INVESTIGATION OF ICP-OES ANALYSIS FOR DETERMINATION OF TRACE LEAD IN LEAD-FREE ALLOY

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Abstract:

This work studied the determination of trace Pb in SnAg3.0Cu0.5 (SAC305) lead-free alloy by ICP-OES. Three emission wavelengths, i.e., Pb I 217.000, Pb II 220.353 and Pb I 283.306 nm, ICP-OES viewing mode, and potential matrix elements were investigated in order to establish a strategy for reliable analysis of trace Pb. The results showed that Pb content obtained from Pb I 283.306 nm with axial viewing mode was noticeably higher than that from Pb I 217.00 and Pb II 220.353 nm. The enhancement of Pb I 283.306 signal accounts for 16% and 18% with respected to Pb I 217.000 and Pb II 220.353 nm, respectively. On the other hand, the three wavelengths showed insignificant difference in measured Pb content when radial viewing mode was used. It was most likely that Sn contributes to the enhancement of emission intensity in Pb I 283.306, whereas Ag and Cu have no influence. The results from standard addition indicated that Pb I 217.00 and Pb II 220.353 are suitable for quantification of trace Pb in SAC305 alloy. These two wavelengths offer accuracy of results at an acceptable level regardless of ICP-OES observation mode and calibration method.

Introduction:

SAC305 alloy (contains 96.5% Sn, 3% Ag, and 0.5% Cu) has received much publicity as the lead-free alloy of choice for electronics assembly since the restriction of the use of certain hazardous substances in electronical and electronic equipment (RoHS) Directive 2002/95/EC [1] has become effective. It has replaced traditional SnPb alloys. According to the RoHS Directive, Pb content contained in lead-free alloys is limited to 0.1% by weight or 1000 ppm. Therefore, it is mandatory to ensure alloy manufacturers' compliance with RoHS regulations. In addition, Pb content in SAC305 alloy used in assembly processes must be controlled and monitored regularly due to the fact that the alloy can absorb trace amounts of Pb and other metals from contamination on components during use.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is widely used as routine technique for elemental analysis in a wide scale of alloy types [2–7]. It is due to its multi-element capability, its high sample throughput and its low limits of detection. Although interferences in ICP-OES are less severe than in other spectrometry techniques, such as FAAS or ICP-MS, matrix effects can be observed. Slight differences in matrix composition of each alloy type may cause relatively large variations in the result in terms of accuracy and precision. One may see the importance of an accurate measurement when the value of the analyte lies at the border of the specification limits. Even a small degradation in the reliability of the result can greatly affect costs or revenue from the sale of the assembled products.

There is considerably more literature regarding SAC305 alloy properties than analytical methods to determine its elemental composition. On-line solid phase extraction coupled with hydride generation atomic fluorescence spectrometry and laser induced breakdown spectroscopy were reported for measuring trace Pb in lead-free alloy and solder finished product [8, 9]. However, to the best of our knowledge, there is no report on ICP-OES method for Pb determination in SAC305 alloy in the readily available literature on analytical chemistry so far. Therefore, this work aims to apply ICP-OES for accurate quantification of trace Pb. Interference in ICP-OES and effect of potential alloy matrix elements were investigated. Moreover, a strategy for ICP-OES analysis of Pb at acceptable accuracy was formulated from the results of the investigations.

Methodology:

Reagents: Analytical grade reagents and deionized water were employed to prepare all solutions. Fluoroboric acid solution used for alloy digestion was prepared by mixing 300 mL of HNO_3 (65%), 5.0 g HBO_3, 50 mL of HF (50%) and 650 mL water. Owing to a negligible matrix effect from digestion reagent (data not shown), calibration standard solutions can be prepared by appropriate dilution of Pb, Sn, Ag and Cu standard solutions for ICP-OES (Merck, Darmstadt, Germany) with either digestion reagent or 5% HNO_3.

Instrumentation: Measurements were carried out with inductively coupled plasma-optical emission spectrometer (Optima 5300 DV, Perkin-Elmer, CT, USA). The Optima 5300DV system makes it possible to use either the axial viewing or the radial viewing mode by means of a periscope. A fair comparison between the two observation modes was thus possible. The ICP-OES conditions were shown in Table 1.

Line selection: The spectral lines shown in Table 1 were selected according to spectral line library and required to be sensitive enough to allow reliable measurements of trace Pb in the alloy to be made.

Alloy sample: SAC305 alloy was used in PCB assembly process. It was sampled from a running wave of molten alloy in alloy bath. The molten alloy was filled into a square mold with dimension of 3 x 3 x 2.5 cm. The solidification of the alloy was allowed to be completed before subjecting to sample preparation for ICP-OES analysis.

Alloy dissolution: At least three holes were drilled into alloy sample at points equally spaced between the ends of the piece along a diagonal line. All drillings were collected. 500 mg of the drillings was weighed into a polyethylene beaker together with 2.5 mL of HF and 12.5 mL of Flouroboric acid solution. The sample was allowed to stand until it was completely digested. Thereafter, the clear digest was transferred into a plastic volumetric flask and the volume make up to 50 mL with deionized water.

Standard addition of alloy sample: 2.50 mL of the digest was transferred into a 25-mL polyethylene volumetric flask and 0, 0.5, 1.0, 1.5 and 2.0 mL of stock standard Pb solution (100 mg L^{-1}) was added. Afterwards, the solutions were made to volume with 5% HNO_3.

Table 1. ICP-OES operating conditions

Parameter	Value
RF power (W)	1300
Argon plasma gas flow rate (L min^{-1})	15
Nebulizer gas flow rate (L min^{-1})	0.8
Auxiliary gas flow rate (L min^{-1})	0.2
Sample uptake rate (mL min^{-1})	1.0
Nebulizer	Cross-flow
Emission line (nm)	
Pb I	217.000
Pb II	220.353
Pb I	283.306

Results, Discussion and Conclusion:

Determination of trace Pb in SAC305 alloy: Axially viewed ICP is usually used for determination of elements at trace level. There is a general agreement that a five-to ten-fold improvement in detection power is obtained for axial viewing compared to radial viewing [10]. However, this observation mode has a poor reputation regarding the matrix effects. Therefore, the effect of observation mode on Pb determination in SAC305 alloy matrix measured from Pb I 217.00, Pb II 220.353 and Pb I 283.306 nm was investigated in the present study. As seen in Table 2, Pb I 283.306 nm with axial viewing mode revealed noticeably difference in Pb content from those of two wavelengths. The difference accounts for 16% and 18% with respect to Pb I 217.000 and Pb II 220.353 nm, respectively. As opposed to axial viewing mode, the differences in Pb content among three wavelengths decreased to below 3.5% in radial view. It is clearly seen that the magnitude of interference depends upon the observation mode and wavelength selected.

Table 2. Pb content (wt%) in SAC305 alloy as obtained by using axially and radially viewed ICP-OES

Alloy type	Pb content (wt%)					
	Axial view			Radial view		
	217.000 nm	220.353 nm	283.306 nm	217.000 nm	220.353 nm	283.306 nm
SAC305	0.197 ± 0.003	0.193 ± 0.002	0.231 ± 0.003	0.199 ± 0.002	0.200 ± 0.001	0.206 ± 0.001

Results are expressed as the mean of three replicates ± standard deviation.

Table 3. Determination of Pb content (wt%) in SAC305 alloy by using standard addition method

Alloy type	Pb content (wt%)					
	Axial view			Radial view		
	217.000 nm	220.353 nm	283.306 nm	217.000 nm	220.353 nm	283.306 nm
SAC305	0.206 ± 0.003	0.202 ± 0.004	0.206 ± 0.004	0.202 ± 0.003	0.203 ± 0.003	0.206 ± 0.003

Results are expressed as the mean of three replicates ± standard deviation.

Compensation of matrix interference by standard addition method: For the purpose of overcoming the matrix interference, standard addition was carried out and the results were presented in Table 3. As expected, Pb content obtained from all three emission lines was compatible regardless of viewing mode. The Pb content was found to be in the range of 0.202–0.206 wt%. The results from standard addition and external calibration methods were also comparatively evaluated (see Table 2 and Table 3). Enhancement of Pb signal was observed in Pb I 283.306 nm when external calibration and axial viewing were applied. The Pb content was 12% higher than that obtained by standard addition method. For radial viewing mode, the quantitative results using external calibration were in good agreement with standard addition method for all three Pb emission wavelengths. The results above indicated that Pb I 217.00 nm and Pb II 220.353 nm are suitable wavelengths for measuring trace Pb in SAC305 alloy. These two wavelengths gave results with appreciable accuracy regardless of detection viewing mode and calibration method.

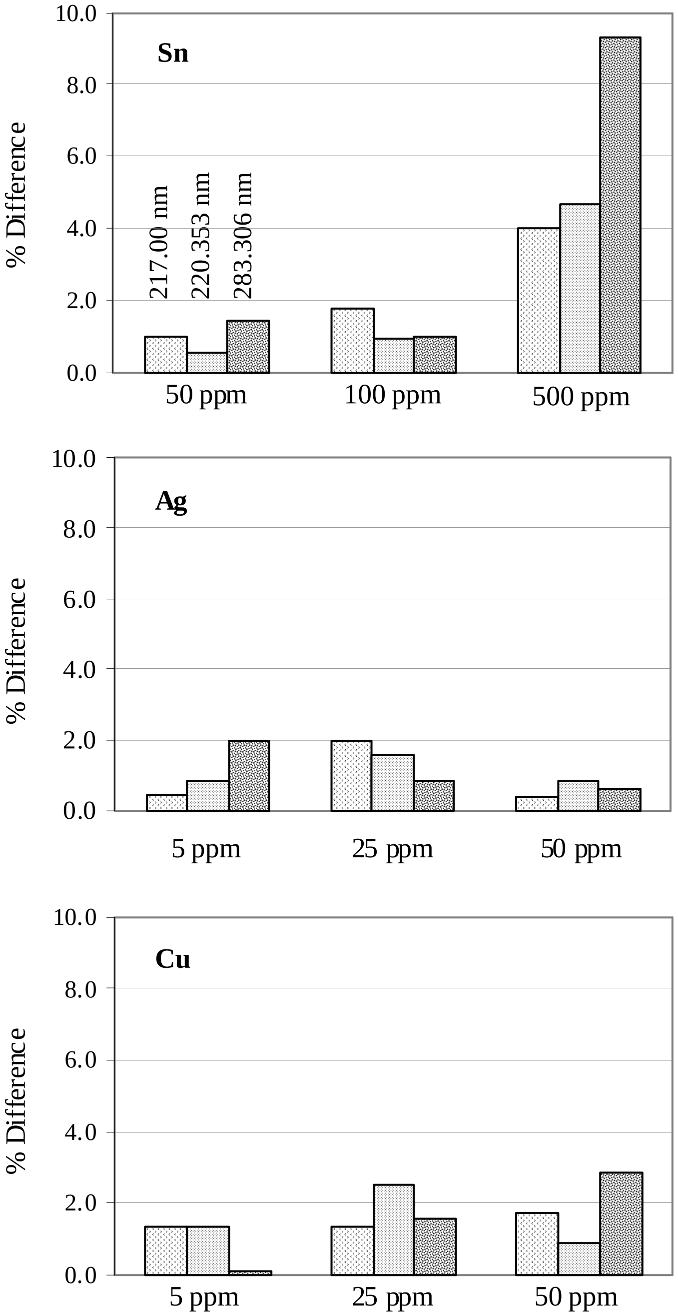

Figure 1. Effect of alloy matrix elements on Pb determination with axially viewed ICP-OES

Effect of alloy matrix elements: Sn, Ag and Cu are major and minor elemental compositions of SAC305 alloy and may have potential to cause matrix interferences. To evaluate the effect of the individual alloy element on the determination of Pb, a digestion reagent containing 10 mg L^{-1} Pb was spiked to contain 0, 50, 100 and 500 mg L^{-1} Sn and 0, 5, 25 and 50 mg L^{-1} Ag or Cu. The experiment was performed only for axially viewed ICP-OES as the fact that no interference was observed for radial observation mode. The change in Pb concentration from the nominal concentration affected by each matrix element at each wavelength was converted to percentage and shown in Figure 1. In the presence of Ag or Cu, three wavelengths showed insignificant differences in Pb concentration. The variations of Pb concentration among the three wavelengths were less than 3%. Conversely, the results showed the tendency of enhancement of Pb signal with increasing Sn concentration. This effect was pronounced at Pb I 283.306 nm. The percent difference of Pb was below 2% when 50 and 100 mg L^{-1} Sn were added but increased to almost 10% with 500 mg L^{-1} Sn. The enhancement effect induced by Sn may be attributed to the change in the efficiency of aerosol generation and transport, and the shift in the plasma equilibrium [11].

In conclusion, the results from this study suggest that the interference can be avoided or minimized by careful selection of emission lines. By using Pb I 217.00 nm or Pb II 220.353 nm, the quantification of Pb can be performed using external calibration method with any viewing configuration. This can avoid the time-consuming and labor-intensive standard addition and simplify laboratory work.

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Acknowledgements:
The authors are indebted to Dr. Martin Reinhard Hühne for helpful discussion and for correction of the manuscript.

Keywords: lead-free alloy, interference effect, alloy matrix elements, axial viewing, radial viewing