
| Co | 0.034 | 0.11 |
| Zn | 1.22 | 4.13 |
| Mn | 0.22 | 1.17 |

For Co, the concentrations found in sea water were above the determination limit. For Zn and Mn some determined concentrations lie between the detection and determination limits, and some above the determination limit.

## 4.9 Reduction of Na, Cl and Br Content

One of the main advantages of preconcentration with chitosan was the reduction of Na, Cl and Br content of sea water which made the NAA determination of Co, Zn and Mn possible without spectral interferences. The concentrations of Na, Cl and Br were reduced by factors of the order of magnitudes, $10^6$, $10^5$ and $10^3$ respectively, in all three cases.

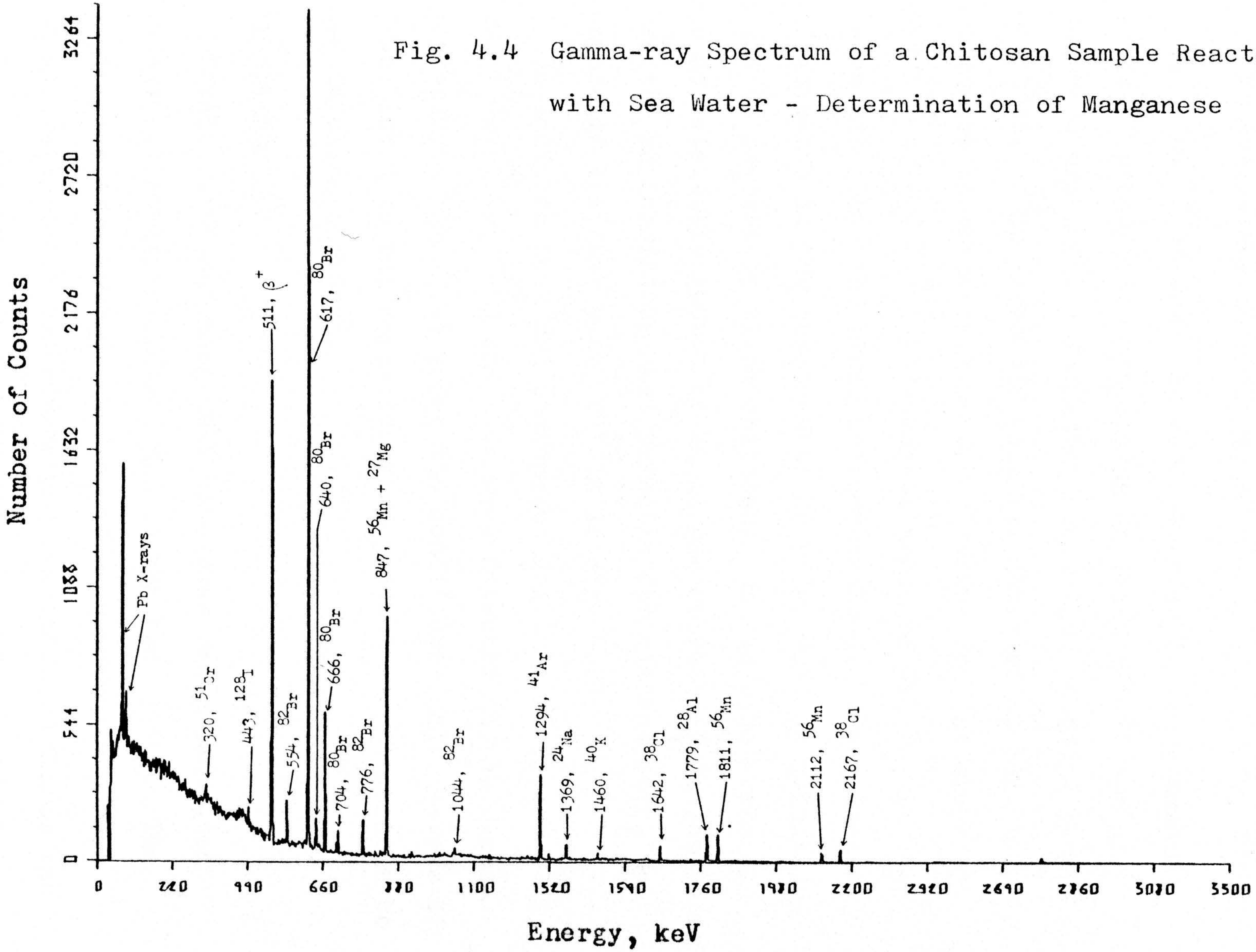


Fig. 4.4 Gamma-ray Spectrum of a Chitosan Sample Reacted with Sea Water - Determination of Manganese

## 4.10 Other Elements Preconcentrated with Co, Zn and Mn

Photopeaks due to nuclides of $^{82}$Br, $^{141}$Ce, $^{51}$Cr, $^{59}$Fe, $^{140}$La, $^{24}$Na, $^{239}$Np and $^{46}$Sc were detected in the gamma-ray spectra of precipitate containing Co (Figure 4.2) and Zn (Fig. 4.3) under the irradiation, decay and counting conditions used. $^{58}$Co (from Ni) peak was detected in Fig. 4.3. An increase in concentration was observed for the elements Ce, Ni($^{58}$Co) and U($^{239}$Np), whereas those of Cr, Fe, La and Sc were not above the blank chitosan values. The presence of $^{60}$Co peaks in the spectrum of Zn (Fig. 4.3) is mainly due to the Co present in blank chitosan. It is also evident that no detectable amount of Zn is concentrated from sea water under the pH conditions most suitable for concentrating Co (absence of 1115 keV peak of $^{65}$Zn in Fig. 4.2).

In addition to $^{56}$Mn, photopeaks due to nuclides of $^{28}$Al, $^{80}$Br, $^{38}$Cl, $^{51}$Cr, $^{128}$I and $^{24}$Na were detected in the gamma-ray spectrum (Fig. 4.4) under the conditions used. Levels of Al, Cr, and I in the coprecipitated product are comparable to those in blank chitosan.

## 4.11 CONCLUSION

Cobalt, zinc and manganese have been preconcentrated from sea water with chitosan, and determined by NAA. The methods developed involve the reaction of chitosan powder with sea water under pre-determined reaction conditions (pH, amount of chitosan and reaction time) to obtain maximum possible recoveries. The methods developed are simple and a number of samples can be analyzed at the same time. Preconcentration with chitosan considerably reduces the major problem associated with analysis of trace metals in sea water, namely the interferences from the major activities of $^{24}$Na, $^{38}$Cl, $^{80}$Br and $^{82}$Br. Both preconcentration of trace elements and reduction of interfering elements are achieved in one step in the methods developed using chitosan. In this respect, the chitosan methods are superior to other preconcentration methods (such as those using chelex-100) where two separate steps (one for preconcentrating trace elements and the other for removing interfering elements) are required.

Chitosan, being an organic matrix is superior to inorganic reagents such as $Fe(OH)_3$ when NAA is the method of determination.

The possibility of performing direct NAA for trace elements on chitosan makes this method simpler than solvent extraction methods where evaporation of the solvent is needed to obtain the product in a physical form (viz. solid) suitable for NAA.

The number and the amounts of elements present in blank chitosan, as well as the capacities for collecting trace metals by chitosan have been found to vary from batch to batch.

# 5. DETERMINATION OF VANADIUM IN SEA WATER

An analytical method has been developed for the determination of vanadium in sea water based on preconcentrating vanadium with magnesium hydroxide followed by neutron activation. An attempt made to develop a method to concentrate vanadium from sea water with chitosan has also been described here, although this method was found to give poor yields. Various factors that can influence the recovery of vanadium with magnesium hydroxide have been studied. The method has been applied to sea water samples collected from **the Atlantic Ocean** and vanadium has been concentrated with an efficiency greater than 95%. A precision of 6.5% and a detection limit of 0.38 μg V $L^{-1}$ sea water have been achieved.

## 5.1 INTRODUCTION

Vanadium is an element of considerable interest in environmental pollution studies. Environmental mobilization of vanadium and its compounds occur by a number of means in the net transport of vanadium into oceans. Some of these transport processes include terrestrial runoff, industrial emissions, atmospheric washout (vanadium in air comes predominantly from industry, as there are no significant natural sources), river transport, and oil spills, resulting in a complex ecological cycle (KLE75). Although the possibility of vanadium deposition due to oil spillage has been discussed (ZER66), no evidence is yet available to confirm the release of vanadium from oil. Since crude oils are rather rich in vanadium (50-200 ppm), it is not inconceivable that some vanadium should be released upon the contact of oil with sea water (NAS74). At low levels, vanadium is an essential element for man and many other biological species, but at somewhat higher levels it is quite toxic. In the aquatic environment it is well known that certain Ascidians and Tunicates concentrate vanadium (GOL51). A concentration factor of 280,000 times has been found in certain marine organisms compared to sea water (NOD38).

Under normal aerobic conditions, thermodynamically most probable species of vanadium are $VO_3^-$ and $HVO_4^{2-}$ (SCH61) although vanadyl cation has been detected at a level of ca. 1% of the total vanadium (KAL63). However, isotopic exchange between V(V) and V(IV) has been reported to be rapid (FUR52, TEW50). Vanadium (III) exists at extremely low concentrations in natural waters except for unusual waters with very high acidity. Occurrence of polyanions is negligible at the concentration levels of sea water, since polyanions are formed at concentrations higher than $10^{-4}$ M (SCH61).

Because of its low concentration, determination of vanadium in sea and natural waters is usually achieved in combination with a preconcentration technique. Determination and preconcentration techniques used in the past include atomic absorption with solvent extraction (CHA70, CRU71), spectrophotometry with ion exchange - coprecipitation (CHA66b) or with ion exchange alone (KIR72), neutron activation with ion exchange - solvent extraction (LIN70) and x-ray fluorescence with solvent extraction (MOR68).

## 5.2 OBJECTIVES

The aim of the present work is to develop a suitable method for determining vanadium in sea water by NAA. Since vanadium produces only one nuclide, namely $^{52}V$ (half-life = 3.75 min), on thermal neutron activation and since vanadium cannot be determined in sea water by INAA due to interferences from the major elements, Na, Cl and Br, it is necessary to preconcentrate vanadium from sea water prior to NAA. The preconcentration method must be quantitative and must reduce interfering activities (e.g. those of $^{24}Na$, $^{38}Cl$ and $^{80}Br$) significantly. Two different approaches have been made to preconcentrate vanadium.

The first method utilizes the natural chelating polymer, chitosan, to preconcentrate vanadium. Several experiments have been carried out to evaluate the feasibility of using chitosan. For reasons described later on, chitosan has been found to be ineffective for quantitative recovery of vanadium from sea water.

Consequently, a second method has been developed. This method is based on coprecipitating vanadium with magnesium hydroxide which is formed when alkali is added to sea water. The method is simple, quantitative, and fairly specific. Concentration of vanadium in sea water is easily determined using this method followed by NAA.

## 5.3 LITERATURE SURVEY

### 5.3.1 Methods for Determining Vanadium in Sea Water

Solvent extraction (CHA70, NIS73), anion or chelating exchange (RIL68b, RIL72, KIR72, MUZ74) methods have been widely used in preconcentrating vanadium from sea water, followed by its determination by spectrophotometry or atomic absorption spectrometry.

Nishimusa et al. (NIS73) have reacted the vanadium with 4-(2-pyridyl)-azo-resorcinal and extracted the resultant complex with chloroform after converting it to an ion pair with tetradecyl-dimethyl-benzyl ammonium chloride. Extraction of other ions was prevented by complexing them with complexone and cyanide ion.

Riley and Taylor(RIL68b) have used chelating resin chelex-100 for concentrating vanadium from sea water at pH5; elution has been carried out with 2M ammonium hydroxide solution. Vanadium has been determined photometrically with 3,3'-diaminobenzidine reagent.

Kirijma and Kuroda (KIR72) adsorbed the element as a thiocyanate complex on the thiocyanate form of Dowex-1 and subsequently eluted it with hydrochloric acid; determination has been done colorimetrically with 4-(2-pyridylazo)resorcinal.

Muzzarelli (MUZ74) has used chitosan to preconcentrate vanadium from sea water in its determination by atomic absorption spectrometry.

A method for vanadium based on absorption of ammonium pyrrolidine dithiocarbamate complex on activated carbon followed by neutron activation has been reported by van der Sloot (VAN76a).

Coprecipitation with iron (III) hydroxide has been used to preconcentrate vanadium from sea water (CHA66b) and quantitative recoveries have been obtained over the pH range 3.5-8. Vanadium has been separated from iron and other elements by ion-exchange, using hydrogen peroxide as a very selective eluting agent. The element has been determined photometrically with diaminobenzidene. Same authors have reported that quantitative coprecipitation can also be achieved with chromium (111) hydroxide at pH 6.5 and with hydrous manganese dioxide at pH 3.2-5.3.

In a spectrographic determination of vanadium in sea water, Black and Mitchell (BLA52) have used a method based on coprecipitation of vanadium with a mixed precipitate obtained by adding tanin, thioanilide, oxine, $Fe^{3+}$ and $Al^{3+}$ ions.

Chau and Chan (CHA70) have investigated 13 chelating agents for their suitability for extraction of vanadium for atomic absorption spectrometry. Dichloro-oxine has been found to extract V(IV), V(V) and 90% of V(III).

A catalytic method based on oxidation of gallic acid by bromate, after separating and concentrating vanadium by a combined cation-anion exchange procedure in 0.05M

HCl-0.1% $H_2O_2$ media, have been reported by Fukasawa and Yamane (FUK77) for the determination of vanadium in lake and river water. They recommend the applicability of this method to sea water, if vanadium is separated before ion-exchange procedure, by the coprecipitation method of Chan and Riley (CHA66b).

Most of the methods described above involve two-step preconcentration procedures and frequently a third step to eliminate interferences; consequently, they are time consuming. The literature survey shows that there is a need for developing a simple, rapid and quantitative method for preconcentrating vanadium from sea water. The objective of the present work is to develop such a preconcentration method.

### 5.3.2 Vanadium Concentrations in Sea Water

Some of the values reported in the literature for the concentration of vanadium in sea water are summarized in Table 5.1. Two observations emerge from these data: (i) Levels of vanadium are low in the world's oceans, and (ii) Vanadium content does not vary much from ocean to ocean.

## 5.4 Preconcentration of Vanadium with Chitosan

As stated in the objectives, attempts were first made to preconcentrate vanadium with chitosan. At the beginning, the aim was to concentrate vanadium, most probably present as $VO_3^-$($H_2VO_4^-$) and $HVO_4^{2-}$ in sea water on

Table 5.1 Literature Values for Vanadium Concentration in Sea Water

| Origin | Concentration, $\mu g\ L^{-1}$ | Reference |
|---|---|---|
| Northeast Atlantic | 0.2-5.1 | RIL72 |
| Pacific Ocean | 1.73-2.00 | WEI77 |
| Adriatic Sea | 1.64-1.73 | WEI77 |
| Irish Sea | 1.77-1.87 | CHA66b |
| Dutch Sea | 1.25-1.85 | VAN77c |
| Northeast Atlantic | 0.83-1.57 | MOR75 |
| British in-shore Waters | 2.4-7.0 | BLA52 |
| East China Sea | 0.2-7 | KIR72 |

chitosan, followed by its determination by neutron activation analysis.

### 5.4.1 Vanadium Content of Chitosan

Levels of vanadium in chitosan were found to be very low (see Table 4.3), compared to the blank values for the elements studied in the previous chapter (viz., Co, Zn and Mn). Because of this low vanadium concentration, relative to vanadium concentrations reported in literature for sea water, no special cleaning procedure was necessary.

### 5.4.2 Vanadium Tracer

$^{48}V$ tracer was obtained from the Radiochemical Centre, Amersham, Buckinghamshire, England, as $^{48}VOCl_2$. A diluted solution of this tracer was reacted with hydrogen peroxide in alkaline media to convert V(IV) to V(V). Vanadium tracer solution was carrier free. Absence of $^{51}V$ in the tracer solution was also confirmed by irradiating and counting a 500 μl aliquot of the tracer solution.

### 5.4.3 Reagents

Baker analyzed reagent grade ammonium hydroxide and nitric acid were used in tracer experiments. ULTREX reagents were used when actual determinations were carried out with sea water.

### 5.4.4 Preparation of Sea Water Samples

Sea water samples filtered through 0.4 μm Nuclepore membrane filters were irradiated with UV light for 3 h.

### 5.4.5 Gamma-ray Spectrometry

A NaI(Tl) detector connected to Canberra 8100/e model 4096 multichannel analyzer was used in tracer experiments and a Ge(Li) detector connected to TN-11 multichannel analyzer was used for neutron irradiated samples.

### 5.4.6 Preliminary Experiments with Sea Water

As has been mentioned in the previous chapter, the trace elements to be concentrated with chitosan were studied in preliminary experiments with 1L samples of sea water and 200 mg of 100-200 mesh chitosan. It was also **found that the NAA determinations through short-lived nuclides were impossible** in experiments carried out at pH 2.5 and 5.5, because of the high activities of $^{38}Cl$ and $^{80}Br$. Three experiments later carried out at the pH of sea water (viz. 8.0-8.1), gave vanadium concentrations of 0.02 μg $L^{-1}$ with a precision within ± 10%. However, this value is about two orders of magnitudes less than the vanadium levels reported in literature.

### 5.4.7 Experiments with Deionized Water

A set of experiments was carried out, following the above observations at different pH values with deionized water (1L) spiked with vanadium (as $VO_2^+$) to have a concentration of 2 $\mu gL^{-1}$, in order to investigate the feasibility of using chitosan as a collector for vanadium. Two hundred mg of precipitated chitosan was used in these experiments and the shaking time was 1 hr. Precipitates were collected by filtration, air dried and sealed in small polyethylene vials and irradiated for 10 min, and counted with the Ge(Li) detector for 10 min after a decay of 3 min. Recoveries were calculated by comparing the 1434 keV photopeak areas of $^{52}V$ of samples with that of a vanadium comparator standard spiked on chitosan in a small vial. The results obtained from these experiments are presented in Table 5.2.

The higher recovery obtained at pH 7.0 compared to pH 5.0 can be explained as due to the competition of $NO_3^-$ ions (from $HNO_3$ used to adjust the pH) with $VO_3^-$ ions for the available $-\overset{+}{N}H_3$ sites of chitosan, concentrations being about $10^{-7}$M for $VO_3^-$ and about $10^{-5}$M for $NO_3^-$ (pH adjusted to 5). Since the $pK_a$ value of chitosan is 6.3, a significant fraction of it is present as the protonated form at pH 7.0 and that the collection of anions is feasible. In these experiments, the time elapsed between the addition of vanadium spike as $VO_2^+$ and the reactions with chitosan was

Table 5.2 Vanadium Recoveries from Deionized Water at Different pH Values

| pH | Recovery, %* |
|---|---|
| 3.0 | 0.5 ± 0.15 |
| 5.0 | 24 ± 0.35 |
| 7.0 | 68 ± 0.63 |
| 8.0 | 2 ± 0.17 |
| 10.0 | 0.5 ± 0.15 |

* - the given deviations are due to counting statistics

about 1 h. It is assumed that the fraction of $VO_2^+$ converted to $VO_3^-$ in 1 h is the same for all the above experiments, if this conversion is not complete within this time. Chitosan was found to be partially dissolved at pH 3.

### 5.4.8 $^{48}V$ Tracer Experiments with Sea Water

Following the above deionized water experiments a series of experiments were carried out with 100 ml of filtered, and UV-irradiated sea water samples spiked with $^{48}V$ tracer, using 100 mg of 200-400 mesh chitosan for each experiment. Time elapsed between the addition of the tracer and the reaction with chitosan was about 1 h and the shaking time was 1 h. Chitosan was collected on a Whatman Number 1 filter and transferred into a medium size polyethylene vial for counting the activity. Recoveries were calculated by comparing the peak areas of samples with a $^{48}$V-standard as before. Table 5.3 represents the results obtained in these experiments.

Table 5.3 Collection of Vanadium on Chitosan at Different pH Values

| pH | Recovery, %* |
|---|---|
| 3.0 | 37 ± 0.9 |
| 4.0 | 27 ± 0.9 |
| 6.3 | 22 ± 0.8 |
| 7.3 | 17 ± 0.7 |
| 8.0 | 6 ± 0.6 |
| 9.0 | 2 ± 0.6 |
| 9.5 | -[a] |
| 10.2 | 98 ± 1.7 |

* - the given deviations are due to the counting statistics.

a - recovery below the detection limit.

Collection efficiency of vanadium on chitosan increases with decreasing pH below 9.0. The low recoveries of vanadium in these experiments compared to those with deionized water should mainly be due to the higher concentration of chloride ions (about 0.5M in sea water) in these experiments. Fraction of chitosan present as $-\overset{+}{N}H_3$ increases with decreasing pH. The high recovery obtained at pH 10.2 is mainly due to the collection of vanadium by magnesium hydroxide. This was verified by carrying out an experiment at this pH (i.e. 10.2), with a solution of 3% NaCl, all the other experimental conditions being the same as above. Recovery of vanadium was zero in this experiment, indicating that there is no contribution from chitosan for the collection of vanadium at this pH. In order to investigate if manganese at low concentration levels contributes to the collection of vanadium, two experiments were carried out with sea water at pH 10, where 0.5 µg of inactive manganese was added to each of them. The recoveries of vanadium were 3%. As discussed in chapter 4, manganese was collected with a recovery of about 80% under these conditions. At pH 10, only about 10 µg of magnesium were precipitated from 100 mL of sea water as mentioned there. Concentration of iron present in sea water is also too low to coprecipitate vanadium. The $Mg(OH)_2$ precipitate obtained in an experiment carried out later at pH 10.2 with 100 mL of sea water (with no chitosan) was irradiated for 16 h, and counted after a decay of about 2 w. Iron (through the gamma-ray peaks of $^{59}Fe$) was not detected under these conditions. These experiments show that it is magnesium hydroxide which is responsible for the collection of vanadium.

### 5.4.9 Remarks

Tracer experiments carried out with 100 mL of sea water samples showed that the vanadium recoveries are very low at all pH values studied. In order to obtain significantly good recovery of vanadium a large amount of chitosan has to be used. However, because of the very high concentration of chloride ions present in sea water compared to that of vanadate ions, subsequent NAA would always be a problem because of the interferences from $^{38}$Cl. Hence, no attempt was made to improve the recovery by increasing the amount of chitosan. Since the half-life of $^{52}$V is 3.76 min and that of $^{38}$Cl is 37.2 min, a longer decay time would not help to overcome the problem of interference from $^{38}$Cl. Extremely low recoveries obtained at higher pH values, where the interference from chloride ions is less, are not suited to be applied for a quantitative determination of vanadium. Hence, the use of chitosan to preconcentrate vanadium from sea water was not further investigated.

However, Muzzarelli and Rocchetti (MUZ74) have reported a collection efficiency of 60% at pH 4 using 500 mg of chitosan conditioned with $H_2SO_4$ at pH 4 in a column, for 1L of sea water. In his study vanadium concentration has been determined by atomic absorption spectrometry on 5 mg portions of chitosan. This high recovery obtained by them compared to the recoveries obtained in this study could mainly be due to the differences in degree of deacetylation of chitin. The use of a chitosan column was tried at the beginning of this work. However, because of the significant swelling which took place within about one-half hour, and the long time necessary for a single experiment, the use of a column was rejected.

Quantitative recoveries obtained at pH 10.2 in the experiments carried out with chitosan (Table 5.3), led to a development of a preconcentration method based on coprecipitation of vanadium with magnesium hydroxide.

## 5.5 PRECONCENTRATION OF VANADIUM WITH MAGNESIUM HYDROXIDE

### 5.5.1 General Procedure for Tracer Studies

One mL of $^{48}V$ tracer with a specific activity of about 2 x $10^5$ counts $\mu g^{-1}$ $s^{-1}$ was added to 100 mL of sea water in a 250 mL beaker, and the pH was adjusted to 10.2 with ammonium hydroxide where a slight precipitate of magnesium hydroxide was formed. The mixture was transferred to a 250 mL erlenmeyer flask, stoppered and shaken in a mechanical shaker for a desired length of time. All experiments were carried out at room temperature. The precipitate was allowed to settle for about 15 min and filtered through a Whatman Number 1 filter, and washed three times with about 5 mL portions of deionized water. Precipitate was dried under suction for about 10 min and transferred with the filter to a medium size polyethylene vial, for radioactive counting measurements with a NaI(Tl) detector. The recoveries of $^{48}V$ tracer were calculated by comparing the areas of 984 keV photopeak of the samples from tracer experiments with that of a 1 mL portion of the tracer solution.

### 5.5.2 Exchange Between Radioactive and Inactive Vanadium

The first factor studied was the time for the $^{48}V$ tracer to reach equilibrium with the vanadium in sea water. This time was varied from 5 min to 5 d and the results are given in Table 5.4. In these experiments, pH was adjusted to 10.2, and a shaking time of 1 h was used.

Table 5.4 Isotopic Exchange Between the Added Spike and Natural Vanadium in Sea Water

| Time[a] | Recovery, %* |
|---|---|
| 5 min | 100 ± 1.6 |
| 30 min | 99 ± 1.6 |
| 1 h | 96 ± 1.4 |
| 3 h | 100 ± 1.0 |
| 2 d | 97 ± 1.0 |
| 5 d | 99 ± 2.0 |

a - time elapsed between the addition of $^{48}V$-spike and the precipitation of $Mg(OH)_2$

* - the given deviations are due to counting statistics

These results show that the exchange between the added tracer and the vanadium in sea water is attained rapidly.

### 5.5.3 Reaction Time

The effect of shaking time on the recovery of vanadium was studied at pH 10.2. The time elapsed between the addition of $^{48}V$ tracer and the precipitation of $Mg(OH)_2$ was about 15-30 min in these experiments; the results are presented in Table 5.5.

Table 5.5 Effect of Shaking Time on $^{48}V$ Tracer Recovery

| Shaking Time | Recovery, %* |
|---|---|
| 0[a] | 85 ± 1.2 |
| 15 min | 93 ± 1.4 |
| 1 h | 99 ± 1.6 |

a - immediate filtration

* - the given deviations are due to counting statistics

Collection efficiency increases when the reaction time is increased up to 1 h, and it was decided to use a shaking time of 1 h and let the precipitate settle for about 15 min before filtration.

### 5.5.4 Determination of Vanadium in Sea Water

A similar procedure to that used in tracer studies was adapted. Experiments were carried out with 100 mL sea water samples and ULTREX $NH_4OH$ was used to precipitate $Mg(OH)_2$. $^{48}V$ tracer was added to sea water in each experiment and the necessary yield corrections were made in calculating the vanadium concentration in sea water. Recoveries of more than 95% were obtained. Precipitates collected on Whatman Number 1 filters were dried under suction and sealed in precleaned polyethylene bags. Samples were irradiated for 3 min at a flux of $5 \times 10^{11}$ n $cm^{-2}$ $s^{-1}$ and counted with the Ge(Li) detector for 10 min after a decay period of 3 min. This short irradiation time made it possible to keep the dead time below 20%. However, necessary dead time corrections were made for the decay of $^{52}V$ during the counting time of 10 min. $^{27}Mg$ was the major activity in these experiments. Concentrations of vanadium were calculated by comparing the corrected (for the recovery and dead time) photopeak areas of the 1434 keV photopeak of $^{52}V$ with that of a standard spiked on Nuclepore filter, irradiated and counted under the same conditions. No vanadium was detected in blank Whatman Number 1 filters, irradiated and counted under the same conditions. Five sea water samples collected at a depth of 1m, from five different stations were analyzed and the results are presented in Table 5.6. A typical gamma-ray spectrum obtained under these conditions is presented in Figure 5.1 (a and b).

Table 5.6 Vanadium Concentration in Sea Water

| Station Number | Vanadium Concentration, $\mu gL^{-1}$ |
|---|---|
| 2 | 1.36 |
| 3 | 1.46 |
| 4 | 1.42 |
| 5 | 1.61 |
| 6 | 1.46 |

Fig. 5.1a Gamma-ray Spectrum of a $Mg(OH)_2$ Precipitate Containing Vanadium

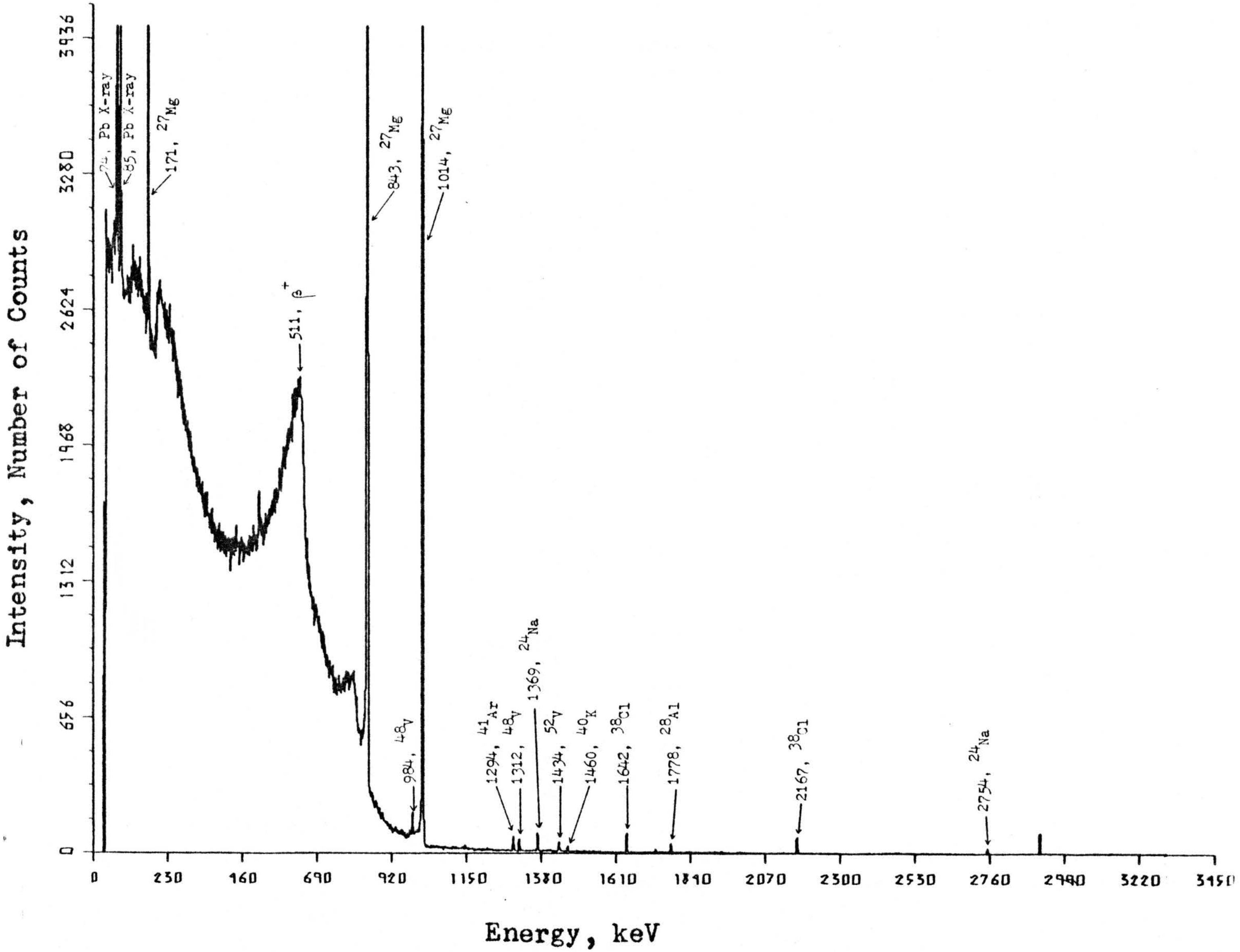
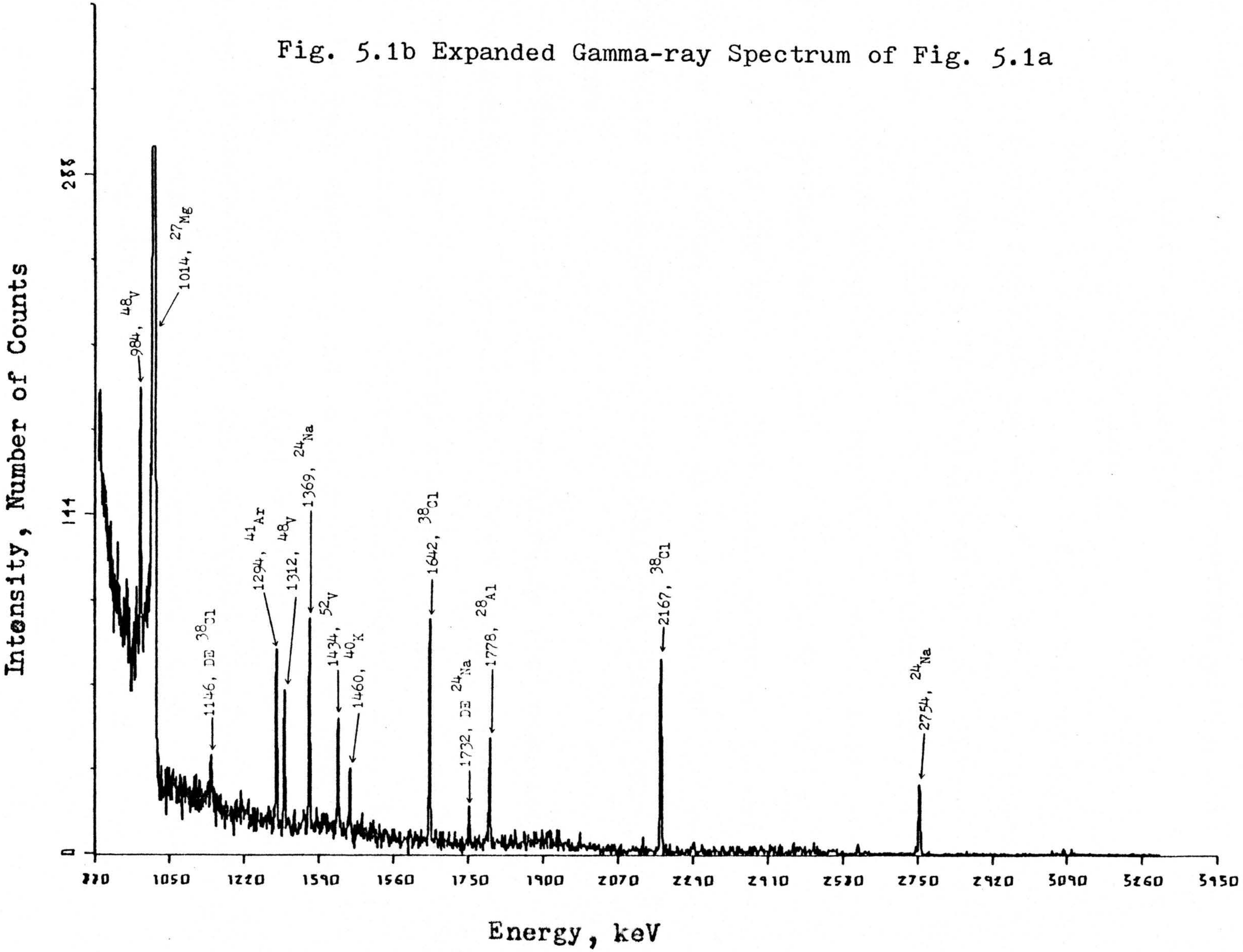


Fig. 5.1b Expanded Gamma-ray Spectrum of Fig. 5.1a



According to these results, vanadium concentration in surface sea water is relatively constant within the area studied (c.f. Zn concentrations).

### 5.5.5 Other Coprecipitated Elements

In addition to vanadium, peaks due to magnesium, sodium, chloride and aluminum were detected in the gamma-ray spectrum under the irradiation, decay and counting conditions used. Photopeaks with lower energies would not be detected under these conditions, unless they have very high intensities, because of the high Compton continuum of $^{27}$Mg photopeaks. Sodium and chloride concentrations were found to be reduced by a factor of $3 \times 10^4$ compared to those in sea water by this preconcentration procedure.

To investigate if any other elements producing long-lived nuclides are coprecipitated with $Mg(OH)_2$ under the experimental conditions used, a sample was irradiated for 16 h, and counted after different decay times. Molybdenum was the only element found to be coprecipitated under these conditions. It is possible that some other elements are coprecipitated with $Mg(OH)_2$ from sea water; however, since only 100 mL were used in these experiments their concentrations in the $Mg(OH)_2$ precipitate may be below their detection limits.

Some tracer experiments (with $^{56}$Co, $^{54}$Mn and $^{65}$Zn) carried out with 100 mL sea water samples showed that these elements could also be quantitatively coprecipitated with $Mg(OH)_2$. Therefore it is possible to extend the $Mg(OH)_2$ coprecipitation procedure to include determination of a few other elements in sea water.

### 5.5.6 Precision of the Method

Precision of the method was studied by analyzing three sea water samples from a depth of 50m from station number 3 and a value of $1.12 \pm 0.06\ \mu g\ V\ L^{-1}$ was obtained, giving a precision of 6.5%.

### 5.5.7 Detection and Determination Limits

The detection and determination limits of the method were calculated using Currie's (CUR68) method and found to be $0.38\ \mu g\ L^{-1}$ and $1.50\ \mu g\ L^{-1}$ respectively. The vanadium concentrations found in sea water samples analyzed in this study lie in between the detection and determination limits.

### 5.5.8 CONCLUSION

The method developed in this study to preconcentrate vanadium from sea water using coprecipitation with $Mg(OH)_2$ is quantitative, simple and rapid. One of the important advantages of the present method is the possibility of performing analysis on 100 mL samples of sea water as a result of the high sensitivity of V in NAA. The determination of a trace element producing a short-lived nuclide with a low sensitivity for NAA would be almost impossible by this method. The necessity of using larger volumes of sea water in such a case would result in large amounts of $Mg(OH)_2$ precipitates, which in turn would be highly activated on neutron irradiation, leading to a need for long decay times before they could be counted.

The possibility of contamination by the reagents is negligible, since only $NH_4OH$ is needed to be added to precipitate $Mg(OH)_2$ from sea water. Reduction of Na and and Cl concentrations by a factor of $3 \times 10^4$ made the determination of V by NAA interference-free. High $^{27}Mg$ activity produced on neutron irradiation of the samples would not interfere in the determination of vanadium since the gamma-rays emitted by $^{27}Mg$ (at 171 keV, 843 keV and 1014 keV) have lower energies than that of $^{52}V$ (at 1434 keV).

# 6. CONCLUSIONS AND RECOMMENDATIONS

Neutron activation analysis methods have been developed in this study to determine multielement concentrations in marine SPM and some selected elements in the soluble fraction of sea water.

The concentrations of trace elements in marine SPM have been determined by INAA. With the extremely low weights of samples used in this study, CINNA or EINNA methods have not been found to offer any advantage over the conventional TINNA method. The distribution of trace elements among the various fractions in SPM has been studied by evaluating the inter-element correlation coefficients. The main objective of this study has been to investigate the possibility of determining the trace elements in micro samples of SPM collected from the ocean water. In order to investigate the trace element distributions, for example with depth, a large number of samples need to be collected.

The determinations of selected trace elements in the soluble fraction of sea water have been achieved using three different reagents in the preconcentration steps.

A detailed investigation has been made on the suitability of $\beta$-naphthoin oxime as a selective and quantitative collector for Mo from sea water. The method developed has also been applied to determine Mo concentrations in some estuarine water samples and a steel sample. Preconcentration of other elements, in addition to Mo, from the steel sample illustrated the possibility of cocrystallizing these elements with $\beta$-naphthoin oxime. Tungstun has been found to be collected with a higher recovery than molybdenum from the steel sample; however, due to the very low concentration of W in sea water, it was not detected in the product cocrystallized from sea water samples. The selectivity of $\beta$-naphthoin oxime to cocrystallize Mo and W from steel has been found to be increased by decreasing pH to 0.5. The precision and accuracy of the method have been evaluated by analyzing a few standard reference materials. The detection and determination limits for determining Mo in various matrices have been observed to be adequate for Mo measurements.

The ability of a natural chelating polymer, called chitosan, to collect trace metals from sea water has been investigated. Chitosan has been used here to develop methods for preconcentrating Co, Zn and Mn. Applicability of the methods has been studied by analyzing a few sea water samples. To obtain chitosan (which comes as flakes) in a suitable physical form to use as a collector for trace metals, several attempts were made to homogenize it. Finally, homogenization in a micromill with rotating blades has been found to be useful in this study. Chitosan has been found to yield highest recoveries for the three elements studied at three different pH values. Collection of Co and Zn by chitosan has been postulated to be due to complex formation. Manganese has been preconcentrated by coprecipitation of $Mn(OH)_2$ with chitosan. The possibility of using chitosan to collect V has also been investigated. However, this has not been found to be successful as a result of the low recoveries obtained and the interferences from high activity of $^{38}$Cl on neutron irradiation of the concentrate. The use of chitosan to preconcentrate trace metals present as anions in sea water is not recommended, because of the interferences by Cl, both in the concentration and determination (in NAA) steps. However, the method may be extended to include other elements present in sea water, which can form complexes with chitosan (for example, Cu, Ni) if larger volumes of sea water and higher neutron fluxes are used.

Vanadium has been quantitatively concentrated with $Mg(OH)_2$. High sensitivity of V by NAA made it possible to carry out the determinations in products coprecipitated from 100 mL samples. This method could also be extended to include some other elements, for example, Zn, Mn, Co and Mo, depending on the concentration of these elements in sea water and their sensitivities by NAA.

All the above preconcentration methods have the advantages of reducing Na and Cl concentrations to levels which do not interfere in NAA determinations of the elements of interest, and of obtaining the final concentrates on solids.

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# 8. APPENDICES

# APPENDIX A

## Description of Suspended Particulate Matter Samples

| Station Number | Bottom Depth (cm) | Sample Number | Depth (m) | Volume Filtered,L | Total Weight (µg) | Concentration µg L-1 | Salinity ‰ |
|---|---|---|---|---|---|---|---|
| 2 | 180 | 4505 | 1 | 8.86 | 60 | 6.8 | 28.086 |
| | | 4506 | 20 | 4.87 | 490 | 100.6 | 29.756 |
| | | 4508 | 150 | 7.32 | - a | - a | 31.360 |
| 3 | 448 | 4524 | 1 | 1.75 | 130 | 74.3 | 29.130 |
| | | 4523 | 20 | 10.86 | 180 | 16.6 | 30.979 |
| | | 4522 | 50 | 7.11 | 270 | 38.0 | 32.338 |
| | | 4521 | 150 | 6.10 | 60 | 9.8 | 34.145 |
| 4 | 488 | 4557 | 1 | 11.35 | 120 | 10.6 | 30.910 |
| | | 4560 | 20 | 4.34 | 200 | 46.1 | 31.712 |
| | | 4564 | 50 | 11.71 | 590 | 50.4 | 32.201 |
| | | 4535 | 150 | 7.23 | 510 | 70.5 | - |
| 5 | 440 | 4574 | 1 | 2.59 | 200 | 77.2 | 30.938 |
| | | 4575 | 10 | 9.85 | 290 | 29.4 | 31.019 |
| | | 4588 | 20 | 7.03 | - a | - a | 31.277 |
| | | 4589 | 20 | 4.23 | - a | - a | 31.269 |
| | | 4590 | 20 | 10.79 | 210 | 19.5 | 31.267 |
| | | 4591 | 20 | 6.67 | 150 | 22.5 | 31.264 |
| | | 4576 | 50 | 9.50 | 400 | 42.1 | 32.360 |
| | | 4577 | 100 | 8.61 | 60 | 7.00 | 33.107 |
| | | 4568 | 150 | 8.14 | 180 | 22.1 | 34.017 |
| 6 | 336 | 4618 | 1 | 2.71 | 260 | 95.9 | 27.667 |
| | | 4617 | 20 | 3.10 | 220 | 71.0 | 27.626 |

a - sample weights could not be determined accurately

# APPENDIX B

## Trace Element Concentrations in SPM, μg/filter

| | Sample Number and Weight | | | | | |
|---|---|---|---|---|---|---|
| Element | 4577 (60 μg) | 4521 (60 μg) | 4505 (60 μg) | 4557 (120 μg) | 4524 (130 μg) | 4591 (150 μg) |
| Al | 2.78 | 0.162 | 0.699 | 0.685 | 0.849 | 1.27 |
| Au** | 40.9 | 62.8 | 74.5 | 82.6 | 107 | 179 |
| Ba | - | - | - | - | - | - |
| Br | 0.140 | 0.0971 | 0.176 | 0.203 | 0.269 | 0.261 |
| Ca | 2.67 | - | 0.814 | 17.3 | 1.63 | 14.4 |
| Ce* | 13.1 | - | - | - | - | 6.65 |
| Cl | 8.47 | 5.69 | 5.52 | 8.74 | 1.88 | 6.63 |
| Fe | 2.90 | 0.526 | - | 1.18 | - | 2.41 |
| Hg* | 9.46 | 6.41 | 4.88 | 9.46 | 11.6 | 8.85 |
| I | 0.0653 | 0.0185 | 0.0983 | 0.137 | 0.203 | 0.0461 |
| K | 1.06 | 0.589 | 0.479 | - | 0.305 | 0.733 |

** - pg/filter        * - ng/filter

(continued) APPENDIX B

Trace Element Concentrations in SPM, µg/filter

| | Sample Number and Weight | | | | | |
|---|---|---|---|---|---|---|
| Element | 4577 (60 µg) | 4521 (60 µg) | 4505 (60 µg) | 4557 (120 µg) | 4524 (130 µg) | 4591 (150 µg) |
| La* | 3.15 | - | - | - | 2.49 | 2.11 |
| Mg | 1.70 | - | - | - | - | - |
| Mn | 0.286 | 0.0248 | 0.366 | 0.0611 | 0.318 | 0.255 |
| Na | 5.33 | 3.47 | 3.39 | 5.18 | 1.27 | 3.82 |
| Sc* | 0.778 | 0.482 | 0.556 | 0.389 | 0.556 | 0.648 |
| Sm* | 0.398 | - | 0.183 | 0.114 | 0.273 | 0.325 |
| Sr | - | - | - | - | - | - |
| Ti | - | - | - | - | - | - |
| V* | 5.78 | - | 2.09 | 1.21 | 1.55 | 3.11 |
| Zn | - | - | - | 0.108 | 0.296 | 0.128 |

* - ng/filter

(continued) APPENDIX B

Trace Element Concentrations in SPM, µg/filter

| Element | 4568 (180 µg) | 4523 (180 µg) | 4560 (200 µg) | 4574 (200 µg) | 4590 (210 µg) | 4617 (220 µg) |
|---|---|---|---|---|---|---|
| Al | 4.17 | 0.105 | 2.04 | 0.806 | 0.505 | 3.58 |
| Au** | 124 | 32.8 | 90.6 | 90.6 | 10.8 | - |
| Ba | - | - | - | - | - | - |
| Br | 0.189 | 0.163 | 0.272 | 0.322 | 0.311 | 0.109 |
| Ca | 3.49 | - | 51.9 | 13.3 | 29.3 | 5.00 |
| Ce* | 15.1 | - | 7.76 | 13.3 | - | 25.1 |
| Cl | 21.8 | 23.0 | 11.1 | 31.3 | 39.0 | 1.36 |
| Fe | 3.00 | - | 2.43 | 1.25 | - | 3.79 |
| Hg* | 2.44 | - | 14.6 | 2.14 | 13.4 | 7.02 |
| I | 0.0774 | 0.0179 | 0.0856 | 0.302 | 0.0425 | 0.0505 |
| K | 2.03 | - | 0.960 | 1.56 | 1.58 | 1.16 |

** - pg/filter * - ng/filter

## (continued) APPENDIX B

### Trace Element Concentrations in SPM, µg/filter

| | Sample Number and Weight | | | | | |
|---|---|---|---|---|---|---|
| Element | 4568<br>(180 µg) | 4523<br>(180 µg) | 4560<br>(200 µg) | 4574<br>(200 µg) | 4590<br>(210 µg) | 4617<br>(220 µg) |
| La* | - | - | 4.17 | - | 4.76 | 4.72 |
| Mg | 3.75 | - | 1.41 | 2.76 | 3.60 | 0.919 |
| Mn | 0.482 | 0.00489 | 0.473 | 0.122 | 0.172 | 1.35 |
| Na | 14.0 | 13.5 | 7.04 | 18.6 | 22.8 | 1.98 |
| Sc* | 1.19 | 0.296 | 0.870 | 0.444 | 0.389 | 0.126 |
| Sm* | 0.549 | - | 0.716 | 0.534 | 0.319 | 0.735 |
| Sr | - | - | 0.289 | - | - | - |
| Ti | 0.295 | - | - - | - | - | - |
| V* | 9.60 | - | 9.13 | 2.08 | - | 7.05 |
| Zn | 0.286 | - | 0.138 | 0.108 | 0.286 | 0.187 |

* - ng/filter

(continued) APPENDIX B

## Trace Element Concentrations in SPM, µg/filter

| Element | Sample Number and Weight<br>4618<br>(260 µg) | 4522<br>(270 µg) | 4575<br>(290 µg) | 4576<br>(400 µg) | 4506<br>(490 µg ) |
|---|---|---|---|---|---|
| Al | 4.63 | 2.24 | 0.602 | 2.61 | 2.82 |
| Au** | 252 | 69.8 | 94.9 | 34.1 | 19.2 |
| Ba | - | - | - | - | - |
| Br | 0.134 | 0.341 | 0.344 | 0.413 | 0.579 |
| Ca | 25.1 | 9.77 | 61.2 | 9.19 | 46.4 |
| Ce* | 24.6 | 11.1 | - | 18.6 | 25.1 |
| Cl | 3.19 | 62.8 | 20.3 | 76.8 | 98.4 |
| Fe | 4.61 | 3.36 | 2.21 | 2.61 | 3.36 |
| Hg* | 7.32 | 13.7 | 18.3 | 67.1 | 15.0 |
| I | 0.0467 | 0.0653 | 0.315 | 0.0754 | 0.252 |
| K | 1.68 | - | 0.916 | 4.16 | 2.45 |

** - pg/filter      * - ng/filter

(continued) APPENDIX B

## Trace Element Concentrations in SPM, μg/filter

| Element | 4618<br>(260 μg) | 4522<br>(270 μg) | 4575<br>(290 μg) | 4576<br>(400 μg) | 4506<br>(490 μg) |
|---|---|---|---|---|---|
| | Sample Number and Weight | | | | |
| La* | 8.99 | 4.24 | 4.33 | - | 7.47 |
| Mg | 2.16 | 6.80 | 2.13 | 6.93 | 4.75 |
| Mn | 1.51 | 0.742 | 0.0639 | 1.05 | 2.02 |
| Na | 2.95 | 34.6 | 12.6 | 42.7 | 55.7 |
| Sc* | 1.22 | 0.648 | 0.370 | 0.833 | 1.13 |
| Sm* | 1.21 | 0.480 | 0.502 | 0.694 | 0.894 |
| Sr | - | - | 0.354 | - | - |
| Ti | - | - | - | - | 0.213 |
| V* | 1.06 | 1.71 | 1.58 | 7.02 | 2.80 |
| Zn | 0.197 | 0.217 | 0.128 | 0.0985 | 0.857 |

* - ng/filter

(continued) APPENDIX B

## Trace Element Concentrations in SPM, µg/filter

| Element | Sample Number and Weight<br>4535<br>(510 µg) | <br>4564<br>(590 µg) | <br>4588 | <br>4508 | <br>4589 |
|---|---|---|---|---|---|
| Al | 8.45 | 6.09 | 0.961 | 1.93 | 2.45 |
| Au** | 53.8 | 241 | 155 | - | 167 |
| Ba | - | - | 0.788 | - | 0.155 |
| Br | 0.495 | 0.587 | 0.374 | 0.160 | 0.225 |
| Ca | 31.4 | 40.8 | 11.1 | 4.65 | 70.9 |
| Ce* | 15.5 | 22.8 | - | 15.8 | 17.7 |
| Cl | 84.0 | 107 | 88.4 | 11.8 | 5.56 |
| Fe | 10.9 | 7.47 | 2.11 | 1.71 | 1.43 |
| Hg* | 44.2 | 52.2 | 10.7 | 24.4 | 50.3 |
| I | 0.115 | 0.114 | 0.0385 | 0.0605 | 0.0531 |
| K | 4.19 | 4.54 | 0.616 | 1.49 | 0.978 |

** - pg/filter * - ng/filter

(continued) APPENDIX B

Trace Element Concentrations in SPM, µg/filter

| Element | 4535<br>(510 µg) | 4564<br>(590 µg) | 4588 | 4508 | 4589 |
|---|---|---|---|---|---|
| La* | 5.19 | 7.32 | 5.01 | 2.27 | 7.82 |
| Mg | 9.33 | 9.51 | - | 2.37 | 1.90 |
| Mn | 0.678 | 3.65 | 0.223 | 1.14 | 0.521 |
| Na | 47.1 | 60.7 | 5.08 | 6.53 | 3.82 |
| Sc* | 1.82 | 1.94 | 0.852 | 0.685 | 0.648 |
| Sm* | 0.843 | 1.50 | 0.344 | 0.288 | 0.866 |
| Sr | - | - | - | - | 0.363 |
| Ti | 0.594 | - | 8.57 | - | 0.219 |
| V* | 10.3 | 17.2 | - | 6.55 | 4.97 |
| Zn | 3.04 | 0.669 | 0.177 | 0.0690 | 0.158 |

Sample Number and Weight (column heading above sample numbers)

* - ng/filter

# APPENDIX C

## Trace Element Concentrations in SPM, ng $L^{-1}$

| Element | 4577 | 4521 | 4505 | 4557 | 4524 | 4591 |
|---|---|---|---|---|---|---|
| | | | Sample Number | | | |
| Al | 323 | 26.6 | 78.9 | 60.4 | 485 | 190 |
| Au* | 473 | 10.3 | 8.41 | 7.28 | 61.1 | 26.8 |
| Ba | - | - | - | - | - | - |
| Br | 16.3 | 15.9 | 19.9 | 17.9 | 154 | 39.1 |
| Ca | 310 | - | 91.9 | 1520 | 931 | 2160 |
| Ce | 1.52 | - | - | - | - | 0.997 |
| Cl | 984 | 933 | 623 | 770 | 1070 | 994 |
| Fe | 337 | 86.2 | - | 104 | - | 361 |
| Hg | 1.10 | 1.05 | 0.551 | 0.834 | 6.63 | 1.33 |
| I | 7.58 | 3.03 | 11.1 | 12.1 | 116 | 6.91 |
| K | 123 | 96.6 | 54.1 | - | 174 | 110 |

* - pg $L^{-1}$

## (continued) APPENDIX C

### Trace Element Concentrations in SPM, ng $L^{-1}$

| Element | Sample Number<br>4577 | 4521 | 4505 | 4557 | 4524 | 4591 |
|---|---|---|---|---|---|---|
| La | 0.366 | - | - | - | 1.42 | 0.316 |
| Mg | 197 | - | - | - | - | - |
| Mn | 33.2 | 4.07 | 41.3 | 5.38 | 182 | 38.2 |
| Na | 619 | 569 | 383 | 456 | 726 | 573 |
| Sc* | 90.4 | 79.0 | 62.8 | 34.3 | 318 | 97.2 |
| Sm* | 46.2 | - | 20.7 | 10.0 | 156 | 48.7 |
| Sr | - | - | - | - | - | - |
| Ti | - | - | - | - | - | - |
| V* | 625 | - | 236 | 107 | 886 | 466 |
| Zn | - | - | - | 9.52 | 169 | 19.2 |

* - pg $L^{-1}$

## (continued) APPENDIX C

## Trace Element Concentrations in SPM, ng $L^{-1}$

| | Sample Number | | | | | |
|---|---|---|---|---|---|---|
| Element | 4568 | 4523 | 4560 | 4574 | 4590 | 4617 |
| Al | 512 | 9.67 | 470 | 311 | 46.8 | 1160 |
| Au* | 15.2 | 3.02 | 20.9 | 35.0 | 1.00 | - |
| Ba | - | - | - | - | - | - |
| Br | 23.2 | 15.0 | 62.7 | 124 | 28.8 | 35.2 |
| Ca | 429 | - | 12000 | 5140 | 2720 | 1610 |
| Ce | 1.86 | - | 1.79 | 5.14 | - | 8.10 |
| Cl | 2680 | 2120 | 2560 | 12100 | 3620 | 439 |
| Fe | 369 | - | 600 | 423 | - | 1220 |
| Hg | 0.300 | - | 3.36 | 0.826 | 1.24 | 2.27 |
| I | 9.51 | 1.65 | 19.7 | 117 | 3.94 | 16.3 |
| K | 249 | - | 221 | 602 | 146 | 374 |

* - pg $L^{-1}$

## (continued) APPENDIX C

### Trace Element Concentrations in SPM, ng $L^{-1}$

| Element | Sample Number<br>4568 | 4523 | 4560 | 4574 | 4590 | 4617 |
|---|---|---|---|---|---|---|
| La | 0.146 | - | 0.961 | - | 0.441 | 1.52 |
| Mg | 2560 | - | 325 | 1070 | 334 | 297 |
| Mn | 59.2 | 0.450 | 109 | 47.1 | 15.9 | 436 |
| Na | 1720 | 1240 | 1620 | 7180 | 2110 | 639 |
| Sc* | 146 | 27.3 | 201 | 171 | 36.1 | 407 |
| Sm* | 67.5 | - | 165 | 206 | 29.6 | 237 |
| Sr | - | - | 66.6 | - | - | - |
| Ti | 36.2 | - | - | - | - | - |
| V* | 1180 | - | 2100 | 803 | - | 2270 |
| Zn | 35.1 | - | 31.8 | 41.7 | 26.5 | 60.3 |

* - pg $L^{-1}$

## (continued) APPENDIX C

### Trace Element Concentrations in SPM, ng $L^{-1}$

| Element | 4618 | 4522 | 4575 | 4576 | 4506 |
|---|---|---|---|---|---|
| | **Sample Number** | | | | |
| Al | 1710 | 315 | 61.1 | 275 | 579 |
| Au* | 93.0 | 9.82 | 9.63 | 3.59 | 3.94 |
| Ba | - | - | - | - | - |
| Br | 49.5 | 48.0 | 34.9 | 43.5 | 119 |
| Ca | 9260 | 1370 | 6210 | 967 | 9530 |
| Ce | 9.08 | 1.56 | - | 1.96 | 5.15 |
| Cl | 1180 | 8830 | 2060 | 8080 | 20200 |
| Fe | 1700 | 473 | 224 | 275 | 690 |
| Hg | 2.70 | 1.93 | 1.86 | 7.06 | 3.08 |
| I | 17.2 | 9.18 | 32.0 | 7.94 | 51.7 |
| K | 620 | - | 93.0 | 438 | 503 |

* - pg $L^{-1}$

(continued) APPENDIX C

Trace Element Concentrations in SPM, ng $L^{-1}$

| Element | Sample Number<br>4618 | 4522 | 4575 | 4576 | 4506 |
|---|---|---|---|---|---|
| La | 3.32 | 0.596 | 0.440 | - | 1.53 |
| Mg | 797 | 956 | 216 | 730 | 975 |
| Mn | 557 | 104 | 6.49 | 111 | 415 |
| Na | 1090 | 4870 | 1280 | 4500 | 11400 |
| Sc* | 650 | 91.1 | 37.6 | 87.7 | 232 |
| Sm* | 447 | 67.5 | 51.0 | 73.1 | 184 |
| Sr | - | - | 35.9 | - | - |
| Ti | - | - | - | - | 43.7 |
| V* | 391 | 241 | 160 | 739 | 575 |
| Zn | 72.7 | 30.5 | 13.0 | 1.04 | 176 |

* - pg $L^{-1}$

(continued) APPENDIX C

Trace Element Concentrations in SPM, ng $L^{-1}$

| lement | 4535 | 4564 | 4588 | 4508 | 4589 |
|---|---|---|---|---|---|
| | | | Sample Number | | |
| Al | 1170 | 520 | 137 | 263 | 601 |
| Au* | 74.4 | 20.6 | 22.1 | - | 39.5 |
| Ba | - | - | 112 | - | 368 |
| Br | 68.5 | 50.1 | 53.2 | 21.8 | 53.3 |
| Ca | 4340 | 3480 | 1570 | 635 | 16800 |
| Ce | 214 | 1.95 | - | 2.16 | 4.18 |
| Cl | 11600 | 9140 | 12600 | 1610 | 1320 |
| Fe | 1510 | 638 | 300 | 234 | 338 |
| Hg | 6.11 | 4.46 | 1.52 | 3.33 | 11.9 |
| I | 15.9 | 9.74 | 5.47 | 8.26 | 12.5 |
| K | 580 | 388 | 87.6 | 204 | 231 |

* - pg $L^{-1}$

(continued) APPENDIX C

Trace Element Concentrations in SPM, ng $L^{-1}$

| | Sample Number | | | | |
|---|---|---|---|---|---|
| Element | 4535 | 4564 | 4588 | 4508 | 4589 |
| La | 0.718 | 0.625 | 0.713 | 0.310 | 1.85 |
| Mg | 1290 | 812 | - | 323 | 450 |
| Mn | 93.8 | 312 | 31.7 | 156 | 123 |
| Na | 6520 | 5180 | 723 | 892 | 903 |
| $Sc^{*}$ | 252 | 166 | 121 | 93.6 | 153 |
| $Sm^{*}$ | 117 | 128 | 48.9 | 39.3 | 205 |
| Sr | - | - | - | - | 85.9 |
| Ti | 82.2 | - | 1220 | - | 51.9 |
| $V^{*}$ | 1430 | 1470 | - | 896 | 1180 |
| Zn | 421 | 57.1 | 25.2 | 9.43 | 37.4 |

* - pg $L^{-1}$

# APPENDIX D

## Trace Element Concentrations in SPM, mg $g^{-1}$

| | Sample Number | | | | | |
|---|---|---|---|---|---|---|
| Element | 4577 | 4521 | 4505 | 4557 | 4524 | 4591 |
| Al | 46.3 | 2.70 | 11.7 | 5.72 | 6.54 | 8.44 |
| Au* | 0.678 | 1.05 | 1.24 | 0.688 | 0.823 | 1.19 |
| Br | 2.34 | 1.62 | 2.94 | 1.69 | 2.07 | 1.74 |
| Ca | 44.6 | - | 13.6 | 14.4 | 12.5 | 96.1 |
| Ce | 0.218 | - | - | - | - | 0.0443 |
| Cl | 141 | 94.9 | 92.1 | 72.9 | 14.5 | 44.2 |
| Fe | 48.3 | 8.77 | - | 9.83 | - | 16.1 |
| Hg | 0.158 | 0.107 | 0.0813 | 0.0788 | 0.0892 | 0.0590 |
| I | 1.09 | 0.309 | 1.64 | 1.14 | 1.57 | 0.307 |
| K | 17.7 | 9.82 | 7.98 | - | 2.35 | 4.89 |

* - µg $g^{-1}$

## (continued) APPENDIX D

Trace Element Concentrations in SPM, mg g$^{-1}$

| | Sample Number | | | | | |
|---|---|---|---|---|---|---|
| Element | 4577 | 4521 | 4505 | 4557 | 4524 | 4591 |
| La | 0.0525 | - | - | - | 0.0192 | 0.0141 |
| Mg | 28.3 | - | - | - | - | - |
| Mn | 4.76 | 0.413 | 6.10 | 0.509 | 2.45 | 1.70 |
| Na | 88.8 | 57.8 | 56.5 | 43.1 | 9.80 | 25.5 |
| Sc* | 13.0 | 8.03 | 9.27 | 3.24 | 4.28 | 4.32 |
| Sm* | 6.63 | - | 3.05 | 0.950 | 2.10 | 2.17 |
| Sr | - | - | - | - | - | - |
| Ti | - | - | - | - | - | - |
| V* | 96.3 | - | 34.9 | 10.1 | 12.0 | 20.7 |
| Zn | - | - | - | 0.900 | 2.28 | 0.853 |

* - μg g$^{-1}$

## (continued) APPENDIX D

### Trace Element Concentrations in SPM, mg g$^{-1}$

|  | Sample Number |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Element | 4568 | 4523 | 4560 | 4574 | 4590 | 4517 |
| Al | 23.2 | 0.589 | 10.2 | 3.84 | 2.40 | 16.3 |
| Au* | 0.689 | 0.182 | 0.453 | 0.453 | 0.0514 | - |
| Br | 1.05 | 0.908 | 1.36 | 1.66 | 1.48 | 0.498 |
| Ca | 19.4 | - | 259 | 66.3 | 140 | 22.7 |
| Ce | 0.0838 | - | 0.0388 | 0.0665 | - | 0.114 |
| Cl | 121 | 128 | 55.6 | 157 | 186 | 6.16 |
| Fe | 16.7 | - | 12.2 | 6.25 | - | 17.2 |
| Hg | 0.0136 | - | 0.0730 | 0.0107 | 0.0638 | 0.0319 |
| I | 0.430 | 0.100 | 0.428 | 1.51 | 0.213 | 0.230 |
| K | 11.3 | - | 4.80 | 7.80 | 7.52 | 5.27 |

* - µg g$^{-1}$

## (continued) APPENDIX D

### Trace Element Concentrations in SPM, mg $g^{-1}$

| Element | Sample Number<br>4568 | 4523 | 4560 | 4574 | 4590 | 4617 |
|---|---|---|---|---|---|---|
| La | - | - | 0.0209 | - | 0.0227 | 0.0215 |
| Mg | 20.8 | - | 7.06 | 13.8 | 17.9 | 4.18 |
| Mn | 2.68 | 0.0272 | 2.37 | 0.609 | 0.819 | 6.14 |
| Na | 77.6 | 75.0 | 35.2 | 92.9 | 109 | 8.98 |
| Sc* | 6.61 | 1.64 | 4.35 | 2.22 | 1.85 | 5.73 |
| Sm* | 3.05 | - | 3.58 | 2.67 | 1.52 | 3.34 |
| Sr | - | - | 1.45 | - | - | - |
| Ti | 1.64 | - | - | - | - | - |
| V* | 53.3 | - | 45.7 | 10.4 | - | 32.1 |
| Zn | 1.59 | - | 0.690 | 0.540 | 1.36 | 0.850 |

* - μg $g^{-1}$

## (continued) APPENDIX D

## Trace Element Concentrations in SPM, mg g$^{-1}$

| Element | Sample Number<br>4618 | 4522 | 4575 | 4576 | 4506 | 4535 | 4564 |
|---|---|---|---|---|---|---|---|
| Al | 17.8 | 8.29 | 2.08 | 6.53 | 5.76 | 16.6 | 10.3 |
| Au* | 0.969 | 0.259 | 0.327 | 0.0852 | 0.0392 | 1.06 | 0.409 |
| Br | 0.515 | 1.26 | 1.15 | 1.03 | 1.18 | 0.971 | 0.996 |
| Ca | 96.6 | 36.2 | 211 | 23.0 | 94.7 | 61.6 | 69.2 |
| Ce | 0.0946 | 0.0411 | - | 0.0465 | 0.0512 | 0.0304 | 0.0386 |
| Cl | 12.3 | 233 | 700 | 192 | 201 | 165 | 182 |
| Fe | 17.7 | 12.4 | 7.62 | 6.53 | 6.86 | 21.4 | 12.7 |
| Hg | 0.0282 | 0.0507 | 0.0631 | 0.168 | 0.0306 | 0.0867 | 0.0885 |
| I | 0.180 | 0.242 | 1.08 | 0.189 | 0.514 | 0.225 | 0.194 |
| K | 6.46 | - | 3.16 | 10.4 | 5.00 | 8.22 | 7.70 |

* - $\mu$g g$^{-1}$

## (continued) APPENDIX D

### Trace Element Concentrations in SPM, mg $g^{-1}$

| | Sample Number | | | | | | |
|---|---|---|---|---|---|---|---|
| Element | 4618 | 4522 | 4575 | 4576 | 4506 | 4535 | 4564 |
| La | 0.0346 | 0.0157 | 0.0149 | - | 0.0153 | 0.0102 | 0.0124 |
| Mg | 8.29 | 25.2 | 7.34 | 17.3 | 9.69 | 18.3 | 16.1 |
| Mn | 5.81 | 2.75 | 0.220 | 2.63 | 4.13 | 1.33 | 6.19 |
| Na | 11.4 | 128 | 43.3 | 107 | 114 | 92.3 | 103 |
| Sc* | 4.69 | 2.40 | 1.28 | 2.08 | 2.31 | 3.57 | 3.30 |
| Sm* | 4.65 | 1.78 | 1.73 | 1.74 | 1.83 | 1.65 | 2.54 |
| Sr | - | - | 1.22 | - | - | - | - |
| Ti | - | - | - | - | 0.434 | - | - |
| V* | 40.9 | 6.32 | 5.46 | 17.6 | 5.70 | 20.2 | 29.2 |
| Zn | 0.758 | 0.804 | 0.441 | 0.246 | 1.75 | 5.96 | 1.13 |

* - µg $g^{-1}$