Trace element quantification

From lithium to uranium

The challenge

Accurately measuring trace elements within solid materials is essential for discerning their origins, tracing chemical processes, identifying contamination, and ensuring precise process control. Many industries require high-sensitivity measurements to ensure both product effectiveness and the health and safety of consumers. In metallurgy and materials science, high-purity metals typically exceed 99.99%, which indicates trace impurities are less than 100 ppm. For geologic materials, geologists and earth scientists seek high sensitivity, especially for rare earth elements (REEs), to unravel complex geological processes and phenomena.

Despite the demand for high-sensitivity measurement tools, achieving such low detection limits can be difficult and time consuming. Methods with acceptable detection capabilities typically have at least one of the following challenges: 1) intricate sample preparation processes, 2) complicated calibration procedures, and 3) expensive, confounding packages of several different instruments. Because techniques like Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Optical Emission Spectroscopy (ICP-OES) require a liquid solution, precise sample digestion and dilution procedures are necessary. These plasma-source techniques also suffer from spectral interferences and matrix effects, which demand matrix-matched standards for proper calibration. Achieving low detection limits directly from solid samples requires the combination of ICPMS and a compatible Laser Ablation (LA) system. Due to the complexity, establishing an efficient workflow is very challenging. Furthermore, the large footprint of the combined LA-ICP-MS system is suitable for a laboratory environment only.

The solution

The EXUM™ MASSBOX™ LALI-TOF-MS introduces a groundbreaking solution for trace element quantification, revolutionizing analytical capabilities across industries reliant on precise chemical analysis. Using Laser Ablation Laser Ionization Time-of-Flight Mass Spectrometry (LALI-TOF-MS), the MASSBOX mass spectrometer offers rapid and comprehensive characterization of major, minor, and trace elements within diverse solid materials. This breakthrough streamlines the analytical process by eliminating the need for extensive sample preparation. Quantifying trace elements precisely allows users to gain deeper insights into chemical processes, investigate trace origins, identify contamination sources, and ensure stringent quality control standards. Moreover, this innovative approach holds significant promise for industries such as advanced manufacturing, materials science, and resource extraction, where precise measurement of trace elements is crucial for advancing research, innovation, and product development.

MASSBOX LALI-TOF-MS

Engineered to overcome prevalent challenges in traditional analytical techniques, the MASSBOX LALI-TOF-MS technology offers swift and high-sensitivity quantification across a broad spectrum of elements. By employing two lasers, the ionization source, LALI, efficiently ablates material from solid samples and ionizes neutrals present in the ablated material. The laser ablation process enables direct analysis of solid materials, eliminating the need for complex sample preparation procedures associated with liquid sample introduction methods. The ionization laser targets neutral particles generated by ablation, ensuring a more accurate representation of the sample's constituents compared to plasma-generated ions. This targeted approach allows more automatic elemental verification and minimizes sample matrix effects, contributing to the overall stability of the analytical process. Following ionization, the time-of-flight mass analyzer generates a full mass spectrum at each laser spot, facilitating detailed elemental analysis and providing insights into the composition of the sample.

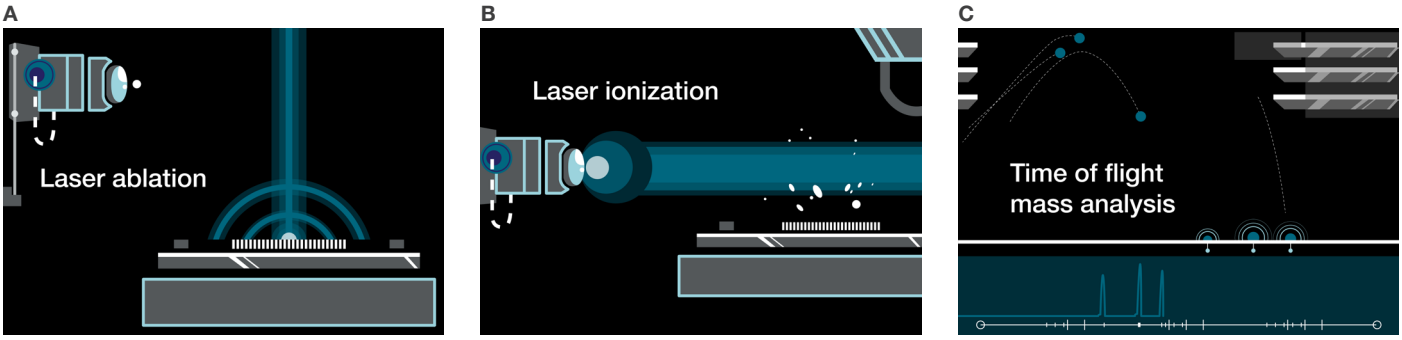

Figure 1. A) Ablation laser fires perpendicular to the sample's surface. The laser spot size is adjustable from 5-150 micron.
B) Secondary laser performs multiphoton ionization of neutral particles created by ablation process.
C) Ions are separated by Time-of-Flight mass spectrometry and detected with a multichannel plate (MCP).

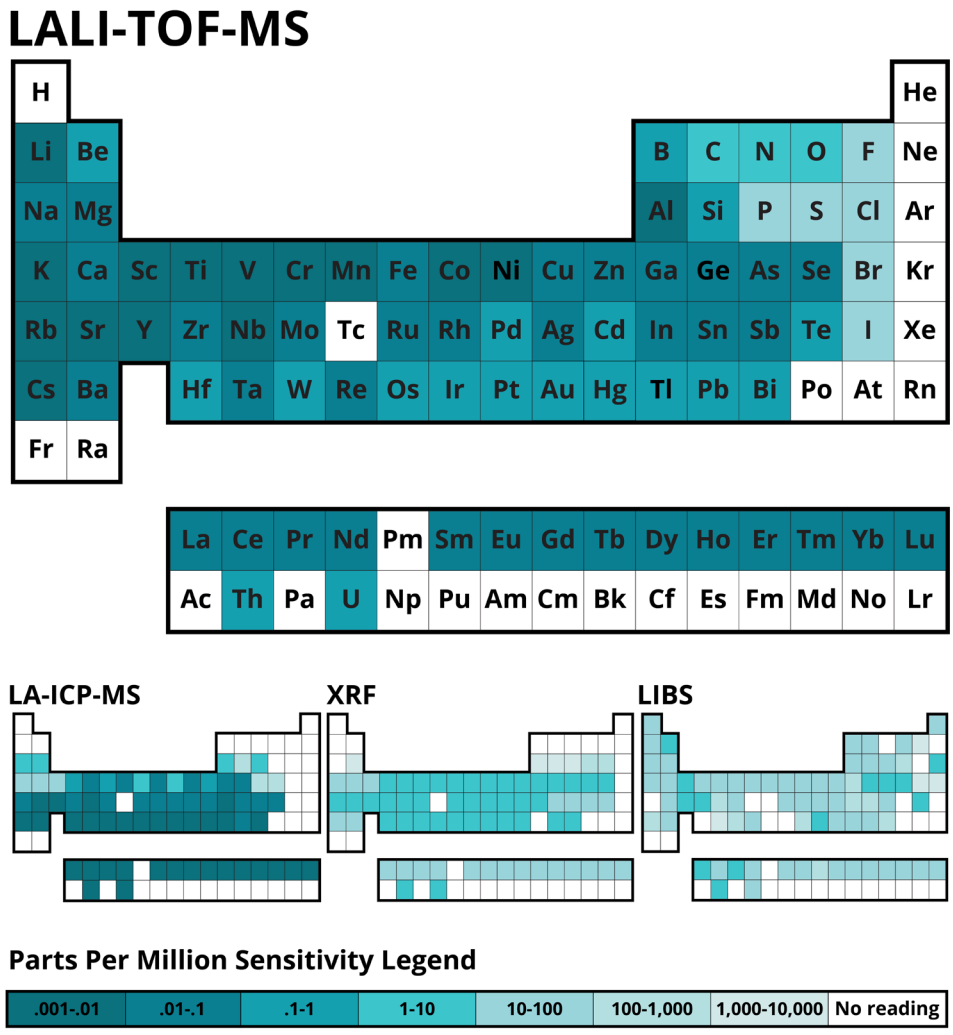

Figure 2. Detection limits for MASSBOX, LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry), XRF (X-Ray Fluorescence), and LIBS (Laser Induced Breakdown Spectroscopy). Each element is colored by its respective limit of detection. Darker colors represent lower detection limits.

Quantifying trace elements

This study demonstrates the MASSBOX LALI-TOF-MS's proficiency in detecting and accurately quantifying major, minor, and trace elements in the same analytical session. We used USGS black glass reference materials as test samples, as shown in Figure 3. Treating GSE 1G as an unknown, we quantified its constituents from a single point calibration using known values from GSE 2G. Our results, presented in Figures 4 and 5, revealed an average accuracy of 10% for major elements and 9% for trace elements. The results include light elements like lithium (Li) and beryllium (Be) as well as high-mass elements like tungsten (W) and uranium (U). Few techniques can reliably quantify low-mass and highmass elements simultaneously. Figure 3 shows an image of the two test samples taken by MASSBOX macrocamera. For each analytical session, the camera captures an image of the sample tray so the user can use it to view the samples and define areas for analysis. On each sample, we analyzed three raster areas (800 x 800 micrometers each) with a 40-micron ablation laser spot size. The results included in Figures 4 and 5 are the average of the analytical areas. The error bars represent the standard deviations from the three areas, which show the consistency and reliability of the measurements.

Detection capabilities

Figure 2 shows color-contoured periodic tables comparing detection limits of the MASSBOX LALI-TOF-MS to those of other common analytical techniques for solid sample analysis: 1) LA-ICP-MS, 2) X-ray Fluorescence (XRF), and 3) Laser Induced Breakdown Spectroscopy (LIBS). The graph's color gradient denotes detection limits, and darker colors represent the lowest levels.

For the MASSBOX LALI-TOF-MS, detection limits for most elements are in the high ppb range. Compared to the detection limits of XRF and LIBS, MASSBOX LALI-TOF-MS's limits of detection are approximately three orders of magnitude lower, making it an appropriate tool for high quality control applications.

Because of MASSBOX LALI-TOF-MS's ionization source, LALI, and its analysis under vacuum, it can reliably detect and quantify low-mass elements (e.g., lithium, carbon, oxygen, nitrogen, etc.) that are difficult for other techniques to reliably detect.

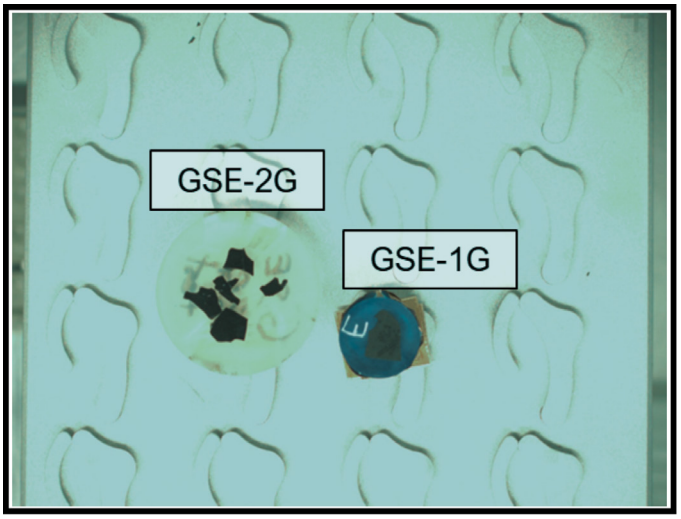

Figure 3. Image of GSE-1G and GSE-2G samples. The image was captured by the MASSBOX macrocamera. From this image, the user chooses points, lines, or areas to analyze on the sample. The samples were placed on a typical sample holder, which required only a few minutes of sample preparation. The MASSBOX LALI-TOF-MS can analyze an area up to 83 mm by 83 mm in each analytical session.

Results

Figure 4 shows results from the sample's major elements (in weight %) and minor elements (in ppm). Figure 5 includes the rare-earth and other trace element results (in ppm). Note that all elements were detected and quantified in the same analytical session, demonstrating the MASSBOX LALI-TOF-MS's wide dynamic range. Each graph compares the results acquired by the MASSBOX LALI-TOF-MS (in blue) with the material's certified values (in gray). Compared to known values, MASSBOX LALI-TOF-MS's results have an average accuracy of 10% for major elements and 9% for trace elements. Because the MASSBOX LALI-TOF-MS can directly analyze solid materials, it minimizes the time involved in acquiring data. In this case, the sample preparation, analysis, and data processing required ~45 minutes total.

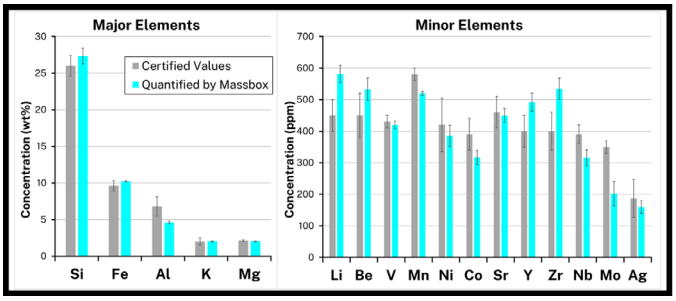

Figure 4. Comparison of the MASSBOX LALI-TOF-MS's results quantified across three raster areas (blue) compared to the GSE 1G certified results (gray), demonstrating 10% average accuracy. Major elements, in wt%, are on the left and minor elements (in ppm) are on the right. For the MASSBOX LALI-TOF-MS's results, error bars depict the standard deviation from triplicate raster areas. On the certified values, the error bars show a confidence interval for 95% uncertainty.

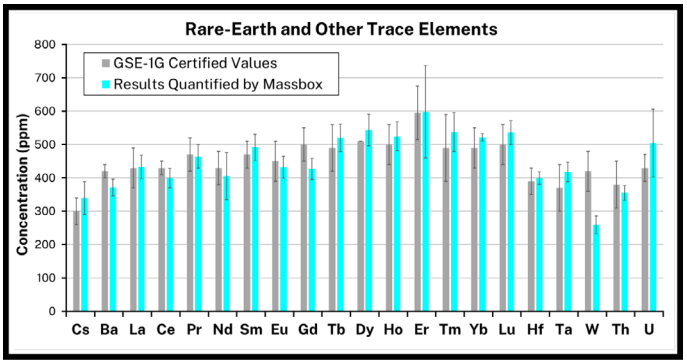

Figure 5. Comparison of MASSBOX LALI-TOF-MS's results quantified across three raster areas (blue) compared to the GSE 1G certified results (gray), demonstrating 9% average accuracy. The composition of rare-earth and other trace elements is presented in ppm. On MASSBOX LALI-TOF-MS's results, error bars depict the standard deviation from triplicate raster areas. On the certified values, the error bars show a confidence interval for 95%uncertainty.

MASSBOX LALI-TOF-MS Results

The MASSBOX LALI-TOF-MS represents a groundbreaking advancement in trace element quantification, addressing the critical need for high-sensitivity chemical analysis across various industries. With its LALI-TOF-MS technology, the MASSBOX instrument offers rapid and comprehensive characterization of trace elements within diverse materials, streamlining the analytical process with unprecedented operational efficiency. Its versatility extends to industries such as manufacturing, energy, and materials science, enabling researchers and engineers to delve deeper into understanding chemical processes, tracing origins, identifying contamination sources, and ensuring stringent quality control standards.

This study demonstrates the MASSBOX LALI-TOF-MS's ability to reliably quantify trace elements from Li to U at ppm-level sensitivities with high accuracy compared to known values.

In addition to accurate compositional analysis of the full periodic table, from lithium to uranium, the MASSBOX LALI technique has other unique capabilities. Because the MASSBOX software automatically verifies the elements present in the material based on naturally occurring isotope patterns, it facilitates rapid screening applications. Rapid screening allows users to immediately identify the composition of any unknown material, including trace contaminants or impurities in low-ppm levels.

Each of the ablation laser's spots generates a full mass spectrum, which allows the user to create elemental maps and depth profiles. The MASSBOX LALI-TOF-MS can analyze an area up to 83 mm by 83 mm. The resulting map's spatial resolution is determined by the ablation laser's spot size, which is adjustable from 5-150 microns. Mapping reveals the spatial distribution of any element of interest.

To create a depth profile, the user can analyze the same area with repeated elemental maps, which shows how the distributions change layer-by-layer. Each elemental map typically removes 100s of nanometers per layer, depending on the material, and this can be modified by adjusting the ablation laser's power. The MASSBOX LALI-TOF-MS also creates depth profiles using a single laser spot. Depending on the material type and user-defined laser power, spot dwelling typically removes 10s of nanometers per laser pulse, resulting in ~1 micron removed per second. Combining these impactful abilities into a compact desktop package, the MASSBOX LALI-TOF-MS is a versatile solution throughout the materials lifecycle.

Elemental mapping

Depth profiling

Rapid screening

Quantitative analysis

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Learn more at **thermofisher.com/massbox**

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