

Instrumental Achievements

Determination of Cadmium in High-Purity Zinc by Electrothermal Atomic Absorption Spectrometry after Coprecipitation with Iron(III) Hydroxide

Tetsuya ASHINO and Kichinosuke HIROKAWA

*Institute for Materials Research, Tohoku University, Katahira, Sendai 980-77, Japan***Keywords** Electrothermal atomic absorption spectrometry, high-purity zinc, coprecipitation, iron(III) hydroxide, cadmium

The characteristics of high-purity metals have been widely investigated. In order to assess the purity of metals it is necessary to determine trace amounts of elements in them. For the smelting of zinc metal, a mineral ore (zinc sulfide (ZnS), oxide (ZnO) or carbonate (ZnCO₃)) has been used which contains several elements, especially cadmium. Therefore, in order to evaluate the purity of high-purity zinc metal it has been necessary to develop a procedure for highly sensitive determinations of trace amounts of cadmium in a large quantity of zinc. Trace amounts of cadmium have been determined by voltammetry¹, spectrophotometry^{2,3}, inductively coupled plasma atomic emission spectrometry (ICP-AES)^{4,5} and electrothermal atomic absorption spectrometry (ET-AAS).⁶ In these methods ET-AAS is well suited due to its high sensitivity. However, it is necessary to separate and concentrate trace amounts of cadmium from zinc, because the sensitivity of the determination of cadmium by ET-AAS is affected by a large quantity of zinc. Various preconcentration methods of cadmium have been reported: coprecipitation methods with iron(III) hydroxide (Fe(OH)₃)⁷, molybdenum sulfide (MoS₃)⁸ and diethyldithiocarbamic acid (DDTCA);⁹ a liquid-liquid extraction method with sodium diethyldithiocarbamate (Na-DDTC) using 4-methyl-2-pentanone (MIBK) as a solvent¹⁰ and a cation-exchange method.^{11,12} However, when MoS₃ or DDTCA is used as a carrier, or when Na-DDTC is used as an extraction ligand, both cadmium and zinc are precipitated and extracted. The cation-exchange method is not suitable for analyzing a large number of samples. Therefore, in order to develop an easy procedure for highly sensitive determinations of trace amounts of cadmium in high-purity zinc, a coprecipitation method with Fe(OH)₃ using NaOH and a determination by ET-AAS was investigated and employed. Because cadmium hydroxide (Cd(OH)₂) and Fe(OH)₃ are precipitated in a strong alkali solution, but zinc is dissolved in the solution as ZnO₂²⁻, cadmium can be separated from a large quantity of zinc.

Table 1 Instrument and operating conditions

Instrument	Hitachi Z-9000 simultaneous multi-element atomic absorption spectrophotometer
Background correction	polarized Zeeman effect
Wavelength	228.8 nm
Lamp current	7.5 mA
Argon flow rate	
Carrier gas	300 ml min ⁻¹
Interrupted gas	20 ml min ⁻¹
Graphite furnace	tube type
Injection volume	10 µl
Temperature program	
Drying	80 – 150°C 30 s
Ashing	150 – 600°C 30 s 600 – 600°C 30 s
Atomizing	1500°C 10s
Cleaning	3000°C 10s

Experimental

Apparatus

For the determination of cadmium, a Hitachi Z-9000 simultaneous multi-element atomic absorption spectrophotometer was used; the background was corrected by the polarized Zeeman effect. A hollow-cathode lamp was used as the light source. The operating conditions are listed in Table 1. For the dissolution and coprecipitation of a sample, a polytetrafluoroethylene (PTFE) beaker was used. For filtration, polypropylene filter funnel and filter paper (No. 5C) were used. For decomposing the precipitate and filter paper, a Pyrex glass beaker was used.

Reagents

Cadmium standard solution (0.01 µg ml⁻¹): 100 mg of metallic cadmium (99.999%, Wako Pure Chemical Industries Ltd.) was dissolved in 10 ml of 7 M HNO₃, and diluted to 100 ml with water. It was diluted with water

before use.

Iron(III) standard solution (2 mg ml^{-1}): 200 mg of metallic iron (99.99%, Johnson Matthey Material Technology) was dissolved in 5 ml of 7 M HNO_3 and 5 ml of 6 M HCl , and diluted to 100 ml with water. Distilled and ion-exchanged water was used for all preparations of the standard and sample solutions. All of the reagents used were of analytical-reagent grade.

Samples

High-purity zinc: a High Pure Chemicals Co. Ltd. product (99.999%), a Mitsuwa Chemicals Co. Ltd. product (99.999%) and a Mitsui Mining & Smelting Co. Ltd. product (99.999%), were analyzed.

Procedure

A 1 g sample was weighed into a PTFE beaker; 7.5 ml of 14 M HNO_3 , 2.5 ml of 12 M HCl and 10 ml of water were then added, and the sample was dissolved on a heating plate at about 200°C . After cooling at room temperature the solution was diluted with 80 ml of water. Then, 5 ml of a 2 mg ml^{-1} iron(III) standard solution was added, 80 ml of a 20w/v% NaOH solution was added dropwise with stirring. Next, the mixture was boiled for 10 min, and cooled at 20°C for 30 min. After cooling, the precipitate was collected through filter paper, and the precipitate was thoroughly washed with a 0.5w/v% NaOH solution. The filter paper along with the collected precipitate was decomposed in 20 ml of 14 M HNO_3 and 5 ml of 18 M H_2SO_4 , and the solution heated to fumes. Finally, the solution was exactly diluted to 25 ml with water. The blank was prepared using the same procedure as described above without the sample. After 10 μl of the sample solution or the blank solution was injected into a graphite furnace, the atomic absorbance was measured under the conditions given in Table 1. The solutions for calibration were prepared as follows: 0–25 ml of the cadmium standard solution were transferred into volumetric flasks, followed by the addition of 10 ml of iron(III) standard solution and 10 ml of 18 M H_2SO_4 . Finally, the solutions were exactly diluted to 50 ml with water.

Results and Discussion

Effects of a matrix modifier on the determination of cadmium by ET-AAS

The effects of a matrix modifier on the determination of trace amounts of cadmium by ET-AAS were examined; the results are given in Fig. 1. The employed method was as follows: solutions containing $0.002 \mu\text{g ml}^{-1}$ cadmium and $100 \mu\text{g ml}^{-1}$ (50000-times concentration of cadmium) of various metals or 3.2 M H_2SO_4 as matrix modifiers were prepared, and the atomic absorbance of cadmium measured. As matrix modifiers, Fe, Pd, Pt, Au, Ag, Cu, Ni, Zn, H_2SO_4 and Fe- H_2SO_4 were selected. The increase in the atomic absorbance was found for all of the described matrix modifiers;

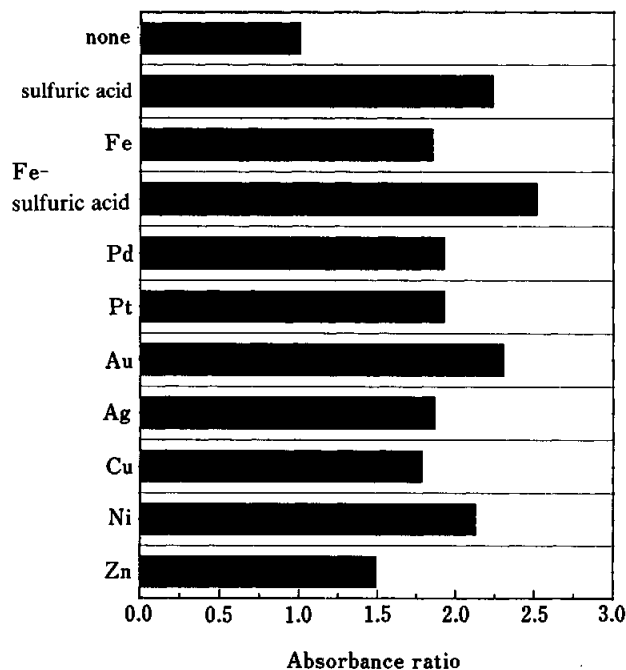


Fig. 1 Effects of matrix modifiers on the atomic absorbance of cadmium: $\text{Cd}=0.002 \mu\text{g ml}^{-1}$; matrix modifiers= $100 \mu\text{g ml}^{-1}$; $\text{H}_2\text{SO}_4=3.2 \text{ M}$. Atomic absorbance ratios are normalized to 1 when no modifiers are present.

especially, the presence of Fe- H_2SO_4 was effective. Therefore, Fe- H_2SO_4 appeared to be the most useful modifier on the selected modifier. A direct determination method for cadmium in high-purity zinc is difficult, because effects of zinc on the determination of cadmium by ET-AAS were found, and synthetic standard solutions matrix-matched to the samples are needed. Accordingly, the authors adopted the coprecipitation method with iron(III) hydroxide and a determination by ET-AAS, because iron can be used as a carrier for coprecipitation and a matrix modifier for determination by ET-AAS.

Concentration of iron as a matrix modifier

The effects of the concentration of iron on the atomic absorbance of cadmium by ET-AAS were examined; the relationship between the concentration of iron and the absorbance of cadmium is shown in Fig. 2. The employed method was as follows: solutions containing $0.002 \mu\text{g ml}^{-1}$ cadmium and in the concentration range from 200 to $600 \mu\text{g ml}^{-1}$ iron were prepared, respectively, and the atomic absorbance of cadmium measured. As a result, in more than $300 \mu\text{g ml}^{-1}$ iron, the atomic absorbance of cadmium was constant. Therefore, for determination of cadmium by ET-AAS the concentration of iron was selected to be $400 \mu\text{g ml}^{-1}$; accordingly, the authors adopted that the quantity of iron as the carrier for coprecipitation should be 10 mg.

Volume of a sodium hydroxide solution for coprecipitation

The effects of the volume of a 20w/v% NaOH solution

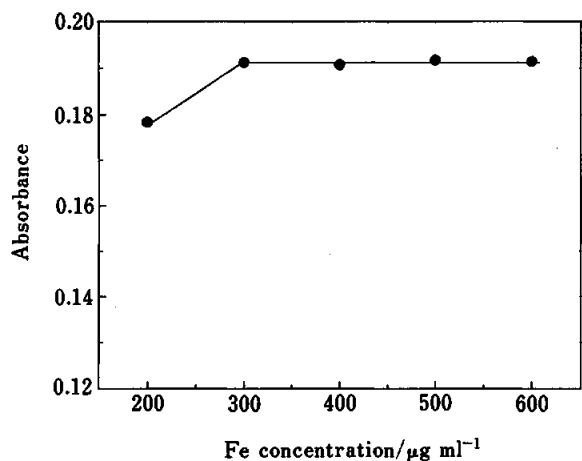


Fig. 2 Relationship between the concentration of iron and the atomic absorbance of cadmium: $\text{Cd}=0.002 \mu\text{g ml}^{-1}$; $\text{H}_2\text{SO}_4=3.6 \text{ M}$.

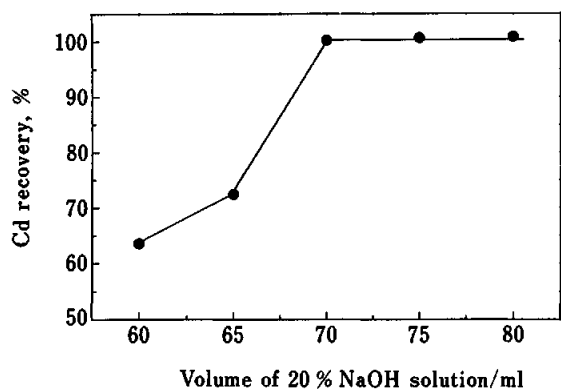


Fig. 3 Relationship between the volume of sodium hydroxide solution for coprecipitation and the recovery of cadmium: $\text{Zn}=1 \text{ g}$; $\text{Cd}=0.05 \mu\text{g}$; $\text{Fe}=10 \text{ mg}$.

on the recovery of cadmium were examined; and the relationship between the volume of NaOH solution and the recovery of cadmium is shown in Fig. 3. The employed method was as follows: after 1 g of high-purity zinc and 0.05 μg of cadmium were dissolved, cadmium was separated by coprecipitation in the range from 60 to 80 ml of NaOH solution. The precipitate was then dissolved and diluted to 25 ml using the same procedure as described above, and cadmium was determined by ET-AAS. As a result, when more than 70 ml of NaOH solution was used, cadmium was quantitatively precipitated. Therefore, the volume of a 20w/v% NaOH solution for coprecipitation was chosen to be 80 ml. The reason for using a 20w/v% NaOH solution for coprecipitation was that not only zinc was hardly dissolved as ZnO_2^{2-} in less than 20%, but also the filter paper decomposed in more than 20% of NaOH solution.

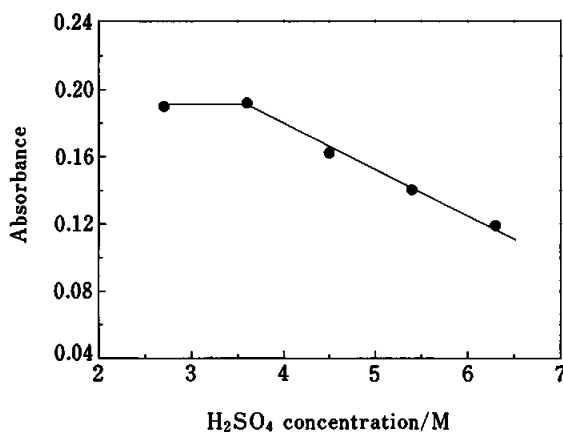


Fig. 4 Relationship between the concentration of sulfuric acid and the atomic absorbance of cadmium: $\text{Cd}=0.002 \mu\text{g ml}^{-1}$; $\text{Fe}=400 \mu\text{g ml}^{-1}$.

Concentration of sulfuric acid for a sample solution

The effects of H_2SO_4 on the determination of cadmium by ET-AAS were examined; the relationship between the H_2SO_4 concentration and the atomic absorbance of cadmium is shown in Fig. 4. The employed method was as follows: solutions containing $0.002 \mu\text{g ml}^{-1}$ cadmium, $400 \mu\text{g ml}^{-1}$ iron and in the concentration range from 2.7 to 6.3 M H_2SO_4 were prepared, respectively, and the atomic absorbance of cadmium measured. As a result, in more than 3.6 M H_2SO_4 , the atomic absorbance was lower. Therefore, the concentration of H_2SO_4 for the sample solution was selected to be 3.6 M; accordingly, the authors adopted that the volume of H_2SO_4 for decomposition of the filter paper with collected precipitate to be 10 ml.

Effects of sodium ion on the determination of cadmium by ET-AAS

The effects of Na^+ on the atomic absorbance of cadmium by ET-AAS were examined, because, in the proposed coprecipitation procedure small amounts of Na^+ were contained in the sample solution. The employed method was as follows: solutions containing $0.002 \mu\text{g ml}^{-1}$ cadmium, $400 \mu\text{g ml}^{-1}$ iron, 3.6 M H_2SO_4 and in the concentration range from 0 to 6 mg ml^{-1} of Na^+ were prepared, respectively, and atomic absorbance of cadmium measured. As a result, no effects of Na^+ were found in this range.

Calibration curve

For preparing calibration graphs, an aqueous standard was used and the relationship between the concentration of cadmium and the atomic absorbance examined. A straight line was obtained for a concentration from 0 to $0.007 \mu\text{g ml}^{-1}$ for cadmium. The detection limit (3-times the relative standard deviation of the blank) of the proposed method was $0.0003 \mu\text{g g}^{-1}$ for cadmium in 1 g of sample.

Table 2 Analytical results of the mixed solution samples ($n=5$)

Sample	Cd found/ μg	Recovery, %	RSD, %
Zn 1 g+Cd 0.0563 μg	0.0713 \pm 0.0007	101.6	1.23
Zn 1 g	0.0141 \pm 0.0003	—	1.42

Zn: purchased from Mitsui Mining & Smelting Co. Ltd.

Table 3 Analytical results of zinc metals ($n=5$)

Sample	Cd certified/ $\mu\text{g g}^{-1}$	Cd determined/ $\mu\text{g g}^{-1}$	RSD, %
A	<1	0.133 \pm 0.005	3.76
B	<1	0.0712 \pm 0.0007	0.986
C	—	0.0141 \pm 0.0003	1.42

Sample: A, High Pure Chemicals Co. Ltd., 99.999% Zn; B, Mitsuwa Co. Ltd., 99.999% Zn; C, Mitsui Mining & Smelting Co. Ltd., 99.999% Zn.

Analysis of a mixed solution sample

Cadmium in a mixed solution sample, which contained 0.05 μg of cadmium and 1 g of high purity zinc, was determined according the proposed method; the results are given in Table 2. As a result, cadmium was determined quantitatively.

Analysis of real samples

The proposed method was applied for the determination of cadmium in zinc metals. The results are given in Table 3. Trace amounts of cadmium in high-

purity zinc were quantitatively separated, and high-sensitively determined by the proposed method. The proposed method is useful, since not only the procedures are easy and simple, but also high-precision analytical values can be obtained.

References

1. T. Nedeltcheva, L. Costadinova and K. Minneva, *Fresenius' J. Anal. Chem.*, **348**, 648 (1994).
2. T. Ishizuki, K. Matsumoto, A. Yuchi, T. Ozawa, H. Yamada and H. Wada, *Talanta*, **41**, 799 (1994).
3. T. Yoshida and S. Okawa, *Bunseki Kagaku*, **42**, 145 (1993).
4. L. Elci, *Anal. Lett.*, **26**, 2667 (1993).
5. M. C. Valdes Hevia y Temprano, M. R. Fernandez de la Campa and A. Sanz Medel, *J. Anal. At. Spectrom.*, **9**, 231 (1994).
6. E. Tserovsky, S. Arpadzham and I. Karadzova, *J. Anal. At. Spectrom.*, **8**, 85 (1993).
7. A. M. Wifladt, R. Bye and W. Lund, *Fresenius' J. Anal. Chem.*, **344**, 541 (1992).
8. R. Chakravorty and R. von Grieken, *Mikrochim. Acta*, **1986 III**, 81.
9. G. S. Golden and M. G. Atwell, *Appl. Spectrosc.*, **24**, 514 (1970).
10. H. Watanabe, S. Barman and D. S. Russell, *Talanta*, **19**, 1363 (1972).
11. K. M. Bone and W. D. Hibbert, *Anal. Chim. Acta*, **107**, 219 (1979).
12. T. Watanabe and S. Nakagawa, *Materia Jpn.*, **33**, 380 (1994).

(Received April 24, 1995)

(Accepted June 14, 1995)