Determination of Cadmium by Inductively Coupled Plasma Atomic Emission Spectrometry after Suction-Flow On-Line Preconcentration on 8-Quinolinol-Loaded Active Carbon

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The suction-flow on-line column preconcentration of cadmium from an aqueous solution for inductively coupled plasma atomic emission spectrometry (ICP-AES) was investigated utilizing a column packed with gas chromatographic-grade porous active-carbon impregnated with 8-quinolinol. A sample solution (pH 2.5–7) and a buffer solution were sucked, mixed and pumped through the column; subsequently, the analyte was eluted directly into the nebulizer of the ICP with 1 cm³ of 0.5 mol dm⁻³ hydrochloric acid. Using 5 cm³ of the sample solution, this method gave a signal enhancement of 1 order of magnitude for cadmium, better than that obtained by a conventional nebulization system; the detection limit was 0.25 ng cm⁻³ with a sampling rate of 35 h⁻¹. The relative standard deviation for 500 ng cadmium was 1.1% ($n=10$). This column could be used for more than 80 replicate analyses when 5 cm³ of a standard solution containing 100 ng cm⁻³ cadmium(II) was introduced into the system each time. The proposed method was applied to the determination of cadmium in certified biological reference materials.

Keywords Inductively coupled plasma atomic emission spectrometry, cadmium, suction-flow, on-line preconcentration, active carbon, 8-quinolinol

Recently, on-line sample introduction systems incorporated with ion-exchange preconcentration for atomic spectrometry have been attempted.^{1–12} In addition to other benefits, these systems have the advantage of being able to carry out automatic operation in a closed system. Particularly suitable are simple and rapid techniques that facilitate a discrete introduction of small amounts of a sample solution, such as flow injection^{1–8} and suction-flow.^{9–12} With respect to the size of the sample used, these techniques allow analyses at low volume of the order of microliters or milliliters of a sample solution. In any event, these techniques are capable of improving the detection limit by 1 or 2 orders of magnitude with the additional advantage of separating the analyte from an interfering matrix.

Regarding an on-line preconcentration column, various chelating resins^{1–4,9,10}, and active alumina^{5,6,11}, as well as silica gel, glass or polymer immobilized complexing agents^{7,8,12} have been used as a vehicle packed in the column, depending on the elements to be determined and the matrix analyzed. On the other hand, in batch procedures, despite the smaller exchange capacity and less hydrophilicity, active carbon has been used as a sorbent.^{13–16} In order to improve the collection capacity, several batch methods for the concentration of trace metals on chelating agent-loaded active carbon have been reported.^{16–20} Furthermore, by using a suitable chelating agent, single or multiple

elements of interest can be separated selectively from the various coexisting elements. However, these methods are somewhat tedious for a preconcentration procedure, and none of them makes replicate use of the active carbon. We found that multiple use of porous active carbon of high purity impregnated with 8-quinolinol (oxine-AC) was possible without any reloading with oxine. This paper describes a low-cost on-line preconcentration system using a column packed with oxine-AC for a sensitive suction-flow on-line inductively coupled plasma atomic emission spectrometry (ICP-AES) of cadmium and its application to determinations for biological samples.

Experimental

Reagents

Water was purified by ion-exchange followed by filtration using an Advantec Toyo (Tokyo, Japan) Model GSU-901 de-ionizer. The conductivity of the purified water was less than 0.1 $\mu\text{S cm}^{-1}$. Analytical-reagent grade chemicals were used in all experiments. A 1000 $\mu\text{g cm}^{-3}$ cadmium(II) standard solution (Kanto Chemical, Tokyo, Japan) was used by appropriate dilution with dilute hydrochloric acid. A citrate buffer solution (0.1 mol dm⁻³) was prepared by dissolving 22.6 g of diammonium hydrogen citrate in 1.0 dm³; the pH was

Fig. 1 Flow diagram of the suction-flow on-line oxine-AC column preconcentration system for ICP-AES. 1, suction cup; 2, column; 3, peristaltic pump; 4, ICP; 5, digital pipet.

adjusted to 8.5 with 1 mol dm⁻³ ammonia water. Gas chromatographic-grade active carbon (AC; 80–100 mesh, GL Sciences, Tokyo, Japan) was used. An 8-quinolinol (oxine)-AC was prepared as follows: to a conical flask, 5 g of pre-dried AC, 5 g of oxine (Wako Pure Chemical, Osaka, Japan) and 125 cm³ of ethanol solution were added and the mixture was stirred overnight. The oxine-AC was separated by suction filtration and washed with water.

Apparatus

A Kyoto-Koken (Kyoto, Japan) Model UOP-1S high-resolution inductively coupled plasma atomic emission spectrometer was used. The flow system comprised a two-channel variable-speed peristaltic pump (Tokyo Rikakikai, Tokyo, Japan), a PTFE suction cup²¹, an oxine-AC column (2 mm i.d., 10 cm long) and a T-joint. The other parts of the flow system were connected with 1-mm i.d. PTFE tubings. The assembly is shown in Fig. 1. The dimensions of the cup were as reported previously.^{21,22} Gilson (Villiers-le-Bel, France) Pipetman Model P-5000 and Microman P-250 digital pipets were used. Double-vessel digestion bombs²³ were used for the decomposition of biological samples. The bomb comprised a Teflon-PFA (perfluoroalkylvinyl ether) Tuf-Tainer vial (Pierce Chemical, Rockford, USA), a PTFE vessel and a stainless-steel jacket (both San'ai Science, Nagoya, Japan).

Analytical procedure

Using the digital pipet, a sample solution (pH 2.5–7; 5 cm³) is transferred to the suction cup and is merged into the buffer line and mixed. Cadmium ions are retained on the oxine-AC column while the buffer solution is continuously introduced into the nebulizer of the spectrometer through the column. Then, 1 cm³ of 0.5 mol dm⁻³ hydrochloric acid is sucked in and the collected ions are subsequently eluted. The transient emission signal is recorded on a strip-chart recorder and the peak height is measured. The emission peak appears within 10 s, just after introducing the eluent.

Table 1 Analytical conditions

ICP atomic emission spectrometer (Kyoto Koken Model UOP-1S)	
Radio frequency power	1.0 kW
Argon gas flow rates	
Outer gas	10 dm ³ min ⁻¹
Intermediate gas	0.5 dm ³ min ⁻¹
Nebulizer gas	0.35 dm ³ min ⁻¹
Observation height	12 mm above load coil
Photomultiplier applied voltage	800 V
Response (time constant)	1 s
Analytical line	214.438 nm (Cd II)
Suction-flow preconcentration system	
Sample (pH 2.5–7) volume	5 cm ³
Eluent (0.5 mol dm ⁻³ HCl)	
volume	1 cm ³
Rinse water volume	1 cm ³
Flow rates	
Sample	4.5 cm ³ min ⁻¹
Eluent	4.5 cm ³ min ⁻¹
Buffer (pH 8.5, 0.1 mol dm ⁻³ ammonium citrate)	4.5 cm ³ min ⁻¹
Column	
Size	2 mm i.d., 10 cm long
Packing (oxine-AC)	170 mg

Fig. 2 Time-sequence for suction-flow.

The recommended operating conditions are summarized in Table 1. After elution, 1 cm³ of water is sucked in for rinsing. The timing of the cycle is shown in Fig. 2.

Results and Discussion

Optimization of operating conditions

The emission intensity in ICP-AES is mainly affected by the incident radio-frequency power, flow rate of carrier gas and observation height of the plasma. The effects of the variation of these parameters on the cadmium emission intensity were thus investigated for optimization. The analytical line used was 214.438 nm (Cd II) showing the highest sensitivity and having

relatively few neighboring lines. From the obtained results, the optimal conditions for cadmium determination were selected (Table 1).

The active carbon for gas chromatography chosen in this work showed a high adsorption activity together with a low back-pressure and minimum background, since it has a porous, coarse (80–100 mesh) structure, and is highly pure. Such features were very favorable for the suction-flow on-line sample introduction system.

The effect of column size on the cadmium emission intensity was investigated while keeping the loaded amount of cadmium(II) at 500 ng. With a column of 2.0 mm i.d., the sharpest and highest peaks were obtained. Using a column wider than 2.0 mm i.d. lowered the emission intensity. Diffusion upon the elution of cadmium(II) seems to have caused this result. Regarding the column length, a minimum length of 5 cm was necessary for a complete collection of cadmium(II). A column longer than 20 cm produced extra back-pressure and disturbed the constant flow. Since while using a column of less than 5 cm length, cadmium(II) could not be retained completely, an optimum 10-cm column length was chosen and used throughout this work.

The effects of the flow rates of the sample, buffer and eluent were examined. In this work, all flow rates of the solutions were kept the same for practical convenience. The emission intensities were almost constant in the flow rate, ranging from 1.5 to 4.5 cm³ min⁻¹. A rate of 4.5 cm³ min⁻¹ was chosen in consideration of the sample throughput.

Hydrochloric acid was used as an eluent; a maximum, constant emission intensity of cadmium was obtained in the range from 0.5 to 1.0 mol dm⁻³. In this work, 0.5 mol dm⁻³ of hydrochloric acid was used throughout. Under the above-mentioned conditions, we confirmed that the constructed column can be used for the analysis of at least 80-replicates without any reloading with oxine, when 5 cm³ of a standard solution containing 100 ng cm⁻³ cadmium(II) is introduced into the system each time.

In order to evaluate the pH response of the oxine-AC column, the pH of a sample solution containing 100 ng cm⁻³ cadmium(II) was varied by adding dilute hydrochloric acid or dilute ammonia water. The analysis was then carried out under analytical conditions in which the pH of the 0.1 mol dm⁻³ diammonium hydrogencitrate buffer solution was adjusted to 8.5 with 1 mol dm⁻³ ammonia water. The results are presented in Fig. 3. When the pH of the sample solution was less than 2.5, a fraction of cadmium(II) broke through the column. Therefore, the pH of a sample should be adjusted to be between 2.5 and 7 prior to analysis.

As Fig. 4 shows, the pH of the buffer solution should be adjusted to 8.5–10.5 when a sample solution of pH 2.5 is introduced into the line.

The relation between sample injection volume (100 ng cm⁻³ cadmium(II)) and the cadmium emission intensity was linear within the tested range, 1–20 cm³.

Fig. 3 Effect of pH of the sample solution on the cadmium emission intensity. Cadmium(II), 500 ng.

Fig. 4 Effect of pH of the citrate buffer solution on the cadmium emission intensity. Cadmium(II), 500 ng.

The apparent sensitivity could therefore be changed by the sample size. In this work, a sample size of 5 cm³ was adopted after considering both the sensitivity and sample throughput.

Calibration and precision

Under analytical conditions, the detection limit (3σ) was 0.25 ng cm⁻³. The sensitivity and detection limit were both 1 order of magnitude better than those obtained by direct aspiration of the aqueous solution. The calibration graph for cadmium was linear up to 1.0 µg cm⁻³, and the relative standard deviation for 10 replicate measurements of 0.1 µg cm⁻³ cadmium was 1.1%. Thirty five samples could be analyzed per hour.

Interference

The effect of ubiquitous ions were investigated by using each solution containing 500 ng of cadmium(II). Tolerable amounts of foreign ions, which gave less than a 10% error for the determination of cadmium, were evaluated. The maximum concentration examined was 1000-times the concentration of cadmium(II) by weight. Within the concentration ratio, foreign ions such as sodium, calcium, strontium, vanadium, ammonium, selenite, chloride, nitrate and sulfate produced no interference. Tolerable amounts of interfering ions are given in Table 2. These tolerance limits would allow the determination of cadmium in biological samples²⁴ without interference by foreign ions.

Table 2 Tolerance limits of foreign ions for the determination of cadmium(II) (results within 10% error)

Ion	Mass ratio (Foreign ion/Cd(II) ^a)	Ion	Mass ratio (Foreign ion/Cd(II) ^a)
Be ²⁺	920	Fe ³⁺	970
Mg ²⁺	860	Co ²⁺	700
Ba ²⁺	880	Ni ²⁺	780
Al ³⁺	610	In ³⁺	850
Ti(IV)	860	Tl ⁺	950
Cr(VI)	890	Sn ²⁺	670
W(VI)	890	Pb ²⁺	740
Mn ²⁺	710	Bi ³⁺	960

Species tolerated up to at least a 1000-fold mass ratio to Cd(II): Na⁺, K⁺, Ca²⁺, Sr²⁺, V(V), NH₄⁺, Se(IV), Cl⁻, NO₃⁻, SO₄²⁻.

a. Cd(II), 100 ng cm⁻³.

Table 3 Determination of cadmium in biological certified reference materials

Sample	Cadmium/ $\mu\text{g g}^{-1}$	
	Found ^a	Certified
Oyster Tissue (NBS SRM 1566)	3.4 $\pm$ 0.3	3.5 $\pm$ 0.4
Pepperbush (NIES CRM No. 1)	7.1 $\pm$ 0.3	6.7 $\pm$ 0.5

a. Mean $\pm$ ave. dev., 3 results.

Application to practical samples

The accuracy of the method was confirmed by analyzing an NBS standard reference material, Oyster Tissue, and an NIES certified reference material, Pepperbush. A decomposition procedure for samples using double-vessel digestion bombs was selected from the literature.²³ Briefly, up to 300 mg (dry weight) of the sample was digested with 3 cm³ of nitric acid in a bomb initially for 2 h at 90°C and then for 4 h at 140°C. After cooling and appropriate rinsing, the digest was adjusted to pH 3 with 1 mol dm⁻³ of ammonia water, and then diluted as required. The results shown in Table 3 are in good agreement with the certified values. Therefore, the proposed method could be successfully applied to the determination of cadmium in such type of samples.

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