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Preparation of monolithic chelating adsorbent inside a syringe filter tip for solid phase microextraction of trace elements in natural water prior to their determination by ICP-MS

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ABSTRACT

A syringe-based sample pretreatment tool, named herein “tip-in chelating monolith”, has been developed for simple and facile solid phase microextraction (SPME) of trace elements in natural waters. The tip-in chelating monolith was directly prepared within the confines of a commercially available syringe filter tip by a two-step process: (1) in situ polymerization of a monomer solution consisting of 22.5% glycidyl methacrylate (GMA), 7.5% ethylene glycol dimethacrylate (EDMA), 35% 1-propanol, 28% 1,4-butanediol, and 7% water and (2) its subsequent modification with 1 mol L^{-1} of iminodiacetate solution (adjusted to pH 10) via ring-opening reaction of epoxide. The adsorption properties of the tip-in chelating monolith thus obtained were evaluated through an adsorption/desorption experiment, where the effects of sample solution pH and eluent on the SPME of trace metals and metalloids were systematically examined. Consequently, when sample solution pH was adjusted to 5.0 and 0.9 mL of 2 mol L^{-1} nitric acid was used as an eluent, good recoveries of more than 80% were obtained for 27 elements in a single-step extraction. The proposed SPME method was validated through the analysis of two river water certified reference materials (CRMs: JSAC 0301-1 and NMIJ 7201-a). After 50-fold preconcentration (from 50 mL of the original river water sample to 1.0 mL of final analysis solution), 22 trace elements including Ti, Fe, Co, Ni, Cu, Ga, Cd, Sn and REEs were quantitatively determined by inductively coupled plasma mass spectrometry (ICP-MS). The analytical detection limits were in the range from 0.000003 $\mu g\,L^{-1}$ for Ho to 0.18 $\mu g\,L^{-1}$ for Fe. Good agreement of the observed values with the certified or reference values indicates that the proposed SPME using the tip-in chelating monolith is practically applicable.

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1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has been accepted as the most powerful and sophisticated atomic spectrometric technique, because of its excellent features such as high sensitivity, wide dynamic range, and simultaneous multielement detection capability, and so on [1–3]. However, direct analysis of natural water samples by ICP-MS is still a difficult task, not only because the concentration levels of trace elements are quite low, but also because high salt matrix often interferes with their determination [4–10]. Thus, an enrichment/separation has become an essential part of spectrometric analysis, including solvent extraction [11,12], coprecipitation [13–15], and solid phase extraction (SPE) [16–24]. Among them, SPE on chelating resin has attracted the most attention due to its simplicity, high concentration factor, small sample requirement, and no need for harmful organic solvent, and has widely been used in both batch and column modes. This SPE technique has continued to undergo improvement, and recently syringe connected-minicolumn (SCM) method has emerged as a hybrid technique combining the characteristics of batch and column methods [25–27].

In chromatographic separation and purification, over the past several years, a single piece of porous material so-called “monolith” has gained popularity as an alternative to particle-packing configuration [28–31]. Due to the novel characteristics such as low-flow resistance, efficient mass transfer, and high reaction efficiency, their applications are now extended from the original separation media to extraction media and catalyst supports. Monoliths can be classified into two categories; silica-based and organic polymer-based monoliths, each with their own advantages and disadvantages. The major advantages of polymer-based monoliths include wide pH stability and less irreversible adsorption of biomolecules, and we have so far tried to prepare well-ordered

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porous polymer monoliths for high-throughput and high-efficiency separations [32–35].

Organic polymer monoliths have also the advantage of facile synthesis and modification, and they have great potential in solid phase microextraction (SPME) of trace elements (metals and metalloids) in natural water samples [36–39]. However, little work has been reported on the use of monolithic materials in such a chelating resin adsorption. In the present work, thus, the preparation of a monolithic adsorbent has been attempted for SCM-mode SPME. Glycidyl methacrylate (GMA), which has a reactive epoxy group for further derivatization, was copolymerized with ethylene glycol dimethacrylate (EDMA) inside a commercially available syringe filter tip. Subsequently, the epoxides at the monolith surface were reacted with one of the most popular chelating ligands, iminodiacetic acid (IDA) [40]. The SPME properties of the obtained chelating adsorbent "tip-in monolith" were evaluated through an adsorption–desorption experiment, where the effect of sample solution pH on the adsorption of a total of 53 elements was systematically examined. In addition, the accuracy of the proposed SCM-mode SPME tool and technique was tested by analyzing two river water certified reference materials (CRMs).

2. Experimental

2.1. Apparatus

A syringe filter tip for HPLC (model DISMIC-3JP from Advantec, Tokyo, Japan) was used as a vessel and chamber for SPME. A conventional Termo-syringe (Terumo Corporation, Tokyo, Japan) was used for loading the samples solution, rinsing the tip-in monolith with Milli-Q water, and eluting target metals with nitric acid. A model LC-10Ai pump (Shizuoka, Kyoto, Japan) was used for the measurement of pressure drop across the tip-in monolith. For parallel multi-sample pretreatment, a gravity-driven 8-port syringe pump was laboratory-made and used [42].

A high resolution ICP-SFMS instrument of model Finnigan Element 2 (Thermo Fisher Scientific, Bremen, Germany) equipped with a single collector and a concentric-type nebulizer (Conikal, AR35-1-FC1E, Glass Expansion Pty. Ltd., West Melbourne, Australia) was used for the measurement of trace elements. The operating conditions for ICP-SFMS are summarized in Table 1. An ICP-AES instrument of model IRIS intrepid II XPS DUO (Thermo Fisher Scientific) was also used for the measurement of high concentrations of elements. The morphology of GMA-based monoliths formed inside the filter tip was examined using a scanning electron microscope (model S-3000N, Hitachi High-Technologies Corporation, Tokyo, Japan).

Table 1
Operating conditions for the HR-ICP-MS instrument.

HR-ICP-MS Element 2	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16.0 L min^{-1}
Auxiliary gas flow rate	Ar 0.8 L min^{-1}
Carrier gas flow rate	Ar 0.9 L min^{-1}
Nebulizer:	Concentric-type
Sample uptake rate	0.2 mL min^{-1}
Data acquisition:	
Mass window	150%
Integration window	80%
Sampling points per peak	15 points
Integration times (runs × passes)	3 × 3 times

2.2. Chemicals

Glycidyl methacrylate, ethylene glycol dimethacrylate, and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Wako Pure Chemicals (Osaka Japan). Solvents (1-propanol, 1,4-butandiol, cyclohexanol, toluene) and inorganic salts (NaCl, Na_2CO_3, $Cu(NO_3)_2$) were also obtained from Wako Pure Chemicals. Iminodiacetic acid (IDA) was obtained from Sigma–Aldrich (Steinheim, Germany). Nitric acid, acetic acid and aqueous ammonia solution were of electronic industry grade from Kanto Chemicals (Tokyo, Japan). Multielement standard solutions for calibration were prepared from single-element standard stock solutions (1000 μg mL^{-1}) for atomic absorption spectrometry (Wako Pure Chemicals). Pure water used throughout the present experiment was prepared by a Milli-Q purification system of model Element A-10 (Nihon Millipore Kogyo). Two river water CRM samples, JSAC 0301-1 issued by the Japan Society for Analytical Chemistry and NMIJ 7201-a issued by the National Metrology Institute of Japan, were purchased from Tama Chemicals (Kawasaki, Japan) and Seishin Trading Co. Ltd., respectively.

2.3. Preparation of tip-in chelating monolith for SPME

The procedure for preparation of tip-in chelating monolith was almost the same as that for monolithic capillary column [33]. Briefly, GMA, EDMA and a porogenic solvent were mixed at an appropriate ratio in a bottle, into which AIBN (1 wt.% with respect to the amount of total monomers) was added. After stirring and degassing, an aliquot of the mixture was drawn into a syringe and was immediately poured into the gap space confined between the DISMIC-3JP filter tip and the syringe. The filter tip filled with the monomer solution was sealed with tape, and then was put into a water bath for thermal polymerization. After the polymerization was completed, the tip-in monolith was washed with ethanol and then pure water to remove any unreacted reagents. Subsequently, the coupling of IDA to the monolith surface was carried out by reacting with an aqueous sodium iminodiacetate solution. Schematic illustration of the tip-in monolith is shown in Fig. 1. As can be seen in Fig. 1, the diameter and length of the cylindrical monolithic adsorbent were 4 mm and 3–4 mm, respectively, and its volume was 40–50 μL (ca. 20 mg).

2.4. Measurement of chelating capacity

A chelating capacity of the tip-in monolith was estimated from the amount of Cu^{2+} adsorbed on the monolith in the following manner. First, a plenty amount (10 mL) of 0.5 mol L^{-1} $Cu(NO_3)_2$ aqueous solution (pH around 4.3) was passed through the tip-in monolith at a flow rate of 0.3 mL min^{-1}. Secondly, the tip-in monolith was rinsed with 10 mL pure water to eliminate Cu^{2+} ions remaining in the through-pores of the monolith. Thirdly, the Cu^{2+} ions adsorbed on the monolith were eluted with a plenty amount (5 mL) of 2 mol L^{-1} HNO_3. Finally, the concentration of Cu^{2+} in the eluate solution was measured by ICP-AES.

The chelating capacity was calculated from the following expression:

$$Q = \frac{C \times V}{W}$$

where Q (mmol g^{-1}) is the adsorption capacity of the chelating polymer, C (mmol L^{-1}) is the concentration of Cu^{2+} in the eluate. V (L) and W (g) are the volume of the eluate and the dry weight of chelating polymer monoliths, respectively.

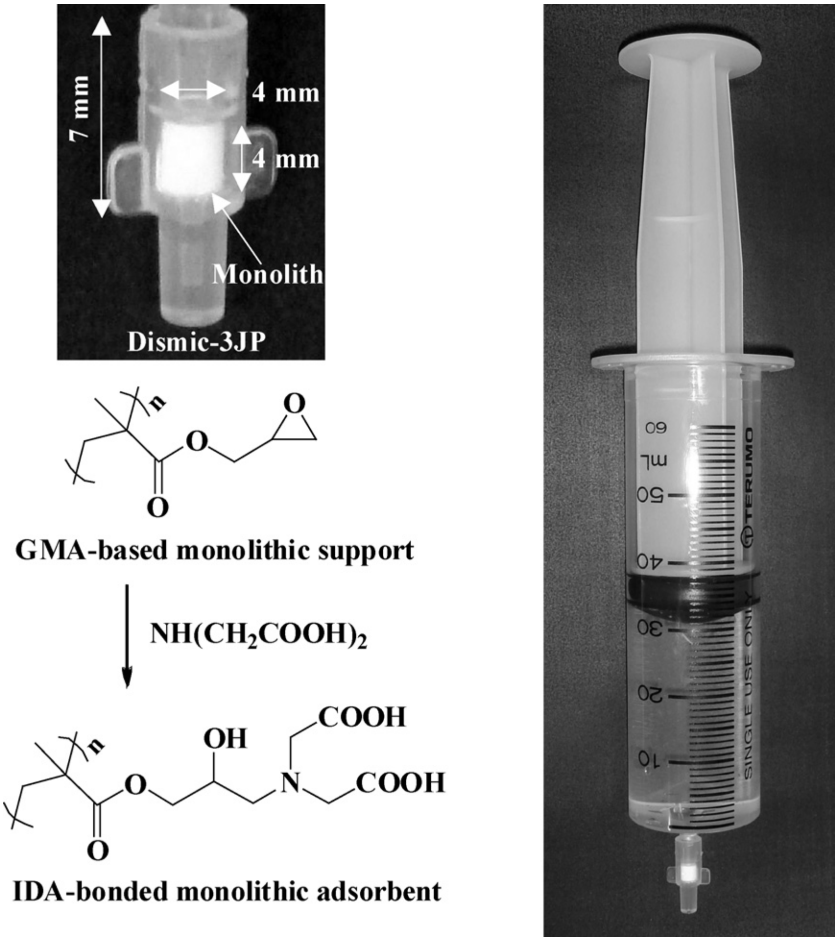

Fig. 1. Schematic illustration of tip-in chelating monolith.

Table 2
Composition of the test solution used for the addition-recovery experiment.

Element[a]	*m*/*z*	Amount spiked[b] ($\mu g L^{-1}$)	Element	*m*/*z*	Amount spiked[b] ($\mu g L^{-1}$)
Al [$Al(NO_3)_3$]	27	10	Te [$TeCl_4$]	125	0.1
Sc [$Sc(NO_3)_3$]	45	1	Cs [$CsNO_3$]	133	0.1
Ti [$Ti(SO_4)_2$]	47	1	Ba [$Ba(NO_3)_2$]	138	10
V [NH_4VO_3]	51	1	La [$La(NO_3)_3$]	139	0.1
Cr [$K_2Cr_2O_7$]	52	10	Ce [$Ce(NO_3)_3$]	140	0.1
Mn [$Mn(NO_3)_3$]	55	1	Pr [$Pr(NO_3)_3$]	141	0.1
Fe [$Fe(NO_3)_3$]	56	10	Nd [$Nd(NO_3)_3$]	143	0.1
Co [$Co(NO_3)_2$]	59	1	Sm [$Sm(NO_3)_3$]	147	0.1
Ni [$Ni(NO_3)_2$]	60	10	Eu [$Eu(NO_3)_3$]	151	0.1
Cu [$Cu(NO_3)_2$]	63	10	Gd [$Gd(NO_3)_3$]	157	0.1
Zn [$Zn(NO_3)_2$]	64	10	Tb [$Tb(NO_3)_3$]	159	0.1
Ga [$Ga(NO_3)_3$]	69	1	Dy [$Dy(NO_3)_3$]	163	0.1
As [As_2O_3]	75	1	Ho [$Ho(NO_3)_3$]	165	0.1
Rb [RbCl]	85	0.1	Er [$Er(NO_3)_3$]	167	0.1
Sr [$SrSO_4$]	88	10	Tm [$Tm(NO_3)_3$]	169	0.1
Se [SeO_2]	82	10	Yb [$Yb(NO_3)_3$]	172	0.1
Y [$Y(NO_3)_3$]	89	0.1	Lu [$Lu(NO_3)_3$]	175	0.1
Zr [$ZrO(NO_3)_2$]	91	1	Hf [$HfCl_4$]	178	1
Nb [NbF_5]	93	1	Ta [TaF_4]	181	1
Mo [$(NH_4)_6Mo_7O_{24}$]	95	10	W [Na_2WO_4]	182	10
Ru [$RuCl_3$]	99	0.1	Pt [H_2PtCl_6]	195	0.1
Rh [$RhCl_3$]	103	0.1	Au [AuCl]	197	0.1
Pd [$Pd(NO_3)_2$]	105	0.1	Pb [$Pb(NO_3)_2$]	208	1
Ag [$AgNO_3$]	109	1	Bi [$Bi(NO_3)_3$]	209	1
Cd [$Cd(NO_3)_2$]	111	1	Th [$Th(NO_3)_4$]	232	1
Sn [$SnCl_2$]	118	1	U [$UO_2(NO_3)_2$]	238	1
Sb [$SbCl_3$]	121	0.1			

[a] Chemical form of metal/metalloid in parenthesis denotes the reagent used for the element standard solution.
[b] The concentration in the final solution. Each element standard solution was added to 0.1 M HNO_3.

Table 3
Compositions of polymerization reaction mixtures and characteristics of the monoliths.

Tip-in monolith	Composition of monomers				Composition of porogenic solvent		Permeability[a] ($n = 3$)
	GMA	EDMA	%T	%C	C/T[b]	P/B/W[c]	
I	22.5	7.5	30	25	40:60, v/v	–	3.4 ± 0.4
II	22.5	7.5	30	25	50:50, v/v	–	3.2 ± 0.5
III	22.5	7.5	30	25	60:40, v/v	–	2.1 ± 0.4
IV	22.5	7.5	30	25	–	30:60:10, v/v	3.4 ± 0.3
V	22.5	7.5	30	25	–	40:50:10, v/v	3.0 ± 0.3
VI	22.5	7.5	30	25	–	50:40:10, v/v	2.7 ± 0.3
VII	22.5	7.5	30	25	–	60:30:10, v/v	2.2 ± 0.2

[a] Flow volume at 5 atm in Milli-Q water (mL min^{-1}).
[b] Cyclohexanol/toluene.
[c] 1-Propanol/1,4-butanediol/water.

2.5. *Procedure for SCM-mode SPME*

The effect of sample pH on the extraction of trace elements from water samples was examined through the following experiment. First, 50 mL of a pH-adjusted test solution containing 0.1, 1 or 10 μg L^{-1} each of metals and metalloids (as shown in Table 2) was loaded into the tip-in monolith at a flow rate of 0.3 mL min^{-1} by using a 50 mL-volume syringe. Then, 1 mL of Milli-Q water was passed through the monolithic adsorbent at a flow rate of 1 mL min^{-1} to reduce matrix elements (Na, K, Mg, Ca) remaining in the tip-in monolith. After that, trace metals and metalloids adsorbed on the monolith were eluted with 0.9 mL of 2 mol L^{-1} HNO_3 and collected in a test tube, into which 0.1 mL of internal standard solution (Ge, In, Re, and Tl; 10 μg L^{-1} each) was added to monitor the stability of signal intensities obtained by ICP-MS. Finally, the eluate solution was subjected to analysis by ICP-SFMS.

3. Results and discussion

3.1. *Effect of porogenic solvent on porous property of monolith*

Support material bearing reactive epoxide groups in its matrix permits further modification with functional molecules and/or ligands. To form such a reactive epoxide-containing polymer matrix, GMA was chosen and polymerized with EDMA as a cross-linker for forming a 3-dimensional network structure. In general, there are several parameters that influence the porous properties and the resulting extraction performance, including the type and concentration of porogenic solvent, polymerization temperature and time, and the percentage of cross-linker and initiator [34]. Among them, porogenic solvent in the polymerization mixture plays the most important role in monolithic morphology. Thus, the composition and ratio of porogenic solvent were first adjusted, taking into account the following points: low-flow resistance and high surface area. Low-flow-resistance monoliths are preferable to reduce working pressure as low as possible, making manual operation easy, but such highly permeable monoliths usually have low surface area and low adsorption capacity, leading to poor extraction performance. According to previous papers and our preliminary results, in the present paper, two kinds of porogenic solvents, (1) a ternary mixture of 1-propanol, 1,4-butanediol, and water (P/B/W) and a binary mixture of cyclohexanol and toluene (C/T) were examined, where total monomer concentration (%T) and the proportion of cross-linker (%C) were fixed at 30% (w/v) and 25% (w/w), respectively [33,34].

The recipes of the polymerization mixtures used in this experiment are summarized in Table 3. The permeability of each monolith given in Table 3 was evaluated by measuring the flow volume at a constant pressure of 5 atm across the monolith. As can be seen in Table 3, the flow volumes ranged from 2 to 4 mL min^{-1} at 5 atm. These results support that all the monoliths prepared can be easily operated by hand without need for high pressure. In terms of preparation reproducibility, the monoliths obtained from P/B/W ternary porogenic solvent were a little bit better than those from C/T binary porogenic solvent.

The relationships between the flow rate and the pressure drop were represented in Fig. 2 for the evaluation of mechanical strength of the monoliths. Linear relationship was observed between the flow rate and the pressure drop in the range of up to at least 10 atm. It was found that the produced monoliths have adequate mechanical strength for SPME. The SEM photos are also shown in Fig. 2. As in the case of monolithic columns for HPLC, heterogeneous polymer globules with diameters of 3–8 μm were observed, and the globules were interconnected to form a monolithic structure. As a result of the best balance of low-flow resistance, high surface area, and good preparation reproducibility, in the present paper, the ternary porogenic solvent of 1-propanol, 1,4-butandiol, and water at the volume ratio of 5:4:1 was selected and used for further experiments.

3.2. *Coupling of IDA to monolith surface*

Iminodiacetic acid is one of the most popular ligands with the ability to bind a variety of metal/metalloid ions [40]. Therefore, as the next step, the optimization of the coupling of IDA to GMA-based monolith was carried out. The scheme for covalent attaching of IDA to epoxy group is shown in Fig. 1.

The preparation of chelating monoliths with higher capacities is the most important subject. The chelating capacity is dependent on many parameters such as the IDA concentration, reaction pH, reaction temperature, and reaction time. In the present experiment, IDA concentration and reaction pH were optimized to obtain higher chelating capacity. The prepared IDA solution was filled into

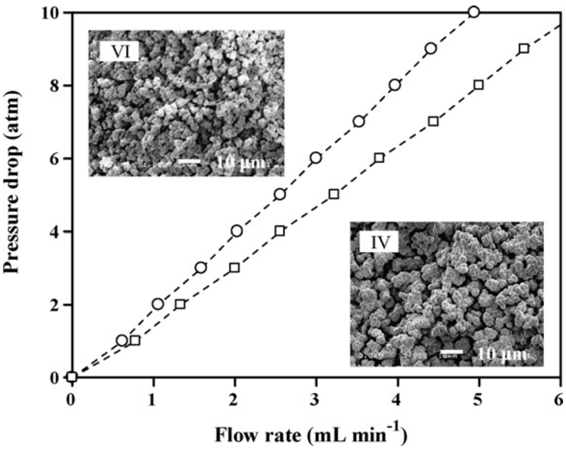

Fig. 2. Relationship between flow rate and pressure drop. (□) monolith IV; (○) monolith VI.

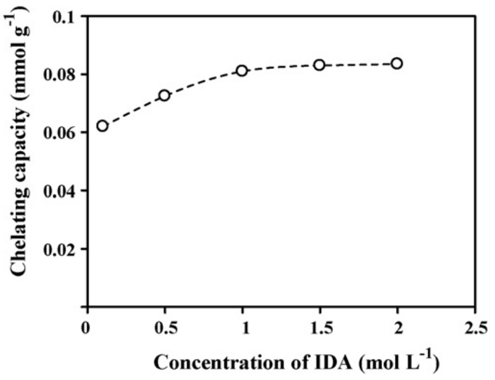

Fig. 3. Chelating capacity as a function of IDA concentration. Reaction time, temperature, and pH were fixed at 20 h, 80 °C, and 10, respectively.

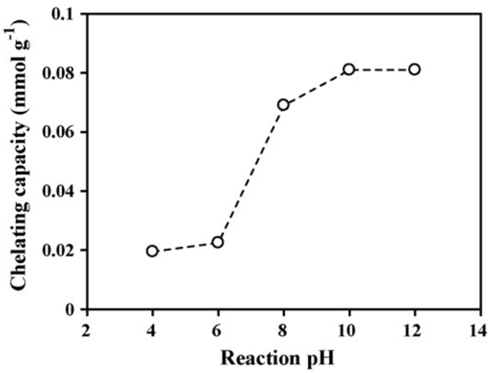

Fig. 4. Variation in chelating capacity with the ring-opening reaction pH of epoxide with IDA. IDA concentration, reaction time, and temperature were fixed at 1 M, 20 h, and 80 °C, respectively.

the flowthrough pores of the tip-in monolith. According to our preliminary experiments [32], reaction temperature and reaction time were set at 80 °C and 20 h, respectively. IDA modification solution was prepared by dissolving IDA and NaCl at a weight ratio of 5:1 into 50 mL of 2 M Na_2CO_3, and the solution pH was adjusted to the intended value with NaOH or HNO_3.

The effect of IDA concentration on the chelating capacity was first examined in the concentration range of 0.1–2 M. Fig. 3 shows the chelating capacity of the adsorbent as a function of the IDA concentration, where the reaction was carried out at pH 10. It was found that maximum chelating capacity could be obtained at IDA concentrations higher than 1 M. Fig. 4 shows the variation in the chelating capacity with the pH of the 1 M IDA solution. As the solution pH increased from 6 to more alkaline pH values, the capacity increased and reached maximum value of 0.082 mmol g^{-1} for Cu(II). According to these results, the optimum conditions of IDA concentration and reaction pH were found to be 1 M and pH 10, respectively.

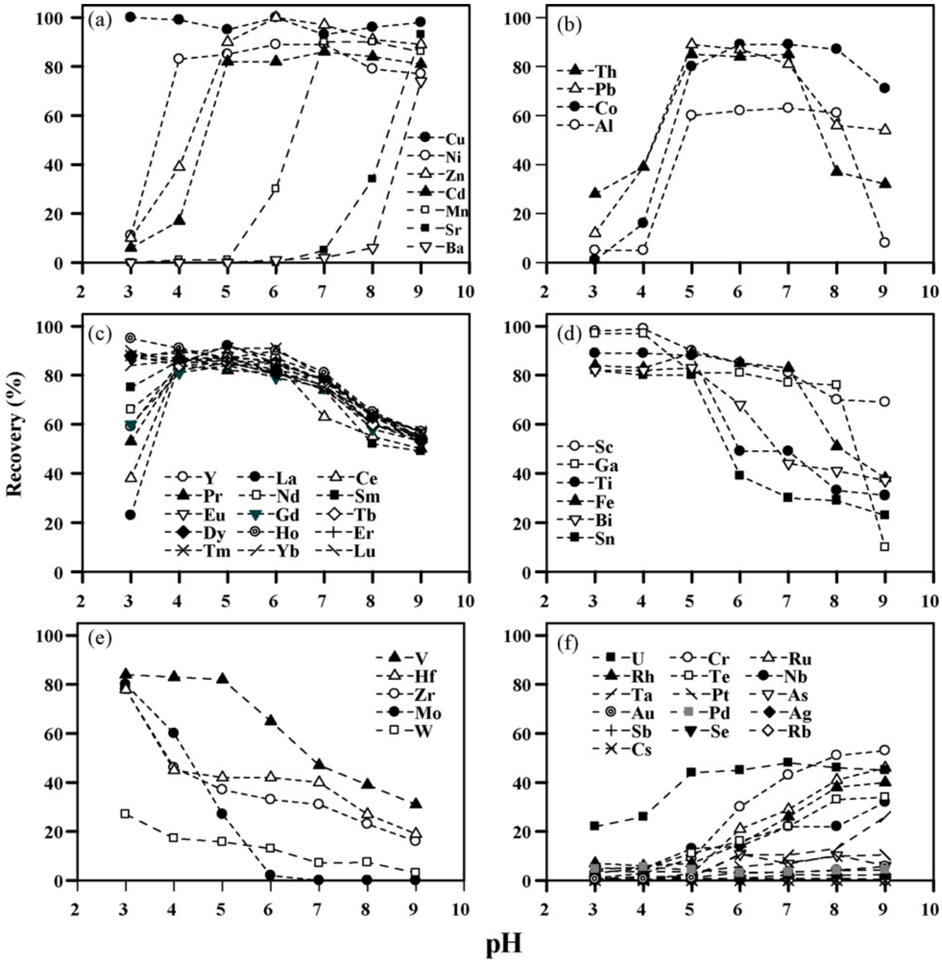

Fig. 5. pH-dependent recoveries for different metals and metalloids. (a) ●: Cu, ○: Ni, △: Zn, ▲: Cd, □: Mn, ■: Sr, ▽: Ba. (b) ▲: Th, △: Pb, ●: Co, ○: Al. (c) ○: Y, ●: La, △: Ce, ▲: Pr, □: Nd, ■: Sm, ▽: Eu, ▼: Gd, ◇: Tb, ◆: Dy, ◎: Ho, +: Er, ×: Tm,/: Yb, \: Lu. (d) ○: Sc, □: Ga, ●: Ti, ▲: Fe, ▽: Bi, ■: Sn. (e) ▲: V, △: Hf, ○: Zr, ●: Mo, □: W. (f) ■: U, ○: Cr, △: Ru, ▲: Rh, □: Te, ●: Nb,/: Ta, \: Pt, ▽: As, ◎: Au, ▨: Pd, ◆: Ag, +: Sb, ▼: Se, ◇: Rb, ×: Cs.

Table 4
Analytical figures of merit of the present method[a].

Element	*m*/*z*	Recovery at pH 5[b] (%)	Blank value[b] ($\mu g\,L^{-1}$)	Analytical detection limit[c] ($\mu g\,L^{-1}$)
Sc	45	89 ± 2	0.003 ± 0.0001	0.0003
Ti	47	93 ± 3	0.014 ± 0.001	0.003
Fe	56	89 ± 6	0.22 ± 0.06	0.18
Co	59	80 ± 5	0.0036 ± 0.0003	0.0009
Ni	60	83 ± 1	0.028 ± 0.002	0.006
Cu	63	86 ± 9	0.015 ± 0.005	0.015
Zn	64	85 ± 7	0.1 ± 0.03	0.09
Ga	69	84 ± 2	n.d.[d]	0.00001
Y	88	84 ± 1	0.00034 ± 0.00001	0.00003
Cd	111	96 ± 2	0.00074 ± 0.00003	0.00009
Sn	118	80 ± 4	0.0036 ± 0.0005	0.0015
La	139	92 ± 2	0.0043 ± 0.0003	0.0009
Ce	140	92 ± 1	0.0004 ± 0.00008	0.00024
Pr	141	89 ± 1	0.000033 ± 0.000005	0.000015
Nd	143	83 ± 1	<0.00009	0.000027
Sm	147	84 ± 1	<0.00004	0.000012
Eu	151	86 ± 4	<0.00003	0.000009
Gd	157	83 ± 4	<0.00005	0.000015
Tb	159	86 ± 1	<0.00003	0.000009
Dy	163	83 ± 2	<0.00004	0.000012
Ho	165	88 ± 1	0.000013 ± 0.000001	0.000003
Er	167	81 ± 2	<0.00004	0.000012
Tm	169	91 ± 1	0.000016 ± 0.000003	0.000009
Yb	172	90 ± 2	0.000097 ± 0.000009	0.000027
Lu	175	92 ± 1	<0.00004	0.000012
Pb	208	97 ± 2	0.017 ± 0.002	0.006
Bi	209	84 ± 4	0.0003 ± 0.00004	0.00012

[a] Multielement preconcentration (50-fold) at pH 5 followed by ICP-SFMS measurement.

[b] Mean value ± standard deviation, $n = 3$.

[c] Equivalent concentration to 3-fold standard deviation of blank value. When the blank was not quantitatable, the ADLs were calculated from the instrumental detection limits, considering the preconcentration factor and the recovery values.

[d] Not detected.

3.3. Effects of sample solution pH and eluent on recoveries of trace metals and metalloids

For SPME of metals and metalloids by the IDA-bonded chelating monolith, sample solution pH and eluent were optimized. In order to obtain higher concentration factors, firstly, minimum requirement of the eluent was examined. Referring to previously reported data [41–43], nitric acid was used as an eluent, and the recovery of Cu^{2+} from the tip-in monolith was measured at different eluent conditions. It was found from the experiment that over 85% of Cu^{2+} adsorbed on the monolith was eluted only with 0.5 mL of 2 M HNO_3, and that the adsorbed Cu^{2+} was almost completely (more than 95%) recovered under the elution condition of 0.9 mL of 2 M HNO_3. Thus, 0.9 mL of 2 M HNO_3 was used for subsequent studies.

Sample solution pH has significantly influenced both the chemical forms of ligand (IDA) and analytes (metals/metalloids) and the resulting adsorption of trace elements on the chelating monolith. Then, the effect of sample pH on the recoveries for different elements was systematically examined in the range of pH 3 to pH 9. For the addition-recovery (adsorption–elution) experiment, a test solution shown in Table 2 was prepared and employed. The solution pH was adjusted to the intended value just before use.

The pH-dependent recoveries for 53 elements are summarized in Fig. 5. As can be seen in Fig. 5, the IDA-bonded chelating monolith provided different recovery characteristics for each element. The recovery characteristics were generally in good agreement with those obtained with commercially available Chelex-100 resin, because which has the same IDA groups in a styrene–divinylbenzene matrix. From the result, it was found that a useful IDA-type chelating resin can be home-made from raw materials easily and at a low cost by using the proposed monolithic column technique (in situ polymerization and modification technique).

In general, IDA–metal complex has higher stability constant at higher pH values, and then it is expected that the recovery (adsorption) would be enhanced by increasing the sample pH. But, at pH values higher than 5, the hydrolysis of metals may have an adverse effect on their recoveries. Thus, maximum recoveries were obtained in the pH range of 4–6 for large majority of transition metals. In the case of some elements such as V, Mo, W, Hf, and Zr, higher recoveries were obtained at the lower pH, and their recoveries exceeded 80% at pH 3. The recoveries for several elements such as Au, Pd, As, Ag, Sb, Se, Rb and Cs were poor and did not exceed 30% in the pH range examined. The recoveries are strongly dependent on the chemical form in the sample, and now a more detailed examination is in progress.

3.4. Application to analysis of river water samples

As can be seen in Fig. 5, the chelating monolith provides highest recoveries for most of the metals at pH 5. Thus, further experiments were carried out using samples adjusted to pH 5. Trace metals adequately recovered from the chelating monolith at pH 5 are summarized in Table 4. Good recoveries exceeding 80% were obtained for 27 elements including REEs, Ti, Fe, Co, Ni, Cu, Zn, Ga, Cd, Sn, Pb and Bi in a single-step extraction. In Table 4, analytical detection limits and blank values are also represented. As a result of the combination with 50-fold preconcentration, quite low analytical detection limits could be achieved, ranging from 0.000003 $\mu g\,L^{-1}$ for Ho to 0.18 $\mu g\,L^{-1}$ for Fe. On the other hand, significantly high blank values were observed for some metals such as Zn, Ni, Cu, and Pb.

In order to validate the SPME using the IDA-bonded methacrylate monolith, two river water CRMs, JSAC 0301-1 and NMIJ 7201-a, were analyzed. For this experiment, 50 mL of the river water sample was passed through the tip-in monolith. The elements adsorbed on the monolith were eluted with 0.9 mL of 2 M HNO_3, and into which

Table 5
Analytical results for trace metals in CRMs (JSAC 0301-1 and NMIJ 7201-a).

Element	m/z	JSAC 0301-1 ($\mu g\,L^{-1}$)		NMIJ 7201-a ($\mu g\,L^{-1}$)	
		Observed value[a]	Certified or reference[b] value	Observed value[a]	Certified value
Sc	45	(0.0036 ± 0.0002)[c]	0.0025[b] ± 0.0002	(0.0042 ± 0.0001)[c]	
Ti	47	0.152 ± 0.011	0.148[b] ± 0.005	0.072 ± 0.008	
Fe	56	4.2 ± 1.4	4.7 ± 0.3	2.04 ± 0.12	2.02 ± 0.14
Co	59	0.0078 ± 0.0005	0.0080[b] ± 0.0003	0.004 ± 0.001	
Ni	60	0.036 ± 0.002	0.032[b] ± 0.002	0.047 ± 0.004	0.048 ± 0.002
Cu	63	0.49 ± 0.01	0.57 ± 0.07	0.130 ± 0.002	0.137 ± 0.015
Zn	64	(0.22 ± 0.04)[c]	0.19 ± 0.03	(0.278 ± 0.065)[c]	0.294 ± 0.013
Ga	69	0.015 ± 0.001	0.013[b] ± 0.003	0.0018 ± 0.0001	
Y	88	0.0042 ± 0.0003	0.0041[b] ± 0.0001	0.0074 ± 0.0002	
Cd	111	0.0023 ± 0.0007	0.0023 ± 0.0007	0.0020 ± 0.0004	0.0018 ± 0.0002
Sn	118	0.0057 ± 0.0009	0.0060[b] ± 0.0030	0.0132 ± 0.0006	
La	139	(0.00316 ± 0.00020)[c]	0.00090[b] ± 0.00003	(0.015 ± 0.008)[c]	
Ce	140	0.00148 ± 0.00008	0.00112[b] ± 0.00006	0.0058 ± 0.0002	
Pr	141	0.00029 ± 0.00001	0.00025[b] ± 0.00002	0.00167 ± 0.00007	
Nd	143	0.00155 ± 0.00010	0.00147[b] ± 0.00008	0.0065 ± 0.0002	
Sm	147	0.00041 ± 0.00003	0.00039[b] ± 0.00006	0.00124 ± 0.00002	
Eu	151	0.00015 ± 0.00002	0.00013[b] ± 0.00002	0.000338 ± 0.000007	
Gd	157	0.00067 ± 0.00004	0.00056[b] ± 0.00004	0.00186 ± 0.00004	
Tb	159	0.000084 ± 0.000006	0.000076[b] ± 0.000008	0.000204 ± 0.000005	
Dy	163	0.00061 ± 0.00002	0.00059[b] ± 0.00002	0.00104 ± 0.00003	
Ho	165	0.00016 ± 0.00001	0.00014[b] ± 0.00001	0.00024 ± 0.00001	
Er	167	0.00063 ± 0.00003	0.00053[b] ± 0.00001	0.00071 ± 0.00007	
Tm	169	0.000115 ± 0.000007	0.000080[b] ± 0.000006	0.000110 ± 0.000004	
Yb	172	0.00086 ± 0.00003	0.00068[b] ± 0.00006	0.00074 ± 0.00005	
Lu	175	0.000226 ± 0.000008	0.000186[b] ± 0.000003	0.000129 ± 0.000002	
Pb	208	(0.018 ± 0.006)[c]	0.005	(0.0264 ± 0.0039)[c]	0.0063 ± 0.0008
Bi	209	(0.000455 ± 0.000114)[c]	0.000053[b] ± 0.000009	(0.00127 ± 0.00007)[c]	

[a] Mean ± standard deviation, $n = 3$. The analytical result of each element was corrected with its recovery.
[b] Reference [42].
[c] The value in the parentheses was close to the blank value.

0.1 mL of internal standard solution was added, resulting in concentration factor of 50. The analytical results for metals in the river water CRMs are given in Table 5. As can be seen, the observed values, which were corrected with their recoveries, were consistent with certified or information values, and it was confirmed that the produced tip-in monolith could be practically used for SPME.

4. Conclusion

A syringe filter tip fitted with a monolithic chelating adsorbent, tip-in chelating monolith, was prepared by in situ copolymerization of GMA and EDMA in the presence of a ternary porogenic solvent of 1-propanol, 1,4-butanediol, water and subsequent modification with IDA via epoxide opening reaction. Extraction conditions were optimized to measure as many trace elements as possible with a minimum effort required for sample preparation. As a result, adequate recoveries exceeding 80% were obtained for 27 elements at pH 5. The proposed SPME method using IDA-bonded methacrylate monolith can be successfully applied to simultaneous determination of transition and rare-earth metals in river water samples by ICP-MS.

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