

NUCLEAR FORENSIC INTERNATIONAL TECHNICAL WORKING GROUP

## ITWG GUIDELINE LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

## **EXECUTIVE SUMMARY**

Laser ablation is a solid sample introduction technique for analysis by atomic spectrometry. In nuclear forensic applications, it is mainly used with inductively coupled plasma mass spectrometry – ICP-MS<sup>1</sup>. Any solid sample may be categorized and characterized rapidly (within few hours) with little or no sample preparation. A high energy laser is used to ablate the sample in a controlled manner. The resulting aerosol containing particles, vapor and agglomerates is introduced into the plasma by a suitable gas, where they are ionized, and then analyzed by a mass spectrometer. Surface analysis and depth profiles can be obtained to a depth of a few  $\mu$ m. Since the laser ablation is carefully controlled, the sample consumption is minimal (almost non-destructive), thus the sample remains available for other investigations. Besides uranium and plutonium isotopic measurement, trace impurity analyses are of high importance to gather "fingerprint" information for comparison with nuclear forensics library data for eventual provenance attribution. It is also possible to perform spatial and depth analyses by measuring isotopic and elemental profiles in inhomogeneous samples, to obtain information on production process. In this role LA-ICP-MS it is less expensive than Secondary Ionization Mass Spectroscopy (SIMS). Age determination (radiochronometry measurements), which can provide date of last purification of the material, can also be performed on the sample with acceptable precision using LA-ICP-MS.

<sup>1</sup> Laser Induced Breakdown Spectroscopy (LIBS), which also uses high energy laser to vaporize and excite sample particles for atomic emission spectroscopy detection, is not be covered in this Guideline.

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ITWG Guidelines are intended as consensus-driven best-practices documents. These documents are general rather than prescriptive, and they are not intended to replace any specific laboratory operating procedures.

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### **1. INTRODUCTION**

Laser ablation was first reported as a sample introduction system for ICP-MS in 1985 [1]. Since then, LA-ICP-MS has successfully been used in geology, biology, and chemistry, as well as in classical and nuclear forensics [2-6]. The principle of the technique is to use a high energy laser to generate sample particles, vapor and agglomerates, which are then flushed into the plasma of the ICP-MS by a gas flow, where they are broken down, atomized and ionized to be analyzed in the mass spectrometer. The typical schematic of laser ablation used with ICP-MS is shown in Figure 1 (from [7]). Laser ablation of a solid sample is a complex process which is not completely understood. The ablation depends on the nature of the material in the sample, laser wavelength, pulse duration, energy density, spot size, and the gas used to sweep the particles out of the ablation cell into the mass spectrometer. It is particularly susceptible to elemental fractionation, which is the selective release of certain elements as a consequence of the interaction of laser energy with a sample and subsequent formation of a complex plume.



The schematic shows a solid state Nd:YAG laser (in this case with a frequency quintupled 213 nm wavelength), a cell on a movable stage, a light source and a camera. The sample is positioned within the air-tight ablation cell, which is flushed through by a gas that carries the ablated sample material into the ICP-MS. The movable stage is used to carefully position the sample under the laser spot for ablation and move the sample to the spot or line to be investigated. The laser filter and beam expander serve to control the laser energy hitting the sample, as measured by the energy probe. The polarized light source, objective lens, and other optics are used to see the sample surface, define the ablation protocol and monitor and record the progress of ablation using a digital camera.

In contrast to some other surface analysis techniques, e.g. glow discharge mass spectrometry - which is mostly used with electrical conducting materials, LA-ICP-MS can be used for any type of sample, i.e. non-conducting, conducting and soft tissue or polymer samples [8]. There is an emerging application of LA-ICP-MS in the analysis of electrophoresis gels for metal containing proteins.

The lasers which are commonly used in LA-ICP-MS are listed in Table 1 and the ICP-MS instruments in Table 2. The advantages and disadvantages of common laser and ICP-MS equipment are also summarized.

Laser	Wavelength	Pulse duration	Characteristics	Table 1. Commonly used lasers and their	
Nd:YAG	1064; 532; 266 and 213 nm	3 – 20 ns (Q-switched)	Solid-state, easy to maintain, most frequently used; UV-lasers (266 and 213 nm) have improved ablation characteristics and are preferred over IR lasers.	y used; UV-lasers aracteristics and [8])	
Ti:saphire	266 nm	<200 fs	Femtosecond lasers produce smaller particles, which are better ionized in the plasma. Less material is ablated per pulse than with nanosecond lasers resulting in a lower sensitivity. The price approximately doubles for the same wavelength. (2019 prices)		
XeCl (excimer)	308 nm	10 – 25 ns	Gas lasers. They are more difficult and expensive to		
ArF (excimer)	193 nm	10 – 25 ns	maintain.		

ICP-MS (Type)	Mass Resolving Power (m/Δm)	Scan frequency <sup>a</sup>	Duty Factor <sup>d</sup>	Characteristics	Table 2. Commonly used ICP-MS	
Quadrupole	<350	2b-500c Hz	2-45%	Robust, inexpensive, used for routine multi-element analysis. Low mass resolution and sensitivity often hamper accuracy of isotope ratio analysis and detection of minor isotopes.	instruments and their advantages and disadvantages	
Triple- quadrupole	<350	2b-500c Hz	2-45%	Robust, more expensive (~2x price of quadrupole), used for routine multi- element analysis with higher accuracy than single quadrupole (better interference elimination). Excellent abundance sensitivity (~1x1014) enables more accurate isotope ratio analysis.	(adapted from [8])	
Sector Field	300, 4000, 10000	2b-500c Hz	2-45%	Better mass resolution at the expense of sensitivity (loss of signal by ~ 10x at each order of magnitude gain of mass resolution) for precise isotope ratio analysis. Expensive (~10x quadrupole). Isobaric interferences, if not removed by using higher mass resolution, must be accounted and corrected for.		
Time of flight	300-2000	20 kHz	~10%	Emerging technology for isotope ratio LA applications. Duty factor cannot be changed but simultaneous accurate detection of different isotopes makes it ideal for isotope ratio measurements. Lower sensitivity and low abundance sensitivity (~103) may hinder accurate measurements of minor isotopes.		
Multi- collector	300-8000	Not applicable	>90%	Excellent mass resolution and sensitivity for precise isotope ratio analysis. Expensive (10-20x quadrupole); usually require clean room conditions and are not suitable for multiple element analysis		

<sup>a</sup>One resolution setting

<sup>b</sup>Typical multi-element applications, including 40 isotopes over the entire mass range

<sup>c</sup>'Best of' values: 2 isotopes only in a close mass range (no magnet jump in sector field MS)

<sup>d</sup>Defined as the ratio of measurement time for one isotope relative to the entire scan duration.

UV lasers, such as quadrupled and quintupled frequency Nd:YAGs at wavelengths of 266 and 213 nm, are currently the most frequently used. In comparison with infrared, e.g. 1064 nm, the use of UV wavelength leads to more efficient ablation, especially for transparent samples, such as glasses. Interaction of the UV laser pulse with the sample material results in better absorption of the laser energy, which in turn leads to more material being vaporized.

Femtosecond lasers have less heating effect and have been shown to produce smaller particles in a more uniform manner than nanosecond lasers, leading to less pronounced element fractionation. However, the amount of ablated material is smaller, which lowers the sensitivity. A femtosecond laser is approximately twice as expensive as a nanosecond equivalent. (as of 2019)

Use of helium gas to sweep the ablated material into the ICP-MS has proven to result in higher sensitivity compared with argon [9, 10]. This is presumably because of the higher thermal conductivity of helium, which promotes faster expansion and cooling of ablated vapour, thus yielding less agglomerates. In addition, using a mixture of helium and argon results in slightly "hotter" plasma in the ICP-MS.

The sensitivity of LA-ICP-MS depends on the laser spot size. Assuming a cylindrical crater shape and constant ablation efficiency, the amount of ablated material is proportional to the square of the radius of the spot size.

Another laser parameter affecting sensitivity and selectivity of LA-ICP-MS is the pulse repetition rate. Faster repetition rates, such as 20 Hz, lead to a train of pulses ablating the sample within the time of signal acquisition in time resolved mode of the mass analyzer. This enhances the sensitivity of detection while averaging any spatial variation within the sample.

It is noteworthy that laser ablation results in so-called 'dry' plasma conditions. This means there is considerably less probability for hydride and oxide formation than when aqueous samples are introduced into the ICP-MS. For example, for analysis of a UO2 pellet, the  $^{238}$ U<sup>1</sup>H<sup>+</sup>/ $^{238}$ U<sup>+</sup> ratio by LA is ~ 1x10<sup>-5</sup>, as compared with ~5x10<sup>-5</sup> in the case of sample introduction in 2% nitric acid aqueous solution.

Proper use of LA-ICP-MS necessitates the optimization of both the laser ablation and ICP-MS stages. For example, the extent of LA induced elemental fractionation may be assessed by monitoring the signals of <sup>232</sup>Th and <sup>238</sup>U in NIST 610 or 612 glasses. The difference between the two signals should be minimized (the Th/U signal ratio ~1) by careful optimization of LA conditions and tuning of the ICP-MS. In addition, the signal ratio of ThO<sup>+</sup>/Th<sup>+</sup> should be kept to less than 1 %. Next, the signal stability and sensitivity should be verified and adjusted as necessary.

The ICP-MS is operated in the time resolved mode when used with LA sample introduction. The time of signal acquisition should be selected considering the number of isotopes monitored, available sample quantity, as well as required accuracy and precision. For example, for a trace element analysis of a nuclear forensic sample when 20 isotopes are monitored with 0.1 s dwell time per isotope, the ICP-MS will generate and record a single point every 2 seconds. To have at least a 10 point trace, one should record sample ablation over a minimum 20 second time interval. In a typical experiment, a blank trace should be generated by operating the laser with the shutter closed for at least 10 seconds, and then opening the shutter and collecting the data for a set time interval.

# 2. USE OF LA-ICP-MS IN NUCLEAR FORENSICS

#### **Isotope Ratio Measurements**

The LA-ICP-MS is well suited for a rapid determination of isotope ratios [11-15]. It is noteworthy that the elemental fractionation of LA combined with space-charge effects of ICP-MS contributes to the mass bias, which needs to be corrected for by using an appropriate standard reference material.

The ability of LA-ICP-MS to rapidly and accurately measure isotope ratios with minimal sample preparation can be utilized in enrichment studies and in age determination. For example, in the case of uranium age determination in fuel pellets, employing the ratio between <sup>230</sup>Th and <sup>234</sup>U, it is possible to use New Brunswick Laboratories CRM 125-A (fuel pellet), which has a certified date of last purification, to correct for the mass bias.

Figure 2 shows the traces collected in LA-ICP-MS of CRM-125 A, useful for the determination of mass bias, and Figure 3 traces for an unknown uranium fuel pellet, whose age was being determined. LA-ICP-MS is well suited for isotope ratio determination of plutonium containing samples. In a recent article, Stefanie Konegger-Kappel and Thomas Prohaska [12] measured plutonium isotopes in the micro-particles from Chernobyl directly by LA-ICP-MS with excellent accuracy, thus providing a new method for assessing the burn-up of the reactor from which the plutonium originated.

#### **Spatial Analysis**

LA-ICP-MS can be used to perform spatial analysis of a solid sample, such as pellets, shards, metal pieces, powders, and swipe samples [2,5,15]. Since the laser beam can be operated to ablate at a controlled speed in any direction, the surface sample homogeneity can be investigated down to a resolution of a few µm. Similarly, modern laser ablation systems enable so-called depth profiling, where the laser "drills" into the material to provide information on the homogeneity of the sample along the drilling axis with a resolution of less than 0.1 μm depending on the material hardness. For depth profiling, measurement of the extent of ablation in one shot needs to be performed (e.g. with profilometer), since the operator controls the number of pulses and not the speed of "drilling".



**Figure 2**. Signal for <sup>230</sup>Th (black line) and <sup>234</sup>U (pink line) collected during ablation of uranium fuel pellet CRM-125 A. Using areas integrated from 30 to 110 seconds, the correction for the ratio <sup>230</sup>Th/<sup>234</sup>U was calculated as 1.12 to obtain the certified age of CRM-125A.



**Figure 3.** Signal for  $^{230}$ Th (black line) and  $^{234}$ U (pink line) collected during ablation of an unknown uranium fuel pellet under the same conditions as CRM-125A. When the 1.12 correction factor was applied to  $^{230}$ Th/ $^{234}$ U, the calculated age of 4.3±0.4 years was in an excellent agreement with 4.2±0.4 years determined by dissolution of the sample aliquot and separation of Th and U.

Both elemental and isotope spatial profiles can be measured.

An example of spatial analysis of uranium fuel pellet by LA-ICP-MS using the U-isotope profile is shown in Figure 4. The results from LA-ICP-MS analyses of fuel pellet samples were useful for determining the inhomogeneity of one of the fuel pellets in the fast evacuation of the LA cell ~10 ms compared to a conventional cell washout of ~500 ms limits scanning ICP-MS to analyse for 2 or 3 elements or isotopes and precludes a multi-element profiling.

#### **Trace Element Analysis**

Trace element analysis requires a suitable external calibration to quantify the elements in the sample.



**Figure 4.** Laser ablation of uranium fuel pellet scanning along a line at 50 µm/s. The variations of 234U and 235U traces along the path of ablation are indicative of inhomogeneous enrichment. Detailed analysis of the traces shows the 235U enrichment ranges from 0.3 to 4.4 % 235U. Similar results were obtained using SIMS.

Collaborative Materials Exercise organized by the ITWG in 2016, CMX-5.

The spatial resolution depends on the extent of ablated material in the aerosol and combined volume of ablation cell and gas line bringing the aerosol to ICP-MS. Small dispersion high speed evacuation LA cells [16] enable high resolution imaging of the surface of the ablated material, down to a 5  $\mu$ m lateral resolution. However, very

External calibration for LA-ICP-MS analysis is very probably the most challenging, because the interaction of the laser beam with the solid sample surface generates an aerosol significantly different from that obtained by aspiration and nebulization of acidic sample solution. In general, the best strategy in obtaining useful external calibration is to have calibration standards closely matrix-matched with the samples and choose isotope(s) of known concentration added, or present, in the matrix as internal standards.

It is possible to perform one- and multi-point calibrations. Similar to the wet sample-introduction configuration, multi-element calibration is more accurate. For example, when samples are prepared as glass beads, e.g. in the case of powdered samples, the calibration standards can be prepared by increasing the concentrations of the elements of interest in the glass beads and using an ubiquitous isotope in glass, such as <sup>44</sup>Ca, as an internal standard.

For uranium rich materials, such as uranium oxides, Crain and Gallimore [17] successfully used uranium ore concentrate certified references materials, New Brunswick Laboratories CRM 124 series, which contain different concentration of impurities, pressed in to pellets and <sup>234</sup>U as an internal standard.

There are other possible strategies for external calibration, such as mixing the laser ablated aerosol with one from the nebulizer coupled with a desolvator. The problem with this strategy is possible distortion of the calibration curve (non-linearity) due to elemental fractionation caused by LA, which may cause over-estimation of the concentration in the ablated material. More information on various strategies for external calibration may be found in [2, 4, 18].

For a comparison of an unknown sample with a known material using impurity and/or spatial homogeneity pattern (similar to "fingerprint" matching), there is no need to perform external calibration. However, it is essential that the experimental conditions are matched as closely as possible. Preferably, the comparison should be made after both samples were ablated using the same equipment operating under the same conditions.

### **3. SAMPLE REQUIREMENTS**

LA-ICP-MS requires minimal or no sample preparation.

Any solid object can be analyzed by LA-ICP-MS, provided that it fits in the LA cell. If this is impossible, a sub-sample has to be created for analysis.

Powdered samples can be pressed into pellets with or without an organic binder or fused into glass beads. Alternatively, powders spread over a surface may be sampled with a swipe cloth. There is also a so-called "dried-droplet" sample preparation technique, where a sample solution or suspension is dried on an inert surface. More details on various sample preparation techniques in LA-ICP-MS can be found in [4, 12].

Given that the LA-ICP-MS is predominantly a surface analysis technique, it is very important to have the sample surface clean of impurities. When possible, prior to analysis, the sample surface should be wiped clean with an un-intrusive solvent, e.g. water or alcohol and gently dried, or the laser can be used to clean the surface (pre-ablation).

LA-ICP-MS is in essence a trace analytical technique, requiring minute amounts of sample. The ablation, which is proportional to the extent of sample damage, can be carefully controlled, thus leaving the sample minimally changed. This is especially important for forensic analysis, since the sample should be preserved as much as possible for other examinations/analyses.

# 4. PRO'S AND CON'S OF THE TECHNIQUE

#### Pros:

• Less expensive than SIMS, easy to set-up, no cleanroom requirement

• Minimal or no sample preparation (e.g. no waste or hazardous chemicals)

• Minimal sample consumption/damage

• Trace element analysis at limits of detection comparable with wet sample preparation techniques, i.e. dissolution and dilution (without extraction and concentration of the analyte).

- Sensitive and accurate isotope ratio analysis
- $\bullet$  Spatial analysis with a few  $\mu m$  resolution
- Very fast (within a few hours)
- Cons:

• Sensitivity is lower by about 1000x than with aqueous nebulization

• Challenging external calibration for accurate concentration measurements

• Limited number of useful standard reference materials for nuclear forensic analysis

• Challenging tuning for maximum sensitivity at minimal elemental fractionation

• Condensation of sample material in the LA system generates powder deposits. Inadvertent and uncontrolled transport of deposited particles leads to spurious spikes during the analysis. To avoid such contamination effects, the LA system requires regular cleaning

## 5. FAQ

• Cost of a Laser Ablation nanosecond system with Nd:YAG 213 nm laser and the 100 cm<sup>3</sup> cell is approximately 110,000 US Dollars. (2019 prices)

• Used predominantly for solid samples.

• Requires minimal sample preparation. Can be used for micro analysis.

• Fast, accurate and precise trace element (impurity "fingerprint"), isotope ratio (enrichment, radiochronometry) and spatial analysis (surface and depth profiles).

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### **DOCUMENT REVISION HISTORY**

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