Notes

Anion-Exchange Behavior of 12 Elements in Potassium Iodide Media. Application to the Determination of Traces of Bismuth, Cadmium, Copper and Lead in Zinc Metals

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For quality-control purposes it is important to determine traces of impurities in pure zinc metals. Analytical methods for the determination of the traces of bismuth, cadmium, copper and lead have been specified in JIS^{1,2} or ISO.^{3,4} Those methods are simple and can be employed to determine each impurity accurately. However, these classical analytical methods are not suitable for some impurities, such as cadmium, bismuth, copper and lead at the sub- $\mu\text{g g}^{-1}$ level, because a standard addition or matrix matching technique and certified reference materials or high purity materials are required for the accurate determination of these elements. If a matrix separation technique is employed, the determination of trace impurities may be carried out with a simple calibration method using matrix free standard solutions. Furthermore, trace metal ions can be determined precisely and accurately by combining a matrix separation and a sensitive instrumental method such as ICP-AES, ICP-MS or GF-AAS. Solvent extraction, precipitation⁵ and ion-exchange^{6,7} methods have been widely applied to the preconcentration of metal ions at trace levels in pure zinc metals. Because various solvent media are available for eluents, the ion-exchange method is the most suitable for the separation of impurities from pure zinc metals among the techniques mentioned above.

Systematic information on the adsorbability of a number of elements on a strongly basic anion-exchange resin from halide solutions has already been reported by many workers.⁸⁻¹⁰ The hydrochloric acid system has been proved to be particularly useful for the simple separation of heavy metals from alkali and alkaline earth metals, but its selectivities among heavy metals are poor. Especially, in the case of separation of impurities in pure zinc metals, a large amount of ion-exchange resin is required to adsorb matrix zinc. It is difficult to reduce blank level, because of the necessity of a large volume of eluant to recover analytes. On the other hand, bismuth(III), cadmium(II), copper(II) and some other non-metal ions form iodo-complexes, which are more stable than respective chloro- or bromo-complexes.

Marsh *et al.* have presented the adsorption behavior of many elements in hydroiodic acid media¹¹, but they have not reported the details of the distribution coefficients.

Based on the capability of ion-exchange chromatography in iodide media, the present work has been carried out to reveal the adsorption behavior of a number of elements on AG 1-X8 in potassium iodide media acidified with nitric acid. It will be demonstrated that the ion-exchange system combined with inductively coupled plasma-atomic emission spectrometry provides a quantitative basis for the accurate determination of bismuth, cadmium, copper and lead in pure zinc metals.

Experimental

Instruments

A Nippon-Jarrell Ash inductively coupled argon plasma-atomic emission spectrometer (Model ICAP-88) with two monochromators was used throughout the determination of metal ions. The operating parameters of the ICAP-88 were adjusted to the conditions under which the highest sensitivity was obtained. The analytical lines chosen are listed in Table 1.

Chemicals

All of the chemicals used were of analytical reagent grade. Distilled and de-ionized water was used throughout the experiments. Metal stock solutions ($1000 \mu\text{g cm}^{-3}$) were prepared to be 3 M in nitric acid (Cu, Pb, Se, As, Bi, Ga, In, Zn, Cd) or hydrochloric acid (Te, Sb, Sn). These stock solutions were used after appropriate dilution and conversion of chlorides to nitrates (Te) or sulfates (Sb, Sn).

Column preparation

A strongly basic anion-exchange resin Bio-Rad AG 1-X8 (Bio-Rad Laboratories, Richmond, CA, USA) of 100–200 mesh in the chloride form was used throughout. The resin was stored for more than one week over

Table 1 Instrumental and operating conditions

ICP-AES	Nippon Jarrell-Ash, Model ICAP-88
RF power	1.4 kW
Coolant gas	16 dm ³ min ⁻¹
Plasma gas	0.6 dm ³ min ⁻¹
Observation height	13 mm above work coil
Integration time	3 s
Spectrometer	twin monochromator
Mount	cross Czernyl-Turner, 2-channel
Focal length	0.75 m
Grating	1800 grooves mm ⁻¹ ruled grating for channels 1 and 2
Slits	channel 1 with 10 μ m channel 2 with 25 μ m
Torch type	high solids Fassel type
Analytical lines	channel 1: Bi 306.772 nm, Cd 214.438 nm channel 2: Cu 324.754 nm, Pb 220.353 nm

saturated potassium bromide solution in a desiccator. A two gram amount of the resin suspended in water was slurry-packed in a polyethylene column (10 mm i.d.) fitted with an appropriate amount of cotton wool. Before use, the column was preconditioned with 20 ml of 0.5 M potassium iodide–0.1 M nitric acid at a flow-rate of 2.0 ml min⁻¹. After each run, the column was washed with 50 ml each of 1.0 M sodium thiosulfate and water and then stored for the next run.

Procedure

Measurements of distribution coefficients. Weight distribution coefficients (amount of ion per g of dry resin/amount of ion per ml of the solution) were determined by the batch equilibrium method at 20°C. The mixtures 40 ml of potassium iodide solution of various concentrations (0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.0 and 2.0 M) containing 1 mg of the metal ions and 1.00 g of AG1-X8 resin were shaken for 20 h. The metal ions in the

solution were then determined after removal of the resin by filtration.

Procedure for the determination of bismuth, cadmium, copper and lead in pure zinc metals. Digest a sample weighing about 2.0 g on a hot plate with 20 ml of nitric acid. Evaporate gently nearly to dryness. Take up the residue with 50 ml of 0.5 M potassium iodide–0.1 M nitric acid. Condition the anion-exchange column with 20 ml of 0.5 M potassium iodide–0.1 M nitric acid. Load the sample solution onto the top of the column and allow it to pass down the column at a flow rate of 2.0 ml min⁻¹. Wash the column with 30 ml of 0.5 M potassium iodide–0.1 M nitric acid and 100 ml of 0.1 M nitric acid at a flow rate of 2.0 ml min⁻¹. Strip the analytes by elution with 130 ml of 3 M nitric acid at a flow rate of 1.0 ml min⁻¹. Discard the early 3 ml portion of the effluent which contains much zinc salt. Evaporate the effluent nearly to dryness. Then take up the residue in 5 ml of nitric acid and dilute exactly to 25 ml with water. Determine each analyte with ICP-AES.

Results and Discussion

Adsorption of metals from potassium iodide–nitric acid mixtures

Anion-exchange distribution coefficients of 12 elements in potassium iodide–nitric acid mixtures are summarized in Table 2. The coefficients are listed as a function of potassium iodide concentration. Adsorptivity values of many elements in hydroiodic acid media have already been published by Marsh *et al.*¹¹ The results suggested that alkali metals, alkaline earth metals, polyvalent cations including iron(III), vanadium(V), titanium(IV) and zirconium(IV) are not adsorbed on the anion-exchange resin or only weakly adsorbed there, whereas the platinum group, groups 2B to 5B cations are strongly adsorbed, particularly, from the lower concentration range of hydroiodic acid. But details of the distribution coefficient at lower concentrations of

Table 2 Distribution coefficients (K_d) on AG 1-X8 in potassium iodide^a

Element	KI/mol l ⁻¹								
	0.01	0.02	0.05	0.1	0.2	0.5	1	2	5
As(III)	<10	<10	<10	<10	<10	<10	<10	<10	<10
Bi(III)	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	—	—	—
Cd(II)	2300	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	—	—	—
Cu(II)	precipitated →					>10 ⁴	3000	690	170
Ga(III)	<10	<10	<10	<10	<10	<10	—	—	—
In(III)	<10	<10	<10	<10	50	340	—	—	—
Pb(II)	precipitated →					>10 ⁴	>10 ⁴	3300	180
Sb(III) ^b	precipitated →				140	620	—	—	—
Sn(II) ^b	60	30	50	40	80	80	—	—	—
Te(IV)	<10	330	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	—	—	—
Tl(III)	1100	7000	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	—	—	—
Zn(II)	<10	<10	<10	<10	<10	10	—	—	—

a. The solutions were acidified to 0.1 M HNO₃. b. The solutions were acidified to 0.1 M H₂SO₄.

hydroiodic acid have not been reported. As can be seen in Table 2, gallium(III), tin(II), indium(III) and zinc(II) exhibit no or weakly adsorption over the potassium iodide concentration ranges tested, whereas bivalent cations including copper(II), lead(II), cadmium(II), trivalent cations including bismuth(III) and tellurium(III), and thallium(III) are adsorbed strongly from the lower concentration range of potassium iodide tested. It is well known that ionic iodide reduces copper(II) to copper(I) and thallium(III) to thallium(I), respectively. At the lower concentrations of potassium iodide, copper(II) precipitates but its stable iodo-complex exists in acidic potassium iodide solution ($[I^-] > 0.5$ M). Zinc(II) was adsorbed very slightly on the resin in 0.5 M of acidic potassium iodide solution, whereas weakly adsorbed in 0.5 M of hydrochloric acid solution. These results suggest that this ion-exchange system is very suitable to separate groups 2B, 3B, 4B and 5B elements from zinc matrix. The acidic potassium iodide solution turns clear-yellow, which shows the liberation of iodine (I_2), but the presence of iodine does not affect the adsorption behavior of the elements indicated above.

Determination of bismuth(III), cadmium(II), copper(II) and lead(II) in zinc

From 0.5 M potassium iodide–0.1 M nitric acid medium, bismuth(III), cadmium(II), copper(II) and lead(II) are adsorbed strongly on Bio-Rad AG1, as shown in Table 2. For convenience the free acid concentration in sample solutions was kept at 0.1 M and the sample volume was adjusted to 50 ml. Under these conditions the above four elements are quantitatively adsorbed on a 2 g-resin column. Most other elements, including zinc, are not adsorbed on the column from the sample solution and are removed completely by the subsequent washing with 100 ml of 0.1 M nitric acid solution. A small portion of matrix zinc (about 20 μ g) is co-eluted from the column with analytes, but it does not affect the determination of bismuth(III), cadmium(II), copper(II) and lead(II) with ICP-AES. Cadmium(II), copper(II) and lead(II) can be recovered easily by elution with 30 ml of 3 M nitric acid solution. Judging from its distribution coefficient data, we think thallium(III) may be adsorbed on the column and accompanied by these elements, if it is present in zinc samples. However, it is partially retained, probably because of the precipitation

of thallium iodide, and tends to show tailing and to contaminate the fraction of cadmium(II), copper(II) and lead(II). Tellurium may also be recovered from the column with these three elements. However, thallium and tellurium do not interfere with the determination of cadmium(II), copper(II) and lead(II) by ICP-AES. Bismuth(III) is strongly adsorbed on the resin and tends to show the tailing, so that the quantitative elution of bismuth(III) required as much as 130 ml of 3 M nitric acid.

Table 3 shows the results for the separation and determination of bismuth(III), cadmium(II), copper(II) and lead(II) in the presence of zinc. Recoveries are obtained in the range 90 to 110%. Three zinc metal (99.99%) samples were analyzed for bismuth, copper, cadmium and lead, the results are shown in Table 4. These samples were also analyzed in our laboratory by an ICP-AES method according to JIS H 1108¹ and H 1110.² The results obtained by the proposed method are in good agreement with those obtained by JIS methods.

The above results indicated that the proposed potas-

Table 3 Anion-exchange separation of bismuth(III), cadmium(II), copper(II) and lead(II) in potassium iodide media

Element	Sample A		Sample B	
	Added/ μ g	Found/ μ g	Added/ μ g	Found/ μ g
Bi(III)	0	0.2	0	N.D.
	10	10.9	500	467
	20	19.5		
Cd(II)	0	7.9	0	17.6
	10	13.6	500	527
	40	47.8		
Cu(II)	0	5.0	0	5.8
	10	13.6	500	483
	20	21.5		
Pb(II)	0	59.5	0	65.9
	30	95.6	500	569
	60	121		

Sample A contained 2 g of 99.99% Zn, and B contained 2 g of 99.95% Zn. Values are expressed as average of duplicate determinations. N.D.: not detected.

Table 4 Determination of Bi, Cd, Cu and Pb in zinc metals (μ g g⁻¹)

Element	Sample A ^a	Sample B ^a	Sample C ^a		Blank ^b
			This work	JIS method ^{1,2}	
Bi(III)	N.D.	N.D.	N.D.	—	0.20 $\pm$ 0.02
Cd(II)	1.9 $\pm$ 0.04	9.0 $\pm$ 0.33	0.65 $\pm$ 0.01	0.66 $\pm$ 0.06	N.D.
Cu(II)	1.3 $\pm$ 0.06	0.37 $\pm$ 0.08	5.5 $\pm$ 0.23	5.6 $\pm$ 0.57	0.39 $\pm$ 0.03
Pb(II)	16 $\pm$ 0.97	9.4 $\pm$ 0.60	9.0 $\pm$ 0.37	9.1 $\pm$ 0.82	0.44 $\pm$ 0.09

Samples A, B and C contained 2 g of 99.99% Zn. a. Average of triplicate determinations $\pm$ the standard deviation.

b. Determined throughout the whole procedure. N.D.: not detected.

sium iodide–nitric acid anion–exchange system is suitable for the determination of trace bismuth(III), cadmium(II), copper(II) and lead(II) in zinc metal. Copper(II) and lead(II) are easily reduced to lower oxidation state and are precipitated by iodide ion. We found, however, that the μg levels of copper(II) and lead(II) form stable iodo-complexes and are strongly adsorbed on the resin in acidic potassium iodide solution in the range above 0.5 M. High purity zinc for matrix matching or certified reference materials are not necessary and a simple calibration method can be applied for the determination of these impurities. The proposed method will be applicable to the zinc matrix separation for the determination of ultra-trace levels of bismuth(III), cadmium(II), copper(II) and lead(II).

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