Determination of Trace Elements in Lead and Lead-based Alloys by Inductively Coupled Plasma Optical Emission Spectrometry After Separation of Lead as Lead Chloride Fluoride Precipitate

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INTRODUCTION

Lead is used in batteries, TV screens, as shielding material in nuclear reactors, and also in the manufacture of alloys such as PbBi and PbLi (1-3). Lead-bismuth eutectic (PbBi) is a potential candidate material for spallation target and coolant in accelerator-driven systems (ADS) (4,5). Similarly, lead-lithium eutectic (PbLi) is proposed for use as multiplier, breeder, and coolant in fusion reactors (6-8). The presence of impurities limits their utility, and hence, it is important to determine trace elements present in these materials as a quality check. Direct determination of impurities after dissolution of the sample by ICP-based techniques is difficult due to matrix interferences, both spectroscopic and non-spectroscopic in nature (9). Solid state techniques such as spark source mass spectrometry, though reported for the determination of impurities in lead, require matrix-matched standards (10). Hence, for accurate determinations, the matrix element needs to be separated from the trace impurities. Normally, Pb is separated from trace impurities as PbCl₂ precipitate (11). However, some of the hydrolyzable elements such as Nb, Sb, Sn, Ta, and Ti are not recovered by this procedure. Solvent extraction and ion exchange procedures are already developed, but they are tedious, time-consuming, and all of

ABSTRACT

A method has been developed for the separation of Pb from trace impurities such as Nb, Ni, Sb, Sn, Ta, and Ti for their determination in Pb, PbLi, and PbBi alloy samples. Lead was separated as chloride fluoride (PbClF) precipitate. The method also enables the determination of hydrolyzable elements which are otherwise not recovered. The separation of Pb was found to be 99.5%, whereas the recovery of impurities was in the 82-94% range. Matrix-free solutions were analyzed for Nb, Ni, Sb, Sn, Ta, and Ti by inductively coupled plasma optical emission spectrometry (ICP-OES). The method was applied for the analysis of Pb, PbLi, and PbBi alloy samples. Relative standard deviations were in the 1.8-10.2% range and the process blank levels were at the lower µg/g level.

the elements of interest cannot be separated and determined using a single separation procedure (12-14). Therefore, a better alternative to the existing procedures is necessary.

The procedure reported in the present study deals with the separation of Pb as chloride fluoride (PbClF) precipitate from Pb, PbLi, and PbBi samples. Matrix-free supernatants are analyzed for Nb, Ni, Sb, Sn, Ta, and Ti by inductively coupled plasma optical emission spectrometry (ICP-OES). The procedure is applied to the analysis of Pb and PbLi, PbBi alloy samples. A comparison between PbCl₂ and PbClF methods is also reported.

EXPERIMENTAL

Instrumentation

An inductively coupled plasma optical emission spectrometer Model No. JY-2000, equipped with a 40.68 MHz radio frequency generator, was used for these studies and determinations (Jobin Yvon, Horiba, France). The operating parameters used are listed in Table I.

TABLE I. ICP-OES Operating Parameters

Instrument	JY 2000 Sequential ICP-OES Spectrometer
RF Power	1 kW at 40.6 MHz
Plasma gas flow rate	12 L min ⁻¹
Nebulizer gas flow rate	0.1 L min ⁻¹
Sample uptake rate	1.2 mL min ⁻¹
Slit width	20 µm/20 µm (Entrance/Exit)
Monochromator	0.64 m focal length, 2400 groves/mm Czerny Turner mounting

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Reagents

Analytical reagent grade chemicals were used throughout. Pure water (18 MΩ cm) was prepared by passing potable water through a mixed-bed ion exchanger and then through a Millipore® Milli-Q™ system. The standard solutions of the metals were procured as multi-element standard solution from E. Merck, Germany. Pb was procured from E. Merck, Germany, PbLi and PbBi samples were purchased from local suppliers.

Analytical Procedure

Pb, PbLi, or PbBi alloy (0.5 g) was dissolved in 3 mL nitric acid (HNO₃) and 2 mL hydrofluoric acid (HF) in a water bath and diluted to 20 mL. To the solution, 2 mL hydrochloric acid (HCl) was added to precipitate Pb as PbClF and was then diluted to 25 mL. The resultant precipitate was centrifuged and the supernatant was analyzed for Nb, Ni, Sb, Sn, Ta, and Ti by ICP-OES. To verify the recoveries of the analytes, sample solutions spiked with traces of standard solutions of the analytes of interest were treated as mentioned above and analyzed by ICP-OES. The process blanks were also prepared as mentioned above without sample. The percentage recoveries were calculated by comparing the signal of the pure standards and those of the spiked standards.

The above procedure was repeated without HF to compare the recoveries of the analytes with and without HF. The procedure was applied for the analysis of Pb, PbLi, and PbBi alloys. The same ICP-OES system (JY-2000) was used for the measurements. The calibration standards used for quantification were in the 0.5–5 µg/mL range and external calibration was used for quantification.

RESULTS AND DISCUSSION

The simplest procedure for the separation of Pb from trace impurities is precipitation as PbCl₂. Hence, lead samples dissolved in HNO₃ were analyzed by trace impurities after separation of Pb as PbCl₂. However, the recoveries of Nb, Sb, Sn, Ta, and Ti were less and found to be decreasing with time due to hydrolysis. Hence, quantification could not be performed. The elements whose recoveries were found to be poor are known to form stable fluorides.

To improve the recoveries, the sample was dissolved in HNO₃ and HF. Precipitation was carried out using HCl in the presence of HF, leading to lead chloride fluoride (PbClF) precipitation. This procedure ensures the complete precipitation of lead and also avoids hydrolysis of the elements mentioned above.

A comparison of recoveries in the presence and absence of HF is shown in Table II. It can be seen that the recoveries of Nb, Ni, Sb, Sn, Ta, and Ti were found to be near quantitative when Pb was precipitated as PbClF compared to those obtained when Pb was precipitated as PbCl₂. The improvement in the recoveries of the analytes is due to the formation of stable fluorides of impurities in the

presence of HF. In the absence of HF, most of the analytes were hydrolyzed leading to poor recoveries.

The percentage separation of lead was also found to improve from 92±2.0% (for PbCl₂) to 99.5±0.5% (for PbClF). This procedure was applied to the determination of Nb, Ni, Sb, Sn, Ta, and Ti in Pb, PbLi, and PbBi samples, and the results are listed in Table III. The method detection limits (MDL) was calculated (in µg/g in the sample after applying the multiplication factor) as signal equivalent to three times the standard deviation of repeated blank measurements (n=5). The limit of quantification (LOQ) is considered as 10 times the standard deviation of repeated blank measurements. The values obtained are reported as <LOQ.

This procedure requires only acids which are commercially available in pure form. Since no external complexing agent or other reagents are required to be added, the process blank levels were in the lower µg/g range. The relative standard deviation was found to be in the 1.8–10.2% range. The concentrations of the impurities in the three samples were at the lower µg/g levels, except the concentration of Sn in PbLi was 22.5 µg/g and of Ni in PbBi was 11.1 µg/g.

TABLE II
Comparison of Recoveries of Nb, Ni, Sb, Sn, Ta, Ti
Using Chloride and Chloride Fluoride Precipitation

Element	Wavelength (nm)	Recovery (%)	
		PbClF precipitation (n=3)	PbCl ₂ precipitation (n=3)
Nb	269.706	93 ± 2	59 ± 6
Ni	221.647	91 ± 1	76 ± 3
Sb	206.833	90 ± 2	65 ± 7
Sn	235.484	82 ± 1	52 ± 10
Ta	223.980	92 ± 4	52 ± 7
Ti	334.904	94 ± 2	42 ± 12

Note: Uncertainties are expressed as standard deviation of three experiments.

TABLE III
Concentration of impurities in Pb, PbLi, and PbBi

Element	MDL ^a (μg/g)	Process Blank ^b	Concentration (μg/g) (n=3)		
			Pb	PbLi	PbBi
Nb	1.5	<5	<5	<5	<5
Ni	0.3	2	5.4 ± 0.2	<1	11.1 ± 0.2
Sb	1.8	<6	6.7 ± 0.2	<6	<6
Sn	1.8	<6	9.4 ± 0.5	22.5 ± 1.0	<6
Ta	1.5	<5	<5	<5	<5
Ti	0.3	<1	4.3 ± 0.3	3.9 ± 0.4	<1

Note: Uncertainties are expressed as standard deviation of three experiments.

^a MDL = Method detection limit.

^b Process Blank of present procedure.

CONCLUSION

The chloride fluoride precipitation method was used for the separation of lead from trace impurities and for their determination in Pb, PbLi, and PbBi alloy samples. The percentage separation of Pb and also the recoveries of the hydrolyzable elements were improved by the addition of HF. The procedure is simple, fast, and better than the PbCl₂ precipitation method in recovering the hydrolyzable elements of Nb, Ni, Sb, Sn, Ta, and Ti.

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