

## CHAPTER I



### INTRODUCTION

#### 1.1 The Problem

It is well recognized that environmental problems are playing an important role in Thailand at present. Toxic elements which are contaminated in/on air, water, soil and food is one of the factors. The main sources of toxic contaminants come from industrial wastes and pesticide residues. The study of trace toxic elements in varieties of environmental samples e.g. rice, fish, soil, vegetables and fruits etc. in Thailand has been widely conducted. Nevertheless the investigation of these trace elements on water samples is still quite rare, and a reason for this is probably due to the lack of appropriate pre-concentration techniques available and the applied analytical technique.

Since neutron activation technique is well known as one of the promising techniques owing to its high sensitivity and adaptability to a wide varieties of sample materials. Meanwhile a suitable neutron source in form of the research reactor Thai Research Reactor-1/modification-1 (TRR-1/M-1) is readily available at the Office of Atomic Energy for Peace (OAEP). Additionally, OAEP has established a co-ordinated program with Department of Fisheries and Department of Agriculture on the baseline study of pesticide residues and toxic contaminants in Thai environmental samples.

Therefore, it is the purpose of this study to develop a technique in analytical chemistry for the determination of trace toxic elements in water by neutron activation analysis.

## 1.2 Scope of this Present Study

Some techniques in pre-concentration of trace elements from (sea) water were developed :-

- a) Co-precipitation of As with  $\text{Fe}(\text{OH})_3$
- b) Adsorption of APDC-Metal chelates of Co, Hg, Zn, Sb, W, Mo, Cr (VI) and elemental Se on activated charcoal.

In combination with neutron activation the preconcentration techniques have been applied to some investigations :-

- a) The determination of arsenic in tap water, canal water and sea water.
- b) Leaching behaviour of some trace elements from an alkaline ash in contact with sea water.
- c) The determination of some trace elements in water and related samples in the Western Scheldt Estuary.

## 1.3 Literature Search of Previous Work

### 1.3.1 The Chemical Composition of Water

Sea water as well as fresh water contains dissolved salts, gases, organic compounds and suspended particles which usually consists of an inorganic core partially coated with organic material. [1]

The chemical composition of sea water and fresh water can be briefly described as follow :-

#### 1.3.1.1 Sea Water

The total concentrations of surface sea water cover the following ranges :-

Dissolved constituents :- salts 33-37 g./kg.  
 gases 4-7 ml.O<sub>2</sub>(STP)/kg.  
 9-12 ml.N<sub>2</sub>(STP)/kg.  
 organic compounds 1-2 mg./kg.  
 Suspended particles :- 0.5-5.0 mg./kg. (up to 50 mg./kg. was found in coastal water)

The dissolved salts consist of the ions listed in table 1.1 in order of decreasing concentration. Elements present in concentration below 1 mg./kg. are referred to as "trace elements". Average concentration of trace elements in sea water are given in table 1.2. About 92% of the total amount of trace elements is due to five elements only i.e. Li, Rb, P, I and Ba.

The concentration of trace elements in sea water are influenced in different ways, i.e.

a) By natural processes, such as movement of watermasses, precipitation, adsorption on or desorption from suspended matter or bottom sediments, river transport of eroded matter to sea and uptake by marine organisms.

b) By pollution due to volcanic events. Mercury is released in large quantities during submarine volcanism.

c) By pollution due to discharge of industrial and domestic waste. As to this fact the inflow of contaminated rivers, the direct discharge of metallic pollutants into estuaries and sea, and the contribution from arial fallout are regarded as the main sources of pollution to seas and oceans.

#### 1.3.1.2 Fresh Water

Riverwater composition varies with climate, local geology and presence of large cities and intensive agriculture, since rivers effectively integrate the soluble materials from the basin they drain. In temperate regions the major species present are usually calcium and bicarbonate ions, while in the humid parts of the tropics the rivers are more diluted and contain more Al, Fe, Si, and organic matter. River waters usually contain much larger amounts of organic matter than does sea water. It seems that most of the transition elements are either complexed or adsorbed by colloidal matter. Since the average resident time of its water is of the order of days, river composition can change rather rapidly in response to external conditions. The summary on elemental composition of fresh water is presented in table 1.3.[2]

Table 1.1 Major ionic constituents of sea water [1]

| Element            | Concentration (g./kg.) |
|--------------------|------------------------|
| $\text{Cl}^-$      | 19.353                 |
| $\text{Na}^+$      | 10.752                 |
| $\text{SO}_4^{2-}$ | 2.701                  |
| $\text{Mg}^{2+}$   | 1.295                  |
| $\text{Ca}^{2+}$   | 0.416                  |
| $\text{K}^+$       | 0.390                  |
| $\text{HCO}_3^-$   | 0.145                  |
| $\text{Br}^-$      | 0.066                  |
| $\text{Sr}^{2-}$   | 0.008                  |
| $\text{HBO}_3^-$   | 0.0046                 |
| $\text{Si}^{4+}$   | 0.002                  |
| $\text{F}^-$       | 0.0013                 |
| trace elements     | 0.0005                 |
| Total              | <u>35.1344</u>         |

Table 1.2 Trace elements levels in sea water

| Element | Average concentration ( $\mu\text{g.}/\text{kg.}$ ) | Predominant inorganic forms   |
|---------|---|---|
| Li      | 170   | $\text{Li}^+$   |
| Be      | $6 \times 10^{-4}$                                  | $\text{Be}(\text{OH})_2$  |
| Al      | 5   | $\text{Al}(\text{OH})_2^+$  |
| P       | 70  | $\text{PO}_4^{3-}$  |
| Sc      | $7 \times 10^{-4}$                                  | $\text{Sc}(\text{H}_2\text{O})_5\text{OH}^{2+}$                       |
| Ti      | 1   | $\text{Ti}(\text{OH})_2^{2+}$   |
| V       | 1.9   | $\text{HVO}_4^{2-}, \text{VO}_3^-$                                    |
| Cr      | 0.2   | $\text{CrO}_4^{2-}, \text{Cr}[(\text{H}_2\text{O})_4(\text{OH})_2]^+$ |
| Mn      | 0.4   | $\text{Mn}^{2+}, \text{Mn}(\text{OH})^+$                              |
| Fe      | 1.5   | $\text{Fe}(\text{OH})_4^-, \text{Fe}(\text{OH})_2^+$                  |
| Co      | 0.1   | $\text{Co}^{2+}, \text{CoCl}^+, \text{Co}(\text{OH})^+$               |
| Ni      | 0.7   | $\text{Ni}^{2+}, \text{NiCl}^+, \text{Ni}(\text{OH})^+$               |
| Cu      | 0.9   | $\text{Cu}^{2+}, \text{CuCl}^+, \text{Cu}(\text{OH})^+$               |
| Zn      | 2   | $\text{Zn}^{2+}, \text{ZnCl}^+$                                       |
| Ga      | 0.03  | unknown   |
| Ge      | 0.06  | $\text{Ge}(\text{OH})_4$  |
| As      | 2.5   | $\text{HASO}_4^{2-}, \text{AsO}_4^{3-}, \text{AsO}_3^{3-}$            |
| Se      | 0.09  | $\text{SeO}_3^{2-}, \text{SeO}_4^{2-}$                                |
| Rb      | 120   | $\text{Rb}^+$   |
| Y       | 0.3   | $\text{Y}(\text{OH})^{2+}$  |
| Zr      | 0.02  | unknown   |

Table 1.2 (Cont.)

| Element | Average concentration( $\mu\text{g.}/\text{kg.}$ ) | Predominant inorganic forms                                |
|---------|--|--|
| Nb      | 0.01   | unknown  |
| Mo      | 10   | $\text{MoO}_4^{2-}$  |
| Ru      | $7 \times 10^{-4}$                                 | unknown  |
| Ag      | 0.29   | $\text{AgCl}_2^-$  |
| Cd      | 0.11   | $\text{CdCl}^+$ , $\text{CdCl}_2$ , $\text{Cd}^{2+}$       |
| In      | 0.1  | $\text{In}(\text{OH})_2^+$                                 |
| Sn      | 0.8  | $\text{Sn}(\text{OH})^+$ , $\text{Sn}(\text{OH})_2^{2+}$   |
| Sb      | 0.3  | $\text{Sb}(\text{OH})_2^+$ , $\text{Sb}(\text{OH})_6^-$    |
| I       | 60   | $\text{I}^-$ , $\text{IO}_3^-$                             |
| Cs      | 0.3  | $\text{Cs}^+$  |
| Ba      | 30   | $\text{Ba}^{2+}$   |
| La      | $1.2 \times 10^{-2}$                               | $\text{La}(\text{OH})_2^{2+}$ , $\text{La}(\text{OH})_2^+$ |
| Ce      | $5.2 \times 10^{-3}$                               | $\text{Ce}(\text{OH})_2^{2+}$                              |
| Nd      | $9.2 \times 10^{-3}$                               | unknown  |
| Hf      | $< 8 \times 10^{-3}$                               | unknown  |
| Ta      | $< 3 \times 10^{-3}$                               | unknown  |
| W       | 0.1  | $\text{WO}_4^{2-}$   |
| Re      | $8 \times 10^{-3}$                                 | $\text{ReO}_4^-$   |
| Au      | 0.01   | $\text{AuCl}_4^-$  |
| Hg      | 0.03   | $\text{HgCl}_4^{2-}$                                       |
| Tl      | $< 0.01$   | $\text{Tl}^+$  |

Table 1.2 (Cont.)

| Element | Average concentration ( $\mu\text{g.}/\text{kg.}$ ) | Predominant inorganic forms        |
|---------|---|------------------------------------|
| Pb      | 0.03  | $\text{Pb}^{2+}$ , $\text{PbCl}^-$ |
| Bi      | 0.02  | $\text{BiO}^+$ , $\text{BiOCl}$    |
| Ra      | $1 \times 10^{-7}$                                  | unknown                            |
| Th      | $4 \times 10^{-4}$                                  | $\text{Th}(\text{OH})_2^{2+}$      |
| U       | 3.3   | $\text{UO}_2(\text{CO}_3)_3^{4-}$  |

Table 1.3 Elemental composition of fresh water

| Element | Median ( $\mu\text{g.}/\text{kg.}$ ) | Range ( $\mu\text{g.}/\text{kg.}$ ) | Species                 |
|---------|--------------------------------------|-------------------------------------|-------------------------|
| Ag      | 0.3                                  | 0.01-3.5                            |                         |
| Al      | 300                                  | 8-3500                              | Colloid                 |
| As      | 0.5                                  | 0.2 -230                            | Anion                   |
| Au      | 0.002                                | 0.001-0.02                          | Anion?                  |
| B       | 15                                   | 7 -500                              | $\text{B}(\text{OH})_3$ |
| Ba      | 10                                   | < 3 -150                            | $\text{Ba}^{2+}$        |
| Be      | 0.3                                  | 0.01 -1                             |                         |
| Bi      | 0.02                                 |                                     |                         |
| Br      | 14                                   | 0.05 -55                            | $\text{Br}^-$           |
| C       | 11K                                  | 6K -19K                             | $\text{HCO}_3^-$        |



Table 1.3 (Cont.)

| Element | Median<br>( $\mu\text{g.}/\text{kg.}$ ) | Range<br>( $\mu\text{g.}/\text{kg.}$ ) | Species          |
|---------|---|--|------------------|
| Ca      | 15K                                     | 2K - 20K                               | $\text{Ca}^{2+}$ |
| Cd      | 0.1                                     | 0.01-3                                 | Org.             |
| Ce      | 0.2                                     | 0.1-0.2                                | Colloid          |
| Cl      | 7000                                    | 1K-35K                                 | $\text{Cl}^-$    |
| Co      | 0.2                                     | 0.04-8                                 |                  |
| Cr      | 1                                       | 0.1-6                                  |                  |
| Cs      | 0.02                                    | 0.005-1                                | $\text{Cs}^+$    |
| Cu      | 3                                       | 0.2 -30                                | Org.             |
| Dy      |   | 0.005                                  |                  |
| Eu      | 0.006                                   | 0.002-0.009                            |                  |
| F       | 100                                     | 50-2700                                | $\text{F}^-$     |
| Ga      | 0.09                                    |  |                  |
| Hf      | 0.01                                    | 0.005-0.13                             |                  |
| Hg      | 0.1                                     | 0.0001-2.8                             | Org.             |
| I       | 2                                       | 0.5 -7                                 | $\text{I}^-$     |
| K       | 2200                                    | 500 -10K                               | $\text{K}^+$     |
| La      | 0.1                                     | < 0.05 -0.8                            |                  |
| Li      | 2                                       | 0.7 -40                                | $\text{Li}^+$    |
| Lu      | 0.003                                   | 0.002-0.005                            |                  |
| Mg      | 4000                                    | 400-6K                                 | $\text{Mg}^{2+}$ |
| Mn      | 8                                       | 0.02-130                               |                  |



Table 1.3 (Cont.)

| Element | Median<br>( $\mu\text{g.}/\text{kg.}$ ) | Range<br>( $\mu\text{g.}/\text{kg.}$ ) | Species                   |
|---------|---|--|---------------------------|
| Mo      | 0.5                                     | 0.03-10                                | $\text{MoO}_4^{2-}$       |
| N       | 50                                      | 2 -1800                                | $\text{NO}_3^-$           |
| Na      | 6000                                    | 700-25K                                | $\text{Na}^+$             |
| Nd      | 0.15                                    | < 0.06-0.25                            |                           |
| Ni      | 0.5                                     | 0.02-27                                |                           |
| P       | 20                                      | 1-300                                  | $\text{PO}_4\text{H}_2^-$ |
| Pb      | 3                                       | 0.06-120                               |                           |
| Ra      | $4 \times 10^{-7}$                      |  |                           |
| Rb      | 1                                       | 0.6-9                                  | $\text{Rb}^+$             |
| Rn      | $1.7 \times 10^{-12}$                   |  | Rn                        |
| S       | 3700                                    | 200-40K                                | $\text{SO}_4^{2-}$        |
| Sb      | 0.2                                     | 0.01-5                                 | Sb(V)                     |
| Sc      | 0.01                                    | 0.004-0.04                             |                           |
| Se      | 0.2                                     | 0.02-1                                 | $\text{SeO}_3^{2-}$       |
| Si      | 7000                                    | 500-12K                                |                           |
| Sm      | 0.06                                    | 0.01-0.12                              |                           |
| Sn      | 0.009                                   | 0.004-0.09                             | Sn (IV)                   |
| Sr      | 70                                      | 3 -1000                                | $\text{Sr}^{2+}$          |
| Ta      | < 0.002                                 |  |                           |
| Tb      | 0.003                                   | 0.001-0.005                            |                           |

Table 1.3 (Cont.)

| Element | Median<br>( $\mu\text{g.}/\text{kg.}$ ) | Range<br>( $\mu\text{g.}/\text{kg.}$ ) | Species                 |
|---------|---|--|-------------------------|
| Th      | 0.03                                    | 0.007-0.1                              | Zn <sup>2+</sup> , Org. |
| Ti      | 5                                       | 3-18                                   |                         |
| U       | 0.4                                     | 0.002-5                                |                         |
| V       | 0.5                                     | 0.01 -20                               |                         |
| W       | 0.03                                    | <0.02 -0.1                             |                         |
| Yb      | 0.01                                    | 0.005-0.2                              |                         |
| Zn      | 15                                      | 0.2 -100                               |                         |
| Zr      | 0.8                                     | 0.05 -20                               |                         |

### 1.3.2 Water Pollution [3]

There are two ways of looking at the problem of water pollution. The first, or global view, attempts to compare the amounts of the elements added to rivers and sea each year by natural and human origins. The second, or local view, investigates the effects of single substance polluting limited volumes of water. /

By global point of view the elements can be divided into four classes according to their potential to pollution, as following :-

- a) Very high potential pollution :- Ag, Au, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Tl and Zn

- b) High potential pollution :- Ba, Bi, Ca, Fe, Mn, Mo, P, Ti, and U
- c) Moderate potential pollution :- Al, As, B, Br, Cl, Co, F, Ga, K, Li, Na, Ni, Rb, V and W
- d) Low potential pollution :- Ga, I, La, Mg, Nb, Si, Sr, Ta and Zr.

Local effects of fresh water pollution have been reviewed by many investigators. Among the many different types of pollution these authors recognize inorganic, particulate and organic variants.

Inorganic pollution arises from industrial, mining and agricultural wastes. The commonest toxic materials are Cyanides, Copper, Lead and Zinc. These materials may effect organisms for many kilometres along a stream.

### 1.3.3 Toxicology

#### 1.3.3.1 Arsenic [4]

All compounds of arsenic are toxic and in sufficient concentration will cause death or illness to humans, animals and plants. The particular of acute poisoning by arsenic compounds due to ingestion or inhalation are of little interest in relation to environmental pollution, but in summary many vital functions are affected, and death may result from relative small amounts of arsenic. Chronic intoxication due ingestion or inhalation has been

described and unlike the acute disease, early manifestations include subjective complaints and such non-specific symptoms as weakness, malaise, abdominal complaints, and pains involving the extremities.

Arsenic is usually included on the list of substances suspected of being carcinogenic to humans. This potential carcinogenicity is the single most important aspect of concern with arsenic in the environment.

#### 1.3.3.2 Cadmium [4]

Cadmium has been known since 1858 to exert toxic effects. The acute effects of oral ingestion in man are those of immediate nausea and vomiting which can occur from as little as 15 mg. of total cadmium.

Since cadmium accumulates to a very high degree in the liver and kidney one might expect that these organs would be the site of any possible malignant changes; however, these appear to have been no epidemiologic studies indicating that this is occurring. The significance for human cancer of animal experiments in which relatively large quantities of reactive metals are injected in a variety of sites is difficult to interpret with reference to the care of very low level exposures in the human environment. Considerable interest has been sparked recently by reports of a syndrome occurring in Japan and attributed by many to environmental pollution with cadmium. Itai-itai appears to be an endemic condition, seen particularly in elderly females, characterized by pain in the bones and joints,

waddling gait, aminoaciduria, glycosuria, severe osteomalacia, and multiple pathological fractures. Cases began to be observed about 1912 in an area potentially contaminated with metals from a lead mine. The number of cases increased about the time that the mine began to produce zinc and cadmium. Over a period of 15 years, some 200 persons living along the banks of the Jintsu River suffered from the syndrome. Half of them died. Women 50-60 years of age who had borne many children were especially at risk.

#### 1.3.3.3 Chromium [4]

It is probably true that all compounds of chromium are toxic in sufficiently high concentrations, but certain compounds have been demonstrated to be much more toxic than the others. By far the most important effects of exposure to chromium result from the hexavalent compounds, or chromates. Depending upon their solubility to some extent, these compounds are usually irritating and toxic to all tissues. Cancer in the respiratory tract is the known type of cancer related to chromium compounds and in the great majority of cases this is found to be bronchogenic carcinoma.

#### 1.3.3.4 Mercury [4]

Man-made alterations in patterns of distribution of mercury in the hydrosphere have been of increasing concern in several parts of the world. In Japan a mysterious illness, subsequently named Minamata disease, first made its appearance in the latter part of 1953, the highest incidence being among fishermen and their

families. Later, when it was recognized that seabirds and household cats were being affected, attention was focused on fish and shellfish as etiological factors. This in turn led to a study of the water in Mimanata Bay and to the identification of mercury in a factory effluent as the cause of the disease. Late in 1967, the Swedish Medical Board found it necessary to ban the sale of fish from about 40 Swedish rivers and lakes, due to the finding of high concentrations of methyl mercury in fish caught in these waters. Some investigators have shown that microorganisms isolated from the sedimentary beds of rivers, canals, Lakes and even from aquaria are capable of methylating inorganic mercury. Mercury is thus converted into a highly diffusible form capable of leaving the sediment entering the water phase and there by into a variety of organisms, including fish. The hazard to man is increased by the fact that most of the methyl mercury found is in the edible portion of fish and the degree of accumulation in human brain is much greater than in most other species. Accumulation in liver, kidney, heart, lung and muscular tissues has also been reported. Chronic syndrome is characterized by self-consciousness, timidity, embarrassment with insufficient reason, anxiety, indecision, depression; these appear sometimes to cause a complete change of personality. Headache, fatigue, weakness and either drowsiness or insomnia are frequent complaints. Other symptoms of chronic mercurialism has been reported elsewhere. [5]

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#### 1.3.3.5 Cobalt [6]

Cobalt is an essential element for human metabolism but in high concentration may cause some disorder behaviours. The possible toxic effects of cobalt compounds have been studied. Cobalt is very toxic to plants.

#### 1.3.3.6 Antimony, Molybdenum, Tungsten, Selenium and Zinc [3]

Antimony is moderately toxic to all organisms. Sb in industrial smoke may cause lung disease. Molybdenum is essential to all organisms except perhaps some green algae. It has a moderate toxicity, excessive Mo inhibits reduction of sulphate. Tungsten is moderately toxic to plants and slightly toxic to mammals. Selenium is essential to mammals, where it can replace vitamin E and to a few angiosperms. It occurs in a few aminoacids and many proteins. Selenium toxicity to mammals is relatively higher than to plants. Zinc is also essential to all organisms. It has a moderate toxicity to plants and slightly toxic to mammals.

#### 1.3.4 Residence times of the elements in man and cumulative poisons [3]

The residence times of the elements in man has been estimated and results in table 1.4. The very long residence times found for some elements means that these elements can be classified as accumulative poisons.



Table 1.4 Residence times of the elements in Man. [3]

| Element   | Residence times in the body<br>(days) |
|---|---------------------------------------|
| Hg, K, Mo   | 50 - 100                              |
| Co, Cs, Mn, Rb                                    | 100 - 200                             |
| As, Sb, Se  | 200 - 400                             |
| Cd  | 400 - 800                             |
| Ba, Ca, Cu, Ni, Ra, Sn,<br>Sr, Ac, Am, Cm, Fe, Pb | 800 - 1600                            |
| Pu, Th, Zn  | > 1600                                |

### 1.3.5 Water Analysis

#### 1.3.5.1 Sample collection

Whatever the type and sensitivity of the analysis of microconstituents to be used, the problem of primary importance namely contamination arises during sampling. Many data are of doubtful value because of improper sampling operations, even though they were obtained through precise and sophisticated methods of analysis.

Sampling procedures are discussed in some details in **Reference Methods for Marine Radioactivity Studies**. [7] A brief recommended procedures are presented here. Water samples from the

surface level are taken by pumping or with a polythene bucket. Sampling at various depths is performed by pumping or by using Nansen bottles which are shut at the desired depth by sending a 'messenger' down the hydrographic wire, to which the samplers are attached. A separation between dissolved salts and suspended matter is achieved by filtration through 0.45  $\mu\text{m}$ . membrane filters or centrifugation. This should be done as soon as possible to avoid the chemical exchange between the two phases.

#### 1.3.5.2 Sample storage

Water samples should preferably be stored in containers of linear polyethylene, polypropylene or PTFE. Acidification to pH less than 1.5 is often recommended. [7] Some investigators [8,9] reported on changing in trace elements during storage in glass or even polyethylene bottle both quantitatively (adsorption losses, leaching of contaminants from the storage vessel) and qualitatively (change of the chemical form). So if preconcentration is necessary, it should be carried out as soon as possible after sampling. The preconcentration procedure should be simple and result in a concentrate that can be stored for considerable time without deterioration.

#### 1.3.5.3 Sample preparation

Preconcentration and separation of the elements of interest from bulk sample from other major dissolved salts respectively resulting small size of concentrate samples is preferable

for neutron activation analysis. Thus sensitivity of the analytical system is increased, radiolysis of water is prevented and radiation burden can be avoided. Non destructive neutron activation analysis of trace elements in fresh water after preconcentration by freeze-drying has been studied. [11] This technique is timeconsuming and limited to only long-lived radionuclides for sea water since the major salts with high radiation burden are still present. Further study using Hydrated antimony pentoxide (HAP) to eliminate  $^{24}\text{Na}$  in combination with Dowex 1x8 anion exchange resin has been done. Any how, this method is still inconvenient.

Solvent extraction procedure avoiding the instability of chelate-complexes in an organic solvent during storage is described. The method is restricted only to short-lived radionuclides as irradiation in a reactor causes considerable radiation damage. Ion exchange chromatography using Chelex-100 resin is especially appropriate for the preconcentration of a group of trace elements from sea water. [12,13] It permits the treatment of large volume of sea water and yields a high concentration factor. Direct activation of the resin, containing the retained elements, is sometimes performed, but impurities in the resin often prevent an accurate determination. Usually the resin is eluted and the eluate evaporated to dryness. This is too complicate.