

Integration of Solid-phase Extraction with Electrothermal Atomic Absorption Spectrometry for Determination of Trace Elements

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An enrichment step in a sample treatment is essential for trace analysis to improve the sensitivity and to eliminate the matrix of the sample. Solid-phase extraction (SPE) is one of the widely used enrichment technique. Electrothermal atomic absorption spectrometry (ETAAS) is a well-established determination technique for trace elements. The integration of SPE with ETAAS leads to further improvement of sensitivity, an automation of the measurement and the economy in the sample size, amounts of the reagents and time for the sample pretreatment. The integration is achieved by introducing the solid phase used for the enrichment directly into ETAAS for a batch method, or on-line coupling of a SPE column with ETAAS. Fine particles of various materials, including an activated carbon, an ion-exchange resin, a cellulose nitrate resin and biomass materials were used as adsorbents for batch method. A membrane filter was also used. A simultaneous multi-elements extraction and a speciation analysis were accomplished. A microcolumn packed with resin beads or an open tubular column such as a PTFE tube or a silica capillary tube having the chemically modified inner wall were used for the on-line coupling.

Key Words : Solid-phase extraction, Electrothermal atomic absorption spectrometry, slurry injection, lob-on-valve, in-tube solid-phase microextraction, inner wall preconcentration

1. Introduction

A trace element has an important role in organisms or materials, so its determination is carried out widely for environmental samples, biological samples, industrial products, etc. Inductively coupled plasma-mass spectrometry (ICP-MS) is a multi-element determination technique with the extremely low detection limit, however, the expensive instrument and the high running cost are critical especially for a small laboratory. On the other hand, electrothermal atomic absorption spectrometry (ETAAS), a well-established single-element determination technique, is able to perform a measurement comparable in sensitivity to ICP-MS [1]. The other important characteristics of ETAAS is a size of sample solution required for an analysis. Only 5-100 μ L of sample solution is enough for one measurement and this is advantageous for the analysis of rare or precious samples which can be obtained in a small size.

A sample pretreatment is done for the dissolution of the solid sample and the enrichment of a desired element in the sample. Enrichment is a process in which the ratio of the amount of a desired trace element to that of the original matrix increased [2]. It leads to the reliable analytical data that is crucial to evaluate the property of the materials analyzed. Solid-phase extraction (SPE) is widely used in the enrichment procedures to improve the sensitivity of the determination techniques and/or to remove the interference substances [3]. There are wide variety of solid-

phases to widen the scope of the enrichment procedures. And the use of a harmful organic solvent would decrease compared with liquid-liquid extraction.

In a batch method, the procedure generally includes five steps; 1) the addition of resin beads or particles to a sample solution, 2) the extraction of a desired element under stirring for an appropriate time, 3) the collection of the particles holding a desired element by filtration or centrifugation, 4) the washing of the particles with an appropriate solution if necessary, and 5) the elution of the desired element with a suitable eluent for the determination. In a column method, resin beads or modified silica gel particles are packed into a small plastic or glass column or embedded into a membrane, and the procedure includes four steps; 1) the conditioning of the column, 2) the extraction of a desired element by applying a sample solution to the column, 3) the washing of the column, and 4) the elution of the desired element.

The sensitivity depends on the size of a sample solution and an eluent. Although a definite portion of eluent is required for the complete elution of the extracted element, the use of large volume of eluent results in the lowering of the sensitivity, and may also cause the danger of contamination.

The elution step can be miniaturized or omitted by the integration of SPE with a detection technique. For example, in solid-phase spectrophotometry, a colored complex of a desired element is collected on a thin layer of ion-exchange resin or a

membrane filter and determined directly, without elution, on the solid-phase by spectrophotometry or densitometry [4]. Thus the integration of SPE and spectrophotometry is attained to improve the sensitivity [5].

The integration with SPE is also useful for ETAAS. The merits of the integration are 1) to improve the sensitivity and to avoid the risk of the contamination by eliminating a elution step or restriction by the size of an eluent and 2) to assemble an automatic or semiautomatic ETAAS analytical systems including SPE. The former is attained by the direct injection of the solid phase used for the extraction of a desired element into ETAAS. The solid phase is injected as a suspension or a slurry, as a solution dissolving solid-phase, or as a dry form. The latter by flow injection (FI)/sequential injection (SI) on-line sample pretreatment or in-tube solid-phase microextraction (ITSPME) coupled to ETAAS.

In this short review, we describe on the integration of SPE, batch and on-line methods, with ETAAS. Comprehensive reviews on enrichment techniques integrated with ETAAS are available [6,7].

2. Batch methods

2.1 General

Figure 1 shows the scheme of general procedure for SPE integrated with ETAAS. Prior to the extraction, a desired element is usually converted into a hydrophobic species such as its complex. Then, a adsorbent is added to the solution. When resin beads such as anion-exchange resin (AR) is used for the adsorbent, it is convenient to add the resin beads as a suspension. After fixation of a desired element, the adsorbent are collected on a membrane filter (MF) by filtration under suction. In some cases, a MF acts as the adsorbent. The adsorbent holding the desired element are introduced into a graphite furnace after suspended in the other solution, as a dry form, or after dissolved

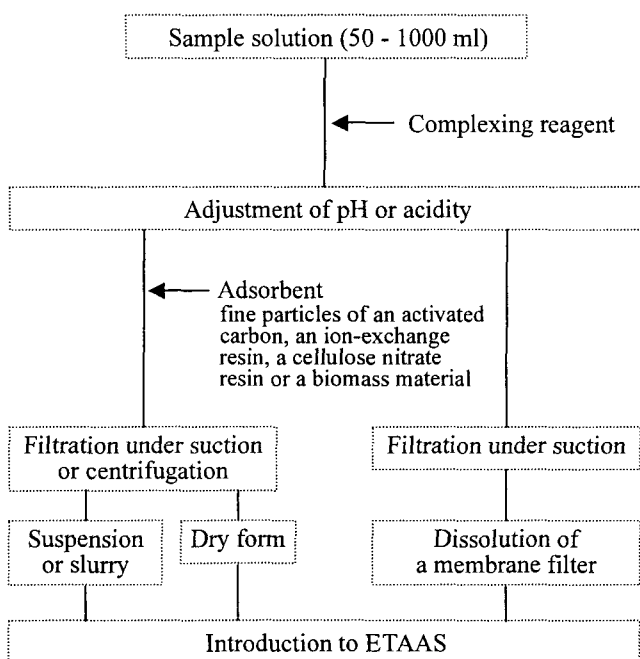


Figure 1 Scheme of general procedure for a batch SPE integrated with ETAAS.

in a appropriate solvent or solution in the case of the MF.

2.2 Solid phase

Solid phases used should have both a hydrophilic and a hydrophobic property to easily disperse in an aqueous sample and to strongly adsorb a desired element converted into its hydrophobic species, respectively. A fine activated carbon (AC) would satisfy these conditions [8].

A finely divided anion-exchange resin suspension (ARS) is also suitable for this purpose [9], because a charged group on its surface makes it hydrophilic and a base of an ion-exchange resin, copolymer of styrene and divinylbenzene, has a strong hydrophobicity. In addition, fine particles have a high specific surface area preferred for adsorption, and an effect to keep the uniformity of the sample when the aliquots of the resin are injected into a graphite furnace.

A cellulose derivative resins such as cellulose nitrate (CNR), cellulose acetate (CAR), and cellulose triacetate (CTAR) is a possible raw material for MFs that were used to enrich hydrophobic compounds in an aqueous sample [10]. Therefore, it is worthwhile to compare with ARS for the sorption ability of a hydrophobic metal complex.

The suspensions of CNR, CAR, and CTAR were prepared by pouring a mixture solvent of dichloromethane and tetrahydrofuran (2:1) containing them into an aqueous solution of benzalkonium chloride under vigorous stirring, volatilizing dichloromethane and tetrahydrofuran at about 98°C, and concentrating the suspension by centrifugation. [11]. It was found that the resulting resin particles could rapidly dispersed into water and be easily removed from water by membrane filtration. Then, the adsorption ability was compared with ARS for the extraction of the Mo-phenylfluorone complex. The results shown in Figure 2 indicate that CNR is comparable to ARS for the extractability of

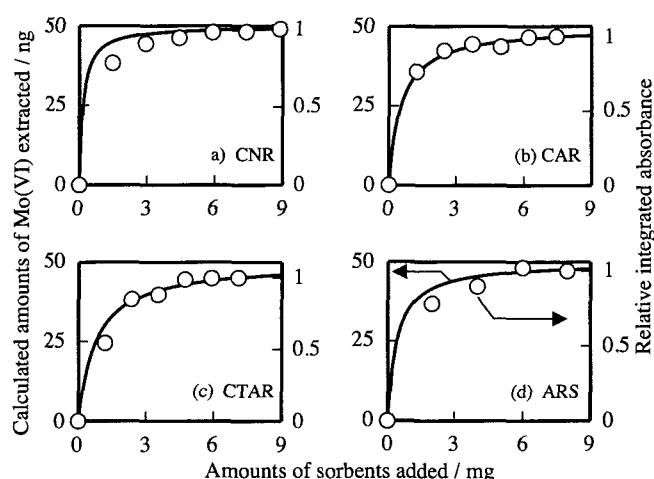


Figure 2 Relationship between the amounts of sorbents added and the calculated amounts of molybdenum(VI) extracted (the left hand ordinate) or the relative absorbance (the right hand ordinate). The absorbance obtained using the largest amount of sorbent was set to be unity and was adjusted to fit the calculated amount of molybdenum(VI) at the corresponding sorbent amount. The solid lines and the open circles indicate the calculated amounts of molybdenum(VI) extracted and the relative absorbance, respectively. Reference [11].

Table 1 ETAAS integrated with SPE by batch method

ion ^a	Matrix	Chelating reagent ^b	Solid phase ^c	Injected as ^d	Detection limit or determination range ^e	Reference
As	seawater, well water	as molybdoarsenate	AC	S	20 ng L ⁻¹ (1000 mL)	17
As(III), As(III+V) ^{SP}	seawater, river water, tap water	APDC	ARS	S	6.7 ng L ⁻¹ (150 mL)	25
As(V), As(III+V), total As ^{SP}	river water, seawater	as molybdoarsenate	MF	L	40 ng L ⁻¹ (100 mL)	29
Cd ^{ML}	seawater	Ox	AC	S	0.3 ng L ⁻¹	24
Cd ^{ML}	tap water	APDC	ARS	S	0.17 ng L ⁻¹ (150 mL)	23
Co ^{ML}	seawater	Ox	AC	S	7 ng L ⁻¹	24
Co	river and sea bottom sediments	DOX	AC	S	up to 0.25 μg	21
Cr(III), Cr(VI) ^{SP}	pond water, mineral water, seawater, serum	N	Lemna minor	S	10 ng L ⁻¹ Cr(III), 30 ng L ⁻¹ Cr(VI) (100 mL)	27
Cu	river water	APDC	micro-MF	L	40 ng L ⁻¹ (5 mL)	34
Ga	mine drainage, river water	PV	ARS	R	3 ng L ⁻¹ (500 mL)	31
Ga	river water, spring water, seawater	Ox	AC	S	1 μg L ⁻¹ (100 mL)	19
Hg ^{ML}	seawater	Ox	AC	S	120 ng L ⁻¹	24
Hg	natural gas liquid and condensate	N	AC	S	2.0 ng mL ⁻¹ (500 mL)	22
Mo	rice flour-unpolished	Phenylfluorone	CNR	S	50 ng L ⁻¹ (60 mL)	11
Ni	river water	APDC	micro-MF	L	100 ng L ⁻¹ (5 mL)	34
Ni ^{ML}	seawater	Ox	AC	S	7 ng L ⁻¹	24
Ni	river and sea bottom sediments	DOX	AC	S	up to 0.25 μg	21
Pb	river water, tap water	APDC	miniature-MF	L	10 ng L ⁻¹ (10 mL)	35
Pb ^{ML}	tap water	APDC	ARS	S	5.7 ng L ⁻¹ (150 mL)	23
Ru	river water, seawater, wastewater	TPTZ	AC	S	0.8 μg L ⁻¹	20
Sb(III) ^{SP}	river water	PV	ARS	R	11 ng L ⁻¹ (500 mL)	33
Sb(III+V)	river water, snowfall	BPR	ARS	R	9.8 ng L ⁻¹ (500 mL)	32
Sb(III), (III+V) ^{SP}	natural water	Pyrogarol	AC	S	25 ng L ⁻¹ (1000 mL)	28
Se	sedeiment, lake water, seawater	Bismuthiol II	AC	S		18
Ti	electrolyte replenishers, KCl	APDC	CNR	S	20 ng L ⁻¹ (50 mL)	16
Tl	seawater, snowmelt	APDC	CNR/miniSPE	S	1.9 ng L ⁻¹ (100 mL)	36
Tl ^{SP}	river water	APDC	CNR	S	18 ng L ⁻¹ (50 mL)	12
V(IV), V(V), V(IV+V) ^{SP}	seawater, artificial seawater	CAB, CXA	ARS	S	20 ng L ⁻¹ (40 mL)	26
Pesticides	river water	as the Cu complexes	MF	L	0.2-0.5 μg L ⁻¹ (200 mL)	30

^aML, multi-element extraction; SP, speciation.

^bAPDC, ammonium pyrrolidinedithiocarbamate; BPR, Bromopyrogallol Red; CAB, Chromazurol B; CXA, *N*-Cinnamoyl-*N*-2,3-xylylhydroxylamine; DOX, 1,2-cyclohexanediondioxime; Ox, 8-hydroxyquinoline; PV, Pyrocatechol Violet; TPTZ, 2,4,6-tri-2-pyridyl-1,3,5-triazine; N, not used.

^cAC, activated carbon; ARS, anion-exchange resin suspension; CNR, cellulose nitrate resin; MF, membrane filter.

^dL, solution dissolving a MF; R, dry resin; S, suspension or slurry.

^eSample volume is given in parenthesis.

the hydrophobic complex, and that the sorption ability decreases in the following order: CNR > ARS > CAR > CTAR. It was found that the CNR is useful for the ETAAS of such an element that the presence of ARS causes interference with the determination [12].

2.3 Chelate reagent

Generally, a desired element is converted into its complex prior to the extraction on a solid phase. The effect of the 11 chelate agents was studied for the extraction of copper on a finely divided anion-exchange resin as shown in Figure 3 [9]. The chelate reagents used were *N,N*-donors such as bathocuproine (BC), bathocuproinedisulfonate (BCS) and bathophenanthrolinedisulfonate (BPS). As shown in Figure 3, the Cu(I)-BC, -BCS, and Cu(II)-BPS complexes were quantitatively fixed on the anion-exchange resin. On the other hand, the BC complex was quantitatively adsorbed on the membrane filter, however, 12% of the BCS complex and 72% of the BPS complex were not adsorbed on the membrane filter. It implies that the BC complex was adsorbed due to a hydrophobic interaction whereas the BCS and BPS complexes were adsorbed due to an ion-exchange reaction in addition to a hydrophobic interaction. Furthermore, it can be concluded that the order of the hydrophobicity could be the BC complex > the BCS complex > the BPS complex.

Table 1 tabulated the literatures on ETAAS integrated with

SPE by a batch method since 1995. It was found that ammonium pyrrolidinedithiocarbamate (APDC) was used for several elements. The possible reasons are as follows; 1) APDC is an *S,S*-donor ligand which reacts with many elements including heavy metal ions, so a multi-element extraction is possible. 2) The metal-PDC complexes are insoluble in water and hydrophobic. 3) APDC itself is soluble in water. 4) Speciation is possible if an element in the different oxidation states have the difference in the reactivity. An *O,N*-donor ligand, 8-quinolinol (Ox), is also used for several elements.

2.4 Suspension or slurry injection

The first attempts to introduce an ion-exchange resin containing the adsorbed metal into a graphite furnace of ETAAS were carried out in 1979 in our knowledge [13,14]. Later, a single anion-exchange bead was inserted into ETAAS [15]. However, the use of fine particles as the adsorbent has a great advantage as described above.

In resin suspension injection ETAAS (RSI-ETAAS), the fine particles of a resin are used to extract a desired element. After the extraction, the resin particles holding a desired element are suspended into 1 mL of a suitable aqueous solution under sonication, and then, an aliquot of the suspension is injected into a graphite furnace. The acidity of the suspension should be suitable for an atomization of the desired element and may contain

a chemical modifier. The desired element may not desorb from the resin particle in the suspension.

AC could be used with a similar procedure, however, the final volume of suspension was usually 5 mL.

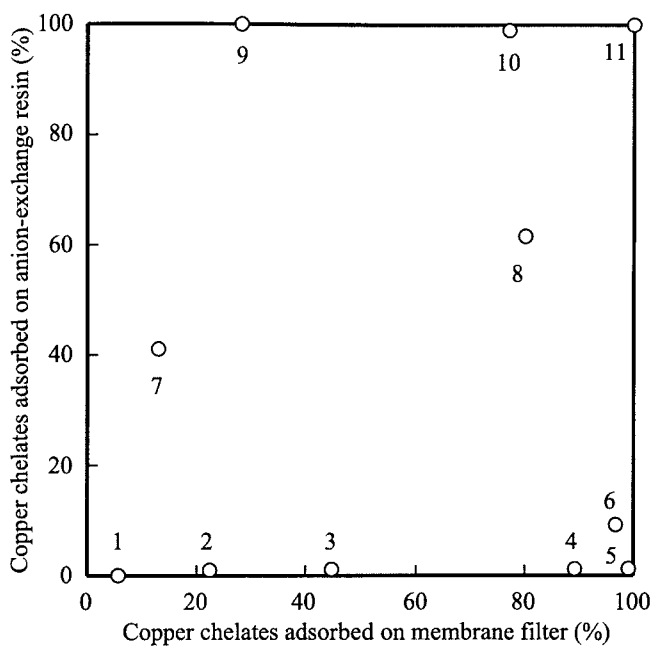


Figure 3 Adsorption of copper chelates on the anion-exchange resin and membrane filter. Anion-exchange resin: Amberlyst A-27. Membrane filter: mixed cellulose ester, $0.45 \mu\text{m}$ pore size, 25 mm in diameter. Copper(II) complexes with 1, 2,2'-bipyridine; 2, 1,10-phenanthroline; 3, 5,6-dimethyl-1,10-phenanthroline; 6, bathophenanthroline; and 9, BPS. Copper(I) complexes with 4, neocuproine; 5, 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine; 7, 3-(2-pyridyl)-1,2,4-triazin-5,6-diyl di(benzene-p-sulphonate); 8, 2,2'-biquinoline; 10, BCS; and 11, BC. Reference [9].

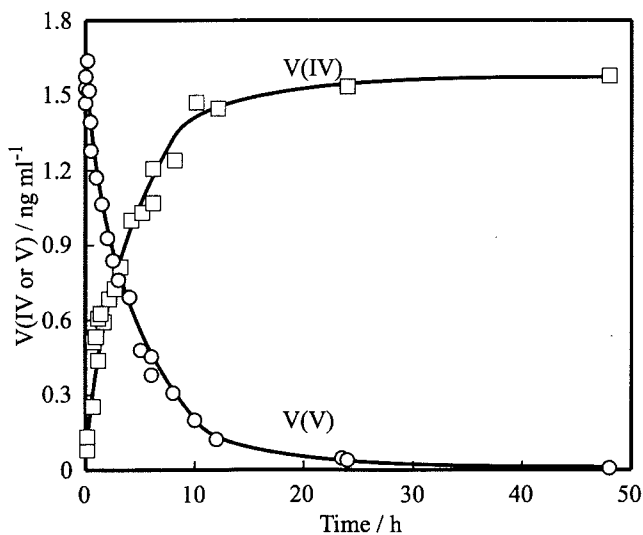


Figure 4 The effect of the acidification of a seawater sample on the oxidation state of vanadium. An aliquot of hydrochloric acid was added at 0 to adjust pH of the sample to 2.0. Reference [26].

Copper in river water and seawater samples were extracted using ARS as the Cu(I)-BCS complex for the determination with RSI-ETAAS. The sample sizes required were 100-250 mL [9]. Molybdenum in NIES-certified reference material (Rice flour-unpolished) was extracted on CNR as the Mo(VI)-Pfn complex after a digestion with a mixed acid [11]. The memory effect observed in ETAAS of Mo was suppressed in the presence of CNR. Thallium in potassium chloride and electrolyte replenishers were extracted on CNR and determined by RSI-ETAAS [16]. Thallium(I) was oxidized with bromine water and extracted as the Tl(III)-PDC complex. The addition of a chemical modifier such as palladium(II) nitrate to a graphite furnace was not required in the presence of CNR.

Arsenic in seawater and well water was adsorbed on AC as a molybdoarsenate [17]. Selenium in sediment, lake water, and seawater [18] was adsorbed on AC as the pyrogarol complex and the Bismuthiol II complex, respectively. A reagent impregnated ACs were prepared. Ox impregnated AC was used for adsorption of gallium in river water and spring water [19] and 2,4,6-tri-2-pyridyl-1,3,5-triazine impregnated AC was used for ruthenium in river water, seawater, and waste water [20]. 1,2-cyclohexanedionedioxime impregnated AC was used to extract cobalt and nickel in a sample solution of digested sediments, however, a simultaneous extraction of nickel and cobalt was not attained [21]. For the ETAAS determination of Hg in non-aqueous samples such as natural gas liquid and condensate, AC was added to the samples to collect Hg on AC surface [22].

In a favorable case, more than one element could be extracted simultaneously. For the extraction of cadmium and lead using APDC and ARS, when the effect of the pH was studied in the pH range 2-8, it was found that the constant and maximum atomic absorption of cadmium was obtained above 4 and that of lead was observed above 5. In the result, the simultaneous extraction of the Cd- and Pb-PDC complexes were attained at pH 6. Cadmium and lead in tap water were determined by RSI-ETAAS for ten days with three or four repeated runs for each day. The relative standard deviations were in the ranges 2.4-11.4% and 2.8-8.7% for the determination of cadmium and lead, respectively [23]. For the preconcentration of Cd, Co, Hg and Ni in seawater, their Ox complexes were adsorbed on AC. The AC was prepared as a slurry in glycerol or in boiled tapioca suspension before ETAAS [24].

Speciation is an important area in a trace analysis for natural water. A differential determination of an element in the different oxidation states was done based on their different reactivity to certain chelating reagent. For example, As(III) reacted with APDC to form the extractable As(III)-PDC complex in the pH range 1-3.7, whereas As(V) and dimethylarsinic acid did not. In the result, a selective extraction of As(III) using ARS was attained for RSI-ETAAS. As(III+V) was obtained after the reduction of As(V) with sodium thiosulfate. The proposed method was applied to the determination of arsenic in sea, river and tap water. The result showed that the amount of As(III) in natural water samples decreased in the order: hot spring, river and seawater, and the ratio of As(III) to total As(III,V) also decreased in this order [25].

To study the changes in the oxidation state of vanadium in seawater, the selective determination techniques by RSI-ETAAS were developed. V(IV) was extracted as the complex with Chromazurol B using ARS and V(V) was as the complex with *N*-cinnamoyl-*N*-2,3-xylylhydroxylamine, respectively. V(IV+V)

was extracted after the reduction of V(V) with ascorbic acid. The results in this study showed that the reduction of V(V) to V(IV) in seawater was occurred with the addition of hydrochloric acid to adjust the pH of the sample to 2.0, as shown in Figure 4. Since only the slight reduction was observed in 0.01 M HCl, the presence of the organic matters in seawater and their complexing ability may be attributed to the reduction [26].

Lemna minor, one of biomass materials, was used to the separation and preconcentration of Cr(III)/Cr(VI) with no chelating reagent. First, Cr(III) was adsorbed on 10 mg of 160 mesh pre-treated *Lemna minor* at pH 1.0, and then Cr(VI) in the supernatant solution after centrifugation was adsorbed at pH 5.0 by the addition of another portion of *Lemna minor*. The adsorbents holding Cr(III) or Cr(VI) were injected into ETAAS as slurries in agar solution [27].

Antimony(III) was preconcentrated on AC as the Sb(III)-pyrogallol complex. Prior to the preconcentration, Sb(V) was reduced to Sb(III). The method was applied to differential determination of antimony in natural water [28].

The possibility of differential determination of Tl(I+III) and Tl(III) by the extraction as Tl(III)-PDC complex was suggested [12].

2.5 Injection as a solution and as a dry form

A MF was used for the collection of a desired ion, and dissolved in an appropriate solution to introduce into ETAAS. For As(V) determination, arsenomolybdate was collected on a mixed cellulose ester MF as the ion association complex with a tetraphenylphosphonium ion. The MF holding the complex was dissolved in 400 μ L of 12.5% tetramethylammonium hydroxide by heating. The solution was mixed with 1.2 mL 0.02 M zirconyl nitrate (a chemical modifier) and diluted to 2 mL with water. A portion of the resulting solution was analyzed for As by ETAAS. As(III+V) were determined by adding 1 g potassium peroxodisulfate to the sample solution before the formation of the ion association complex [29]. Pesticides which react with copper were collected on a mixed cellulose ester MF as their copper complexes. The copper complex of thiram, ziram and disulfiram were formed after decomposition of the pesticides in the presence of ascorbic acid and copper sulfate at pH 2. The MF holding the complexes was dissolved in 5 mL of warm 2-methoxyethanol for the determination of copper by ETAAS. [30].

The resin particles on a membrane filter was introduced into ETAAS without a formation of suspension. For the determination of gallium in mine-drainage and river water, the Ga-Pyrocatechol Violet complex formed in pH 4.5-5.5 was extracted using ARS and the resin suspension was filtered and washed with 2-3 mL of water. The resin remaining on the filter was held in position with a cellophane tape after drying in a desiccator for 15 min, and 3 mm disks were removed by punching. Each disks was inserted into a cup-type cuvette for the determination [31]. This technique was also applied to the determination of total Sb(III+V) and Sb(III) in river water and snowfall samples. Sb(III+V) was extracted as the Sb(III)-, Sb(V)-Bromopyrogallol Red complexes at pH 2 [32], whereas Sb(III) was extracted as the Pyrocatechol Violet at pH 7 [33]. Sb(III) and Sb(V) in river water samples were 0-0.1 μ g L⁻¹ and 0.2-1 μ g L⁻¹, respectively.

2.6 Miniaturized SPE

A miniaturization of SPE has advantage in the economy in a sample size, amounts of the reagents and time for the sample pretreatment. The smaller the final volume of the enrichment step, the higher the sensitivity is obtained. The high sensitivity can result from not only the large enrichment factor but also the greater ratio of an injection volume to a final volume. If the whole of the final solution is injected to ETAAS, the maximum sensitivity is attained. However, the lower limit of the final volume may be about 100 μ L because of the difficulties arising from handling a small size solution in a batch method.

A mixed cellulose ester MF with a diameter of 4 mm was used for the extraction of a Cu(II)- and Ni(II)-PDC complexes at pH 4 and 7, respectively. The complexes could be extracted from 5 mL of sample solution by simple pressure filtration using a modified luer lock type gastight syringe. The whole of the membrane was inserted into a cup-type cuvette to determine Cu or Ni in river water by ETAAS [34]. Lead was concentrated as a PDC complex from 10 mL of a sample solution on a MF of 5 mm in diameter and 2 mm in effective filtering diameter. The MF holding the complex was cut so as to be 3 mm in diameter, and dissolved in 100-200 μ L of methyl cellosolve to introduce into ETAAS [35].

To preconcentrate a desired element from a large sample volume with a short filtration time, it is important to keep the effective filtration area as large as possible. In mini SPE system (Figure 5) [36], the funnel has an effective filtration area of 0.64cm², and it takes only 7 min to complete filtration of 100 mL of sample solution. Thallium in a 100 mL of seawater and snowmelt samples was extracted as Tl(III)-PDC complex on a minute amount of CNR after the oxidation of Tl(I) to Tl(III) with bromine water. The CNR extracting Tl was collected on a MF (25 mm ϕ) by filtration under suction using a glass funnel with the expanded throat (9 mm ϕ). The MF holding CNR was then transferred and place on an acrylate resin puncher with 10 mm ϕ hole. The resin thin layer was carved out to put it into a

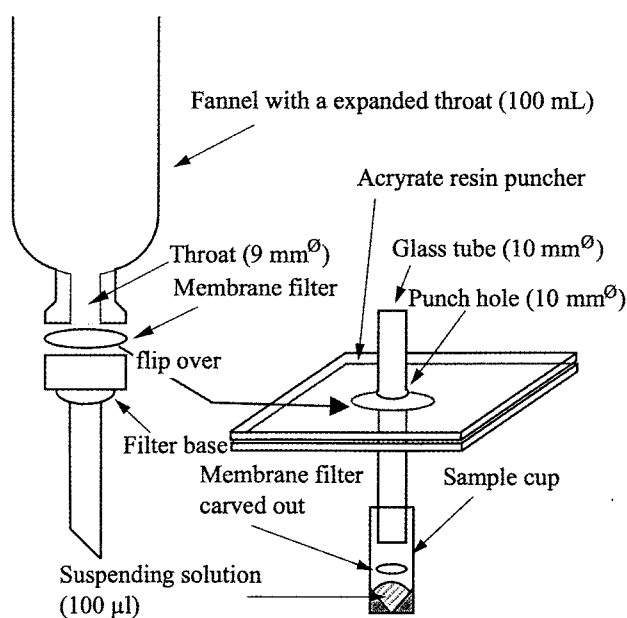


Figure 5 Filtration apparatus and a purpose-built acrylate resin puncher. Reference [36].

Table 2 Comparison of RSI-ETAAS following mini and conventional SPE for a 1000-fold enrichment

	Mini	Conventional ^a
Membrane filtration		
Effective filtration area/cm ²	0.64	2.26
Sample size/mL	100	1000
Finals olution/mL	0.1	1
Filtration time/min	7	20
Amounts of reagent required		
30 mM APDC/mL	1.5	15
Bromine water/mL	0.1	0.1
CNR/mg	4	15
Calibration graph		
Range/pg mL ⁻¹	0–40	0–30
Slope/mL pg ⁻¹	3.59×10^{-3}	3.91×10^{-3}
Standard deviation/mL pg ⁻¹	0.07×10^{-3}	0.07×10^{-3}
Correlation factor	0.999	0.999
Detection limit/pg mL ^{-1b}	1.9	1.3

^aA filtration apparatus having a 17 mm throat diameter for a 25 mm^φ membrane filter.

^bCalculated by the equation $3 \times s_{yx}/b$, where b is the slope of the calibration graph and s_{yx} is the estimate of the standard deviation of the blank given by regression analysis of the calibration graph. Reference [36].

sample cup containing 100 μ L of 10 mM HNO₃ and 0.5 mM NaCl. The solution was subjected to ultrasonication for 1 min to disperse the CNR particles on the MF and prepare the suspension of CNR. In the result, a 1000-fold concentrated solution was introduced into ETAAS [36].

Table 2 shows the comparison of RSI-ETAAS following mini and conventional SPE for 1000-fold enrichment. It was found that mini SPE has the advantages of economy in sample volume, filtration time, and reagents, whereas has a comparable precision and sensitivity. A small sample solution required is effective to eliminate the danger of contamination arising from the treatment of large sample solutions.

3. On-line methods

3.1 General

SPE has been coupled on-line with continuous flow systems such as flow injection (FI) analysis by inserting a column packed with a solid phase into the flow line. It is possible to introduce a sample solution using FI in flame atomic absorption spectrometry (FAAS), therefore, the coupling with SPE is rather easy. On the other hand, for ETAAS the difficulties arise from the fact that the sampling is made in a discontinuous way in ETAAS, whereas the sample zone is continuously transported to the detector in flow systems. Furthermore, it is necessary to consider that only small volumes are generally injected (<100 μ L) into the graphite furnaces. Thus, the ETAAS technique requires more sophisticated coupling devices when compared to FAAS etc [6].

The on-line coupling methods for ETAAS are divided into two main branches. One uses a packed microcolumn for the collection of a desired element. The desired element is introduced into ETAAS after elution, or by transporting the solid-phase beads holding the desired element into a graphite furnace. These procedures can be performed automatically [37].

The other uses an inner wall of an open tubular as the solid phase. A polytetrafluoroethylene (PTFE) tube has been used under the name "knotted reactor" [38]. In-tube solid-phase microextraction (ITSPME), which does not have a large difference in principle with other FI-SPE techniques using an open tubular column, uses a chemically modified silica capillary tube

[39] or a PTFE tube [40] as the solid phase.

Generally, a microcolumn preconcentration has advantage in a retention efficiency and an enrichment factor when compared with an inner wall preconcentration. The retention efficiency can reach to >90% and up to about 100-fold enrichment can be attained. On the other hand, an inner wall preconcentration using an open tubular has advantages of low flow resistance/hydrodynamic impedance, which allows high sample-loading flow rates for obtaining better enrichment factors.

Since reviews have been published lately [37,38], the on-line coupling of SPE with ETAAS appeared in the most recent papers are described here.

3.2 On-line microcolumn preconcentration

A microcolumn (1.0 mm i.d., 15 mm length) packed with about 10 μ L of C18 phase was used for on-line preconcentration of Pt with subsequent determination by ETAAS. The anionic Pt-Sn complexes formed in the sample solution were on-line adsorbed on a *N,N*-diethyl-*N'*-benzoylthiourea loaded C18 phase. The formed Pt complex was eluted with 50 μ L of ethanol and directly introduce into the graphite furnace. The detection limit was 0.1 μ g L⁻¹ for 1.57 mL of a sample solution. The relative standard deviation was 5.5% at 0.5 μ g L⁻¹ Pt (n=10). The method has been applied to the analysis of platinum in aerosol samples in a highway-tunnel [41]. The Cu-PDC complex loaded microcolumn (6 \times 2 mm i. d.) packed with the sorbent from cigarette filter was used for the collection of Pd(II) by on-line displacement reaction between Pd(II) and the Cu-PDC complex on the microcolumn. The retained analyte was subsequently eluted with 40 μ L of ethanol for on-line ETAAS determination. Interference from coexisting heavy metal ions with lower stability of their PDC complexes relative to the Cu-PDC complex were minimized. The detection limit was 18 ng L⁻¹ for 2.8 mL of the sample solution. The relative standard deviation was 2.5% at the 1 μ g L⁻¹ level. The method has been applied to the selective determination of Pd(II) in local road dusts and roadside soils [42].

Renewable microcolumn was used in a "Lab-on-Valve" (LOV) system coupled to ETAAS. A six-port selection valve was used to select the flow lines connecting syringe pumps with the microcolumn and the reservoirs containing a sample solution, a reagent solution, and an eluent. For the enrichment of Cd(II), Cd(OH)₂ precipitate was adsorbed onto the C18 surface, which was afterward eluted with 20 μ L of 1% nitric acid. After about 100 cycles of precipitation/dissolution, the used beads were discarded and new beads were packed into the microcolumn automatically. The detection limit was 1.7 ng L⁻¹ for 600 μ L of sample solutions. The relative standard deviation was 2.1% at the 0.05 μ g L⁻¹ level. The procedure was validated by analyzing cadmium in certified reference materials [43]. Chelating Sepharose beads were used for the extraction of Cd(II), Pb(II) and Ni(II) in standard reference materials. The samples were adjusted to pH 5.0 on-line in the system. The target ions were adsorbed by chelation on the surface of beads, contained in a 20 μ L microcolumn within the LOV, and following elution by 50 μ L of 2 M nitric acid, the eluate was introduced into ETAAS. The determination limits were 1, 70 and 20 ng L⁻¹ for Cd(II), Pb(II) and Ni(II), respectively for 1.8 mL of a sample solution. The retention efficiencies were 95, 75 and 90%, and the enrichment factors were 34, 27, and 32. The beads can be used repeatedly for at least 20 times without decrease of performance,

yet can be renewable at will [44].

3.3 Inner wall preconcentration

As(III) in seawater samples were selectively adsorbed as the PDC complex onto inner walls of the PTFE knotted reactor (0.5 mm i.d., 125 cm length) and eluted with 40 μL of ethanol. The detection limit was 8 ng L^{-1} . The relative standard deviation was 4.5% at 0.1 $\mu\text{g L}^{-1}$ As(III) ($n=11$). The accuracy was demonstrated by total arsenic determination in certified reference material after pre-reduction of As(V) with L-cysteine [45]. Pd(II) was adsorbed as the ion association complex between the K^+ 18-crown-6 and $\text{Pd}(\text{SCN})_4^{2-}$ on the inner wall of a PTFE knotted reactor (0.5 mm i.d., 100 cm length), and eluted by 50 μL of methanol acidified with 1% (v/v) HNO_3 . The enrichment factor was 29. The detection limit was 16 ng L^{-1} for 6.6 mL of a sample solution. The relative standard deviation was 2.3% at 0.4 $\mu\text{g L}^{-1}$ Pd(II). The method was validated by recovery measurement on spiked blood and road dust samples [46].

A Ox modified silica capillary tube (0.53 mm i.d., 20 or 40 cm length) was prepared for the determination of Cd(II) by ITSPME/ETAAS [47]. Ox was covalently bound to the inner wall of the silica capillary tube by circulating reagent solutions. The manifold for ITSPME/ETAAS is shown in Figure 6. The capillary column was placed between the nozzle of the autosampler and the syringe pumps. Two three port valves were used for selecting flow lines; one is that for the extraction and the other is for the elution. Obviously, a more sophisticated flow system can be constructed if a fully automated modules are used.

A sample solution is sucked through the capillary column and discharged to the original reservoir. Therefore, the percent extraction (E%) can be improved by the reciprocation of the sample solution as shown in Figure 7. This is one of the characteristics of ITSPME. The E% increased from 25% to 42% in this case. As the E% depended on the flow rate, the constant flow rate is required for the good reproducibility. The optimum pH was in the range 7.7-8.2. The linear calibration graph was obtained in the range 0-0.05 ng mL^{-1} , and the detection limit was 0.004 ng mL^{-1} (3s of the blank).

The effects of foreign ions were studied using 0.05 ng mL^{-1} Cd(II). The presence of 1 mg mL^{-1} of Na^+ , 0.3 mg mL^{-1} K^+ and 0.3 mg mL^{-1} Ca^{2+} were tolerable. However, in the presence of a 100-fold amount of Mg^{2+} , Mn(II) and Zn(II), the relative errors were -7%, -8% and -50%, respectively. This may be caused by the low capacity of the capillary column.

Cd(II) in a certified reference material, river water (JAC 0032), was determined by a standard addition method using 900 μL of a 40-fold diluted sample solution. The agreement between the obtained result, $1.07 \pm 0.02 \text{ ng mL}^{-1}$, and the certified value, $1.00 \pm 0.02 \text{ ng mL}^{-1}$, was achieved.

4. Conclusion

The integration of SPE with ETAAS is useful for improving the sensitivity and avoiding the danger of the contamination due to the large volume of eluent.

In the batch method, an adsorbent such as AC, ARS, CNR or a biomass materials was added to the sample solution to extract a desired element, usually in the form of the hydrophobic species. The adsorbent holding the desired element was collected on a MF by filtration under suction. A MF as such acted as the adsorbent in the absence of resin beads. And then, the adsorbents

were introduced into ETAAS without elution as a dry form, as a suspension or slurry, or after dissolved in an appropriate solution. Thus, integration of SPE with ETAAS was accomplished. Since elution step is eliminated, the enrichment factors up to 1000 were easily attained. In a favorable case, more than one element could be simultaneously extracted. Speciation of the element in the

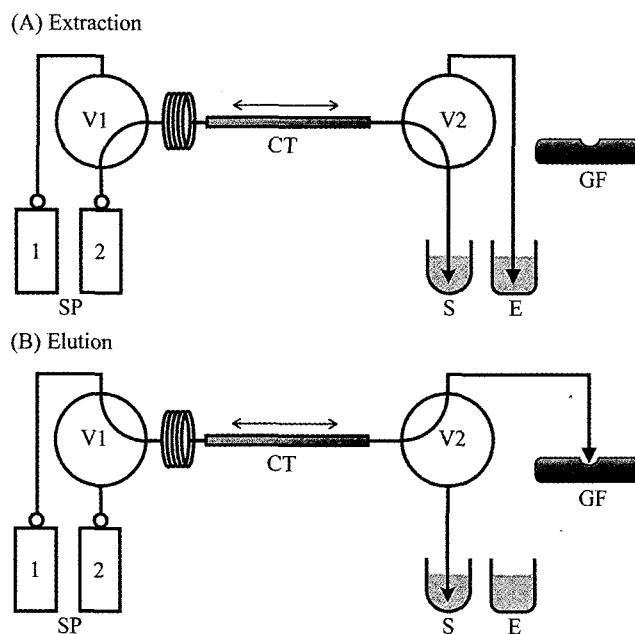


Figure 6 Manifold for ITSPME/ETAAS. (A) A 800- μL aliquot of the sample solution (S) was sucked into the silica capillary tube having Ox modified inner wall (CT) by a syringe pump (SP), and then discharged into the original sample cup. (B) A 80- μL aliquot of eluent (E: 0.1 M HNO_3) was sucked into CT, and then injected into the graphite furnace (GF). V1 and V2, three-way valve.

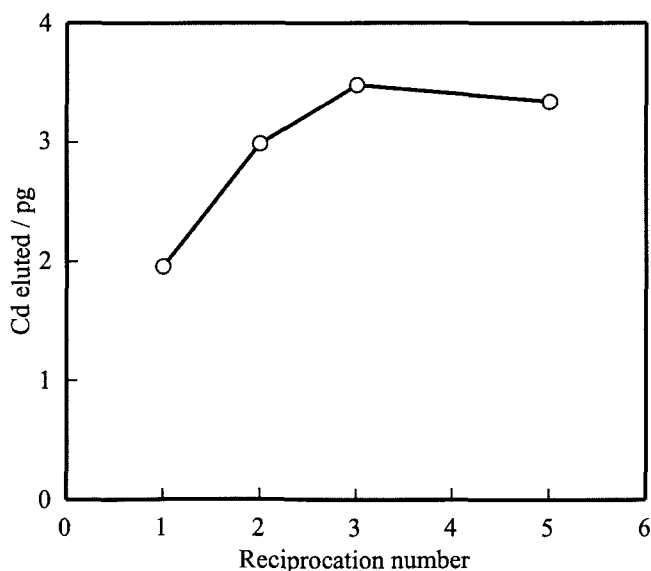


Figure 7 Effect of reciprocation number. Cd(II), 8 pg mL^{-1} ; column length, 40 cm; flow rate, 10 $\mu\text{L s}^{-1}$; sampling volume, 800 μL .

different oxidation states could be carried out based on their different reactivity to certain chelating reagents. A miniaturization of SPE has advantage in the economy in a sample size, amounts of the reagents and time for the sample pretreatment.

The on-line coupling of SPE with ETAAS required sophisticated coupling devices because of the discontinuity of ETAAS measurements. However, an automation of ETAAS measurements could be achieved by the on-line coupling with a microcolumn. The microcolumn was connected with a nozzle tip of an autosampler, or, in LOV, a six-port selection valve was used to select the flow lines connecting syringe pumps with the microcolumn and the reservoirs containing a sample solution, a reagent solution, and an eluent. In inner wall preconcentration, an inner wall of open tubular such as a PTFE tube or a chemically modified silica capillary tube (ITSPME) acted as the adsorbent. A 40-80 μ L of eluent was introduced directly into ETAAS. Generally, the enrichment factors of on-line system are smaller than that of the batch extraction.

The handling of 40-100 μ L of eluent was successfully performed in Miniaturized SPE and the on-line systems. It enables to obtain a high enrichment factor from a small size of samples. It is advantageous for rare and precious materials which can be obtained only in a small size.

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