

Determination of Lead (Pb) Concentration Level in Solder Finished Product Using Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract

In February, 2003, the European Union adopted the RoHS Directive 2002/95/EC (Restriction on Hazardous Substances). The directive sets limits on the concentration of six environmentally toxic substances in various electronic products and electrical equipment. These six substances include Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium (Cr+6), Polybrominated biphenyls (PBB) and Polybrominated diphenyl ether (PBDE). One of the RoHS regulated substances, Lead (Pb), is linked to nerve, blood and brain disorders in humans, especially in young children. Currently, the RoHS concentration limit for Pb stands at 1000 ppm[1]. Since some manufacturers are producing products with and without lead at a single manufacturing facility, it stands to reason that a fast, sensitive, in-line analytical technique is necessary to monitor lead concentration levels. Such a technique would ensure compliance with ROHS regulations for solder finished products, while also checking the consistency of the manufacturing process.

This paper introduces an innovative, alternative method of monitoring the Lead (Pb) concentration levels in solder finished products based on Laser Induced Breakdown Spectroscopy (LIBS). An extensive experimental investigation has been performed to compare the LIBS analytical results with other analytical techniques that are available for Pb concentration analysis, namely ICP-OES, AAS, EDXRF, micro-EDXRF and LA-ICP-MS.

While providing accuracy and performance comparable to ICP-OES (the currently accepted industry standard) LIBS provides additional advantages such as rapid analysis and the elimination of complex sample preparation involving acid dissolution.

Introduction

Lead (Pb) is an element often present in the solder finished products at Spansion. Due to the global adoption of RoHS directives, the Spansion customers require in-house verification of RoHS compliance for final packaged products. Consequently, it would be of great benefit to implement a screening method capable of rapid and accurate analysis of Pb in solder finished products.

Typically, there are three types of solder finished products produced: Matte Tin (Sn100%), Tin Bismuth (SnBi) and Tin Lead (SnPb). The ideal technique should identify a possible mixing of SnPb with lead-free products. More importantly, this technique could also be used to ensure that Pb concentrations in monitored products do not exceed 1000 ppm, thus effectively screening the products for satisfying RoHS compliance.

There are two possible reasons for elevated Pb levels in solder finished products. The first reason may be a plating anode ball that is not 100% pure tin and may contain excessive Pb. The second reason may be the cross-

contamination from process equipment that handled SnPb products prior to lead-free products. Due to a lack of standard analytical methods for Pb analysis, various analytical techniques are used to confirm RoHS compliance. These analytical techniques offer different levels of detection sensitivity, measurement precision and analytical throughput. They also require different sample preparation processes. Furthermore, logistical factors such as the number of samples to be monitored, the environment in which the analysis needs to be performed, and the availability of highly trained scientists/operators may influence the decision to choose one analytical technique over the other.

The commonly used analytical methods for measuring Pb in lead-free solder finished products include ICP-OES (or AES) (Inductively Coupled Plasma – Optical or Atomic Emission Spectroscopy), AAS (Atomic Absorption Spectroscopy), LA-ICP-MS (Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry), and XRF (X-ray Fluorescence) based techniques such as EDXRF, and micro-EDX.

ICP-OES is accepted as a standard industry method for final RoHS compliance verification. However, ICP-OES requires a complex and time-consuming acid dissolution of solid samples prior to the actual analysis steps. This makes the technique unsuitable for rapid Pb monitoring of a large volume of samples for manufacturing quality control.

XRF-based techniques have gained popularity in recent years for monitoring Pb in final products due to its ability to perform the analysis with minimal sample preparation and no physical damage to the final products. Although convenient, XRF-based techniques face challenges in providing accurate and precise concentration analysis for thin and small samples (as in tin solder plating for leadframe packages). Consequently, the XRF-based techniques have been used for screening of RoHS elements rather than final determination of the elemental content.

This paper presents the comparative studies involving six different methodologies to measure Lead (Pb) content in solder platings. The study focused on pure Tin plating (Sn100%) products on Thin Small Outline Package (TSOP) package. As a part of the comparative study, Spansion has also evaluated LIBS (Laser Induced Breakdown Spectroscopy), an analytical technique based on the emission spectroscopy of the plasma generated from laser ablation. LIBS has been determined to be a rapid, accurate, and cost effective solution for Pb monitoring of tin plating products. It eliminates complex sample preparation procedures and the toxic waste generated during acid dissolution steps of other techniques.

Laser Induced Breakdown Spectroscopy (LIBS) and LIBS instrument calibration for quantitative Pb analysis

LIBS is an elemental analysis technique in which emitted light from a microplasma generated by laser ablation is

analyzed for both qualitative and quantitative elemental analysis. Laser Ablation (LA) is a term used for describing mass removal from the sample using a focused laser beam. Figure 1 illustrates a typical LIBS measurement scheme. A short pulse laser beam from an Nd:YAG solid state laser (~ a few nanoseconds) is focused on a sample surface using optical mirrors and lenses. When a focused laser beam is irradiated on the sample surface, it triggers a series of physical processes that lead to formation of energetic, transient plasma.

The plasma emission is composed of atomic and ionic lines that are characteristics of the sample's chemical composition. The plasma light is collected by a set of optical lenses and is further coupled to the LIBS system detector module, comprised of a spectrometer and an ICCD/CCD camera. The detector module allows clear separation and identification of LIBS emission peaks. For quantitative analysis, LIBS peak intensity (either absolute or normalized) can be recorded and compared against the pre-defined calibration curve to estimate the concentration of different elements in the sample.

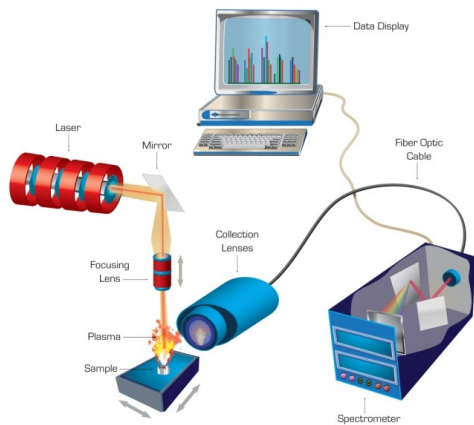


Figure 1: Schematic diagram of LIBS measurement

The pre-defined calibration curve is generated by recording the LIBS intensity of Pb emission lines at 405.7 nm for four different CRMs (Certified Reference Materials) with known Pb concentrations. The CRMs were obtained from NIST and MBH Analytical Ltd. The CRM's Pb concentration values are verified by a third party laboratory with greater than 95% confidence based on ICP-MS analysis. The certified Pb concentration values for the four selected CRMs were 36 ppm, 146 ppm, 403 ppm, and 960 ppm. Non-contaminated, RoHS compliant Spansion Tin plating products contain Pb content between 50 to 100 ppm. Establishing the calibration curve using CRMs with concentration values ranging from low 10's of ppm to 1000 ppm allows LIBS to accurately monitor Pb content variation in the tin plating products and thus detect occurrences of RoHS non-compliance.

Figure 2 shows the typical calibration curve generated based on four CRMs. As seen from the figure, LIBS intensity of 405.7 nm Pb emission line with respect to different concentration values can be described by a simple linear relationship.

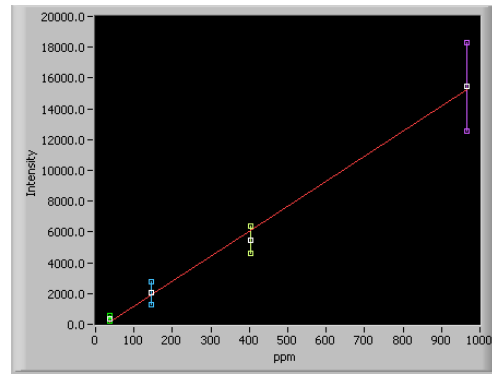


Figure 2: Representative LIBS Calibration curve using four selected CRM's for quantitative Pb analysis in Tin solder finished products

Experimental Study

Six different analytical techniques were used to evaluate the lead content in Sn plating used for TSOP packages. The samples were prepared in three groups: 1) pure tin plating that were deposited on the stainless steel plate at three different current densities, 2) pure tin plated TSOP56 leadframe packages at three different current densities, and 3) pure tin plated TSOP56 leadframe packages that were handled by process equipment that handled SnPb products without any tool cleaning. Prepared samples were submitted to an external third party laboratory for ICP-OES, AA, EDXRF, micro-EDXRF, and LA-ICP-MS analysis. For LIBS analysis, the samples were submitted to a LIBS instrument manufacturer, Applied Spectra, Inc., in Fremont, CA, USA.

A. Description of Analytical Methodologies and Instruments

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

ICP-OES is currently considered the “gold standard” method to confirm RoHS compliance for many electronic components. This method offers ppm level sensitivity for many elements in the periodic table and the method is certified for measuring elemental content in a wide range of sample matrices by international standard organizations such as ASTM (American Society for Testing and Materials).

In ICP-OES analysis of solid samples, the samples are first dissolved in an acid solution; the entire solid samples are digested in the acid solution. The solution is then introduced in the form of fine aerosols into the plasma torch by the instrument nebulizer. The aerosols are ionized in the plasma torch, leading to emission of distinct atomic and ionic lines characteristic of the chemical composition of the samples. Accurate and precise quantitative analysis of elements is achieved by recording the intensity of emission lines and extrapolating the intensity value into the actual concentration using the calibration curve.

ICP-OES typically requires a skilled scientist to operate the instrument and analyze the data. ICP-OES instruments also require an elaborate lab facility to handle acid solutions, to exhaust the toxic fumes generated during the acid dissolution and treatment processes, and to dispose of the chemical waste generated during sample preparation steps. For sensitive ICP-OES analysis, usually a few grams of sample mass is ideal and for TSOP56 package analysis, tin plating

was scraped off from many packages before being digested in the acid solution.

Atomic Absorption Spectroscopy (AAS)

The second technique evaluated in the current study is AAS (Atomic Absorption Spectroscopy). With detection limits approaching ppm level for many elements in the periodic table, AAS has been considered as an alternate elemental technique for RoHS compliance of electronic components. In AAS, the sample is introduced into flame or inductively coupled plasma in the form of fine aerosols using an instrument nebulizer. The light source is then directed to the flame or the plasma. By correlating the amount of light intensity absorbed at a specific wavelength (unique to different elements) to the actual concentration of elements, accurate and precise quantification of elements present in the sample can be performed. As is the case of ICP-OES, solid samples first need to be dissolved completely in a suitable solution before being injecting into a flame or plasma source for analysis.

Energy Dispersive X Ray Fluorescence (EDXRF)

Other techniques considered in the comparative study include XRF-based techniques, namely EDXRF (Energy Dispersive X-Ray Fluorescence) and micro-EDXRF. In XRF-based techniques, the X-rays emitted from the X-ray tube or radioisotope are irradiated on the sample surface, causing tightly held inner core electrons (K, L, and M shells) to be expelled from an atom. Electrons in the higher orbital fall back to the lower orbital to fill the void left behind. The energy transition of electrons from the higher orbital to the lower orbital results in the release of characteristic X-rays, which are unique to different elements.

Quantitative analysis based on XRF techniques is performed by correlating the intensity of the characteristic X-rays associated with a specific element to those measured from solid standards of known concentrations. Alternatively, XRF instruments may offer an internal calibration database and with additional information about the sample such as the number of material layers, composition, geometry, etc, a theoretical model can be used to estimate the concentration of different elements in the sample.

Laser Ablation- Inductive Coupled Plasma –Mass Spectrometry (LA-ICP-MS)

In LA-ICP-MS, a laser beam is focused on the sample surface to remove a tiny portion of sample mass in the form of fine particles (clusters of nano-particles). These tiny particles are transported into the ICP torch of a mass spectrometer instrument by the appropriate carrier gas (typically Argon or Helium). The plasma in the ICP torch digests transported particles and ionizes them. For the analysis involving quadrupole ICP-MS, ions with specific m/z (mass to charge ratio) are able to reach the detector and by sweeping m/z value rapidly, a multi-elemental analysis is possible. Detector signal intensity is proportional to the elemental concentration. For an accurate quantitative analysis, standard reference materials with known amounts of analytes are used to generate the calibration curve. LA-ICP-MS typically provides detection sensitivity that is several orders of magnitude greater than the plasma emission based spectroscopic technique such as ICP-OES (or ICP-AES). Furthermore, LA-ICP-MS eliminates the need for the sample preparation and allows direct solid sampling.

Laser Induced Breakdown Spectroscopy (LIBS)

LIBS is similar to ICP-OES analysis in that both techniques are based on plasma emission spectroscopy. However, for LIBS, the plasma is generated by laser ablation while for ICP-OES, it is generated by radio frequency (RF) generator. As in LA-ICP-MS, LIBS is a direct solid sampling technique using laser ablation; LIBS does not require any sample preparation.

For LIBS analysis, the laser beam spot size on the sample surface can be varied from a few micrometers to several hundred micrometers. Another measurement variable is the number of laser shots per sampling area; both single shot and multiple shot analysis is possible, with the laser shot repetition rate from 1 Hz to 30 Hz.

The LIBS measurement protocol was optimized for bulk analysis of tin plating of the leadframe packages. Typical tin plating thickness on the individual lead is 13 ~ 15 microns. The optimum laser energy was selected to first maximize the Pb LIBS intensity to the noise and the background signal. At the optimized laser energy, each laser pulse ablated 3 microns of tin plating. A total of three laser pulses were applied per lead to ablate as much tin plating as possible (without ablating the copper substrate underneath) and to accumulate the LIBS signal to increase the measurement sensitivity. The laser spot size was 120 microns to cover the whole width of the lead. Finally, the LIBS signal was further averaged over multiple leads with lead number ranging from 2 to 20.

For LIBS sampling of individual leads, the laser ablation was done at the bottom side. The bottom side of the package comes into physical contact with punching dies during the End-of-Line processes. The final test process may also contribute to Lead (Pb) contamination due the contacts between sockets and package external leads. The optical microscope image of a lead before and after laser ablation is shown in Figures 3(a) and 3(b).

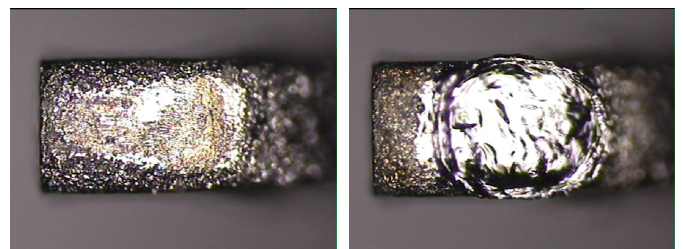


Figure 3(a): Bottom side of the plated lead before laser ablation, Figure 3(b): Bottom side of the plated lead after laser ablation

B. Description of samples used in the comparative study

Three different groups of samples were prepared for the analytical method comparative study. The first group was a pure Tin (Sn) plated TSOP56 leadframe package. Three different plating current conditions were used during the tin plating step to produce samples with different levels of Pb content (see Table 1). Another batch acted as a control lot with no tin plating deposited on the leads (just bare copper leadframe). The leadframes from each group were sent to third party laboratories for ICP-OES, AAS, EDXRF and micro-EDXRF, LA-ICP-MS and LIBS testing.

Table 1: Summary of TSOP56 packages prepared with three different levels of Pb content of Sn plating

No	Lead Level	Plating Current	Total Quantity
1	Low	Tin Plating at 50ASF	28 Strips
2	Regular	Tin Plating at 140ASF	28 Strips
3	High	Tin Plating at 200ASF	28 Strips
4	Copper bare frame	No Tin Plating	28 Strips

The second group of samples were a simulated pure Tin (Sn) plating deposited on a stainless steel thin plate at the same current conditions as in the first group. The purpose of analyzing thicker Tin plating is two-fold. First, analytical techniques requiring acid dissolution of solid samples such as ICP-OES, ICP-MS, and AAS require at least a few grams of sample mass for sensitive analysis; therefore, the mass of thin Sn plating accumulated from a few leadframe packages may not be sufficient. Secondly, for EDXRF or micro-EDXRF, a small quantity of mass (i.e thin films) result in weak X-ray fluorescence signals, causing lengthy measurement times and sometimes lower precision. Furthermore, for a stack of thin films, the fluorescence signal originating from the substrate underneath could interfere with the signal coming from the film of interest. To investigate these concerns, thicker Sn platings were deposited on the steel plate and submitted to the third party analytical labs. The plated films were scraped off from the substrate and about 5 grams of the plating material alone was used for ICP-OES, EDXRF, micro-EDXRF, and LA-ICP-MS analysis.

The third group of samples consists of the dummy tin plated TSOP56 leadframe packages just after the plating and final test process. Just before the final test of dummy samples, the SnPb plated products were tested and there was no subsequent tool cleaning. The motivation for studying these samples is to understand the potential contribution of Pb contamination during the final test process and to assess detection sensitivity of different analytical techniques to analyze the Pb contamination. The dummy leadframe packages were sampled from different final test lots and submitted for ICP-OES, EDXRF, LA-ICP-MS, and LIBS analysis for correlation study.

C. Results and Discussion

Group 1: TSOP56 packages after plating process with different current density conditions

Figure 4 presents the summary of Pb concentration results among AAS, ICP-OES, LA-ICP-MS and LIBS. These results show a close agreement of Pb content among ICP-OES, LA-ICP-MS and LIBS. The graph shows that Pb content was close for tin plating produced at medium and high current density, while it was lower for tin plating produced at the lowest current setting. It is noted that the greater the plating current density, the higher the expected value for the Pb content. For micro-EDXRF measurement, Pb was not detected for all three levels of current settings. μ -EDX instruments had a limited detection of 200 ppm. EDXRF also was not able to provide Pb concentration values; the EDXRF instrument (with 5 mm collimator) used for the measurement had a measurement detection limit of \sim 50 ppm.

ICP-OES did not detect any Pb in the Sn plating at the lowest current setting. The detection limit with ICP-OES

instrument for Pb is \sim 2 ppm. On the other hand, during sample preparation processes, especially during acid purification steps, analyte loss does occur. For the samples with lower analyte concentration, the analyte loss during sample preparation and solution handling can hamper sensitive analysis. This may have been the case for the Sn plating produced at the lowest current setting. AAS yielded lower Pb concentration for the samples produced at all three current settings compared to other techniques. Also AAS detected about 12 ppm of Pb in bare Cu substrates while other techniques did not detect the presence of Pb. This difference may have been due to potential contamination of samples or prepared solutions.

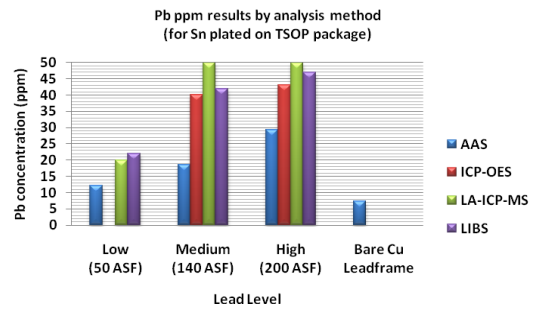


Figure 4: Pb concentration comparison between AAS, ICP-OES, LA-ICP-MS, and LIBS for Sn plated TSOP56 leadframe packages at different current settings.

Group 2: Simulated pure Tin (Sn) plating deposited on a stainless steel thin plate

Figure 5 summarizes the Pb concentration results for simulated pure Sn plating deposited on stainless steel plate. For \sim 15 micron Tin plating, both EDXRF and μ -EDX did not provide sufficient instrument sensitivity to measure Pb. 25 grams of scraped off tin plating from the stainless steel plate was collected and sent to the same third party analytical labs for ICP-OES, AAS, EDXRF, μ -EDX, and LA-ICP-MS analysis. The graph shows that even for the thicker Sn film, both EDXRF and μ -EDX instruments used by the third party testing lab lacked the detection sensitivity to measure Pb. XRF-based instruments offer a wide range of hardware options including a size of collimator, X-ray source, solid state detectors, etc. Commonly available handheld XRF and lower cost standalone EDXRF and μ -EDX instruments may not offer the necessary detection sensitivity for measuring trace elements in the thin films.

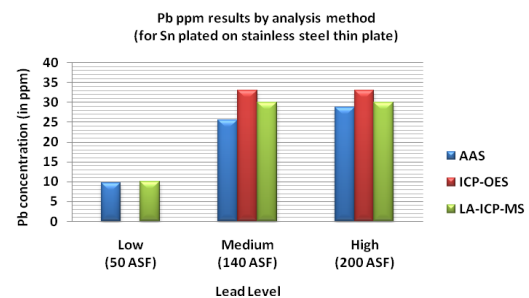


Figure 5: Pb concentration comparison between AAS, ICP-OES, LA-ICP-MS for simulated Sn plated films at different current settings

However, the Pb results among AAS, ICP-OES, and LA-ICP-MS show a good agreement among the three techniques. As in the case of the Sn plating on TSOP56 leadframe package, there was little difference in Pb concentration between the two films produced at the medium and the high current setting. Furthermore, ICP-OES did not report Pb presence for the simulated Sn plating deposited with the lowest current setting.

Group 3: Correlation of different analytical techniques evaluated for Pb monitoring at different leadframe manufacturing steps

For the third group, different analytical techniques were evaluated for suitability for Pb monitoring in various package manufacturing processes. The TSOP56 leadframe packages were sampled just after the Sn plating process from different production lots.

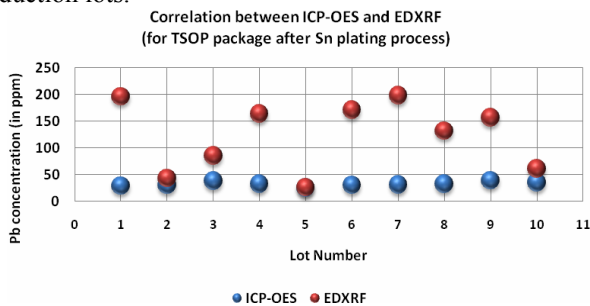


Figure 6: Pb concentration correlation between EDXRF and ICP-OES for TSOP56 leadframe packages just after Sn plating process from different production lot

μ -EDX was not able to detect the presence of Pb. Figure 6 shows the comparison between EDXRF results with ICP-OES. In general, EDXRF data did not correlate well with ICP-OES results. While ICP-OES data shows a tight concentration range of Pb from the minimum value of 25 ppm to the maximum value of 39 ppm among 10 production lots tested, EDXRF data showed the Pb concentration ranging from 26 ppm to 198 ppm. In terms of measurement accuracy, the EDXRF Pb concentration value was greater than the ICP-OES result by a factor close to 600% for some production lots. Finally, the precision of EDXRF data was sometimes greater than 3σ . In general, it was difficult to establish a good data correlation between ICP-OES and EDXRF due to the insufficient detection limit and poor precision of the EDXRF data.

Figure 7 shows the Pb concentration results from ICP-OES, LA-ICP-MS, and LIBS for the TSOP56 packages just after the final test. During the final test, individual leads may come into physical contact with the process instruments that have handled SnPb plated products. Consequently, elevated Pb concentration may arise from the Pb contamination from the process equipments during the final test. Due to insufficient detection sensitivity and poor precision, EDXRF and μ -EDX were not included as a part of this correlation study.

For ten production lots tested after the final test, the Pb concentration by ICP-OES ranged from 31 to 68 ppm, which was a higher range compared to that for the leadframe packages just after Sn plating (25 ~ 39 ppm). Although the lot to lot Pb concentration trend of LA-ICP-MS and LIBS followed closely with that of ICP-OES, the actual

concentration values were highest for LIBS, followed by LA-ICP-MS. For lot # 28, LIBS also yielded substantially higher values than ICP-OES: 126 ppm versus 42 ppm.

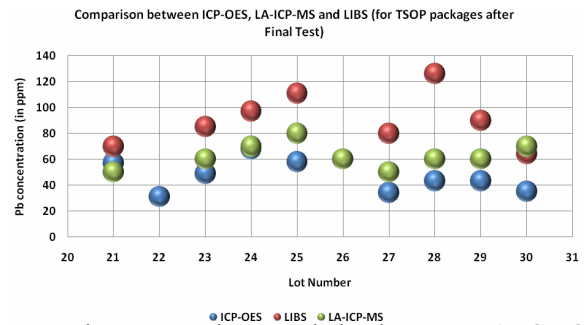


Figure 7: Pb concentration correlation between LA-ICP-OES, LIBS and ICP-OES for TSOP56 leadframe package after the final test.

The possible explanation for higher Pb concentration values for laser ablation-based techniques such as LA-ICP-MS and LIBS compared ICP-OES could be in-homogeneous distribution of the Pb contamination on the leadframe package leads. The Pb contamination resulting from the process equipment parts contacting the leads may occur primarily on the surface at localized areas of the leads. For ICP-OES, the entire plating from all the leads is dissolved and the reported value is the average of the Pb content from the thin Sn plating and localized Pb contaminations from the final test process equipment. For LA-ICP-MS and LIBS, insufficient sampling sites and laser pulses may cause preferential sampling of mass from the locally contaminated regions near the lead surface. This, in turn, could lead to higher Pb concentration values. Proper sampling protocol development that truly represents the bulk analysis of the entire plated film may improve the consistency of concentration data between ICP-OES, LA-ICP-MS, and LIBS.

Three month's data correlation between LIBS and ICP-OES

Due to its rapid analysis – as short as a few seconds per sampling spot – and its elimination of sample preparation, a LIBS instrument has been installed at the manufacturing site at Spansion to monitor Pb concentration on the soldered finished product and investigate Pb contamination from the process equipment at various manufacturing steps.

Figure 8 shows the Pb concentration correlation between ICP-OES and LIBS during the first three months of the LIBS system installation. The samples analyzed for this correlation study were TSOP56 leadframe packages just after the Sn plating process.

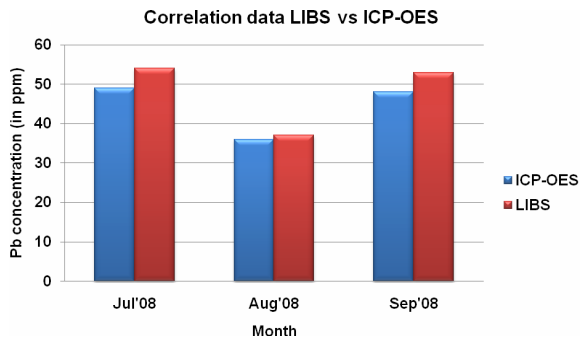


Figure 8: Pb concentration correlation between ICP-OES and LIBS just after Sn plating process for TSOP56 leadframe package

For ICP-OES analysis, 30 leadframe samples were collected from one production lot and sent to the third party testing lab for the analysis. All the leads from 30 units were detached and the Sn plating from the leads was dissolved as a part of the sample preparation process for ICP-OES analysis. For LIBS analysis, 30 additional leadframe samples from the same production lot were analyzed by the installed LIBS instrument. For each leadframe package, three laser pulses were applied per lead and the LIBS intensity for Pb was averaged over 20 leads. For comparison with ICP-OES, Pb concentration estimated for each leadframe package was averaged over 30 units. Figure 8 shows an excellent agreement on the Pb concentration values determined by ICP-OES and LIBS.

Conclusions

The comparative study has been performed to evaluate AAS, ICP-OES, EDXRF, μ -EDX, LA-ICP-MS, and LIBS for monitoring Pb content in TSOP56 leadframe packages. It was determined that XRF-based techniques may not provide sufficient detection limits and precision performance necessary to accurately determine and monitor the Pb content for the leadframe package products with typical product Pb concentration, ranging from single digit ppm levels to above 1000 ppm for RoHS non-compliant products. AAS and ICP-OES are well-accepted techniques within the electronics industry but due to extensive sample preparation that requires acid dissolution and treatment, they are unfit as a fast, on-line monitoring technique. LA-ICP-MS provides a great sensitivity performance but is costly to implement and requires a scientist to calibrate the instrument and analyze the data. It has been demonstrated that under the right sampling protocol development, LIBS can provide Pb analysis results that correlate well with ICP-OES methods. In addition, LIBS provides the fast measurement time and an ability to monitor the Pb content at various leadframe manufacturing steps. Because LIBS requires no sample preparation LIBS can be a viable alternative elemental technique for RoHS compliance monitoring without generating toxic chemical waste.

References

- [1] European Commission, "Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment". Official Journal of the European Union, February, 2003.