NOTE

Loss of Traces of Antimony and Arsenic due to Volatilization during Dissolution of Aluminum Metal Samples

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1. Introduction

In trace element analysis of metals, especially for impurities at the low ppm or ppb level, the samples are often dissolved in various acids and other solvents prior to separation or determination steps. Loss by partial volatilization of desired trace elements may occur during the dissolution and result in significant negative errors in final analytical values. However, the literature which deals with this subject is scanty. In the present work, loss of fractional ppm of antimony and arsenic in high-purity aluminum metal (99.99%) during the dissolution step is investigated because of possible volatilization of both elements as hydrides or halides. Antimony-124 and arsenic-76 produced in the metal samples by thermal neutron irradiation in a nuclear reactor act as tracers in this experiment. The solvents used include 5 M sodium hydroxide, concentrated and 9 M hydrochloric acid containing traces of nickel ions* and *aqua regia*.

2. Experimental

2.1 Nuclear reactor

Japan Atomic Energy Research Institute research reactor JRR-2 (10 MW).

2.2 Radiation detectors and pulse height analyzers

A Harshaw and a Fujitsu NaI(Tl) scintillation detector.

A TMC 400-channel, a TMC 256-channel and a Fujitsu 100-channel pulse height analyzer.

2.3 Decomposition and absorption vessels

A decomposition vessel and absorption tubes are shown in Fig. 1. Also, 100-ml Erlenmeyer flasks and beakers are used instead of the

Fig. 1 Decomposition vessel and absorption tubes.

2.4 Material and reagents

Aluminum metal: 99.99% purity ingot.

Antimony calibration standards, 0.1 μg Sb: Dissolve 1.00 g of antimony metal (99.999%) in 20 ml of *aqua regia*, add 30 ml of HCl, and dilute to 100 ml with water. Dilute this stock solution (10 mg Sb/ml) to appropriate concentrations with a 1:20 mixture of *aqua regia* and water. Place a 0.1-ml aliquot on a 4×4 cm² aluminum foil (ca. 0.09 g), neutralize with 1 M NH₄OH, and evaporate to dryness under an infrared lamp.

Arsenic calibration standards, 0.1 μg As: Dissolve 1.32 g of As₂O₃ in 5 ml of HCl, 10 ml of HNO₃, and 10 ml of water. Evaporate the solution to 5 ml, and dilute to 100 ml with water. Dilute this stock solution (10 mg As/ml) to appropriate concentrations with a 1:20 mixture of *aqua regia* and water. Place a 0.1-ml aliquot on a 3-cm filter paper (No. 7), and evaporate to dryness under an infrared lamp.

Antimony(III) carrier solution, 10 mg Sb/ml: Dissolve 4.68 g of SbCl₃ in 45 ml of HCl, and dilute to 250 ml with water.

Antimony(V) carrier solution, 10 mg Sb/ml: Dissolve 1.00 g of antimony metal in 20 ml

* Nickel ions accelerate the dissolution.

of *aqua regia*, add 30 ml of HCl, and dilute to 100 ml with water.

Arsenic(III) carrier solution, 10 mg As/ml: Dissolve 3.30 g of As_2O_3 in 16 ml of 2.5 M NaOH, add 20 ml of 6 M HCl, and dilute to 250 ml with water.

Arsenic(V) carrier solution, 10 mg As/ml: Dissolve 10.4 g of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in 10 ml of 1 M NaOH, and dilute to 250 ml with water.

Cadmium carrier solution, 10 mg Cd/ml: Dissolve 2.74 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in water, and dilute to 100 ml with water.

Copper(II) carrier solution, 10 mg Cu/ml: Dissolve 3.93 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, and dilute to 100 ml with water.

All the reagents used were of reagent grade. Water purified by distillation and ion exchange was used throughout the work.

2.5 Procedures

For antimony Wash 1-g cube aluminum samples with petroleum benzine, ethanol, hydrochloric acid, and water, and dry at 40°C in an oven. Wrap each sample in aluminum foil, pack into an aluminum capsule (24 mm dia. $\times$ 62 mm) together with antimony calibration standards, and irradiate in a reactor at a thermal neutron flux of $4 \times 10^{13} \text{ n/cm}^2 \cdot \text{sec}$ for 200~300 hrs.

After cooling, cut the irradiated samples into small chips (ca. 1 mm in size) using a chisel and nippers, wash with petroleum benzine, ethanol, hydrochloric acid, and water, and dry at 40°C in an oven.

Transfer ca. 1 g of the chips to a decomposition vessel, connect absorption vessels containing absorbents, add 20 ml of 5 M sodium hydroxide, 30 ml of hydrochloric acid containing 0.1 mg of nickel ions, or 30 ml of *aqua regia* to the decomposition vessel, and heat gently to dissolve. When the sample has completely dissolved, rinse the sidearm of the decomposition vessel with a small amount of water, transfer each solution in the decomposition and the absorption vessels to a 100-ml beaker, and add 5 ml of antimony(V) carrier solution** and 1 ml of cadmium carrier solution. Evaporate the solution to dryness***, and add hydrochloric acid and water to give 90 ml of 4 M

hydrochloric acid solution.

Transfer the solution to a 200-ml Erlenmeyer flask, and pass hydrogen sulfide for 5 min. Filter off the precipitate on a filter paper (5C), and wash with 20 ml of 4 M hydrochloric acid. Dissolve the precipitate in 25 ml of hydrochloric acid, catching the solution in a 100-ml beaker. Add 15 ml of water to the solution and boil for 2 min. Transfer the solution to a 300-ml Erlenmeyer flask, add 85 ml of water, and pass a rapid stream of hydrogen sulfide at 90°C until the orange precipitate turns black.

Filter off the precipitate on a glass filter crucible (1G4), and wash with 20~30 ml of water followed by 10 ml of ethanol. Pour five 5 ml portions of carbon disulfide into the crucible, stir for a few min to dissolve sulfur, and then remove the solvent by suction. Finally, wash the precipitate with 30 ml of ethanol, and dry at 105°C for 90 min. Cool the precipitate, transfer to a polyethylene test tube, weigh as Sb_2S_3 , and measure the gamma spectrum. Correct the radioactivity (photopeak area) using the chemical yield, and determine the amount of antimony by reference to a calibration curve. Confirm the radiochemical purity by measuring the decay.

For the construction of the calibration curve, dissolve each irradiated antimony calibration standard in 30 ml of hydrochloric acid, add 5 ml of antimony(III) carrier solution and 1 ml of cadmium carrier solution, dilute with water to give 90 ml of 4 M hydrochloric acid solution, pass hydrogen sulfide, and proceed as described above.

For arsenic Wash aluminum chips (ca. $1 \times 2 \times 8 \text{ mm}^3$, prepared by a lathe) with petroleum benzine, ethanol, hydrochloric acid, and water, and dry at 40°C in an oven. Wrap the chips in polyethylene sheet, pack into a polyethylene capsule (24 mm dia. $\times$ 62 mm) together with arsenic calibration standards, and irradiate in a reactor at a thermal neutron flux of $8 \times 10^{13} \text{ n/cm}^2 \cdot \text{sec}$ for 20 min.

** Omit this solution when antimony carrier is present. Use antimony(III) carrier when nitric acid is absent from the solution.

*** Omit this operation when nitric acid is absent from the solution.

After cooling, transfer 1 g of the sample to a decomposition vessel, connect absorption vessels containing absorbents, add 20 ml of 5 M sodium hydroxide, 30 ml of hydrochloric acid (12 M and 9 M) containing 0.1 mg of nickel ions, or 30 ml of *aqua regia*, and heat gently to dissolve. When the sample has completely dissolved, rinse the sidearm of the decomposition vessel with a small amount of water, transfer each solution in the decomposition and the absorption vessels to a 200- or 400- ml beaker, and add 5 ml of arsenic(V) carrier solution****. Evaporate the solution to dryness***, and add hydrochloric acid and water to give 40~120 ml of 9 M hydrochloric acid. Filter off the precipitate, on a filter paper (5C), if any,

catching the filtrate in another 400- ml beaker. Add ca. 1 mg of potassium iodide to the filtrate, and pass sulfur dioxide for 10 min. Dilute the solution with water to 4 M in acidity, and pass nitrogen for 40 min to expel sulfur dioxide. Add 1 ml each of copper(II) and antimony(III) carrier solutions, and hydrochloric acid to give 6 M hydrochloric acid solution.

Pass hydrogen sulfide into the solution at 60°C for 5 min. Allow to stand for 20~30 min at 60°C, filter off the precipitate on a filter paper (5C), and wash with 10 ml of 6 M hydrochloric acid followed by 30 ml of water. Dissolve the precipitate in 40 ml of 1 M sodium hydroxide, and add 10 ml of hydrochloric acid at 60°C to reprecipitate the arsenic(III) sulfide.

Table 1 Experimental results for antimony

Exp. No.	Sample taken (g)	Solvent	Vessel	Chemical yield (%)	Radioactivity*7 (cpm)	Sb	
						μg	ppm in Al
1*1	1.10	5 M NaOH, 20 ml	Decomposition	84	6992	0.25	0.23
			1 st absorption*3	82	343	0.03	0.03
			2 nd absorption*4	78	349		
	1.06	HCl, 30 ml (+0.1mg Ni)	Decomposition	80	7830	0.28	0.26
			1 st absorption*3	83	0	0	0
			2 nd absorption*4	77	0		
	1.11	<i>Aqua regia</i> , 30 ml	Decomposition	53	8787	0.31	0.28
			1 st absorption*3	56	0	0	0
			2 nd absorption*4	46	0		
2*2	1.05	5 M NaOH, 20 ml	Decomposition	79	9922	0.23	0.22
			1 st absorption*5	80	323	0.01	0.01
			2 nd absorption*5	80	139		
	0.87	HCl, 30 ml (+0.1mg Ni)	Decomposition	78	9297	0.22	0.25
			1 st absorption*5	81	48	0.001	0.001
			2 nd absorption*5	80	0		
	1.07	<i>Aqua regia</i> , 30 ml	Decomposition	58	10759	0.25	0.23
			1 st absorption*6	49	0	0	0
			2 nd absorption*6	(not determined)			

*1 Irradiation time: 200 hrs. Cooling time: 71 days.

*2 Irradiation time: 288 hrs. Cooling time: 70 days.

*3 100-ml Erlenmeyer flask containing 30 ml of water.

*4 100-ml Erlenmeyer flask containing 30 ml of HCl.

*5 Absorption tube containing 30 ml of HCl and 5 ml of Sb(III) carrier solution.

*6 Absorption tube containing 30 ml of HCl and 5 ml of Sb(V) carrier solution.

*7 Measured 71 days after the end of irradiation, and corrected for chemical yield.

Allow to stand for 10~15 min at 60°C, and filter off the precipitate on a glass filter crucible (1G4). Wash the precipitate with hydrochloric

**** Omit this solution when arsenic carrier is present. Use arsenic(III) carrier when nitric acid is absent from the solution.

acid, water, ethanol, carbon disulfide, and ethanol, dry at 105°C for 1 hr, cool, weigh as As_2S_3 , measure the gamma spectrum, and determine the amount of arsenic, as described for antimony. (N.B. Measure the radioactivity of the irradiated arsenic calibration standards without further treatment).

3. Results and discussion

The time required for complete dissolution of a 1-g sample was ca. 30 min for 20 ml of 5 M sodium hydroxide, ca. 150 min for 30 ml of hydrochloric acid containing 0.1 mg of nick-

el ions, and ca. 90 min for 30 ml of *aqua regia*. Even after the most vigorous decomposition with 5 M sodium hydroxide, a decrease of the solvent volume was 1 ml or less and the aluminum found in the first absorption vessel was less than 1 mg. Therefore, loss due to mechanical entrainment of tiny liquid particles containing the desired trace elements in the escaping vapor seems to be negligible.

Experimental results for loss of antimony and arsenic due to partial volatilization during dissolution are summarized in Tables 1 and 2. All calibration curves were linear over the

Table 2 Experimental results for arsenic

Exp. No.	Sample taken (g)	Solvent	Vessel	Chemical yield (%)	Radioactivity (cpm)	As	
						μg	ppm in Al
1*1	0.91	5 M NaOH, 20 ml	Decomposition	88*8	1495*10	0.12	0.13
			Absorption*4	82*8	876*10	0.07	0.08
	1.01	9 M HCl, 30 ml (+0.1 mg Ni)	Decomposition	84*9	2658*10	0.23	0.23
			Absorption*4	84*9	290*10	0.03	0.03
2*1	0.78	5 M NaOH, 20 ml	Decomposition	98*9	1244*10	0.10	0.13
			1st absorption*5	90*9	79*10	0.01	0.01
			2nd absorption*5	39*9	82*10		
	0.66	HCl, 30 ml (+0.1 mg Ni)	Decomposition	54*9	974*10	0.08	0.12
			1st absorption*5	26*9	246*10	0.03	0.04
			2nd absorption*5	40*9	195*10		
3	0.95*2	5 M NaOH, 20 ml	Decomposition	87	176*11	0.11	0.12
			1st absorption*6	91	85*11	0.06	0.06
			2nd absorption*6	94	21*11		
	1.00*3	HCl, 30 ml (+0.1 mg Ni)	Decomposition	88	525*12	0.15	0.15
			1st absorption*6	92	71*12	0.03	0.03
			2nd absorption*6	92	31*12		
	1.01*3	<i>Aqua regia</i> 30 ml	Decomposition	90	623*12	0.18	0.18
			1st absorption*7	91	0*12	0	0
			2nd absorption*7	(not determined)			

*1 Irradiation time: 20 min. Cooling time: 3 hrs.

*2 Irradiation time: 20 min. Cooling time: 70 hrs.

*3 Irradiation time: 20 min. Cooling time: 46 hrs.

*4 100-ml beaker containing 30 ml of 9 M HCl.

*5 100-ml Erlenmeyer flask containing 30 ml of HCl.

*6 Absorption tube containing 30 ml of HCl and 5 ml of As(III) carrier solution.

*7 Absorption tube containing 30 ml of HCl and 5 ml of As(V) carrier solution.

*8 Nitrogen was passed into 9 M HCl solutions to expel SO_2 .

*9 Nitrogen was passed into hot 9 M HCl solutions to expel SO_2 .

*10 Measured 25 hrs after the end of irradiation, and corrected for chemical yield.

*11 Measured 79 hrs after the end of irradiation, and corrected for chemical yield.

*12 Measured 55 hrs after the end of irradiation, and corrected for chemical yield.

range of 0~1 μg of antimony or arsenic. Because of relatively low temperatures during the dissolution, the chief volatile species are likely to be hydrides, i.e., stibine and arsine. While there is some possibility of incomplete absorption of the volatile species, the following may be concluded from the above results.

For aluminum metal samples containing fractional ppm of antimony and arsenic, *aqua regia* is most recommended as a solvent. On the contrary, 5 *M* sodium hydroxide, which is often preferred because of rapid dissolution, should not be used. Hydrochloric acid can be used only for antimony.