

Solid-Liquid Extraction for the Determination of Impurities in High-purity Lead by Atomic Absorption Spectrometry With Electrothermal Atomization

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After dissolving a lead sample in 4.5 mol l⁻¹ nitric acid, the solution was evaporated to dryness. The trace impurities were extracted from lead nitrate crystals with an ethanolic solvent, that is, a 99 + 1 mixture of ethanol (99.5% v/v) and 15 mol l⁻¹ aqueous ammonia (for silver) or a 99 + 1 mixture of ethanol (99.5% v/v) and 12 mol l⁻¹ hydrochloric acid (for iron, copper and cadmium). The desired trace metals were recovered in >93% yields and determined by electrothermal atomic absorption spectrometry. The separation factor for the lead matrix was about 10⁻³. The proposed method was applied to the determination of impurities at ng g⁻¹ levels in high-purity lead metal.

Keywords: Lead metal; solid-liquid extraction; ultrasonic irradiation; electrothermal atomic absorption spectrometry

Introduction

Solid-liquid extraction offers a useful separation technique, where trace constituents in a solid sample are selectively dissolved in an appropriate solvent.¹ A solid sample is first dissolved in acids or other solvents and then evaporated to dryness to redistribute the trace constituents on the surfaces or in the interstitial spaces of agglomerates of pure matrix crystals. This technique is simple and often permits the simultaneous multi-element separation of trace elements prior to the instrumental determination step. Mizuike and co-workers studied solid-liquid extraction systematically from the viewpoint of inorganic trace analysis. Different solvents were examined for the extraction of trace impurities from basic bismuth nitrate^{2,3} and chlorides⁴ of sodium, potassium, nickel, cadmium, barium and lead for atomic emission spectrometry and square-wave polarography.

For the analysis of lead metal, however, the solid-liquid extraction proposed hitherto has the following disadvantages. The extraction from lead chloride⁴ requires the conversion of the chemical form of lead from nitrate to chloride before the extraction. In addition, it cannot be applied to the determination of trace amounts of silver because of the very poor extraction recoveries (<4%). Although the combination of solid-liquid extraction with matrix precipitation (as lead nitrate from concentrated nitric acid solutions)⁵ improved silver recoveries significantly, the procedure was troublesome and time consuming. The separation factor* for the lead matrix is not good (approximately 10⁻²) and concentrated nitric acid may be undesirable for most instrumental determination techniques.

Because silver is the typical trace constituent in lead metal, it should be determined along with other ubiquitous heavy

metals. In this work, a mixture of ethanol and aqueous ammonia was found to be most suitable for the quantitative extraction of silver. The combined use of ethanolic ammonia and ethanolic hydrochloric acid allows the direct extraction of silver, iron, copper and cadmium from lead nitrate, with a separation factor of 10⁻³. This simple separation method was applied successfully to the analysis of high-purity lead by electrothermal atomic absorption spectrometry (ETAAS).

Experimental

Apparatus

A Seiko (Tokyo, Japan) SAS-715 graphite furnace atomizer was used in conjunction with an SAS-760 atomic absorption spectrometer fitted with a deuterium-effect background corrector. Profiles of the analytical signal and background absorption were displayed on a cathode-ray tube incorporated in the instrument. The furnace programme was as follows. The graphite tube, 30 × 6 mm i.d., made of pyrolytic graphite, was first heated during 20 s to 150 °C, held for 10 s and then heated during 5 s to 400 °C and held for 15 s; the tube was further heated to atomization temperatures of 2000 °C for 2 s (Ag and Cd) and 2400 °C for 4 s (Fe and Cu) for measuring the peak height absorbance. The wavelengths used were Ag 328.1, Fe 248.3, Cu 324.8 and Cd 228.8 nm. Hollow cathode lamps were operated at 10 mA (except for Cd, 5 mA).

The evaporation apparatus consisted of a Yamato (Tokyo, Japan) HF 41 heater and an aluminium heating block (12 holes of 25 mm diameter × 65 mm depth), where a Pyrex glass test-tube (20 mm i.d., 24 mm o.d., 100 mm high) containing sample solution (approximately 3 ml) was inserted. The test-tube was sealed with a silicone-rubber stopper bearing two glass tubes. Nitrogen (preliminarily filtered through a 0.1 µm membrane filter) was introduced into the test-tube at a flow rate of 0.5 l min⁻¹ to provide a clean atmosphere and to sweep out evaporating solvents.

A Branson (Danbury, CT, USA) ultrasonic cleaning bath (47 kHz, 120 W, 295 × 150 × 150 mm high) was used for the extraction of trace metals from the lead matrix. A sample test-tube was irradiated at a height of 50 mm from the bottom of the ultrasonic bath. A Hitachi (Hitachi, Japan) ECV-843 BY clean-bench was used for separation procedures.

Reagents

All reagents were of analytical-reagent grade (Katayama Chemicals, Osaka, Japan), unless stated otherwise. Water was purified by distillation and ion exchange, and then passed through a Millipore (Japan Millipore, Yonezawa, Japan) Milli-Q purification system.

Standard silver solution. Silver nitrate (100 mg as Ag) was dissolved in 100 ml of 15 mol l⁻¹ aqueous ammonia and a 1 ml

* Separation factor = (Q⁰_T/Q⁰_M)/(Q_T/Q_M), where Q⁰_T is the amount of the trace element in the sample, Q⁰_M the amount of the matrix element in the sample and Q_T and Q_M are the corresponding amounts after the separation.

aliquot of the solution ($1 \text{ mg ml}^{-1} \text{ Ag}$) was diluted to 100 ml with ethanol (99.5% v/v). The solution ($10 \text{ } \mu\text{g ml}^{-1} \text{ Ag}$) was further diluted to appropriate concentrations with a 99 + 1 mixture of ethanol (99.5% v/v) and 15 mol l^{-1} aqueous ammonia immediately before use. Another standard silver solution ($10 \text{ } \mu\text{g ml}^{-1} \text{ Ag}$, in 0.1 mol l^{-1} nitric acid) was separately prepared and stored for making synthetic sample solutions.

Standard solutions of iron(III), copper(II) and cadmium(II). Commercial metal standard solutions were diluted with 12 mol l^{-1} hydrochloric acid to prepare stock standard solutions of $100 \text{ } \mu\text{g ml}^{-1} \text{ Fe}$, $100 \text{ } \mu\text{g ml}^{-1} \text{ Cu}$ and $10 \text{ } \mu\text{g ml}^{-1} \text{ Cd}$. A 1 ml aliquot of each solution was diluted to 100 ml with ethanol (99.5% v/v), then further diluted to appropriate concentrations with a 99 + 1 mixture of ethanol (99.5% v/v) and 12 mol l^{-1} hydrochloric acid immediately before use. Other standard solutions ($10\text{--}100 \text{ } \mu\text{g ml}^{-1}$ metal in 0.1 mol l^{-1} nitric acid) were also prepared and stored for making synthetic sample solutions.

Lead nitrate solution. Pure lead nitrate was prepared by the matrix precipitation method,⁶ in which the lead was precipitated as nitrate from concentrated nitric acid solution. A 1.5 g amount of lead metal (1–2 mm granular form) was dissolved in 10 ml of 4.5 mol l^{-1} nitric acid. The solution was evaporated to form a moist crystal conglomerate, which was then treated with slight heating with 15 ml of 14 mol l^{-1} nitric acid. After cooling, the acid was removed by centrifugation. The lead nitrate crystals were washed twice ultrasonically with 10 ml portions of 14 mol l^{-1} nitric acid without heating. The purified precipitate was dissolved in water (usually 20 ml). The concentration of lead was standardized by AAS. The purification method was very effective because no contamination was detected for silver, iron, copper and cadmium.

Procedure

A 3 ml volume of lead nitrate sample solution (containing 100–300 mg of lead) was placed in a Pyrex glass test-tube and evaporated to dryness by heating at 100°C for 30 min and further heating at 140°C for 10 min. The residue was cooled to room temperature and pulverized manually for 1 min with a Teflon rod (5 mm diameter). After adding 2–5 ml of extraction solvent, the test-tube was closed tightly with a silicone-rubber stopper and irradiated with ultrasound for 30–60 min. The extraction solvent was separated by centrifugation (1000g for 10 min) and 10 μl aliquots of the solvent were transferred into the graphite furnace for the determination of silver, iron, copper and cadmium by ETAAS. The measurement was repeated three times and the absorbance readings were averaged.

Calibration graphs were prepared by using ethanolic standard solutions containing appropriate amounts of trace metals.

Results and Discussion

Selection of Solvents for Extracting Trace Metals From Lead Nitrate

Suitable solvents were surveyed from the viewpoints of (1) high solubility of the desired trace metals, (2) minimum solubility of the lead matrix and (3) no interference with subsequent determination by ETAAS. Because the utility of ethanol containing small amounts of hydrochloric acid had been previously reported for the extraction of iron, cobalt, copper and zinc from lead chloride,⁴ 99 + 1 and 999 + 1 mixtures of ethanol (99.5% v/v) and 12 mol l^{-1} hydrochloric acid were examined in this work.

A 3 ml volume of lead nitrate solution (containing 100 mg of lead and nanogram amounts of trace metals) was evaporated

to dryness and then treated ultrasonically for 30–60 min with 5 ml of different kinds of extraction solvents (see Procedure). As shown in Table 1, a mixture of ethanol (99.5%) and 12 mol l^{-1} hydrochloric acid was effective for the extraction of iron, copper and cadmium from lead nitrate, although it was not useful for silver. Compared with a 999 + 1 mixture, a 99 + 1 mixture always provided quantitative trace recoveries. On the other hand, trace amounts of silver were nearly completely extracted into a 99 + 1 mixture of ethanol (99.5% v/v) and 15 mol l^{-1} aqueous ammonia. A significant amount of cadmium was also extracted along with the silver, but the recovery was insufficient and variable. Small or negligible extractability was observed for copper and iron, respectively.

Pulverization of the evaporation residue with a Teflon rod was helpful for complete extraction. Without trituration, the trace recoveries were decreased by 3–10%. The lead accompanying the trace metals was determined by ETAAS and found to be 120–150 μg , which did not interfere in the subsequent determination of trace metals. The separation factor for the lead matrix can be calculated to be $(1.2\text{--}1.5) \times 10^{-3}$.

Effect of Extraction Time on Trace Recovery

Ultrasonic irradiation is known to increase substantially the extraction of trace elements,⁴ probably owing to the pulverization of solid particles and adequate mixing. Fig. 1 shows the percentage of trace metals extracted into 2 ml of solvent as a function of ultrasonic irradiation time. With a 99 + 1 mixture of ethanol (99.5% v/v) and 15 mol l^{-1} aqueous ammonia,

Table 1 Extraction of trace amounts of silver(I), iron(III), copper(II) and cadmium(II) from 100 mg of lead

Extraction solvent	Extraction time/min	Trace metal added	Amount added/ng	Trace metal extracted (%)
Ethanol– $12 \text{ mol l}^{-1} \text{ HCl}$ (999 + 1)	60	Ag	5	7
		Fe	50	87
		Cu	50	86
		Cd	5	89
	60	Ag	25	2
		Fe	250	94
		Cu	250	82
		Cd	25	98
Ethanol– $12 \text{ mol l}^{-1} \text{ HCl}$ (99 + 1)	60	Fe	50	97
		Cu	50	94
		Cd	5	96
	60	Fe	250	93
		Cu	250	94
		Cd	25	96
Ethanol– $15 \text{ mol l}^{-1} \text{ aq. NH}_3$ (999 + 1)	30	Ag	5	87
		Fe	50	0
		Cu	50	18
		Cd	5	67
	30	Ag	25	90
		Fe	250	0
		Cu	250	19
		Cd	25	89
Ethanol– $15 \text{ mol l}^{-1} \text{ aq. NH}_3$ (99 + 1)	30	Ag	5	93
		Fe	50	0
		Cu	50	27
		Cd	5	60
	30	Ag	25	95
		Fe	250	0
		Cu	250	20
		Cd	25	56

nearly complete recovery (>95%) was attained after 30 min (for silver) and after 60 min (for cadmium). Copper and iron were hardly extracted even after 60 min. On the other hand, iron, copper and cadmium behaved similarly with ethanol (99.5% v/v)–12 mol l⁻¹ hydrochloric acid (99 + 1), showing a recovery of 96–98% with irradiation for 60 min. More than 90% of silver remained unextracted, however.

The volume of extraction solvent was not changed even after 60 min, because the test-tube was tightly sealed with a silicone-rubber stopper.

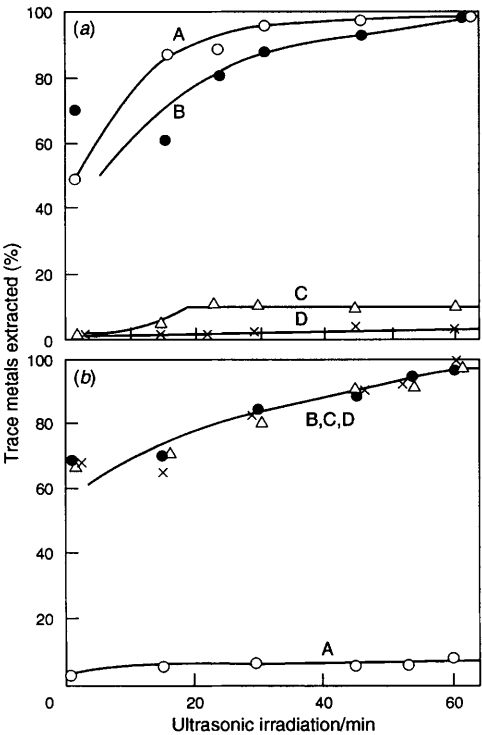


Fig. 1 Effect of ultrasonic irradiation on the extraction of silver (10 ng, A), iron (100 ng, D), copper (100 ng, C) and cadmium (10 ng, B) from 100 mg of lead matrix with a 2 ml mixture of (a) ethanol and 15 mol l⁻¹ aqueous ammonia (99 + 1) and (b) ethanol and 12 mol l⁻¹ hydrochloric acid (99 + 1).

Effect of Amount of Lead on Extraction Recovery

After evaporating 3 ml of lead nitrate solution (containing nanogram amounts of trace metals and 100–500 mg of lead), the residue was treated ultrasonically with 2 ml of extraction solvent. Silver was extracted with a 99 + 1 mixture of ethanol (99.5% v/v) and 15 mol l⁻¹ aqueous ammonia for 30 min; iron, copper and cadmium were extracted with a 99 + 1 mixture of ethanol (99.5% v/v) and 12 mol l⁻¹ hydrochloric acid for 60 min.

Table 2 shows that trace metals are extracted in >94% yields from a solution containing 100–300 mg of lead, but the trace recoveries decrease slightly in the presence of 500 mg of lead.

Analysis of High-purity Lead Metal

The proposed separation method was applied to the analysis of high-purity lead. A 2 g sample of commercial lead metal (99.999% purity, 2–3 mm granular form; Katayama Chemicals) was dissolved in 15 ml of 4.5 mol l⁻¹ nitric acid; the solution was evaporated to dryness and the residue was dissolved in 20 ml of water. A 1 ml aliquot of the solution was placed in a test-tube and evaporation, extraction and determination were carried out as described under Procedure.

The results are summarized in Table 3. Good reproducibilities were obtained for trace constituents, with relative standard deviations of 2–4%. A 10 ng amount of silver added to the sample was quantitatively recovered and successfully determined. Blank values through the whole procedure were less than the detection limits: <0.5 ng for silver, <2 ng for iron, <2 ng for copper and <0.5 ng for cadmium.

Table 2 Effect of amount of lead matrix on trace recovery

Lead taken*/mg	Trace metal extracted (%)			
	Ag [†]	Fe [‡]	Cu [‡]	Cd [‡]
100	97	102	101	99
200	97	99	99	99
300	94	98	98	96
500	76	90	89	90

* Amounts added were Ag 10 ng, Fe 100 ng, Cu 100 ng and Cd 10 ng.

Table 3 Determination of impurities in high-purity lead (99.999% purity)

Sample/g	Aliquot taken	Found/ng				Concentration/ng mg ⁻¹			
		Ag	Fe	Cu	Cd	Ag	Fe	Cu	Cd
1/2*	1/10		54	55	13.0		0.52	0.53	0.125
	1/10		50	52	14.0		0.48	0.50	0.135
	1/10		53	54	12.7		0.51	0.52	0.122
	1/10		54	55	13.1		0.52	0.53	0.126
	1/10		53	54	13.0		0.51	0.52	0.125
						Average 0.51 0.52 0.127			
2.07	1/10	13.7				0.132			
	1/10	14.1				0.136			
	1/10	13.0				0.125			
	1/10	13.4				0.129			
	1/10	12.7				0.122			
	1/10†	23.0				0.125			
						Average 0.128			

* Extraction with ethanol–12 mol l⁻¹ hydrochloric acid.
† Extraction with ethanol–15 mol l⁻¹ aqueous ammonia.
‡ 10 ng of Ag were preliminarily added.

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