

**Studies on Sensitive and Precise Analysis of
Trace Heavy Metals in Environmental Samples**

January 2005

Junichi Nakajima

**Graduate School of Science and Technology
CHIBA UNIVERSITY**

(千葉大学学位申請論文)

**Studies on Sensitive and Precise Analysis of
Trace Heavy Metals in Environmental Samples**

環境試料中微量重金属の
高感度・高精度分析法に関する研究

2005 年 1 月

千葉大学大学院自然科学研究科
物質高次科学専攻応用化学講座

中島 淳一

Contents

	page
Chapter 1	1
General Introduction	
1.1 Characteristics of heavy metals	2
1.1.1 Cadmium	3
1.1.2 Cobalt	4
1.1.3 Lead	4
1.1.4 Manganese	5
1.1.5 Zinc	6
1.2 Analysis of heavy metals	6
1.2.1 Preconcentration methods	7
1.2.1.1 General	7
1.2.1.2 Solvent extraction	11
1.2.1.3 Solid-phase extraction	16
1.2.1.4 Coprecipitation	23
1.2.2 Automation of analysis	29
1.2.2.1 Air-segmented continuous flow analysis	33
1.2.2.2 Flow injection analysis	35
1.2.2.3 Advantages of FI on-line separation and preconcentration systems interfaced to ETAAS	39
1.3 Synopsis of the present investigation	48
References	49

	page
Chapter 2	52
Determination of Lead in Seawater by Flow-Injection On-line Preconcentration–Electrothermal Atomic Absorption Spectrometry after Coprecipitation with Iron(III) Hydroxide	
2.1 Introduction	53
2.2 Experimental	54
2.2.1 Reagents and samples	54
2.2.2 Instrumentation	56
2.2.3 Procedure of coprecipitation with iron(III) hydroxide	59
2.2.4 Determination of lead by on-line FI–ETAAS	59
2.3 Results and discussion	60
2.3.1 Coprecipitation of lead with iron(III) hydroxide	60
2.3.2 Adsorbent for preconcentration of lead	62
2.3.3 Effect of eluents	65
2.3.4 Effect of the concentration of EDTA	67
2.3.5 Analysis of seawater sample	67
References	72
 Chapter 3	 74
A Novel Separation and Preconcentration Method for Traces of Manganese, Cobalt, Zinc and Cadmium Using Coagulation of Colloidal Silica	
3.1 Introduction	75
3.2 Experimental	77
3.2.1 Reagents and samples	77

	page
3.2.2 Instrumentation	78
3.2.3 General Procedure	78
3.3 Results and discussion	80
3.3.1 Choice of electrolyte and alkali for coagulation of colloidal silica	80
3.3.2 Effect of the colloidal silica concentration by preconcentration of single element	82
3.3.3 Effect of the calcium chloride concentration	82
3.3.4 Adsorption behaviors of manganese, cobalt, zinc and cadmium on colloidal silica	85
3.3.5 Effect of the colloidal silica concentration by simultaneous preconcentration of multi elements	85
3.3.6 Analysis of river-water samples	87
References	93
Chapter 4	94
Conclusion	
Acknowledgments	97

Chapter 1
General Introduction

Recently, the precise and accurate analysis of trace heavy metals, especially toxic metals, has been drawing the attentions of various fields, such as environmental science, earth science, agronomy, biochemistry, pharmacy, archaeology, mining industry, electronic industry and food industry. In environmental science, the evaluation of the impact of human activity on the environment is one of the main subjects. In industry, on the other hand, the quality of products often depends on trace heavy metals in material, the content of which must be frequently checked to assure the certain quality. Thus, the function of heavy metals at lower level (less than $\mu\text{g l}^{-1}$) has been recognized, and it becomes more important to develop the precise and accurate analysis methods of trace heavy metals.

1.1 Characteristics of heavy metals

Some of the heavy metals play very important roles in improving the chemical and physical properties of various industrial products. On the other hand, some are among the elemental pollutants and are of particular concern because of their toxicities to humans and animals. Most of such elements are in general the transition metals, and some of the representative elements such as lead and tin are in the lower right-hand corner of the periodic table. Heavy metals include essential elements like iron and zinc as well as toxic metals like cadmium and mercury. Cadmium and mercury have a tremendous affinity for sulfur and disrupt enzyme function by forming bonds with sulfur groups in enzymes. Protein carboxylic acid ($-\text{CO}_2\text{H}$) and amino ($-\text{NH}_2$) groups are also chemically bound to heavy metals. Cadmium, copper, lead, and mercury ions bind to cell membranes, hindering transport processes through the cell membranes. Heavy metals may also precipitate phosphonate biocompounds or catalyze their decomposition.¹

The characteristics of cadmium, cobalt, lead, manganese and zinc tested in this study are described below in more details.¹⁻³

1.1.1 Cadmium

Cadmium is mainly used for electroplating, anticorrosive coating, pigments, stabilizer in PVC, batteries Ni/Cd, alloys and nuclear reactors. Although the uses of cadmium in pigments are replaced by other less toxic materials, the uses in batteries and nuclear reactors are more difficult to replace and the world yearly consumption have been plateau in the last decade.

The chemical properties of cadmium are very similar to those of zinc, and these two metals frequently undergo geochemical processes together. Both metals are found in natural waters in the +2 oxidation state. Major species of cadmium in fresh water are Cd^{2+} , CdCO_3 , while in seawater is CdCl_2 .⁴

The effects of acute cadmium poisoning in humans are very serious and the most serious situation is the disease called “Itai Itai disease”. Among them are high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells. It is believed that much of the physiological action of cadmium arises from its chemical similarity to zinc. Specifically, cadmium may replace zinc in some enzymes, thereby altering the stereostructure of the enzyme and impairing its catalytic activity. Disease symptoms ultimately results from these effects of cadmium poisoning.

1.1.2 Cobalt

The industrial products containing cobalt are fertilizers, super-alloys used in jet engines, stainless steel, electroplating, magnets, catalysts, paints and plastic hardener.

Cobalt is one of the essential elements and a central atom in vitamin B₁₂. As toxicity problem, in 1960s, addition of cobalt, CoCl₂, as beer head stabilizer has caused endemic outbreaks of cardiomyopathy among heavy beer drinkers, resulting in a number of fatalities. The dust of cobalt is carcinogenic. On the contrary, cobalt deficiency problem becomes an issue as well as toxicity. For example, cobalt depletion in agricultural soils presently comes to an issue. Additionally, it is known that the deficiency of cobalt for human causes pernicious anemia.

In natural waters, cobalt is found in the +2 oxidation state and major species are Co²⁺ and CoCO₃.⁴

1.1.3 Lead

Lead is used as a material for lead batteries, rolled and extruded products, pigments, alloys, cable sheathing and ammunition. Although a fairly large amount of lead had been used as a petrol additive, such use of lead has been restricted by law in some countries because of its great environmental impacts. Recently, there is an environmental problem that lead in solders, which are used in the parts of electric instruments such as a computer, is dissolved by acid rain and causes the pollution of the environment, such as soil, groundwater and river water.

Lead is found in the +2 oxidation state in natural waters. Major species is PbCO₃ in fresh water and are PbCl⁺ and PbCO₃ in seawater.⁴

Acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, and the brain and central nervous system. These effects result in sickness or death. Lead poisoning from environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anemia. The victims usually have headaches and sore muscles, and feel fatigued and irritable.

1.1.4 Manganese

Manganese is mainly used as a material for steel alloys (*e.g.*, with Al, Mg, Cu), batteries, catalyst, fertilizers, pigment, wood preservative, fungicide, antiknock agent in gasoline (as a replacement for Pb in unleaded fuel).

Manganese is an essential element for all organisms and a component of some enzymes. Excessive exposure via inhalation has been shown to cause effects on the lung and excessive absorption in the lung will cause accumulation in the brain. Manganese causes an irreversible brain disease, to some extent similar to Parkinson's disease. However, deficiency problem in human and animals are more important than toxicity problem as cobalt and zinc. Manganese deficiency causes growth disturbances in plants and causes failure in reproduction and impaired growth.

In natural waters, manganese is usually found in the +4 oxidation state and major species is MnO_2 .⁴

1.1.5 Zinc

Zinc are used as a material for galvanizing alloys, pigments, chemicals, paint, glass, plastics, lubricants, batteries, pesticide (wood preservative), pharmaceutical products.

Zinc is also an essential metal and necessary for the function of various enzymes. The daily zinc requirement has been recommended as 9 to 30 mg for adults in Japan. It is known that zinc deficiency causes retarded growth, anemia, hepatosplenomegaly, and hyperpigmentation. Recently, several other symptoms and diseases have been related to zinc deficiency, *e.g.* acne, poor wound healing, loss of taste and smell and poor growth in children.

In natural waters, zinc is found in the +2 oxidation state. Major species in fresh water are Zn^{2+} and $ZnCO_3$, while in seawater are Zn^{2+} and $ZnCl_2$.⁴

As mentioned above, constant monitoring of the concentration of these trace heavy metals in the environmental samples is desirable. Thus, it is very meaningful to develop the more accurate and precise analysis methods for the determination of traces of heavy metals mentioned above.

1.2 Analysis of trace heavy metals

The analysis of heavy metals in environmental samples usually is carried out by instrumental techniques such as neutron activation analysis (NAA), isotope dilution mass spectrometry (IDMS), anodic stripping voltammetry (ASV), flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP–AES) and inductively

coupled plasma mass spectrometry (ICP–MS). Among these, AAS, ICP–AES and ICP–MS are widely used for the determination of trace heavy metals because of their good versatilities and detection limits. The detection limits of typical heavy metals for AAS, ICP–AES and ICP–MS are listed in **Table 1.1**.⁵

The concentration of heavy metals in environmental samples is generally extremely low, namely $\mu\text{g l}^{-1}$ or less. On the other hand, alkali, alkali earth metals and natural organic matter are present at the higher concentration than heavy metals and might interfere with the determination of trace heavy metals by AAS, ICP–AES or ICP–MS. For instance, the compositions of metals in river-water and seawater are shown in **Table 1.2**.^{2,6}

Therefore, it is mostly required to separate analytes from matrix components and preconcentrate it to eliminate the potential interferences and improve the sensitivity prior to the measurement. Hence, various separation and preconcentration methods have so far been developed and reviewed in detail by Alfassi *et al.*⁷ Among them, solvent extraction, solid-phase extraction and coprecipitation have been widely used as preconcentration and separation method of heavy metals, because these methods are simple, useful and versatile for various samples. In addition, the automation of analysis, including preconcentration steps, has been developed for trace heavy metals and extensively applied to routine analysis.

1.2.1 Preconcentration methods

1.2.1.1 General

The preconcentration methods are usually judged their usefulness by the following four criteria:⁷

1. Preconcentration factor — P

Table 1.1 Detection limits of typical heavy metals for AAS, ICP–AES and ICP–MS⁵

Element	FAAS ^a	ETAAS ^{a,b}	ICP–AES ^a	ICP–MS ^a
Ag	5	0.01	0.2	0.005
Au	20	0.24	0.9	0.005
Bi	50	0.08	10	0.004
Cd	5	0.004	0.07	0.005
Co	5	0.16	0.1	0.005
Cr	5	0.08	0.08	0.04
Cu	5	0.08	0.04	0.04
Hg	500	0.8	1	0.018
Fe	5	0.06	0.09	0.58
Mn	3	0.02	0.01	0.006
Mo	100	0.24	2	0.006
Ni	5	0.4	0.2	0.013
Pb	10	0.8	1	0.02
Pd	20	1.6	2	0.009
Pt	100	1.6	0.9	0.005
Sb	200	0.16	10	0.012
Sn	60	0.08	3	0.01
Ti	200	0.8	0.03	0.011
V	40	0.8	0.06	0.008
Zn	2	0.006	0.1	0.035

a. $\mu\text{g l}^{-1}$. b. sample volume, 50 μl .

Table 1.2 Concentrations of metal constituents in river-water and seawater^{2,6}

Light metals	River-water/ mg l ⁻¹	Seawater/ mg l ⁻¹
Na ⁺	2.1 – 6.7	10770 – 10800
K ⁺	0.18 – 2.3	380 – 399
Ca ²⁺	6.3 – 15	412
Mg ²⁺	0.75 – 4.1	1280 – 1290
Heavy metals	River-water/ µg l ⁻¹	Seawater/ µg l ⁻¹
Mn	0.1 – 2750	0.02 – 0.2
Co	0.03 – 78	0.0012 – 0.02
Zn	0.1 – 324	0.35 – 5
Cd	0.002 – 9.6	0.07 – 0.11
Pb	0.04 – 81	0.0005 – 0.03

2. Interferences removal or decontamination factor — D
3. Recovery yield — R
4. Specificity

If before the preconcentration step we have a sample which weighs M_0 grams including W_0 grams of element of interest (its concentration is C_0), and after the procedure of the preconcentrations the weight are M_f and W_f respectively (the concentration is C_f), then the first three, P , D and R , are given by the equations:

$$P = \frac{C_f}{C_0} = \frac{W_f}{W_0} \cdot \frac{M_0}{M_f} \quad (1)$$

$$D = \frac{M_0}{M_f} \quad (2)$$

$$R = \frac{100 \cdot W_f}{W_0} \quad (3)$$

The connection between the three factors is given by the equation:

$$P = \frac{R \cdot D}{100} \quad (4)$$

Preconcentration makes sense only if the original sample cannot be analyzed as is, due to the limit of detection being larger than the actual concentration. The preconcentration step is intended to reduce the limit of detection, both by removal of interferences and increase of the concentration of the species of interest. In some cases these aims might be contradictory. For example, in a coprecipitation process an excess of the coprecipitating agent will increase the recovery yield, but will also increase the limit of detection due to larger signal of the blank. An optimization should be done between these factors. The optimization depends on the process for the preconcentration and the following method of quantitative determination.

1.2.1.2 Solvent extraction

Solvent extraction is one of the widely used techniques for preconcentration and separation of trace elements because of its simplicity, speed, and wide scope. With proper choice of extracting agents, this technique can achieve selective separation of trace elements with high efficiencies. In case of heavy metals in water samples, heavy metals are changed to non-polar species with extracting agents, and then they are effectively extract into the organic phase. Solvent extraction is usually conducted with an excess amount of an extracting agent for quantitative transfer of the trace elements of interest from the aqueous phase into the organic phase. Extracting agents are usually chelating reagents, such as derivatives of dithiocarbamic acid and crown ethers. The main chelating reagents used as an extracting agent are shown in **Fig. 1.1**.⁸

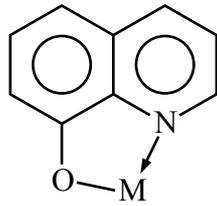
The distribution of a solute between two immiscible phases is usually described by the Nernst distribution law:

$$K_D = \frac{C_{\text{org}}}{C_{\text{aq}}} \quad (5)$$

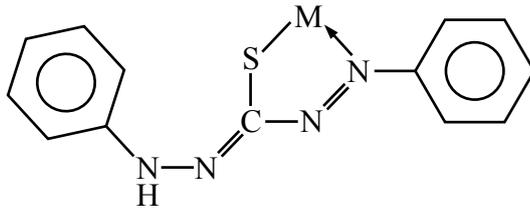
where K_D is the partition coefficient, C_{org} and C_{aq} are the concentration of organic phase and solution, respectively. Actually, this equation is valid only for very dilute solutions where the activity coefficients of the solute can be assumed to be unity. In real cases, a solute usually exists in more than one chemical form in either an aqueous or an organic phase; therefore, a more useful parameter to describe its distribution during solvent extraction is the distribution coefficient D :

$$D = \frac{\sum C_{\text{org}}}{\sum C_{\text{aq}}} \quad (6)$$

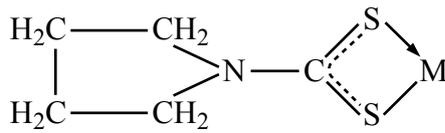
where $\sum C_{\text{org}}$ and $\sum C_{\text{aq}}$ are the total concentration of the solute in the organic phase and in the aqueous phase, respectively. The extraction efficiency E is related to the distribution coefficient by the following equation:



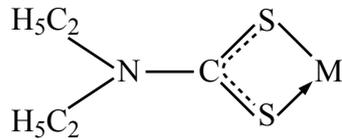
8-Quinolinol
(oxine; 8-hydroxyquinoline)



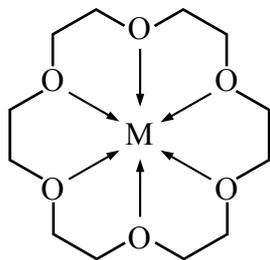
Diphenylthiocarbazono
(dithizone)



Ammonium pyrrolidine
dithiocarbamate (APDC)
(ammonium ions displaced by
metal in the figure)



Sodium diethyldithiocarbamate
(sodium ion displaced by metal
in the figure)



18-crown-6

Fig. 1.1 Typical chelating reagents used as extracting agent.⁸

$$E = \frac{100D}{D + (V_{\text{aq}}/V_{\text{org}})} \quad (7)$$

where V_{org} and V_{aq} are the volumes of the organic phase and the aqueous phase, respectively. The extraction efficiency E depends on the value of D and the ratio of $V_{\text{aq}}/V_{\text{org}}$. The relationships between E and D for $V_{\text{aq}}/V_{\text{org}}$ values of 1, 10, 100 are given in **Fig. 1.2**. For preconcentration purposes, a solute is usually extracted from an aqueous phase into a small volume of an organic phase in order to gain a concentration factor > 1 . If quantitative recovery is achieved in an extraction process, then the equilibrium ratio $V_{\text{aq}}/V_{\text{org}}$ represents the preconcentration factor of the solute. Generally speaking, an extraction can be considered quantitative if E is greater than 99%. To achieve this efficiency in one cycle of extraction, the D value must be greater than 10^3 for a $V_{\text{aq}}/V_{\text{org}}$ ratio of 10. If the $V_{\text{aq}}/V_{\text{org}}$ ratio is 100, the D value must be greater than 10^4 in order to have $> 99\%$ of extraction.

If some cases, repetition of an extraction process may be necessary in order to achieve quantitative extraction of a solute. The weight of a solute remaining in the aqueous phase after n cycle of extraction can be expressed by the following equation:

$$w_n = \left(\frac{V_{\text{aq}}/V_{\text{org}}}{D + (V_{\text{aq}}/V_{\text{org}})} \right)^n \times w_0 \quad (8)$$

where w_n and w_0 is the weight of a solute remaining in the aqueous phase after n cycle of extraction and that in initial aqueous phase. For example, if $V_{\text{aq}}/V_{\text{org}}$ is 10 and D is 100, 9.1% of the solute will remain in the aqueous phase after one cycle of extraction. Repeating the extraction once again will reduce the percentage of the solute in the aqueous phase to 0.8%.

The distribution coefficient is an important parameter in determining the efficiency of extraction of a trace element. Separation of two trace elements which form extractable species with a specific reagent can be described by the separation factor α , which is related to the D values by the following equation:

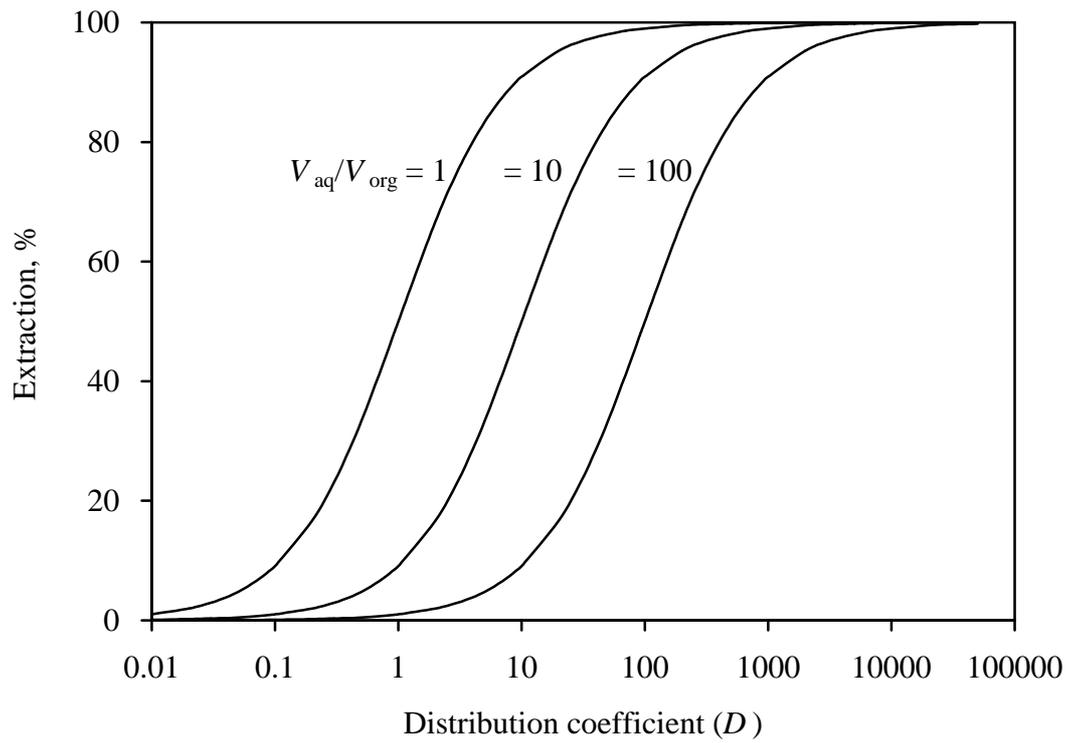
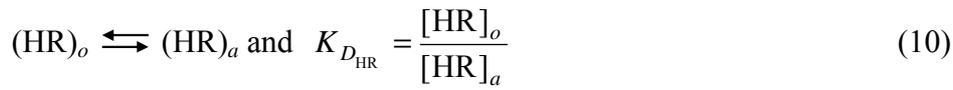


Fig. 1.2 Relationship between extraction efficiency (E) and distribution coefficient (D) for different V_{aq}/V_{org} values.

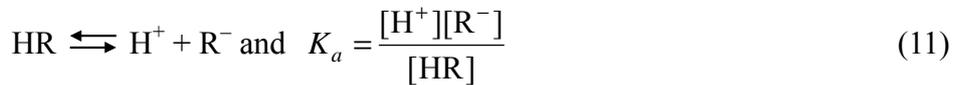
$$\alpha_{2,1} = \frac{D_2}{D_1} \quad (9)$$

Utilizing a selective reagent which favors the D value of one element over another is one way of achieving a high separation factor by solvent extraction. In many extraction systems involving metal chelates, the D values usually depend on pH. Therefore, with proper control of pH, selective extraction of trace elements may be achieved even with a general chelating agent.

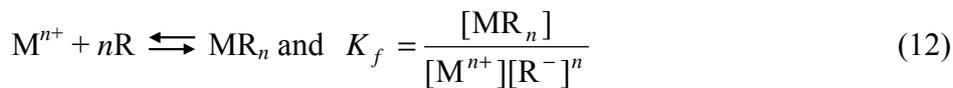
For separation and preconcentration of heavy metals, the most used method of extracting metal ions is formation of a chelating molecule with an organic chelating agent. The usual practice is to add the chelating agent to the organic phase. The extraction process can be thought to consist of four equilibrium steps, each with an equilibrium constant. First, the chelating agent HR distributes between the aqueous and the organic phases:



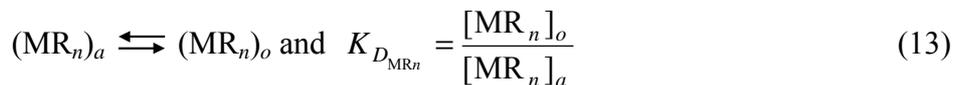
Second, the reagent in the aqueous phase ionizes:



Third, the metal ion chelates with the reagent anion to form an uncharged molecule:



Finally, the chelate distributes between the organic and aqueous phases:



$K_{D_{\text{HR}}}$ and $K_{D_{\text{MR}_n}}$ are the distribution coefficients of the reagent and the chelate, respectively; K_a is the ionization constant of the reagent; and K_f is the formation constant of the chelate.

Assuming that the chelated portion of the metal distributes largely into organic phase, the metal ion does not hydrolyze in the aqueous phase, and the chelate is essentially undissociated in the nonpolar organic solvent, the distribution ratio is given by

$$D \approx \frac{[\text{MR}_n]_o}{[\text{M}^+]_a} \quad (14)$$

By substituting the appropriate equilibrium concentration from Equation (10) through (13) into Equation (14), so that all four equilibrium constants are included, the following equation can be derived:

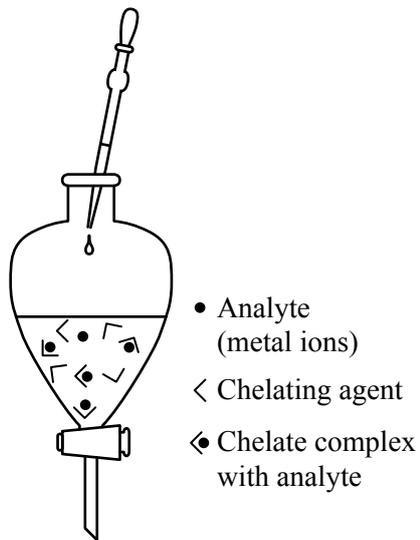
$$D = \frac{K_{D_{MRn}} K_f K_a^n}{K_{D_{HR}}^n} \cdot \frac{[\text{HR}]_o^n}{[\text{H}^+]_a^n} = K \cdot \frac{[\text{HR}]_o^n}{[\text{H}^+]_a^n} \quad (15)$$

For instance, the simplest solvent extraction procedure for separation and preconcentration of heavy metals is shown in **Fig. 1.3**.

The extraction efficiency depends on solubility of organic solvent in water. The widely used organic solvents are listed in **Table 1.3**.⁹ Recently, toxicity problems of some organic solvents are increasing and solvent extraction tends to be replaced by alternative preconcentration methods.

1.2.1.3 Solid-phase extraction

Solid-phase extraction involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase instead of two immiscible liquid phases as in solvent extraction. The principle of solid-phase extraction is similar to that of solvent extraction, involving a partitioning of solutes (analytes) between two phases, and is based on their adsorption behaviors on a solid sorbent. The mechanism of adsorption depends on the nature of the sorbent used, and may include simple adsorption (by van der Waals forces or hydrophobic

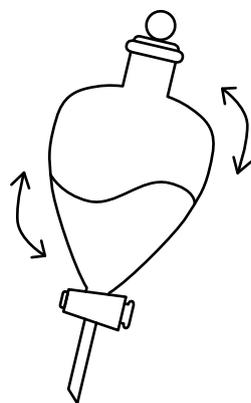


Complexation of chelate with analyte

Addition of buffer solution to adjust appropriate pH

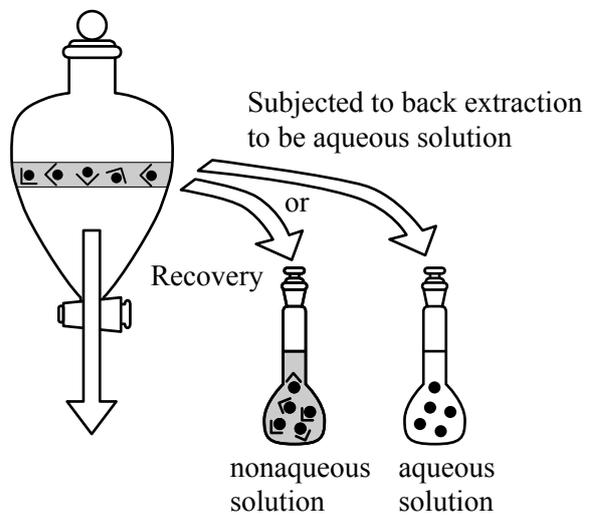


Addition of organic solvent



Shaking solution

Extraction of analyte to organic phase



Separation of two phases and Recovery of analyte

Fig. 1.3 Simple procedure of solvent extraction (batch method).

Table 1.3 Properties of typical organic solvents used for liquid-liquid extraction⁹

Solvent	MW ^a	bp ^b / °C	Density/ g cm ⁻³	Solubility in H ₂ O, wt%
Nonane	128.3	150.8	0.718 ^c	–
2,6-Dimethyl-4-heptanone (DIBK)	132.0	168.2	0.806 ^c	0.05
4-Methyl-2-pentanone (MIBK)	100.2	116.5	0.796 ^c	1.70
Butyl acetate	116.2	125.5	0.883 ^c	0.83
Benzene	78.1	80.1	0.879 ^d	0.18
Chloroform	119.9	61.2	1.499 ^d	0.82
Carbon tetrachloride	153.8	76.7	1.594 ^c	0.08
Nitrobenzene	123.1	210.8	1.208 ^d	0.19
2-Chlorotoluene	126.6	158.9	1.083 ^c	insoluble
1,2-Dichlorobenzene	147.0	180.4	1.300 ^c	0.01

a. MW: molecular weight. b. bp: boiling point. c. 20°C. d. 15°C

interaction), chelation, or ion-exchange. Based on the principle of solvent extraction, we can define that distribution coefficient K_D indicates the ratio of the analytes remained in solution to those adsorbed on the solid phase. Strictly speaking, this distribution coefficient should be defined in terms of activities of the analyte in either phase. However, convenience dictates that concentrations are used and the equation is expressed as follows:

$$K_d = \frac{C_{\text{sorbent}}}{C_{\text{solution}}} = \frac{\text{Mole of analyte adsorbed on sorbent (mmol g}^{-1}\text{)}}{\text{Mole of analyte remained in solution (mmol ml}^{-1}\text{)}} \quad (16)$$

The values of K_d are usually determined by “batch method” and have been reported for metal ions on various sorbents and in different solutions. If K_d is larger, analyte can be strongly adsorbed on solid sorbent. If it is smaller, on the other hand, analyte tends to remain in sample solution. Hence, we can preconcentrate analyte (is larger K_d value) and remove matrix components (are smaller K_d values) based on the difference of their K_d values (*i.e.* the difference of their adsorption behaviors) on a solid sorbent.

The basic procedure based on solid-phase extraction involves passing the liquid sample through a column, a cartridge, a tube or a disk containing a sorbent that retains the analytes (**Fig. 1.4**). After the sample solution has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solution (eluent). The entire process of the solid-phase extraction is represented in **Fig. 1.5**.

It is also important to consider the properties of sorbent in order to achieve excellent separation and preconcentration. Hence, manufacturers of solid-phase extraction devices have developed an extensive range of sorbents — ones that utilize varying strengths of van der Waals (non-polar), hydrogen bonding or dipolar (polar) or coulombic (ion exchange) interactions. For instance, various sorbent types based on bonded silica gel are shown in **Table 1.4**.¹⁰ Until now, on the other hand, many investigators have developed chemically modified sorbents. The main solid sorbents used for solid-phase extraction are shown in

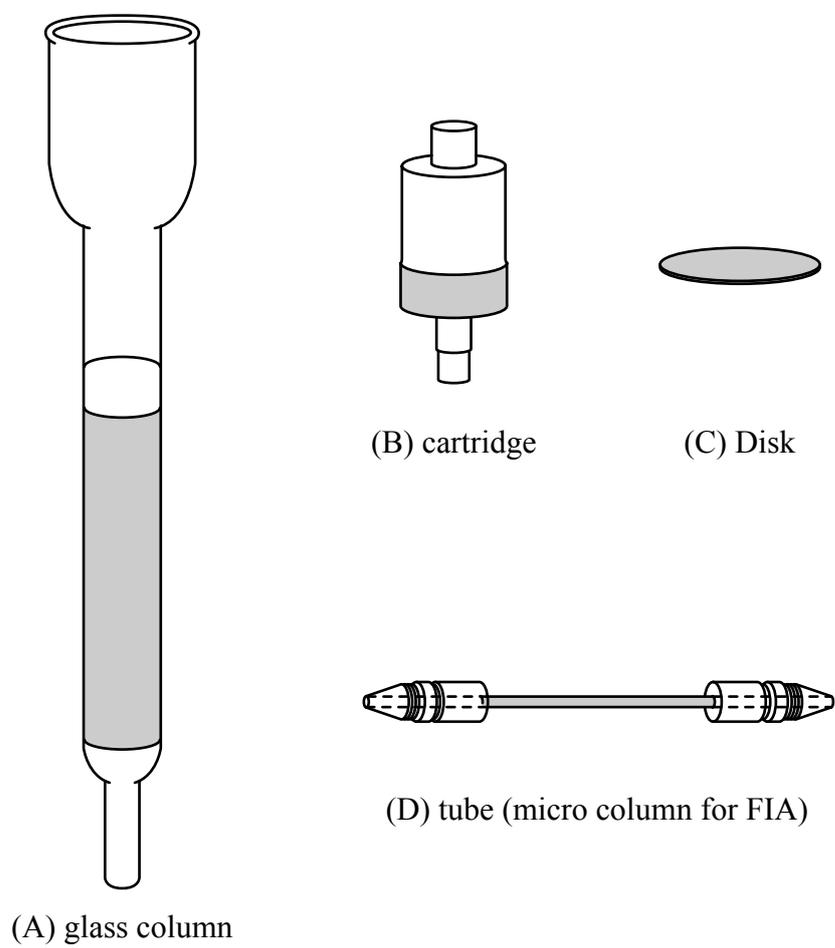
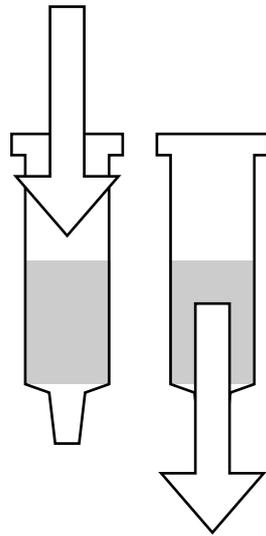
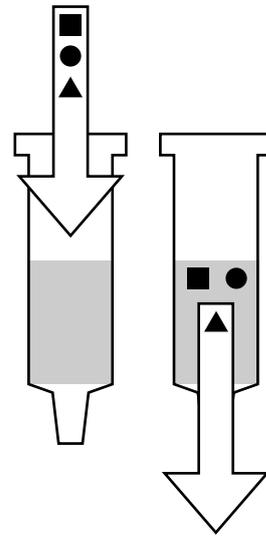


Fig. 1.4 Containers for sorbent.



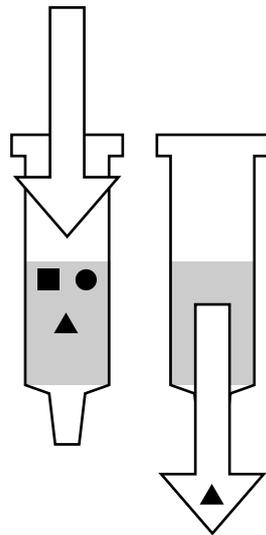
Conditioning

Conditioning the sorbent prior to sample application ensures reproducible retention of the compound of interest (analyte)



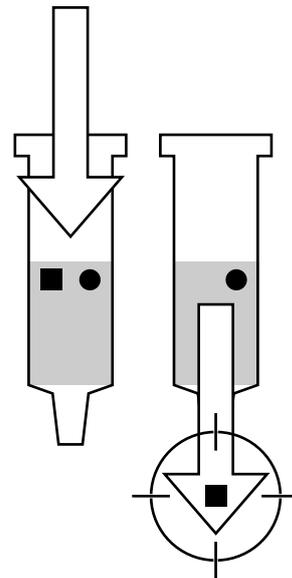
Retention (Loading sample)

■ Adsorbed analyte
 ● Undesired matrix constituents
 ▲ Other undesired matrix components



Rinse (Washing)

▲ Rinse the columns to remove undesired
 □ matrix components



Elution

● Undesired components remain
 ■ Purified and concentration analyte ready
 □ for analysis

Fig. 1.5 Principles of solid-phase extraction.

Table 1.4 Sorbent types, acronyms and extraction properties of common solid-phase extraction sorbents based on bonded silica gel¹⁰

Bonded phase	Acronym	Primary properties
Octadecyl	C18, ODS	Non-polar
Octyl	C8	Non-polar
Ethyl	C2	Non-polar
Phenyl	PH	Non-polar
Cyclohexyl	CH	Non-polar
Cyanopropyl	CN (Cyano)	Non-polar/polar
Propanediol	2OH (Diol)	Polar/non-polar
Silica (unbonded)	SI	Polar
Alumina (unbonded)	AL	Polar
Florisil (unbonded)	FL	Polar
Diethylaminoethyl	DEA	Weak anion exchange/polar
Aminopropyl	NH ₂	Weak anion exchange/polar
Carboxyethyl	CBA	Weak cation exchange
Propylsulfonic acid	PRS	Strong cation exchange
Ethylbenzene sulfonic acid	SCX	Strong cation exchange
Trimethylammonium propyl	SAX	Strong anion exchange

Fig. 1.6 and **1.7**.¹¹ Among these, commercial ion exchangers used as sorbent for separation and preconcentration of heavy metals are listed in **Table 1.5**.

Publication of applications of solid-phase extraction has exploded during the 1990s (**Fig. 1.8**).¹⁰ For heavy metals, this method has been successfully used for the separation and sensitive determination in environmental samples, mainly in water samples, instead of solvent extraction, because solid-phase extraction reduces the consumption of organic solvents, their disposal costs and extraction time. In addition, solid-phase extraction can be easily interfaced on-line with analytical techniques, such as AAS, ICP–AES or ICP–MS. Solid-phase extraction of trace elements was reviewed by Camel in 2003.¹¹

1.2.1.4 Coprecipitation

Coprecipitation is also one of preconcentration and separation methods which have been widely used in various fields.

When a precipitant is added to a solution containing trace quantities of an ionic species (0.1 – 100 µg in 100 – 250 ml, 10^{-8} – 10^{-5} mol l⁻¹), the ionic species may be only partly precipitated (or not at all), even though the solubility product has been exceeded.

The formation of a precipitate, *i.e.* crystal growth, is a complex and slow process. Preconcentration begins with nucleation, which results from association of oppositely charged ions. When nucleation and further growth of nuclei occur slowly, a condition of permanent supersaturation exists in the solution. Nuclei are formed when the first portion of precipitant is added to the solution. If the ions to be precipitated occur in macro-amounts in the solution, further addition of the precipitant causes rapid transformation of the nuclei into crystals by the formation of more of the sparingly-soluble compound. If, however, the

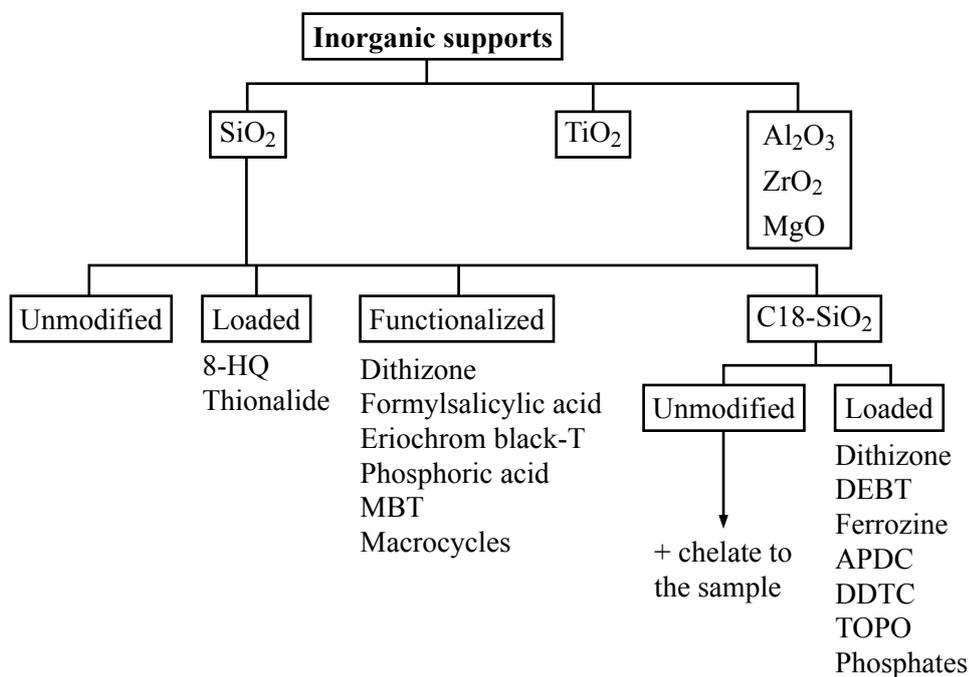


Fig. 1.6 Sorbents based on inorganic supports.¹¹

APDC, Ammonium pyrrolidine dithiocarbamate; DDTC, Diethyldithiocarbamate; DEBT, *N,N'*-Diethyl-*N'*-benzoylthiourea; 8-HQ, 8-Quinolinol; MBT, 2-Mercapto-benzothiazole; TOPO, Tri-*n*-octylphosphine oxide.

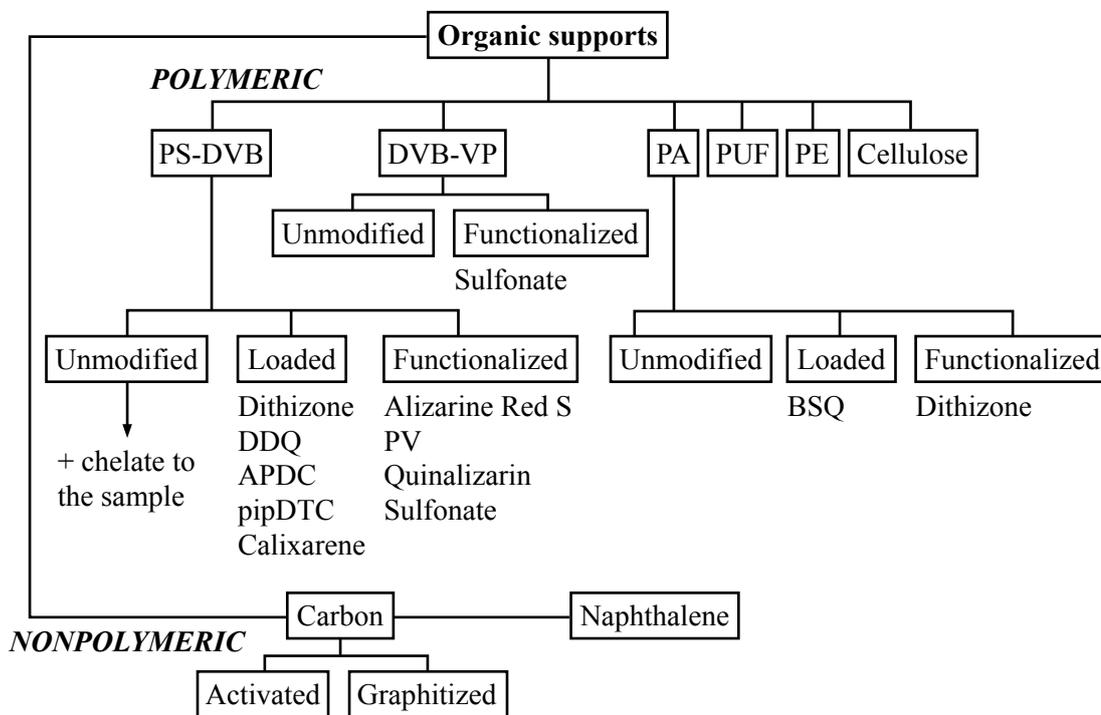


Fig. 1.7 Sorbents based on organic supports.¹¹

APDC, Ammonium pyrrolidine dithiocarbamate; BSQ, 8-(Benzenesulfonamido)-quinoline; DDQ, 7-Dodeceny-8-quinolinol; pipDTC, Piperidine dithiocarbamate; DVB-VP, Divinylbenzen-vinylpyrrolidone; PA, Polyacrylate; PE, Polyethylene; PS-DVB, Polystyrene-divinylbenzene; PUF, Polyurethane foam; PV, Pyrocatechol violet.

Table 1.5 Types and properties of ion exchange resin for separation and preconcentration of heavy metals

Type	Exchange group	pH	Exchange capacity/ meq ml ⁻¹	Example
<i>Cation exchange resin</i>				
Strongly acidic	-SO ₃ H	0 ~ 14	1.9	Diaion SK 1
		0 ~ 14	1.4	Dowex 50W
		0 ~ 14	1.9	Amberlite IR 120 B
Medium acidic	-PO(OH) ₂	4 ~ 14	8	Duolite C-60, C-61
Weakly acidic	-COOH	5 ~ 14	2.8	Diaion WK 10
		5 ~ 14	4.1	Dowex CCR 2
		5 ~ 14	3	Amberlite IRC 50
<i>Anion exchange resin</i>				
Strongly basic	-N(CH ₃) ₃ Cl	0 ~ 14	1.3 ~ 1.7	Diaion SA 100
		0 ~ 14	2	Dowex 1
		0 ~ 14	1.4	Amberlite IRA 400
Weakly basic	-N(CH ₃) ₂	0 ~ 9	2.5	Diaion WA 20
		0 ~ 7	1.8	Dowex 66
		0 ~ 9	1.6	Amberlite IRA 67
<i>Chelating resin</i>				
Iminodiacetate	-CH ₃ N(CH ₂ COOH) ₂	1 ~ 5	0.5 ^a	Diaion CR 10
		1.5 ~ 14	0.8	Amberlite IRC 718
		1.5 ~ 14	0.4	Chelex 100

a. Cu²⁺, mmol ml⁻¹

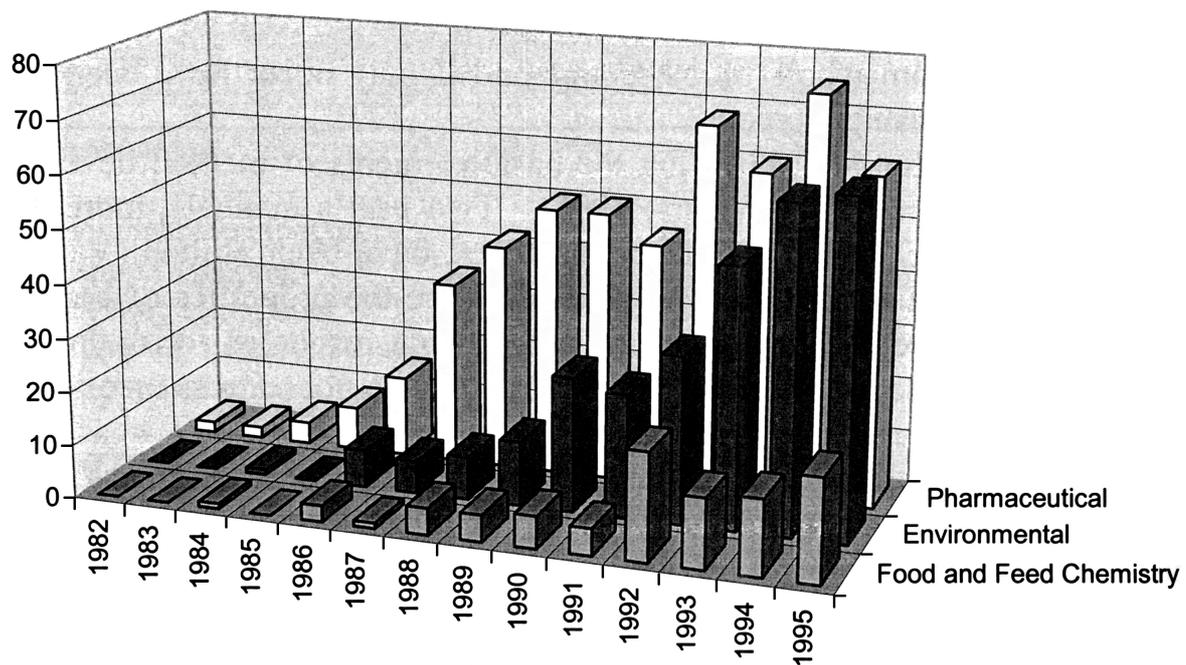


Fig. 1.8 The number of citations having the term “solid-phase extraction” in the title of the article, during the time period 1982 through 1995, according to whether the type of application was pharmaceutical, environmental, or food and feed chemistry.¹⁰

solution contains only trace amounts of the ions to be precipitated, the process is virtually complete after the nucleation stage.

Nucleation, transformation of the amorphous nuclei into crystal nuclei, and growth of the crystals proceed rapidly if the quantity of the resulting solid phase is appreciable. That is why the precipitation of trace from a solution undergoes an essential change when the traces are coprecipitated with a collector (coprecipitant).

The mechanism of coprecipitation depends on experimental conditions and the chemical and physical properties of both the trace element and the collector. The ions coprecipitated from the solution accumulate with the forming particles of the collector precipitate.

Coprecipitation may involve isomorphous solid solution, mixed-crystal formation, or adsorption. Sometimes it occurs by mechanical retention of the trace substance in the collector precipitate. Many cases of coprecipitation of traces with collectors such as sulphides or hydroxides are ascribed to isomorphism.

Separation by coprecipitation is not restricted by the very low concentration of the trace species. Smaller traces can be separated by coprecipitation than by solvent extraction, which is limited by the stability of the complex extracted.

The formation of a solid solution, *e.g.* the separation of traces of lead with lanthanum hydroxide as collector, may occur by occupation of some crystal-lattice site by the trace ion instead of the collector ion. This mechanism of coprecipitation is possible provided the ionic radii of the trace and collector are similar, as is the case with La^{3+} (1.34 Å) and Pb^{2+} (1.47 Å). However, when the collector and the trace species are chemically similar, the latter may be coprecipitated, apparently by mixed crystal formation, even though this would not be predicted on the basis of crystallography and ionic radii. This is known as anomalous mixed crystal formation.

Coprecipitation may result in the formation of chemical compounds, provided the trace element and the collector have opposite chemical properties (acid and basic). For example, traces of germanium or vanadium coprecipitated with Fe(III), Al or La hydroxide yield the respective germanates and vanadates, while trace tungsten or molybdenum coprecipitated with Fe(OH)₃ yield ferric tungstate or molybdate.

Elements which can be preconcentrated by precipitation with collectors are listed in **Table 1.6**¹² and the examples of preconcentration of trace elements with coprecipitation are listed in **Table 1.7**.¹³ Among them, coprecipitation using iron(III) hydroxide has found in many applications, because the method is simple and the precipitate is easily dissolved in acid. For instance, the preconcentration procedure of heavy metals by coprecipitation is shown in **Fig. 1.9**.

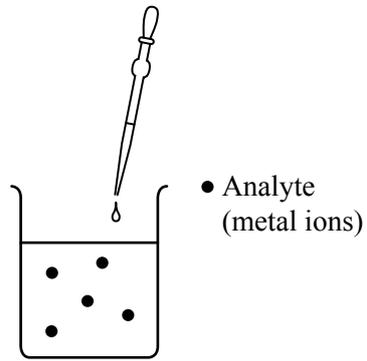
Coprecipitation is highly efficient to collect a wide range of analytes but it has some disadvantages. The precipitate, which has a mass many orders of magnitude greater than that of the analyte, can be a major source of contamination and interference materials during measurements of analyte. Hence, we should use as high pure materials of collector as possible, and the separation of analyte from the precipitate matrix may be required before the measurements.

1.2.2 Automation of analysis

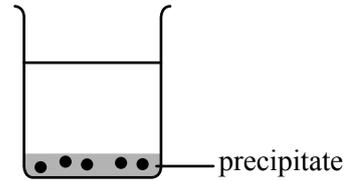
The automation of analysis has been attracting the attentions of various fields, because automated instruments can reduce the manpower cost of laboratory operations, enhance sample throughput, and improve the accuracy and precision of analytical results obtained. Additionally, they can be also used to minimize hazard in laboratory work.

Table 1.7 Examples of preconcentration of trace elements with coprecipitation^{12,13}

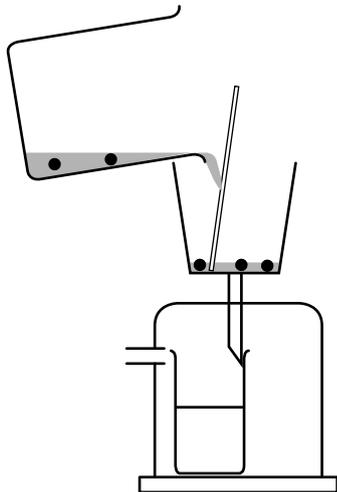
Type	Collector	Coprecipitated traces
hydroxide	Fe(OH) ₃	Pb, As, Mo, W, Co, Ag, Ni, Mn, Zn, Cr, V, Be, Sc, Ti, Ga, Ge, Se, Th
	Sn(OH) ₄	Au, Pt, Ag
	Al(OH) ₃	Ti, Fe, Zr, Cr, U
	Mg(OH) ₂	Mn
sulphide	CuS	Mo, Zn, Pb, Hg, Sb, Bi, Cd, Pd, Pt
	CdS	Hg, Fe, Cu, Sn
	PbS, NiS	Cu
sulphate	BaSO ₄	Pb, Sr
phosphate	FePO ₄	Al, Be
	Ca ₃ (PO ₄) ₂	Co, Bi, Fe, In, Pb, Ga, Zn
	ZrPO ₄	Th
	MgNH ₄ PO ₄	As
	BiPO ₄	Pu
chromate	PbCrO ₄	Ba
	BaCrO ₄	Pb, Tl
others	Ni(BrO ₃) ₂	Ir
	Hg(IO ₃) ₂	Sc, Th
	CaCO ₃	Sr, Pb, Po, Ra
	MnO ₂	Mo, Sb
	Te	Au, Hg, Ag, Pt, Pd, Ir, Se, Sc, Ce, Th, rare earth metals



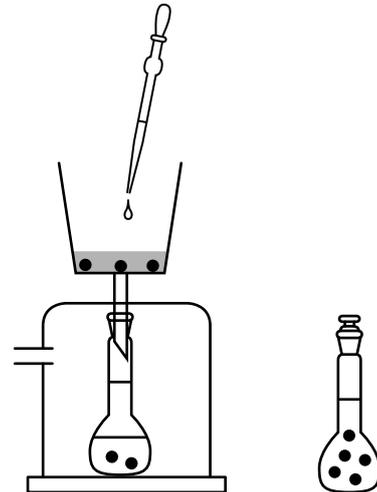
Addition of collector
Adjustment of pH



Formation of precipitate
Staying for 1 to 24 hours



Filtration of precipitate



Recovery of analyte
Dissolution of precipitate by appropriate acid

Fig. 1.9 Procedure of coprecipitation for preconcentration of metals.

The first attempt for automation of solution handling which made up the bulk of labor in an analytical laboratory was simply mechanizing and simulating the traditional manual batch operations under a conveyer-belt concept. This was an approach which never proved to be cost effective and efficient enough to gain widespread acceptance. Batch analyzers which were more successful include the Dupont “sample bag” analyzers and the parallel centrifugal analyzers. They are, however, expensive devices, and their use is rather limited, moreover, they are not designed to perform separation.

1.2.2.1 Air-segmented continuous flow analysis

As one of automation of the sample treatment, the segmented continuous flow analyzer was developed to improve a sample throughput by Skeggs in 1957.¹⁴ With this system analytical chemistry was for the first time performed in conduits instead of discrete vessels, which greatly improved the efficiency of serial assays. This type of analyzer has been commercially refined by Technicon and is marketed under the trade name AutoAnalyzer[®] (**Fig. 1.10**).¹⁵ However, total modernization of the sample handling step of analysis requires a reduction in time and improvements in the types of sample handling steps that can be automated such as matrix modification and dilution. The Autoanalyzer, in most situations, must allow the chemistry to proceed to steady state and has limited flexibility, especially in terms of timing, thereby making kinetic based measurement impractical. Therefore, a new technique instead of the Autoanalyzer for automated sample handling was need.

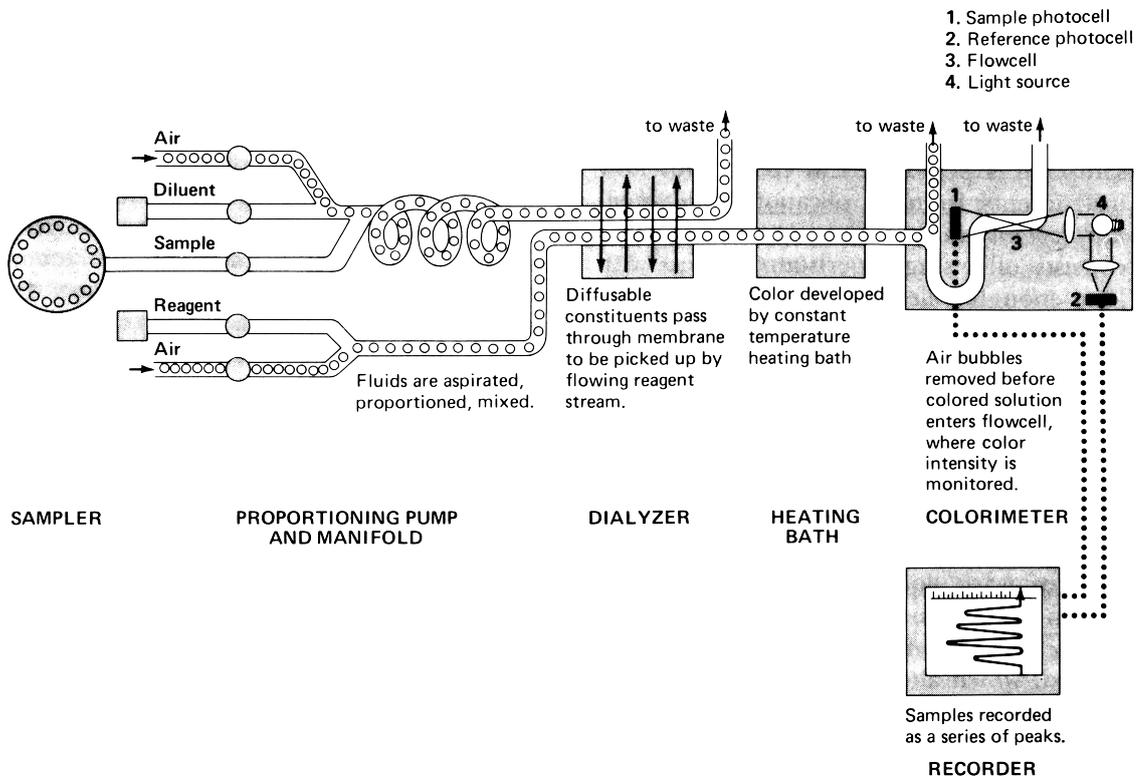


Fig. 1.10 A single channel Technicon AutoAnalyzer® System.¹⁵

1.2.2.2 Flow injection analysis

Flow injection analysis (FIA) is such a technique, proposed by Růžička and Hansen in 1975.^{16,17} In the first edition of their well-known monograph, “Flow-injection Analysis”, published in 1981,¹⁸ they defined FIA as “A method based on injection of a liquid sample into a moving unsegmented continuous stream of a suitable liquid. The injected sample forms a zone, which is then transported toward a detector that continuously records the absorbance, electrode potential, or any other physical parameter, as it continuously changes as a result of the passage of sample material through the flow cell”, and the technique “is based on a combination of sample injection, controlled dispersion, and exact timing”.

For principle of FIA, an example of one of the simplest FIA methods, the spectrophotometric determination of chloride in a single-channel system, is shown in **Fig. 1.11**;¹⁹ this is based on the release of thiocyanate ions, SCN^- from mercury(II) thiocyanate, $\text{Hg}(\text{SCN})_2$ and its subsequent reaction with iron(III) and measurement of red color of the resulting iron(III) thiocyanate complex ion, $\text{Fe}(\text{SCN})^+$. The samples, with chloride contents in the range 5 – 75 ppm chloride, are injected (S) through a 30- μl valve into the carrier solution containing the mixed reagent, pumped at a rate of 0.8 ml min^{-1} . The iron(III) thiocyanate is formed on the way to the detector (D) in a mixing coil (M, 0.5 m long, 0.5 mm i.d.), as the injected sample zone disperses in the carrier stream of reagent. The mixing coil minimizes band broadening (of the sample zone) due to centrifugal forces, resulting in sharper recorded peaks. The absorbance A of the carrier stream is continuously monitored at 480 nm in a micro flow-through cell (volume of 10 μl) and recorded (**Fig. 1.12**). To demonstrate the reproducibility of the analytical readout, each sample in this experiment was injected in quadruplicate, so that 28 samples were analyzed at seven different concentrations of chloride. As this took 14 minutes, the average sampling rate was 120 samples per hour. The fast scan on the 75- and 30-ppm sample peaks (shown on the right in

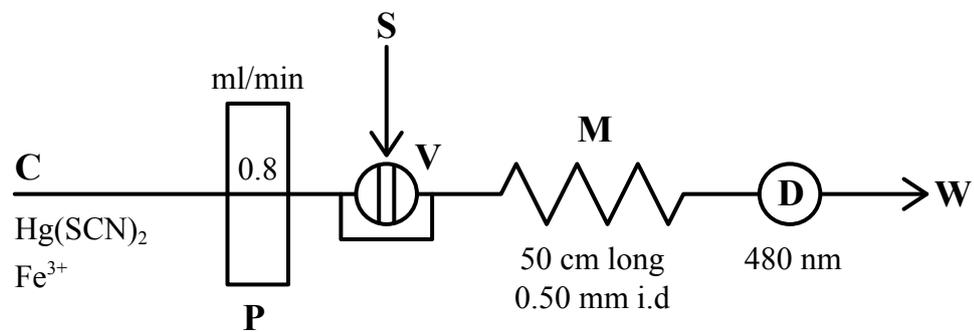


Fig. 1.11 Flow injection diagram for the spectrophotometric determination of chloride.¹⁹
 S, sample; C, carrier; P, pump; V, injector valve; M, mixing coil; D, flow through detector; and W, waste.

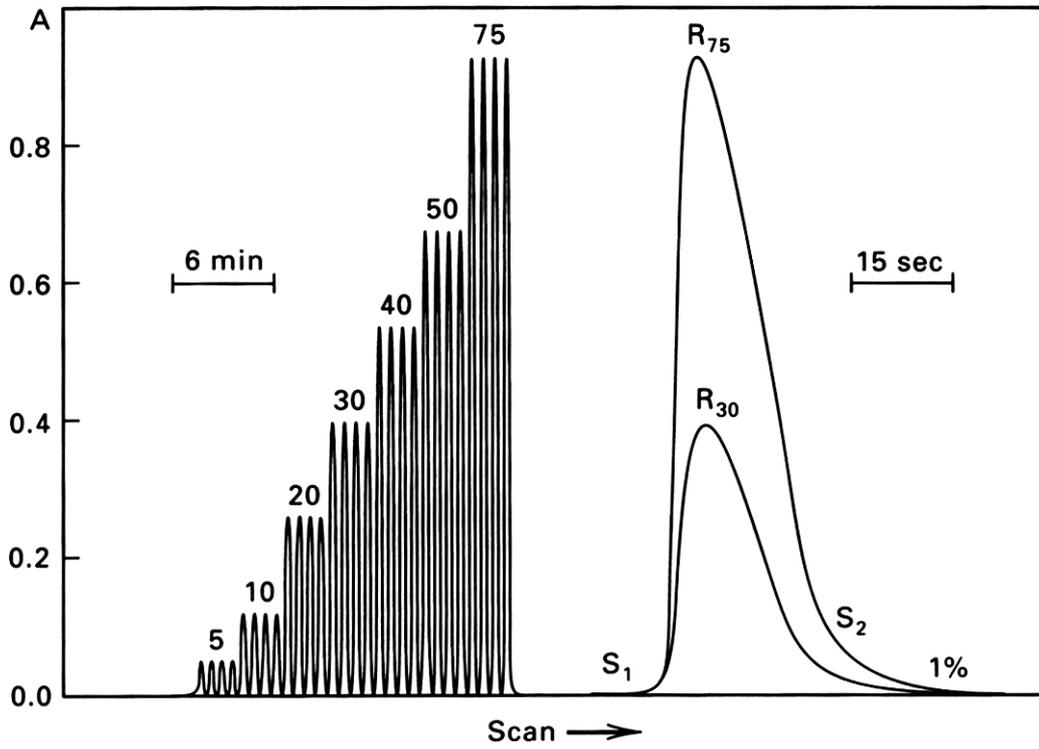


Fig. 1.12 Analog output showing chloride analysis in the range of 5 – 75 ppm Cl with the system depicted in Fig. 1.8.¹⁹

Fig. 1.12) confirms that there was less than 1% of the solution left in the flow cell at the time when the next sample (injected at S2) would reach it, and that there was no carryover when the samples were injected at 30-second intervals.

A peristaltic pump is typically used to propel the stream. For process analysis, these are not suitable because the pump tubing must be frequently changed, and more rugged pumps are used, such as syringe pumps, or pumping is by means of air displacement in a reservoir. The injector may be a loop injector valve as used in high-performance liquid chromatography. A bypass loop allows passage of carrier when the injection valve is in the load position. The injected sample volumes may be between 1 and 200 μl (typically 25 μl), which in turn requires no more than 0.5 ml of reagent per sampling cycle. This makes FIA a simple microchemical technique that is capable of having a high sampling rate and minimum sample and reagent consumption. The pump, valve, and detector may be computer controlled for automated operation.

FIA is a general solution-handling technique, applicable to a variety of tasks ranging from pH or conductivity measurement to colorimetry and enzymatic assays. To design any FIA system properly, one must consider the desired function to be performed. For pH measurement, or in conductivity, or for simple atomic absorption, when the original sample composition is to be measured, the sample must be transported through the FIA channel and into the flow cell in an undiluted form in a highly reproducible manner. For other types of determinations, such as spectrophotometry, the analyte has to be converted to a compound measurable by given detector. The prerequisite for performing such an assay is that during the transport through the FIA channel, the sample zone is mixed with reagents and sufficient time is allowed for production of a desired compound in a detectable amount.

Besides the single-line system, described in **Fig. 1.11**, a variety of manifold configurations may be used to allow application to nearly any chemical system. Several are

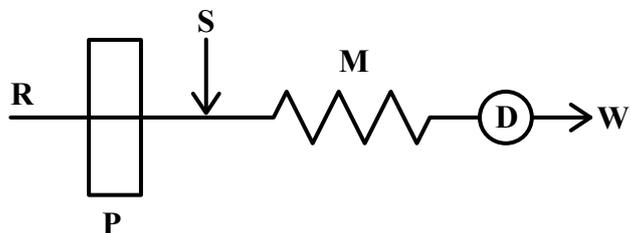
shown in **Fig. 1.13**. The two-line system (B) is the most commonly used, in which the sample is injected into an inert carrier and then merges, with reagent. In this manner, the reagent is diluted by a constant amount throughout, even when the sample is injected, in contrast to the single-line system; reagent dilution by the sample in a single-line system is all right as long as there is excess reagent and the reagent does not exhibit a background response that would shift upon dilution. If two reagents are unstable when mixed, then they may be mixed on-line in (C) or (D), or they may merge with the sample following injection in (E). Mixing coils may be interspersed between confluence points to allow dispersion before merging.

In FIA the sample is very reproducibly controlled in the flowing stream. Steady state measurements are no longer necessary because of this high reproducibility based on the above basic FIA properties. This yields significantly reduced analysis time. With FIA, matrix modification and kinetic based measurements become practical. In addition, FIA prevents the contaminations from the laboratory atmosphere because it is based on the closed system.

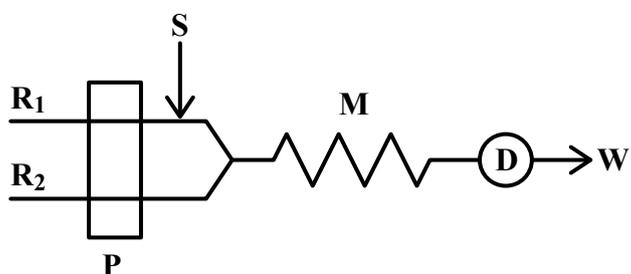
1.2.2.3 Advantages of FI on-line separation and preconcentration systems interfaced to ETAAS

Most sample pretreatment procedures such as preconcentration and separation are still performed manually and suffer from high risks of the contamination. Therefore, the elimination of human interaction in this tedious stage is obviously of great interest, particularly when large numbers of samples are involved. Thus, the FI on-line separation and preconcentration systems coupled with AAS, ICP–AES or ICP–MS may play major roles in the delicate stages of preconcentration of analyte and separation from matrix.

(A) Single-line system



(B) Two-line system with a single confluence point



(C) Single-line system with reagent premix

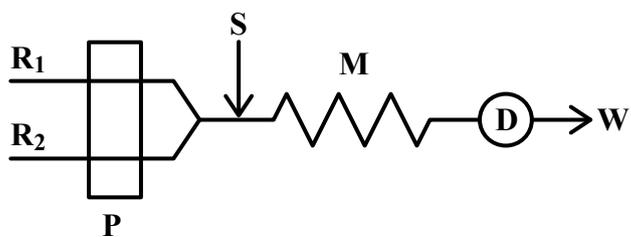
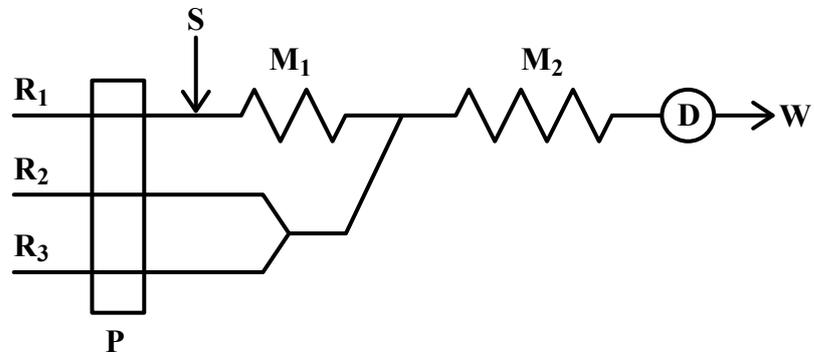


Fig. 1.13 Types of FIA manifolds.

S, sample; R_x , reagent (involving carrier solution); P, pump; M_x , mixing coil; D, detector; and W, waste.

(D) Two-line system with a single confluence point and reagent premix



(E) Three-line system with two confluence points

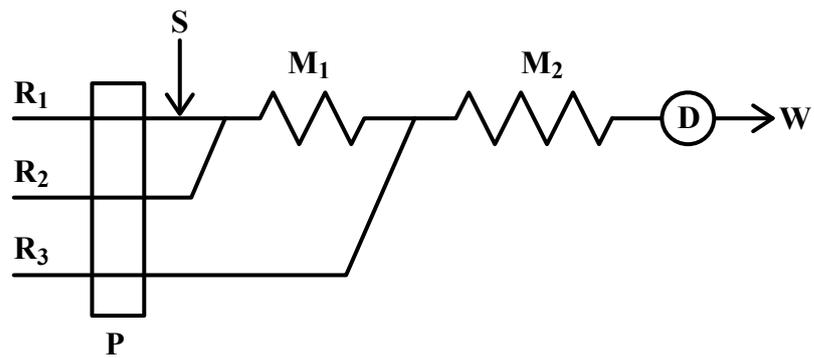


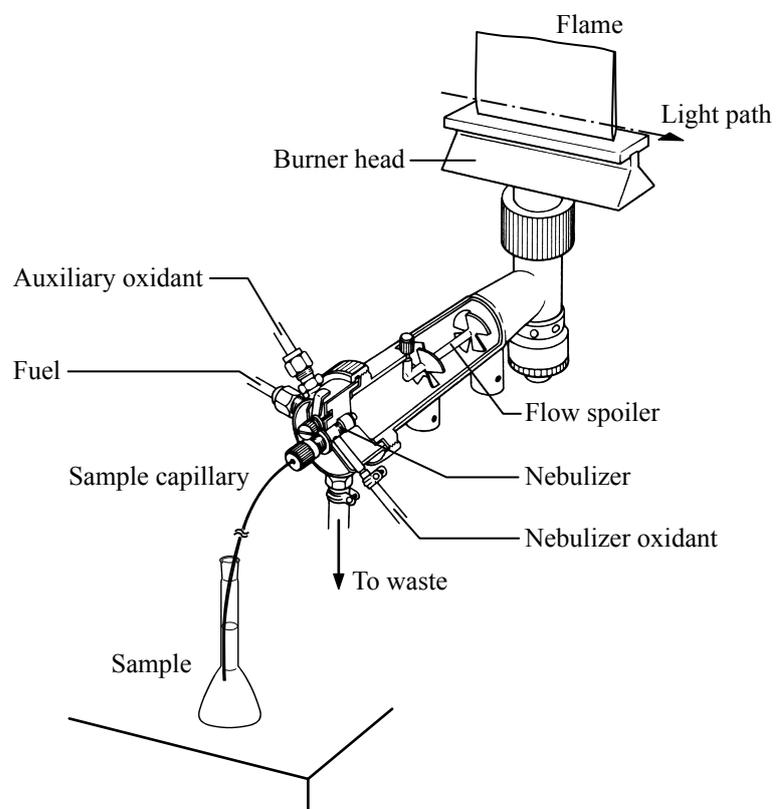
Fig. 1.13 (continued).

For FI systems, solid-phase extraction is most widely used as separation and preconcentration method because it is inherently easier to operate than other methods, and the equipment is generally more robust, although it has some problems of hydraulic pressure often caused by the drastic changes of pH solution between sample and eluent since the inner diameter of column used in FI system is usually extremely small, *e.g.*, 0.5 – 2 mm (see **Fig. 1.4**, (D)). An additional benefit over other method is its extremely high versatility, owing to the availability of a broad range of choice for different sorbents, complexing systems, and eluents.

FAAS, ICP–AES and ICP–MS are easily coupled with FI on-line solid-phase extraction system since they are inherently flow-through techniques, and these FI systems have received most attention. However, FAAS, ICP–AES and ICP–MS have some disadvantages; the detection limits of FAAS and ICP–AES are unsatisfied to determine some heavy metals, especially some toxic metals such as cadmium, lead and tin at sub- $\mu\text{g l}^{-1}$ or ng l^{-1} levels in environmental samples, and ICP–MS needs higher cost and skill than other instrumental techniques.

On the other hand, ETAAS is sufficiently sensitive to be directly applied for the routine determination of most metallic elements at $\mu\text{g l}^{-1}$ levels and the detection limit can be easily lowered to sub- $\mu\text{g l}^{-1}$ or ng l^{-1} levels by increase of sample volume or addition of proper chemical modifier. ETAAS is therefore the best compromise between the cost and the sensitivity. However, the development of the automated FI system coupled with ETAAS is quite difficult because ETAAS is a discontinuous technique due to the limited volume of the graphite furnace up to 100 μl . The structures of typical atomizers of FAAS and ETAAS are illustrated in **Fig. 1.14**.²⁰ Until recently, FI on-line preconcentration–ETAAS systems by solid-phase extraction have been developed for the determination of heavy metals and are summarized in **Table 1.8**.²¹ However, only a few were practically able to perform all the steps automatically.

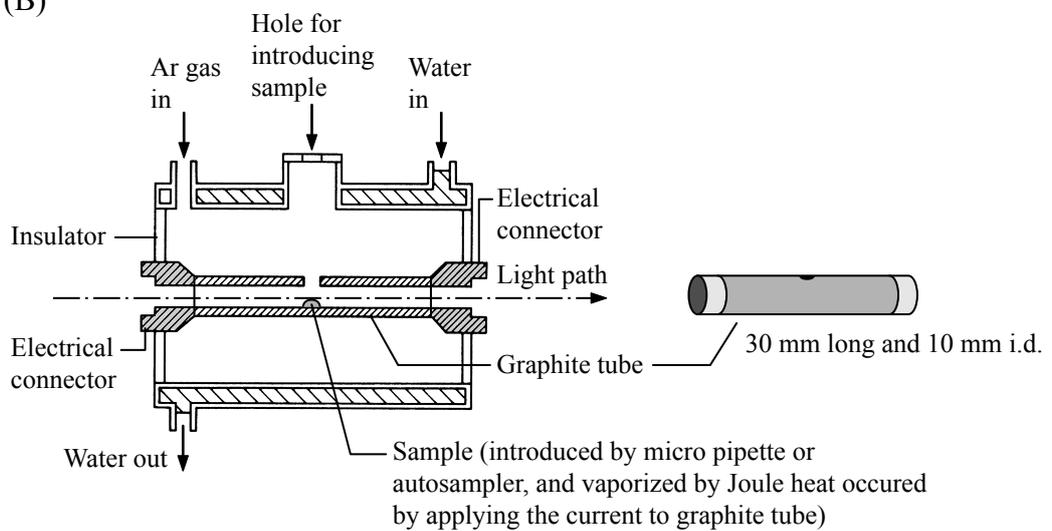
(A)



- *Sample solution can be continuously aspirated into the burner.*
- × *Retention time of vapor of analyte is shorter, so the detection limit is higher than ETAAS.*

Fig. 1.14 Typical atomizers of FAAS (A) and ETAAS (B).²⁰

(B)



Using small volume of graphite tube ---

- Vapor of analyte can retain longer in tube, so the detection limit is lower than FAAS.
- × Sample solution can not be continuously introduced into the graphite tube, so the development of FI connected with ETAAS is difficult.

Fig. 1.14 (continued).

Table 1.8 FI on-line preconcentration–ETAAS systems by solid-phase extraction for the determination of heavy metals²¹

Species	Solid-phase	Sample	Sample volume (mL)	Enhancement factor	LOD ^a	Analysis of CRM ^b or other approaches for method	Ref.
Bi	Activated carbon	Steel, aluminium alloys	10	14	50	Alloy steel	22
Cd	C ₁₈	Sea, river, drinking, reservoir and mineral water	1	19	0.5	Sea and river waters	23
		Seawater	0.5–1.0	–	1.7	Saline waters	24
	Muromac A-1	Ground and river waters	4–12	90	0.2	River water	25
Cd species	Chelex-100 and C ₁₈	Natural waters	5.18	51	12	Internal calibration technique	26
Cd, Pb, Cu, Ni	C ₁₈	River, sea estuarine waters	3	1.2–3.0	0.6(Cd), 8.5(Cu), 21(Ni), 4(Pb)	Sea, estuarine and river waters	27
Cd, Co, Ni	Muromac A-1	Seawater	0.4(Cd), 1.8(Co) and 0.8(Ni)	–	0.1(Cd), 7(Co) and 33(Ni)	Seawater	28
Cd, Cu, Fe, Mn, Ni, Pb, Zn	Silica-immobilized 8-quinolinol	8-Sea water	0.83–5	Up to 250	0.3(Cd), 6.9(Cu), 4.2(Fe), 1.8(Mn), 10.2(Ni), 5.7(Pb) and 1.8 pg (Zn)	Seawater	29

Table 1.8 (Continued)

Species	Solid-phase	Sample	Sample volume (ml)	Enhancement factor	LOD ^a	Analysis of CRM ^b or other approaches for method	Ref.
Cd, Pb, Cu, Ni	C ₁₈	River, lake, tap and seawaters	3	20	0.8(Cd), 6.6(Pb), 17(Cu) and 36(Ni)	Coastal and open ocean seawaters and river waters	30
Cd, Pb, Ni	Fullerene C ₆₀	Water reference materials	3	100–150	2.2(Cd), 23(Pb) and 75(Ni)	Lake, river and drinking waters	31
Co	Fullerene C ₆₀	Wheat flour	25	40	8	Analysis by conventional ETAAS	32
	C ₁₈	Seawater	28	210	1.7	Seawater	33
Co, Ni, Pb	C ₁₈	Seawater	3	29–32	7.8(Cd), 12.8(Ni) and 3.9(Pb)	Seawater	34
Cr(VI)	Innner wall of a knotted reactor made PTFE	Drinking and sea waters	5	19	4.2	Seawater	35
Cr(VI), total Cr	C ₁₈	Natural waters	3	12	16(Cr(VI)) and 18(total Cr)	Seawater and river waters	36
Cu, Mo	Muromac A-1	Seawater	0.2–0.6	3–12(Cu) and 1–4(Mo)	9(Cu) and 60(Mo)	Saline waters	37,38

Table 1.8 (Continued)

Species	Solid-phase	Sample	Sample volume (mL)	Enhancement factor	LOD ^a	Analysis of CRM ^b or other approaches for method	Ref.
Ni	Silica gel functionalized with 1-(di-2-pyridyl)methylenethiocarbonylhydrazine	Seawater	3	58	0.06	Seawater, spiked seawater and spiked synthetic waters	39
Pb	C ₁₈	River and seawaters	3	26–42	3	Coastal and open ocean seawates	40
	Macrocyclic immobilized silica gel sorbent (PB-O2)	Biological materials (rice flour, blood and urine)	3	77	2	Rice flour, blood and urine	41,42
Pd, Pt, Rh	Amberlite XAD-4	Standard solutions	4.6	78	30(Pd), 100(Pt) and 10(Rh)	Analytical addition technique	43
Tl	Amberlite XAD-8	Geochemical materials	1.0	15	18	Geochemical materials	44

a. LOD = limit of detection in ng l⁻¹, unless otherwise stated. b. Certified reference materials.

1.3 Synopsis of the present investigation

Chapter 2 describes an FI on-line preconcentration–ETAAS coupled with a coprecipitation method for the determination of lead in seawater. The combination of two preconcentration procedures, coprecipitation with iron(III) hydroxide and solid-phase extraction with a lead-selective resin, Pb-Spec[®], will be employed to carry out the sensitive determination of lead at the ng kg⁻¹ level.

Chapter 3 states a novel separation and preconcentration method using coagulation of colloidal silica by addition of calcium chloride has been developed for traces of manganese, cobalt, zinc and cadmium. The proposed method will be applied to the determination of manganese, cobalt, zinc and cadmium in river-water.

References

1. S. E. Manahan, "*Environmental Chemistry*", 7th ed., **1999**, Lewis Publishers, Boca Raton, 190.
2. C. Reimann and P. Caritat, "*Chemical Elements in the Environment*", **1998**, Springer, Berlin.
3. J. E. Ferguson, "*The Heavy Elements*", **1990**, Pergamon Press, Oxford.
4. W. Stumm and J. J. Morgan, "*Aquatic Chemistry*", 3rd ed., **1996**, John Willey & Sons, New York, 293.
5. The Japan Society for Analytical Chemistry, Kyushu Branch ed., "*Kiki Bunseki Nyumon (Primer of Instrumental Analysis)*", 3rd ed., **1996**, Nankodo, Tokyo, 108.
6. M. Nishimura, "*Kankyo Kagaku (Environmental Chemistry)*", **1991**, Shokabo, Tokyo, 26.
7. Z. B. Alfassi and C. M. Wai, "*Preconcentration Techniques for Trace Elements*", **1992**, CRC Press, Boca Raton.
8. A. G. Howard and P. J. Statham, "*Inorganic Trace Analysis*", **1993**, John Willey & Sons, Chichester, 145.
9. Y. Takata, K. Oguma, Y. Hirano, and M. Sakata, "*Kankyo Sokutei to Bunseki Kiki (Environmental Measurement and Analytical Instruments)*", **2003**, Japan Environmental Measurement & Chemical Analytical Association, Tokyo, 133.
10. N. Simpson, "*Solid-Phase Extraction*", **2000**, Marcel Dekker, New York.
11. V. Camel, *Spectrochim. Acta, B*, **2003**, 58, 1177.
12. Z. Marczenko, "*Separation and Spectrophotometric Determination of Elements*", 2nd ed., **1986**, Ellis Horwood, Chichester, 32.
13. T. Koyama, N. Handa, and Y. Sugimura, "*Kosui-Kaisui no Bunseki (Analysis of Lake-water and Seawater)*", **1972**, Kodansha, Tokyo, 271.

14. L. Skeggs, *Am. J. Clin. Path.*, **1957**, 28, 311.
15. D. A. Skoog, “*Principles of Instrumental Analysis*”, 3rd ed., **1984**, Saunders College Publishing, Philadelphia.
16. J. Růžička and E. H. Hansen, *Anal. Chim. Acta*, **1975**, 78, 145.
17. J. Růžička and J. W. B. Stewart, *Anal. Chim. Acta*, **1975**, 79, 79.
18. J. Růžička and E. H. Hansen, “*Flow Injection Analysis*”, 1st ed., **1981**, John Wiley & Sons, New York.
19. G. D. Christian, “*Analytical Chemistry*”, 5th ed., **1994**, John Wiley & Sons, New York, 594.
20. A. Vogel, “*A Textbook of Quantitative Inorganic Analysis*”, 4th ed., **1978**, Longman, London.
21. J. L. Burguera and M. Burguera, *Spectrochim. Acta, B*, **2001**, 56, 1801.
22. J. B. Silva, A. J. Curtius, and M. B. Giacomelli, *Analyst*, **1999**, 124, 1249.
23. Z. R. Xu, H. Y. Pan, S. X. Xu, and Z. L. Fang, *Spectrochim. Acta, B*, **2000**, 55, 213.
24. P. G. Su and S. D. Huang, *Anal. Chim. Acta*, **1998**, 376, 305.
25. Y. Hirano, J. Nakajima, K. Oguma and Y. Terui, *Anal. Sci.*, **2001**, 17, 1073.
26. F. M. Fernandez, M. B. Tudino, and O. E. Troccoli, *J. Anal. At. Spectrom.*, **2000**, 15, 687.
27. B. Welz, X. Yin, and M. Sperling, *Anal. Chim. Acta*, **1992**, 261, 477.
28. H. J. Chang, Y. H. Sung, and S. D. Huang, *Analyst*, **1999**, 124, 1695.
29. L. C. Azeredo, R. E. Sturgeon, and A. J. Curtius, *Spectrochim. Acta, B*, **1993**, 48, 91.
30. M. Sperling, X. F. Yin, and B. Welz, *J. Anal. At. Spectrom.*, **1991**, 6, 295.
31. M. M. Silva, M. A. Z. Arruda, F. J. Krug, P. V. Oliveira, Z. F. Queiroz, M. Gallego, and M. Valcárcel, *Anal. Chim. Acta*, **1998**, 368, 255.
32. M. M. González, M. Gallego, and M. Valcárcel, *J. Anal. At. Spectrom.*, **1999**, 14, 711.

33. M. Sperling, X. Yin, and B. Welz, *J. Anal. At. Spectrom.*, **1991**, 6, 615.
34. Q. H. Jin, X. G. Su, F. Liang, and H. Q. Zhang, *Microchem. J.*, **1999**, 62, 316.
35. S. Nielsen and E. H. Hansen, *Anal. Chim. Acta*, **1998**, 366, 163.
36. M. Sperling, X. Yin, and B. Welz, *Analyst*, **1992**, 117, 629.
37. Y. H. Sung, Z. S. Liu, and S. D. Huang, *J. Anal. At. Spectrom.*, **1997**, 12, 841.
38. Y. H. Sung, Z. S. Liu, and S. D. Huang, *Spectrochim. Acta, B*, **1997**, 52, 755.
39. M. T. Siles, C. E. I. Vereda, A. P. Canãda, R.A. Torres, and J. M. Cano, *J. Anal. At. Spectrom.*, **1999**, 14, 1033.
40. Z. Fang, M. Sperling, and B. Welz, *J. Anal. At. Spectrom.*, **1990**, 5, 639.
41. M. Sperling, X. Yan, and B. Welz, *Spectrochim. Acta, B*, **1996**, 51, 1875.
42. X. Yan, M. Sperling, and B. Welz, *J. Anal. At. Spectrom.*, **1999**, 14, 1625.
43. M. L. Lee, G. Tölg, E. Beinrohr, and P. Tschöpel, *Anal. Chim. Acta*, **1993**, 272, 193.
44. Z. Xu, S. Xu, and Z. Fang, *At. Spectrosc.*, **2000**, 21, 12.

Chapter 2

Determination of Lead in Seawater by Flow-Injection On-line Preconcentration-Electrothermal Atomic Absorption Spectrometry after Coprecipitation with Iron(III) Hydroxide

2.1 Introduction

The concentration of lead in the seawater varies and can be very low, *e.g.*, 0.5–30 ng l⁻¹.¹ An analysis of environmental samples for lead was carried out by ASV,^{2–4} FAAS,^{5–7} ETAAS,^{8–11} ICP-AES¹² and ICP-MS.^{13–16} Recently, ETAAS has been extensively used because it is more sensitive than ASV, FAAS and ICP-AES, and more economical than ICP-MS. The determination of lead in natural water by ETAAS requires a preliminary separation and preconcentration step to eliminate any matrix components, and to improve the detection limit. Therefore, some on-line flow injection (FI) systems coupled with ETAAS for the determination of lead have been reported,^{17–19} although these detection limits are still near, or above, the concentration of lead in environmental water.

The coprecipitation method has been widely used for the preconcentration of trace metals and their separation from the matrix components associated with various determination techniques. Several coprecipitants, such as iron(III) hydroxide,^{20–22} magnesium hydroxide,^{16,23} hafnium hydroxide²⁴ and pyrrolidinedithiocarbamate (PDC) of cobalt,²⁵ copper and iron(III),^{26,27} have been proposed. The method using hafnium hydroxide is expensive. Although magnesium hydroxide is an excellent collector, magnesium, itself, causes serious high-background absorption in ETAAS. Digestion of the PDC precipitate of cobalt²⁵ takes a long time to simplify the sample matrix. Among them, the iron(III) hydroxide method is simple and the precipitate is easily dissolved in acid.

In the present work, a flow-injection (FI) on-line preconcentration–ETAAS system after coprecipitation with iron(III) hydroxide was developed for the determination of lead in seawater. The developed system employs a Pb-Spec[®] microcolumn for preconcentration and separation from a large amount of iron present in the sample after the coprecipitation procedure. The Pb-Spec is prepared by loading an isodecanol solution of *bis*-4,4'(5')-[*tert.*-butylcyclohexano]-18-crown-6 on Amberchrom CG-71 md. Lead in the

sample was first coprecipitated with iron(III) hydroxide. Then, the precipitate was dissolved in nitric acid and introduced into the FI system. Lead in the sample solution was adsorbed on the Pb·Spec microcolumn and eluted with EDTA. The eluate zone corresponding to the highest analyte concentration was introduced into a graphite tube by the cooperation of a peristaltic pump and an autosampler pump. The proposed method has yielded reproducible results for lead at slightly higher levels in seawater samples.

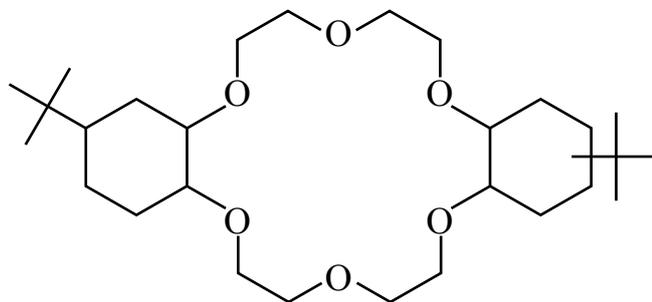
2.2 Experimental

2.2.1 Reagents and samples

All reagents used were of analytical reagent grade. Distilled and deionized water was further purified *via* passage through a Milli-Q[®] Ultrapure water purification system (Millipore, Bedford, USA).

A lead stock standard solution (1000 mg l^{-1}) was prepared by dissolving 0.4 g of lead nitrate in nitric acid (1+1) and diluting to 250 ml with water, and standardized by EDTA titration. Lead working solutions were daily prepared from 1000 mg l^{-1} stock standard solution. A lead working curve was prepared using lead standard solutions without the coprecipitation procedure.

An iron(III) solution (10000 mg l^{-1}) used for coprecipitation was prepared by dissolving 1.0 g of iron wire (99.52%, Mallinckrodt Chemical Works, St. Louis) in nitric acid (1+2) and diluting to 100 ml with water. The iron(III) solution was purified by a small column packed with Pb·Spec. A 5% (m/v) diammonium hydrogenphosphate (Wako Pure Chemical Industries, Osaka) solution was used as a chemical modifier. A lead-selective resin, Pb·Spec (100–150 μm , Eichrom Industries, Darien, IL, **Fig. 2.1**), was used for preconcentration of lead in FI system. The eluent was a $1.0 \times 10^{-4} \text{ mol l}^{-1}$ EDTA solution,



bis-4,4'(5')-[tert.-butyl-cyclohexano]-18-crown-6

Stationary phase

- 0.75 mol l⁻¹ *bis-4,4'(5')-[tert.-butyl-cyclohexano]-18-crown-6*
- in isodecanol

Support

- Amberchrom[®] CG-71

Particle diameter

- 100 ~ 150 μm

Capacity

- 20.5 mg Pb/ml of bed (experimental)

Fig. 2.1 Structure of Pb·Spec[®] resin.

which was prepared from EDTA·2NH₄ (Dojin Laboratory Chemicals, Kumamoto). For the preliminary experiments, ammonium carbonate, ammonium citrate, ammonium oxalate, sulfuric acid and L-cysteine (Kanto Chemicals, Tokyo) were used as the eluents for lead.

A seawater sample collected at Kujukuri seashore (Chiba, Japan) was filtered through a 0.45- μ m membrane filter (Millipore) and acidified to pH 1.5 with nitric acid.

2.2.2 Instrumentation

A Hitachi (Tokyo) prototype flow injection system was used for on-line preconcentration after a partial modification (**Fig. 2.2**). The system was constructed with 1-mm i.d. polytetrafluoroethylene (PTFE) tubing, peristaltic pumps and three-way solenoid valves. A PTFE microcolumn (C₁; 2 mm i.d. and 30 mm long) packed with Pb·Spec resin was used for the preconcentration of lead. Both ends of the column were sealed with glass wool (1mm long). For purification of the conditioning solution, a microcolumn (C₂; 4 mm i.d. and 10 mm long) packed with Pb·Spec resin was used. The preconcentration column was connected with an autosampler of ETAAS by 0.5-mm i.d. PTFE tubing. A Hitachi programmable controller H-200 was employed to control the valves and the autosampler.

A Hitachi Z-5000 atomic absorption spectrometer with a polarized Zeeman-effect background corrector was used. The absorbance was measured under the operating conditions recommended by the manufacturer. A graphite furnace autosampler was employed to inject the eluate from the Pb·Spec microcolumn and a chemical modifier solution into a graphite tube. A pyrolytically coated graphite tube was used throughout the work. The graphite furnace temperature program is shown in **Table 2.1**. For the determination of lead, a 5- μ l portion of the chemical modifier solution was injected into a graphite tube. The carrier gas flow of argon was stopped during atomization, and the

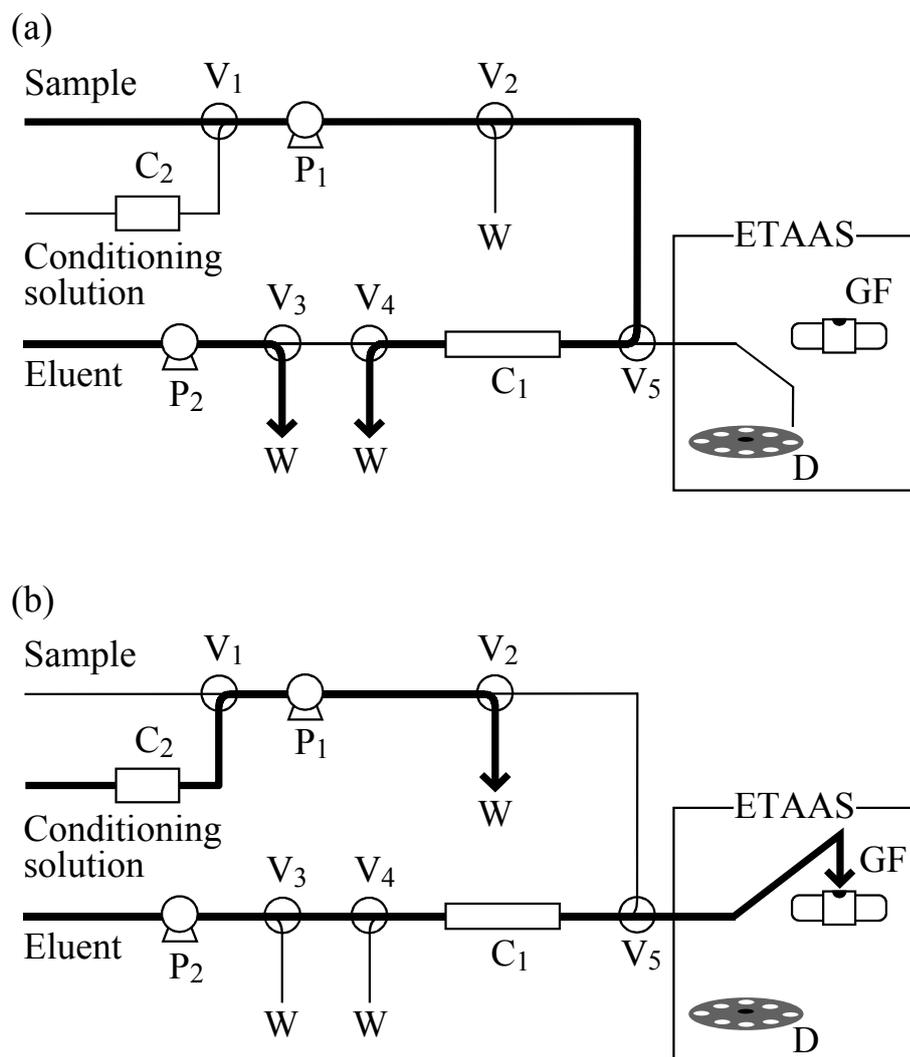


Fig. 2.2 Flow-injection manifold for the determination of lead by an on-line preconcentration-ETAAS analysis. (a), Sample loading; (b), elution. C₁ – C₂. column; V₁ – V₅, three-way solenoid valve; P₁ – P₂, peristaltic pump; GF, graphite furnace; W, waste; D, autosampler disk..

Table 2.1 Temperature program of the graphite furnace

Step	Temperature/ °C	Ramp/ s	Hold/ s
Drying	60 - 125	60	–
Ashing	125 - 500	15	10
Atomization	2100	–	5
Cleaning	2700	–	4

peak-height absorbance was used for quantification. For some experiments to find the optimum experimental conditions, a flame mode of AAS was also used under the operating conditions recommended by the manufacturer. In the flame mode, the column in the FI system was connected to the nebulizer of the flame atomizer *via* 1-mm i.d. PTFE tubing.

2.2.3 Procedure of coprecipitation with iron(III) hydroxide

A 250-g portion of an acidified sample solution was mixed with 1 ml of 10 mg iron(III)/ml solution. The pH of the solution was then adjusted to about 8 with dilute ammonia water, and lead was coprecipitated with iron(III) hydroxide. After standing for about 2 h, the precipitate was filtered with a 0.45- μm membrane filter (Millipore) and washed with Milli-Q water. The precipitate was then dissolved and diluted to 25 ml with 1 mol l^{-1} nitric acid. Four milliliters of the solution prepared as described above was introduced into the FI-ETAAS system.

2.2.4 Determination of lead by on-line FI-ETAAS

For preconcentration and separation of lead from iron, a sample solution in 1 mol l^{-1} nitric acid (4 ml min^{-1}) was passed through the Pb-Spec column in the FI system for 1 min (**Fig. 2.2, a**). After rinsing the column with 1 mol l^{-1} nitric acid (4 ml min^{-1}) for 1 min, the lead retained on the column was eluted with 1.0×10^{-4} mol l^{-1} EDTA and the eluate was introduced into the tip of an autosampler through the valve 5 (**Fig. 2.2, b**). The eluate flow was stopped by turning the valve 3 when the eluate zone containing the highest analyte concentration had just reached the tip of the autosampler.

The procedure for the injection of a small zone of the eluate into the graphite tube has been previously developed.²⁸ The analyte zone flow at the autosampler in the elution step is shown in **Fig. 2.3**. When the autosampler started, the tip of the autosampler was inserted into a sample cup and the syringe moved backward in order to aspirate the sample solution. However, in this system, empty cups were set on the autosampler disk and the eluate was expelled from the autosampler tip into the cup. The autosampler and the FI system were synchronized by a programmable controller so that the eluate flow would be stopped when the backward movement of the syringe was stopped. Although a small portion of the eluate was drawn into the syringe ($3 \mu\text{l s}^{-1}$), most of the eluate flowed into the tip. The tip was then inserted into the graphite tube and a 30- μl portion of the eluate collected in the tip was injected into a graphite tube by the normal autosampler operation, followed by injection of 5 μl of the chemical modifier solution.

Before loading the next sample solution, an EDTA solution (1.5 ml min^{-1}) was pumped to clean-up the tubing between the valve 4 and the autosampler for 1 min. The time required for preconcentration and elution for a 4-ml sample, of which the loading time was 1 min, was 5 min. After injection of the eluate and the chemical modifier into the graphite tube, the heating program of the furnace was started. As the next run of FI preconcentration was started in the drying step of the present run, 12 measurements could be conducted per hour.

2.3 Results and discussion

2.3.1 Coprecipitation of lead with iron(III) hydroxide

A coprecipitation method with iron(III) hydroxide has been widely used for the preconcentration of trace metals in water samples. The properties of iron(III) hydroxide as

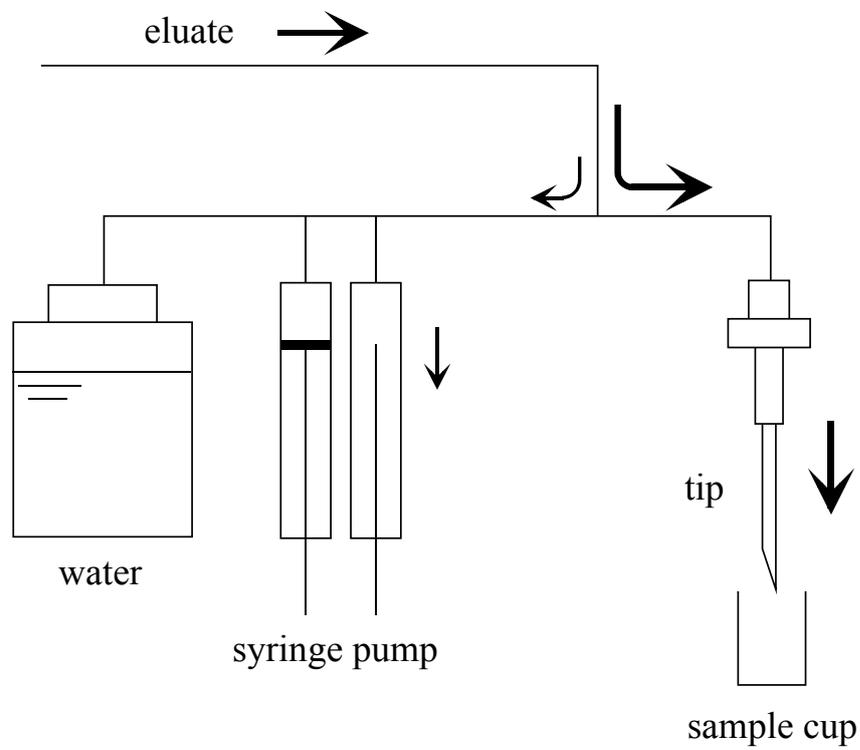


Fig. 2.3 Eluate flow at the autosampler for ETAAS in the elution step of FI-preconcentration.

a coprecipitant for metal ions were investigated by Bruninx *et al.*^{20,21} Lead is known to be one of the elements with the highest coprecipitation yield. The coprecipitation yield of lead increased with an increase in the pH and reached the highest value in the pH range 7.5 to 8.5 (**Fig. 2.4**). On the other hand, the contamination of lead from reagents may become serious at the pH above 8.5. Therefore, the pH was adjusted to about 8 with dilute ammonia water in further experiments.

The coprecipitation of 5 ng lead in 250 g of a solution was examined over an iron(III) concentration range of 4 to 80 mg kg⁻¹. The results are shown in **Fig. 2.5**. The recoveries of lead were about 80% in the iron(III) concentration range 4 to 20 mg kg⁻¹ and almost 100% in the iron(III) concentration range of 40 mg kg⁻¹ or above. Therefore, an iron(III) concentration of 40 mg kg⁻¹ was selected.

2.3.2 Adsorbent for preconcentration of lead

Two adsorbents, Muromac[®] A-1 and Pb-Spec[®], were tested for preconcentration of lead. Muromac A-1 is one of chelating resins containing iminodiacetate group and a suitable adsorbent for a flow-injection column because of its resistance to swelling and shrinkage. It is well-known that chelating resins containing iminodiacetate group can strongly adsorb most multivalent metal ions such as heavy metals and separate them from monovalent metal ions such as sodium and potassium ions. Therefore, they have been widely applied to the determination of most heavy metals in high saline waters. Adsorption of heavy metals on the resins depends on pH and needs the use of proper buffer solutions. In trace heavy metal analysis, some buffer solutions often cause the contamination of analyte because high pure buffer solutions are not available. Acetate-ammonium acetate

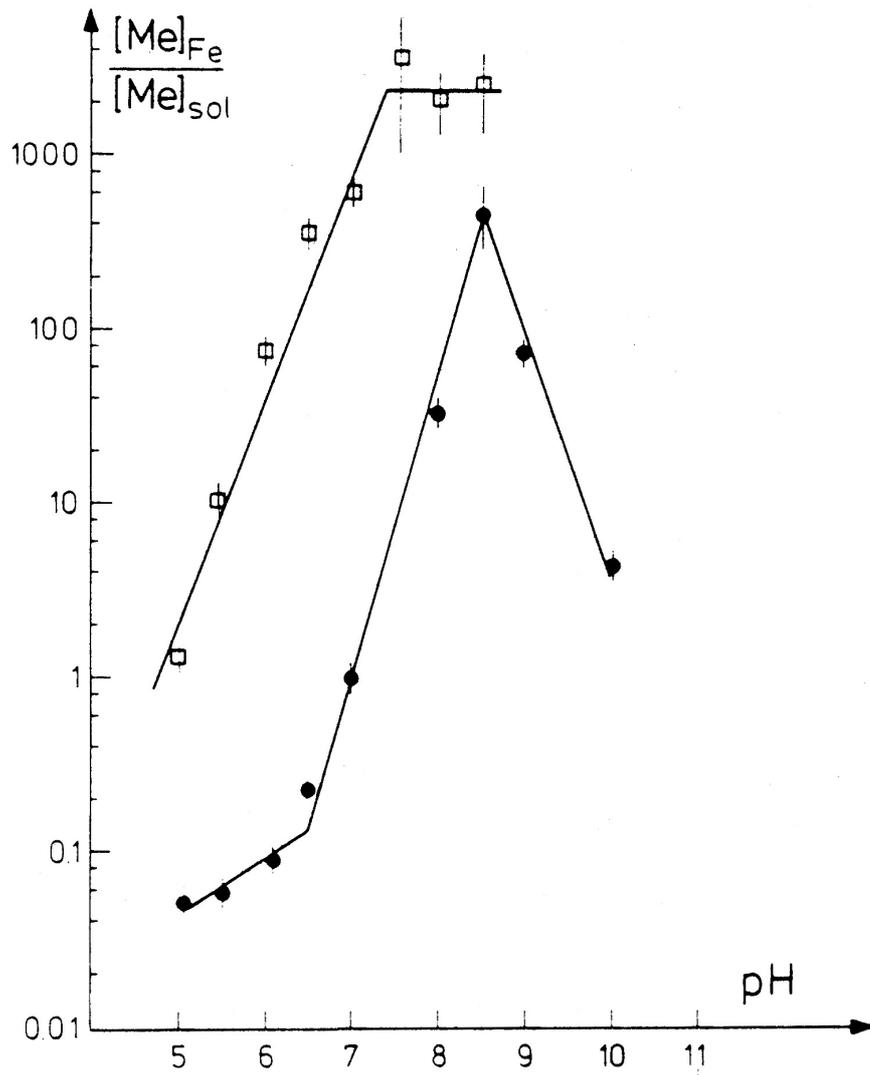


Fig. 2.4 Distribution ratio for varying pH.²¹
 Volume 40 ml; Fe, 400 μg; (□) Pb, 4 μg; (●) Zn, 4 μg. Error bars indicate 1σ counting statistics.

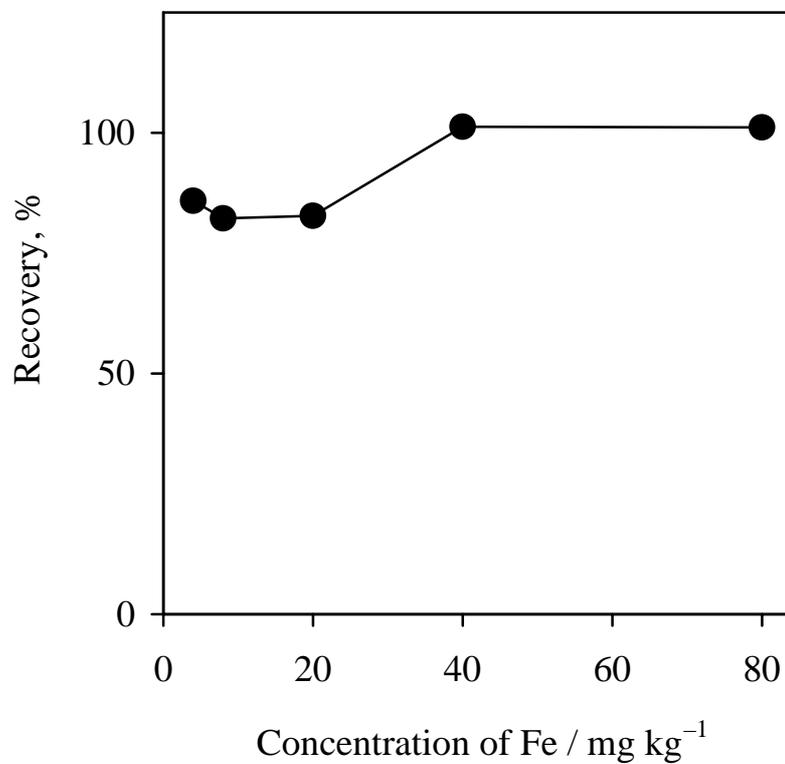


Fig. 2.5 Effect of the concentration of iron(III) on the recovery of lead by coprecipitation-FI-ETAAS. Sample solution, 250 g of 20 ng kg⁻¹ lead.

buffer tested in this work also contained lead at a sub- $\mu\text{g l}^{-1}$ level, although it was purified by the chelating resin column before use.

Pb-Spec is the trade name of a solid-phase extractant which was prepared by loading an isodecanol solution of *bis*-4,4'(5')-[*tert.*-butylcyclohexano]-18-crown-6 onto Amberchrom CG-71 md (Supelco). This resin shows a high selectivity to lead in nitric acid media, giving a capacity factor (k') of almost 1000 for lead at 1 mol l^{-1} nitric acid, so it does not need any buffer solutions. Among the metal ions investigated by Horwitz *et al.*, strontium(II) and thallium(I) have a k' value of about 20 and barium(II) has a k' value of about 10 (**Fig. 2.6**).³⁰ Sodium(I), potassium(I), calcium(II), magnesium(II), iron(III), and aluminum(III), which were the major constituents of environmental water samples, were not adsorbed on Pb-Spec. The application of Pb-Spec to the on-line preconcentration and separation of lead from iron in FI-FAAS has so far been reported for the determination of lead in iron and steel.³⁰ The high selectivity of Pb-Spec resin enable us to preconcentrate and separate lead from a large amount of iron(III) in the sample solution after coprecipitation. The concentration of nitric acid in the sample solution to be subjected to FI-ETAAS was adjusted to 1 mol l^{-1} , because it is most suitable for lead adsorption on Pb-Spec resin.

2.3.3 Effect of eluents

Several eluents (EDTA, ammonium oxalate, ammonium citrate, ammonium tartrate, ammonium carbonate, ammonium sulfate, sulfuric acid and L-cysteine) were examined by monitoring their lead profiles by FI-FAAS, because a sharp peak profile is suitable for the sensitive determination of lead by ETAAS. The eluents prepared at a concentration of 0.1 mol l^{-1} were tested to desorb 4 μg of lead from Pb-Spec column; the obtained peak height

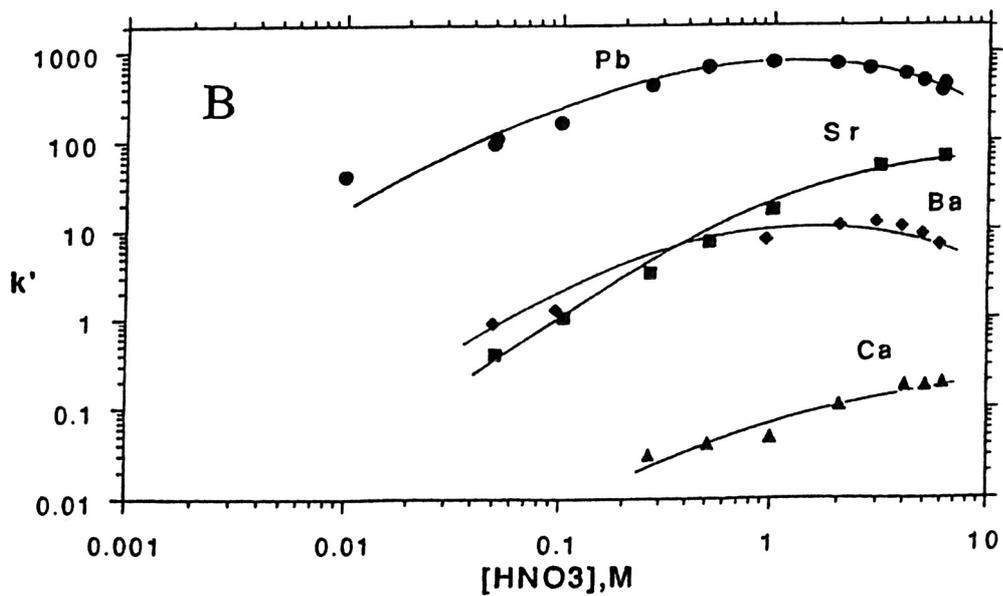
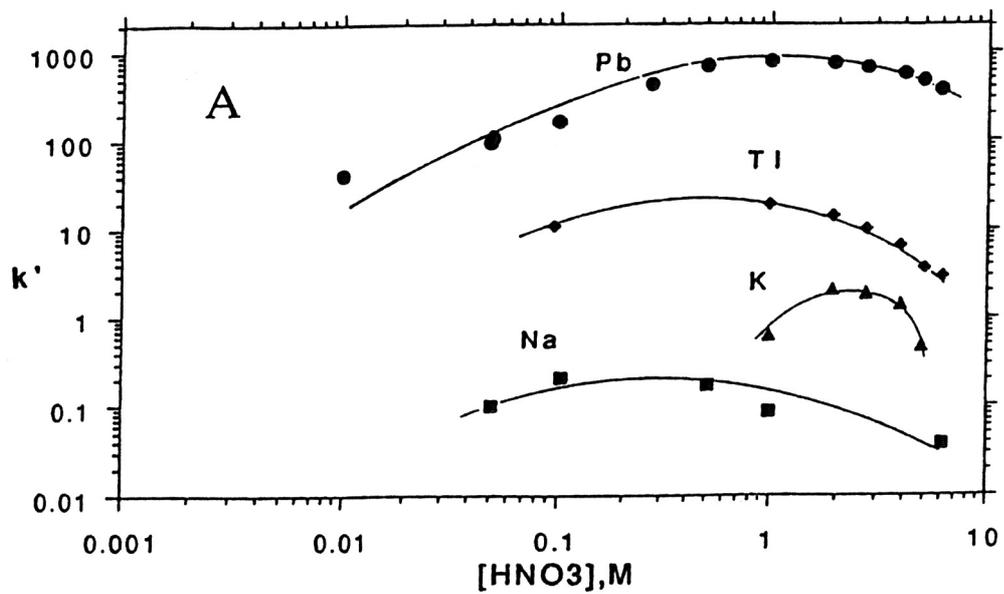


Fig. 2.6 Nitric acid dependency of k' for selected monovalent (A) and divalent (B) metal ions on Pb-Spec[®] resin.²⁹

absorbances are shown in **Fig. 2.7**. Because EDTA gave the highest absorbance, it was selected as an eluent in further experiments.

2.3.4 Effect of the concentration of EDTA

In order to investigate the effect of the concentration of EDTA 4 ml of $1 \mu\text{g l}^{-1}$ lead standard solution in 1 mol l^{-1} nitric acid was loaded onto a Pb-Spec column and the retained lead was eluted with 1.0×10^{-5} to $5.0 \times 10^{-4} \text{ mol l}^{-1}$ EDTA. The time required for the absorbance to reach the maximum value after the start of elution varied with the varying concentration of EDTA. When the concentration of EDTA was higher than $5.0 \times 10^{-4} \text{ mol l}^{-1}$, improducible absorbances were obtained, because carbon residues were accumulated in the graphite tube. The peak height was almost constant over an EDTA concentration range of 5.0×10^{-5} to $5.0 \times 10^{-4} \text{ mol l}^{-1}$, and was reduced to half at $1.0 \times 10^{-5} \text{ mol l}^{-1}$ (**Fig. 2.8**). Although the peak height at $5.0 \times 10^{-4} \text{ mol l}^{-1}$ EDTA was slightly higher than that at $1.0 \times 10^{-4} \text{ mol l}^{-1}$, the contamination of lead from the EDTA solution became serious. Therefore, $1.0 \times 10^{-4} \text{ mol l}^{-1}$ EDTA was adopted as an eluent.

2.3.5 Analysis of seawater sample

The applicability of the proposed method was evaluated by examining the recovery of lead from a seawater sample. A lead working curve was constructed using lead standard solutions by the FI system without the coprecipitation procedure. The results are summarized in **Table 2.2**. The concentration of lead in seawater collected at Kujukuri seashore was $4.7 \pm 0.7 \text{ ng kg}^{-1}$ and the recovery was $93.7 \pm 5.0\%$ for the seawater spiked

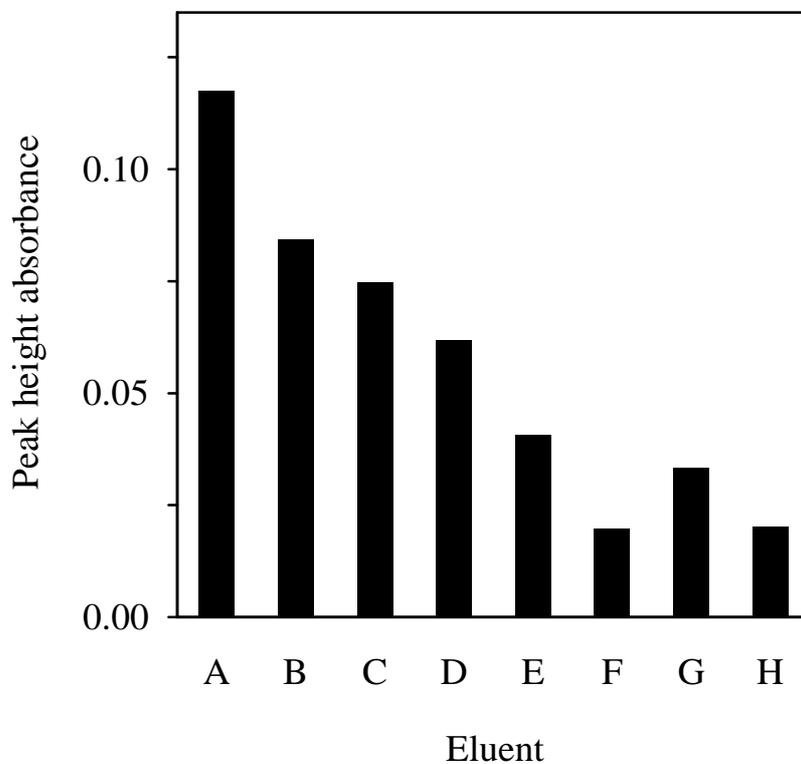


Fig. 2.7 Effect of different eluents on the absorbance of lead by FI-FAAS. Sample solution, 4 ml of 1 mg l⁻¹ lead; A, 0.1 mmol l⁻¹ EDTA; B, 0.1 mmol l⁻¹ ammonium oxalate; C, 0.1 mmol l⁻¹ ammonium citrate; D, 0.1 mmol l⁻¹ ammonium tartrate; E, 0.1 mmol l⁻¹ ammonium sulfate; F 0.1 mmol l⁻¹ ammonium carbonate; G, 0.1 mmol l⁻¹ sulfuric acid; H, L-cystein.

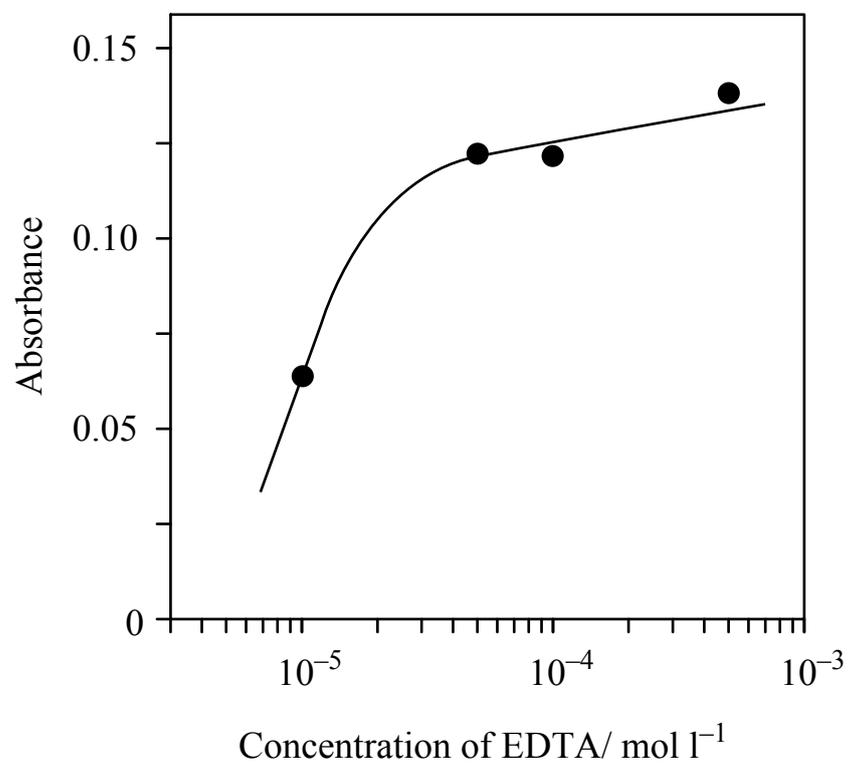


Fig. 2.8 Effect of concentration of EDTA on absorbance of lead by FI-ETAAS. Sample solution, 4 ml of 1 $\mu\text{g l}^{-1}$ lead.

Table 2.2 Determination of lead in seawater^a

Sample taken/ g	Added/ ng kg ⁻¹	Found/ ng kg ⁻¹	Recovery, %
255.4	0	4.9	
250.1	0	5.2	
248.2	0	3.9	
		av. \pm s.d.	4.7 \pm 0.7
253.5	19.7	22.5	90.3
249.4	20.0	24.6	99.4
251.5	19.9	22.8	91.4
		av. \pm s.d.	23.3 \pm 1.1
			93.7 \pm 5.0

a. Taken in Kujukuri (Chiba, Japan).

with 20 ng kg^{-1} lead. The overall enhancement factor, which was estimated by comparing the absorbances of lead with and without preconcentration, was about 200 for 250 g of sample solution. The average and standard deviation of ten blank values obtained by the proposed method are 1.7 ng and 0.38 ng, respectively. These results indicate the applicability of the present method to the determination of lead in seawater at slightly higher levels.

References

1. C. Reimann and P. Caritat, "*Chemical Elements in the Environment*", **1998**, Springer, Berlin, 248.
2. E. Kirowa-Eisner, M. Brand, and D. Tzur, *Anal. Chim. Acta*, **1999**, 385, 325.
3. M. Panigati, M. Piccone, G. D'Alfonso, M. Orioli, and M. Carini, *Talanta*, **2002**, 58, 481.
4. D. G. Green, L. W. Green, J. A. Page, J. S. Poland, and G. van Loon, *Canad. J. Chem.*, **1981**, 59, 1476.
5. A. Tessier, P. G. C. Campbell, and M. Bisson, *Int. J. Environ. Anal. Chem.*, **1979**, 7, 41.
6. S. M. Sella, A. K. Avila, and R. C. Campos, *Anal. Lett.*, **1999**, 32, 2091.
7. J. R. Baena, M. Gallego, and M. Valcárcel, *Spectrochim. Acta, B*, **1999**, 54, 1869.
8. I. L. Grinshtein, Y. A. Vilpan, L. A. Vasilieva, and V. A. Kopeikin, *Spectrochim. Acta, B*, **1999**, 54, 745.
9. O. Acar, A. R. Türker, and Z. Kiliç, *Talanta*, **1999**, 49, 135.
10. A. Salido and B. T. Jones, *Talanta*, **1999**, 50, 649.
11. M. S. Fragueiro, F. Alava-Moreno, I. Lavilla, and C. Bendicho, *J. Anal. At. Spectrom.*, **2000**, 15, 705.
12. J. A. Salonia, R. G. Wuilloud, J. A. Gásquez, R. A. Olsina, and L. D. Martinez, *J. Anal. At. Spectrom.*, **1999**, 14, 1239.
13. H. W. Liu, S. J. Jiang, and S. H. Liu, *Spectrochim. Acta, B*, **1999**, 54, 1367.
14. F. Poitrasson and S. H. Dundas, *J. Anal. At. Spectrom.*, **1999**, 14, 1573.
15. R. S. Olofsson, I. Rodushkin, and M. D. Axelsson, *J. Anal. At. Spectrom.*, **2000**, 15, 727.
16. D. Weiss, E. A. Boyle, V. Chavagnac, M. Herwegh, and J. Wu, *Spectrochim. Acta, B*,

- 2000**, 55, 363.
17. B. Welz, X. Yin, and M. Sperling, *Anal. Chim. Acta*, **1992**, 261, 477.
 18. M. M. Silva, M. A. Z. Arruda, F. J. Krug, P. V. Oliveira, Z. F. Queiroz, M. Gallego, and M. Valcárcel, *Anal. Chim. Acta*, **1998**, 368, 255.
 19. Q. H. Jin, X. G. Su, F. Liang, and H. Q. Zhang, *Microchem. J.*, **1999**, 62, 316.
 20. E. Bruninx and V. Meyl, *Anal. Chim. Acta*, **1975**, 80, 85.
 21. E. Bruninx, *Philips J. Res.*, **1978**, 33, 264.
 22. Y. Harada, N. Kurata, and Y. Goto, *Bunseki Kagaku*, **1984**, 33, 71.
 23. L. Elçi and S. Saraçoğlu, *Talanta*, **1998**, 46, 1305.
 24. J. Ueda and N. Yamazaki, *Bull. Chem. Soc. Jpn.*, **1986**, 59, 1845.
 25. E. A. Boyle and J. M. Edmond, *Anal. Chim. Acta*, **1977**, 91, 189.
 26. R. W. Dabeka and A. D. McKenzie, *Can. J. Spectrosc.*, **1986**, 31, 44.
 27. R. W. Dabeka, *Sci. Total Environ.*, **1989**, 89, 271.
 28. Y. Hirano, J. Nakajima, K. Oguma, and Y. Terui, *Anal. Sci.*, **2001**, 17, 1073.
 29. E. P. Horwitz, M. L. Dietz, S. Rhoads, C. Felinto, N. H. Gale, and J. Houghton, *Anal. Chim. Acta*, **1994**, 292, 263.
 30. T. Seki, H. Takigawa, Y. Hirano, Y. Ishibashi, and K. Oguma, *Anal. Sci.*, **2000**, 16, 513.

Chapter 3

A Novel Separation and Preconcentration Method for Traces of Manganese, Cobalt, Zinc and Cadmium Using Coagulation of Colloidal Silica

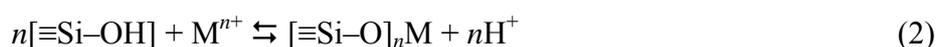
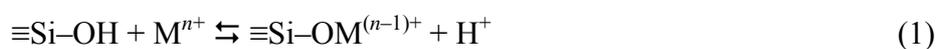
3.1 Introduction

The importance of trace elements has been recognized in various fields, especially in environmental chemistry, medical science and electronic industry. Therefore, trace elements in diverse samples are routinely so often determined. In such a case, it is often required to separate an analyte from matrix components and to preconcentrate it to eliminate the potential interferences and improve the sensitivity. Hence, various separation and preconcentration methods have so far been developed and reviewed in detail by Alfassi *et al.*¹ (see **Section 1.2.1**) Among these are solvent extraction and coprecipitation, which are simple, useful and versatile for various samples, and have been extensively used for trace element analysis. However, both of them have some drawbacks; namely, organic solvents used in solvent extraction are toxic and the formation of precipitates is usually time-consuming.

Thus, in order to overcome these drawbacks, a solid phase extraction technique has recently aroused interest widely; solid phase extraction of trace elements has been reviewed by Camel.² The present authors have also employed solid phase extraction for the flow injection on-line preconcentration of lead in steel³ and natural waters⁴ using Pb-Spec resin[®], and of molybdenum in steel using TEVA resin[®].⁵ However, commercially available adsorbents for solid phase extraction are usually expensive and preparation of homemade adsorbents is tedious, so that the development of an alternative separation and preconcentration method based on other principles is meaningful.

Various types of silica are easily available and exhibit characteristics properties. Silica gel is used for separation and preconcentration of metal ions and chemically modified silica gels have also been developed for improvement of selectivity for metal ions.⁶ On the other hand, colloidal silica has never been used as an adsorbent for separation of metal ions even though highly purified one is recently available at a low cost. However, the

adsorption of metals on colloidal silica and the stability of colloidal silica in presence of electrolytes have been studied by many investigators.⁷⁻¹⁵ The stability of colloidal silica may arise by repulsion by an electric double layer on the silica surface and hydration by hydrogen bonding between silanol groups and water. If the pH of a colloidal silica solution is increased to more than 8 and any electrolytes are added to it, the most silanol groups of the silica dissociate and metal cations are then adsorbed on the silica surface by ion exchange as shown by Eqs. (1) and (2), resulting in disappearance of repulsive force by the electric double layer due to neutralization of silanol groups and dehydration of the surface of the silica.



where $\equiv\text{Si-OH}$ is a silanol group and M^{n+} is a metal ion of charge $n+$. These lead to coagulation of colloidal silica.

In this work, a rapid and precise preconcentration method of manganese, cobalt, zinc and cadmium was developed using coagulation of colloidal silica by addition of calcium chloride. The silica coagulated was easily separated with centrifugal machine and the metals collected by the silica were simultaneously determined by ICP-AES after treatment of the silica with hydrofluoric and perchloric acids. The coagulation of colloidal silica is faster as compared with the time needed for conventional precipitate formation. The proposed method also has yielded reproducible results for determination of manganese, cobalt, zinc and cadmium in saline water such as river-water. The selectivity of colloidal silica for the metals tested was found to be $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+}$.

3.2 Experimental

3.2.1 Reagents and samples

All reagents used were of analytical reagent grade. Distilled and deionized water was further purified via passage through a Milli-Q[®] Ultrapure water purification system (Millipore, Bedford, USA).

The 1000 mg l⁻¹ stock solutions were prepared by dissolving their metal, chloride, or sulfate in suitable dilute mineral acid. Working standard solutions were daily prepared from each stock standard solution.

A 10% (m/m) colloidal silica solution was prepared by diluting 20 g of high purity colloidal silica, Quartron PL-3 (silica concentration, 20% (m/m); average particle size, 35 nm; Fuso Chemicals, Osaka), to 40 g with water. A 5 mol l⁻¹ calcium chloride (Kanto Chemicals, Tokyo) solution was used for coagulation of colloidal silica, and hydrofluoric and perchloric acid (Kanto Chemicals) were used for digestion of coagulated silica. A 10% tetramethylammonium hydroxide solution (Tokuyama, Tokyo) was used for pH adjustment.

An artificial river-water sample that contained 5 mg l⁻¹ of Na⁺, 1 mg l⁻¹ of K⁺ and 3 mg l⁻¹ of Mg²⁺, was prepared from each 1000 mg l⁻¹ stock standard solution according to the literature.¹⁶

An actual river-water sample were collected at Yoro River (Chiba, Japan), filtered through a 0.45- μ m membrane filter (Millipore) and acidified with nitric acid. A river-water certified reference material, NMIJ CRM 7202-a, was obtained from National Metrology Institute of Japan (NMIJ) in National Institute of Advanced Industrial Science and Technology (AIST).

3.2.2 Instrumentation

A Seiko Instruments Plasma Spectrometer SPS 1700HVR (Seiko Instruments, Chiba) was used through the experiments. The optimized operating parameters are listed in **Table 3.1**.

A pH Meter F-13 (Horiba, Kyoto) was used for measurement of pH and a centrifugal machine H-103N (Kokusan, Tokyo) was used for separation of colloidal silica after coagulation.

3.2.3 General Procedure

About 100 g of sample solution was taken in a polypropylene centrifuge tube and mixed with 300 μl of 10% colloidal silica solution. The pH of the solution was adjusted to about 11 with 10% tetramethylammonium hydroxide solution; 10 μl of 5 mol l^{-1} calcium chloride solution was then added to coagulate silica. The coagulated silica was immediately centrifuged at 3000 rpm for 3 min and the supernatant was discarded. The silica was transferred to a 7-ml perfluoroalkoxylalkane (PFA) jar with 3 ml of hydrofluoric acid, and 1 ml of 4.5 mol l^{-1} perchloric acid was added to it, followed by evaporation nearly to dryness on a hot plate. The residue was then diluted to 5 ml with 0.1 mol l^{-1} nitric acid. The solution prepared as above was subjected to the determination of metals by the ICP-AES.

Table 3.1 Operating condition of ICP-AES^a

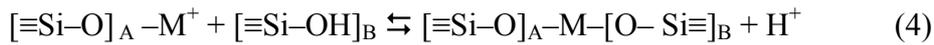
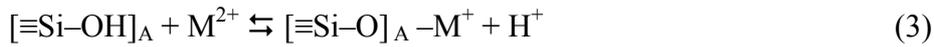
Plasma conditions	
Incident RF power/ kW	1.3
Plasma gas/ l min ⁻¹	16.0
Auxiliary gas/ l min ⁻¹	0.5
Carrier gas/ l min ⁻¹	1.0
Sampling conditions	
Observation height/ mm	12
Sample flow rate/ ml min ⁻¹	1.0
Wavelength/ nm	Mn : 257.687
	Co : 228.687
	Zn : 213.924
	Cd : 214.506

a. Seiko Instruments Plasma Spectrometer SPS 1700HVR

3.3 Results and discussion

3.3.1 Choice of electrolyte and alkali for coagulation of colloidal silica

Ammonium, sodium, magnesium and calcium chlorides were tested as an electrolyte for coagulation in term of low toxicity and cost, and the coagulation concentrations were visually observed. The silica was not coagulated by ammonium chloride. The coagulation concentrations of magnesium and calcium chlorides were much lower than that of sodium chloride. The divalent metal cations such as magnesium and calcium ions act as positive sites after adsorption on a silica particle and then can bridge another particle as shown by the following equations.



where $[\equiv\text{Si-OH}]_A$ and $[\equiv\text{Si-OH}]_B$ stand for silanol groups on separate silica particles. Therefore, bigger silica can be generated by divalent metal cations, and the coagulation concentrations of divalent metals are lower than those of monovalent metals. Among them, calcium chloride gave the lowest coagulation concentration. In addition, Milonjić *et al.*¹³ studied the effect of pH on the coagulation concentrations of chlorides of alkali earth elements and found that the coagulation concentrations of all electrolytes tested dramatically decreased at higher pH than 8 (**Fig. 3.1**). Accordingly, we chose calcium chloride as an electrolyte for the coagulation of colloidal silica and adjusted the pH of the sample solution at 11 to coagulate colloidal silica.

Some alkali is required to adjust the pH of a sample solution at higher than 8 to coagulate colloidal silica. Highly purified sodium or potassium hydroxide is not commercially available. Ammonia water is not suitable to adjust the pH of a sample solution at higher than 10 because of its irritating smell. On the other hand, highly purified tetramethylammonium hydroxide is now commercially available at a reasonable cost.

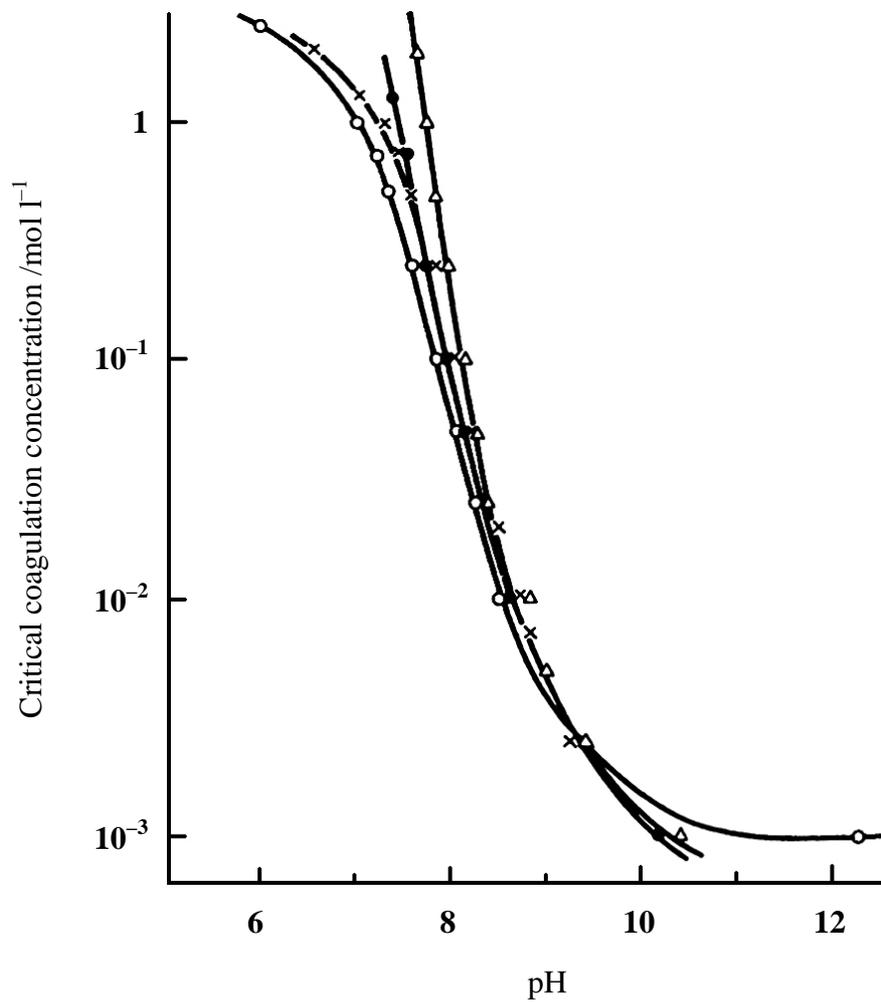


Fig. 3.1 Effect of pH on critical coagulation concentrations of alkali earth chlorides.¹³
MgCl₂, ○; CaCl₂, ×; SrCl₂, △; and BaCl₂, ●.

Therefore, tetramethylammonium hydroxide was used as alkali to adjust the pH of sample solutions.

3.3.2 Effect of the colloidal silica concentration by preconcentration of single element

The effect of the colloidal silica concentration on the recoveries of 1 μg of cobalt or zinc in 100 ml of Milli-Q water was studied over the range of 0.001 to 0.03%. The results obtained are shown in **Fig. 3.2**. The recoveries of zinc and cobalt were almost constant at higher than 0.003% and 0.005%, respectively. Therefore, the colloidal silica concentration of 0.01% was adopted for preliminary experiments for single element preconcentration.

3.3.3 Effect of the calcium chloride concentration

The recovery of 1 μg of zinc in 100 ml of Milli-Q water was examined over the calcium chloride concentration range of 0 to 3 mmol l^{-1} . The results obtained are shown in **Fig. 3.3**. The colloidal silica did not coagulate without calcium chloride and so the recovery of zinc was 0%. At 0.3 mmol l^{-1} , the particle size of coagulated silica was not enough to separate it from solution by centrifugation and the recovery was about 36%. The recovery was almost constant at concentrations higher than 0.5 mmol l^{-1} . The calcium chloride of 0.5 mmol l^{-1} was used hereinafter, since use of any higher concentration of calcium might result in contamination due to its impurities.

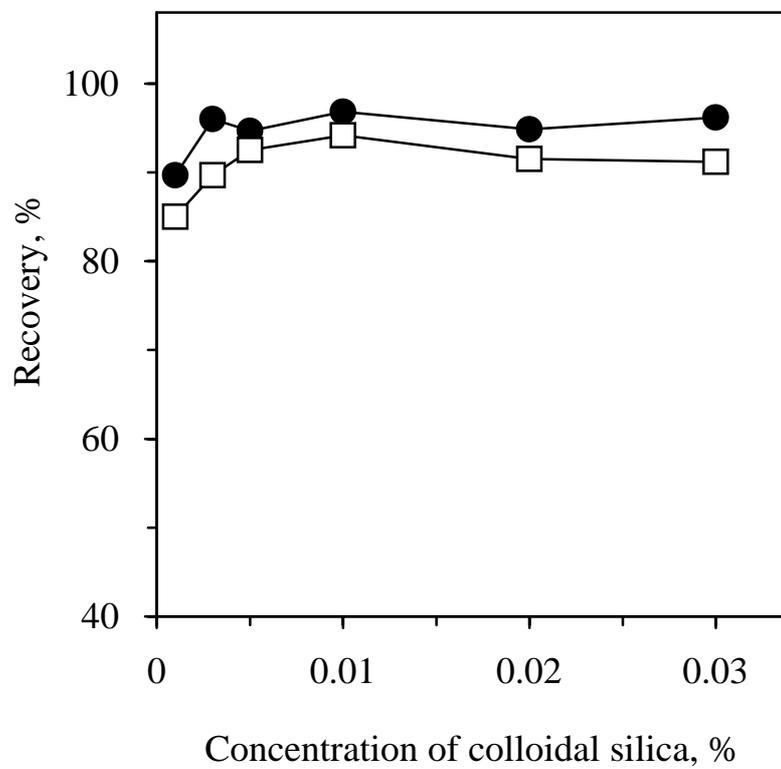


Fig. 3.2 Effect of concentration of colloidal silica on recovery of cobalt and zinc. Sample solution, 1 μg of cobalt (□) or zinc (●) in 100 ml; calcium chloride, 3 mmol l^{-1} .

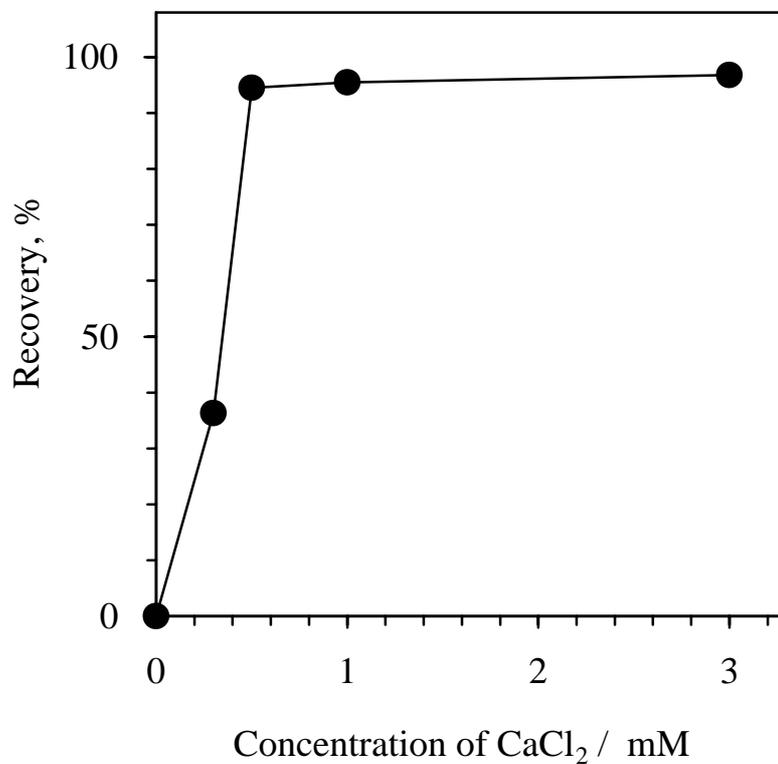


Fig. 3.3 Effect of concentration of calcium chloride on recovery of zinc. Sample solution, 1 μ g of zinc in 100 ml; colloidal silica, 0.01%.

3.3.4 Adsorption behaviors of manganese, cobalt, zinc and cadmium on colloidal silica

In order to investigate adsorption behavior of manganese, cobalt, zinc or cadmium on colloidal silica, we determined the recoveries of 1 or 10 µg of each element in 100 ml of Milli-Q water. The results obtained are shown in **Table 3.2**. Manganese and cobalt were about 92% adsorbed and zinc and cadmium were about 95% adsorbed. The relative standard deviations of the recovery of these ions were about 1%. The high and precise recoveries can be achieved because divalent metal ions are not only adsorbed on the surface of silica but also can be capture among silica by coagulation.

The recoveries of 1 µg each of manganese, cobalt, zinc and cadmium in 100 ml of Milli-Q water by simultaneous preconcentration of them were 88.3, 87.2, 95.8 and 92.8%, respectively. The recoveries of Manganese, cobalt and cadmium by simultaneous preconcentration of them were slightly lower than those by preconcentration of single element. Therefore, the order of ion selectivity series of colloidal silica is guessed as $Zn^{2+} > Cd^{2+} > Mn^{2+} > Co^{2+}$. This order is similar to that on hydrated silica reported by Dushina *et al.*¹⁷ In addition, Hg^{2+} , Fe^{3+} , Al^{3+} , UO_2^{2+} and Cu^{2+} might be strongly adsorbed on colloidal silica except four metal ions tested and applied to their preconcentration, since their order of adsorption on hydrated silica was reported as $Hg^{2+} > Fe^{3+} > Al^{3+} > UO_2^{2+} > Cu^{2+} > Zn^{2+}$.

3.3.5 Effect of the colloidal silica concentration by simultaneous preconcentration of multi elements

The effects of the colloidal silica concentration on recoveries of manganese, cobalt, zinc and cadmium by simultaneous preconcentration of them were reinvestigated over the

Table 3.2 Recoveries of manganese, cobalt, zinc and cadmium^a

Added/ ng ml ⁻¹				Recovery ^b , %			
Mn ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺	Mn ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺
10	0	0	0	92.9 ± 0.9	–	–	–
0	10	0	0	–	92.3 ± 0.6	–	–
0	100	0	0	–	95.8 ± 1.0	–	–
0	0	10	0	–	–	94.7 ± 1.6	–
0	0	100	0	–	–	94.0 ± 0.9	–
0	0	0	10	–	–	–	95.5 ± 0.0
10	10	10	10	88.3 ± 1.0	87.2 ± 0.8	95.8 ± 0.8	92.8 ± 0.6

a. Colloidal silica, 0.01%.

b. Mean ± SD ($n = 3$).

concentration range of 0.01 to 0.03% because the recoveries of manganese, cobalt and cadmium were lower than those for each preconcentration of these ions. The results are shown in **Fig. 3.4**. The recoveries of these ions at 0.03% were almost same as that for each preconcentration at 0.01%. Therefore, the colloidal silica concentration of 0.03% was adopted for simultaneous preconcentration of multi elements.

3.3.6 Analysis of river-water samples

The applicability of the proposed method to real samples was evaluated by examining the recoveries of manganese, cobalt, zinc and cadmium from artificial river-water and actual river-water samples. The results are summarized in **Table 3.3** to **3.5**. The recoveries of these metal ions in the artificial river-water were almost close to those in Milli-Q water, although sodium, potassium and magnesium ions might interfere with the adsorption of cobalt on silica.

The concentrations of zinc and manganese in the sample collected at Yoro River were found to be $0.6 \pm 0.03 \text{ ng g}^{-1}$ and more than 10 ng g^{-1} , respectively. The concentration of manganese in the sample was so high that its accurate concentration was not obtained. Cobalt and cadmium could not be detected. The recoveries for the additions of $1 \mu\text{g}$ each of cobalt, zinc and cadmium to 100 g of river-water sample were 81.8, 95.6 and 90.0%, respectively. Additionally, the concentration of manganese, zinc and cadmium obtained for the river-water certified reference material NMIJ CRM 7202-a were almost close to their certified values (see **Table 3.5**). The recoveries of manganese, cobalt and cadmium in the river-water sample were slightly lower than those in Milli-Q water probably due to the presence of some interfering substances (*e.g.* natural organic matter) in the sample, which might have reduced the free concentrations of cobalt and cadmium through complexation.

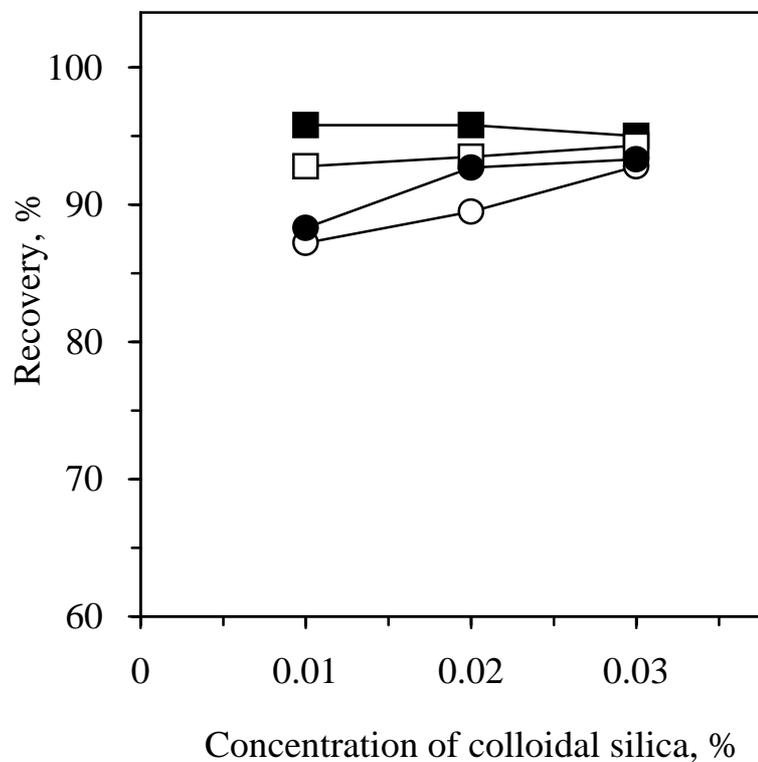


Fig. 3.4 Effect of concentration of colloidal silica on recoveries of manganese, cobalt, zinc and cadmium by simultaneous preconcentration. Sample solution, 1 μg of manganese (●), cobalt (○), zinc (■) and cadmium (□) in 100 ml; calcium chloride, 0.5 mmol l^{-1} .

Table 3.3 Determination of manganese, cobalt, zinc and cadmium in artificial river-water^a

Added/ ng ml ⁻¹				Recovery ^b , %			
Mn ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺	Mn ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺
<i>Milli-Q water</i> ^c							
10	10	10	10	93.3 ± 1.3	92.8 ± 0.6	95.0 ± 1.0	94.3 ± 0.8
<i>Artificial river-water</i> ^d							
10	10	10	10	92.9 ± 2.0	88.8 ± 2.1	95.7 ± 2.2	94.0 ± 1.4

a. Colloidal silica, 0.03%.

b. Mean ± SD.

c. $n = 3$.

d. $n = 6$.

Table 3.4 Determination of cobalt, zinc and cadmium in river-water^a

Added, ng g ⁻¹			Found ^b , ng g ⁻¹		
Co ²⁺	Zn ²⁺	Cd ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺
0	0	0	N.D. ^c	0.6 ± 0.0 ₃	N.D.
10	10	10	8.2 ± 0.1	10.2 ± 0.2	9.0 ± 0.1

a. Taken in Yoro river (Chiba, Japan).

b. Mean ± SD ($n = 3$).

c. Not detected.

Table 3.5 Determination of manganese, zinc and cadmium in NMIJ CRM 7202-a^a

Element	Certified, $\mu\text{g kg}^{-1}$	Found ^b , $\mu\text{g kg}^{-1}$
Mn	5.03 ± 0.14	4.31 ± 0.10
Zn	10.3 ± 0.3	9.7 ± 0.1
Cd	1.02 ± 0.02	0.93 ± 0.02

a. NMIJ: National Metrology Institute of Japan.

b. Mean \pm SD ($n = 4$).

However, the recoveries obtained for NMIJ CRM 7202-a are sufficient for trace metal analysis and indicate the applicability of the present method to the river-water analysis. For seawater samples, the effect of the high salt concentration on the recoveries of trace metals must previously be investigated.

The overall reagent blank value of zinc was found to be 16 ng (average of three runs). Those of manganese, cobalt and cadmium were less than their lower limits of determination (Mn: $0.0010 \mu\text{g ml}^{-1}$, Co: $0.0025 \mu\text{g ml}^{-1}$, and Cd: $0.0015 \mu\text{g ml}^{-1}$).

The present method is simple and rapid as compared with the coprecipitation methods since the coagulation of silica occurs within a few minutes after the addition of calcium chloride. This method is reproducible as can be seen from the standard deviations of analytical results, since divalent metal ions might be strongly captured among some silica particles by coagulation. Furthermore, the cost is lower because high purity colloidal silica is now inexpensive and the consumption of the required reagents is relatively low. Since the order of adsorption on hydrated silica was reported as $\text{Hg}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{UO}_2^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ by Dushina *et al.*,¹⁷ Hg^{2+} , Fe^{3+} , Al^{3+} , UO_2^{2+} and Cu^{2+} may be strongly adsorbed on colloidal silica and easily concentrated from saline water samples.

References

1. Z. B. Alfassi and C. M. Wai, "Preconcentration Techniques for Trace Elements", **1992**, CRC Press, Boca Raton.
2. V. Camel, *Spectrochim. Acta, B*, **2003**, 58, 1177.
3. T. Seki, H. Takigawa, Y. Hirano, Y. Ishibashi, and K. Oguma, *Anal. Sci.*, **2000**, 16, 513.
4. T. Seki, Y. Hirano, and K. Oguma, *Anal. Sci.*, **2002**, 18, 351.
5. T. Seki, K. Oguma, and Y. Ishibashi, *Tetsu-to-Hagane*, **2003**, 89, 939.
6. P. K. Jal, S. Patel, and B. K. Mishra, *Talanta*, **2004**, 62, 1005.
7. L. H. Allen and E. Matijević, *J. Colloid Interface Sci.*, **1969**, 31, 287.
8. L. H. Allen and E. Matijević, *J. Colloid Interface Sci.*, **1970**, 33, 420.
9. J. Depasse and A. Watillon, *J. Colloid Interface Sci.*, **1970**, 33, 430.
10. R. O. James and T. W. Healy, *J. Colloid Interface Sci.*, **1972**, 40, 42.
11. R. O. James and T. W. Healy, *J. Colloid Interface Sci.*, **1972**, 40, 65.
12. P. W. Schindler, B. Fürst, R. Dick, and P. U. Wolf, *J. Colloid Interface Sci.*, **1976**, 55, 469.
13. S. K. Milonjić, V. L. Razin, and Y. G. Frolov, *Kolloidn. Zh.*, **1980**, 42, 147.
14. S. K. Milonjić, *Colloids Surf.*, **1992**, 63, 113.
15. J. Depasse, *J. Colloid Interface Sci.*, **1997**, 194, 260.
16. M. Nishimura, "Kankyo Kagaku (Environmental Chemistry)", **1991**, Shokabo, Tokyo, 26.
17. A. P. Dushina and V. B. Aleskovskii, *Zh. Neorg. Khim.*, **1963**, 8, 2194.

Chapter 4
Conclusion

In chapter 2, a flow injection on-line preconcentration–electrothermal atomic absorption spectrometric (ETAAS) method coupled with a coprecipitation method has been developed for the determination of lead in seawater. By using both the preconcentration procedures, the coprecipitation with iron(III) hydroxide and the solid-phase extraction with a lead selective resin, Pb.Spec[®], the total enhancement factor was about 200 for 250ml of the sample solution. The average and standard deviation of ten blank values obtained were 1.7 ng and 0.38 ng, respectively. The recovery was $93.7 \pm 5.0\%$ for seawater spiked with 20 ng kg^{-1} lead. The proposed method is applicable to the analysis of seawater for lead at slightly higher levels. By the improvement of the coprecipitation, such as the expansion of the difference in the sample volumes before and after coprecipitation, the detection limit will be lowered (sub-ng l⁻¹).

In chapter 3, a novel separation and preconcentration method using the coagulation of colloidal silica by addition of calcium chloride has been developed for traces of manganese, cobalt, zinc and cadmium. The coagulation of colloidal silica is faster as compared with the conventional precipitate formation. The proposed method has yielded reproducible results for the determination of manganese, cobalt, zinc and cadmium in river-water samples. The concentration of zinc and manganese in the sample collected at Yoro River were found to be $0.6 \pm 0.03 \text{ ng g}^{-1}$ and more than 10 ng g^{-1} , respectively. The concentration of manganese in the sample was so high that its accurate concentration was not obtained. Cobalt and cadmium could not be detected. The recoveries for the additions of $1 \text{ } \mu\text{g}$ each of cobalt, zinc and cadmium to 100 g of the river-water sample were 81.8, 95.6 and 90.0%, respectively. Additionally, the analytical results obtained for manganese, zinc and cadmium in the river-water certified reference material NMIJ CRM 7202-a were 4.31 ± 0.10 , 9.7 ± 0.1 , and $0.93 \pm 0.02 \text{ } \mu\text{g kg}^{-1}$, respectively, and were close to their certified values. The recoveries of manganese, cobalt and cadmium added to the river-water sample might be slightly lower than those for the metals added to Milli-Q water probably due to the

presence of some interfering substances (*e.g.* natural organic matter) in the sample which might have reduced the free concentrations of cobalt and cadmium through complexation. However, the recoveries obtained for NMIJ CRM 7202-a are sufficient for trace analysis and indicate the applicability of the present method to river-water analysis. For seawater samples, the effect of the high salt concentration on the recoveries of trace metals must previously be investigated.

The selectivity of colloidal silica for the metals tested was found to be $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+}$. Since the order of adsorption on hydrated silica has been previously reported as $\text{Hg}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{UO}_2^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$, mercury, iron, aluminum, copper and uranyl ions may be strongly adsorbed on colloidal silica in addition to four metal ions studied and effectively concentrated from saline water samples. Study of adsorption behaviors of other metals on colloidal silica is in progress. Using chelating or masking reagents will improve the selectivity of the proposed method.

Acknowledgements

I wish to express my gratitude to Professor Koichi Oguma for his unfailing guidance and suggestions throughout the course of this work, to Associate Professor Masanori Fujinami, Dr. Yoshihiro Hirano, Dr. Nobutaka Yoshikuni and Mr. Hiroaki Tanaka for their valuable discussion and encouragements, and to Miss Chatchalida Boonpanaid, Mr. Takayuki Baba and all the other members (Laboratory of Analytical Chemistry, Department of Applied Chemistry and Biotechnology, University of Chiba) for their support.

I am deeply grateful to Dr. Tatsuya Seki (Nissan Chemical Industries Ltd.) for support during the development of the novel preconcentration method using colloidal silica.