

AAS

APPLICATION NOTES

The determination of trace elements (Ag, Bi, Cu, Sb, Ni) in lead-tin solders

AAS



Introduction

The trace element composition of solders is an important aspect for solder manufacturers as it can affect the wettability, metal compatibility, flow characteristics and brightness of the solder. Atomic absorption spectrophotometry (AAS) is an ideal technique for the major and trace element analysis of lead-tin alloys. Most of the major and trace components can easily be analysed using flame AAS, with the remainder being measured using electrothermal furnace atomization AAS.

Experimental

Sample preparation

The dissolution of lead-tin alloys has given analysts many problems in the past due to tin precipitating in the presence of nitric acid as insoluble metastannic acid ($\text{SnO}_2 \times \text{H}_2\text{O}$). Lead metal with a very low Sn content can usually be dissolved completely in nitric acid but this is not possible with solders with an appreciable Sn content. The usual dissolution technique for solders is to use a 3 to 1 hydrobromic acid : bromine solution but many analysts prefer not to use the noxious and messy bromine.

The method used in this analysis was based on the method of Hwang and Sandanato¹. Fluoroboric acid was used in the technique and this was freshly prepared before use as follows. To a plastic beaker, 100 mL of 40% HF was added, and then 40 g boric acid was slowly added. This was allowed to dissolve and then stored in a plastic bottle. Then 2 g of diced solder (approx. 200 mg pieces) was precisely weighed into a 150 mL plastic beaker. To this was added 40 mL water, 6 mL fluoroboric acid and 12 mL 70% nitric acid. The beaker was covered with a plastic watch glass and warmed on a hot water bath to dissolve the solder. When the solder had dissolved it was cooled to room temperature and 0.5 mL of 10% tartaric acid solution was added. The solution was then diluted with water to 100 mL in a plastic volumetric flask. All plastic ware was used due to the possibility of the HF leaching contaminating ions from the surface of any glassware used.

Standards

The standards used were a combination of all elements analysed including Ni which was determined by furnace AAS. The Auto-Mix facility on the GBC automated graphite furnace system allows the operator to have just one standard from which all other lower concentration standards are diluted automatically. Standard 1 was used for this purpose. Plastic ware was used for the standards because they were made up in the same hydrofluoric, nitric, boric, and tartaric acid mixture as used with the samples.

Table 1 below gives details of the standards used. Concentrations are in mg/L (ppm).

Standard	Ag	Bi	Cu	Sb	Ni
1	1	2	0.1	1	0.1
2	2	8	0.5	5	–
3	4	20	2.0	20	–

Table 1: Standards composition

Air-Acetylene Flame AAS was used to determine Ag, Bi, Cu and Sb, while Furnace AAS was used to determine Ni.

The standards, blank and dilution solution were made up with the same fluoroboric acid, nitric acid, tartaric acid, water mixture as was used with the samples.

Instrumentation

The GBC atomic absorption spectrophotometer and the GBC automated graphite furnace system was used. The GBC graphite furnace system comprises the graphite furnace (GF) and programmable automatic sample loader (PAL).

Results

The major element composition (in %) for the two solder samples analysed are given in Table 2 below.

	Pb	Sn	Ag	Sb
Wire	97.05	2.5	0.45	–
Bar	94.5	5.4	–	0.1

Table 2: Major element composition

Table 3 below gives the results obtained for the two types of solder analysed for both the analysed solutions and solid solder samples. Concentrations are in mg/L (ppm).

	Sb	Bi	Ag	Cu	Ni
Solder wire sample solution	1.17	0.220	0.882	0.074	0.0030
Solder bar sample solution	17.5	5.30	0.074	0.130	0.021
Solder wire sample	59	11	4115	3.7	0.150
Solder bar sample	827	250	3.5	6.1	1.00

Table 3: Analytical results in mg/L (ppm). Note that the solution used for the Ag determination of the wire solder sample was diluted a further 100 times before analysis

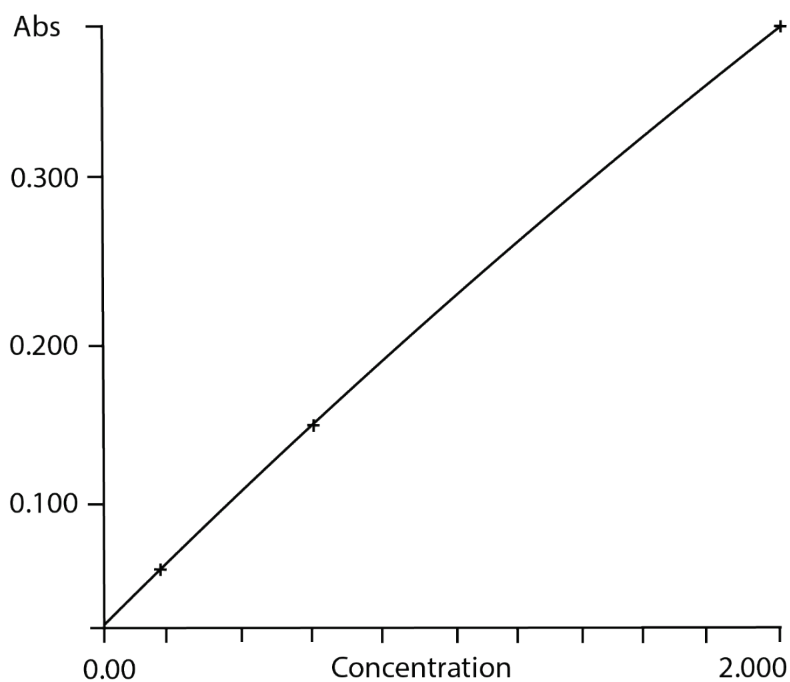
Normal calibration and standard additions were used to determine all elements analysed and it was found that there was no difference between the two methods of calibration except in the analysis of Ni by graphite furnace AAS, where it was found that the sample matrix depressed the Ni signal by a factor of approximately 2. Therefore the result for Ni was obtained using the method of standard additions, while the other elements analysed were determined by the normal calibration method.

Figure 1 and Figure 2 is an output generated by the GBC software.

Element	Cu
Wavelength (nm)	324.7
Slit Width (nm)	0.5
Atomization	Air-Acet
Lamp Current (mA)	4.0
EHT (gain)	–308 V
Scale Expansion	1.000
Integration Time (sec)	1
Beam Mode	Double Beam

Calibration						
Standard/Blank	Reading 1	Reading 2	Reading 3	Reading 4	Mean	RSD (%)
Blank	-0.001	-0.000	0.002	-	0.000	-
Standard 1	0.018	0.017	0.017	-	0.018	1.91
Standard 2	0.091	0.093	0.093	-	0.092	1.35
Standard 3	0.352	0.356	0.346	0.350	0.351	1.19

Calibration Table		
Standard	Absorbance	Concentration
1	0.017	0.100
2	0.082	0.500
3	0.351	2.000



Concentration – Sample Number 1	
Reading	Concentration
1	0.069
2	0.070
3	0.073
4	0.077
5	0.072
6	0.075
Mean: 0.073 RSD: 3.80%	

Concentration – Sample Number 2	
Reading	Concentration
1	0.129
2	0.132
3	0.126
4	0.129
5	0.128
6	0.134
Mean: 0.130 RSD: 2.21%	

Figure 1: Software output for the analysis of Cu

Element	Ni
Matrix	solder
Instrument Mode	Absorbance BC On
Beam Mode	Double Beam
Measurement Mode	Peak Area
Wavelength (nm)	232.0
Slit Width (nm)	0.2
Slit Height	Reduced
Lamp 1 Current (mA)	3.5
Lamp 2 Current (mA)	0.0
Integration Time (sec)	0.1
No. of Replicates	3
Calibration Mode	Standard Additions
Recal. Std No.	2

Calibration		
Blank/Standard	Standard or Added Concentration (ppb)	Mean Standard Absorbance
Blank/Sample	0.00	0.455
Standard 1	5.00	0.563
Standard 2	10.00	0.670

Graphite Furnace Parameters					
Step No.	Final Temp °C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	90	3.0	5.0	Inert	No
2	120	30.0	2.0	Inert	No
3	850	10.0	10.0	Inert	No
4	850	0.5	1.0	None	No
5	2600	1.4	2.0	None	Yes
6	2800	0.5	0.8	Inert	No

Sampling Mode	Auto Sampling
Standards Preparation	Auto-Calculated

Autocalc Sampler Volumes	
Standard 1 Volume (µL)	2
Sample Volume (µL)	20
Modifier Volume (µL)	0
Total Volume (µL)	20

No. of Injections	1
Inject before Step No.	1
Recalibration Rate	1

Solder Samples						
Blank/Addition	Standard/Added Concentration (ppb)	Reading 1	Reading 2	Reading 3	Mean Abs.	RSD (%)
Ni Blank	0.00	0.182	0.147	0.176	0.169	10.99
Addition 1	5.00	0.543	0.557	0.590	0.563	4.29
Addition 2	10.00	0.638	0.666	0.705	0.670	4.99
Bar	21.16	0.453	0.450	0.463	0.455	1.58

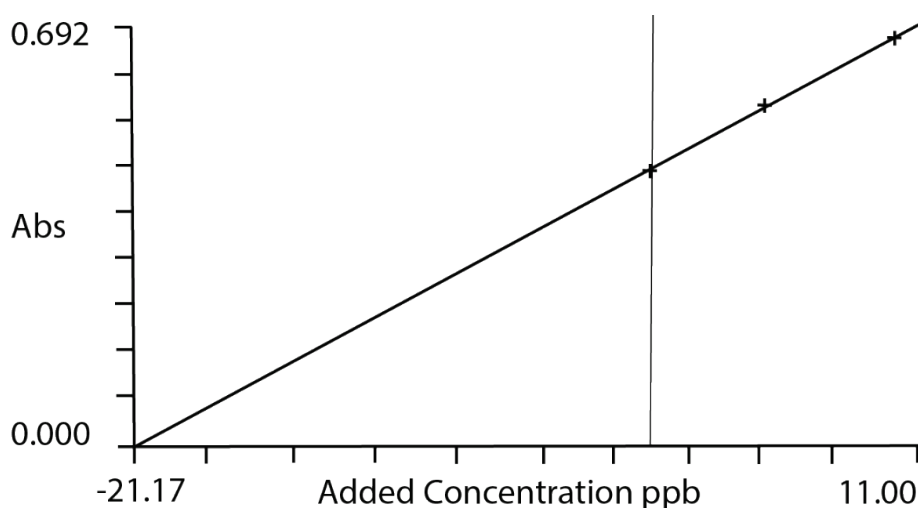


Figure 2: Software output for the graphite furnace analysis of Ni

Conclusion

The trace element analysis of lead/tin solders presents the analyst with a difficult analytical problem. The first obstacle to overcome is the dissolution procedure. The method used here, involving the use of fluoroboric and nitric acids, is both simple and very fast. The use of the GBC Double Beam AAS with its sophisticated report generation facilities allows the analyst to perform detection limit assays with the maximum precision and the minimum of fuss. For graphite furnace work, the GBC AAS is coupled with GBC software gives the operator total control over the instrumental parameters to give accurate and readable reports.

This method is suitable for lead-tin solders, for similar types of metals containing antimony, and cadmium and its alloys.

References

1. Hwang J.Y. and Sandanato L.M., Anal. Chem., 1970, 42, 744.