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Multielement Analysis of Tin-Lead Solder by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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Abstract. The quality control of the chemical composition of tin-lead solder is one of the routine analytical applications in the department of inorganic chemistry. A rapid and reliable method of analysis was established by use of the inductively coupled plasma atomic emission spectrometry (ICP-AES), which allows multielement quantitative determination of the impurities below criteria levels, as well as the determination of the major elements in solder. The most difficult part of the method remains the solder disintegration, as the dissolution of tin and lead together is a difficult chemical procedure. The samples were dissolved in a mixture of HCl and HNO_3. A 4 g/l solder solution was found to be suitable for analyzing traces of Ag, Al, As, Au, Bi, Cd, Cu, Fe, In, Ni, Sb, and Zn with a better precision and accuracy compared to the combined spark-ICP AES method used previously. The results for Sn and Pb obtained with dilute solutions were in good agreement with those obtained by the wet chemical methods. Spectral interferences from Sn and Pb, as well as matrix effects were found to be negligible for most of the trace elements. The reliability of the analytical results achieved in routine programs was proved with commercially certified reference materials. The discrepancies found for some elements between the certified mean values and the ICP results are discussed.

1. Introduction

Solder metal alloys are used for joining together two or more metals at temperatures below their melting points. They have been used since Roman times as mechanical adhesives. With the rapid growth of the electronic industry the tin-lead eutectic solder is commonly used for soldering printed circuit boards. The restoration of ancient music organs requires the knowledge of the exact solder composition used for the preparation of the organ's pipes. Solders are of great importance in all metallurgical processes and the applications are multiple.

The determination of the nominal tin content in solders demands a high accuracy because tin is much more expensive than lead. Each solder alloy contains permissible levels of minor and trace elements such as Ag, Al, As, Au, Bi, Cd, Cu, Fe, In, Sb, Zn specified by ASTM [1] or by customers. The amounts of these elements can affect strongly the solderability of the solder. For example, antimony gives high tensil strenght and low electric conductivity. Gold enrichment can cause solder embrittlement. Therefore, it is necessary to monitor the contamination levels in production solder pots.

The main disadvantages of the classical wet chemistry methods of solder analysis as specified by ASTM [2] are that the samples have been partially dissolved for further single element determinations. These procedures are not only time-consuming, but require also a skilled operator and are rather expensive.

The elemental analysis by use of X-ray fluorescence (XRF) and arc/spark atomic emission spectrometry (AES) are industry standard practices. Most of the solder analysis data presented in the literature have been obtained by these techniques because they do not require sample dissolution [3–5]. However, these methods suffer severely from a poor choice of commercially available standard reference materials containing the large number of elements routinely determined. In practice it is extremely difficult to obtain a sample of solder that is free from concentration gradients. These steep gradients develop during the solidification of the tin-lead solder. On the other hand, the alloys undergo a process of ageing during several years influenced strongly by temperature changes. Sample surface preparation is a lengthy process as incorrect polishing can also cause erroneous results due to smearing of the sample surface [6]. XRF is useful for the major alloy elements, but does not have the sensitivity required for the trace impurities. Arc/spark AES can perform elemental analysis, but the precision is rather poor.

The idea with the introduction of a conductive solid nebulizer (CSN) was to combine the speed and simplicity of the spark excitation technique with the advantages of the inductively coupled plasma (ICP): broad linear dynamic range, and relative freedom from interelement effects [7]. Unfortunately, here again the lack of certified multielement solid standards, the difficult surface preparation and the inhomogeneous element distribution in the samples were the reasons for inaccurate analysis and poor precision. Obviously, for reliable routine analysis of tin-lead solders, a simpler multielement method, which could also handle small samples is desirable.

A significant improvement in the instrumental performance was achieved by the ICP-AES liquid method of analysis. This technique has found a wide acceptance due to its multielement capability and low detection limits. The use of vacuum spectrometers permits the detection of elements like S, P, As, Sn in the UV spectral range. For the accurate trace determination in complex matrices the spectral interferences have to be corrected. The availability of a motorized, computer-controlled scanning drive permits the determination of these corrections quickly and accurately. The combination of a poly- and monochromator facilitates the choice of the most appropriate spectral lines for different kinds of samples.

The critical part is the chemistry as the dissolution of tin-lead alloys is difficult by most procedures. Different digestion procedures have been reported using mineral acids such as HBr, fluoroboric acid, HNO_3 + H_2O_2, and aqua regia [8–12]. Complete dissolution was almost always achieved if

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the major element composition was not varying too much, thus confirming the rule that to bring all elements into solution using a single procedure is sometimes not possible.

After testing different wet-acid attacks, a combined hydrochloric-nitric acid digestion procedure was developed with further analysis of the solutions by ICP-AES. The concentration of the solder solutions was 4 g/l for alloys containing up to 60% lead.

2. Instrumentation

All measurements were performed on an ICP-AES spectrometer. Type: *Applied Research Laboratories/Fisons SA (ARL) 3580B ICP-AES Minitorch* combined 1-m polychromator (36 built-in spectral lines) and monochromator vacuum spectrometer with concave gratings 1080 lines/mm in a *Paschen-Runge* mounting. The 20 μm secondary slits mounted on the *Rowland* circle of the monochromator provide a resolution of 0.009 nm in the 3rd order. The excitation source was a 27.1 MHz RF-generator, 750 W. The sample introduction system was: *Meinhard* glass concentric K type nebulizer, ARL conical glass spray chamber, and a *Fassel* type concentric silica Minitorch. The computer used with the ICP system was an *Olivetti M 480-20 PC*. The Plasmavision software analytical programs were supplied by ARL. The ICP operating conditions are listed in *Table 1*.

3. Experimental Procedure

3.1. *Reagents and Stock Solutions*

The single element stock solns. 1000 mg/l were purchased from *E. Merck AG* (CH–8953 Dietikon), with the exception of gold 1000 mg/l, tin 10 000 mg/l and lead 10 000 mg/l which were purchased from *Johnson Matthey Brandenberger AG* (CH–8052 Zürich). They were used to prepare the ICP calibration standards and the matrix element solns.

Suprapur grade (*E. Merck*) nitric acid sp.gr. 1.40 and hydrochloric acid sp. gr. 1.15 were used to dissolve the samples and to prepare the calibration solns.

Deionized water Milli-Q+ 18 MΩ, *Millipore AG* (CH–8604 Volketswil), was used for all dilutions and washing steps.

3.2. *Sample Preparation*

Chippings of the solder samples were obtained by use of a machine lathe after removing a layer of *ca.* 1 mm from the surface. Care was taken to avoid contamination.

XRF qualitative scans were made on a *Philips AG PW 1404* spectrometer to check the tin-lead composition as well as the minor elements of the solder samples.

The dissolution procedure was as follows:

0.200 g of solder in duplicate were accurately weighed into 50 ml *Duran*-glass beakers. The samples were treated by cautious addition of 15 ml of HCl and 5 ml of HNO_3, swirled and after completion of the reaction gently heated on a Ceran (*E. Merck AG*) ceramic hot plate for *ca.* 30 min until full dissolution of the chippings. Excessive heating of the solns. is not recommended, since the heat helps to form insoluble metastannic acid. The warm solns. were transfered to 50 ml *Duran* glass measuring flasks with the addition of HCl 1:4 vol/vol. The samples were cooled to r. t., and filled up to volume. Care should be taken at this stage not to dilute the solns. with H_2O, since the addition of water results in forming insoluble $PbCl_2$. The maintenance of this high HCl concentration is important in order to keep the lead as soluble lead-chloride complex and to prevent the precipitation of lead. This procedure proved to be suitable for solder alloys with lead content up to 50 wt.% Pb. At higher lead concentrations $PbCl_2$ precipitate was formed in solns. which were older than 1 d. This process was irreversible: neither the addition of more acid or the use of an ultrasonic bath could dissolve the precipitate. Even if the analysis of the trace elements and the tin on the solns. containing $PbCl_2$ precipitate showed no deterioration in the recovery, such solns. being the source for inaccurate results due to coprecipitation effects. XRF scans performed on the acid washed precipitate indicated only the presence of lead. At concentrations less than 50 wt.% Pb (2 g/l Pb in the soln.) the solns. were stable for more than a month.

Table 1. *ICP Operating Conditions*

Forward power:	650 W, 4-turn coil
Viewing height:	9 mm above the plasma coil
Coolant Ar flow:	7.5 l/min
Auxillary Ar flow:	0.8 l/min
Nebulizer Ar flow:	0.8 l/min
Sample uptake:	2 ml/min; *Gilson* Minipuls peristaltic pump
Integration time:	3 x 5 s integrations

The determinations of tin and lead were made by diluting 50-times an aliquot of the 4g/l solns. with HCl 1:10 *v/v*. These solns. were further analyzed with the ICP spectrometer which was calibrated with synthetic reference solns. The calibration range used was up to 100 mg/l for both Sn and Pb.

4. Results and Discussion

4.1. *Wavelength Selection and Interferences*

The first task in setting up the ICP for multielement analysis of samples with varying matrix is the choice of suitable spectral lines and the determination of spectral interferences due to direct spectral overlap and/or background (Bg) shifts [13].

Wavelength scans were made across all the simultaneous and several sequential spectral lines to determine the interferences. For each line, deionized water, acid blank, 2 g/l Sn, 2 g/l Pb, 1 mg/l standard and a reference solder solution (*MBH S63PR10*) were run. The region on either side of the peak was scanned by the simultaneous direct reading polychromator or by the monochromator for the sequential lines. The scans covered a range of 0.05 nm on either side of the emission line.

Table 2 summarizes the investigated spectral wavelengths together with the background equivalent concentration

Table 2. *Spectral Lines Together with Determined BEC and DL* (corresponding to the solid) *in a 4 g/l Soln. 60% Sn-40% Pb*

Element	Line nm	BEC [%]	DL [%]	Interferences
Ag	328.07	0.006	<0.001	
Al	308.21	0.044	0.002	weak OH band
As	189.04	0.026	0.005	weak Sn lines
Au	242.69	0.008	<0.001	Pb 242.86 (resolved)
Bi	223.06	0.012	0.001	Cu 223.01 (resolved)
Cd	226.59	0.004	<0.001	
Cu	324.75	0.006	<0.001	
Fe	259.94	0.009	<0.001	
In	303.94	0.090	0.003	
Ni	231.60	0.020	0.001	Sn: weak Bg shift
Sb	206.83	0.025	0.005	Sn 206.86
Zn	213.86	0.002	<0.001	
		mg/l	mg/l	
Pb	220.35	1.14	0.04	diluted solutions 1:50
Sn	189.99	0.41	0.01	diluted solutions 1:50

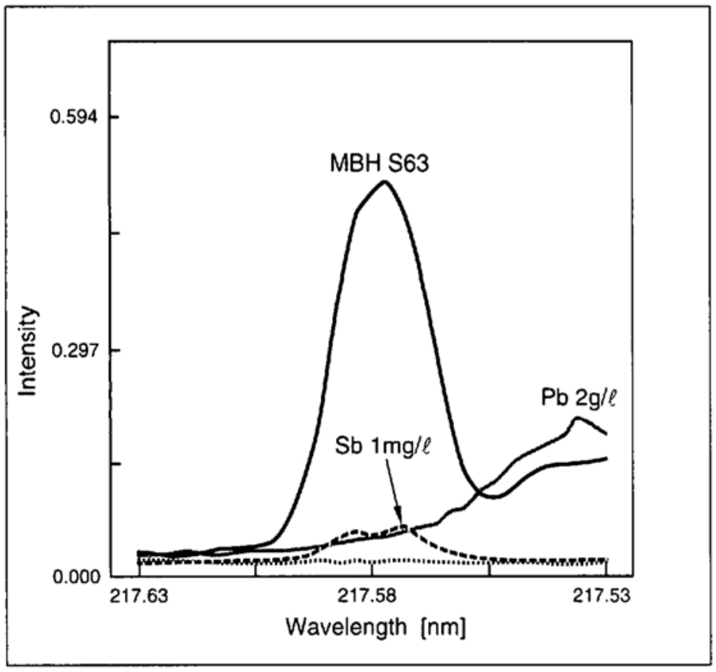

Fig. 1. *Scan around Sb 217.58 nm showing the interference from Pb 217.56 nm*

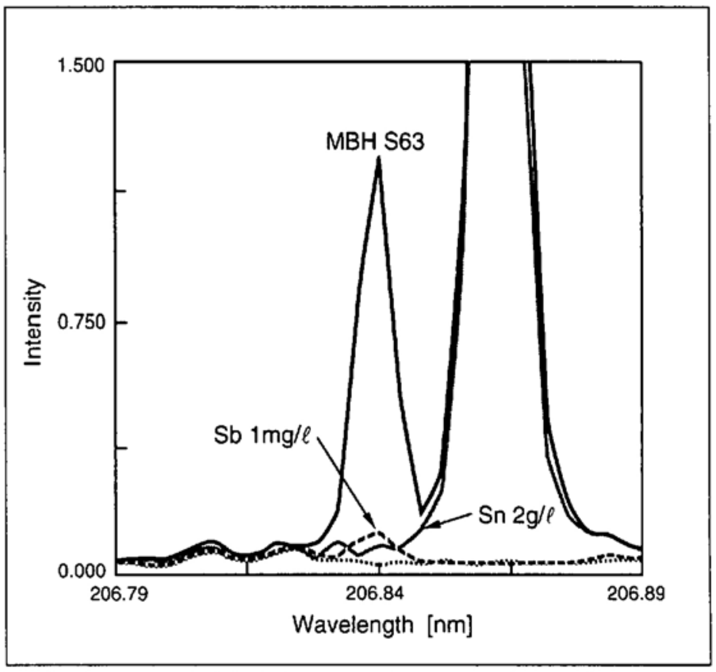

Fig. 2. *Scan around Sb 206.84 nm showing the interference from Sn 206.86 nm*

Table 3. *Analysis of SRM MBH S63PR10 and MBH S63PR3 in wt.-%*

	MBH S63PR10			MBH S63PR3		
Element	Certified		ICP	Certified		ICP
Ag	0.01	±0.00	0.009	0.020	±0.004	0.019
Al	–		0.001	–		<0.001
As	0.007	±0.0006	0.006	0.027	±0.004	0.028
Au	0.046	±0.0137	0.025	0.16	±0.001	0.165
Bi	0.06	±0.002	0.055	0.26	±0.005	0.261
Cd	0.006	±0.000	0.005	0.002	±0.0004	0.002
Cu	0.009	±0.0008	0.008	0.10	±0.001	0.100
Fe	0.003	±0.001	0.001	0.012	±0.0002	0.016
In	–		<0.003	–		0.004
Ni	0.001	±0.000	0.001	0.016	±0.0004	0.016
Sb	0.28	±0.01	0.275	0.29	±0.021	0.285
Zn	<0.001		<0.001	0.015	±0.0008	0.014
Sn	63.0	±0.40	63.0	60.3	±0.22	60.7
Pb	Rest		35.6	Rest		39.4

(BEC) and the detection limits (DL) for those elements which were analyzed for the routine quality control of the solders. The BEC is the concentration of an analyte that will give a signal equal to the background emission at that wavelength. The DL is the concentration of an analyte that will give a signal defined generally as 3 times the standard deviation of the background emission. Empirically the DL is *ca.* 1/30 of the BEC assuming a relative SD of 1%. Precision near the detection limit is ± 50% and the analytical results are semiquantitative. The spectral lines were carefully examined to find the degree of spectral interference. All the elements with the exception of tin and lead were present in concentrations which would not cause interferences. *Figs. 1* and *2* show typical examples of spectral overlap due to very intense adjacent lines of Pb on Sb 217.58 nm and of Sn on Sb 206.84 nm. The corrections have been linear for the investigated concentration range. BEC and DL were evaluated from the calibration performed by use of matrix solutions corresponding to a 60% Sn-40% Pb alloy composition, spiked with 10 mg/l of the elements. For Sn and Pb the BEC and DL are given in mg/l as these elements were determined in the 50 times diluted solutions. It is evident that the sensitivity has been reduced for As and Sb due to spectral overlaps. But even if the chosen lines are not interference-free, they are still more sensitive compared to other investigated spectral lines of As and Sb.

The other wavelength scans detected none of the following elements in the reference solder: B, Ba, Be, Bi, Ca, Co, Cr, K, Li, Mg, Mn, Mo, Na, Nb, P, S, Sc, Si, Sr, Ti, V, W, Zr.

They are in general not required for the quantitative monitoring of trace contaminants in solder baths but their analysis should represent no problem (DL <0.005 wt.%).

4.2. *Precision and Accuracy*

As a general rule analysts are asked to do the analysis with the best possible accuracy, which is often time consuming and expensive. A more realistic approach would be that the results must be accurate enough to fulfil the aim of the investigation without wasting time and money.

The reference solutions used for the trace element calibration of the ICP spectrometer were prepared in two ways:

a) multielement solutions in HCl 1:4 *v*/*v* acid without the addition of Sn and Pb, by applying the spectral interferences correction factors; *b*) multielement solutions with a 4g/l matrix solution 60% Sn-40% Pb in HCl 1:4 *v*/*v* acid.

The analysis of the trace elements in solder samples against both calibrations show no significant difference due to sample transport and sample excitation effects due to the tin-lead matrix (less than 5% relative for all the elements). For routine analysis the first calibration was adopted, as the prepared multielement synthetic solutions with Sn and Pb tend to precipitate.

The short-term precision for all measured elements was less than 1% RSD. The long-term instrumental stability over 2 h was *ca.* 2% RSD.

Two standard reference materials (SRM) purchased from *MBH Analytical Ltd.*, England: S63PR10 and S63PR3 (solder composition 63% Sn-37% Pb), were prepared in triplicate to determine the accuracy of the analysis. The results are presented in *Table 3*. The ICP results agree well with the certified values, with the exception of Au for the first SRM. This difference can be explained when taking into consideration the great deviation on the single analytical values. The reason could be either due to inaccurate gold analysis or inhomogenious gold distribution in the analyzed sample. *Table 4* demonstrates the precision of the analysis for this SRM over a period of one year. The consistent recovery of elements from reference solder materials in multiple replicates was a good test for both the precision and accuracy of the method.

Table 5 summarizes the results for Sn obtained by the ICP and ASTM wet chemistry methods on different tin-lead alloy composition samples. The discrepancy found between both methods for some of the samples, and the sometimes worse precision on the replicates is probably due to concentration gradients in the sample. As a general rule the sum of Sn and Pb concentrations determined by ICP for solder alloys with less than 0.5% impurities was 100 ± 1%.

5. Conclusions

The results reported herein prove that the dissolution of tin-lead solders with a $HCl-HNO_3$ mixture is a satisfactory procedure for the preparation of stable solutions for multielement ICP-AES analysis of the major and trace elements. The reference solutions required for the calibration of the ICP spectrometer are prepared from commercially available element standards. The precision and accuracy of the ICP method are in general better in comparison with the combined CSN-ICP spectrometry and the wet chemistry methods of analysis. The sensitivity is sufficient to enable the detection of the routinely analyzed trace elements at the maximum specification limits. A further advantage is the application of the method for the multielement analysis of small samples compared with other analytical methods.

Table 4. *Element Concentrations in wt.-% on MBH S63PR10 over a 1-Year Period*

	Identification Number				
Element	5292	2393	2693	5193	6193
Ag	0.009	0.009	0.009	0.010	0.010
Al	0.001	<0.001	<0.001	0.001	<0.001
As	0.006	0.006	0.006	0.007	0.006
Au	0.025	0.025	0.025	0.026	0.026
Bi	0.056	0.056	0.058	0.058	0.060
Cd	0.005	0.004	0.005	0.005	0.005
Cu	0.008	0.009	0.008	0.008	0.008
Fe	0.001	0.001	0.002	0.002	0.001
In	<0.003	<0.003	<0.003	<0.003	<0.003
Ni	0.001	0.001	0.001	0.002	0.001
Sb	0.275	0.265	0.270	0.275	0.275
Zn	<0.001	<0.001	<0.001	<0.001	<0.001
Sn	63.0	63.0	62.9	63.4	63.0
Pb	35.9	36.9	36.8	35.9	37.0

Table 5. *Tin Concentration in Solders in wt.-%*

Sample	ICP[a])	Wet chemistry[a])	Certified
MBH S63PR10	63.0 ±0.50	63.5 ±0.57	63.0 ±0.40
MBH S63PD	62.5 ±0.30	63.2 ±0.10	62.4 ±0.20
MBH 63PR1	62.8 ±0.60	62.7 ±0.20	63.0 ±0.14
MBH 63PR2	63.6 ±0.30	63.4 ±0.20	63.5 ±0.22
MBH S63PR3	60.8 ±0.50	59.9 ±0.30	60.3 ±0.22
MBH S40PR3A	42.0 ±0.30	41.8 ±0.20	41.6 ±0.19
MBH S50PR2A	51.1 ±0.40	51.4 ±0.10	50.2
ALPHA SSCA1	59.7 ±0.60	59.4 ±0.20	59.1
ALPHA 63A10	63.0 ±0.30	63.1 ±0.10	63.1
ALPHA 63A11	63.4 ±0.20	62.9 ±0.20	63.4
ALPHA 63A12	63.7 ±0.30	63.0 ±0.20	63.0
Organpipe-1	24.5 ±0.30	25.5 ±0.80	
Organpipe-2	42.8 ±0.25	43.2 ±0.10	
Organpipe-3	67.0 ±0.22	67.0 ±0.10	
Organpipe-4	31.5 ±0.20	32.2 ±0.10	
Organpipe-5	42.1 ±0.35	42.6 ±0.30	
Organpipe-6	76.4 ±0.60	77.9 ±0.60	
5993	63.1 ±0.10	63.2 ±0.20	
6193	62.5 ±0.10	62.8 ±0.10	

[a]) Average and standard deviation for triplicate analysis

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