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Application of chitosan functionalized with 3,4-dihydroxy benzoic acid moiety for on-line preconcentration and determination of trace elements in water samples

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Abstract

Chitosan resin functionalized with 3,4-dihydroxy benzoic acid moiety (CCTS-DHBA resin) was used as a packing material for flow injection (FI) on-line mini-column preconcentration in combination with inductively coupled plasma-atomic emission spectrometry (ICP-AES) detection for the determination of trace elements, such as silver, bismuth, copper, gallium, indium, molybdenum, nickel, uranium, and vanadium in environmental waters. In this system, a 5-mL aliquot of sample (pH 5.5) was introduced to the minicolumn for the adsorption/preconcentration of the metal ions, and the collected analytes on the mini-column was eluted with 2 M HNO₃, and the eluates was subsequently transported via direct injection to the nebulizer of ICP-AES for quantification. The parameters affecting on the sensitivity, such as sample pH, sample flow rate, eluent concentration, and eluent flow rate, were carefully examined. Alkali and alkaline earth metal ions commonly existing in river water and seawater did not affect on the analysis of metals in the present method. Under the optimum conditions, the proposed method allowed the determination of metal ions with the detection limits of 0.08 ng mL⁻¹ (Ag), 0.9 ng mL⁻¹ (Bi), 0.07 ng mL⁻¹ (Cu), 0.9 ng mL⁻¹ (Ga),

0.9 ng mL⁻¹ (In), 0.08 ng mL⁻¹ (Mo), 0.09 ng mL⁻¹ (Ni), 0.9 ng mL⁻¹ (U), and 0.08 ng mL⁻¹ (V). By using 5 ml of sample solution, the enrichment factor and collection efficiency were found in the range of 8-12 fold and 96-102 %, respectively, whereas the sample throughput was 7 samples/ hour. The proposed method was validated by determining metal ions in standard reference materials of river water (SLRS-4) and nearshore seawater (CASS-4), and its applicability was further demonstrated to river water and seawater samples.

Keywords: Flow injection, chitosan resin, on-line preconcentration, 3,4-dihydroxy benzoic acid, ICP-AES

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Introduction

Flow-injection (FI) in combination with on-line preconcentration/separation techniques has been increasingly popular for simultaneous determination of trace metal ions in industrial and environmental samples using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Compared to batchwise preconcentration method, this technique provides some advantages, such as low sample and reagent consumption, rapid analysis as well as increasing sample throughput, and better measurement reproducibility. Moreover, requirements on the laboratory environment for trace analysis are much less stringent.

The use of solid phase extraction (SPE) materials utilized as an on-line column preconcentration unit has been receiving considerable attention during recent years. Solid phase extraction (SPE) offers high enrichment factors, rapid phase separation of interferent ions, high efficiency and rate of process, and the ability of combination with different detection techniques [1]. SPE applied to on-line preconcentration and separation system

usually is packed in mini-column, which includes nanometer-sized alumina [2], chelating resin [3-5], silica gel [6-7], alumina and its modification [8-9], functionalized polyurethane foam [10], metal oxide [11], and polytetrafluoroethylene fiber [12].

The use of biomass and its modification as solid phase extraction material has been becoming favorable because of its typical properties: availability, mechanical strength, high porosity, hydrophilicity and chemical reactivity in functionalizations. Rice husk modified with NaOH has been reported as a solid adsorbent for on-line preconcentration of cadmium and lead coupled with flame atomic absorption spectrometry [13]. Suvaradhan *et. al* [14] studied *Borassus flabellifer* inflorescence (BFI) loaded with 2-propylpiperidine-1-carbodithioate and its application to on-line determination of Cu, Mn, Pb, Cd, Co, Cr, and Zn. In this method, the collected elements were eluted with 0.4 M HNO₃ before measurement by ICP-AES. Although the method provides high collection efficiency (98-100%) and excellent detection limit (LOD: pg mL⁻¹ – several ten pg mL⁻¹) of the target elements, however, the modified BFI can be used for only four cycles, which is inconvenient from practical view point. Cross-linked chitosan functionalized with 8-hydroxyquinoline [15] has been applied to on-line preconcentration of cadmium and copper in water samples. The metal ions in the samples were previously enriched in a mini-column followed by their determination using flow-injection coupled with FAAS. The detection limits of 0.1 ng mL⁻¹ (Cu) and 0.4 ng mL⁻¹ (Cd) were achieved. However, since the column preconcentration unit is operated at alkaline region (pH 10 for Cu), the formation of insoluble hydroxide species of the metals seem to be not avoided, which may result in poor reproducibility. In our previous work [16], the cross-linked chitosan (CCTS) was chemically modified by attaching carboxylic group of 3,4-dihydroxy benzoic acid moiety (DHBA) to the amino group of chitosan through amide-bond formation (CCTS-DHBA resin). A complete removal of large amounts of alkali and alkaline earth matrices in water samples without any loss of adsorption

efficiency over prolonged usage were attributed to this resin. The CCTS-DHBA resin was applied to collection/concentration of uranium at pH 3 in batch-wise method. Since it is operated in batch-wise method, the large volume of solutions, time-consuming, and stringent environment control during experiment could not be avoided. Moreover, the resin can be used for the collection/preconcentration of simultaneous metal ions when higher pH solution is applied.

Therefore, to overcome such main drawback mentioned above, in this work, the CCTS-DHBA resin was packed in mini-column and utilized as an on-line preconcentration unit coupled with flow injection (FI)-inductively coupled plasma-atomic emission spectrometry (ICP-AES). At slightly acidic regions, Ag, Bi, Cu, Ga, In, Mo, Ni, U, and V could be adsorbed almost completely on the resin [16]. Then, pH 5.5 was selected to allow collection/concentration and simultaneous determination of these elements in river water and seawater samples. This system provides good on-line collection efficiency, as well as, the separation of the analytes from commonly existing matrices in the water samples. The detections limits (LODs) of the proposed method were much improved in comparison with LODs obtained by direct measurement of ICP-AES. Experimental variables considered as factors for improving sensitivity, such as eluent concentration, sample and eluent flow rate, pH of sample were carefully optimized.

Experimental

Apparatus

The ICP-AES system (Vista Pro, Seiko Instrument, Chiba, Japan, www.sii.co.jp) was used for the measurement of the analytes. The operating conditions of ICP-AES were summarized in Table 1. The ICP-AES was coupled with a FIA system (OG-V3-P2) developed by Motomizu and Higuchi of Ogawa & Co., Ltd, Japan, which consists of two peristaltic pumps,

three 6-way valves, and a touch-screen monitor for setting the program to allows automated-control of all flow injection procedures.

(Please place Table 1 here)

A mini-column was prepared from commercially available line filter (6 mm i.d x 4 mm length) purchased from GL Sciences Inc. ([Tokyo, Japan, www.gls.co.jp](http://www.gls.co.jp)). A supporter-filter in the line filter was removed, and the space was used for packing CCTS-DHBA resin (20 mg). This column was equipped with the plugs of quartz wool at both ends to keep CCTS-DHBA resin inside the column. The PTFE tubing (0.5 mm i.d.) was used for assembling all flow lines.

Reagents and Materials

Analytical multielement standard solutions were prepared by the accurate dilution of a mixed stock solution containing 10 $\mu\text{g mL}^{-1}$ metal ions for ICP-MS ([XSTC-13, Spex CertiPrep, NJ, USA, www.spexcsp.com](http://www.spexcsp.com)). The XSTC-13 containing 31 elements of Th, Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, V, Zn, U, and Hg. Another standard solution, Mo, was prepared by accurate dilution of single-element stock solution (1000 $\mu\text{g mL}^{-1}$) for AAS ([Wako Pure Chemical, Osaka, Japan, www.wako-chem.co.jp](http://www.wako-chem.co.jp)). The mixed standard solutions were then adjusted to desired concentration and pH before introduced to FI system.

Acetic acid (minimum 96 %) and ammonia water (29 %) used for the preparation of ammonium acetate buffer were of an electronic industrial reagent grade ([Kanto Chemicals, Tokyo, Japan, www.kanto.co.jp](http://www.kanto.co.jp)). This solution was used for adjusting pH from 3-9. Diluted ultrapure grade nitric acid (60 %, density 1.38 g mL^{-1} , Kanto Chemicals, Tokyo, Japan) was used for adjusting pH 1-2 of the samples. Ultrapure water (18.3 $\text{M}\Omega\text{ cm}^{-1}$ resistivity) prepared

by an Elix 3/Milli-Q Element system ([Nihon Millipore, Tokyo, Japan, www.millipore.com](http://www.millipore.com)) was used throughout.

The standard reference material of river water (SLRS-4) and nearshore seawater (CASS-4) were provided by National Research Council Canada (NRCC). The CCTS-DHBA resin was clean up by stirring it at low speed for 6 h in 2 M nitric acid followed by washing with ultrapure water before being packed in mini-column as on-line preconcentration unit.

Operational procedures for on-line preconcentration coupled with FI-ICP-AES system

The schematic diagram for on-line preconcentration coupled with FI-ICP-AES system employed in this work was shown in Fig. 1. The preconcentration procedures involve the conditioning step, in which the CCTS-DHBA resin in the mini-column was conditioned with 2 mL of 0.5 M ammonium acetate solution (pH 5.5) for 2 min, followed by the collection step: Five milliliters of samples containing analytes (pH 5.5) were automatically passed through the mini-column for collection/concentration of analytes for 5 min. After the collection step, the valve V1 was switched to introduce 1 mL of 0.5 M ammonium acetate solution (pH 5.5) for 1 min to wash the column as well as removing analytes remaining in the tubing of the flow system. The collected analytes were then eluted with 0.5 mL of 2 M nitric acid (flow rate of 1.5 mL min⁻¹) by switching the valve V2 to an inject position. The analyte zones eluted from the column were introduced to ICP-AES for their measurement. The signals of elements obtained from the ICP-AES by using time scan mode measurement were transferred to Microcal Origin software, where the flow signals were graphically plotted and the peak height was used as the analytical signal.

(Please place Figure 1 here)

Results and discussion

Factors affecting the collection/preconcentration of analytes

Several factors affecting to the collection/preconcentration of analytes involving sample pH and sample loading flow rate were examined. Among these factors, the pH of sample solution is the most important parameter for the effective collection and preconcentration of analytes.

Effect of sample pH on the collection of analytes was examined in the pH range of 1-9 by using 10 ng mL⁻¹ each analyte. According to the results shown in Fig. 2, the maximum collection efficiency of analytes indicated as the highest peak height was found at pH 5-7 (Ag), pH 1-9 (Bi), pH 5-9 (Cu, In, Ni), pH 4-6 (Mo), pH 3-9 (Ga, U), and pH 3-8 (V): pH 5.5 was selected as an optimum condition for further experiment to allow simultaneous preconcentration and determination of Ag, Bi, Cu, In, Ni, Ga, Mo, U, and V.

(Please place Figure 2 here)

Faster sample flow rate and higher adsorption yield are desired in preconcentration experiments from the view point of a higher preconcentration factor in a shorter time. However, the kinetics of the adsorption may limit the flow rate, at which the sample is flowed through the resin. In this study the effect of sample flow rate was examined in the range of 0.5-1.5 mL min⁻¹. The peak heights of Ag, Mo, and Ni decreased with an increase in sample flow rate, whereas the peak heights of Bi, Cu, Ga, In, U, and V were almost identical with an increase in sample flow rate up to 1.2 mL min⁻¹. As a compromise to the collection efficiency and analysis time of all analytes, a sample flow rate of 1 mL min⁻¹ was selected as an optimum condition.

Factor affecting the elution of analytes

Nitric acid (HNO₃) was used as an eluent throughout the experiments. The concentration of

HNO₃ on the elution of analytes collected on the column was examined in the range of 0.5-2.0 M. Silver can be eluted completely by using 1 M HNO₃, whereas other elements (Bi, Cu, Ga, In, Mo, Ni, U, and V) were completely eluted by using 1.5 – 2 M HNO₃. Such results indicated that the adsorption of silver is the weakest of all elements examined. From these results, 2 M HNO₃ was chosen for the complete elution of analytes.

The effect of the eluent (2 HNO₃) flow rate was examined from 0.5 - 1.5 mL min⁻¹. The higher flow rate resulted in the higher peak intensity of Ag, Bi, Cu, Ga, In, Mo, Ni, U, and V due to the less dispersion of analytes. However, we could not examine at the flow rate of more than 1.5 mL min⁻¹ due to the limitation of peristaltic pump used in the FI system. Therefore, the flow rate of 1.5 mL min⁻¹ was selected as an optimum condition.

The volume of the eluent (2 M HNO₃) was examined from 0.25 – 2 mL. The peak height of analytes increased with an increase in the eluent volume from 0.25-0.5 mL, whereas the peak heights tend to constant when the volumes of eluent were 0.5-2 mL, which indicated the complete elution of the analytes. Therefore, the eluent volume of 0.5 mL was selected with regard to shorter analysis time, as well as to decrease acid consumption.

The optimized flow injection (FI) on-line preconcentration parameters were summarized in Table 2. Under these optimum conditions, the analysis time of 1 sample was 8.3 min when 5 mL of sample was used.

(Please place Table 2 here)

Analytical properties of merits

In order to evaluate the performance of the proposed method, the linearity of calibration graph in the presence and the absence of matrices were examined. The enrichment factor, collection efficiency, and detection limits were studied, and an assessment of the accuracy and repeatability were also examined.

The matrices, such as Na, K, Mg and Ca, which are present in river water and especially in seawater samples, can cause a variety of problems and make direct determination of trace metals by ICP-AES difficult. Therefore, in this study the effect of matrices on the linearity of the calibration graphs, which was constructed from 0 to 5 ng mL⁻¹ of each element (pH 5.5), was investigated. As shown in Table 3, the calibration graphs with and without the addition of artificial river and seawater matrices resulted in similar slope for all analytes. This demonstrates that the column pre-treatment by using CCTS-DHBA resin was very efficient for collecting the analytes quantitatively, and effectively separating them from common potentially interfering matrix constituents, such as alkali and alkaline earth metal ions. Such results indicated that the CCTS-DHBA resin as solid phase extractant is better than commercially available iminodiacetate-based resins, i.e. Muromac A-1, and Chelex 100. These commercial resins were accompanied by two major drawbacks [17-20], such as (1) major matrices mainly calcium and magnesium could be retained by the resins causing matrix interference in the determination of trace elements by atomic spectrometry, and (2) the resins undergo a drastic volume change with the changes in pH solution and ionic composition. These drawbacks were not found in the CCTS-DHBA resin.

(Please place Table 3 here)

The enrichment factor and collection efficiency were investigated under optimum conditions. The enrichment factor was calculated by comparing the peak height of flow signal obtained with and without the column preconcentration unit. The volume of samples introduced to the flow system was 5 mL of 5 ng mL⁻¹ each analyte, whereas a collection efficiency was calculated by comparing the peak height of 0.5 mL of 50 ng mL⁻¹ each analyte obtained without the column with the peak height for 5 mL of 5 ng mL⁻¹ each analyte obtained after column preconcentration (eluent volume: 0.5 mL of 2 M HNO₃). The detection

limits (LOD) of all analytes were determined by the signal to noise ratio ($S/N = 3$). The summary of the results for enrichment factor, collection efficiency and LOD of analytes were given in Table 4, and the example of flow signals were shown in Fig. 3. As shown in Table 4, LOD of the proposed method was much improved compared with LOD of ICP-AES without column preconcentration unit (direct aspiration).

(Please place Table 4 here)

(Please place Figure 3 here)

The reproducibility of peak heights was examined by using 1 ng mL^{-1} of each element. The results showed that the peak height did not change significantly with relative standard deviation was in the range of 0.5 – 4% ($n=15$). Such results indicated that the collection efficiency of the resin toward target elements was very good. Since the resin, which was packed in min-column, can be used continuously from the initial to the end of the experiment, it resembles that no loss of collection efficiency of the CCTS-DHBA resin after prolonged usage.

Our proposed method, in comparison with other flow injection (FI) on-line preconcentration coupled with ICP-AES methods previously reported, shows some difference features. The detection limits that are obtained in our method are higher than other FI-ICP-AES method [7, 21]. However, it should be taken into account that our method provides much simpler procedures, excellent removal of high background matrices like seawater, not use organic solvent, and lower sample consumption. The method proposed by Karami et al [7] requires a 250 mL sample volume to achieve LOD at several pg mL^{-1} levels. The procedure is somewhat complicated since the analytes must be reacted with chelating agent to form complex before passing through the column preconcentration unit, and the use of organic solvent (methanol) as eluent could not be avoided. Although the method is very

sensitive, however, its application to the determination of trace elements in water sample was in several ng mL⁻¹ levels, which can also be detected by our proposed method. The method proposed by Vassileva et al [21] requires a 100 mL, and the LOD achieved was 6-90 pg mL⁻¹. However, approximately 33 min is necessary for analyzing only one sample. It also seems that the precipitation of the most metal ions determined could not be avoided, since this method is employed at pH 8. In addition this method suffered from high blank value.

Analysis of river water and seawater samples

The precision and accuracy of the proposed method, based on the on-line column pretreatment with ICP-AES detection, were evaluated by analyzing certified reference material (CRM) of river water (SLRS-4) and nearshore seawater (CASS-4). Three replicate analyses were performed for each CRM sample. The analytical results for Ag, Bi, Cu, Ga, In, Mo, Ni, U, and V in CRM obtained by the proposed method are summarized in Table 5. The results obtained by the proposed method, such as Cu, Mo, Ni, V in SLRS-4 and Cu, Mo, Ni, U, V in CASS-4, were in good agreement with the certified values. The concentrations of some of elements could not be detected because their concentrations were below LODs of this method. It is possible, that the larger volumes of samples will improve the LODs, although the analysis time will increase substantially.

(Please place Table 5 here)

The applicability and robustness of the proposed method were further demonstrated by the determination of trace elements in environmental river water and seawater samples. The results of the proposed method (FI on-line preconcentration coupled with ICP-AES detection) were compared with those obtained by off-line column pretreatment with ICP-MS detection as shown in Table 6. For off-line method, water sample (10 mL, pH 5.5) was passed through

the column containing CCTS-DHBA resin (1 mL wet volume; 0.2 g dry weight). After washing with buffer solution and water, the analytes were eluted with 10 mL of 1 M HNO₃ prior to measurement by ICP-MS.

(Please place Table 6 here)

In river water samples, some elements, such as Ag, Ga, and U, can not be detected using the proposed method. This is because such elements exist at very low levels and their concentrations are lower than the LODs. The elements that could be determined by the proposed method (Cu, Mo, Ni, and V) were comparable to those obtained by off-line ICP-MS method. However, both the proposed method and ICP-MS method could not detect In and Bi in the samples. Much more preconcentration is needed since these elements are present at extremely low levels.

In seawater samples, the results for most elements determined using proposed method, such as Ag, Cu, Mo, Ni, U, and V were in good agreement with the results obtained by off-line ICP-MS method. However, indium could not be detected using both the proposed method and also ICP-MS method.

Conclusions

The on-line preconcentration column packed with CCTS-DHBA resin coupled with flow-injection - ICP-AES detection system was found to be a versatile technique with considerable promise for the determination of Ag, Bi, Cu, Ga, In, Mo, Ni, U, and V in river water and seawater samples. Commonly existing matrices, such as alkali and alkaline earths metal ions, were successfully removed by employing CCTS-DHBA resin as solid phase extractant. The system is easy to construct and provide good collection efficiency and detection limits of the target elements.

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by on-line flow injection with inductively coupled plasma atomic emission spectrometry.

Fresenius J Anal Chem 370: 52

Table 1 Operating conditions of ICP-AES

Spectrometer	VISTA PRO
Plasma conditions	
RF power	40 MHz , 1.2 kW
Plasma gas flow rate (l min ⁻¹)	Ar 15.0
Auxiliary gas flow rate (l min ⁻¹)	Ar 1.50
Nebulizer gas flow rate (l min ⁻¹)	Ar 0.9
Spray chamber	Glass cyclonic spray chamber
Nebulizer	K-style concentric glass nebulizer
Torch	One-piece low flow extended torch in the axial view mode
Data acquisition	
Measurement mode	Time scan mode
Emission line (nm)	328.068 (Ag), 223.061 (Bi), 324.754 (Cu), 294.363 (Ga), 230.606 (In), 202.032 (Mo), 231.604 (Ni), 385.957 (U), 292.401 (V)

Table 2 Optimized conditions for flow injection (FI) on-line preconcentration system

Parameter	Range examined	Selected
pH of sample	pH 1-9	pH 5.5
Sample and buffer flow rate	0.5 - 1.5 mL min ⁻¹	1 mL min ⁻¹
Eluent concentration	0.5 - 2 M HNO ₃	2 M HNO ₃
Eluent flow rate (2M HNO ₃)	0.5 - 1.5 mL min ⁻¹	1.5 mL min ⁻¹
Eluent volume (2M HNO ₃)	0.25- 2 mL	0.5 mL
Preconcentration time	-	5 min
Sample throughput	-	7 samples/ hour

Table 3 Effect of matrix on the linearity of calibration graph

Elements	Calibration graph equations		
	Standard ¹	Artificial river water ²	Artificial seawater ³
Ag	$Y = 543.1X - 48.9, R^2 = 0.994$	$Y = 543.7X - 37.3, R^2 = 0.999$	$Y = 555.6X - 45.5, R^2 = 0.998$
Bi	$Y = 11.7X + 0.2, R^2 = 0.998$	$Y = 12.6X - 2.1, R^2 = 0.995$	$Y = 11.5X - 0.9, R^2 = 0.998$
Cu	$Y = 379.4X + 15.4, R^2 = 0.999$	$Y = 366.7X + 20.2, R^2 = 0.998$	$Y = 370.2X + 15.1, R^2 = 0.992$
Ga	$Y = 73.0X - 1.8, R^2 = 0.999$	$Y = 73.2X + 2.3, R^2 = 0.998$	$Y = 72.0X - 2.3, R^2 = 0.989$
In	$Y = 14.1X + 1.3, R^2 = 0.990$	$Y = 13.9X + 1.4, R^2 = 0.991$	$Y = 14.4X + 1.1, R^2 = 0.995$
Mo	$Y = 99.6X + 16.6, R^2 = 0.992$	$Y = 98.0X + 8.2, R^2 = 0.994$	$Y = 100.1X + 18.5, R^2 = 0.989$
Ni	$Y = 67.8X + 3.9, R^2 = 0.997$	$Y = 67.1X + 5.3, R^2 = 0.998$	$Y = 64.3X + 4.4, R^2 = 0.995$
U	$Y = 76.2X - 2.1, R^2 = 0.994$	$Y = 73.9X - 1.4, R^2 = 0.992$	$Y = 74.0X - 3.2, R^2 = 0.989$
V	$Y = 215.8X - 1.6, R^2 = 0.998$	$Y = 212.5X + 1.8, R^2 = 0.998$	$Y = 214.1X + 2.1, R^2 = 0.995$

¹ Standard solutions without addition of cation matrices;

² The cation matrices of Na, 20 $\mu\text{g mL}^{-1}$; K, 10 $\mu\text{g mL}^{-1}$; Mg, 15 $\mu\text{g mL}^{-1}$; Ca, 50 $\mu\text{g mL}^{-1}$, were added to the standard solutions;

³ The cation matrices of Na, 11500 $\mu\text{g mL}^{-1}$; K, 3900 $\mu\text{g mL}^{-1}$; Mg, 1200 $\mu\text{g mL}^{-1}$; Ca, 400 $\mu\text{g mL}^{-1}$, were added to the standard solutions.

Table 4 Enrichment factor, collection efficiency, and limit of detection (LOD)

Element	Enrichment factor	Collection efficiency, %	LOD, ng mL ⁻¹	
			FI-ICP-AES ¹	ICP-AES ²
Ag	8.3 ± 0.1	99 ± 2	0.08	0.8
Bi	8.4 ± 0.2	100 ± 3	0.9	11
Cu	9.4 ± 0.0	102 ± 1	0.07	2
Ga	8.2 ± 0.3	101 ± 2	0.9	8
In	10.6 ± 0.2	101 ± 4	0.9	10
Mo	8.4 ± 0.0	97 ± 1	0.08	3
Ni	11.8 ± 0.1	97 ± 0	0.09	2
U	8.4 ± 0.2	101 ± 2	0.9	10
V	8.8 ± 0.1	96 ± 0	0.08	1

¹ LOD of the proposed method, flow-injection on-line column preconcentration method coupled with ICP-AES;

² LOD of ICP-AES without column preconcentration unit (direct aspiration)

Table 5 Analytical results for the certified reference materials (CRMs)

Elements	SLRS-4 ¹		CASS-4 ²	
	Proposed method, ng mL ⁻¹	Certified, ng mL ⁻¹	Proposed method, ng mL ⁻¹	Certified, ng mL ⁻¹
Ag	< LOD	-	0.26 ± 0.03	-
Bi	< LOD	-	< LOD	-
Cu	1.84 ± 0.02	1.81 ± 0.08	0.57 ± 0.04	0.592 ± 0.055
Ga	< LOD	-	< LOD	-
In	< LOD	-	< LOD	-
Mo	0.22 ± 0.02	0.21 ± 0.02	8.88 ± 0.04	8.78 ± 0.86
Ni	0.67 ± 0.03	0.67 ± 0.08	0.30 ± 0.00	0.314 ± 0.030
U	< LOD	0.050 ± 0.003	3.31 ± 0.02	(3.0) ³
V	0.34 ± 0.02	0.32 ± 0.03	1.21 ± 0.09	1.18 ± 0.16

¹ Certified reference material for river water (National Research Council, Canada);

² Certified reference material for nearshore seawater (National Research Council, Canada);

³ Information only;

Samples volume: 5 mL (pH 5.5);

Samples were measured from average of three measurements

Table 6 Analytical results for the determination of trace elements in water samples

Elements	Found, ng mL ⁻¹							
	River water A ¹		River water B ²		Seawater A ³		Seawater B ⁴	
	Proposed method	ICP-MS ⁵	Proposed method	ICP-MS ⁵	Proposed method	ICP-MS ⁵	Proposed method	ICP-MS ⁵
Ag	< LOD	0.030 ± 0.002	< LOD	0.030 ± 0.001	0.45 ± 0.03	0.43 ± 0.03	0.38 ± 0.02	0.37 ± 0.01
Bi	< LOD	< LOD	< LOD	< LOD	< LOD	0.023 ± 0.000	< LOD	0.018 ± 0.001
Cu	1.58 ± 0.10	1.56 ± 0.03	2.60 ± 0.17	2.65 ± 0.06	0.53 ± 0.05	0.58 ± 0.01	1.11 ± 0.06	1.19 ± 0.04
Ga	< LOD	0.086 ± 0.007	< LOD	0.084 ± 0.005	< LOD	0.034 ± 0.002	< LOD	0.051 ± 0.004
In	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Mo	0.82 ± 0.01	0.84 ± 0.05	0.95 ± 0.04	0.95 ± 0.08	9.03 ± 0.15	9.10 ± 0.04	6.20 ± 0.11	6.14 ± 0.02
Ni	0.54 ± 0.05	0.57 ± 0.03	0.45 ± 0.04	0.49 ± 0.04	0.31 ± 0.03	0.33 ± 0.01	0.27 ± 0.00	0.30 ± 0.02
U	< LOD	0.045 ± 0.002	< LOD	0.044 ± 0.004	2.85 ± 0.15	2.93 ± 0.13	2.36 ± 0.16	2.23 ± 0.18
V	1.24 ± 0.03	1.37 ± 0.04	0.72 ± 0.05	0.77 ± 0.01	1.50 ± 0.03	1.54 ± 0.06	1.29 ± 0.04	1.34 ± 0.06

¹ Water sample was sampled at Asahi River located in Okayama City, Japan;

² Water sample was sampled at Zasu River located in Okayama City, Japan;

³ Water sample was sampled at Shibukawa Sea located in Okayama Prefecture, Japan

⁴ Water sample was sampled at Shin Okayama Port located in Okayama Prefecture, Japan

⁵ Water samples (pH 5.5, 10 mL) were passed through mini-column (off-line method) containing 1 mL CCTS-DHBA resin (0.2 g dry weight), then the collected elements were eluted with 10 mL of 1M HNO₃ before measurement by ICP-MS;

Samples volume: 5 mL (pH 5.5);

Samples were measured from average of three measurements.

Figure

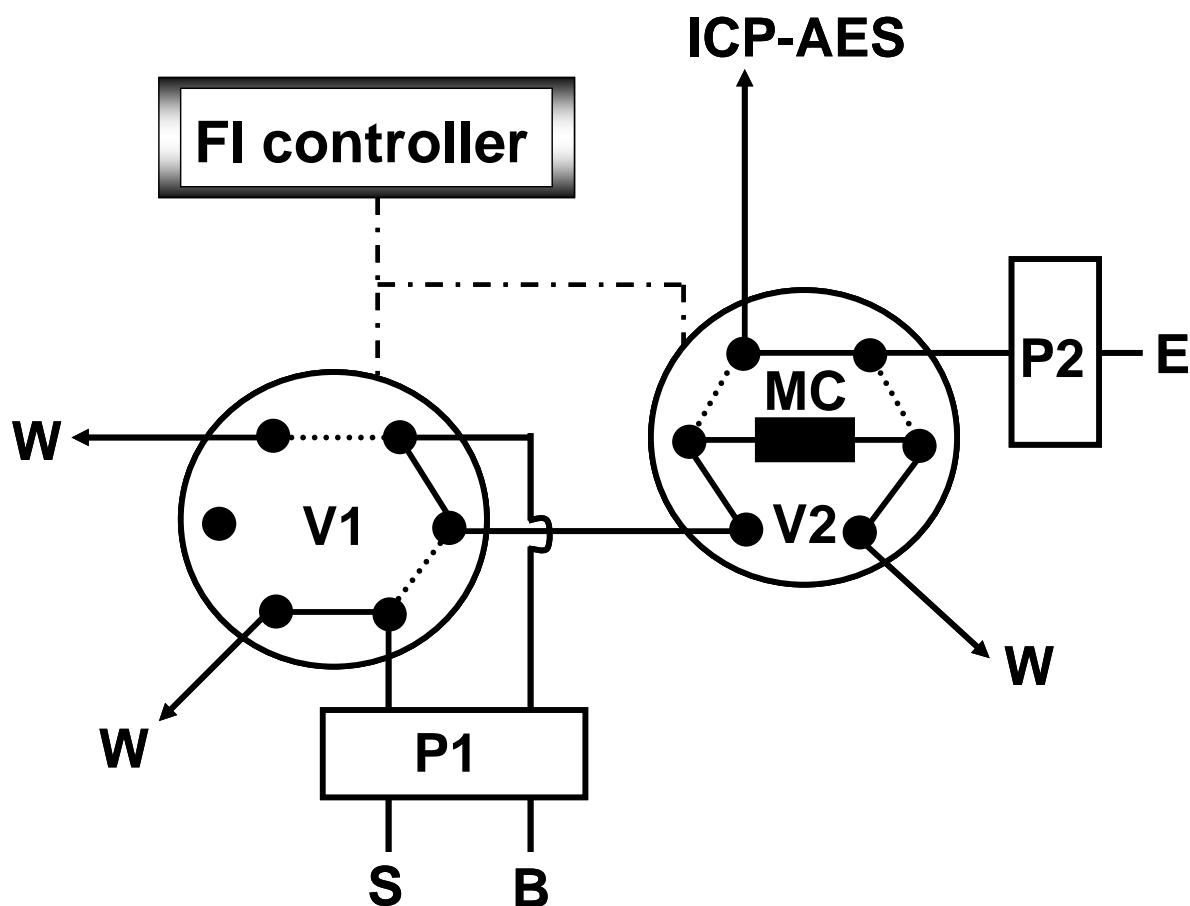
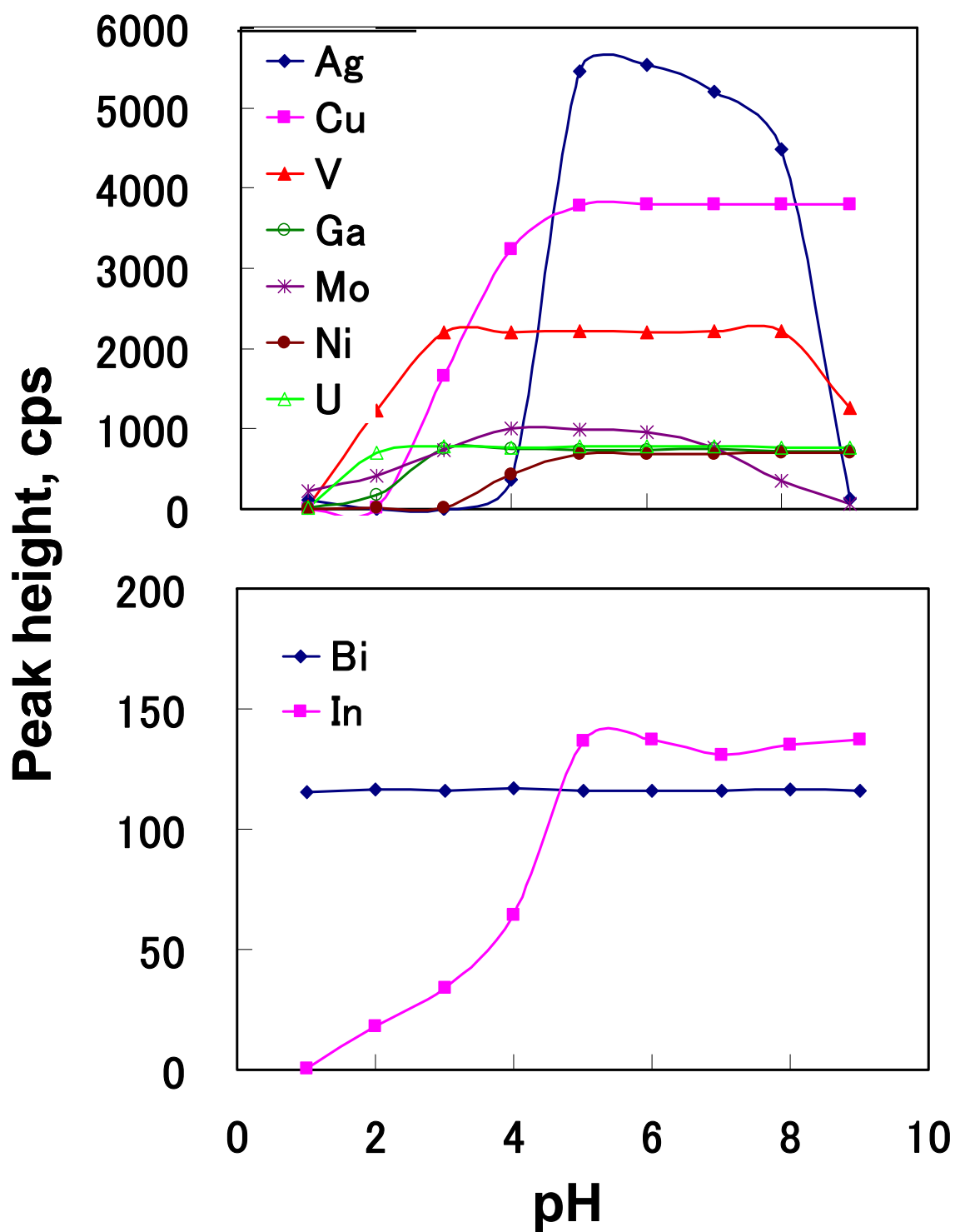


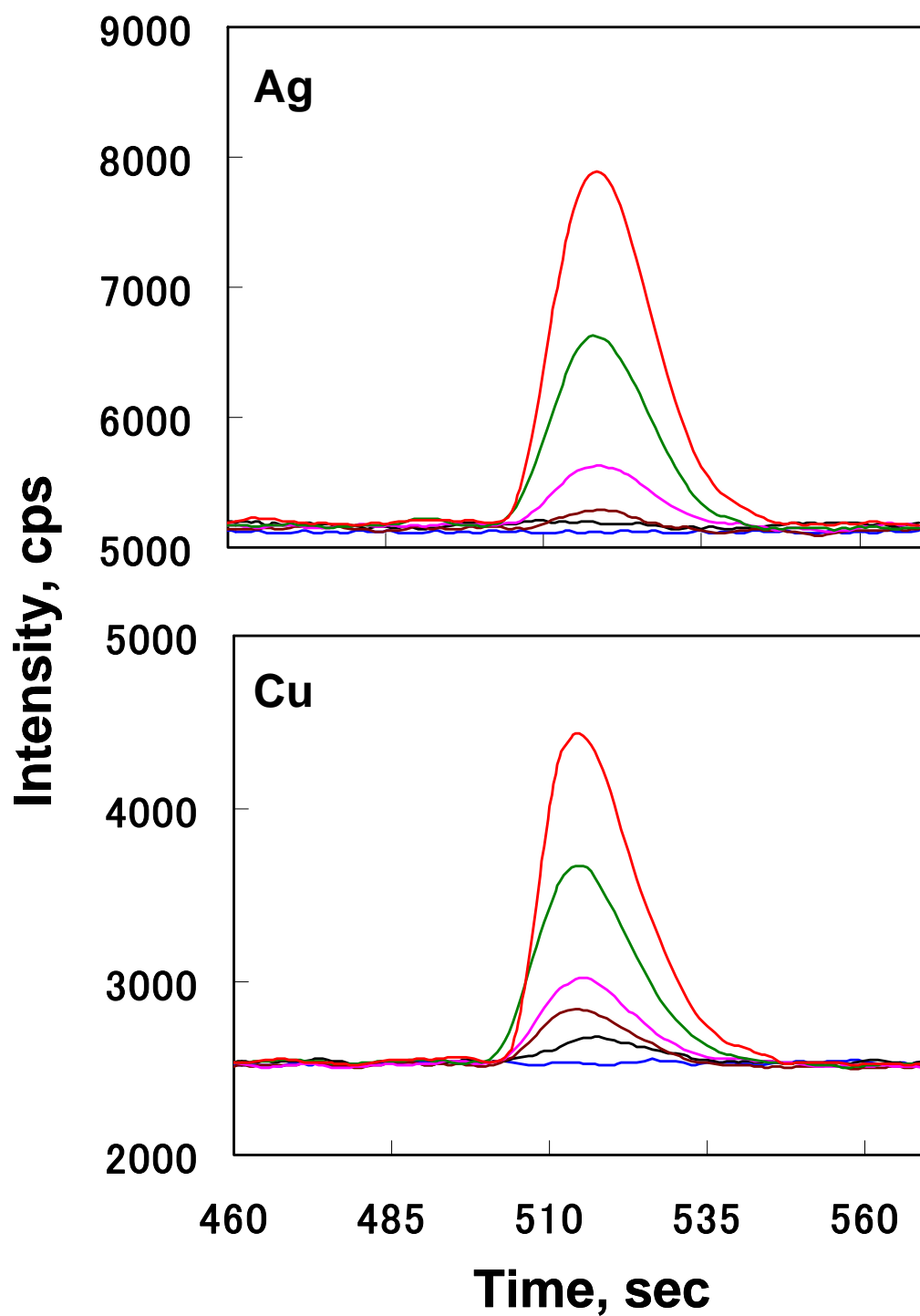
Fig. 1 Schematic diagram for flow injection (FI) on-line preconcentration system

- 5 S: sample or standard solution (5 mL), P1: peristaltic pump (flow rate: 1 mL min⁻¹), P2: peristaltic pump (flow rate: 1.5 mL min⁻¹), W: waste, V1 and V2 : 6-way valve, MC: mini-column containing 20 mg CCTS-DHBA resin, E: eluent (2 M HNO₃), B: 0.5M ammonium acetate buffer solution (pH 5.5)



15 Fig. 2 Effect of sample pH on the peak height

Sample : 10 ng mL^{-1} of each element (5 mL); other conditions are the same as in Table 2



20 Fig. 3 Example peak profiles for Ag and Cu

The flow signals of Ag and Cu were constructed using their concentrations as follows: 0, 0.2, 0.5, 1, 3, and 5 ng mL⁻¹; other conditions are similar as in Table 2.