Novel preconcentration technique using bis(2-ethylhexyl) hydrogen phosphate (HDEHP) loaded porous polytetrafluoroethylene (PTFE) filter tube as a sorbent: Its application to determination of In(III) in seawater by ICP-MS with air segmented discrete sample introduction

Masahiko Murakami *, Naoki Furuta

Faculty of Science and Engineering, Department of Applied Chemistry, Chuo University 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Abstract

Novel preconcetration method involving porous polytetrafluoroethylene (PTFE) filter tube impregnated bis(2-ethylhexyl) hydrogen phosphate (HDEHP) as a sorbent was studied to establish it as a practical preconcentration method for ultra trace analysis with ICP-MS. A 1 ng portion of In(III) in 1000 ml of matrix free solution or 700 ml of synthetic seawater was quantitatively complexed with HDEHP adsorbed onto porous PTFE filter tube by passing the solution through the micro pore of the filter tube. Preconcentrated In(III) was then quantitatively recovered provided that the elution, which consists of a cyclical filtering 0.1 ml of 8 mol dm^{-3} hydrochloric acid through the filter tube for 1 min; therefore, up to 10000- and 7000-fold of enrichment was attained for matrix free solution and synthetic seawater, respectively. To introduce a 0.1 ml of the eluted solution to ICP-MS, flow injection method with air segmented discrete sample introduction (ASDI) was also studied by using manually operated simple valve system. By using ASDI, good linearity of calibration curve ($r = 0.99997$) was observed from 0.01 to 5.0 ng ml^{-1} of In(III). Good reproducibility was also shown in measurements of 0.1 ml of 5 ng ml^{-1} of In(III) (R.S.D. = 1.9%, $n = 5$). The average recovery and R.S.D. of the results for the five duplicates determination of 0.1 ng of In(III) spiked to 200 ml of synthetic seawater were 99 and 2.4%, respectively. The method was applied to the determination of In(III) in coastal seawater sampled at north east of Hachijyo Island, Japan; using 200 ml of sample, 2000-fold preconcentration of In(III) was performed within 30 min for five samples. The analytical detection limit and the blank were 9.8 and 21 pg l^{-1}, respectively. The average concentration was determined to be 96 pg l^{-1}, and R.S.D. of the results was 3.7% ($n = 3$).
© 2005 Elsevier B.V. All rights reserved.

Keywords: Preconcentration; Liquid–solid extraction; Bis(2-ethylhexyl) hydrogen phosphate; HDEHP; PTFE; Filter; In(III); ICP-MS

1. Introduction

In this couple of decades, the ability to quantitatively analyze the trace metals has been enhanced by both advances in clean technologies of sample treatment and in analytical instrumentation for more sensitive elemental detection. The development of inductively coupled plasma mass spectrometry (ICP-MS) is a prime example of instrumental advances. Its excellent analytical feature of multi element detection capability with high sensitivity has allowed the rapid progress in many scientific fields; marine geochemistry is one of typical example of these fields. Since then, concentration levels and oceanic distributions of many trace elements, which serve as an important key to understand the marine geochemical cycle of elements, have been newly obtained, or revised from the old doubtful data. Although there are fewer elements today whose concentrations are not yet known, there are many trace metals whose distributions were obtained only through study at one or a few locations, including Sc, Ti, Zr, In, platinum group elements, Au, Hg and Th.

Indium is highly particle-reactive (47% association in the Mediterranean Sea) [1] and thus must have a short mean oceanic residence time enough to not become thoroughly mixed since it is rapidly removed from seawater; it leads to tremendous spatial and temporal variability, and hence it makes the element poten-

tially useful as tracer of marine processes. Furthermore, indium will be worth monitoring also as a tracer which indicates the effect of human activity on environment, because its environmental load may be increased in near future by rapid increasing in consumption of indium in recent years in the field of electronics industry which has been caused by being utilized as a material of liquid crystal display, light emitting diode, solar cell and lead-free solder, etc. [2]. However, the short ocean residence time also leads to very low concentration of indium in seawater; indium is known as one of the elements which have the lowest levels of concentration in seawater among all the elements that have ever been reported to date and there were few publications which report the reliable value of its concentration in seawater until recent years. Orians and Boyle [3] determined the concentration of indium in open ocean seawater by using ICP-MS followed by the 3000-fold enrichment by the preconcentration with lab-made TSK-8HQ chelating ion exchange resin and the subsequent evaporative concentration. Amakawa et al. [4] performed 300-fold enrichment of the indium in 1000 ml of seawater of North Pacific Ocean by the liquid–liquid extraction which uses HDEHP/2-ethylhexyl dihydrogen phosphate (H$_2$MEHP) and the subsequent evaporative concentration, and then determined by using isotope dilution ICP-MS (ID-ICPMS).

Accurate determination of some ultra trace elements (<ppt) such as indium and rare earth elements (REEs) still difficult even now because both the major ions in sea water cause the spectral and non-spectral interference under ICP-MS measurement and the concentration of analyte is often lower than their limit of detection on ICP-MS. Hence, as shown in the above reports, the determination of such elements requires the sample pretreatment to which separate the analyte from matrix and to enrich them to several hundred-fold or above. Various conventional techniques, e.g., liquid–liquid extraction [4–6], coprecipitation [7–9] and liquid–solid (sorbent) extraction with batch [10,11] or column [3,12–14] technique using ion exchange or chelating resin, have been used for the present purpose. These conventional methods, however, are not always fit to highly sensitive ICP-MS since they were established as a preconcentration and matrix separation method for less sensitive AAS and ICP-AES. They involve many time- and labor-consuming processes which need both proficient operation and large amount of chemicals; furthermore, they often need the additional evaporative concentration because they alone are difficult to achieve the high enough enrichment factor (as over 100-fold). It is difficult for such processes to prevent the contamination which affects the detection of ppt or less, which is available on ICP-MS, because they involve various probable sources of the contamination which cannot be disregarded now although they had been negligible when the concentration of analyte is ppb or so. Thus, the new, clean, and simple preconcentration method which can fit today's, and also future's, ultra trace analysis should be established.

In an effort to develop the novel method more suitable for ultra trace analysis, we have proposed the novel sorbent extraction system involving a porous polytetrafluoroethylene (PTFE) filter tube (pore size 1 μm) which is impregnated with liquid chelating agent, as a solid sorbent [15]. The PTFE filter tube has the porous tube wall which is formed of PTFE fiber. Strong hydrophobicity of PTFE allows firm adsorption of the hydrophobic liquid chelating agent, which often has long hydrocarbon chains, on the surface of the fiber, thus the reagent layer is made on the fiber by impregnating the tube with the liquid chelating agent. In this system, preconcentration is performed as follows: analyte ion is extracted into the reagent layer on the fiber when a sample solution is filtered through the wall of the tube, and then it is eluted by filtering an eluent through the wall of the tube. The attractive feature of the system is that it ensures a high enrichment factor by eluting the extracted analyte to a small volume of eluent; the 'tube-shaped' filter enables treatment of a small volume (like a droplet) of eluent which cannot be treated by conventional disk-type filter, because the filter tube does not need any holder which gives rise to significant dead volume in contrast with the disk-type filter.

To validate our approach, we have preliminarily studied the preconcentration of In(III) with a bis(2-ethylhexyl) hydrogen phosphate (HDEHP) impregnated PTFE filter tube as a sorbent by subsequent AAS detection [15]; in this work, we found that 1 μg of In(III) in 1000 ml of synthetic seawater was quantitatively extracted to the filter tube, and then was also quantitatively eluted into 0.3 ml of 4 mol l^{-1} hydrochloric acid; thus 3300-fold or more enrichment was attained by the one step preconcentration alone, without the evaporative concentration. We have also studied that the applicability of the present system to preconcentration of REEs in seawater; it was observed that ppt levels of REEs in natural sea salt solution were quantitatively preconcentrated by the present system with maximum preconcentration factor of 200- and 20-fold for Nd–Lu and La–Sm, respectively, and were determined by ICP-MS [16].

Whereas there are few recent reports for improved method which is applicable to determination of indium in open ocean seawater, the result of the previous study suggests that our system has potential to apply to the purpose provided that it is properly fitted with ICP-MS detection. However, several additional studies and new tactics to introduce the small volume of eluent to ICP-MS without any loss are still required to fully execute the system as the preconcentration method for ICP-MS determination of indium in real seawater sample, since the concentration of indium in natural seawater is probably lower than that tested in the previous study by a factor of 1000 or more.

Hence, in this paper, we have tried to optimize the system to establish the present technique as the preconcentration method followed by ICP-MS measurement. First, following extraction conditions were investigated by using a matrix free solution or a synthetic seawater containing 1 ng of In(III): pH for extraction, sample volume and sample flow rate. As the conditions for eluting the extracted In(III), acidity of the eluent and eluting time were also studied in order to minimize a volume of the eluent needed. Next, to efficiently introduce a droplet of the eluent to ICP-MS, we have studied the discrete sample introduction technique, which called as segmented flow injection (SFI) [17] or air segmented discrete introduction (ASDI) [18]. The ASDI is the technique which prevents the dilution of a sample caused by the diffusion to the carrier of the sample, by putting small air gaps into the both ends of the sample solution plug to segment the carrier solution and the sample. The ASDI effectively improves the

sensitivity and the detection limit, especially when a small volume of the sample is measured; Stefanova et al. [18] reported that the detection limit has been improved about three times than that obtained on conventional flow injection method, when 0.5 ml of the sample was injected. In spite of such an advantage, however, there are few reports [19] concerning to the practical application of this technique to ultra traces analysis; the one of the probable reasons is that it requires the complicated sampling system in order to insert an air segment between a sample plug and a carrier flow, at suitable timing. Hence, in this work, we have proposed the simple method which enables to manually implement the same sampling sequence which has been performed on the automated ASDI, by manually aspirating up the sample into the simple lab-made valve system which has the sample loop with a bigger volume than the volume of the sample to be introduced.

The preconcentration of indium from coastal seawater with HDEHP impregnated PTFE filter tube followed by measurement on ICP-MS with the manual ASDI flow injection system was also studied, to confirm the practical applicability of the present method.

2. Experimental

2.1. Materials and reagents

Porous PTFE filter tube (pore size 1 μm) was obtained from UNIVERSAL Co., Ltd. (Toshima-ku, Tokyo, Japan). Bis(2-ethylhexyl) hydrogen phosphate was purchased from Tokyo Kasei Co., Ltd. (Kita-ku, Tokyo, Japan). Both nitric and hydrochloric acid were EL (high purity chemicals for the electronics industry) grade, and were purchased from Kanto Chemical Co., Inc. (Chuo-ku, Tokyo, Japan). All chemicals were used as received. The ultra pure water was prepared with Millipore model Milli-Q water purification system. Synthetic seawater was prepared as described by Riley and Skirrows [20], by desorbing the following reagents into 1000 ml of ultra pure water: NaCl 23.487 g; $MgCl_2$ 4.981 g; Na_2SO_4 3.917 g; $CaCl_2$ 1102 g; KCl 0.664 g; $NaHCO_3$ 0.192 g; KBr 0.096 g; H_3BO_3 0.026 g; $SrCl_2$ 0.024 g and NaF 0.003 g.

Coastal Seawater sample was collected during the regular service on Tokyo–Hachijyo island line of passenger steamer of Tokai Kisen Co., Ltd., at about 20 km north east offshore of Hachijyo Island, Japan. The sample was filtered through 0.45 μm Nucleopore membrane filter and acidified to about pH 3 with concentration HNO_3, then was stored in acid-leached polyethylene terephthalate bottle.

2.2. Procedures

2.2.1. Impregnation of HDEHP into porous PTFE filter tube

A porous PTFE filter tube (25 mm × 1 mm i.d., 2 mm o.d.) was sealed at its one end with heat-shrinkable plastic tube. Added the tube and 25 ml of 35% HDEHP in hexane solution into a 50 ml conical flask, and applied ultrasonic wave to the flask for 5 min on an ultrasonic cleaner, to well impregnate the
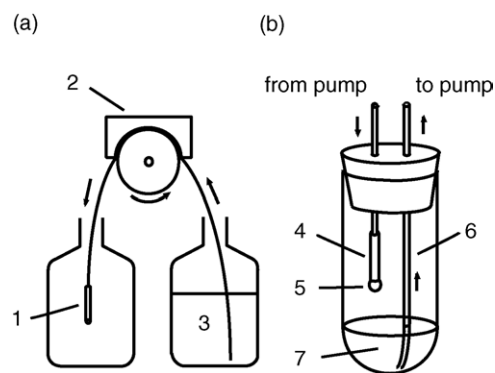

Fig. 1. Schematic diagram of the preconcentration set up (a) and the circulating elution apparatus (b) (from Ref. [14]); 1, PTFE filter tube; 2, peristaltic pump; 3, sample solution; 4, PTFE filter tube; 5, heat-shrinkable plastic tube for end cap; 6, PTFE tubing to pump and 7, eluting acid.

reagent solution into the micro pore of the tube. Then the tube was dried by air at room temperature. The sorption capacity of the 25 mm tube for In(III) has been determined to be 630 μg (5.5×10^{-6} mol) in the previous work [15].

2.2.2. Preconcentration

The preconcentration system consisted of a MasterFlex model 7524-10 peristaltic pump equipped model 751960 multichannel pump head with a Tygon pump tube connected to the HDEHP adsorbed PTFE filter tube, with PTFE tubing (Fig. 1(a)). Then 100–1000 ml of solution containing 0.1–10 ng of In(III), which had been acidified to pH 3 with nitric acid, was seeped through the filter tube at a flow rate of 10–20 ml min^{-1}. Up to five samples were simultaneously processed.

2.2.3. Elution

The preconcentrated In(III) was then eluted by 0.1 ml of 8 mol l^{-1} hydrochloric acid which was added Rh(III) to be a concentration of 1 ng ml^{-1} as an internal standard, at flow rates of 1 ml min^{-1}. To obtain a quantitative elution recovery by using 0.1 ml of 8 mol l^{-1} hydrochloric acid, the acid was added to a conical-bottom vial, and was circulated to the filter tube as Fig. 1(b), for a period of 1–3 min.

2.2.4. Measurements

The concentration of In(III) in the eluent was determined with ICP-MS on Fisons model PQ Ω equipped Meinhard concentric nebulizer and a Scott-type double pass spray chamber. The sample was manually introduced by air segmented introduction technique using a house-made FIA system including Rheodyne type 50 six-ports rotary valve equipped 0.2 ml of sample loop, a disposable plastic syringe and Gilson Minipuls peristaltic pump.

The recovered eluent or 0.1 ml of In(III) standard solution was drawn up through the valve with a disposable plastic syringe until a whole of the sample or the standard solution went into the sample loop, which was initially filled by air; the sample plug was put between small air segments, as shown in Fig. 2, because the volume of the sample (about 0.1 ml) is insufficient to fill the total volume of the sample loop and dead space of the valve.
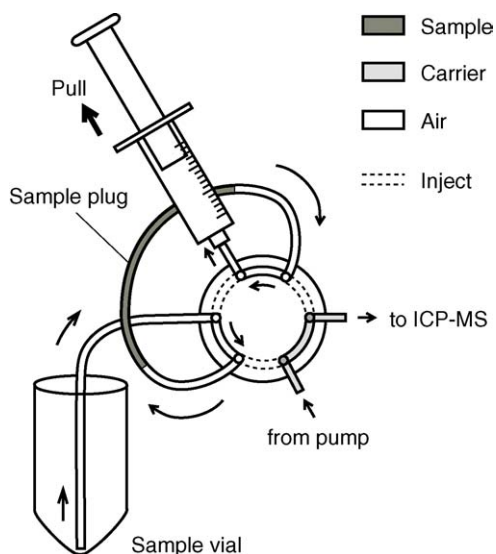
Fig. 2. Sample loading by manual ASDI.

Then, by turning the valve to the inject position, the sample plug and the air gaps transfer into ICP-MS, with 1% nitric acid solution as a carrier, at a flow rate about 0.3 ml min^{-1}. In this process, as the dispersion of the sample into the carrier solution is suppressed because both of the air gaps divide the sample plug from the carrier, the broadening and lowering of the peak could be eliminated. The operational conditions of ICP-MS and measuring sequence are summarized in Table 1. After injecting the sample, turning the valve to the load position and the sampling line and the sample loop were washed with 1 ml of 1% nitric acid solution by completely drawing up the solution with the syringe, then next sample was loaded.

Data were acquired using the time resolved mode. All peaks were evaluated through integration of the area beneath the peak. A calibration curve was prepared by directly measuring the In(III) standard solutions which were made by adding various known amount of In(III) to the hydrochloric acid solution which was prepared to same acidity as that used as eluent; a constant

Table 1
Operating conditions of ICP-MS and sampling sequence

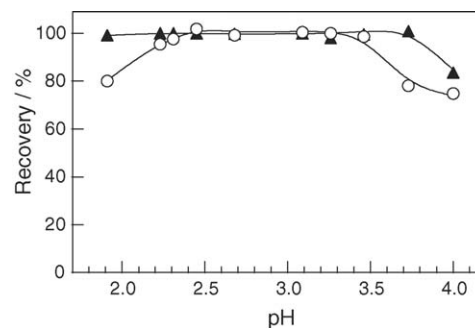| Plasma conditions	
Forward power (W)	1350
Reflected power (W)	<2
Gas flow rate	
Coolant (l min^{-1})	14.0
Auxiliary (l min^{-1})	1.2
Nebulizer (l min^{-1})	1.0
Sample uptake rate (ml min^{-1})	0.3
Data acquisition	
Time resolved mode mass (M/Z)	115 for In, 103 for Rh
Measurement mode	Peak jumping
Dwell time (μs)	200
Measuring sequence	
Sample uptake (s)	50
Rinse (with 5% HNO$_3$) (s)	120

Fig. 3. Effect of pH on extraction of 10 ng of In(III) from 100 ml of (a) matrix free solution (▲) and (b) synthetic seawater sample (○).

amount of Rh(III) were also added to be a concentration of 1 ng ml^{-1} as an internal standard.

3. Results and discussion

3.1. Extraction

3.1.1. pH

The effect of pH of the sample solution on sorption of 1 ng of In(III) was studied for 100 ml of both matrix free samples and high salinity samples consist of synthetic sea water; the results are shown in Fig. 3. For matrix free sample, In(III) was quantitatively extracted from less than pH 1.0 through 3.7 (Fig. 3(a)). In the case of the highly saline sample, quantitative extraction was not observed under pH 2.3; the range of the quantitative extraction was shifted to pH 2.3–3.5 (Fig. 3(b)). On the standpoint of reducing a contamination, it is noted that the use of buffer solution is avoidable since such a range of the pH value can be adjusted with clean nitric acid or hydrochloric acid; it is beneficial for the ultra trace analysis.

Hence, pH 2.5–3.0 was estimated as an optimum because In(III) can be quantitatively extracted regardless of the salinity of the sample.

3.1.2. Flow rate

The effect of sampling flow rate on the extraction recovery of 1 ng of In(III) in 100 ml synthetic seawater was studied over the range of 5–30 ml min^{-1}. The results shown in Table 2; the quantitative recovery was obtained up to 25 ml min^{-1}. It is noteworthy that sampling flow rate of over 20 ml min^{-1} is applicable to the filter tube system; such a high flow rate is not allowed to conventional column system because of its high backpressure.

Table 2
Effect of flow rate on extraction of 10 ng of In(III) from 100 ml solution

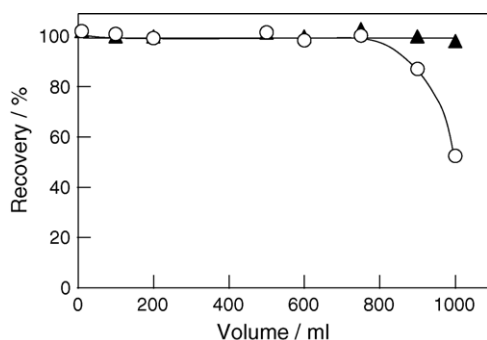| Flow rate (ml min^{-1})	Recovery (%)
5	100
10	101
15	98.0
20	99.8
25	98.0
30	95.2

Fig. 4. Effect of sample volume on extraction of 1 ng of In(III) for (a) matrix free solution (▲) and (b) synthetic seawater sample (○).

Fig. 5. Effect of eluent volume on elution of In(III) with (a) $4\,mol\,l^{-1}$ (○) and (b) $8\,mol\,l^{-1}$ (▲) of hydrochloric acid.

However, when the flow rate was increased to over $20\,ml\,min^{-1}$, leaking of the sample solution was occasionally observed at a connection of the Tygon pump tube and the Teflon tube. Therefore, $10–15\,ml\,min^{-1}$ was used as an optimum in our later studies.

3.1.3. Sample volume

The effect of the sample volume on the extraction recovery of 1 ng of In(III) was studied for samples of matrix free solution or synthetic seawater. For the matrix free solution (Fig. 4(a)), the extraction of In(III) was almost quantitative through 1000 ml. On the other hand, when the synthetic seawater (Fig. 4(b)), quantitative extraction was observed up to 750 ml and the recovery was steeply decreased with more increasing the sample volume. Therefore, the sample volume of up to 700 ml was appropriate in considering safety.

3.2. Elution

3.2.1. Acidity and volume of eluting acid

It is known that HDEHP works as a very strong chelating agent for In(III), REEs and Y(III), and the elution or back extraction of these elements with various mineral acids is very difficult [5]. In our previous study [15], it was observed that the eluting process, which consisted of cyclical filtering a 0.1 ml of $4\,mol\,l^{-1}$ hydrochloric acid through the filter tube for 1 min, must be repeated three times to obtain the quantitative recovery of 2.5 μg of In(III). To achieve the higher enrichment of analyte, the volume of final eluent has to be decreased as much as possible. Thus, elution of preconcentrated In(III) was studied by using 0.1–1.0 ml of 4 or $8\,mol\,l^{-1}$ of hydrochloric acid, at a constant flow rate of $1\,ml\,min^{-1}$.

Fig. 5 shows the results obtained when the eluting acid was only once filtered through the filter tube sorbent loaded 1 ng of In(III). When the $4\,mol\,l^{-1}$ of hydrochloric acid was used, the recovery of In(III) was increased with increase in the acid volume, and was reached 98–100% at 0.8 ml or above (Fig. 5(a)). Although the quantitative recovery of In(III) can be obtained with $4\,mol\,l^{-1}$ of hydrochloric acid by the single elution, it needs large amount of the eluting acid.

On the other hand, It found that increasing the acidity considerably decreases the volume of the eluting acid required to establish the quantitative recovery of In(III); using $8\,mol\,l^{-1}$ of
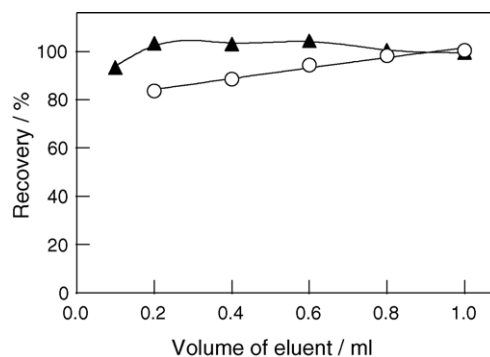
hydrochloric acid, sufficient recovery was observed at 0.2 ml or above although it was still not observed at 0.1 ml (Fig. 5(b)).

3.2.2. Circulating elution

In our previous work [15], we found that the elution recovery increases with "circulating elution", by which the eluting acid had passed through the filter tube is returned back to the tube again and again. Such a decrease in the volume of the eluent is desirable because it directly leads to the increase in the factor of preconcentration. Thus, $8\,mol\,l^{-1}$ of hydrochloric acid was selected as an optimum for the elution of preconcentrated In(III). Hence, to reduce the volume of the eluting acid as much as possible, the influence of circulating a 0.1 ml of $8\,mol\,l^{-1}$ hydrochloric acid through the filter tube on the elution recovery of In(III) was studied. Table 3 shows the results. As mentioned above, the quantitative recovery was not obtained when a 0.1 ml of $8\,mol\,l^{-1}$ hydrochloric acid was only once filtered through the filter tube (it was designated as one time of cycle in Table 2). On the other hand, the quantitative elution recovery was established by two to four times of the circulation.

Thus, two to four times of the circulating was taken as an optimum; it required the period of 1–3 min on our system. Hence, to elute the preconcentrated In(III), a 0.1 ml of $8\,mol\,ml^{-1}$ hydrochloric acid was circulated for 1–3 min at a flow rate of $1\,ml\,min^{-1}$, in our later studies.

3.3. Measurements

3.3.1. Sample introduction

As mentioned above, the present system has allowed quantitatively transferring 1 ng of In(III) in 700 ml of highly saline sample to 0.1 ml of eluent; it means that sensitivity of the ICP-

Table 3
Effect of cycle of elution on recovery of In(III)
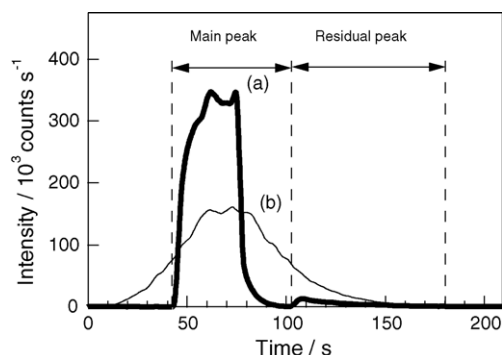
Cycles (time)	Recovery (%)
1	93.3
2	103
3	103
4	102
5	97.7

Fig. 6. Peak shapes of manual (a) ASDI-FI and (b) normal FI.

Fig. 7. Calibration curves made from (a) whole peak area (○) and (b) main peak area (▲).

MS measurement is enhanced by a factor of 7000 if the resulting eluent can be directly measured without any further dilution.

To measure such a small volume of sample by means of ICP-MS, flow injection (FI) method is used as a sample introduction technique. In normal FI system, however, the diffusion of the sample solution into the carrier solution occurs in the course of transportation, and it causes considerable lowering of resulting signal peak, especially when the volume of the sample is less than 0.5 ml [18]. Hence, to avoid such dispersion and to successfully measure the 0.1 ml of resulting eluent, we have applied the technique that is called air segmented discrete introduction which prevents the dispersion by segmenting the sample plug and carrier solution by inserting small air gap between them.

Fig. 6 shows the transient signals for 0.1 ml of In 5 ng ml^{-1} solution obtained on the manual-ASDI (Fig. 6(a)) and on the normal FI equipped 0.1 ml sample loop (Fig. 6(b)). Compared with the normal FI (Fig. 6(b)), higher and narrower peak was observed by manual ASDI (Fig. 6(a)): the height of the signal obtained on ASDI was higher than that obtained by normal FI by a factor of about 2, and the baseline peak width was approximately half that on normal FI. It means that the fraction of noise in the region of the signal which is used to calculate an area intensity of the peak obtained on ASDI is lower than that on normal FI. Thus, ASDI is advantageous especially when the concentration of analyte in the sample is near to its limit of detection.

3.3.2. Integration range of the peak for quantification

In the case of the ASDI, small and broad residual peak was shown following the main peak (Fig. 6(a)); it is caused by the residual sample solution which is carried along with carrier solution. Since it is also originated by part of the analyte in the sample, the intensity should be calculated by the area beneath both peaks. Hence, effect of the integration range on quantification has been studied in both cases of which the intensity of signal was calculated from the area beneath only the main peak and from the area beneath both the main and residual peak. Fig. 7(a) shows the calibration curve which is made from the areas beneath main and residual peak. As shown in Fig. 7(a), linearity of the curve becomes considerably spoiled at low concentration range about less than 1 ng ml^{-1}, e.g., 0.05 ng ml^{-1} of In(III) gave higher intensity than that for 0.1 ng ml^{-1}.

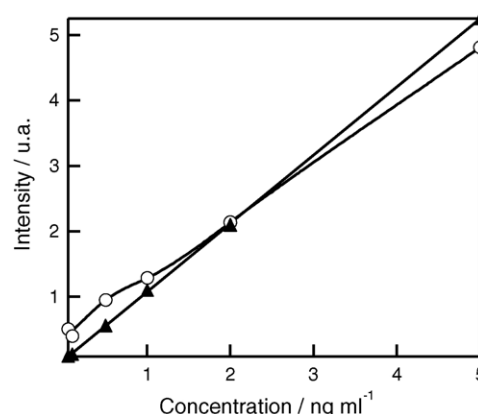On the other hand, it was found that the linearity was much improved when the intensity was evaluated from only the main peak area. Fig. 7(b) shows the calibration curve that is based on the area beneath only the main peak. It is noted that both good linearity (the correlation coefficient (r) = 0.99997) is kept from 0.01 to 5.0 ng ml^{-1}. Such a depress of the linearity of the curve (a) is probably due to the low signal to noise ratio of the residual peak. Hence, the residual peak was ignored and the intensity was capitulated from the area of main peak, to quantify the signal obtained by ASDI.

The intensity measured and quantified under the above condition showed good reproducibility: a 1.9% of relative standard deviation (R.S.D.) was observed at five duplicates measurements of 0.1 ml of 5 ng ml^{-1} of In(III) solution, provided that the internal standard was used.

3.3.3. Recovery for spiked synthetic seawater sample

To verify the applicability of the present method to the preconcentration of trace In(III) from seawater, the extraction and elution of 0.1 ng of In(III) from 200 ml of synthetic seawater was studied. In this study, the preconcentrated In(III) was recovered with 0.1 ml of eluting acid; therefore, the enrichment factor is about 2000-fold.

Table 4 shows the results of five independent measurements of 0.1 ng of In(III) in 200 ml of synthetic seawater. The quantification was carried out with the working curve which were prepared by directly measuring of the In(III) standard solutions without the preconcentration. Quantitative recoverie was obtained from the highly saline sample with good reproducibility, even though 2000-fold enrichment was carried out. The results indicate that the sorption and elution of In(III) is little affected by the coexisting of salt matrices, and suggests that the present method is applicable to real natural water samples such as seawater.

Table 4
Total recovery from synthetic seawater sample ($n = 5$)

Added (pg l^{-1})	500
Found (pg l^{-1})	495
Recovery (%)	99.0
R.S.D. (%)	2.4

Table 5

Analytical results of three independent measurements of In(III) for Japanese coastal sea water

Found (pg l^{-1})	
1	99
2	92
3	95
Mean (pg l^{-1})	96
R.S.D. (%)	3.7
Blank (pg l^{-1})	21
D.L.[a] (pg l^{-1})	9.8

[a] Calculated form 3σ of the blank.

3.3.4. Determination of In(III) in coastal seawater

The present method was applied to the determination of In(III) in the surface seawater sampled at pacific ocean, about 20 km northeast offshore of Hachijyo island, Japan. A 200 ml aliquot of each sample was consumed to give 2000-fold enrichment, and was measured under the condition optimized as above; Table 5 shows results.

Good reproducibility was obtained for natural coastal sea water sample. Both sufficiently low limit of detection and blank value were also observed. The analytical value was comparable to the previously reported values which were obtained by the methods consuming much more time, labor and sample: 0.1–2.0 pM (10–20 pg l^{-1}) for open ocean seawater and 0.06–0.15 pmol kg^{-1} (6–16 pg l^{-1}) for the Pacific and 0.6–1.5 pmol kg^{-1} (60–150 pg l^{-1}) for the Atlantic Ocean [21].

The overall time of the preconcentration for five samples was about 30 min even when 2000-fold enrichment was performed. It is significantly rapid compared with the conventional column or bach preconcentration method. Orians and Boyle [3] carried out the chelating resin column preconcentration which needs 8–10 h, and further evaporative concentration, to obtain 3000-fold enrichment.

4. Conclusions

Using the chelating agent impregnated porous PTFE filter tube provides a rapid, simple and clean system for concentration of trace elements in aqueous sample. The attractive feature of the system is that it permits the treating and recovering of a very small volume of eluent, and hence it yields the high enrichment factor as over 7000-fold in considerably less time and sample consumption than the conventional column system or the liquid–liquid extraction technique, without any further evaporation. The ability of the system was fully brought out by fitting the system to ICP-MS by using the manual ASDI technique as the sample introduction method.

The fact that the reagent is used as an excellent extractant for the rare earth elements (REEs) suggests that this system should also be usable for REEs; the application of the method to the preconcentration of REEs in seawater is now in progress.

References

[1] D.S. Alibo, Y. Nozaki, C. Jeandel, Geochim. Cosmochim. Acta 63 (13–14) (1999) 1991.
[2] USGS. Mineral Commodity Summaries (2005). http://minerals.usgs.gov/minerals/pubs/mcs/2005/mcs2005.pdf.
[3] K.J. Orians, E.A. Boyle, Anal. Chim. Acta 282 (1993) 63.
[4] H. Amakawa, D.S. Alibo, Y. Nozaki, Geophys. Res. Lett. 23 (1996) 2473.
[5] M.B. Shabani, T. Akagi, H. Shimizu, A. Masuda, Anal. Chem. 62 (1990) 2709.
[6] K. Benkhedda, H.G. Infante, E. Ivanova, F.C. Adams, J. Anal. At. Spectrom. 16 (2001) 995.
[7] H. Sawatari, E. Fujimori, H. Haraguchi, Anal. Sci. 11 (1995) 369.
[8] J. Wu, E.A. Boyle, Anal. Chem. 69 (1997) 2462.
[9] C.L. Chou, J.D. Moffatt, Fresenius J. Anal. Chem. 368 (2000) 59.
[10] M.B. Shabani, A. Masuda, Anal. Chem. Acta 261 (1992) 315.
[11] B.K. Esser, A. Volpe, J.M. Kenneally, D.K. Smith, Anal. Chem. 66 (1994) 1736.
[12] A. Miyazaki, R.A. Reimer, J. Anal. At. Spectrom. 8 (1993) 449.
[13] T.-H. Zhang, X.-Q. Shan, R-X. Liu, H.-X. Tang, S.-Z. Zhang, Anal. Chem. 70 (1998) 3964.
[14] K. Oshita, M. Oshima, Y. Gao, K.-H. Lee, S. Motomizu, Anal. Chim. Acta 480 (2003) 239.
[15] M. Murakami, T. Takada, Anal. Commun. 36 (1999) 185.
[16] M. Murakami, E. Hamanaka, T. Takada, Anal. Lett., 38, 14, in press.
[17] J.M. Craig, D. Beauchemin, J. Anal. At. Spectrom. 9 (1994) 1341.
[18] V. Stefanova, V. Kmetov, L. Futekov, J. Anal. At. Spectrom. 9 (1994) 1341.
[19] K.H. Lee, M. Oshima, T. Takayanagi, S. Motomizu, Anal. Sci. 16 (2000) 731.
[20] J.P. Riley, G. Skirrows, Chemical Oceanography 1, Academic Press, New York, 1965, p. 648.
[21] D.S. Alibo, H. Amakawa, Y. Nozaki, P. Indian As. Chem. Sci. 107 (1998) 359.