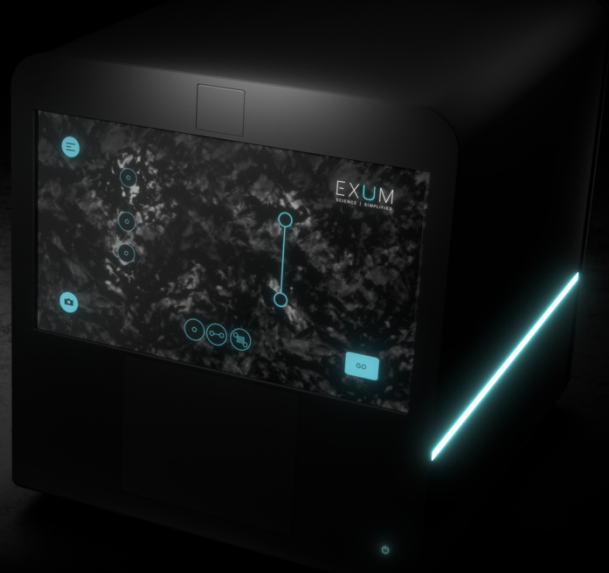


The Massbox

A field portable mass spectrometer capable of high-precision, high-sensitivity, inorganic and organic analysis

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Introduction

The Massbox is the first commercial instrument equipped with a Laser Ablation Laser Ionization (LALI) source. The patented, dual-laser technology of the Massbox extracts and subsequently ionizes material in two discrete steps. Historically, LALI has been referred to by numerous acronyms in the literature i.e. SALI (1) (2), LDI (3) (4), L²MS (5), LD-LPI-TOFMS (6). Most of the research regarding LALI was purely academic and performed between the late 1980s and early 1990s. At the time, cost and electronic limitations prohibited commercialization of LALI technology, and other techniques took center stage. Recent advances in computing technology and miniaturized, high-powered, solid-state lasers make LALI much more commercially viable today, and Exum Instruments is well-positioned to revitalize the technology in the commercial realm with the launch of the Massbox in March 2020.

LALI

Laser-Ablation Laser-Ionization

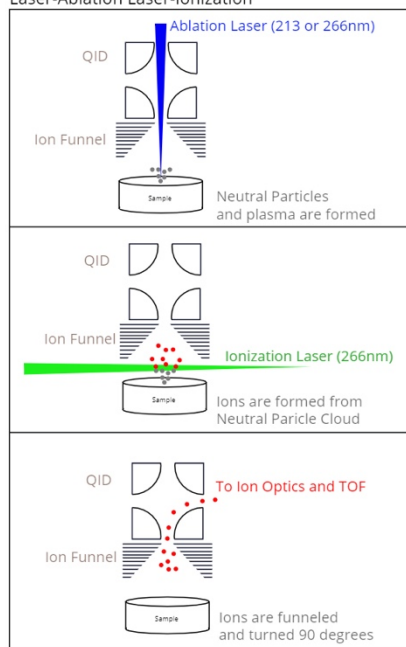


Figure 1: LALI process flow.

The first step of LALI uses a focused laser beam to ablate/desorb material from a solid sample surface. The Massbox utilizes an Nd: YAG desorption laser with an adjustable wavelength, Figure 1. Depending on the application, the desorption/ablation laser can be set to the fourth harmonic (266 nm) or fifth harmonic (213 nm) for ablation, or the fundamental 1064 nm wavelength for desorption. In a process exactly analogous to Laser Ionization Mass Spectrometry (LIMS) and Laser Induced Breakdown Spectroscopy (LIBS), the ablation/desorption laser generates an initial set of ion/electron pairs from a temporal plasma along with a neutral particle cloud that migrates normal to the sample surface. A short delay ($< 1 \mu\text{s}$) allows plasma extinction and the dispersion of plasma-generated ions before a second laser is triggered for ionization (also Nd: YAG set to 266 nm). As shown in Figure 1, the ionization laser is aligned parallel to the sample surface and its beam is focused inside the neutral particle cloud. The focused beam from the ionization laser has an energy density $> 10^9 \text{ W}\cdot\text{cm}^{-2}$, which allows for ionization of neutral particles via multiphoton ionization (MPI). MPI differs from Resonant Enhanced Multiphoton Ionization (REMPI) in that with MPI the laser is not tuned to a specific elemental or molecular frequency for ionization.

By ionizing elements across a wide range of ionization energies MPI serves as a highly efficient ion source and replaces the Ar plasma of ICP instruments. Once ionized, an ion funnel collects and focuses the ions in a low pressure (0.2-0.3 mbar) environment, Figure 1. After exiting the ion funnel, a Quadrupole Ion Deflector (QID) turns the ions 90 degrees and directs the ion beam through an Einzel Lens Stack and a quadrupole to further improve the beam shape. After the transfer quadrupole, the Massbox is equipped with a notch quadrupole filter. For applications that require high sensitivity, the notch filter increases dynamic range by selectively reducing the signal of up to four different ion masses (typically the most abundant matrix elements). Ions are then transferred to the reflectron Time-Of-Flight (TOF) which completes the mass analysis, Figure 2.

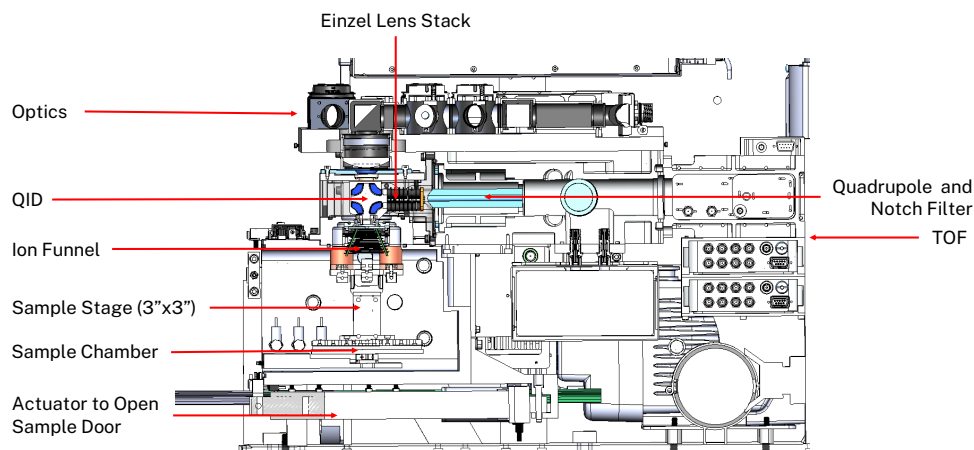


Figure 2: Diagram of Massbox instrument.

Reduced Matrix Effects

Compared to LIBS and LIMS, which both use only the plasma generated by the laser, LALI has more efficient ionization and reduced matrix effects. LALI's ability to reduce/eliminate matrix effects makes quantification a much more straight-forward endeavor. In LIBS for example, matrix-matched standards are a critical requirement for reliable quantification. For applications that require quantification across a variety of matrices, this requirement is a severe limitation of LIBS.

The Massbox's patent-pending LALI source ionizes gas-phase particles within the neutral particle cloud instead of relying on the plasma generated during ablation. Compared to material ionized by the initial ablation plume, material in the neutral cloud is significantly less variable across different matrices. Ionization of neutral cloud material also results in stoichiometric accuracy, which enables quantification of a variety of sample matrices without the need for matrix-matched standards.

Diffusion and Transport

Another major advantage of the Massbox is that ionization occurs under vacuum in the sample chamber. The Massbox is a completely static system held at high-vacuum ($\sim 10^{-7}$ mbar) in the TOF and a pressure gradient to $\sim 10^{-4}$ mbar in quadrupoles and the ion optics. The pressure in the sample chamber is maintained at ~ 0.2 mbar with an inert cooling gas (He). The low pressure of the ion source results in a large improvement in sensitivity because it greatly reduces losses associated with gas transport from atmospheric pressure to a vacuum system. Furthermore, without an inductively coupled plasma source, the Massbox does not require a carrier gas, which eliminates most polyatomic molecular isobaric interferences. Interference reduction improves the detection for a whole host of elements including Si, K, Ca, and Fe. The removal of the plasma source also has the advantage that thermal emission of contaminant ions from the cones and/or injector is eliminated, which greatly improves the ability to analyze many volatile metals along with Na and Pb. Additionally, without a plasma source or any carrier gasses, LALI does not rely on components with dynamic fluctuations, which leads to long-term signal stability without regular instrument tuning.

Interferences

Figure 3 shows LALI mass spectra are remarkably clean and unplagued by polyatomic or multiple charge interferences. shows the mass spectrum from a GSE-2G standard glass that contains almost every trace element. As seen in the zoomed insets, peak area ratios of a LALI mass spectra are isotopically correct across the entire periodic table, which makes quantification easier and more accurate.

Standard Glass: GSE-2G

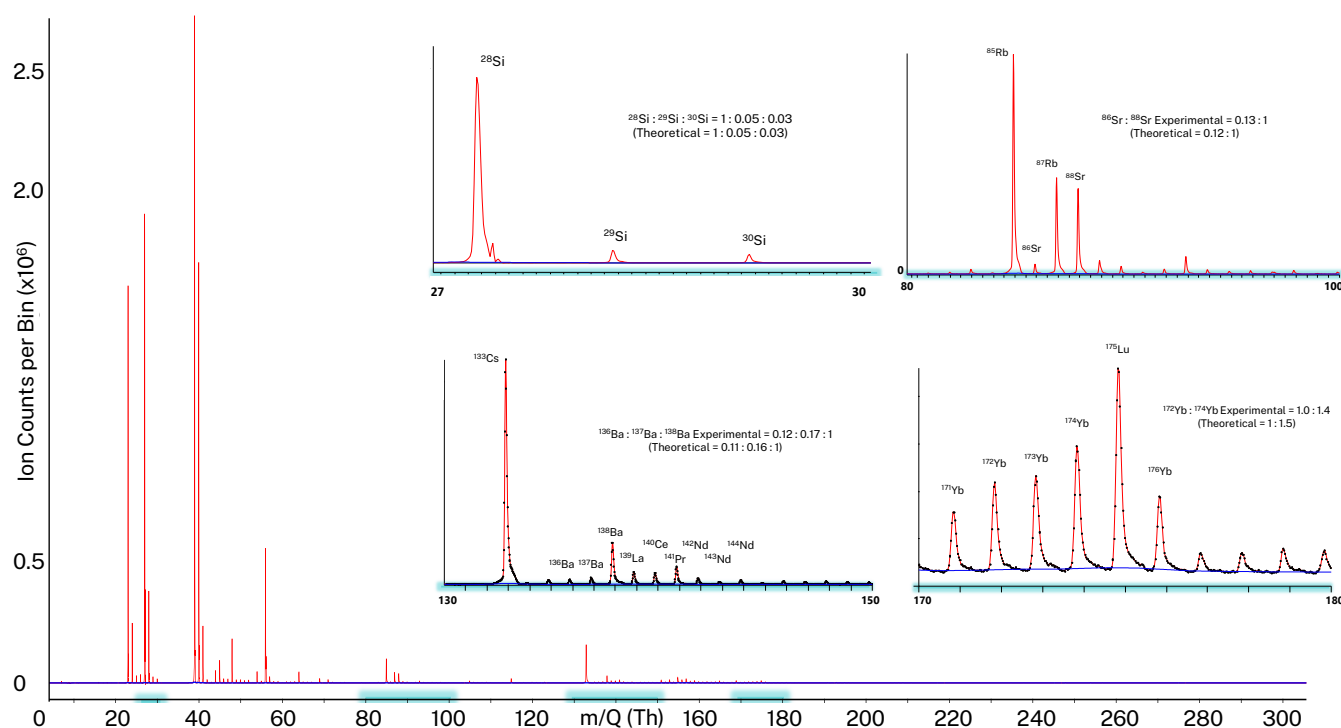


Figure 3: Broadband LALI mass spectrum and zoomed insets from GSE-2G standard glass.

Transmission Efficiency

LALI provides considerable improvements in transmission efficiency of an ion beam compared to techniques that generate ions at atmospheric pressure. Ions generated by a plasma at atmospheric pressure are generally transferred in several stages before reaching the high-vacuum mass analyzer. Each stage transition of cones and/or lenses removes a significant portion of ions. For instance, LA-ICP-MS has a very high ionization efficiency for elements with a first ionization potential (FIP) less than 8 eV, but only ~ 1 in every $10^5 - 10^6$ ions reach the detector (~ 0.01 - 0.001% transmission efficiency). The Massbox's LALI source is already under vacuum, so it does not suffer from transmission loss going from atmospheric pressure to vacuum. Removing the atmospheric/vacuum interface greatly improves transmission efficiency, allows for higher sensitivity, and further reduces matrix effects by removing plasma-ion spatial interaction effects.

Inorganic and Organic Analysis

LALI is capable of analyzing both organics and inorganics, which is difficult to replicate with other techniques that suffer from the problems previously discussed (7).

The ability to analyze organic compounds by LALI has been studied by many groups for applications including planetary missions⁽⁴⁾ and crude oil analysis (5) (8). The analysis of organics utilizes the infrared

component of the Nd: YAG laser (1064 nm). The intense IR pulse flash heats the sample (10^8 K/s) to desorb intact material from the sample surface (9). Following desorption, organic compounds are ionized via MPI using the secondary ionization laser as previously described. The ability to analyze both organics and inorganics in the same analytical session enables mapping (or bulk characterization) of both in the same sample almost simultaneously after a quick mode switch.

Operational

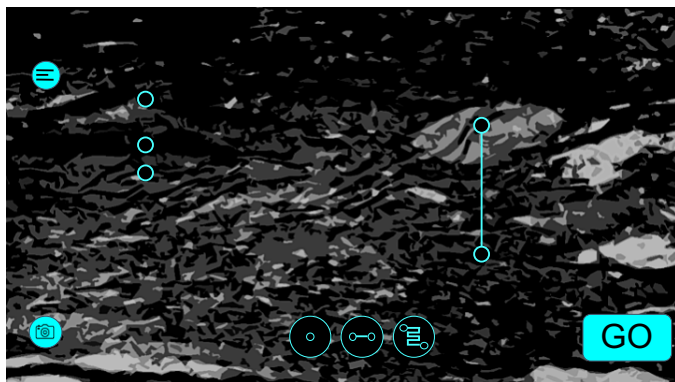


Figure 4: User interface used to identify where characterization occurs.

Away from the completely technical measurements, the Massbox has been developed to be easily deployed across multiple industries and applications. This is a step-change in analytical characterization and pulls from other technical steps changes from this past decade:

- The Massbox is field and lab portable (28" x 24" x 24"). The entire tool can be deployed on a desktop with no additional equipment required.
- The simplicity of design allows for a much-reduced purchase price and operation costs as compared to typical LA-ICP-MS systems.

User Interface

The Massbox has a very straightforward User Interface (UI). Figure 5 shows the sample chamber opening to allow the sample tray to be loaded and accommodating a 3" by 3" stage with nm precision. A macro-camera then opens to take a high precision, spatially located picture, Figure 5. After the sample chamber door closes and begins to pump down to vacuum. Meanwhile, the high-resolution image from the macro-camera is loaded onto the touch screen interface. The macro-image is used to enable navigation around the sample(s) as shown in Figure 4. Moving back and forth on the screen physically moves the sample stage within the chamber and aligns the desired area properly with the lasers. Pinching on the image zooms in and switches to a live microscopy image that allows precision when choosing an area to analyze. From the live view, spots, lines, and/or rasters for maps are chosen. After selecting the type and number sampling areas, analysis and data processing are automated, and all that remains is to apply the results.

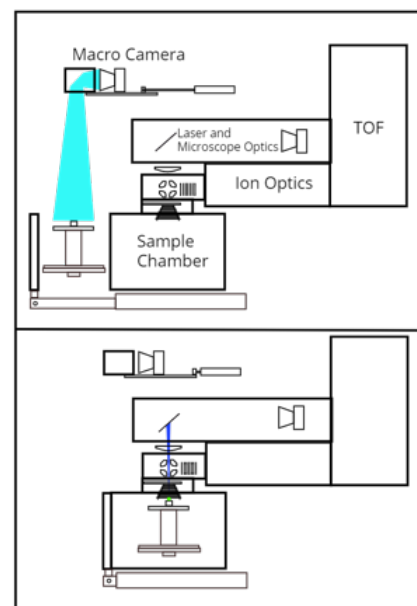


Figure 5: Schematic of sample loading, macro imaging and LALI source

Analytical Capabilities

The Massbox provides industries with high-precision, high-sensitivity data for both inorganic and organic analysis.

Massbox Specifications	
Analysis Type	Inorganic and Organic
Sample Type	Solid or Pseudo Solid (Biological Samples)
Elements Analyzed	Li - U
Detection Limits	10 ppb – 1 ppm (Application Dependent)
Mass Range	1 - 20000 Th
Mass Resolution	CTOF (700-1100Th/Th) LTOF (6000- 14000 Th/Th)
Mass Accuracy	4 ppm
Notch Filter Channels	4
Mapping	80 mm x 80 mm x 30 mm 3-axis with nm repeatability and resolution
Laser Spot Size	Adjustable from 1 μ m – 250 μ m
Repetition Rate	1 – 50 Hz
Ablation Laser Power (266 nm)	10 mJ
Ablation Laser Power (213 nm)	3 mJ
Ionization Laser Power (266 nm)	10 mJ
Beam Characteristics	Flat – Top Profile
Total Analysis Time (Including Pump Down)	< 5 min
Sample Holder	Customizable Depending on Application Standard has 9 Sample Slots
Quantification / Characterization	Completed Automatically Variable Matrix Materials Resolved Without Complex Standardization

Conclusion

The Massbox, which is the only LALI instrument available on the market, delivers both organic and inorganic analyses with high fidelity and high sensitivity. The Massbox provides quantitative chemical mapping and/or bulk analysis without the need for complex quantification schemes or matrix matched standard materials. The instrument's simple design enables field portability, and its easy-to-use, intuitive interface makes personnel and training requirements negligible. Together these factors open a wide range of potential applications.

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