Atomic Absorption Spectrometry of Nanogram Amounts of Cadmium, Lead and Zinc after Precipitation with 8-Quinolinol

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A highly sensitive method was developed for the determination of cadmium, lead and zinc in natural waters by atomic absorption spectrometry after coprecipitation with 8-quinolinol. Quantitative recoveries of the metals were possible over the pH range 8–10 when magnesium was present as a carrier ion. The precipitates thus formed were analyzed directly by an atomic absorption spectrometer equipped with a specially devised graphite furnace and a miniature cup. Reliability of this procedure was confirmed by the determination of the metals in lake and river water samples. For the analysis of a 400-cm³ portion of water sample, detection limits ($3\sigma_b$) for Cd(II), Pb(II) and Zn(II) are 0.6, 2.3 and 1.9 ng dm⁻³, respectively. A corresponding precision of 3–5% was typical.

Keywords 8-Quinolinol coprecipitation, magnesium carrier ion, lake water analysis, river water analysis, atomic absorption spectrometry, cadmium, lead, zinc

The concentrations of toxic trace elements in natural water are of considerable interest at present. In general, electro-thermal graphite furnace atomic absorption spectrometry (GFAAS) is the method of choice because of its high sensitivity for cadmium, lead and zinc. However, GFAAS is currently unable to determine directly cadmium and lead at the lower end of their reported concentration ranges in lake water¹ or other natural waters. Therefore, an appropriate preconcentration is usually required.

8-Quinolinol (8-Q) is a well-characterized reagent and the nonselectivity of the reagent has made possible a wide range of analytical applications. Recently, complexation of trace elements with 8-Q, followed by adsorption on activated carbon² or C₁₈ bonded silica gel³, has been developed. Although these techniques have been successfully employed in natural water analysis^{1,3–5} with GFAAS or ICP–AES, the final analyte specimen must be provided in the form of a liquid.

The coprecipitation method has been used for isolating trace elements from natural water, but GFAAS was until now limited to concentrates in solution. When the coprecipitation method is to be applied for isolation of trace elements, the precipitates must be submitted to analysis in the form of a liquid by dissolving the precipitates into appropriate acids. Redissolution involves several chemical stages in order to remove interfering matrix elements, thus decreasing the versatility of analysis and increasing the possibility of

contamination.

We have already developed^{6–9} a solid sampling technique with AAS for the direct analysis of some powdered biological samples and coprecipitation samples. In the present study the technique has been explored for its usefulness in natural water analysis by coprecipitation of trace elements with 8-Q and the subsequent direct analysis of finely powdered precipitates with GFAAS. Simple, rapid and reliable analytical method for cadmium, lead and zinc with simultaneous multielement preconcentration was found to be possible for the lake water samples within the Japanese background level area.

Experimental

Reagents

Acids and ammonium hydroxide used were of the purest available reagent grade (Kanto Chemical Co.). Ultra clean water which was obtained from a Milli-Q purification system (Millipore Co.) was used. 8-Q (8-hydroxyquinoline, reagent grade, Wako Pure Chemical Co.) was preliminarily purified, and then dissolved in hydrochloric acid, and a 2% (w/v) solution was prepared. The purification procedure was as follows: 8-Q was dissolved in chloroform and the solution was shaken with an 0.05 mol dm⁻³ EDTA aqueous solution at pH 10 in a Teflon separatory funnel. Then, the

organic phase was separated and chloroform was evaporated. The solution of magnesium as a carrier metal ion, which was prepared by dissolving the pure metal (99.995%) in hydrochloric acid, was also purified by the addition of 8-Q solution and a subsequent extraction with chloroform at pH 5 to remove any extractable metal chelates.

Stock standard solutions of each element were prepared by dissolving the pure metals and diluting with water; working standards were obtained by serial dissolutions.

Apparatus

A Hitachi Zeeman atomic absorption spectrometer (Model Z-8000), equipped with a background compensation device, was used in combination with an electro-thermal graphite furnace of a cupped type and a miniature cup which was designed by us.^{6,7} A Hitachi AA data processor was employed for data handling.

A Mettler microbalance, model M-3 (readability 1 µg) was used. The maximum permissible weight for this balance is 2.9 g.

Coprecipitation procedure

The coprecipitation procedure for the sample preparation was carried out in a simplified clean laboratory equipped with laminar flow benches, providing a class 10000 working environment.

In a standard procedure, an aliquot of sample solution (100–400 cm³) was placed in a Teflon beaker, into which 20 mg of magnesium ions and 5 cm³ of the 8-Q solution (100 mg as 8-Q) were added. This solution was adjusted to pH 9 by adding an aqueous ammonia solution, and allowed to age for 1 h at 70°C on a hot plate. It was then filtered by a glass filter (No. 4G). The filter was dried at 110°C for 1 h in a drying oven, and then weighed accurately. With a portion of the precipitate, the quantitative analysis was performed directly with AAS.

The powder standards used for calibration of absorbances were prepared by the standard procedure except that a 100-cm³ portion of a standard solution containing various amounts of the respective metal ions was used. A blank powder standard was also prepared by the use of 100 cm³ of water for each sample preparation.

Direct AAS measurement of precipitate

The miniature cup was accurately weighed by use of the microbalance. After the precipitate was placed in the miniature cup, it was again weighed (difference=net weight of the precipitate). The miniature cup was then inserted into the graphite furnace. The precipitate was dried, ashed and atomized according to the instrumental conditions shown in Table 1.

For measurements of absorbance, at least five aliquots with different weights in the range 0.1–0.5 mg were measured, and the absorbance value corresponding to 1 mg of the precipitate was calculated. Oc-

Table 1 Instrumental conditions

Element	Cd	Pb	Zn
Wavelength/nm	228.8	283.3	213.8 307.6 ^a
Lamp current/mA	7.5	7.5	5.0
Drying temp./°C (s)	—	200 (30)	200 (30)
Ashing temp./°C (s)	400 (30)	500 (60)	400 (30)
Atomization temp./°C (s)	2500 (5)	2500 (5)	2500 (5)

a. This line was used for zinc recovery test.

casionally, to normalize the absorbances obtained in different concentration factors, we defined the total absorbances which were calculated from the absorbance obtained above multiplied by the total weight of precipitate obtained.

Recovery studies

The recoveries were calculated by analyzing the particular elements in the filtrates with ICP-AES (a Hitachi ICP atomic emission spectrometer, model 306 was used), where the original concentrations of the metals examined were 1 mg dm⁻³ (recovery test A). For preconcentration work in the submicrogram level (2–0.01 ppb), the recoveries were estimated by comparing the absorbance of the particular elements in the precipitate sample, which were divided by the concentration factor, to those of respective standard solution or NBS standard reference materials measured by the present AAS technique (recovery test B).

Results and Discussion

Instrumental conditions for direct measurement of precipitate samples

Direct introduction of organic solvent extracts into the graphite furnace, despite reported success by some authors^{10,11}, has been unpopular. Difficulties have been reported in dispensing small volumes of organic solvents accurately. Additionally, the volatility of metal-organic compounds is reported to cause loss of the analyte, particularly in the presence of hydrocarbon halides, during drying and ashing steps of the furnace cycle.^{12,13} However, such difficulties were not encountered in a direct analysis of the powder sample by GFAAS.

The operating conditions for the furnace were investigated. The analyte specimen was prepared according to the standard procedure with magnesium carrier ions. As reported in the previous papers^{6,7}, the

drying step was not always necessary in the proposed solid sampling technique, but it was occasionally effective for ashing organic samples smoothly. Atomization temperatures were selected in view of the sensitivity. As a result, the temperature shown in Table 1 is recommended. The relative standard deviation (RSD) of signals evaluated by the peak-height data was obviously wrong, ranging from 5 to 15%, whereas peak-area absorbance values gave reproducible results, the RSD of which was less than 5%.

The effect of the ashing temperature was investigated in detail for each element. Parallel with this, the effect of the ashing time was also examined. The absorbances (peak area) became constant in the ashing temperature between 350 and 500°C for zinc, and 300 and 500°C for cadmium and lead. No volatility of the three elements in the analyte was observed at temperatures below 500°C. The absorbances of the three elements were independent of the ashing time between 30 s and 120 s under the ashing temperature of 400–500°C.

In order to ascertain the heating conditions, the absorption profiles for the elements were investigated. The profile for lead occasionally showed a two-peak pattern in the ashing conditions of 500°C for 30 s or lower than 400°C for 60 s. However the absorption profiles for the three elements showed a symmetric pattern and no shoulder under the conditions shown in Table 1.

Although aluminum was less effective than magnesium as a carrier for quantitative recovery of the coprecipitation with 8-Q (described below), the heating conditions for the sample prepared with aluminum carrier ions were also examined. As a result, the conditions shown in Table 1 were recommended, except that an ashing temperature of 500°C is better for cadmium and zinc.

Recovery efficiencies

The effect of pH on the recoveries of cadmium(II), lead(II) and zinc(II) was investigated to find the conditions necessary for quantitative recovery from aqueous samples. We examined the recovery of the trace elements by using 8-Q (100 mg) and a carrier ion as coprecipitant, precluding the use of thionalide and tannic acid because these reagents gave high blanks.¹⁴ The experiments were performed with 100 cm³ water containing magnesium or aluminum ions as carrier, according to the recovery test A. The results are shown in Figs. 1 and 2. In Fig. 1, the pH range examined was limited to 6–11. Precipitation of magnesium(II) 8-quinolate did not take place significantly below pH 6. As can be seen in Fig. 1, all of the three elements were quantitatively recovered in the presence of magnesium ions. However, aluminum ions were less effective than magnesium. As shown in Fig. 2, maximum recoveries of the elements were obtained at pH 10–11, but the recoveries were not 100%. Cadmium, lead and zinc

Fig. 1 Effect of pH on the coprecipitation of cadmium, lead and zinc with 8-Q in the presence of magnesium ions as a carrier. Metal ions taken, 100 µg; magnesium ions, 20 mg; 8-Q, 100 mg; total aqueous volume, 100 cm³; ●, Cd(II); ○, Pb(II); ▽, Zn(II).

Fig. 2 Effect of pH on the coprecipitation of cadmium, lead and zinc with 8-Q in the presence of aluminum ions as a carrier. Metal ions taken, 100 µg; aluminum ions, 10 mg; 8-Q, 100 mg; total aqueous volume, 100 cm³; ●, Cd(II); ○, Pb(II); ▽, Zn(II).

provided 96, 92 and 98% recoveries, respectively, at pH 10.7 in the presence of 10 mg of aluminum ions.

A further test of the recoveries for the metals (recovery test B) was carried out when known amounts of the metals in the order of submicrograms were spiked into 100 cm³ of pure water. Quantitative recoveries of all elements were found over the pH range 8–10 with magnesium carrier ions. On the other hand, incomplete recoveries were confirmed with aluminum carrier ions. For cadmium, lead and zinc, 94, 84 and 96% recoveries, respectively, were found at pH 10.5 in the presence of 10 mg of aluminum carrier ions. Consequently, in subsequent experiments, precipitates were prepared at pH 9 in the presence of magnesium ions.

Effect of 8-Q amount and sample size

Submicrogram amounts of the three elements were coprecipitated from 100 cm³ of water containing various amounts of 8-Q up to 200 mg and 20 mg of

Table 2 Detection limits, sensitivities and precision

	Concentration, detection limit (400 cm ³) ^a /ng dm ⁻³	Peak height sensitivity (pg/0.0044 AU)	Precision ^b (%RSD)
Cd	0.6	2.3	4.2
Pd	2.3	50	3.3
Zn	1.9	1.2	4.5

a. Defined as the concentration of analyte which gives a response equivalent to 3 times the standard deviation of the blank, based on a 400-cm³ sample volume.

b. Expressed as a coefficient of variation of the analytical determination at 10-fold detection limits.

Fig. 3 Relationship between sample weight of river water sample and the total amount of metals in the final precipitate. A, cadmium; B, zinc; C, lead.

magnesium. As a result, the recoveries of the elements were independent of the amounts of 8-Q in the range >40 mg.

Next, the standard method was applied to various volumes (100–400 cm³) of test solutions. The recovery yields of the elements were essentially independent of the sample volume (see Fig. 3). In this case (sample volume 400 g), the concentration factor reached around 5500. Examinations on sample volumes larger than 500 cm³ were not made because high signals from reagent blanks were found due to large concentration factors (>9000).

Analytical figures of merits

Detection limits, sensitivities and precision are given in Table 2. The sensitivity was calculated on the basis of the metal weight giving 0.0044 of peak-height absorbance. Detection limits have been estimated from the variation of blank values (*i.e.* 3σ_b). Precision is in

Table 3 Determination of Cd, Pd and Zn in water of Lake Mashu (about 5 m depth)

	Proposed method		ICP-AES by NIES ^a /µg dm ⁻³
	µg kg ⁻¹	Blank value/ng	
Cd	0.0017±0.0004	1.81±0.08	<0.006
Pb	0.045 ±0.003	11.9 ±0.3	0.05±0.03
Zn	0.648 ±0.023	10.7 ±0.3	0.63±0.06

a. The values were reported by Nojiri *et al.* of the National Institute for Environmental Studies (Ref. 1).

the range 3–5% (RSD) at a level 10-fold higher than the detection limits.

Analysis of lake and river water

The present method was applied to the determination of the three elements in river and lake water samples. The elements in the samples at sub-ppb level can be determined by the standard addition method using 100 cm³ of the sample waters. As blank values of the standard procedure were relatively high, the analysis was made by varying the sample weight in the range 100–400 g. The concentration was calculated from the slope of the relationship between sample weight and total amounts of the elements. As an example, analytical results on a river water sample are shown in Fig. 3. The concentrations obtained were as follows: Cd, 0.0081±0.0002 ppb; Pb, 0.145±0.004 ppb and Zn, 0.498±0.010 ppb. The present result for Cd was in acceptable agreement with that obtained by Murozumi and Nakamura¹⁵ by isotope-dilution mass spectrometry for the same sample as that used in present study, *i.e.* 0.0107 ppb. The reference values for Pb and Zn in the river water have not been given yet.

Results for the water of Lake Mashu (about 5 m depth) are summarized in Table 3. The blank value listed in Table 3 was obtained from the Y-intercept of the relationship (*c.f.* Fig. 3), which was in good agreement with the blank value obtained by the standard procedure. In Table 3, the present results are also compared with the values obtained by ICP emission spectrometry reported by Nojiri *et al.*¹

Although the purification of the precipitants has not been investigated in detail, blanks can potentially be further lowered with use of cleaner precipitants. The advantages of the present method lie in its simplicity, good precision, high sensitivity and wide applicability range, since the solid sampling technique with AAS is simple and reproducible.

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