



## CHAPTER I

### INTRODUCTION

The term 'trace metal' when applied to seawater is generally taken to include all metals at concentrations of less than 1 mg/kg. This definition includes almost all of the metals present in the earth's crust.

The purpose of studying trace metals in seawater in the past until now by the chemical oceanographer can be classified into two categories :

(a) Studying the role of trace metals. The purposes are to increase or to gain the knowledges of the role of the trace metals in the open sea, coastal seawater and estuary such as the biochemical and geochemical cycles, horizontal variation, seasonal variation, types of distribution, speciation of trace metals into the ocean etc.

(b) Studying the environmental impacts of trace metals. The determination of trace metals, particularly the heavy metals, has received increasing attention in pollution studies. There are many scientific conferences on metal pollution in the marine environment that help identifying the major pollution problems, examining the critical issues and determining ways in which a meaningful base-line survey can be conducted and a useful monitoring program can be established. The background levels of trace metals in unpolluted water and in polluted water, gained from the monitoring program, are needed in order to access accurately the environmental hazard and to

set a management plan for pollution control and recovery of the marine environment and also natural resources.

Three major stages in determining the level of trace metals in natural water are sampling, sample preconcentration and/or preservation and analysis. Each stage has its own importance and also relates to each other at the same time. If there is an error or mishandling at any stage it will seriously affect the quality of data which are later used for interpretation.

#### Problems in Seawater Analysis.

The main problems facing every chemical oceanographer who analyses seawater for its trace metal content are as follows :

1. The Very Low Concentrations of Trace Metals.

The concentration of many trace metals of current analytical interest fall within the range of 0.01 - 10  $\mu\text{g}/\text{l}$ . There is one thing to notice about the levels of trace metals in seawater. Since 1966's onward the levels of trace metals reported which are determined by the analysts tends to decrease dramatically. This is because there are developments on the accuracies and sensitivities of the analytical techniques (Table 1.1).

2. The High Salt Content of the Matrix.

We know that, as a solution, seawater contains approximately 3 to 3.5 % dissolved solids, primarily halides, sulfates and carbonates of sodium, magnesium, calcium, potassium and strontium. These components having concentrations of 1 mg/kg or greater (Table

**Table 1.1** Analytical techniques and their detection limits for determining trace metal (1).

Analytical Techniques	Approximate amount in g							
	-9 10	-10 10	-11 10	-12 10	-13 10	-14 10	-15 10	-16 10
1) Gravimetry								
2) Titrimetry								
3) Colorimetry in solution								
4) Fluorescence reactions								
5) Inverse Voltametry								
6) Flame emission spectroscopy								
7) Atomic Absorption Spectroscopy								
8) Gas Chromatography								
9) X-ray Fluorescence (XRF)								
10) Radiometry								
11) Activation analysis								
12) Mass Spectrometry								

■ : applicable to most elements  
 □ : applicable to some elements

**Table 1.2** Concentration of the major ions in seawater of various salinities (g/kg)\* (2)

Salinity (‰)	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Sr <sup>2+</sup>	B	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Br <sup>-</sup>	F <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>
5	1.539	0.185	0.058	0.057	0.001	0.001	2.763	0.387	0.010	0.0002	0.020
10	3.078	0.370	0.118	0.114	0.002	0.001	5.527	0.775	0.019	0.0004	0.041
15	4.617	0.555	0.177	0.171	0.003	0.002	8.290	1.162	0.029	0.0005	0.061
20	6.156	0.739	0.235	0.228	0.005	0.003	11.054	1.550	0.038	0.0007	0.081
25	7.695	0.924	0.294	0.285	0.006	0.003	13.817	1.937	0.048	0.0009	0.101
30	9.234	1.109	0.353	0.342	0.007	0.004	16.581	2.325	0.058	0.0011	0.122
31	9.542	1.146	0.365	0.353	0.007	0.004	17.133	2.402	0.059	0.0011	0.126
32	9.850	1.183	0.377	0.365	0.007	0.004	17.685	2.480	0.062	0.0012	0.130
33	10.157	1.220	0.388	0.376	0.007	0.004	18.239	2.557	0.063	0.0012	0.134
34	10.465	1.257	0.400	0.388	0.008	0.004	18.791	2.635	0.065	0.0012	0.137
35	10.773	1.294	0.412	0.399	0.008	0.004	19.344	2.712	0.067	0.0013	0.142
36	11.081	1.331	0.424	0.410	0.008	0.005	19.897	2.789	0.069	0.0013	0.146
37	11.389	1.368	0.435	0.422	0.008	0.005	20.449	2.867	0.071	0.0013	0.150
38	11.696	1.405	0.447	0.433	0.009	0.005	21.002	2.944	0.073	0.0014	0.154
39	12.004	1.442	0.459	0.445	0.009	0.005	21.555	3.022	0.075	0.0014	0.158
40	12.312	1.479	0.471	0.456	0.009	0.005	22.107	3.099	0.077	0.0015	0.162
41	12.620	1.516	0.482	0.467	0.009	0.005	22.660	3.177	0.079	0.0015	0.166
42	12.928	1.553	0.494	0.479	0.009	0.005	23.213	3.254	0.081	0.0015	0.170

\* Cations concentrations: averages of mean results of Cox and Culkin (1967) and Riley and Tongudai (1967). Sulphate and bromide concentration based on mean values from Morris and Riley (1966).

1.2). The concentration of these constituents vary so little that they have been considered to be conservative, or almost so in behaviour.

In analysis of seawater sample, since the concentrations of trace metals are lower than those dissolved solids so the dissolved solid can cause serious interferences. For example, Brook et al (3) found that direct aspiration of seawater into Flame Atomic Absorption Spectrophotometer usually resulted in difficulties associated with clogging of the burner and scattering effects because of the high salt contents. Segar and Gonzalez (4) tried to analyse trace metals in seawater by direct atomization of seawater sample but the results seem to be unsatisfactory, owing to the scattering interferences by the dissolved solids. Bruland et al (5) found that large amount of calcium and magnesium were retained on the Chelex resin and eluted with the acid. Calcium and magnesium in the acid can suppress the absorbance signal of metals during measurement by FAAS. Haraguchi (6) found that concentrated salts and undissolved particulated caused severe interferences with the determination of trace metals by AAS.

### 3. The Contamination and Loss of Trace Metals.

At such extremely low levels of trace metals in seawater, contamination may occur at any stage either during sampling procedure, sample preparation or analysis.

Theirs (7) has grouped contamination errors into three basic types :

- positive contamination resulting from the addition of extraneous matter to the sample;



- negative contamination resulting from unexpected losses from the sample;
- pseudo-contamination arising from factors which are unrelated to the element of concern but produce either positive or negative errors in the final data.

Although positive forms of contamination present the most obvious threat to trace metals studies, all three types must be considered. Negative contamination can be an important factor in sample storage while pseudo-contamination problems may arise with the introduction of compounds or elements which interfere in the analysis but are themselves not measured.

3.1 Contamination from Seawater Samplers. Sampling of seawater sample may be carried out in three ways. Firstly, by using a water sampling bottle or device which is lowered open to an appropriate depth and then closed by a signal sent from the surface. Secondly, by lowering a hose to the depth required and pumping the water to the surface. Thirdly, by adsorbing the required element, or compound in water at the desired depth onto a mass of appropriate adsorbent. Of these, the first approach is undoubtedly the more important, although pumping has advantage if large samples are to be collected and is essential if continuous profiling is to be carried out. An ideal seawater sampling device for trace metals must be able to obtain a representative sample from the designated sampling depth and return the sample uncontaminated to the surface. In addition, the sampling device must be practical in term of cost and ease of handling.

Many sampling devices of different designs, materials and sizes have been used. Until about 1962, sampling devices including the Nansen and Knudsen type were nearly all constructed from brass or other copper-brass alloys which had been heavily coated with metal, or, more recently with Teflon (PTFE) to protect them from corrosion. But, the protective coating becomes pitted or worn, exposing the brass to the corrosive action of seawater resulting in the release of significant amounts of Cu and Zn into the collected sample. Recently, several types of plastic sampling devices, such as Niskin, made of polypropylene, polycarbonate or polyvinyl chloride have been used for seawater sampling. Unfortunately, the material used for the end-caps or springs, rubber or Teflon-coated stainless steel, sometimes release significant amount of Ba, Cu, Sb and Zn (8). Hydrowire is another source of contamination because it can release Fe to the seawater.

Contamination of samples might result not only from sampling devices or hydrowire but also from wastes discharged into the sea from the ship. The latter source of contamination can be minimized by carrying out sampling to windward.

3.2 Contamination from Filtration Suspended particulate matter and marine organisms are present in seawater. The total amount of suspended matter varies greatly according to the environment from ten of milligrams per litre in estuaries to a few micrograms or less per litre in the deep waters of the ocean remote from land. The size distribution of the particulate matter varies considerably with environment, the largest particle often being silt-sized in estuaries and inshore waters, and small clay-sized in deep oceanic waters. A considerable number of trace elements such as Fe, Cu, Zn, Cd, Pb and

Mn are present in the adsorbed form on the suspended inorganic and organic organisms. Bruland and Frank (5) compared the analytical results between filtered and unfiltered seawater samples from deep seawater (1,800 m) and coastal seawater (25 m). They found that the contents of particulate trace metals (Cu, Cd, Pb and Ni) from deep water were less than 1 % of the total concentration and filtering deep seawater did not cause significant differences but differences due to filtration should be taken into account for coastal and surface seawater. Therefore, in seawater analysis, it is important to separate the particulate fraction from the dissolved fraction and to analyse them separately. Although this separation can be done by high-speed centrifugation, it is preferably done by filtration.

However, the filtration may alter the composition of the water sample being filtered either by removing the trace metals species through adsorption by the filter, which is called the negative contamination, or by contaminating the water sample with substances dissolved from the materials of filter which is called the positive contamination. Riley (9) found Millipore HA filters adsorbed appreciable amounts of inorganic Hg from seawater, whereas glass filter caused < 7% loss and in Table 1.3 shows that such filters cause negligible contamination of water samples for most trace metals, provided that a sufficient quantity of water (usually > 10 l) is passed through the filter. To minimize this possibility, filters should be cleaned either by filtration of a sufficiently large volume of water, 10 l or more, or by washing with diluted acid. The filter support should be non-contaminating and teflon is a recommended choice. Filtration can be carried out under partial vacuum or under

Table 1.3 Maximum possible contamination by 47 mm Millipore HA (0.45  $\mu\text{m}$ ) filters using a 10 L water sample (9).

Element	Fe	Cr	Mn	Cu	Zn	Ba	Ni	Ag	Mo	Co
Concentration in filter ash (%)	1.4	0.75	0.12	1.2	0.77	0.05	0.08	0.01	0.02	0.006
Sea water concentration ( $\mu\text{g l}^{-1}$ )	1	0.5	2	3	3	20	7	0.03	10	0.01
Maximum contamination as percentage of sea water concentration	6	6	0.25	1.7	1	0.01	0.04	1.7	0.008	2

Table 1.4 Properties and suitabilities of materials for use in trace metal work (22).

	Comments	Recommendation
Polyvinyl chloride	Often seriously contaminated with trace metals; may adsorb others.	Do not use; but needs more research because of its use in samplers, etc.
Polyethylene		
A. cross-linked (conventional)	May be a source of Sb, Co, Cr, Fe; may sorb Zn and some other trace metals. Batches vary widely.	Can be used, but needs checking before use in any application.
B. linear	Probably better than cross-linked	Can be used, but needs further study
Polypropylene	Removed Ba (and Sr?) at pH > 3.5, also lanthanides and Ag.	Can be used, but needs more study
Polystyrene	Removed Ag.	Needs more study in view of its use in disposable apparatus.
Polytetrafluoroethylene	Probably the best general purpose plastic; but expensive, soft and subject to pinholing when used as coatings. Sorbed Ag.	Recommended.
Acrylate	Levels of impurities very low; sorbed Zn and Ag.	Needs more study in view of use in samplers.
Silica	Composition variable; subject to attack under alkaline conditions.	Recommended, but needs further study
Borosilicate glass	Attacked chemically at sea water pH	Unsafe in many applications.
Vycor glass	Attacked chemically at sea water pH; trace metal content variable.	Unsafe.
Soft glass		Rarely safe for trace metal work.



pressure. Pressure filtration also permits filtration directly from the sampler under an inert atmosphere, an important consideration in preventing air-borne contamination and in the preservation of the redox state of the sample (10,11).

3.3 Contamination from Sample's Container. It is obvious that analysis of seawater samples should be carried out immediately after collection, but this is seldom practical because of lack of time, personnel or adequate analytical facilities on board a ship. Therefore, samples are usually stored in containers. Whenever samples for trace metals analysis are to be stored unconcentrated for more than a few hours, special attention must be paid to the storage conditions and also the choice of suitable materials to be used as container for storing water since the concentrations of such trace metals may be changed as a result of contamination arising from desorption of trace metals from particulate matter, its liberation during breakdown of marine organisms, or the sample may be contaminated by dissolution and desorption of trace metals from container wall. Contamination from the first two of three sources can be prevented by filtration of the sample, although even with this, difficulties may arise because of leaching of the filter as previously mentioned in Section 3.2. In addition, trace metals may be lost from samples by adsorption onto the container walls or by chemical changes such as precipitation or colloidal formation. For many trace metals, these changes are rapid.

Many workers have been investigated the significant loss of trace metals from water samples upon storage (12-18). Eichholz et al (12) found loss of trace metals from water samples when

stored in polyethylene and borosilicate (Pyrex) glass containers. Robertson (19) investigated losses of Ag, Co, Fe, In, Sc and V from seawater stored in Pyrex and polyethylene containers and found significant losses of these metals. The loss of Hg from water samples upon storage has been showed to be a serious problem by many workers (15-17). These losses of Hg are caused by rapid adsorption on container walls (16). Lo and Wai (20) reported that 81 % of Hg in untreated samples was lost to the walls of the polyethylene containers and the remaining 19 % was volatilized from solution, at the atomic state, to the atmosphere. Besides, a decrease in concentration due to loss by adsorption, there may be an increase in concentration due to contamination. Bothner and Robertson (21) reported that seawater samples stored in polyethylene containers, could, under certain conditions, showed an increase in the Hg concentration with time because of contamination. Bowen et al (22) have reviewed the properties of the various materials available for the construction of apparatus for trace metals analysis and sample storage. From their report (Table 1.4), it seems that glass of any kind is generally unsuitable for trace metals work. PTFE (Polytetrafluoroethylene) and fused silica seem to be the best materials since they are chemically inert and contain very low levels of trace metals (Table 1.5), but they are expensive. Silica is also fragile. The much cheaper high density polyethylene is only slightly inferior in purity.

In an effort to remove trace impurities from material surfaces, it is necessary to thoroughly clean the containers prior to use in order to prevent leaching of metals from the container during storage. The cleaning procedures are suggested by many workers

Table 1.5 Trace metal content(ppb) of some materials commonly used in trace metal sampling and storage (23-24).

Material	Zn	Fe	Sb	Co	Cr	Sc	Cs	Ag	Cu
Polyvinyl chloride	$7 \times 10^3$	$2.7 \times 10^3$	$2.7 \times 10^3$	45	.2	4.5	<1	<5	630
Polyethylene	55	7.4	$9 \times 10^3$	140	254	11	<100	<200	nm
hose	28	$10^4$	0.2	$7 \times 10^{-2}$	76	$8 \times 10^{-3}$	$<5 \times 10^{-2}$	<1.1	6.6
container (Nalgene)	9.3	35	0.4	1.7	<30	$<4 \times 10^{-3}$	$<10^{-2}$	<0.3	22
Polytetrafluoroethylene									
Polymethyl methacrylate	<10	<140	$<10^{-2}$	$<5 \times 10^{-2}$	<10	$<2 \times 10^{-3}$	$<6 \times 10^{-2}$	$<3 \times 10^{-2}$	<9.5
Surgical rubber tubing*	$3 \times 10^4$ to $4 \times 10^3$	<100	<100 to 360	<30 to $7 \times 10^3$	$4 \times 10^3$	<8 to 185	<100 to 580	<700 to 1240	<6
Neoprene rubber	$1.8 \times 10^3$	um	290	$2 \times 10^3$	um	$3 \times 10^3$	um	<1000	um
Silica tubing									
(Suprasil)	<1	nm	$<10^{-2}$	12	2.5	0.4	<0.1	$<10^{-2}$	$4 \times 10^3$
(Spectrosil)	1.5	400	$5 \times 10^{-3}$	0.44	6.5	$3 \times 10^{-2}$	1	$5 \times 10^{-3}$	2
Borosilicate glass	730	$3 \times 10^3$	$3 \times 10^3$	81	um	106	<100	$<10^{-3}$	nm
Vycor glass	um	um	$10^4$	um	um	um	um	um	um
Millipore filter	$2 \times 10^3$	330	39	13	$1.7 \times 10^4$	0.8	1.5	$5 \times 10^{-2}$	nm
Kimwipe tissue	$5 \times 10^4$	$10^3$	16	24	500	14	<0.1	~0.8	nm
Steel hydrographic wire	um	—	$5 \times 10^4$	$6 \times 10^4$	um	<50	um	um	$2 \times 10^4$

\* Range of values of samples from 3 different suppliers.

nm = not measured um = could not be measured because of interference from other radionuclides.

Table 1.6 Typical trace metal concentrations(ppb) in some reagents and solvents (from instrumental neutron activation) (23).

Sample	Zn	Fe	Sb	Co	Cr	Sc	Cs	Ag	Cu
Quartz distilled water	1-10	<0.2-1	0.06-0.10	0.04-0.20	2-10	0.002	<0.01-0.1	<0.02	nd
Double distilled water	~1	<0.2	<0.01	<0.02	~2	$<10^{-4}$	<0.01	<0.02	nd
Triple distilled water	~0.5	~1	<0.02	<0.02	12	$\sim 2 \times 10^{-4}$	<0.01	<0.02	nd
Nitric acid <sup>1</sup>	13	~2	~0.03	0.02	72	$7 \times 10^{-4}$	<0.01	~0.24	1.3
Hydrochloric acid <sup>1</sup>	22	~1	0.20	0.09	1.1	0.002	<0.002	<0.1	82
Sodium hydroxide <sup>1</sup>	<20	<900	0.32	5.5	60	0.3	0.7	<0.2	nd
Ammonia solution <sup>1</sup>	2	<0.1	<0.006	~0.009	<0.04	$<3 \times 10^{-4}$	<0.002	<0.1	6.0
Carbon tetrachloride <sup>2</sup>	1.2	10	0.3	~0.003	<50	~0.002	<0.1	<0.005	0.12
Chloroform <sup>3</sup>	2.1	1.6	0.05	~0.003	<100	$\sim 3 \times 10^{-3}$	<0.02	<0.005	0.29
Dithizone	1100	<7000	0.8	1.2	<2000	0.15	10	<10	420
Thionalide	120	<300	3.7	5.1	um	0.29	<10	<2	0.4
Ammonium pyrrolidine dithiocarbamate	1970	~5000	1.9	1.3	um	0.11	<1	<1	4
8-hydroxyquinoline <sup>4</sup>	<40-370	<100-5700	<0.2-1210	<0.2-1.8	<50	<0.02-0.14	<0.1-0.4	0.6	290

<sup>1</sup> Baker and Adamson CP reagent.

<sup>2</sup> Baker Analyzed Reagent, doubly distilled.

<sup>3</sup> Mallinckrodt Analytical Reagent, doubly distilled.

<sup>4</sup> Ranges for 4 samples from different manufacturers.

nd = not determined.

um = could not be determined because of interference by other radionuclides.

(16, 21, 24-26). Exact procedures will depend on materials and the blank level required. Erickson (27) recommended that the procedure described by Zief and Mitchell (28) and the Participants in the Lead in Seawater Workshop (26) should be adequate for most metals.

3.4 Contamination from the Reagents and the Laboratory Atmosphere. Contamination arising from impurities present in reagents is another serious problem in the determination of trace metal in seawater. Analytical grade chemicals should not be used without further purification in the determination of the more ubiquitous elements such as Cu, Zn, Pb and As. Robertson (23) investigated the levels of some trace metals in a wide range of acids, solvents and chemical used in trace metal analysis. The results (Table 1.6) clearly showed the severity of the problem due to impurities present in reagents. Particular care should be taken in the purification of reagents and solvents, including water, to avoid contamination. Some workers (29-32) developed the purification procedure, such as sub-boiling distillation, of reagents especially for the mineral acids. The results of the sub-boiling distillation (or double distillation process) are showed in Table 1.7 (30).

Another serious source of contamination is the ambient air in any analytical laboratory, particularly if the air is moving such as in a fume hood or near a window. Although the control of temperature and humidity of analytical laboratories with sophisticated instrumentation has now become a common practice, the need for regulation of airborne contamination is still not regarded. These contaminants, usually in the form of dusts, mists and fumes, circulate in the atmosphere and can enter laboratories through any



Table 1.7 Average impurity concentration (ppb) in double distilled acids (the method of analysis based on isotope-dilution spark-source mass spectrometry (ID-SSMS)) (30).

Element	HCl	HNO <sub>3</sub>	HClO <sub>4</sub>	HF	H <sub>2</sub> SO <sub>4</sub>
Pb	0.02	0.03	0.22	0.1	0.3
Tl	0.04	0.06	0.07	0.07	0.1
Ba	0.04	0.02	0.17	0.09	0.3
Te	0.02	0.03	0.05	0.05	0.09
Sn	0.12	0.02	0.14	0.15	0.12
Cd	0.03	0.02	0.05	0.05	0.16
Ag	0.21	0.06	0.06	0.18	0.3
Sr	0.03	0.02	0.02	0.03	0.16
Se	0.03	0.06	0.5	0.21	-
Zn	0.13	0.06	0.2	0.19	2.5
Cu	0.08	0.05	0.10	0.26	0.14
Ni	0.12	0.08	0.37	0.45	0.12
Fe	2.5	0.35	1.2	2.5	3.7
Cr	0.16	0.06	3.2	2.1	0.12
Ca	0.12	0.11	0.6	1.3	1.2
K	0.5	0.17	0.37	0.9	2.3
Mg	0.27	0.09	0.12	1.0	2
Al	1.0	0.7	0.4	0.85	1
Na	0.8	0.7	1.2	4.0	6

vent. The common constituents in ambient air are aerosols composed mainly of solids and liquid particulate matter which can cause serious contamination problems at the trace/ultratrace levels (33-35). To solve this problem, the analysis must be performed in controlled laboratory environment to prevent the sample from being contaminated by artifacts contributed by the laboratory atmosphere or worked in positive pressure laminar flow hood. Adeloju and Bond (35) demonstrated the significance of clean room conditions for precise and accurate determination at the lower trace/ultratrace levels as showed in Table 1.8. Apart from Cd for which little or no contamination is experienced, most common trace metals, Cu, Pb and Zn, can not be adequately and accurately determined in uncontrolled laboratory environment even at the lower trace level. We can see that extreme cleanliness in working will very much reduce contamination and, in addition, the analytical chemist should observed at all times clean room disciplines.

#### Analytical Techniques for Determination of Trace Metals in Seawater.

Because of the extremely low concentration at which many trace metals are present in seawater, it is very important to guard against contamination during sampling, storage and seawater analysis.

As mentioned in the previous section, we can see that the third problem of the contamination and loss of trace metals from the sample can be controlled by the care taken in handling the sample and by the method chosen. But the first two problems can not be controlled because it is the natural condition of seawater regardless of the input of trace metals to seawater by human activities.

Table 1.8 Influence of laboratory environment on the determination of some trace elements in seawater (35).

amt of element, $\mu\text{g/L}$				
element	clean lab		conventional lab	
	acidified pH 2.7	nonacidified pH 8.2	acidified pH 2.7	nonacidified pH 8.2
Cd	$0.05 \pm 0.01$	$0.06 \pm 0.02$	$0.06 \pm 0.02$	$0.08 \pm 0.02$
Cu	$0.81 \pm 0.04$	$0.56 \pm 0.05$	$7.22 \pm 1.95$	$4.76 \pm 3.00$
Pb	$0.63 \pm 0.03$	$0.42 \pm 0.04$	$1.72 \pm 0.82$	$1.27 \pm 0.56$
Zn	$1.71 \pm 0.05$	$0.32 \pm 0.09$	$4.07 \pm 2.59$	$3.52 \pm 1.81$

Water sample were kept in the clean room but were exposed to the different laboratories during acidification and determination step. Error is mean deviation based on triplicate determination.

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There are two main approaches in the determination of trace metals.

1. Direct Analysis.

In the case that the levels of trace metals in samples are of appreciable concentration, the direct determination of some trace metals can be done by some techniques such as atomic absorption spectrometry, x-ray fluorescence, radiometry, neutron activation analysis and mass spectrometry.

2. Indirect Analysis.

However, the concentration of many trace metals in seawater of current analytical interest are extremely low. Table 1.9 shows the concentration of some trace metals in seawater. Since the concentrations of trace metals in seawater vary geographically, spatially and in depth and such variations are generally caused by the biological activities and physicochemical process in the ocean. Thus, the concentration of metals in Table 1.9 are not representative of those for all ocean. We can see that from their concentrations, it is insufficient for the direct determination by some analytical techniques (Table 1.1) although some can be detected by other analytical techniques.

By considering the detection limit of the analytical techniques which are used for determining the concentration of trace metals in Table 1.1, the first two techniques can not detect the trace metals in unpolluted seawater, the third, fourth and eighth technique are suitable for determining the organic compounds. Even if the



Table 1.9 Concentration (ppb) of some trace metals in seawater.

Metal	Seawater in 1966 (6)	Open Ocean in 1971 (36)	Seawater in 1973 (37)	Open Ocean in 1975 (38)
Al	10	5	1	1-10
Cd	0.11	0.05	0.11	0.1-0.6
Cr	0.05	0.60	0.20	0.2-2
Co	0.27	0.08	0.05	< 0.1
Cu	3	3	2	< 4
Fe	10	3	3.4	1-10
Pb	0.03	0.03	0.03	0.2-0.1
Mn	2	2	1.9	0.2-4
Ni	5.4	2	2	0.5-3
Zn	10	5	2	0.5-4

Table 1.10 Estimated cost of various analytical techniques for trace metals (1).

Analytical Techniques	Cost ( $10^3$ US\$)	Number of sample
1) Pulse polarography	5 - 10	10 - 20
automated	20 - 25	30 - 40
2) Eletrothermal AAS	8 - 15	50
automated	30 - 45	50 - 100
3) Atomic emission	70 - 120	100
4) Mass spectroscopy	250 - 300	4
5) NNA, multichannel	90	10

detection limit of the tenth to twelfth techniques can be used for direct measurement of trace metals in seawater but considering their cost for analysis in Table 1.10, they cost more than the fifth and seventh techniques. Besides, the fifth technique can measure only the metals which can form amalgam with mercury, so the number of trace metals which can be measured by the fifth technique are limited and smaller than the seventh technique. In addition, if we consider the commonness of instruments that are currently used in Thailand between the fifth and seventh technique, the seventh technique is more common than fifth technique. However, for the seventh technique, itself, still has the problem about interference of salt matrix even though it can be used for direct analysis of trace metals in seawater (39, 41) provided that there are sufficient concentrations of trace metals in seawater.

In trying to overcome the first two problems as described earlier, a sample preparation technique is needed. The sample preparation technique is used to preconcentrate the trace metals present in sample before analysis. This technique is able to enrich the concentrations of trace metals and able to separate them from the salt matrix at the same time.

#### Preconcentration.

There are several techniques that can be chosen for preconcentration namely solvent extraction, coprecipitation, ion exchange, co-crystallization depending on their limitations. A number of workers (42-44) have reviewed the available methods for the concentration and separation of trace metals from seawater. Of all the

method available, coprecipitation, ion exchange and solvent extraction have been most frequently used.

### 1. Solvent Extraction.

Solvent extraction techniques have been widely used for the preconcentration of trace metals from seawater as a preliminary to their determination by colorimetry or by atomic absorption spectrophotometry. The possibility of making the extraction selective or even specific for colorimetric determination is of advantage. When the extraction is used in conjunction with the Flame AAS, the enhanced sensitivity resulting from the spraying of the organic solvent into flame and multielement analysis are appreciated.

In the process of solvent extraction, the metal ions, which are dissolved in the aqueous phase, seawater, are extracted along with chelating ligands into organic solvents. This is because the coordinated water molecules of metal ions are replaced with the ligand groups, so as to produce complexes, chelate complexes, which are essentially non-polar and usually soluble in organic solvents. In forming chelate complex (sometimes called inner complexes when uncharged), the central metal ion coordinates with a polyfunctional organic base to form one or more stable four-, five- or six-membered ring structures.

1.1 Chelating Ligands and Organic Solvents. To be used in simple chelate extraction systems for metals, a chelating ligand must be anionic in nature, so that it is capable of neutralizing the positive charges on metal cations. It must also contain nitrogen, oxygen or sulphur atoms which are capable of donating electrons into

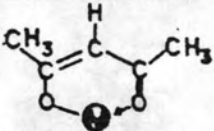
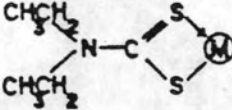
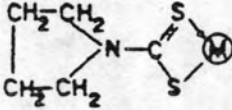

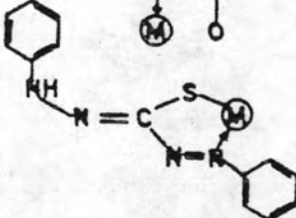
vacant orbitals of metal atoms and, thus, displacing solvating water molecules in such a way that the one or more stable ring structures are formed as showed in Table 1.11. Of the complexing agents, ammonium pyrrolidinedithiocarbamate (APDC) and dithizone have been most frequently used (3, 42, 44, 45, 76, 77, 79). These two chelate extraction systems have been used not only in conjunction with flame atomization procedures but also with graphite furnace (46-49).

The organic solvent used in extracting the metal complexes formed must show a number of desirable characteristics : extract the desired metal-chelates, be immisible with the aqueous solution, not tend to form emulsions and having low toxicity (50-51). There are many kinds of organic solvents which are used in chelate extraction such as 4-methylpentane-2-one (its pseudonym is methylisobutyl ketone, MIBK), carbon tetrachloride ( $CCl_4$ ), chloroform, n-butyl ether, ethyl propionate, 8-quinoline etc. MIBK and chloroform are the most or favorite organic solvent which are used together with APDC and dithizone respectively because they show good extractability. Joyner et al (43) and Stolzberg (52) have reviewed the application of solvent extraction system to seawater analysis.

The great advantages of solvent extraction techniques are their favourable concentration factors, removal of matrix salts and matrix normalization effects besides their simplicity, speed, low cost and ease in manipulation. Many chemical oceanographers use the solvent extraction technique to study the concentration of trace element in seawater such as Nissenbaum (53) who studied the minor and trace elements in Dead Sea, Sturgeon et al (54) or Jickells and Burton (55).



Table 1.11 Some chelating ligands commonly used in solvent extraction (6,45).

Chelating ligand	Complex structures #
1. Pentane-2,4-diene (acetylacetonone)	
2. Sodium diethyldithiocarbamate (DDC)	
3. Ammonium tetramethyllenedithiocarbamate (ammonium pyrrolidinedithiocarbamate, 1-pyrrolidinecarbodithioate ammonium salt, APDC)	
4. 8-Hydroxyquinoline (oxine,8-quinolinol)	
5. Diphenylthiocarbazonone (dithizone)	

\* Although only 1:1 ligand : metal complexes are shown for simplicity, ratio of 2:1 would normally be found.

## 2. Coprecipitation.

Coprecipitation techniques have been favored for the concentration of trace metals from seawater. In general, coprecipitation can occur in two ways. Firstly, the coprecipitated element may be incorporated into the lattice of the precipitate as a solid solution. Because of the requirement for mixed crystal formation, this type of coprecipitation tends to be specific in its action, and its applicability in the concentration of trace elements from seawater is accordingly limited. Secondly, the coprecipitated element may be adsorbed onto the surface of a precipitate having a large surface area. Because of its unspecific nature, this technique is most commonly used to concentrate trace metals from seawater. The percentage of recovery almost always exceeds 90%. Some of the frequently used adsorbents include the hydrous oxides of Fe (II), Mn(IV), and Al(III), and the sulphide of Co(II), Pb(II) and Fe(II). The main advantage of this technique is that very high concentration factors can be achieved. There are, however, a number of drawbacks or limitations such as their separations are lengthy and time consuming, the precipitates are often gelatinous and difficult to handle, yield monitors are necessary since recoveries are irreproducible etc.

A recently developed technique for concentrating trace metals from natural waters prior to atomic absorption analysis utilizes an organic complexing agent. The method is based on the principle that when slightly soluble organic complexing agents crystallize, they tend to carry down any insoluble complexes which they form with the trace metals. Weiss and his co-workers(56-58) have used a number of complexing agents such as potassium rhodizonate (56),

1-nitroso-2-naphtholes and 2-mercapto-benzimidazole(58), to concentrate trace metals from seawater. Boyle and Edmond (59) have used the APDC chelate of cobalt rather than the complexing agent itself to concentrate Cu and Ni from seawater. Many workers have used this Co APDC co-precipitation technique(60-64). Although, it might be possible to achieve a more selective recovery of the analyte and to remove the carrier, it still suffers from the limitations as mentioned previously.

### 3. Ion Exchange.

Ion exchange procedures may be divided into three principal categories on the type of exchanger used, viz. cation exchanger, anion exchanger and chelating ion exchanger. Riley (65) and Chakrabati et al(44) have reviewed the various ion exchange procedures used in concentration of trace metals from seawater. Anion exchange resins have been found to be useful for concentrating those trace metals, which are in the seawater medium, acidified with mineral acid, exists as Chloroanion (65,66).

In recent years, many attempts have been made to produce ion exchange media having chelating groups (complexing or chelating ion exchange) in place of the usual sulphonic acid or quarternary ammonium groups. The chelating resin preconcentration procedure was originally developed by Riley and Taylor (67) for the determination of Cu, Ni, Co, Zn and Cd in seawater using Chelex-100 resin (a copolymer of vinylbenzyliminodiacetic acid, styrene, and divinylbenzene which its commercially trade name of Dowex A1). It is mostly used to concentrate trace metals from seawater (68-71). Muzzarelli and

Rocchetti(73) used chitosan as an inexpensive resin alternative to the expensive Chelex-100 resin.

There are several drawbacks in this technique such as separation are lengthy and time consuming, many trace metals are not completely released from Chelex-100 which would cause considerable error in the determination of the total trace metals concentration and the stability constants of the chelated trace metals are so slightly different that any metals can not be separated well.

In trace analysis, it is advisable to avoid any type of preconcentration wherever possible. If this is not possible, coprecipitation and cocrystallization may be used where large concentration factors are necessary, or where large volumes of water have to be processed, and when concentration from the large excess of carrier or reagent is not a serious problem such as in the collection of natural and artificial radioactive nuclides from seawater. Coprecipitation or cocrystallization should be the method of choice in the determination of trace metals(44). Furthermore, equally efficient concentrations can be obtained by ion exchange or solvent extraction procedure which have the advantages of greater speed and selectivity. They also provide the trace elements in a suitable form for direct capability for sequential multielement analysis. Ion exchange procedure have an advantage over solvent extraction procedure in that they are easy to use at the sampling site. However, solvent extraction is faster than ion exchange.



### Development of Solvent Extraction Technique.

A variety of solvent extraction techniques have been developed and these are applicable to the determination of many elements. Most heavy metals are extracted with chelating reagent into organic solvents. With the proper choice of reagents, an extraction may be selective for either a narrow or a broad range of elements to be transferred from seawater to a solvent concentrate suitable for the analytical method to be used. A selection of solvent extraction systems, which either have been, or could be, used for seawater analysis is presented in Table 1.12.

The solvent extraction technique can be generally classified into two major categories. The first one involves the extraction of metal complexes into organic solvents such as MIBK (Methyl isobutyl ketone) or dithizone and then analyse the solvent directly. The other one is the extraction of the metal complexes into organic solvents followed by a back extraction with acid solvent and then analyse the trace elements in the acid solution.

#### 1. Single Extraction.

1.1 APDC-MIBK Solvent Extraction Technique. Brooks et al (13) pioneered solvent extraction for seawater with an APDC-MIBK Solvent Extraction Technique for the determination of Cu in seawater by flame atomic absorption spectrophotometry. They (77) later modified that technique, in which the scope of the technique is extended to cover the determination of Co, Fe, Pb, Ni and Zn as well as Cu. However, the metal complexes extracted into MIBK were unstable (decomposing within one day), which makes the technique inconvenient

Table 1.12 Solvent extraction systems of proved or possible use for concentrating trace elements in seawater.

Element Analysed	Original Sample	Sequestering Agents	Solvent	Method of Analysis	Ref
Pb	Environmental Sample	NaI, Dithizone	Isopropyl methyl ketone	Radiochemical	(72)
Cd, Cu, Fe Mn, Pb, Zn	River water	DEDTC	Isoamyl alcohol	Atomic absorption	(73)
Cd, Cu, Pb, Zn	Seawater	APDC	MIBK	Atomic absorption	(74)
Mn	Seawater	8-Hydroxyquinoline	MIBK	Atomic absorption	(55,75)
Co, Cu, Ni	Seawater	APDC	Chloroform	Atomic absorption	(55,75)
Cd, Co, Cu, Fe Mn, Ni, Pb, Zn	Seawater	APDC+NaDDC	Chloroform	Atomic absorption	(49)
Cd, Cu, Ni, Zn	Seawater	Dithizone	Chloroform	Atomic absorption	(76)
Ag, Cd, Cr, Cu	Seawater	APDC	MIBK	Atomic absorption	(46)
Fe, Ni, Pb, Zn					
Cd, Co, Cu, Fe Ni, Pb, Zn	Seawater	APDC+DDTC	Freon TF	Atomic absorption	(47)

NOTE APDC : Ammonium pyrrolidinedithiocarbamate  
DEDTC : Diethyldithiocarbamate  
NaDDC : Sodium diethyldithiocarbamate  
DDTC : Diethylammonium diethyldithiocarbamate  
Freon TF : 1,1,2-trichloro-1,2,2-trifluoroethane  
MIBK : Methyl isobutyl ketone

for routine analysis. Koirttyohann and Wen (78) have studied the extraction of Cu, Pb and Zn and found that the intensity of the absorption signals of the metallic ions extracted with APDC in MIBK decreases when the pH increases, although the extraction is quantitative (except for low pH values). Kremling and Petersen (79) have developed the APDC-MIBK Solvent Extraction Technique for the determination of Cu and Fe in 1-cm<sup>3</sup> samples of oceanic waters by flame atomic absorption spectrophotometer with a HGA-72 graphite atomizer. Subramanian and Meranger (80) have studied the stability with time of the APDC complexes of Ag, Co, Cu, Fe, Mn and Ni in the MIBK phase after extraction from aqueous solution at various pH values and determined by flameless atomic absorption spectrophotometer with an HGA-2100 graphite furnace and a deuterium background corrector. Gaurdia and Vidal (81) have revised the optimum extraction conditions for Cu and Fe complexes with APDC and MIBK in order to carry out their analysis by atomic absorption spectrophotometer equipped with copper and iron hollow cathode lamps. Newland and Clements (82) have investigated the effect of the aqueous phase, total Cd (II) concentration on the extraction efficiency using the APDC-MIBK Solvent Extraction Technique and attempted to explain the theoretical aspects of the limitations of the technique. All their experiments were conducted using the radioisotope, <sup>109</sup>Cd. Subramanian (83) explored the feasibility of directly complexing both Cr (II) and Cr (VI) by APDC at room temperature, extracting it subsequently into MIBK, and determining the Cr in the MIBK phase by atomic absorption spectrophotometer equipped with a HGA-500 graphite furnace, an AS-1 autosampler, and hollow cathode lamp. These studies have been done in order to improve the several conditions for the determination of trace

metals by the APDC-MIBK Solvent Extraction Technique. Therefore the atomic absorption spectrophotometry (AAS) as a technique for chemical analysis combined with preconcentration of trace metals as APDC-MIBK systems has rapidly become the method of choice for determination of trace metals in seawater.

Some analysts have tried to use the mixed chelating agents for determining trace metals by solvent extraction technique such as Sachdev and West (84) who used diphenylthiocarbazone, acetyl acetone and 8-quinolinol in ethyl propionate as a combined chelating agent and ethyl propionate as the organic solvent to determine Ag, Al, Be, Cd, Co, Cu, Fe, Ni, Pb and Zn in the aqueous solution or Kinrade and Van Loon (50) used APDC and DDDC (diethylammonium diethyldithiocarbamate) as chelating agent and MIBK as organic solvent to determine Ag, Cd, Co, Cu, Fe, Ni, Pb and Zn in natural water.

1.2 Back Extraction. The APDC-MIBK Solvent Extraction Technique which is developed by Brook et al (13) is limited by the instability of the metal complexes formed (less than one day). By considering this limitation in case of there are large sample populations to be analysed and the analyst cannot do it all within one day, the result from the analysis performed the next day is the wrong result. It is obvious that the main disadvantage of carbamate which is the chelating agent is the poor stability (13,77) of the metal carbamate in the organic solvent, which limits the time available for analysis after extraction. Therefore, the organic solutions with unstable metal chelates, metal carbamate, should be avoided and a final acidic aqueous solution is, thus, the most suitable matrix for final measurements by the graphite furnace technique (48). Such a



solution can be obtained by evaporating the organic solvent, digesting the residue and dissolving it in a small amount of dilute acid (55,85). These rather time-consuming procedure can easily give a total concentration factor up to 100. Another way of obtaining a final aqueous solution is to use back extraction.

Back extraction is the separation step which is used to remove or extract the metals chelate from the solvent, in case of the organic solvent is nonvolatile, by chemical means, such as by shaking the organic solvent with a volume of water containing acids of other reagents, whereby the extractable complex is decomposed. The metal ions are then quantitatively back extracted into the aqueous phase. Back extraction may also be used as the second stage of a two-stage concentration process. Thus, a 100:10 extraction followed by a 10:1 back extraction may give superior precision to a simple 100:1 extraction, although both lead to a 100- fold concentration.

Many studies have reported on the improvements of both the stability and sensitivity of the metal chelates by back extraction. Danielsson et al (47) reported that main advantage of back extraction method is the transfer of the metals to a solution where their concentrations do not change with time and in contrast to most other methods, one extraction is sufficient for the determination of Cd, Cu, Fe, Ni, Pb and Zn in seawater sample. In addition, the final solution, nitric acid, is well suited for analysis with the heated graphite atomizer (HGA). Jan and Young (46) reported that the metal complexes (Cd, Cr, Cu, Fe, Ni, Pb and Zn) in the acid extract were found to be stable for more than 1 week, with the exception of the Ag complex, which was stable only for about 3 days. Subramanian

and Meranger (86) found that both the stability and sensitivity of As(III), Sb(III) and Se(IV) may be improved by back extraction of the chelates from the MIBK into a smaller volume of acidified (pH 1.0) aqueous solution. Many analysts, such as Boniforti et al (85), Bruland and Franks (5) compared the efficiency of back extraction together with solvent extraction technique with other preconcentration techniques.

1.2.1 Types of Acids Used in Back Extraction. There are many kind of inorganic acids which are used in the chemical analysis such as nitric acid, hydrochloric acid, perchloric acid, sulfuric acid and hydrofluoric acid. For the analysis of trace metals in seawater, high purity of inorganic acid is particularly important because the relatively large amount of acid is required for chemical operation. Therefore, accurate determination of metal near the 1-ppm level will depend on the availability of acids containing no more than 1 ppb of the metal. By considering the impurity concentration of elements in the inorganic acids as showed in Table 1.13 (Kuehner et al (30)), we can see that even with ACS reagent grade acids, the total amount of the impurities is still high. Among these acids which are the sub-boiling distilled acids, nitric acid has the least impurity concentration of elements. Magnusson and Westerlund (48) compared the efficiency of different acids between nitric acid and hydrochloric acid by doing back extraction of the metals (Cd, Co, Cu, Fe, Ni, Pb and Zn) from chloroform, MIBK and freon. The result of their study (Table 1.14) shows that back extraction with nitric acid is more effective than with hydrochloric acid. Therefore, by considering the impurity of elements in acids (23,30), the suitability of acid for

Table 1.13 Impurities concentration in ppb by weight (ng/g) of elements in acids (30).

Nitric Acid			Hydrochloric Acid	
	Acid from sub-boiling still	ACS reagent grade acid	Acid from sub-boiling still	ACS reagent grade
Pb	0,02	0,2	0,07	0,5
Tl	...	0,2	0,01	0,1
Ba	0,01	8	0,04	2
Te	0,01	0,1	0,01	0,1
Sn	0,01	0,1	0,05	0,07
In	0,01	...	0,01	...
Cd	0,01	0,1	0,02	0,03
Ag	0,1	0,03	0,03	0,05
Sr	0,01	2	0,01	0,05
Se	0,09	0,2		
Zn	0,04	4	0,2	2
Cu	0,04	20	0,1	4
Ni	0,05	20	0,2	6
Fe	0,3	24	3	20
Cr	0,05	6	0,3	2
Ca	0,2	30	0,06	70
K	0,2	10	0,5	200
Mg	0,1	13	0,6	10
Na	1	80	1	500
	Σ 2,3 ppb	Σ 220 ppb	Σ 6,2 ppb	Σ 820 ppb
Sulfuric Acid			Hydrofluoric Acid	
	Acid from sub-boiling still	ACS reagent grade acid	Acid from sub-boiling still	ACS reagent grade acid
Pb	0,6	0,5	0,05	0,8
Tl	0,1	0,1	0,1	0,2
Ba	0,3	0,2	0,1	0,5
Te	0,1	0,1	0,05	0,1
Sn	0,2	0,6	0,05	11
Cd	0,3	0,2	0,03	2
Ag	0,3	0,6	0,05	0,1
Sr	0,3	0,4	0,1	0,5
Zn	0,5	2	0,2	4
Cu	0,2	6	0,2	3
Ni	0,2	0,5	0,3	12
Fe	7	6	0,6	110
Cr	0,2	0,2	5	20
Ca	2	121	5	14
K	4	9	1	28
Mg	2	4	2	10
Na	9	50	2	100
	Σ 27 ppb	Σ 200 ppb	Σ 17 ppb	Σ 320 ppb

Table 1.14 Efficiency of back extraction with hydrochloric acid instead of nitric acid (48).

Solvent	No back extraction (< 5 %)	Partial back extraction (20-95 %)	Quantitative back extraction (97-100 %)
Chloroform	Co, Cu, Ni, Pb	Fe, Cd	Zn
MIBK	Co, Cu, Ni		Pb, Fe, Cd, Zn
Freon	Co, Cu	Ni, Fe	Pb, Cd, Zn

graphite furnace atomic absorption spectrophotometer (48), the efficiency of acid for back extraction from organic solvent (48), the nitric acid is well suit for back extraction.

Determination by Atomic Absorption Spectrometry.

1. Flame Atomic Absorption Spectrometry (FAAS).

FAAS has been extensively used for determining trace elements in seawater. Even though the detection limit of FAAS have been lowered considerably by improvements in the design and efficiency of both hollow cathode lamps and burner-nebulizer systems, the direct determination of trace elements in seawater samples is still limited for a number of reasons. First, many trace elements in seawater are presented in much lower concentrations than the currently available detection limits of FAAS, and, therefore, preconcentration of sample is mandatory. Second, in addition to the adverse effects produced on the rate and efficiency of atomization by the spraying of solution of high ionic strength such as seawater, a further source of error with such sample is the attenuation of the incident radiation by scattering of salt particles in the flame and deposition of salts inside the burner-nebulizer chamber and along the burner slot. Third, the high concentration of major cations, anions and surfactants in the sample affect the rate at which the sample is drawn into the atomizer, the size of the droplet produced, and the quantity of aerosol which reaches the burner. These factors affect absorption.

2. Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

Many of the undesirable features of FAAS are easily



overcome by GFAAS with electrothermal atomization. The technique provides the possibility of determining the large number of elements (~70), high sensitivity, selectivity, speed of measurement, comparatively low cost of the apparatus, low cost of analysis. The above factors have made GFAAS a technique which is widely used for routine analysis of trace elements. Table 1.15 presents a list of trace metals in seawater which have been determined by flameless atomic absorption spectrometry.

For some elements, GFAAS does not have adequate sensitivity for their direct determination even with 100 ul sample injection. Determination of these elements required preconcentration, and often by solvent extraction. This also removes the salt matrix from the sample, thereby eliminating the potential interference due to background absorption and scattering of incident radiation caused by the salt matrix. Therefore, using GFAAS together with the solvent extraction is the well suited technique for determining trace metals in seawater.

#### Problems in Solvent Extraction and Back Extraction.

As mentioned before, one of the widely used technique for preconcentration of trace metals in seawater samples is solvent extraction, which is liquid-liquid extraction, followed by back extraction and analysed by atomic absorption spectrophotometry. For the solvent extraction, the factors, which affect the extractability of the solute, are the pH of aqueous solution at the time of extraction, the chelating agent concentration, the shaking time for extraction, the volume of organic solvent used and for the back

Table 1.15 Determination of trace metal in seawater with flameless atomic absorption spectrophotometry.

Metals	Particular atomization	Atomizer	References
Fe	Selective volatilization	HGA-70	(4)
Cu	Selective volatilization after addition of ammonium nitrate	HGA-2100	(39)
Pb	Addition ascorbic acid	HGA-72	(87)
Mn	Addition ammonium nitrate	HGA-74	(88)
Pb	Addition ammonium nitrate	Graphite tube	(89)
Fe, Mn, Zn	Selective volatilization	HGA-2200	(90)
Cu, Fe, Mn	Additive ammonium nitrate	Coated graphite tube HGA-2200	(91)
Pb	Additive ammonium nitrate	Tantalum coated graphite tube HGA-2200	(92)
Cd, Zn	Selective volatilization	HGA-72	(93)

extraction by nitric acid, which is frequently used as back extracted agent, the factors are the concentration of nitric acid , the volume of acid and shaking time for extraction.

The use of solvent extraction has been developed for a long time and as the development of this technique is still proceeding. A problem arised along with its development. The problem is that there are vast differences in experimental conditions of the extraction process such as pH of aqueous solution at the time of extraction (Table 1.16), the range of concentration of chelating agent used (Table 1.17), shaking time for extraction (Table 1.17) and for back extraction-by nitric acid such as the concentration of nitric acid which ranged from 1.5 N to concentrated, volume used ranged from 0.2 to 5 ml and shaking time for extraction ranged from 1/3 to 20 min (Table 1.18).

As mention above, even though there are differences in experimental condition of the solvent extraction followed by back extraction but the main principle is still the same. However, if we can collate the good points or steps of each procedure, which are developed by many analysts, we will possibly get not only the useful procedure of preconcentration technique for determining trace metals in seawater sample by solvent extraction and followed by back extraction but also the appropriate technique for studying the trace metals within our country.

In the present study, the preconcentration technique for Cu, Ni, Pb and Zn in seawater by solvent extraction followed by back extraction was chosen. The investigation were done by comparing the

Table 1.16 Range of pH of aqueous solution at the time of extraction.

Sample Matrix	Elements	pH range	Chelating agent +Organic solvent	References
Seawater	Cu	3	APDC + MIBK	(3)
Seawater	Co, Cu, Fe Pb, Ni, Zn	8	"	(77)
Seawater	Cu, Fe	3-4	"	(79)
Seawater	Cd, Cu, Pb Ni, Zn	2.2	"	(52)
Seawater	Ag, Cd, Cr Cu, Fe, Pb Ni, Zn	4	"	(46)
Aqueous	Cu, Pb, Zn	2-6	"	(78)
Aqueous	Ag, Cr, Cu Ni	2 3-8	" "	(80)
Aqueous	Co, Fe, Mn Cu Fe	1-6 1-10 5-6	" "	(81)
Seawater	Cd, Co, Cu Fe, Pb, Ni Zn	5	(APDC + DDDC) + Freon	(47)
Seawater	Cd, Cu, Ni Zn	4	(APDC + DDDC) + Chloroform	(5)
Seawater	Cu Cd, Ni, Zn	2 7.7	Dithizone + Chloroform	(76)
Natural Water	Ag, Cd, Co Cu, Fe, Pb Ni, Zn	5	(APDC + DDDC) + MIBK	(50)



Table 1.17 Range of the chelating agent (APDC) concentration and its use in the solvent extraction.

Chelating agent		Sample volume (ml)	Shaking time (min)	References
Concentration (%w/v)	Volume (ml)			
1%	5	500	10	(3)
1%	7	750	30	(77)
2%	0.05	1	3	(79)
5%	4	800	1	(52)
1%	2	200	20	(46)
4%	1	50	1	(78)
2%	5	20	3	(80)
1%	1	50	>3	(81)
4%	1	200	2	(95)

Table 1.18 Various conditions of back-extraction by nitric acid.

Element Analysed	Concentration (N)	Volumes (ml)	Shaking time (min)	References
Cd, Co, Cu, Fe Ni, Pb, Zn	Concentrated	0.2	1/3	(47)
Ag, Cd, Cr, Cu Fe, Ni, Pb, Zn	4	5	20	(46)
Cd, Cu, Ni, Zn	7.5	4	2	(5)
Cd, Cu, Ni, Zn	Concentrated	0.2	5	(76)
Cd, Co, Cr, Cu Fe, Mn, Ni, Pb, Zn	1.5	NR	NR	(96)
Cd, Co, Cu, Fe Ni, Pb, Zn	Concentrated	0.2	20	(48)
Co, Cu, Cr, Fe Mn, Ni, Zn	14	0.3	1	(86)

NR : Not reported

optimum conditions, which were used in the extraction procedure, of the solvent extraction system between APDC-MIBK and dithizone-chloroform system in order to achieve the best, appropriate and suitable solvent extraction technique followed by back extraction. The optimum conditions, which were investigated, for the solvent extraction were the volume and concentration of chelating agent, the sequence of adjusting pH of the aqueous phase, the additional volume of organic solvent, the pH of aqueous solution at the time of extraction, shaking time for extraction etc., and for back extraction were the concentration of acid used and shaking time for extraction.

Copper was chosen as the first metal in investigating the optimum conditions because its complexing abilities were greater than Ni, Pb and Zn. Therefore, the optimum conditions, which were obtained from the experiments with Cu, would be used as the optimum conditions for the extraction of Ni, Pb and Zn except one condition that was the pH of aqueous solution at the time of extraction of Ni, Pb and Zn were done separately. By considering the concentration of Cu, Ni, Pb and Zn in Table 1.9 and in the seawater in Thailand (94,97,98) together with the concentration factors (20 folds) from the method which was used in this study, therefore, the treated seawater was spiked to make the concentration of Cu, Ni, Pb and Zn to 5 ppb.