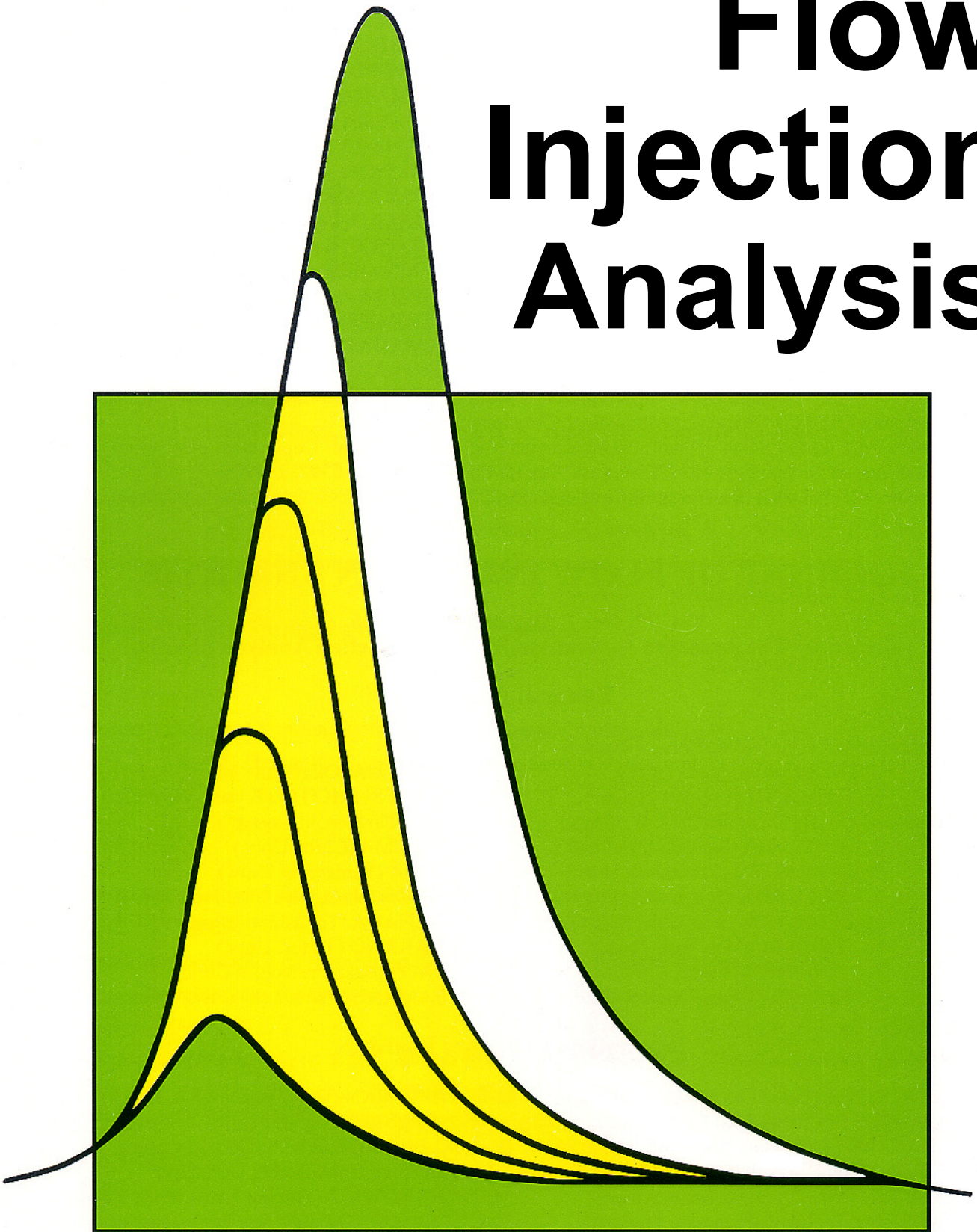


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# Multi-Auto-Pret AES System for Rapid Determination of Trace Metals in Water Samples

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## Abstract

A triply-synchronized automated on-line pretreatment system coupled with ICP-AES, Multi-Auto-Pret AES system, was developed for the rapid determination of trace metals in water samples. The Multi-Auto-Pret AES system consists of three sets of a single Auto-Pret system, one more selection valve and a switching valve. Each single Auto-Pret system has one mini-column (40 mm length x 2 mm i.d.), which was filled with a commercially available resin, Muromac A-1. The Multi-Auto-Pret AES system proposed here consists of 3 mini-columns that could be used for the preconcentration of trace metals sequentially, and can reduce analysis time and running cost. Under the optimum conditions, the repeatability in the same mini-column and the different mini-columns gave similar results, in which were less than 10% the relative standard deviations (RSD). When 5 mL of sample solution was used, the sample throughput was about 30 h<sup>-1</sup>. The proposed system was very useful for analyzing a number of samples and applied to the rapid determination of 11 trace metals in river water samples.

**Keyword:** Multi-Auto-Pret system, triply-synchronized system, determination of trace metals, water samples, Muromac A-1, ICP-AES

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## 1. Introduction

A rapid analysis of trace metals in various kinds of samples becomes more and more important, when a large number of samples need to be investigated. Inductively coupled plasma – atomic emission spectrometry (ICP-AES) is one of the most appropriate techniques for an elemental analysis, because of the capability for rapid multi-element detection over a wide concentration range [1,2]. However, trace metals in natural water samples, such as river and seawater, could not be determined by direct measurement, because of its insufficient sensitivity. Therefore, any sample pretreatment procedure for the enrichment of analytes was necessary before measuring trace metals by ICP-AES [3,4].

Usually, sample pretreatment has been carried out manually, which is labor-intensive, may cause sample contamination and give rise to large sample and reagent consumption [5-7]. In recent years, on-line sample pretreatment methods using chelating resins for the determination of trace metals in water samples have been attractively interested because it is not only eliminated the drawback of batch procedures, but also improves precision, decreases detection limits, and reduces the consumption of reagents and wastes. However, on-line methods themselves could introduce several problems: mainly the separation / preconcentration step took more than 10 min, during this stage, the ICP-AES was idle and waiting for the sample to reach the plasma, thus it wasted expensive resources [8-10]. To shorten the time necessary for the separation / preconcentration procedure, on-line techniques could be much more efficient.

In this study, an automated on-line pretreatment system with 3 collection systems (Multi-Auto-Pret AES), which are synchronized and work sequentially or simultaneously, was

developed for the rapid determination of trace metals in water samples. The Multi-Auto-Pret AES system consists of three sets of the single Auto-Pret system [11], one more selection valve and a switching valve. The selection valve was installed for selecting an eluent and introducing it into the ICP-AES, and the switching valve was installed for supplying water to the ICP-AES while the eluent was not supplied to the ICP-AES. Each single Auto-Pret system had one mini-column (40 mm length x 2 mm i.d.), which was filled with a commercially available resin, Muromac A-1. Therefore, the Multi-Auto-Pret AES system consisted of three mini-columns that could be used for preconcentration of trace metals sequentially or simultaneously, which could reduce analysis time and running cost.

As reported in the previous paper [11], Muromac A-1 was selected because of its suitable characteristics; the resin could adsorb several trace metal ions from pH 4 to 9, and almost all of the metals adsorbed on the resin could be easily recovered using a 1.5 M nitric acid solution prior to the measurement by ICP-AES.

The proposed system was applied for the determination of Ba, Be, Cd, Co, Cu, Mn, Ni, Pb, Sc, V, and Zn in water samples. These trace metals have considerably paid attention in biochemical studies due to micro-nutrients, such as Co, Cu, Mn, V and Zn, while others are non-essential toxic elements, such as Pb and Cd [12]. The proposed system, Multi-Auto-Pret AES system, is very useful for analyzing a number of samples and for rapid and simultaneous determination of trace metals.

## 2. Experimental

### 2.1. Instruments

A Vista-Pro ICP-AES system (Seiko Instruments Co., Chiba, Japan) was used; the operating conditions were listed in Table 1. The ICP-AES was coupled with the Multi-Auto-Pret system. The Multi-Auto-Pret AES system was built from three sets of a single

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Table 1 ICP-AES operating conditions

System	ICP-AES VISTA - PRO
RF generator	Frequency 40 MHz, power 1.1 kW
Plasma gas flow	Ar 15.0 L min <sup>-1</sup>
Auxiliary gas flow	Ar 1.50 L min <sup>-1</sup>
Nebulizer gas flow	Ar 0.75 L min <sup>-1</sup>
Spray chamber	Glass cyclonic spray chamber
Nebulizer	K-style concentric glass nebulizer
Torch	One-piece low flow extended torch in the axial view mode
Measurement mode	Time scan mode

Auto-Pret system, an eight-port selection valve and a six-port switching valve, as shown in Fig. 1. Each single Auto-Pret system equipped with one syringe pump (Hamilton, Reno, NV, USA) with volume capacity of 10 mL, an eight-port selection valve and a six-port switching valve of Hamilton.

## 2.2 Reagents and Solutions

An iminodiacetate chelating resin, Muromac A-1 with 50-100 mesh, Na-form (Muromachi Co., Tokyo, Japan), was used and packed in a mini-column. Before using, the resin was sieved to select the particles; the big particles were used (about 100 mesh). The resin was cleaned for removing any metal impurities in the resin by soaking and stirring it in a hydrochloric acid solution (3 M) for 3 h, and washing with ultrapure water [13]. The resin was kept in 0.5 M ammonium acetate buffer solution (pH 6) until use.

A multielement stock standard solution of XSTC-13 (Spex CertiPrep Inc., Metuchen, NJ, USA), which contained 10 µg mL<sup>-1</sup> of metal ions (Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, Th, and U) was used to prepare working standard solutions. Accurate dilution of the standard solutions was carried out by a weight method.

Nitric acid for the analysis of poisonous metals with 60-62% and density 1.38 g mL<sup>-1</sup> (Wako Pure Chemicals Industries, Ltd., Osaka, Japan) was used and diluted with an ultrapure water to give a 0.01 M or a 1.5 M solution.

A stock solution of 4 M ammonium acetate buffer solution was prepared by mixing appropriate amounts of acetic acid (96%) and ammonia solution (29%). Both acetic acid and

ammonia solutions used were of electronic industrial reagent grade (Kanto Chemicals Co., Inc., Tokyo, Japan). A buffer solution of 0.5 M ammonium acetate was prepared by diluting a 4 M ammonium acetate stock standard solution and adjusting the pH with small amounts of ammonia or acetic acid.

The ultrapure water (18.3 MΩ cm<sup>-1</sup> resistivity) was prepared by an Elix-3/ Milli-Q element system (Nihon Millipore, Tokyo, Japan).

All of the water sample solutions were acidified to pH 2 by adding nitric acid and filtered through 0.45 µm pore size membrane filter made of mixed cellulose ester (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) before storing [14]. The pH of the sample solutions was adjusted to 4 just before the column pretreatment by adding small amounts of an ammonia solution.

SLRS-4 water reference material for trace metals was purchased from Institute for National Measurement Standards (National Research Council of Canada, Ontario, Canada).

## 2.3 Procedure for collection and concentration of trace metals using Multi-Auto-Pret AES system

Procedure for collection / concentration of trace metals using Multi-Auto-Pret AES system was done in 4 steps, and additionally step for resin shaking was added before the preconcentration procedure, as shown in Table 2. The resin-shaking step (Step 1) was applied to restore the resin packing in the column after using in the previous cycle, in order to avoid high pressure that might be happened because of resin packing by flowing solutions.

The preconcentration procedure was carried out as follows. The mini-columns (2.0 mm i.d. x 40 mm) were filled with Muromac A-1. At the loading stage (switching valve, SW, at the position 1), 0.5 mL of 0.5 M ammonium acetate buffer solutions (pH 4) was passed through the column for conditioning (Step 2). After the pretreatment of the column, 5 mL of sample solutions (pH 4) was passed through the column (Step 3) followed by 0.5 mL of ultra-pure water for eliminating sample matrix (Step 4). The switching valve was moved to the position 2 for the eluting stage, then 1 mL of 1.5 M nitric acid was passed through the columns for eluting metals adsorbed on the resin, followed by 2 mL ultra-pure water for cleaning the resin for the next cycle (Step 5). At this stage, all of the solutions were flowed to the ICP-AES.

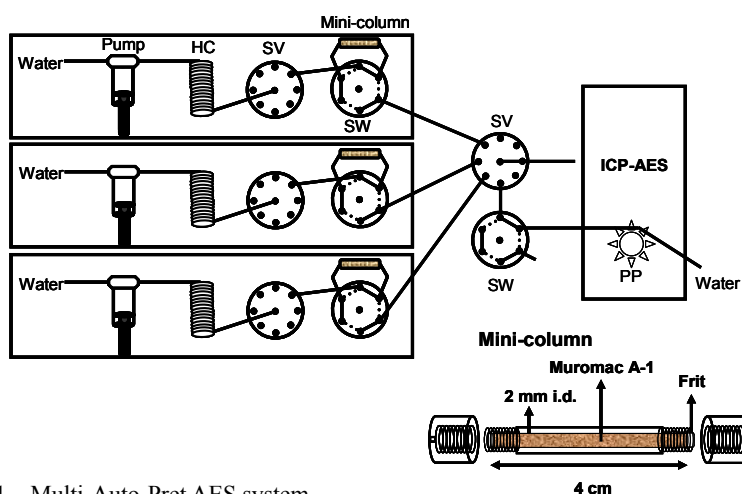


Fig 1 Multi-Auto-Pret AES system.

Pump, 10 mL syringe pump; HC, holding coil; SV, 8-port selection valve; SW, 6-port switching valve; PP, peristaltic pump equipped to ICP-AES system.



Table 2 Procedure for the preconcentration with Multi-Auto-Pret system

Step	Operation description	Pump	SV <sup>a</sup>	SW <sup>b</sup>	Flow rate / $\mu\text{L s}^{-1}$	Volume / $\mu\text{L}$	Action of flow	Time required/s
1	Resin shaking ultra-pure water	IN		1	300	100	aspirate	0.3
		OUT	5	1	40	100	dispense	2.5
		OUT	5	1	40	100	aspirate	2.5
		OUT	5	1	40	100	dispense	2.5
		OUT	5	1	40	100	aspirate	2.5
2	Conditioning 0.5 M buffer	OUT	1	1	100	500	aspirate	5
		OUT	5	1	40	500	dispense	12.5
3	Sample loading sample	OUT	6	1	100	5000	aspirate	50
		OUT	5	1	40	5000	dispense	125
4	Matrix removing ultra-pure water	IN		1	300	500	aspirate	1.7
		OUT	5	1	40	500	dispense	12.5
5	Eluting and cleaning ultra-pure water 1.5 M HNO <sub>3</sub>	IN		1	300	2000	aspirate	6.7
		OUT	3	1	100	1000	aspirate	10
		OUT	5	2	40	3000	dispense	75
Pump / SV / SW moving								48
TOTAL TIME								359.2 s ≈ 6.0 min

<sup>a</sup> SV, selection valve; <sup>b</sup> SW, switching valve

The time required for the whole procedure was about 6 min. As the Multi-Auto-Pret AES system consisted of three sets of the single Auto-Pret system, the sample throughput was about 30 h<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Optimization of the parameters of Auto-Pret procedures

The parameters of Auto-Pret procedures, such as sample pH, sample loading flow rate, eluent flow rate, and eluent concentration, should be optimized in order to obtain the best result.

As reported in the previous paper, Muromac A-1 could adsorb a number of metal ions from pH 4 to 9 [11]. However, at pHs above 6, the chelation became stronger for many metal ions than that at a lower pH, which meant that it was difficult to break up the metal complexes, and thereby to recover metal ions completely from the resin. At pH 4, all of the elements could be recovered completely. With increasing in pH, the adsorption of alkaline metals on the resin was increased. At pH 4, only small amounts of alkaline metals could be adsorbed on the resin, and they could be completely removed by washing the resin with ultrapure water as the washing solution. In order to detect the metals of interest simultaneously, that condition was free from the interferences with alkali or alkaline-earth metals that usually present as water sample matrixes, the sample solution adjusted to pH 4 was selected for preconcentration of metals in the column.

Eluent flow rate, sample loading flow rate, and eluent concentration were optimized using 5 mL of the standard solution containing 1 ng mL<sup>-1</sup> of metal ions. The eluent flow rate was varied from 10 – 50  $\mu\text{L s}^{-1}$ , whereas the sample loading flow rate was kept constant at 40  $\mu\text{L s}^{-1}$ . Peak height intensity was increased by increasing the eluent flow rate from 10 to 30  $\mu\text{L s}^{-1}$ , and became constant when eluent flow rate was faster than 30  $\mu\text{L s}^{-1}$ , and then decreased after 45  $\mu\text{L s}^{-1}$ , as shown in Fig. 2A. A faster flow rate was preferred to decrease measuring time and to

increase sample throughput. Therefore, 40  $\mu\text{L s}^{-1}$  of the eluent flow rate was used.

Sample loading flow rate was studied from 10 to 50  $\mu\text{L s}^{-1}$ . When sample loading flow rate was varied, the eluent flow rate was kept constant at 40  $\mu\text{L s}^{-1}$ . As shown in Fig. 2B, a little increase in signal intensity were obtained for Mn, Ni, and Zn, while for other metal ions there was no significant difference of signal intensity. To avoid generation of high pressure, sample loading flow rate of 40  $\mu\text{L s}^{-1}$  was selected.

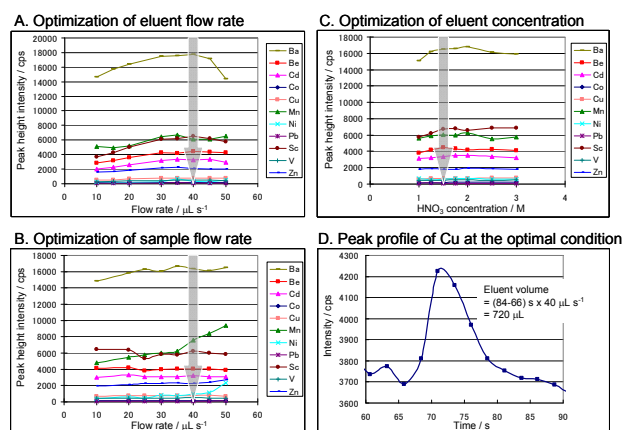


Fig 2 Optimization of condition for Auto-Pret procedures.

As an eluent, nitric acid was used. To optimize the concentration of nitric acid, sample and eluent flow-rate of each 40  $\mu\text{L s}^{-1}$  was employed. Concentration of nitric acid was studied from 1.0 to 3.0 M. As shown in Fig. 2C, increasing nitric acid concentration from 1.0 to 1.5 M could increase the peak height intensity. The signal intensity became stable at the concentration higher than 1.5 M. Lower concentration of nitric acid was preferable to decrease consumption of nitric acid and waste; therefore, 1.5 M of nitric acid was employed as an eluent.

Table 3 Repeatability of Multi-Auto-Pret-AES system

Cycle	Mini-column	Ba	Be	Cd	Co	Cu	Mn	Ni	Pb <sup>a</sup>	Sc	V	Zn
1st	1	31319	8043	5359	343.5	1387	9135	711.5	139.4	12865	732.6	3123
1st	2	30603	8434	5185	317.5	1302	8265	674.4	125.3	12669	762.5	2869
1st	3	30794	8706	4905	373.0	1306	8199	667.5	125.1	13360	818.5	2843
2nd	1	33431	7204	4895	360.6	1386	8675	684.1	124.5	11491	746.6	2942
2nd	2	31501	7232	4894	339.0	1303	8788	728.8	133.8	11935	733.3	2879
2nd	3	31653	7686	5052	330.1	1335	8451	726.2	122.4	10954	769.4	3008
3rd	1	30156	8413	5403	355.7	1265	8399	682.1	132.2	13332	763.1	2863
3rd	2	31233	8799	5560	349.3	1298	8879	758.3	126.8	12131	878.3	3045
3rd	3	31576	7682	5050	331.3	1324	9608	663.7	137.6	11941	760.8	3002
<b>RSD of peak height from different mini-column / %</b>												
1st		1.2	4.0	4.5	8.1	3.6	6.1	3.5	8.2	2.7	5.7	5.3
2nd		3.3	3.7	1.8	4.6	3.1	2.0	3.5	6.1	4.3	2.4	2.2
3rd		2.4	6.8	4.9	3.7	2.3	6.8	7.1	5.4	6.0	8.4	3.2
<b>RSD of peak height from same mini-column / %</b>												
	Mini-column 1	5.2	7.8	5.4	2.5	5.2	4.2	2.4	7.5	7.6	2.0	4.5
	Mini-column 2	1.5	10.0	6.4	4.8	0.2	3.8	5.9	4.5	3.1	9.7	3.4
	Mini-column 3	1.5	7.3	1.7	7.1	1.1	8.6	5.1	8.1	10.0	4.0	3.2

<sup>a</sup> Concentration of Pb is 5 ng mL<sup>-1</sup>, while for other metal ions was 1 ng mL<sup>-1</sup>

### 3.2 Reproducibility of the Multi-Auto-Pret AES system

Reproducibility of the Multi-Auto-Pret AES system was examined by passing through 5 mL of standard solutions containing 1 ng mL<sup>-1</sup> of metal ions through the mini-columns filled with Muromac A-1, in which sample and eluent flow rate of 40  $\mu\text{L s}^{-1}$  and 1.5 M of nitric acid as an eluent were employed. The reproducibility was calculated as a relative standard deviation (RSD) for repeated measurements with the same mini-column, and single measurement with different mini-columns. As shown in Fig 3, the reproducibility of the same mini-column and different mini-column gave similar results, both of which RSD were less than 10%. The results were summarized in Table 3. From Table 3, the Multi-Auto-Pret AES system has good reproducibility, and could be used for the multi-element preconcentration and the determination of trace metals.

From the profiles of the analytical signals of metal ions, it could be seen that 0.72 mL of 1.5 M HNO<sub>3</sub> was enough to elute the metal ions collected on the resin, as shown in Fig. 2D. Therefore, for recovering of the elements completely and cleaning the resin for the next cycle, 1 mL of 1.5 M HNO<sub>3</sub> was used.

### 3.3 Enrichment factors and detection limits

The enrichment factor (EF) and the limit of detection (LOD) of metal ions at their wavelength obtained by the Multi-Auto-Pret AES system were shown in Table 4. The emission wavelengths were selected to give the best intensity without any interference, based on Method 200.7 US-EPA [15].

The enrichment factors were estimated by comparing the peak height obtained by the proposed method using 3 ng mL<sup>-1</sup> of the standard solution, with those obtained by the conventional nebulization method of ICP-AES using 30 ng

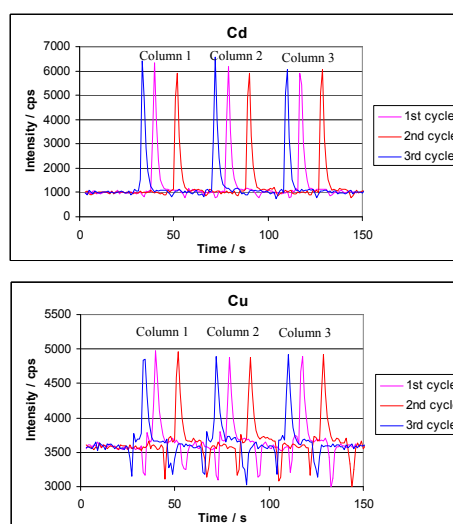


Fig 3 Reproducibility test with Multi-Auto-Pret AES system.

mL<sup>-1</sup> of the standard solution. The enrichment factors of the trace metals were in the range of 14 (Ba) to 24 (Cu), when 5 mL of the sample solution was used. The enrichment factor until 100 fold could be obtained for Pb when 20 mL of sample solution was used.

The LODs obtained in this work were calculated as the concentrations corresponding to three-times of the signal-to-noise ratio of the backgrounds, while the LODs of the ICP-AES instrument were determined as the concentrations corresponding to three-times the standard deviation of the blank signal intensities for each trace metal contained in 0.01 M nitric acid used as a blank solution (for 10 measurement replicates) which were measured by the conventional nebulization of ICP-AES.

Table 4 Enrichment factor and detection limits obtained with the Multi-Auto-Pret AES system

Element	Wavelength nm <sup>a</sup>	Enrichment Factor <sup>b</sup>	LOD, ng mL <sup>-1</sup>	
			This work <sup>d</sup>	Direct ICP-AES <sup>e</sup>
Ba	493.408	14	0.24	0.3
Be	313.042	15	0.003	0.1
Cd	226.502	96 <sup>c</sup>	0.007 <sup>c</sup>	0.3
Co	228.615	78 <sup>c</sup>	0.032 <sup>c</sup>	0.8
Cu	324.754	24	0.12	0.3
Mn	257.610	21	0.14	0.7
Ni	231.604	14	0.20	0.9
Pb	220.353	100 <sup>c</sup>	0.090 <sup>c</sup>	3.7
Sc	361.383	21	0.010	0.3
V	292.401	18	0.18	0.8
Zn	213.856	15	0.08	1.2

<sup>a</sup> Emission wavelengths used are based on Method 200.7 US-EPA [15].

<sup>b</sup> Enrichment factor, the ratios of peak height obtained by the proposed system to those by the conventional nebulization of ICP-AES.

<sup>c</sup> Sample volume was 20 mL for Cd, Co and Pb, and was 5 mL for other elements.

<sup>d</sup> Limit of detections, corresponding to S/N 3.

<sup>e</sup> Limit of detections of instrument, corresponding to 3 SD (standard deviation) of the blank solution (n =10) which were measured by the conventional nebulization of ICP-AES.

From the obtained results, the proposed method with only 5 mL of a sample solution was found to be sensitive enough for determining trace metals in river water samples, except

for Cd, Co, and Pb. Since the concentrations of Cd, Co, and Pb in river water samples were extremely low, a 20 mL of sample solution was necessary to improve their detection limits. Without any preconcentration step, only Cu and Mn in river water could be directly determined, while other metal ions could not be determined without the proposed precollection/ concentration procedure.

#### 3.4. Certification with standard reference material and application to river water samples

Analytical results for Ba, Be, Cd, Co, Cu, Mn, Ni, Pb, Sc, V, and Zn in the standard reference material and river water samples were summarized in Table 5.

River water standard reference material for trace metals, SLRS-4, was analyzed to confirm the accuracy of the proposed method. A good agreement with the certified values could be obtained.

The proposed method was applied to the determination of trace metals in river water samples collected in Okayama City. The river water samples were also spiked with 0.05 and 0.5 ng mL<sup>-1</sup> of the multi-element standard solution to evaluate the proposed procedure. Since the Nishi River and the Zasu River are branches of Asahi River, the concentrations of some metal ions obtained were found to be comparable. A little higher concentration of some metal ions in Nishi River and Zasu River were observed because of the pollution from domestic wastes.

High reliability and the sufficient recoveries (90-109 %) in Table 5, indicate that the proposed method has good accuracy, validity, and is applicable to the determination of trace metals in river water samples.

Table 5 Analytical results for trace metals in standard reference material and river water samples

Elements	Spiked /ng mL <sup>-1</sup>	SLRS-4 <sup>a</sup>		Asahi River		Nishi River		Zasu River	
		Certified values /ng mL <sup>-1</sup>	This work /ng mL <sup>-1</sup>	Found /ng mL <sup>-1</sup>	Recovery %	Found /ng mL <sup>-1</sup>	Recovery %	Found /ng mL <sup>-1</sup>	Recovery %
Ba	-	12.2 ± 0.6	12.6 ± 0.5	6.4 ± 0.1		6.89 ± 0.04		7.49 ± 0.24	
Be	-	0.007 ± 0.002	0.011 ± 0.002	0.022 ± 0.001		0.007 ± 0.002		0.015 ± 0.004	
	0.05			0.074 ± 0.004	101	0.054 ± 0.007	92	0.061 ± 0.007	91
Cd	-	0.012 ± 0.002	0.014 ± 0.005 <sup>b</sup>	0.024 ± 0.009 <sup>b</sup>		0.034 ± 0.006 <sup>b</sup>		0.047 ± 0.005 <sup>b</sup>	
	0.05			0.079 ± 0.006 <sup>b</sup>	109	0.082 ± 0.001 <sup>b</sup>	96	0.098 ± 0.006 <sup>b</sup>	102
Co	-	0.033 ± 0.006	0.036 ± 0.004 <sup>b</sup>	0.048 ± 0.004 <sup>b</sup>		0.047 ± 0.006 <sup>b</sup>		0.035 ± 0.002 <sup>b</sup>	
	0.05			0.096 ± 0.008 <sup>b</sup>	96	0.099 ± 0.008 <sup>b</sup>	104	0.085 ± 0.004 <sup>b</sup>	100
Cu	-	1.81 ± 0.08	1.83 ± 0.07	1.1 ± 0.03		0.85 ± 0.01 <sup>b</sup>		1.02 ± 0.06	
	0.5			1.6 ± 0.01	95	1.32 ± 0.02	94	1.52 ± 0.11	100
Mn	-	3.37 ± 0.18	3.59 ± 0.28	4.8 ± 0.1		4.90 ± 0.17		7.03 ± 0.13	
Ni	-	0.67 ± 0.08	0.61 ± 0.02	0.36 ± 0.01		0.24 ± 0.01		0.20 ± 0.04	
	0.5			0.83 ± 0.06	94	0.75 ± 0.02	103	0.69 ± 0.06	98
Pb	-	0.086 ± 0.007	0.092 ± 0.012 <sup>b</sup>	0.32 ± 0.08 <sup>b</sup>		0.28 ± 0.02 <sup>b</sup>		0.29 ± 0.01 <sup>b</sup>	
	0.5			0.86 ± 0.04 <sup>b</sup>	107	0.75 ± 0.04 <sup>b</sup>	92	0.81 ± 0.06 <sup>b</sup>	105
Sc	-	-	(0.026 ± 0.002) <sup>c</sup>	0.035 ± 0.002		0.041 ± 0.004		0.044 ± 0.004	
	0.05			0.080 ± 0.008	90	0.089 ± 0.001	97	0.092 ± 0.000	96
V	-	0.32 ± 0.03	0.34 ± 0.02	0.52 ± 0.03		0.49 ± 0.03		0.50 ± 0.01	
	0.5			1.05 ± 0.08	106	0.96 ± 0.02	94	1.03 ± 0.02	94
Zn	-	0.93 ± 0.10	0.90 ± 0.05	3.9 ± 0.1		1.17 ± 0.02		1.74 ± 0.08	
	0.5			4.4 ± 0.1	105	1.65 ± 0.01	95	2.27 ± 0.20	106

All data were averaged from three replicates. River water samples were sampled in Okayama City.

<sup>a</sup> River water reference material for trace metals issued by National Research Council Canada.

<sup>b</sup> Sample volume was 20 mL.

<sup>c</sup> Figure in parentheses was information value.

#### 4. Conclusion

The Multi-Auto-Pret AES system incorporated in 3 Auto-Pret systems was developed for the rapid determination of trace metals in water samples. The sample throughput was about 30 h<sup>-1</sup>. Enrichment factors were from 14 to 24 with 5 mL of the sample volume and up to 100 fold for Pb with 20 mL of sample volume. Lower detection limit with high sample throughput was accomplished and the proposed method was applied successfully to the determination of 11 trace elements in river water samples.

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