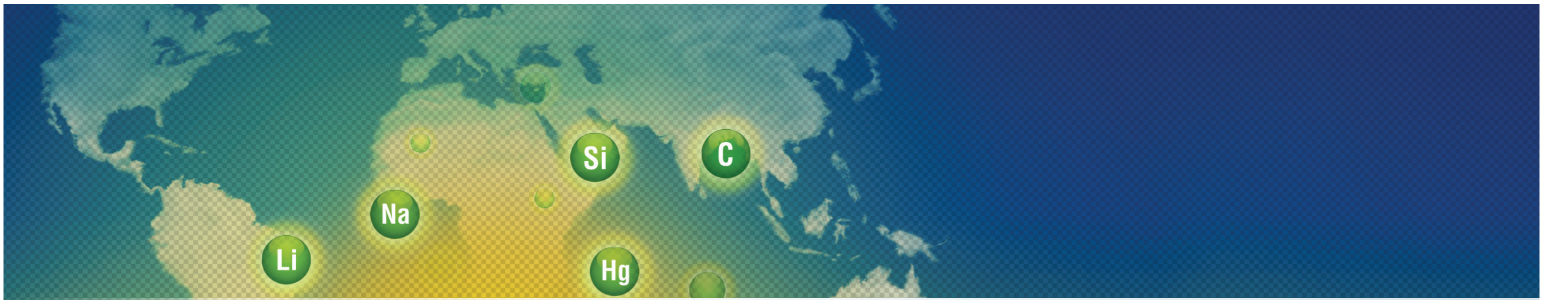

Analysis of Contaminated Plant Leaves Using J200 Tandem LA-LIBS Instrument

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Introduction

Plants have the ability to extract elements from their environment (soil, water, air); the distribution of essential elements and/or toxic elements in plants provides critical information on metal uptake and accumulation. Detailed spatial analysis (2D and 3D) of these elements within the plant structure (root, stem, leaf, and/or flower) can be used to determine available nutrient content, potential health effects from essential and toxic elements, and even environmental conditions like climate change and pollution.

The J200 Tandem LA-LIBS Instrument from Applied Spectra, Inc. provides the unique ability to measure all the elements in a plant throughout its entire structure by combining the analytical benefits of LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry) and LIBS (Laser Induced Breakdown Spectroscopy). LIBS is used for the analyses of major elements and non-metals (such as H, N, O, and halogens). When coupled with an ICP-MS, the J200 Tandem LA-LIBS Instrument simultaneously measures trace elemental and isotopic ratio compositions. This instrument with an ICP-MS expands the elemental coverage and the dynamic range of analysis from sub-ppb levels to % levels, and measures every element on the periodic chart in one instrument.

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Using Applied Spectra's J200 Tandem LA-LIBS Instrument, in combination with our powerful data analysis software, makes acquiring elemental maps seamless. The ability to perform analyses and generate detailed elemental maps is demonstrated in this report for understanding elemental uptake and accumulation in plant leaves.

Operating Parameters

Applied Spectra Inc.'s J200 Tandem LA-LIBS Instrument

- 266 nm Nd:YAG laser (ns) and a broadband CCD detector
- Applied Spectra Axiom Software
- Flex™ sample chamber with helium or argon gas flow
- Sample: Plant leaf exposed to a Pb or As solution
- LIBS & LA-ICP-MS data analyzed and converted into images using Applied Spectra's Data Analysis Software

Analytik Jena Plasma Quant MS Elite

- Time resolved "high sensitivity mode" detection
- Peak hopping mode: $^{39}K^{+}$, $^{63}Cu^{+}$, $^{75}As^{+}$, $^{88}Sr^{+}$, and $^{208}Pb^{+}$
- Synchronized communication triggering with J200 Tandem LA-LIBS Instrument

The laser beam samples individual locations on the plant leaf for analysis using LIBS and ICP-MS simultaneously. Helium was used as the purge gas in the sample chamber.

Sample Analysis

The J200 Tandem LA – LIBS Instrument in combination with the Analytik Jena Plasma Quant Elite ICP-MS was used to analyze contaminated plant leaf samples. Figure 1 is a photograph showing the anatomy of the leaf. The petiole of this leaf was exposed to a solution that contained 500 ppm of Pb or As; the amount of exposure time was varied from 0 to 24 h. The leaf was analyzed using a 150 μm laser spot size (spatial resolution). Smaller or larger spot sizes are available depending on the spatial resolution required by the user. All leaves used in this study were from the same plant, with size of the leaves kept as constant as possible.

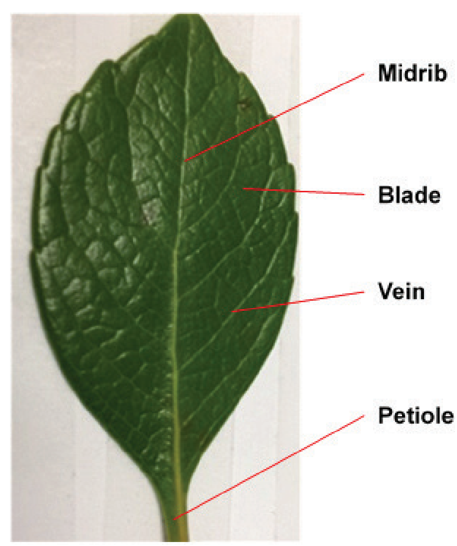

Figure 1. Anatomy of a typical leaf.

$^{39}K^{+}$, $^{63}Cu^{+}$, $^{88}Sr^{+}$, and $^{75}As^{+}$ or $^{208}Pb^{+}$ were chosen as the elements to monitor using LA-ICP-MS. K, Cu, and Sr are naturally occurring elements, while As and Pb were monitored to determine the extent of contamination in each leaf. Figure 2 displays optical photographs (top) of the control leaf, 3 h Pb exposure leaf, and 12 h Pb exposure leaf prior to analysis. Looking at the chemical image maps below each photograph, the control leaf showed no natural Pb accumulation; however, the leaves that were exposed to the Pb solution showed significant uptake of Pb. The Pb solution was taken up by the leaf based on capillary action, and was mainly detected in the petiole, midrib, and vein regions. It could be expected that Pb would travel via cation pathways (possibly mimicking Ca^{2+}) and these results show that the naturally occurring elements K, Cu, and Sr were displaced during the uptake of the Pb.

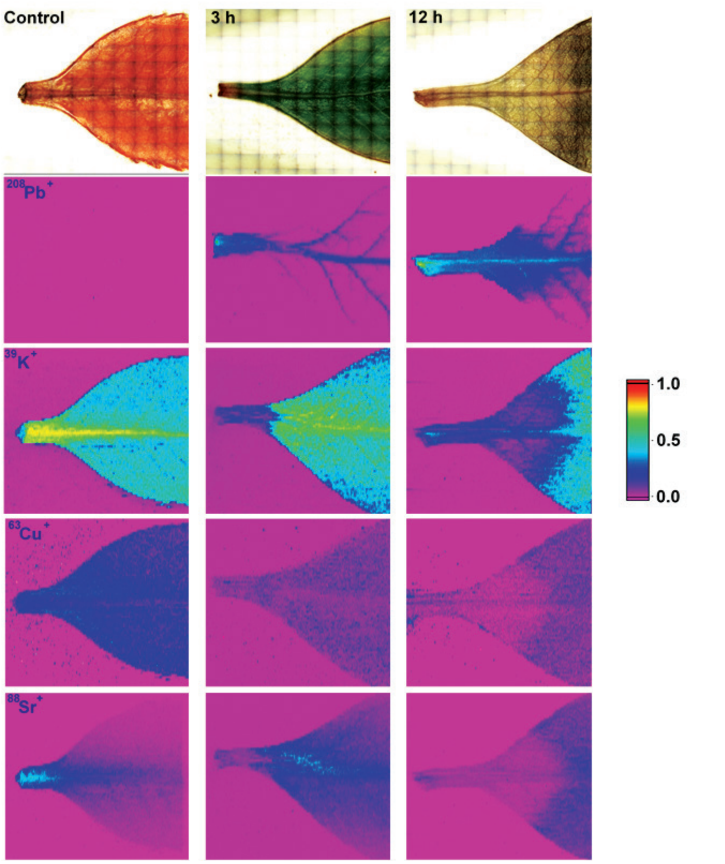

Figure 2. Photographs for the control, 3 h Pb exposure, & 12 h Pb exposure leaves. LA-ICP-MS elemental maps for Pb, K, Cu, and Sr isotopes obtained using an ICP-MS combined with ASI's J200 Tandem instrument.

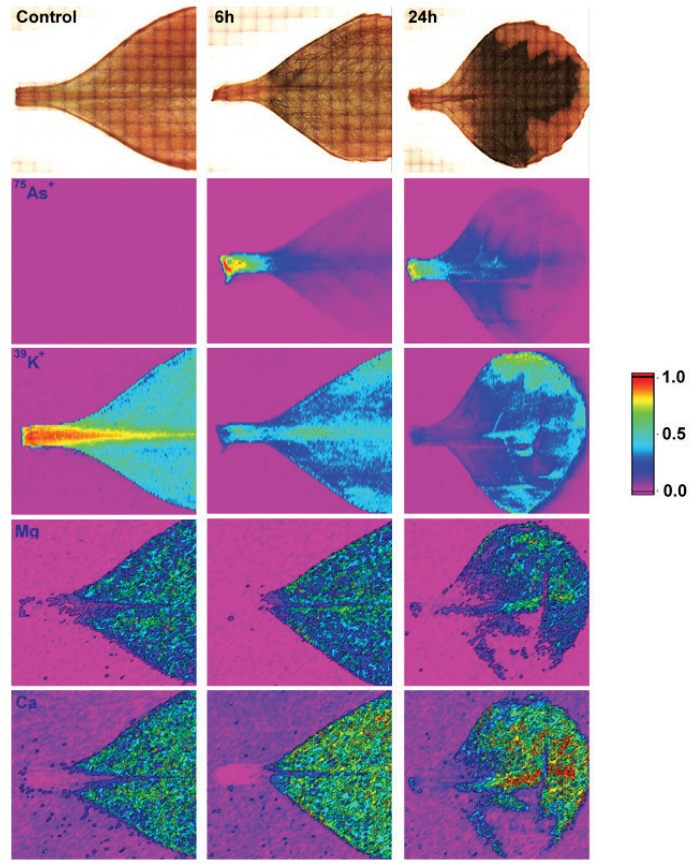

Figure 3. Photographs for the control, 6 h As exposure, & 24 h As exposure leaves. LA-ICP-MS elemental maps for As and K. LIBS elemental maps for Mg and Ca.

The second experiment was an exposure of the plant leaves to As solution for varying time periods (up to 24 h). Figure 3 displays photographs and elemental image maps for the control, 6 h exposure, and 24 h exposure leaves. The control leaf showed no natural abundance of As or prior exposure to As based on the elemental images in Fig. 3.

The leaves that were exposed (6 h and 24 h) to As had contamination detected throughout the leaf structure. Arsenic travels in an unpredictable pathway as compared to the Pb. Uptake throughout the leaf suggests that arsenate [As(V)] follows the phosphate channel pathways. There was significant displacement of the naturally occurring elements (K, Mg, and Ca) with As similar to that measured in the Pb study.

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In addition to the elements measured using the ICP-MS, LIBS provided simultaneously analysis of Ca, Mg, C, H, and O at each spatial location of these leaves. The LIBS optical spectrum was collected from 190 – 1040 nm in order to detect every element in the plant leaves with each laser pulse. Figure 4 displays the elemental maps for C, H, and O from the LIBS measurements using this CCD detector option. The depletion of C, H, and O can be seen in the leaf region demonstrating that the As damaged the natural structure of the leaf.

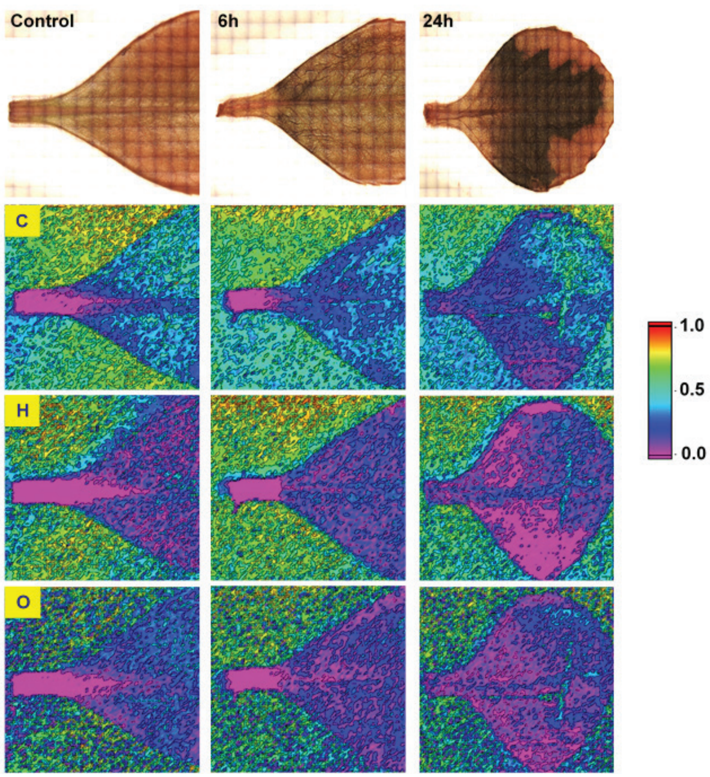

Figure 4. Photographs for the control, 6 h As exposure, & 24 h As exposure leaves. LIBS elemental maps for C, H, and O.

LIBS also was used to measure two of the essential elements (Ca and Mg) that are vital for plant life (Fig. 3). The sensitivity for Ca is excellent for LIBS, but can be low for ICP-MS since the main isotope for Ca is the main isotope for Ar (^{40}Ca and ^{40}Ar). The Ca isotopes (^{42}Ca, ^{43}Ca, and ^{44}Ca) that can be used for ICP-MS analysis, free of interferences, are ≤ 2.1% abundance. This is an excellent example of how the LIBS and LA-ICP-MS complement each other; simultaneous analysis of all elements in the sample, at each spatial location.

Conclusion

Combining LA-ICP-MS and LIBS using Applied Spectra's J200 Tandem LA-LIBS Instrument provides an innovative and unique capability for simultaneously analyzing and mapping every element in a sample, with one instrument! No other instrument provides the analysis of H and O at the same time as the heavy isotopes commonly measured with the ICP-MS. For this study, we showed how LIBS was used to measure Ca, Mg, C, H, and O with As, Pb, K, Cu, and Sr simultaneously measured by LA-ICP-MS, at each spatial location in the leaf samples. Elemental maps showed that the uptake of Pb and As followed different pathways in the leaf. LIBS offered the added advantage of detecting the depletion of C, H, and O within the exposed leaf and correlating it to the accumulation of Pb or As.

Simultaneous elemental mapping can be applied to any sample with the same level of success, including biological tissue, alloys, batteries, etc. The power of these measurements is analyzing *every* element within a sample at each spatial location, made possible by the Tandem capability. The data analysis package offered by Applied Spectra makes data processing (LIBS and LA-ICP-MS) and the creation of elemental maps easy and efficient.

Alison M. Bray, Ph.D., Texas Lutheran University, Department of Chemistry – Dr. Bray is an analytical geochemist at TLU in Seguin, Texas. She is currently funded by the U.S. Department of Agriculture - National Institute of Food and Agriculture for studies on the uptake of arsenic by rice plants. Studies of plant tissue using LA-ICP-MS are complimentary to complete plant tissue digests being utilized on contaminated rice, spinach, and kale samples being conducted by TLU students.