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ANALYSIS OF LEAD ALLOYS BY ATOMIC
ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

The determination of tin in tin-lead alloy and the determination of calcium in calcium-lead alloy is accomplished by atomic absorption spectrophotometry. Solutions of the samples are analyzed using a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a 10 cm pre-mix acetylene-air burner.

Tin-lead alloy samples are dissolved using fluoboric acid, tartaric acid, and a small amount of nitric acid. Replicate analyses of an NBS lead alloy containing 4.94 percent tin gave an average result of 4.93 percent with a relative standard deviation of 2.66 percent.

The calcium-lead alloys are put into solution with nitric acid, and lanthanum added to eliminate possible interferences. Recoveries on prepared synthetic samples averaged nearly 100 percent. The relative standard deviation at a calcium content of 640 ppm was 0.30 percent.

GENERAL INTRODUCTION

A relatively fast and precise method for the determination of tin in tin-lead alloys and the determination of calcium in calcium-lead alloys was needed in the preparation of these two alloys at Rocky Flats. Published information (1,2) and previous experience indicated that the determination of tin and calcium in lead base materials could be accomplished by atomic absorption methods. The use of an atomic absorption method could possibly offer advantages in speed, simplicity, and precision over X-ray or titrimetric methods. Two methods were developed which encompassed these three advantages.

PART I

Determination of Tin in Tin-Lead Alloys

INTRODUCTION

The tin-lead alloy was prepared for specific tensile strength and elongation properties. A rapid analytical procedure was needed for verification that the alloy met a specification of an 8 to 12 percent tin content.

A combined ion exchange-X-ray fluorescent technique was initially used to determine the tin content of the alloy. A check on the X-ray results was needed by a more precise method. Atomic absorption was chosen as a possible means of supplying the necessary analysis.

EXPERIMENTAL

Instrumentation

Analytical measurements were made with a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer. This is a double beam instrument and is equipped with a 10 cm pre-mix acetylene-air burner. Instrumental parameters follow those suggested by the Perkin Elmer Atomic Absorption Handbook (3) and are shown in Slide 1.

The acetylene-air fuel mixture was adjusted to give a reducing flame. This flame is obtained by aspirating a standard solution containing 100 ppm tin into the burner flame while adjusting the acetylene flow to obtain maximum absorption.

Standard Preparation

A master stock solution of tin was prepared by the dissolution of reagent grade tin metal in fluoboric acid (HBF_4) (1) and 5 N HNO_3 , with tartaric acid added as a complexing agent to keep the tin in solution. Fluoboric acid is not a much-used acid, but it is highly effective for some dissolutions. It is prepared by mixing 10 grams of H_3BO_3 and 25 mls of 48 percent HF in 200 mls distilled water. This solution is diluted to 400 mls with distilled water. If the solution becomes cloudy, more HF is added.

It was found that this HBF_4 - HNO_3 method of standard and sample dissolution was more rapid than methods using HCl or HNO_3 with added HF.

Dilutions of the master stock solutions were made with distilled water to prepare a series of standards to cover the desired analytical range of 20-300 ppm tin.

Sample Preparation

Samples of lead alloy were weighed and then dissolved in the same manner as in the preparation of the tin master stock solution. The lead alloy sample weight was determined by the expected tin content of the sample. The tin content of the sample solution must be within the range of the analytical curve.

A complete dissolution of the average 0.1 gram sample was accomplished using approximately 0.3 gram tartaric acid, 5 mls HBF_4 , and 2-3 mls 5 N HNO_3 . The samples were diluted to a

final volume of 25 ml with distilled water. An excess of tartaric acid must be present during sample dissolution to retain the tin in solution. In order to reduce the corrosive effect of a high acid concentration on the instrument burner and atomizer, a minimum of acid should be used to obtain dissolution of the standards and of the samples.

RESULTS AND DISCUSSION

The analytical curve for the determination of tin concentration in a sample solution is shown on Slide 2. Standards were analyzed concurrently with the samples. The analytical curve for tin in solution was linear over the desired analytical range.

Sensitivity of the method was 4 ppm tin for 1 percent absorption, and the limit of detection was about 1 ppm. The limit of detection could be further reduced by using 5X or 10X scale expansion.

The possibility of interferences in the method as a result of the reagents used and the effect of the lead concentration in the aspirated solution were investigated. Blanks consisting of the approximate concentrations of tartaric acid, HBF_4 , and HNO_3 that would normally be found in a sample solution were aspirated and shown to be free of interfering effects. The results obtained on synthetic samples containing known amounts of tin and lead are given in Slide 3. The amount of tin present ranged from 0.76 percent to 9.43 percent. Samples 1, 2, and 3 contained varying amounts of tin and the same amount of lead. Samples 4, 5, and 6 contained the same

respective amounts of tin as 1, 2, and 3 but double the lead concentration. A comparison of the results shows no significant indication of interference due to the change in the lead concentration.

Slide 3 also shows the percent recovery of the tin, varying from 93.29 percent to 111.84 percent with an average recovery of 100.86 percent.

A National Bureau of Standards certified standard, 53d, containing 4.94 percent tin in a lead base was used to determine the accuracy of the method. Over a period of several days, nine individually weighed samples of the standard were analyzed. Dissolution was accomplished by the previously described method. An average result of 4.93 percent tin and a relative standard deviation of 2.66 percent was obtained.

Slide 4 shows the atomic absorption results on five samples of the tin-lead alloy compared to the results as reported by the X-ray method. The atomic absorption results are the average of three determinations per sample, each determination being made on an individually weighed portion of the sample.

PART II

Determination of Calcium in Calcium-Lead Alloy

INTRODUCTION

The next lead alloy analyzed was a calcium-lead alloy. The addition of calcium to lead results in an alloy having higher strength, superior creep resistance, better fatigue properties, and higher hardness than lead. There are, however, processing problems in holding the calcium content to very close limits at low levels. Previous investigations (4) indicated that acceptable properties could be obtained over a range of 0.04 to 0.1 percent calcium, with a normal content of 0.07 percent calcium.

Preparation of this alloy at Rocky Flats required that an analytical method be developed for the determination of the calcium in the alloy. The previously noted processing problems in alloying the metals made it desirable that a casting be analyzed as soon as possible after pouring to ensure that the calcium content was within specifications. This was especially important during the initial stages of the preparation when various methods of alloying were being tested.

The desirability of a relatively fast method and the level of calcium content to be determined suggested the use of atomic absorption spectrography. A method was therefore developed for the calcium determination by atomic absorption spectroscopy.

EXPERIMENTAL

Instrumental

A Perkin-Elmer 303 Atomic Absorption Spectrophotometer was employed for all analytical measurements. This double-beam instrument was used with a 10 cm laminar flow burner and acetylene-air fuel. The instrumental parameters are given in Slide 5.

Standard Preparation

The standards used to prepare working curves for the analysis contained calcium, lead, and lanthanum. Lanthanum was added to both the standards and the samples to eliminate the effect of interfering ions that might be present (3). The solutions used in the preparation of the standards are listed on Slide 6.

- Calcium Master Solution - A master solution of 400 ppm calcium was prepared by dissolution of reagent grade CaCO_3 in approximately 0.1 N HNO_3 .
- Lead Stock Solution - Reagent grade lead shot was dissolved in a small amount of nitric and brought to volume with distilled water. Final solution contained 10 percent lead by weight.
- Lanthanum Stock Solution - A 5 percent lanthanum solution was prepared by dissolving 15.5 g of reagent grade lanthanum nitrate in 25 mls of concentrated HNO_3 and diluting to a 100 ml final volume.

The standard solutions were made up to cover the 1 to 25 mg/l calcium range. Each standard in a final volume of 25 mls also contained 2 percent lead and 3 mls of the 5 percent lanthanum stock solution. Analytical curves were drawn from standards analyzed concurrently with the samples. Slide 7 shows a typical working curve.

Sample Preparation

Samples of the lead alloy weighing 0.4 to 0.5 g each were dissolved in 2 mls of concentrated HNO_3 and 10 mls of water. After dissolution was complete, 3 mls of the 5 percent lanthanum stock solution were added, and the solution was diluted to a final volume of 25 mls with distilled water. These sample solutions, containing approximately 2 percent lead and 15 ppm calcium, were then aspirated directly into the burner.

RESULTS AND DISCUSSION

Accuracy

There were no standard samples available of a lead-calcium alloy to check the accuracy of the method. Synthetic samples were therefore prepared using solutions of calcium and lead, and analyzed as unknowns. The results obtained on these samples are given in Slide 8. All sample solutions contained 2 percent lead.

Precision

A 10 g portion of the alloy sample was dissolved as in the regular sample procedure and brought to a final volume of

100 mls. Five-ml aliquots of this solution along with 3 mls of the lanthanum stock solution were each diluted to 25 mls and aspirated into the burner. At a calcium level of 640 ppm, the relative standard deviation was found to be 0.30 percent on the eleven aliquots analyzed.

Homogeneity of Received Samples

The material as received from the alloy preparation was in the form of several thick turnings per sample. In order to check the homogeneity of each sample submitted, specimens of alloy from each turning within a given sample were selected. These were then individually weighed and analyzed as separate samples.

From the results shown typically in Slide 9, the samples submitted were homogeneous with respect to different turnings within a given sample.

Some of the reported results on the lead-calcium alloy samples are shown on Slide 10. Sample numbers 1 through 6 show the difficulty incurred in preparing a lead calcium alloy and the need for a rapid method of analysis. Samples 4, 5, and 6 are the slags from the castings of samples 1, 2, and 3. Samples 7 through 12 are typical of the calcium results after the casting method was more fully developed.

The lead-calcium alloy had been previously developed at the Oak Ridge Y-12 Plant. At that installation the calcium determination had been accomplished by flame photometry. This determination, developed before the advent of atomic absorption spectroscopy, had a relative standard deviation of approximately 10 percent (4). The use of an atomic absorption method at this plant enabled the lowering of the relative standard deviation to about 1 percent.

CONCLUSION

We have found that the addition of an atomic absorption spectrophotometer to our laboratory has opened up a new area of sample analysis for us. This is with samples, such as the alloys mentioned in this paper, in which it is necessary to determine a constituent present in the 0.05 to 10 percent range. The standards for the analyses are all solution standards, which are far easier to prepare than solid standards. If the required hollow cathode lamp is on hand, a tentative method can be set up in a short time. A tentative method is one in which "ball park" answers are obtained, but possible interferences have not been fully investigated, nor a statistical evaluation of the method made. This type of analysis has been found to be especially valuable to workers starting up new processes. Then, while they solve their start-up problems, we can more fully investigate the initial "tentative method."

REFERENCES

1. Luis Capacho-Delgado and David D. Manning, Atomic Absorption Newsletter, 4, 317(1965).
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3. Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corp., Norwalk, Conn. (1966).
4. A. B. Townsend, USAEC Report Y-1307(1960).

LIST OF SLIDES

<u>Slide Number</u>	<u>Description</u>
1	Instrumental Parameters for the Determination of Tin
2	Analytical Curve for Tin
3	Results of Synthetic Samples
4	Amount of Tin Found in Prepared Lead Alloys
5	Instrumental Parameters for the Determination of Calcium
6	Standard Preparation Solutions
7	Analytical Curve for Calcium
8	Results of Synthetic Samples
9	Calcium Content of Portions from One Sample
10	Amount of Calcium Found in Prepared Alloys

Atomic Absorption Instrumental Parameters
for the Determination of Tin in Tin-Lead Alloys

Wave Length	2863	A
Lamp Current	20	ma
Slit Width	1.0	mm
Scale Expansion	X2	
Air Flow (Flow Meter Reading)	7.5	
Acetylene Flow (Flow Meter Reading)	12.0	

ANALYTICAL CURVE FOR TIN

SLIDE 2

Results on Synthetic Samples

<u>Sample</u>	<u>Prepared</u>			<u>Found</u>		<u>% Recovery</u>
	<u>Sn</u> <u>μg/ml</u>	<u>Pb</u> <u>μg/ml</u>	<u>%Sn in Pb</u>	<u>Sn</u> <u>μg/ml</u>	<u>%Sn in Pb</u>	
1	310	3288	9.43	315	9.58	101.59
2	124	3288	3.77	119	3.62	96.02
3	93	3288	2.83	87	2.64	93.29
4	310	6576	4.71	302	4.59	97.45
5	124	6576	1.89	122	1.86	98.41
6	93	6576	1.41	88	1.34	95.04
<hr/>						
7	62	3288	1.89	60	1.82	96.30
8	31	3288	0.94	33	1.00	106.38
9	47	3288	1.43	48	1.46	102.10
10	25	3288	0.76	28	0.85	111.84
11	31	3288	0.94	31	0.94	100.00
12	25	3288	0.76	28	0.85	111.84
Average						100.86

Amount of Tin Found in Prepared Lead Alloys

<u>Sample</u>	<u>Atomic Absorption Average of 3</u>	<u>X-ray</u>
1	9.02 %	10% $\pm$ 1%
2	9.40 %	"
3	9.42 %	"
4	9.61 %	"
5	8.96 %	"

SLIDE 4

Atomic Absorption Instrumental Parameters for
the Determination of Calcium in Calcium-Lead Alloys

Wavelength	4227	Å
Lamp Current	15	ma
Slit Width	1	mm
Scale Expansion	1	x
Air (Flowmeter Reading)	7.5	
Acetylene (Flowmeter Reading)	~9*	

*

Exact setting made by aspirating calcium standard and adjusting acetylene flow to obtain maximum absorption.

Standard Preparation Solutions

Calcium Master Solution - A master solution of 400 ppm calcium was prepared by dissolution of reagent grade CaCO_3 in approximately 0.1 N HNO_3 .

Lead Stock Solution - Reagent grade lead shot was dissolved in a small amount of nitric and brought to volume with distilled water. Final solution contained 10 percent lead by weight.

Lanthanum Stock Solution - A 5 percent lanthanum solution was prepared by dissolving 15.5 g of reagent grade lanthanum nitrate in 25 mls of concentrated HNO_3 and diluting to a 100 ml final volume.

ANALYTICAL CURVE FOR CALCIUM

SLIDE 7

Results on Synthetic Samples
(Values in ppm, based on lead)

<u>Calcium Added</u>	<u>Calcium Found</u>	<u>%Recovery</u>
819	812	99.2
1229	1196	97.3
1065	1037	97.3
901	875	97.1
328	338	103.1
573	584	101.9
737	768	104.2
819	829	101.2
655	681	104.0
410	402	98.1
246	261	106.1
737	768	104.1
	Average	101.1

Calcium Content of Portions from One Sample

<u>Sample Weight</u> (grams)	<u>Calcium Content</u> (ppm)
0.4995	641
0.5026	633
0.5118	645
0.5078	628
0.5087	632
0.5212	616
0.5308	623
0.5238	611
0.5247	610
0.5110	626
0.4876	628
	<hr/>
Average	627

Relative Standard Deviation 1.56%

Amount of Calcium Found in Prepared Alloys

<u>Sample</u>	<u>Calcium Content</u> (ppm)
1	<10
2	<10
3	<10
4	1610
5	2820
6	2594
7	761
8	854
9	864
10	914
11	848
12	886