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Computer-controlled fluid-flow chemical analysis (CC-FCA) and its application to environmental analytical chemistry*

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Abstract: Computer-controlled fluid-flow chemical analysis (CC-FCA) was investigated for the determination of trace amounts of toxic pollutants in the environment. For CC-FCA, automated chemical analysis systems were developed by using computer-controllable pumping and valve modules, and polytetrafluorethylene (PTFE) tubing and connectors. The systems demonstrated in this work were a flow injection-type system, a sequential injection-type system, a mini-column pretreatment system (Auto-Pret system), and an Auto-Pret hyphenated with flow injection analysis (FIA) system. Such systems were fully controlled by a computer program; the lab-made programs were written in Visual Basic. The systems can be hyphenated with some detectors, such as a spectrophotometric detector, an electrochemical detector, electrothermal-atomic absorption spectrometry (ET-AAS), a liquid electrode plasma-atomic emission spectrometry (LEP-AES) and inductively coupled plasma (ICP)-AES. Such systems were successfully applied to the determination of trace amounts of toxic pollutants in environmental water samples: they were heavy metal ions (Pb, Cd, Cr, etc.). In this paper, the author aims mainly at investigating the CC-FCA method for the determination of trace amounts of Cr(VI) in environmental water samples by spectrophotometry. The techniques used in this work were FIA, sequential injection analysis (SIA), and Auto-Pret/FIA, which were all computer-controllable. Limits of detection of Cr(VI) by FIA, SIA, and Auto-Pret/FIA were 8×10^{-9} mol/L (0.4 μg/L), 1.1×10^{-8} mol/L (0.6 μg/L), and 1.4×10^{-9} (0.07 μg/L), respectively. The methods were applied to the determination of Cr(VI) in river and drinking waters.

Keywords: Auto-Pret; chromium(VI); cadmium and lead; computer-controllable system (CC); flow injection analysis (FIA); fluid flow chemical analysis (FCA); liquid electrode plasma-atomic emission spectrometry (LEP-AES); sequential injection analysis (SIA); spectrophotometry; toxic heavy metals.

INTRODUCTION

In almost all of chemical analysis, several pretreatment procedures are necessary prior to measuring target analytes by some instrumental or visual observation methods. Though the pretreatment procedures are very important and are requisite to get reliable analytical results, they are often very tedious, complicated, and time-consuming, and sometimes necessitate specialists/technicians or special techniques and know-how. Such pretreatment procedures have sometimes been overcome by using automated techniques or by robots in batch-wise methods.

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In 1975, Ruzicka and Hansen reported flow injection analysis (FIA) [1]. This technique is similar to air-segmented flow analysis (SFA), but the instrumentation is much simpler than SFA, and the concept and principle of FIA are very different from SFA. The FIA technique is considered to be one of the automated pretreatment (Auto-Pret) systems for the preparation/arrangement of samples prior to the measurement. In FIA system, various kinds of pretreatment device, such as reaction columns, separation/concentration devices, UV-irradiation unit, gas diffusion unit, etc., can be installed online. Until now, numbers of pretreatment procedures have been installed in FIA instruments [2–4].

In 1990, Ruzicka and his colleagues reported another fluid-flow chemical analysis (FCA), sequential injection analysis (SIA) [5]. In this technique, they put a lot of new ideas into the SIA system. One of the most important ideas is the use of a computer-controllable (CC) pump and valve. By using a CC pump and selection valve (SLV), the management of solutions can be done freely. Later, from the concept of SIA, new techniques were born; they are a lab-on-valve and a beads injection method.

Recently, several kinds of pump and valve modules, which can be controlled by a personal computer and lab-made software, have been commercially available. By using such CC modules and assembling them together with suitable accessories, tubing, and connectors, CC-FIA or other CC-FCAs have been developed; they are named as, for example, a multicommutated flow injection analysis (MCFIA) system utilizing solenoid valves [6], a multipumping flow system (MPFS) utilizing solenoid pumps and valves [7], a multisyringe flow injection analysis (MSFIA) system utilizing several syringe pumps [8], an all injection analysis (AIA) system utilizing six-way switching valves (SWVs) [9], a simultaneous injection effective mixing analysis (SIEMA) [10], and an Auto-Pret system utilizing syringe pump modules and valve modules [11,12]. Of these, MCFIA, MPFS, MSFIA, AIA, and SIEMA enable one to perform pretreatment procedures in the flowing streams in a similar manner to conventional FIAs, whereas the SIA and Auto-Pret systems enable one to perform several pretreatment steps sequentially; for example, the Auto-Pret system can carry out intermittently several steps of a column pretreatment, a column conditioning, sample loading, column washing, analytes eluting/propelling to a detector, and column cleaning step, sequentially according to the sequences of the steps prepared and installed in a computer beforehand.

In this paper, the author demonstrates interesting and useful examples of the application of the Auto-Pret system to the determination of lead, cadmium, and zinc by anodic stripping voltammetry (ASV) and by liquid electrode plasma-atomic emission spectrometry (LEP-AES) and Cr(VI) by spectrophotometry.

EXPERIMENTAL

Chemicals and reagents

All standard solutions and reagent solutions were prepared with standard and analytical grade reagents using an ultrapure water (resistivity ≥ 18.2 MΩ cm^{-1}) prepared by an Elix 3/Milli-Q Element System (Nihon Millipore, Japan). Working standard solutions of Zn(II), Pb(II), and Cd(II) were prepared daily by the appropriate dilution of the stock standard solutions (1000 mg L^{-1} atomic absorption analysis standard solution, Kanto Chemical, Japan) with 1 M (1 M = 1 mol dm^{-3}) hydrochloric acid (HCl) solution. A 1000 μg L^{-1} (1 L = 1 dm^{-3}) Bi(III) plating solution was prepared by the appropriate dilution of the stock solution of Bi(III) (1000 mg L^{-1} atomic absorption analysis standard solution, Kanto Chemical, Japan) with 1 M HCl solution. An eluent, 1 M HCl, which also can serve as a supporting electrolyte and an electrode cleaning solution, was prepared by the appropriate dilution of concentrated HCl (electronic grade, 36 %, 1.18 g mL^{-1}; Mitsubishi Chemicals, Japan). Sodium acetate trihydrate (analytical reagent grade, Wako Pure Chemicals, Japan), concentrated acetic acid (analytical reagent grade, Wako Pure Chemicals, Japan) and 3 M HCl solution were used to make acetate buffers of a desired pH. Nitrilotriacetate (NTA, Wako Pure Chemicals, Japan) was used as the eluent for the elution of metal ions from TE-05 resin in LEP-AES.

The solid phases, MetaSEP Analig ME-01 and TE-05 (100–200 mesh, GL Sciences, Japan) and Toyopearl QAE-550C as strong anion-exchanger (Tosoh, particle size: 50–150 µm), were packed in a mini-column (2 mm i.d. and 4.5 cm length); both ends of the column were packed with frits (2 mm o.d. × 1 mm thickness) made of resin.

Potassium chromate (Nacalai Tesque, Japan) was used to prepare the standard solution of CrO_4^{2-}. The coloration reagent for Cr(VI), 1,5-diphenylcarbazide (DPC), and nitric acid (Wako Pure Chemicals, Japan) were used for preparing a reagent solution, which was prepared by dissolving DPC in a small amount of ethanol and diluting it with 1 M nitric acid. The final concentration of DPC in 0.3 M HNO_3 was 6×10^{-4} M.

A buffer solution of acetic acid and ammonia for Cr(VI) determination was prepared using acetic acid and ammonia (electronic grade, Mitsubishi Chemicals, Japan).

Apparatus

An Auto-Pret system was assembled with one syringe pump (Hamilton PSD/4) or two syringe pumps (Hamilton PSD/8) with a 0.5-, 5-, or 10-mL glass syringe, an SLV (Hamilton MVP with a valve head of eight-port distribution flow path) and an SWV (Hamilton MVP with a valve head of eight-port distribution flow path). A mini-column made of acrylic resin was installed on an SWV; an anion-exchange resin or a chelating resin was packed in the mini-column. The Auto-Pret system was controlled by a personal computer with lab-made Auto-Pret controlling software (LMPro ver. 2.5).

Spectrophotometric detection was carried out using a spectrophotometer (SPM), Soma Visible detector S 3250 with a 20-mm path length flow cell. A strip chart recorder (TOA Dempa FBR-251A, Japan) and an FIA monitor (Ogawa & Co., Japan) were used for recording peak signals. Liquid electrode plasma-atomic emission spectrometry was carried out with a LEP-AES, MH-5000 (Micro Emission, Japan) with a quartz flow cell.

Procedures

Determination of Cr(VI) with Auto-Pret system hyphenated with a spectrophotometer (Auto-Pret/SPM)

Cr(VI) could be collected on an anion-exchange resin [13,14]. In this work, Toyopearl QAE-550C was packed in a mini-column, which was installed on the SWV of the Auto-Pret system (Fig. 1). The collection/concentration of CrO_4^{2-} was carried out using a syringe pump, and finally Cr(VI) was eluted with 0.30 M HNO_3 solution. The effluent was merged with the reagent stream, which was propelled with the other syringe pump, and the absorbance of the Cr complex with DPC was measured by the SPM at 542 nm.

Also, Cr(VI) was measured with the Auto-Pret/SPM by a conventional SIA mode and a double-syringe CC-FIA mode.

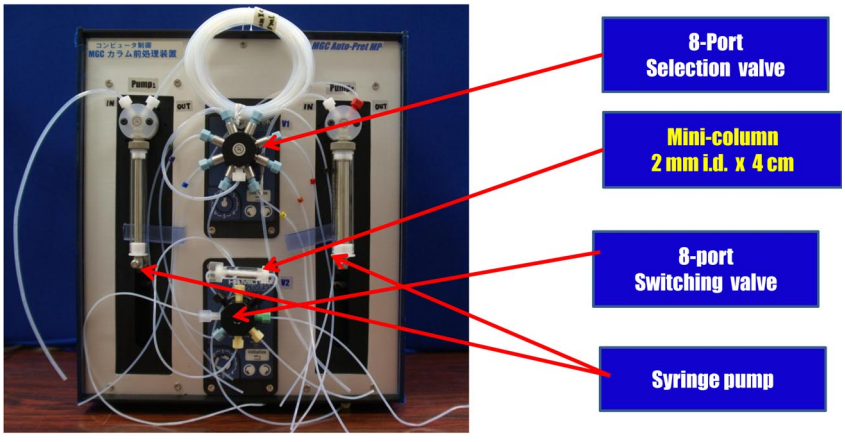

Fig. 1 CC-Auto-Pret system for solid-phase extraction with a mini-column.

Determination of Pb(II), Cd(II), Cu(II), and Zn(II) with a double-syringe type Auto-Pret system hyphenated with LEP-AES (Auto-Pret/LEP-AES)

Several heavy metal ions, such as Pb(II), Cd(II), Cu(II), and Zn(II), could be almost completely collected and concentrated on the mini-column packed with TE-05 resin as is shown in Fig. 2. In ICP-AES measurement, the collected metal ions could be eluted with 2 M HNO_3, and the analytes in the effluent were measured online.

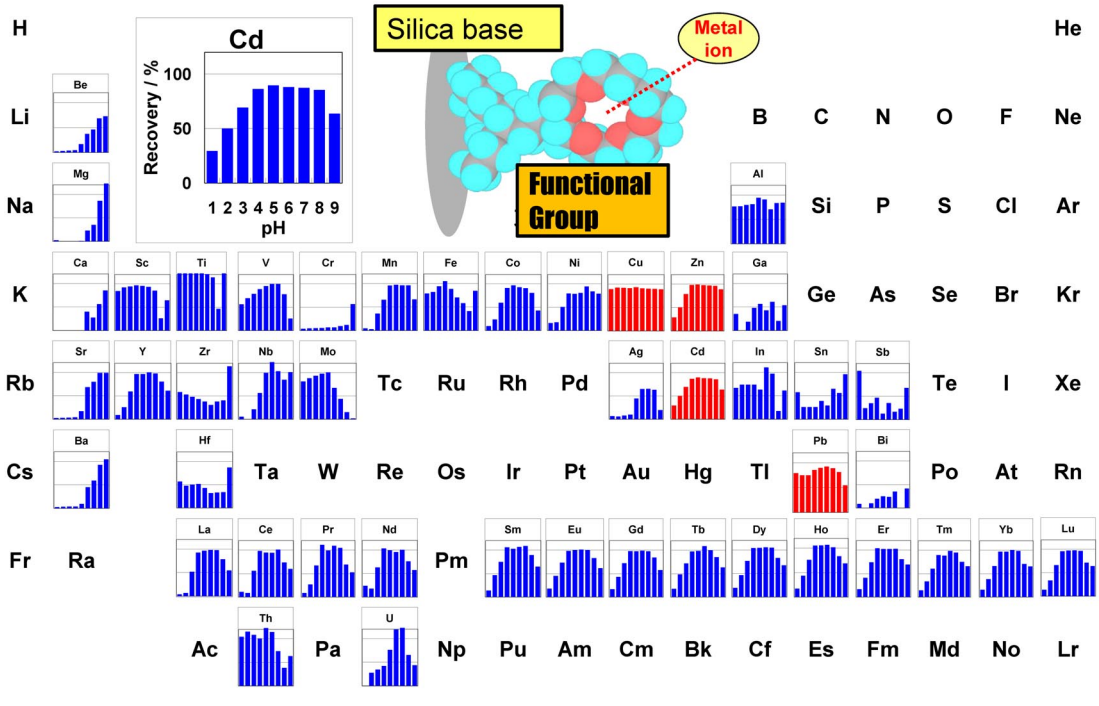

Fig. 2 Collection efficiency of metal ions on Analig TE-05. Sample: 5.0 mL; concentration of each element: 20 ppb; eluent: 5.0 mL of 2.0 M HNO_3. These data were obtained by measuring with ICP-AES.

In this work, TE-05 was packed in the mini-column, which was used for the collection/concentration of metal ions installed in the Auto-Pret system; the elution of metal ions can be carried out with 0.09 M NTA solution by using the syringe pump (P2; total volume: 0.5 mL). The effluent was flowed into the flow cell of LEP-AES, and the emission of each metal was measured.

RESULTS AND DISCUSSION

Comparison of sensitivity of Cr(VI) determination by three modes of CC-FCA method, CC-FIA, SIA, and Auto-Pret/FIA mode, and the application to practical water samples

CC-FIA mode

By using the double-syringe Auto-Pret system shown in Fig. 1, the determination of Cr(VI) was carried out by using an FIA mode. The schematic diagram of the flow manifold is shown in Fig. 3, in which one pump (P1) propels the reagent solution, and the other the carrier and the sample (400 µL) zone. The sample solution (400 µL) was aspirated into the holding coil, and the two pumps were started simultaneously at the flow rate of 1 mL min^{-1}. The experimental conditions, such as reagent concentration, acid concentrations in the carrier and the reagent solution, sample volume, flow rate and reaction coil length, were optimized. As the results, the conditions used for Cr(VI) in water samples were shown in Fig. 3. The example of typical flow signals and its calibration graph are shown in Fig. 4.

In the peak profiles in Fig. 4, "D" shows the background or baseline of the solution caused by mixing the carrier and the reagent solution, and peaks C correspond to Cr complex, and sharp peaks B appear before the peak C. The peaks B appear from the Shlieren effect, which occurs by the difference between refractive index of two bordered solutions. Before the sharp peak B, rectangular-shaped dips, A, are appeared. While these dips appear, the pump of the reagent is aspirating the reagent solution and the other is arranging the sample aspiration and water; that is, any solution does not flow into the flow cell. The peak height of Cr is measured from the baseline.

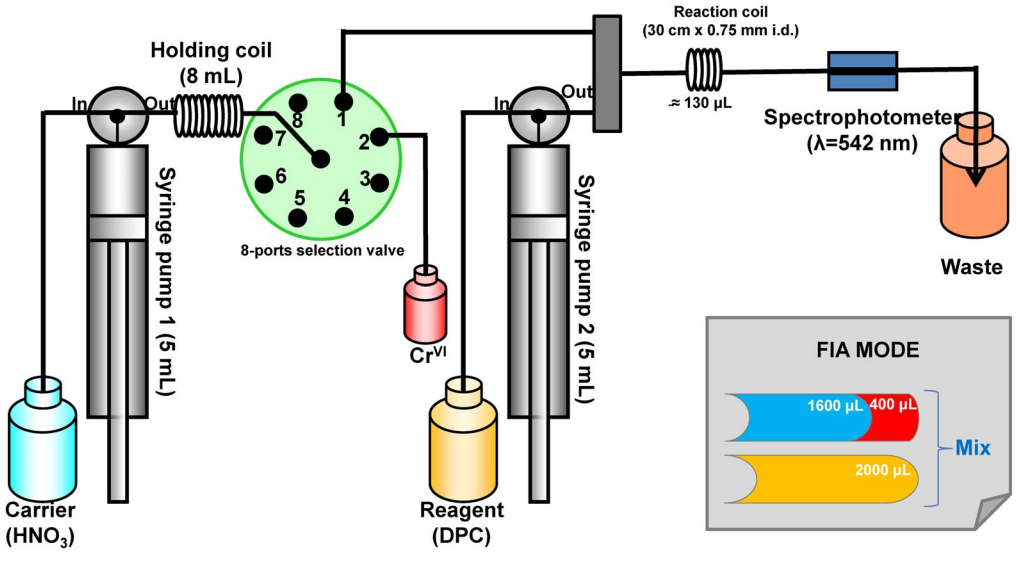

Fig. 3 Manifold of CC-FIA for the determination of Cr(VI) by spectrophotometry. Carrier stream: 0.3 M HNO_3, reagent stream: 6 × 10^{-4} M DPC in 0.3 M HNO_3, sample volume injected: 400 µL, flow rate of each stream: 1.0 mL/min, reaction coil: 0.75 mm i.d. × 30 cm, wavelength: 542 nm.

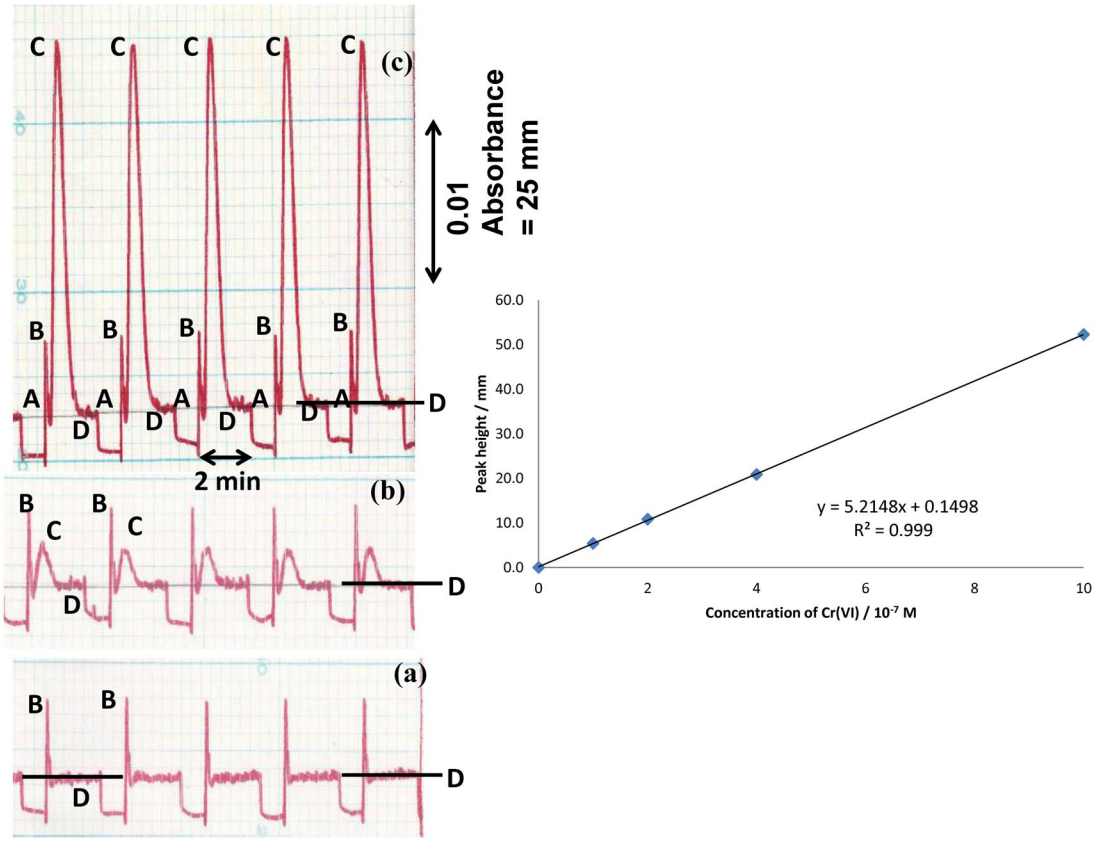

Fig. 4 Signal profiles and a typical calibration graph obtained by using CC-FIA system for Cr(VI). Cr(VI): (a) 0, (b) 1.0×10^{-7} M, (c) 1.0×10^{-6} M; calibration graph: $y = 6.57$, $x = 0.806$, $R^2 = 0.9994$. In the calibration graph, 10 mm of peak height corresponds to the absorbance of 0.004. Symbols A, B, C, and D are explained in the text.

The calibration graph shows good linearity over the range of 0 to 1×10^{-6} M, and the regression curve is shown as: $y = 6.57x - 0.806$, $R^2 = 0.9994$, where y is peak height (mm), x the molar concentration (10^{-7} M) of Cr(VI). The limit of detection (LOD) of Cr(VI), which is defined as the Cr(VI) concentration corresponding to the three times of the standard deviation (σ) of the peak height of 1.0×10^{-7} M Cr(VI) (3σ), is 0.8×10^{-8} M (0.4 µg L^{-1}). Sample throughput is more than 30 samples h^{-1}.

Cr(VI) has been suspected to be one of the carcinogenic substances, though Cr(III) has been considered to be essential to living organism [15,16]. The World Health Organization (WHO) provides a provisional guideline level of 0.05 mg L^{-1} of total Cr for drinking water [15,16]. Now, the maximum tolerable concentration of Cr(VI) in drinking water regulated in Japan and WHO is 50 µg L^{-1} (1.0×10^{-6} M).

Considering the guideline or regulated values, the sensitivity of the proposed CC-FIA method is sufficient for monitoring Cr(VI) in drinking or environmental waters.

SIA mode

The Auto-Pret system shown in Fig. 1 (the photo of the system) can be used for conventional SIA. For SIA mode, only one syringe pump and one SLV is used, as is shown in Fig. 5. In SIA for the determination of Cr(VI), the reagent solution used was the same as in CC-FIA. The other experimental conditions were optimized by using the reagent solution and the background solution (0.3 M HNO_3). As the results, the zones formed in the holding coil were in the following order: (1) 1200 µL of the background

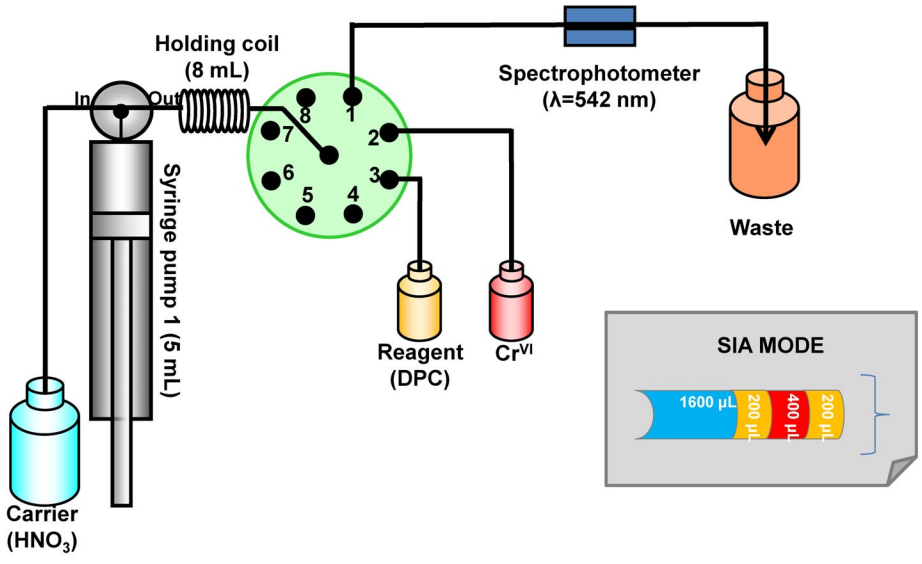

Fig. 5 Schematic diagram of SIA system: one syringe pump mode.

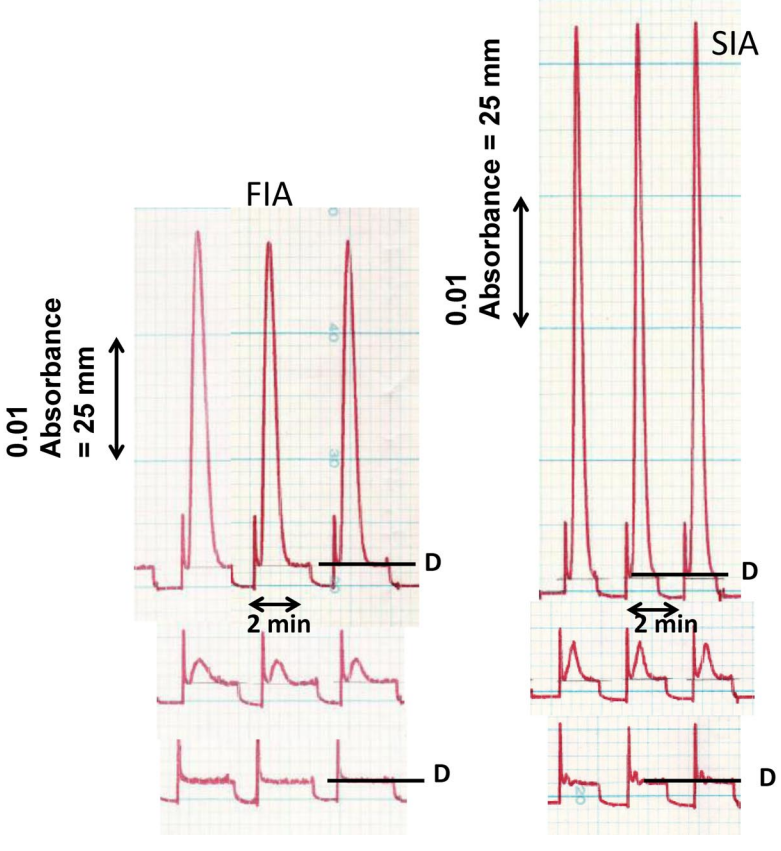

Fig. 6 Comparison of peak profiles obtained by SIA and FIA.

solution, (2) 200 μL of the DPC solution, (3) 400 μL of a sample solution, and (4) 200 μL of the DPC solution. The zones aspirated in the holding coil were propelled toward the detector at the flow rate of 30 μL s^{-1} (1.8 mL min^{-1}) for 80 s. The sample throughput was more than 45 samples min^{-1}.

The example of typical flow signals is shown in Fig. 6. In Fig. 6, a symbol D means the baseline, from which the peak height is measured as the height. The calibration graph shows good linearity over the range of 0 to 1×10^{-6} M, and the regression curve is shown as $y = 10.6x - 1.632$, $R^2 = 0.9991$, where y is peak height (mm), x the molar concentration (10^{-7} M) of Cr(VI). The LOD of Cr(VI) is 1.1×10^{-8} M (0.6 μg L^{-1}).

Comparing the signals of SIA with CC-FIA, the peak height of SIA is about 1.6 times higher than that of CC-FIA. This is because the sample zone is not so dispersed or diluted with both reagent zones as is in CC-FIA, whereas the sample zone in the carrier is diluted twice with the reagent solution in CC-FIA. In FIA, when a slower flow rate of the reagent solution compared to the flow rate of a sample zone was used, the peak height was increased; for example, the flow rate of the reagent solution was 0.3 mL min^{-1}, the peak height was almost the same as in SIA. By using the present syringe pump, the slower flow rate, for example, 0.1 mL min^{-1}, can be possible, and therefore much higher peak height can be obtained. By the same reason, the peak width of SIA is about 0.6 times narrower than that of CC-FIA as shown in Fig. 6.

Comparing the LOD of CC-FIA with that of SIA, the former shows lower LOD than the latter. This is because in CC-FIA the dispersion or the mixing between a sample and a reagent solution is very reproducible, and the peak and its shape of CC-FIA are more stable and reproducible than those of SIA. In conclusion, however, the difference in LOD between SIA and CC-FIA is not so large and meaningless in a practical analysis for environmental samples. SIA can be available for the determination of Cr(VI) in real water samples.

Auto-Pret/FIA mode

SIA and CC-FIA proposed here can be favorably applied to the determination of Cr(VI), and these techniques satisfy the demands of WHO guidelines, Japanese environmental regulations, etc. However, someone wants to know how much Cr(VI) is present in natural and drinking waters, whose concentrations of Cr(VI) are less than the guideline or the regulated values, and are possibly less than 10^{-8} M. For such a purpose, more sensitive methods were developed by using the double syringe-type Auto-Pret system shown in Figs. 1 and 7 with the mini-column packed with the anion-exchange resin.

The principle of the techniques is as follows.

Procedures of the collection/concentration of Cr(VI) and the spectrophotometric method by FIA are:

(1) Cr(VI) is collected/concentrated on the column installed on an 8-port SWV.
(2) Cr(VI) on the column is eluted.
(3) Some parts of the effluent zone are kept in a loop on an 8-port SWV.
(5) A carrier stream and a reagent stream are flowed simultaneously as is in CC-FIA.
(6) SWV is turned and the effluent in the loop flows out with the carrier stream while the two streams are flowing.
(7) The carrier stream with the effluent is merged with the reagent stream, and the mixture flows into a reaction coil and finally flows into the flow cell of the SPM.

In these procedures, step 6 is very important for the sensitivity and reproducibility of Cr(VI) determination; that is, in the effluent, it is very important to investigate where the most concentrated zone of Cr(VI) is present.

In Table 1, all of the sequences for the collection/concentration procedures and the spectrophotometric detection procedures are summarized.

Table 1 Operating procedure for the Auto-Pret/FIA system.

Sequence step	SP1 (SP2)[a]	Subject	SLV	SWV	Flow rate, μL s^{-1}	Volume, mL
Filling reagent	(aspirate from bottle)	reagent		1	100	2.5
Cleaning	aspirate from bottle	water	Port3(P3)	1	100	0.5
	dispense	water	P5	1	50	0.5
Conditioning	aspirate	buffer	P1	1	100	1.0
	dispense	buffer	P5	1	50	1.0
Sample loading	aspirate	sample	P2	1	100	5.0
	dispense	sample	P5	1	40	5.0
Washing	aspirate from bottle	water	P5	1	100	0.5
	dispense	water	P5	1	40	0.5
Eluting	aspirate	eluent	P3	2	100	2.5
	dispense	eluent	P5	2	40	0.3
Flowing for FIA	(dispense)[a,b]	reagent		2	15	2.5
	dispense[a,b,c]	carrier	P6	2	15	0.6
	dispense[a,b,c]	carrier	P6	1	15	1.9

[a]Syringe pump 2 for reagent.
[b]SP1 and SP2 start dispensing the solution simultaneously, and the SWV turned from 1 to 2.
[c]While SP1 is continuously propelling the solution, SWV turns to SWV1 from SWV2, and the effluent in the loop is pushed out.
SP1: syringe pump 1; (SP2): syringe pump 2; SLV: selection valve; SWV: switching valve.
SWV 1, P5 of SLV → column → waste, and P6 of SLV → loop → mixing joint; SWV 2, P5 of SLV → column → loop → waste.

By using the manifold of the double-syringe Auto-Pret system shown in Fig. 7, some parts of the effluent zone of the highest concentration of Cr(VI) were investigated. In Fig. 7, Port 6 of SLV was connected to Port 5 of SWV and Port 4 of SWV was free, and the loop of 300 μL was exchanged for a 1100 μL loop. The procedures were carried out according to the above-mentioned procedures 1–3: the front part, 1100 μL, of the effluent was kept in the loop. After that, as in the similar manner to SIA described in the section "SIA mode", Cr(VI) concentration in the effluent was measured: each 10 μL of the effluent in the loop was aspirated from Port 5 of SWV through Port 6 of SLV into the holding coil and the Cr(VI) concentration was measured. The results obtained are shown in Fig. 8. From Fig. 8, the zone of the highest concentration of Cr(VI) was present at around 90 μL in the front area of the effluent. Therefore, in the Auto-Pret/FIA mode, the front area of the effluent from the mini-column was kept in the 300 μL loop, considering the dispersion of the zone during the FIA measurement.

The typical signal profiles obtained by using the operating procedures in Table 1 are shown in Fig. 9. In the signal profiles in Fig. 9, during A any solution is not flowing into the flow cell, while a series of the procedures, the collection/concentration of Cr, the elution of Cr from the column and keeping the effluent in the effluent loop, is performed, and at B, the measurement procedures for Cr by FIA is started. Just after starting the measurement procedures, a sharp peak B caused by SWVs and starting the flow of the solution into the flow cell appears, and a set of a minus and a plus peak appears, which is caused by the Schlieren effect. After the Schlieren effect peak, a background or a baseline appears in a short time, which corresponds to the water present in the front zone (Zone 1 in Fig. 7) and again the Schlieren effect peak C1 in Fig. 9, which includes a peak of Cr, appears; the second peak is composed

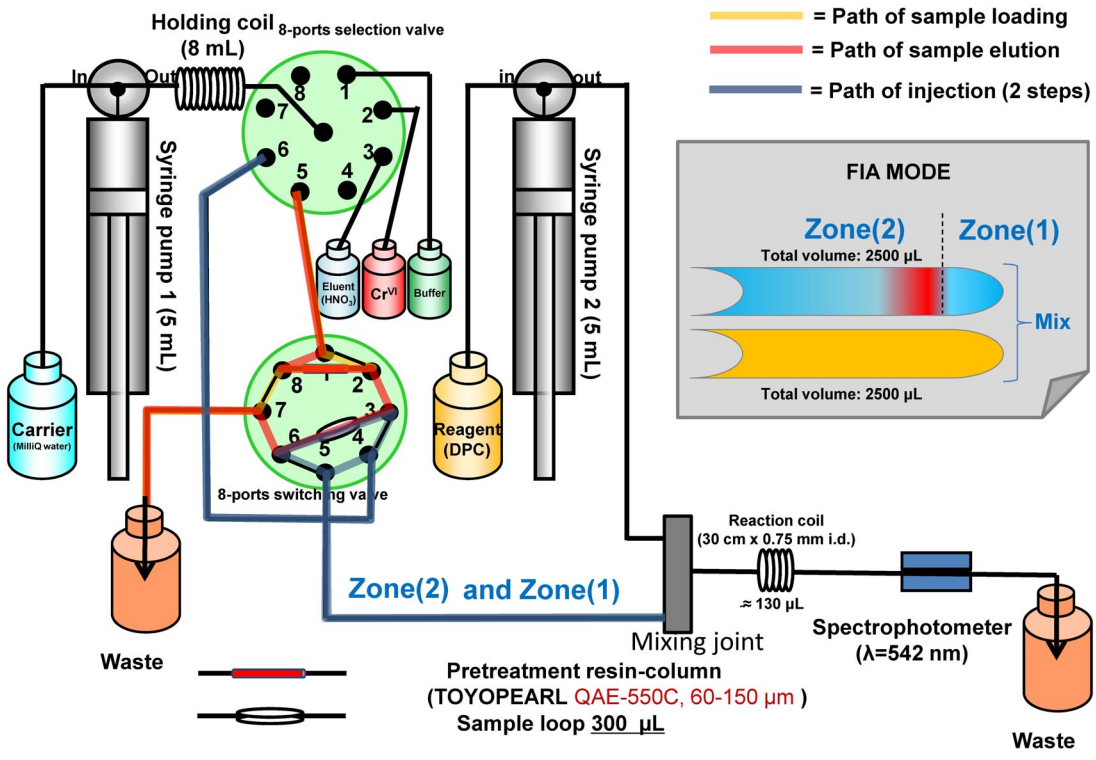

Fig. 7 Manifold of Auto-Pret/FIA system for the determination of Cr(VI) by spectrophotometry. Carrier stream: 0.3 M HNO_3, reagent stream: 6×10^{-4} M DPC in 0.3 M HNO_3, sample volume used for column loading: 5 mL, loop for keeping effluent: 300 µL, flow rate of each stream for FIA: 15 µL/s, reaction coil: 0.75 mm i.d. × 30 cm, wavelength: 542 nm.

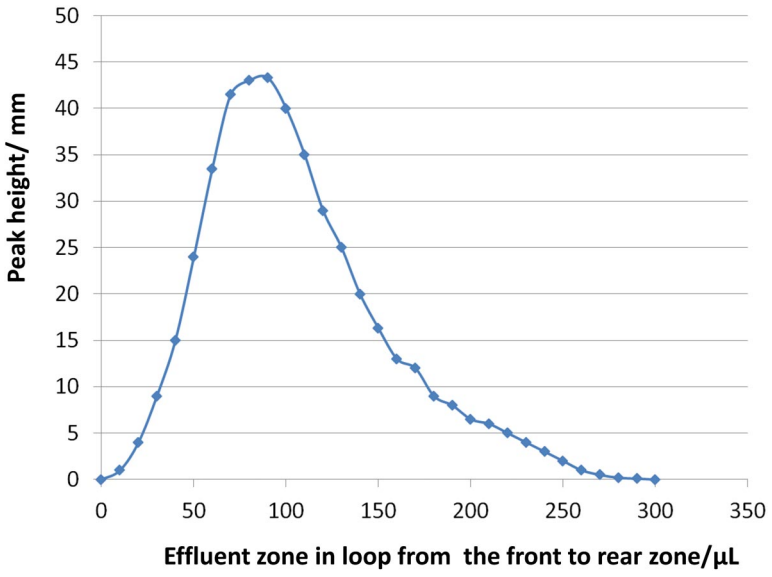

Fig. 8 Relative concentration profile of Cr(VI) in effluent zone kept in the loop on an SWV.

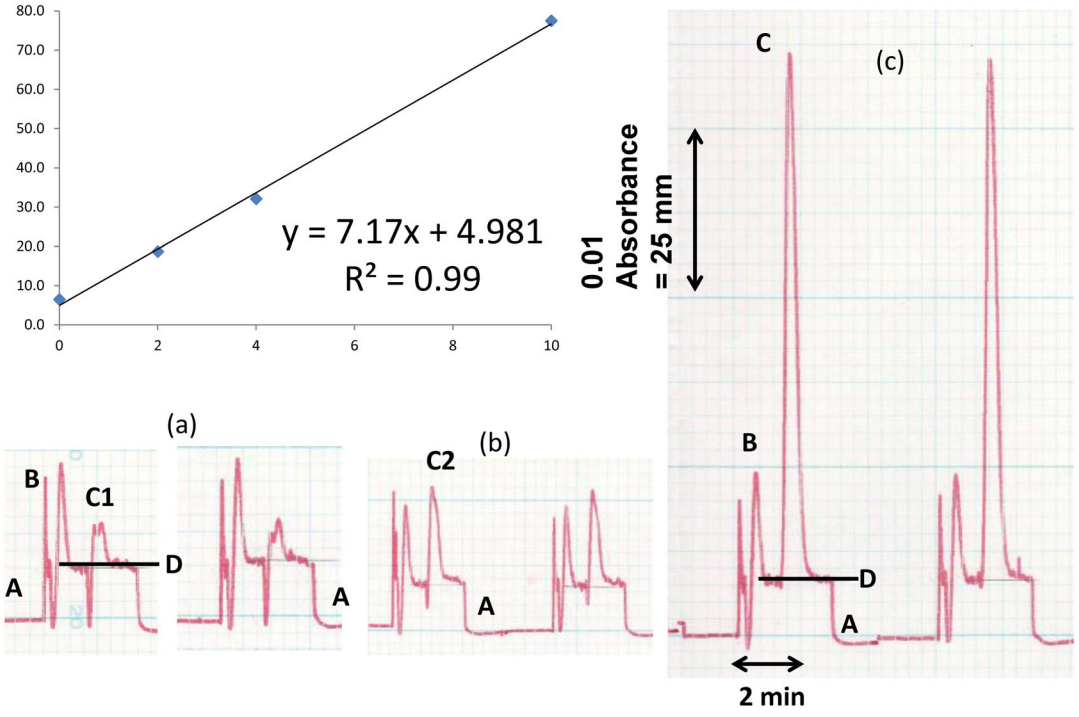

Fig. 9 Signal profiles and a typical calibration graph obtained by using Auto-Pret/FIA system for Cr(VI). Cr(VI): (a) 0, (b) 2.0×10^{-8} M, (c) 1.0×10^{-7} M; calibration graph: $y = 7.17x + 4.981$, $R^2 = 0.99$. In the calibration graph, 10 mm of peak height corresponds to the absorbance of 0.004. Symbols A, B, C, C1, C2, and D are explained in the text.

of the Schlieren effect peak and the Cr peak of trace amounts in the water and the reagent solution. In C2 in Fig. 9, a relatively large peak of Cr overlaps the Schlieren effect peak, and finally, in C in Fig. 9, the Schlieren effect peak cannot be seen.

Peak height can be measured as the height from the baseline D. The calibration graph shows good linearity: $y = 7.17x + 4.981$, $R^2 = 0.99$. The LOD, which is defined as the Cr(VI) concentration corresponding to the three times of the standard deviation (σ) of the peak height of the reagent blank (3σ), was 1.4×10^{-9} M (0.07 µg/L).

The sensitivity of the Auto-Pret/FIA mode was much increased compared with the CC-FIA mode. However, a small peak of the reagent blank appeared. This peak may be caused by trace amounts of Cr(VI) contained in the water and the reagents.

Application of Auto-Pret/FIA mode to the determination of Cr(VI) in practical water samples

By using the proposed method using the Auto-Pret/FIA mode, the concentrations of Cr(VI) in water samples were determined. Most of the cations and anions commonly existing in environmental water samples and drinking waters did not interfere with the determination; the tolerable concentrations of ions are: Na^+, F^- (1×10^{-1} M), K^+, HCO_3^- (2×10^{-2} M), Cl^-, Br^-, NO_3^-, SO_4^{2-} (1×10^{-3} M), Mg^{2+}, Ca^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+} (1×10^{-4} M), where the tolerable concentration means that the percentage of the deviation compared with the standard sample is within ±2 %.

Table 2 show the analytical results obtained for river water samples and pet-bottled waters commercially available, which were imported into Japan from a foreign country.

Table 2 Analytical results for Cr(VI) in water samples obtained by the Auto-Pret/FIA system.

Sample	Cr(VI) found/10^{-9} M
Tap water (Okayama City)	<1 (0.05 μg/L)
Drinking water (Japan)	<1 (0.05 μg/L)
Drinking water A (imported)	3.0 (0.16 μg/L)
Drinking water B (imported)	4.0 (0.21 μg/L)
JSAC Standard river water*	<1 (0.05 μg/L)

*Certified value of total Cr: 10.1 μg/L: chromium can exist as Cr(III).

Some of the drinking waters contained ultra-trace amounts of Cr(VI), whose concentrations are much less than the WHO or other guidelines. The Cr(VI) contents in tap waters and JSAC (Japan Society for Analytical Chemistry) standard material were less than the LOD of the method. In our previous papers using ICP-AES with a column pretreatment [13,17], the Cr(VI) and Cr(III) concentrations in tap water samples are 0.05 ± 0.03 and 0.07 ± 0.01 μg L^{-1}, respectively. From these results, tap water examined in this work contained very low concentrations of Cr(VI), which are around 10^{-9} M or less.

LEP-AES COUPLED WITH DOUBLE-SYRINGE AUTO-PRET SYSTEM

Recently, Takamura, for the first time, found a principle of LEP-AES, which was a newly developed instrument for AES [18,19]. The system is a compact and portable type, and works with a battery. Other advantages of LEP-AES are: sample volume necessary for the measurement of atomic emission is only several μL, and the running cost is very low—several dollars for several days—and a flow cell for water samples is installed in the system. By utilizing such advantages, the LEP-AES system has been applied to the determination of metals, such as alkaline metals and heavy metals (Pb, Cd, etc.) in soils and water samples [20–22]. LEP-AES is very useful for the determination of metal ions in water samples. However, the sensitivity itself is at the levels of several ppm (mg L^{-1}) to sub-ppm (0.1 mg L^{-1}), which are somewhat insufficient for the determination of analytes at ppb (μg L^{-1}) levels. Therefore, some preconcentration techniques must be adopted prior to the measurement [20–22].

The double-syringe Auto-Pret system (Fig. 1) was hyphenated with LEP-AES, in which the syringe P2 was exchanged for a smaller one (0.5 mL). The mini-column was packed with TE-05 chelating resin, and installed on SWV. The column was conditioning with 1 mL of acetate buffer (pH 7), and 5–30 mL of a sample solution was loaded on the mini-column. After the mini-column was washed with 1 mL of water, the eluent, 0.09 M NTA, was flowed into the column by using the syringe P2 at the flow rate of 15 μL s^{-1}: the effluent was flowed into the quartz flow cell, where the atomic emission was measured with applying voltage of 1100 V. The calibration graphs for Cd, Pb, Cu, and Zn shows good linearity over the ranges of 0–100 μg L^{-1} by using 30 mL of sample solutions; for example, the calibration graph for Cd shows the linear line with $y = 4176x + 43.18$, $R^2 = 0.9962$, where x is metal concentration, 0.1 mg L^{-1}. The LODs of Cd, Pb, Cu, and Zn were 20, 20, 430, and 500 μg L^{-1}, respectively, when 5 mL of samples was used. In larger volume of samples loaded on the mini-column, the detection sensitivity was much improved; the LODs of Cd and Pb were 5 μg L^{-1} when 30 mL of samples was loaded, as is shown in Fig. 10.

The method can be applied to the determination of metals in contaminated soil and sediment samples.

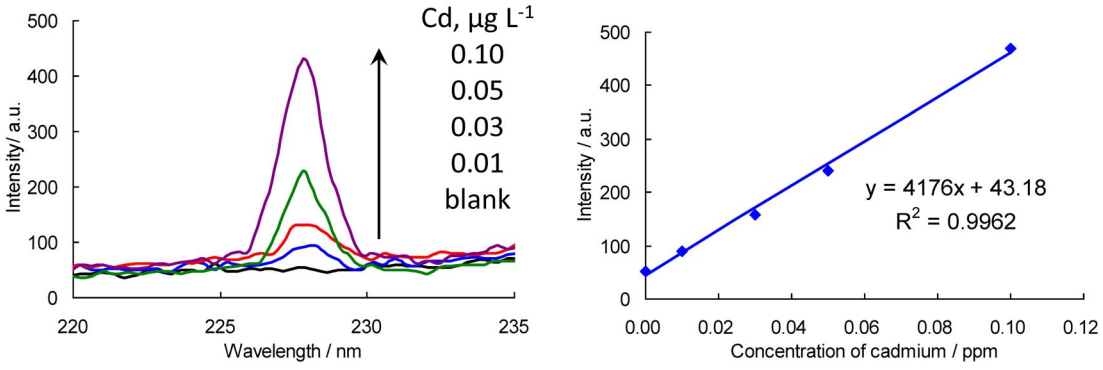

Fig. 10 Signal profiles and a typical calibration graph obtained by AES using LEP-AES system. Sample: 30.0 ml of cadmium solution, pH 7; Eluent: 0.09 M NTA, pH 7.

ANODIC STRIPPING VOLTAMMETRY (ASV) HYPHENATED WITH SIA AND AUTO-PRET SYSTEM

In recent years, ASV has been used for trace metal ions in environmental samples. For highly sensitive ASV methods, a thin-film coated carbon electrode has been used. One of the most effective and less toxic metal ions for the thin-film coating is Bi [23]; Bi compounds have been used for medicine, which is a less toxic substance, and can be easily electro-deposited on the surface of carbon electrodes. However, there are some problems in the reproducibility and complexity of the procedures, which include the formation of thin films on the surface of electrodes, the deposition of analyte metals on the electrode, the stripping of analyte metals from the electrodes and the cleaning of the electrodes.

The complex and tedious procedures in the thin-film ASV can be avoided by using CC-FCA, such as SIA or the Auto-Pret system. For ASV-hyphenated CC-FCA, a screen-printed carbon electrode (SPCE) is a very versatile, convenient, and less expensive electrode. Further, it can be used in a flow system, and all the procedures necessary for the thin-film SPCE-ASV can be performed by SIA system, and for much more highly sensitive detection, the Auto-Pret system with a mini-column can be used, as is shown in Fig. 11.

When SIA was used for Bi-film SPCE-ASV, trace amounts of C(II), Pb(II), and Zn(II) were simultaneously measured, and the LODs of Cd and Pb were 0.89 and 0.69 µg L^{-1}, respectively [24], and using a screen-printed carbon nanotube electrode (SPCNTE), the LODs of Pb, Cd, and Zn were improved; they were 0.2, 0.8, and 11 µg L^{-1}, respectively [25].

When the Auto-Pret system with the mini-column packed with ME-01 was used, LODs of Cd and Pb were improved: the lowest detectable concentrations were as low as 0.05 µg L^{-1} for Pb, 0.3 µg L^{-1} for Cd, and 17 µg L^{-1} for Zn [26].

ASV hyphenated with SIA and Auto-Pret system will become more useful and interesting for the determination of trace amounts of other metal ions, such as As, Hg, and Cr, by coupling with the improvement of thin-film SPCEs.

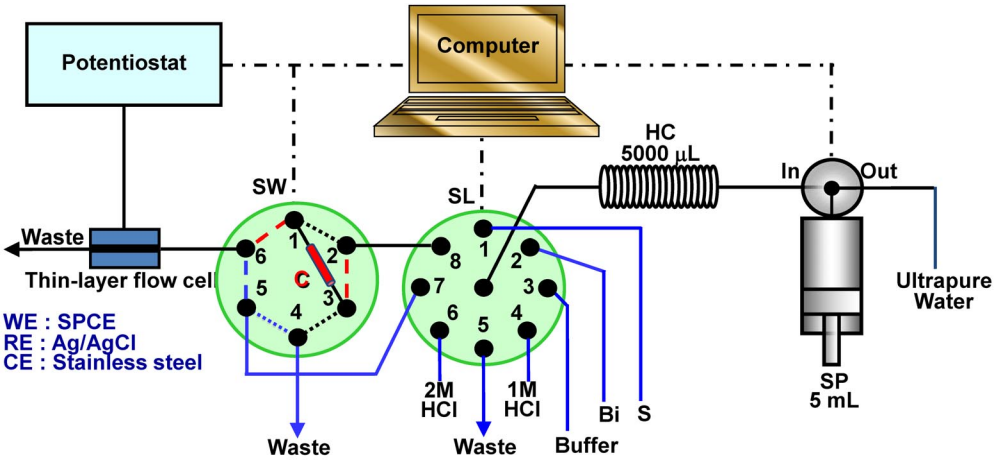

Fig. 11 Auto-Pret system hyphenated with SPCE-ASV. SP: syringe pump; SLV: selection valve; SWV: switching valve; ….. loading, —— eluting; HC: holding coil; C: mini-column (2 mm i.d., 4 cm length) of chelating resin; 2 M HCl: column cleaning solution; 1 M HCl: eluent and electrode cleaning solution; buffer: 0.1 M acetate buffer; Bi: Bi plating solution (Bi(III) in 1 M HCl); S: sample/standard solution in acetate buffer; WE: working electrode; RE: reference electrode; CE: counter electrode (ref. [24]).

APPLICATION OF AUTO-PRET SYSTEM TO THE DETERMINATION OF TRACE AMOUNTS OF HEAVY METALS BY ELECTROTHERMAL-ATOMIC ABSORPTION SPECTROMETRY (ET-AAS) AND ICP-AES

Auto-Pret system with a mini-column packed with chelating resins was applied to the determination of trace amounts of metal ions in water samples. One hundred µL of the analyte zone in the effluent, which contains highest concentrations of the analyte, was kept in the nozzle of the sample injection into a graphite furnace of ET-AAS. After that, an autosampler of ET-AAS started to work, and 40–100 µL of the analyte zone in the nozzle was injected into the furnace, and atomic absorbances were measured.

The sensitivity of the methods was much improved, and usually LODs are several ng L^{-1} to several tens of ng L^{-1} [27].

Similarly, Auto-Pret systems with a mini-column has been applied to the determination of metals in water samples. Various kinds of chelating resins have been tested, and the sensitivities were much improved by such a hyphenated system as Auto-Pret/ICP-AES [28–30].

CONCLUSION

Now several sophisticated analytical instruments can be used for chemical analysis in scientific, social, and industrial areas, and so on. They, of course, are very useful for trace and ultra-trace chemical analysis. However, such instruments, for example, those hyphenated with mass spectrometers, are very expensive, and further special maintenance and high running cost are necessary. On the other hand, the cost of conventional CC-FCAs demonstrated in this paper is less than one-tenth of the hyphenated mass spectrometers, and special maintenance is not necessary.

As was reported in the paper, chemical species at nano or sub-nano mol/L levels can be measured by using conventional CC-FCAs, which will satisfy more than 90 % of increasing demand on chemical analyses [31].

From the consideration reported [31], several examples for the chemical analyses of trace and ultra-trace amounts of toxic metals in environmental samples were demonstrated by using several promising CC-FCA systems. Recently, we can utilize various kinds of CC-FCA as it is, or by hyphenating

them with various kinds of less expensive and less sophisticated detection systems with good cost-performance and compact and good mobility.

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