

Laser Ablation in Analytical Chemistry - A Review

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Abstract

Laser ablation is becoming a dominant technology for direct solid sampling in analytical chemistry. Laser ablation refers to the process in which an intense burst of energy delivered by a short laser pulse is used to sample (remove a portion of) a material. The advantages of laser ablation chemical analysis include direct characterization of solids, no chemical procedures for dissolution, reduced risk of contamination or sample loss, analysis of very small samples not separable for solution analysis, and determination of spatial distributions of elemental composition. This review describes recent research to understand and utilize laser ablation for direct solid sampling, with emphasis on sample introduction to an inductively coupled plasma (ICP). Current research related to contemporary experimental systems, calibration and optimization, and fractionation is discussed, with a summary of applications in several areas.

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1. Introduction

Laser ablation in analytical chemistry has grown substantially over the past few years; several recent reviews each list approximately 200 references describing fundamental or applied studies related to analytical chemistry [1-3]. Conceptually, laser ablation is a simple and straightforward process. A short-pulsed high-power laser beam is focused onto a sample surface. The laser beam converts a finite volume of the solid sample instantaneously into its vapor phase constituents. The vapor then is analyzed by measuring atomic/ionic emission in the induced plasma (LIBS) or by transporting the vapor to **another measurement system**, such as the inductively coupled plasma (ICP).

Compared to conventional dissolution techniques, laser ablation has many advantages. Most analytical techniques involve **removing** a portion of the solid sample, which is then dissolved in acid solutions. **With this procedure, there is a** greater chance of exposure to hazardous **materials** and there is a risk of introducing contaminants or losing volatile components during **sample preparation**. For laser ablation, any type of solid sample can be ablated for analysis; there are no sample-size requirements and no sample preparation procedures. Chemical analysis using laser ablation requires a smaller amount of sample (< micrograms) than that required for solution nebulization (milligrams). Depending on the analytical **measurement** system, picogram to femtogram **sample** quantities may be sufficient for laser ablation analysis. In addition, a focused laser beam permits spatial characterization of heterogeneity in solid samples, with typically micron resolution both in terms of lateral and depth conditions.

Interest in analytical optical and mass spectrometry associated with laser ablation for sample introduction has increased markedly during the past few years. Laser ablation optical and mass spectrometry with inductively coupled plasma (LA-ICP-AES/MS) appears to be the only analytical approach for nearly non-destructive determination of a large number of elements with very low detection limits [1-6]. Applications of LA-ICP-AES/MS now span a great range of academic and industrial fields that include environmental, geological, archaeological, forensic, and semiconductor manufacturing sectors.

A primary goal of laser ablation for analytical chemistry is quantitative analysis. Calibration typically requires matrix-matched standards, which, however, can be difficult to obtain or fabricate. Developing reliable, possibly universal calibration standards will be essential for laser ablation to become more widely adopted in analytical chemistry. Without matrix-matched calibration, fractionation (mass removal based on thermal properties) becomes an issue during laser ablation sampling. Fractionation limits accurate chemical analysis, as the ablated mass composition is not the same as the actual sample composition. These challenges (calibration and fractionation) along with perspectives of laser ablation as a viable analytical tool will be discussed in this review.

In addition to the challenges of calibration and fractionation, the fundamental physical processes of laser ablation are not fully understood. Understanding fundamental laser ablation mechanisms is necessary in order to efficiently couple the laser beam into the sample, ablate a reproducible quantity of mass, minimize fractionation and plasma shielding, control ablated particle transport, and produce stoichiometric ablation. A thorough review of the fundamental

issues of laser ablation (e.g., ultrafast laser-solid interactions, vapor and plasma dynamics) falls beyond the scope of this article. We direct readers to **several** recent articles and conference proceedings devoted to **these** topics [7-10].

This review will summarize current laser ablation research in analytical chemistry, focusing on standard laser ablation experimental systems, calibration, fractionation, and numerous analytical applications. LA-ICP-AES and LA-ICP-MS will be emphasized in this review. As evident from a large number of publications in the field of laser ablation – approximately two **thousand** published papers over the past ten years, interest in laser ablation continues to flourish.

2. Experimental Systems

A typical laser ablation system consists of a laser, an ablation stage, and a detection system (Figure 1) [1]. Pulsed lasers are used most often to produce coherent light for ablation. The samples are usually **placed** on a mechanically adjustable ablation stage. **The** detection system **is often** an ICP-MS or ICP-AES. **Argon** or other inert gases **typically carry the ablated sample** into the ICP.

2.1. Lasers for ablation

Many types of pulsed lasers **have been** used for ablation. Ruby lasers were among the first applied to ablate solid materials for **chemical analysis applications** [2, 11,12]. Currently, most laser ablation experiments **utilize** Nd:YAG or excimer lasers [4]. Solid state Nd:YAG systems have been widely employed because they are relatively inexpensive, require little

maintenance, and are easily incorporated into **small** commercial ablation systems. **Excimer lasers utilize halogen gas-filled chambers rather than solid-state crystals.**

Ablation is affected by the laser wavelength. In general, the shorter the laser wavelength, the higher the ablation rate **and lower the** fractionation [13-18]. For Nd:YAG lasers, the fundamental wavelength **is in the near-IR** at 1064 nm. Optical frequency doubling, tripling, quadrupling, and quintupling (wavelengths at 532, 355, 266, and 213 nm) of the Nd:YAG lasers have been achieved and employed for laser ablation chemical analysis [4,18,19]. For excimer lasers, the operating gas determines the lasing wavelength. An excimer laser produces a choice of output wavelengths at 308, 248, 193, or 157 nm, using XeCl, KrF, ArF, or F₂, respectively. Generally speaking, shorter wavelengths offer higher photon energies for **efficient** bond breaking and ionization of the solid sample. For laser wavelengths at 266, 213, and 157 nm, the equivalent photon energy is 4.66, 5.83, and 7.90 eV. **Absorption of laser energy by target material and by the laser-induced plasma varies significantly with laser wavelength.**

Ablation may involve thermal and/or non-thermal mechanisms, depending on the wavelength. For a thermal process, electrons directly absorb the laser light, transferring this energy into the atomic lattice. Melting and vaporization of the target material occurs. Because of the difference in latent heat of vaporization for different chemical elements, a thermal mechanism may induce strong fractionation. If the photon energy is higher than the bonding energy between neighboring atoms in the solid (a few eV), the electromagnetic laser radiation can directly break the atomic lattice, inducing ion and atom ejection without traditional heating effects [20-21].

Another process that strongly depends on laser wavelength is plasma shielding [22-24]. The laser beam can interact with the expanding plasma-plume generated at the early stage of the ablation process, depending on the duration of the pulse. Laser energy can be strongly absorbed or reflected by the plasma. The absorption coefficient of the plasma depends on the laser wavelength; typically, plasma absorption is greater at longer wavelengths [23,24]. The high photon-energy, short UV wavelength penetrates the plasma more efficiently and directly initiates bond breaking in the sample. These two conditions lead to a larger ablation rate and less fractionation.

Picosecond laser pulses may provide improved accuracy versus nanosecond laser pulses [25]. An additional feature of picosecond laser ablation is enhanced ablation efficiency compared to nanosecond laser ablation [26]. Significantly more mass can be removed per unit energy using picosecond laser pulses. **The improvement is related to reduced plasma shielding and smaller heat affected zone in the sample.** Femtosecond laser pulses might be favorable for providing reduced fractionation because of minimal thermal effect [27]. Preliminary studies using femtosecond lasers for analytical spectroscopy have been reported recently [28,29].

Other than wavelength and pulse duration, the laser-beam spatial energy profile also **influences** mass removal. Solid state Nd:YAG lasers usually have a Gaussian beam profile, which can be readily focused to a very small beam area. The beam waist at the **lens focal point** is a function of initial beam size and the lens' focal length. For Gaussian beams, the radius at a distance δ from the waist of the focal point can be expressed as [30]:

$$w(\delta) = w_0 \left[1 + \left(\frac{\delta}{z_R} \right)^2 \right]^{1/2}, \quad (1)$$

where

$$z_R = \pi w_0^2 / \lambda, \quad (2)$$

and

$$w_0 = \lambda f / \pi w_l. \quad (3)$$

In the above expressions, w_l is the laser beam radius at the lens, λ is laser wavelength, and f is the focal length of the lens. z_R represents the Rayleigh length defined as the distance at which the diameter of the laser beam increases by a factor of $\sqrt{2}$ from its waist; w_0 is the laser beam radius with the intensity $1/e$ of its maximum.

By using a Gaussian laser-beam energy profile, the shape of ablation crater becomes cone-like after, for instance, hundreds of pulses [31]. On the other hand, flat-top laser beam profiles are capable of producing straight-wall craters in a wide range of materials [4, 32]. Excimer lasers generally have ‘flat-top’ beam profiles. With appropriate imaging optics, both Nd:YAG and excimer lasers can generate flat-bottom craters (figure 2). The shape of the crater walls will influence depth resolution and fractionation may increase with the development of the ablation crater [31]. However, the degree of fractionation is not strictly related to the beam profile; fractionation is not eliminated by having a flat-top beam profile.

2.2. Ablation Stage

A typical laser ablation stage consists of a lens, an ablation chamber, and an adjustable platform. The lens may be incorporated into an optical microscope so that optical and visual focusing coincides. Often the sample surface can be viewed remotely via a CCD camera. The sample is located inside the ablation chamber that has a fused silica window. The adjustable platform, typically under computer control, allows positioning of the sample in the X, Y, and Z directions. Displacement as small as a few microns can be achieved without difficulty. Depending on the timing between individual laser pulses and platform movement, different tasks such as depth profiling, spatial profiling, surface and bulk analyzes are possible.

For applications using LA-ICP (figure 1), the chamber is flushed with an inert gas to transport the ablated sample to the ICP. Argon and helium have been employed with the latter gas providing improved ablation and transport rates [2, 15]. An arrangement for chamber purging must be included, usually by a three-way valve. Since the 1980s, a variety of different ablation chamber designs have been developed and tested [4, 33-38] for LA-ICP-AES and LA-ICP-MS. The volume of the chamber and the transport tube can influence the sample density in the ICP. Smaller volumes (below 1 cm³) may reduce “sample-washout” time. A high carrier gas flow can reduce sample deposition in the chamber and transfer tube, thereby decreasing memory effects and increasing transport efficiency. To improve transport efficiency, the sample and or chamber can be placed directly under the ICP torch [37]. In general, chamber designs need to be further studied and optimized for improved laser ablation analysis.

2.3. Detection Systems

2.3.1 ICP-MS

Most ICP-MS systems use quadrupole mass analyzers. However, double focusing electrostatic-magnetic sectors, multiple Faraday analogue detector instruments, time of flight (TOF), and ion trap mass analyzers have all been utilized with ICP-MS [1]. A characteristic of quadrupole mass analyzers is their ability to scan between selected masses. The settling time at a particular mass is less than 1 ms; 1000 masses per second can be measured. Although the measurement is not simultaneous, the speed is fast compared to the time response of laser ablation sample introduction. A disadvantage of using quadrupoles occurs when large particles are present in the ablated vapor; large particles lead to spatial changes (enhancements or depressions in the signal level and chemistry) in the ion cloud in the ICP. The transit time through the ICP for this particle-induced ion cloud is only a few ms. Therefore, only one mass measurement may be obtained from such particles. Particle influences on the ICP and fractionation need to be thoroughly investigated.

Double focusing electrostatic-magnetic sector instruments exhibit very low background levels and high resolution. Such instruments can acquire data at high speed within limited regions, but the instruments cannot switch rapidly over large mass regions required for full trace element analysis [39]. Multiple Faraday analog detector instruments were designed for specific isotope ratio applications. These are simultaneous instruments that can determine isotope ratios with very high precision [1,40]. Analog detection reduces detection limits by approximately 1000-fold. TOF instruments [41,42] potentially are better suited for laser ablation sampling ICP-MS; signal detection is sequential but sampling is simultaneous [42]. The TOF system may be capable of eliminating the errors due to large particle in the ICP.

2.3.2 ICP-AES

Spectral emission lines identify elemental composition within the ICP. The emission line intensity is an indication of the ablated mass quantity and the concentration of constituents in that mass. ICP-AES provides a large dynamic range that extends from trace to major constituent analysis [43]. The major advantage of ICP-AES is its high simultaneous multi-element capability. High-resolution spectrometers are necessary for trace analysis of samples with elements exhibiting line-rich spectra (e.g., Fe, Co, Ni, U, Th, and rare earth's) [43]. Isotopic ratios also can be measured using ICP-AES systems with high-resolution spectrometers [44,45]. Reduced sensitivity and spectral interferences are disadvantages of AES over MS systems. The sensitivity of any component in a multi-element system depends on the concentration of other components. Interference correction for multi-element analysis using ICP-AES has been studied extensively [46].

2.4 Sample preparation

A significant benefit of laser ablation is that little or no sample preparation is required for direct solid **chemical analysis**. Laser ablation generally can be categorized as microprobe or bulk analysis. **Microprobe analysis includes depth profiling and lateral surface area analysis, neither which requires sample preparation procedures.** No sample preparation is necessary for bulk analysis, if the sample is homogenous. If the sample is inhomogeneous, it can be pulverized to a fine powder and pressed, or fused to form a glass [47-49]. Phenols or polyethylene binders can be mixed with powder samples and pressed under high pressure to produce a sturdy homogeneous material [49,50]. **For analysis of pressed powders, a large laser beam diameter or rastering should be used to scan a large area of the sample [1].**

3. Calibration Strategies in LA-ICP-MS and LA-ICP-AES

There is little doubt that laser ablation is very attractive for direct solid sampling with ICP-AES and ICP-MS. Qualitative and semi-quantitative analysis are almost routine. However, for quantitative analysis, calibration remains a challenge for analysis of a wide variety of samples. There is no universal method of calibration for all of solid-sample types. There are three general groups of calibration strategies (Figure 3) that are described below.

3.1 Matrix-Matched Direct Solid Ablation

External calibration utilizing matrix matching is the most common method for LA-ICP-MS. Matrix matching is necessary because the ablation rate (quantity of mass ablated per laser pulse) varies with the sample matrix. Certified reference materials are commercially available for some types of solids matrices (glass, ceramic, cement, metals). However, available reference materials do not cover every type of sample. Many laboratories prepare matrix-matched standards, which include a mixture of an appropriate matrix material with the analyte. Techniques used to obtain matrix-matched standards include: addition of compounds to a powdered matrix, mixing and pressing with or without a binder [51,52], addition of standard solutions to a powdered matrix, co-precipitation of elements into a matrix with single element solution [53], drying and pressing [2] glass fusion, and the production of sintered compacts (co-precipitation gel techniques) [54]. External calibration with matrix-matched standards has been used successfully for quantification [51,54-60]. A sample type in which external calibration is considered relatively easy is metals. Many metal standards are available that have similar

properties to the sample. However, the standard must be carefully chosen so that fractionation does not exist or it is similar in the standard and sample [55, 61].

Gagean and Mermet [61] reported Cu and Zn calibration from a series of brass standards using LA-ICP-AES. An enhancement of Zn signal intensity with increasing Zn concentration in the brass resulted in a non-linear calibration plot. Borisov et al. [55] reported that this behavior was related to changes in the amount of ablated material. Good calibration for the analysis of Cu-Zn binary alloys (commercially available, Glen Spectra References Materials) was possible when signal normalization was used. Two normalization procedures were used, one in which Cu was used as an internal standard and another in which the amount of mass was measured (the amount of ablated mass was determined by measuring ablation crater volume with a white-light interferometric microscope). The principal disadvantage is the difficulty in determining the precise amount of ablated mass from micron-sized craters.

Craig et al. [54] evaluated three calibration strategies for the quantitative determination of trace elements in natural CaCO₃ matrices. These strategies included: 1) commercially available glass calibration standards; 2) high-purity CaCO₃ powder spiked with trace element standard solutions; and 3) geological reference materials with a predominantly CaCO₃ matrix. They also evaluated calcium and indium as internal standards to correct for differences in ablation efficiency, and to compensate for differences in physical and chemical properties between samples. Indium was added with binder to fabricate synthetic pressed-pellet. However, the indium showed large (> 50%) variations in signal response from one ablation site to another, in contrast to the behavior of other trace elements. Calcium, a major component of the geological samples, was used directly as an internal standard. Both short-term precision and long-term reproducibility were improved using Ca.

Calibration curves have been plotted using internal standardization for a **suite** of glasses and **pressed pellets** [54]. For the synthetic pressed-powder pellets, calibration data were linear, with R^2 values more scattered than those measured for the glass standards. Some elements in specific samples, for example Mn and Fe in DWA-1 (**Table 1**), measured higher than **nominal values, whereas** the same elements in NIST-1b **measured** low. **Synthetic pressed-powder pellets were not sufficiently similar in either physical structure or chemistry to be ablated in the same way as the natural materials.**

Leach and Hiefje [62] **described** two data analysis techniques for improving single shot measurement precision. Both **techniques** employed the simultaneous full-spectrum acquisition capability of a time-of-flight mass spectrometer. The first approach was an extension of internal standardization. Instead of generating a ratio of an analyte signal to that of a single reference element, the entire mass spectrum was summed to yield a value that should be proportional to the total mass ablated. This approach resulted in **a precision improvement greater than two**, better than was possible with a single internal standard. The enhancement in measurement precision was found to be concentration dependent, with the greatest improvement **measured for** high concentration elements. The second method correlated the attenuation of plasma matrix ions to analyte intensities. This attenuation technique demonstrated no statistically significant improvement in precision, which was limited by the relatively low signal-to-noise ratio of the attenuated signals.

In general, challenges remain for both external and internal calibration **procedures**. External calibration is difficult due to the fact that an exact sample match is not an easy task. Internal standardization is limited by the requirements of one element present or added with known concentration. Also, **elements used as the internal standard** need to be homogeneously distributed and behave similarly with the majority of other analytes during the laser ablation process.

3.2 Dual Introduction (Sample-Standard)

It would be favorable, if possible, to have a calibration method that did not require the reference standards to be introduced by laser ablation. A calibration technique developed by Thompson et al. [63] involved the use of two sample introduction channels to obtain matched plasma conditions, **one for the ablated material and another for nebulized aqueous solution standards**. Figure 4 shows a diagram of a dual sample introduction system. Cromwell and Arrowsmith [64] applied this method for semi-quantitative analysis with LA-ICP-MS. **They studied Fe in steel and Ba in glass (Standards References Materials, SRMs); the difference between measured and certified concentrations was less than $\pm 40\%$ for most elements**. The relative atomization and ionization efficiency, as well as instrument response of elements introduced into the plasma as aqueous solvated ions, were similar to those for elements introduced as solid micro-particulates by laser ablation.

Falk et al. [65] used a 250 mg/L Cu solution, with a series of increasing amounts of elements to be analyzed. The spike concentrations were 0, 0.5, 1, and 5 $\mu\text{g/L}$, which were equivalent to a concentration in a solid sample of 0, 2, 4, and 20 mg/kg. The results based on the

percentage of recovery – measured (mg/kg) / given (mg/kg) – were good (the mean value 106.8%). The slightly higher value of the measurements was attributed to fractionation during the laser ablation process.

Mao and Russo [66] reported optimization and calibration of LA-ICP-AES by measuring vertical spatial intensity profiles. Because the excitation mechanism and ICP response will be different for aqueous solution nebulization and laser ablation sampling, it was necessary to characterize the ICP response for these two cases before using solutions as standards. The vertical spatial profiles were not always the same for laser ablation and solution nebulization, even if all ICP operating conditions were constant (e.g., total gas flow, rf power, and amount of water to maintain similar excitation characteristics and temperature spatial profiles). Hilbert space distance was used to quantify the difference between two emission intensity profiles; the smaller the distance value, the more similar the profiles. The difference between laser ablation and solution nebulization of standards was calculated for different gas flow rates and rf powers. The authors found that at a gas flow rate of 0.2 l/min, the difference between laser ablation and solution nebulization was approximately 0.05, i.e., the spatial profiles for the above two cases were essentially identical. They concluded that by measuring vertical spatial emission intensity profiles, ICP-AES operating conditions can be established for optimized response during laser ablation sampling process, and that the influence of rf power on emission intensity was not as sensitive as gas flow rate for the elements investigated.

Horn et al. [38] described a method to correct mass discrimination of the instrument using combined solution nebulization and laser ablation sample introduction with ICP-MS. They

studied U-Pb geochronology and found that two mechanisms **caused** deviations from the “true” ratios, instrumental mass discrimination and laser-induced elemental fractionation. The first mechanism occurs in all spectrometers and is typically corrected either by a comparison with an internal standard measured under the same experimental conditions (e.g., in Hf and Nd isotopic analyses, where at least two isotopes are non-radiogenic), or by a comparison to a multi-isotopic element of similar atomic mass that is present in the analyte (e.g., using Tl isotopes to correct for Pb mass discrimination).

To correct for instrumental mass discrimination, which is generated by space charge effects in the sample-skimmer cone region and the ion transfer optics, external mass discrimination was applied [38]. A solution containing a known amount of Tl and ^{235}U (enriched to 99.9% ^{235}U) was continuously nebulized and mixed with the laser ablation gas flow. Ablation was described as mainly photolic (**non-thermal bond breaking by direct photodissociation**) as all elements should be ablated from the sample into a vapor plume with the same efficiency. The authors demonstrated that a combined solution nebulization and laser ablation sample introduction technique could be an accurate and precise micro-analytical tool for in situ isotope ratio determinations of minerals. They compared their results to that of SHRIMP (sensitive, high-resolution ion micro-probe) and achieved an analytical precision of ~2% RSD.

Bi et al. [67] described a solution calibration method by matching the signal intensity of a matrix element with a solution of a known concentration. Metal samples were considered, **although** the feasibility of applying solution-based calibration to more complex matrices, such as NIST soil and glass, was explored. The authors introduced three normalization factors: 1)

correction for variation in ICP-MS operating conditions; 2) correction for the response of each element measured in the solid sample by solution standard and correction of laser power variation; and 3) correlation of signals from solution and solid for the calibration of trace **elements** in the solid. By analyzing NIST soil (Pb, V, Ba, Cr, Zn, Cd, and Sb) and NIST glass (Ni, Cu, Rb, Ag, and Co), they found that the measured values were **within $\pm 10\%$ of the certified values**. The method was not capable of accurately measuring concentrations below 10 ppm in soil samples. Several elements exhibited different behavior in soil and glass samples. Poor accuracy was observed for Cu and Ni in soil samples, whereas good results were obtained for these elements in glass samples. The cause of the error was believed to be due to the heterogeneity of **elements** in the sample. The limitation of the method is that an internal standard of known concentration must be present in the solid sample.

The use of nebulized aqueous standards is an attractive alternative **to finding matrix-matched solids**. However, the plasma produced with laser ablation is “dry” relative to the plasma produced using a “wet” sample introduction system, such as a conventional nebulizer. Therefore, analyte response from the two introduction methods can differ to some extent, and the benefits of using a “dry” plasma, such as reduced oxide interference, are lost. If the solution aerosols are desolvated before they reach the plasma, the response from the calibration aerosol should be closer to that of a “dry” sample introduction source.

Gunther et al. [52] reported that signal intensity was improved by a factor of 10 using “Mistral” nebulization compared instead of liquid nebulization. They suggested that these results were due to low molecular interferences (e.g. oxide formation) compared with liquid

nebulization. However, high RSDs were measured for Mistral nebulization, this behavior was mainly the result of poor stability of the nebulizer. They proposed that more effective desolvation and detailed studies of air entrainment could lead to more sensitive dual gas flow systems.

Leach et al. [68] used dried solution aerosols to calibrate LA-ICP-MS. The solution standards were introduced by flow injection to the baseline of ions produced by laser ablation. An ultrasonic nebulizer with desolvation was employed. The method could essentially be thought of as standard additions, with nebulized solution pulses serving as the “spikes”. By observing that solid particles from the sample behave like dried particles from the calibrant solution, the sensitivity could be optimized using only standard solutions introduced through the nebulizer.

3.3 Direct Liquid Ablation

Gunther et al. [69] demonstrated direct liquid ablation as a calibration strategy for LA-ICP-MS. They used different solutions for quantitative analyses of NIST 610 and 612 glasses. Na (all elements) and Yb (rare earth elements only) were used as internal standards. 75 out of 96 determinations were within 10% of the expected values. Yb as an internal standard showed no significant difference compared to the values based on Na. To explain the similar ablation behavior of liquids and solids, particle size distributions were measured and the contribution to the total ablation volume was calculated. The particle size distribution from ablation was dominated by small particles, whereas, a broader particle size distribution was measured for solution ablation. For solution ablation, approximately 90% by volume of droplets were between

3 and 10 μm , and the signal suggested complete ionization of all droplets. Good linearity over more than 4 orders of magnitude was measured in concentration.

Boué-Bigne et al. [70] described a new method of calibration for quantitative analysis using LA-ICP-MS using aqueous standard solutions. Optical absorption characteristics of the solutions were modified by the addition of a chromophore in order to obtain a desired degree of ablation. The authors studied 1) plasma conditions for ablating standard solutions, 2) optimization of modified standard solutions, 3) ablation mechanisms of the solutions, and 4) the application of this method to the analysis of NIST 613 and low density polyethylene (LDPE). The purpose of the chromophore was to improve laser energy coupling to the aqueous solution in such a way that the threshold ablation fluence was reached within the surface layers of the liquid, thereby producing a fine aerosol. The ideal chromophore should have the following characteristics, it should absorb strongly at the lasing wavelength; it should not precipitate in contact with the analytes; and it should be non-toxic. The amount the chromophore needed depended on the concentration of the analytes. The principal advantage of this method was that the standard offered a renewable surface of fresh solution for each laser pulse. All calibration curves had a correlation coefficient greater than 0.993. The data for analysis of LDPE and NIST reference materials, along with data obtained using other methods, are presented in table 1.

The calibration schemes for laser ablation chemical analyses reviewed above provide a framework for recent advancements, consisting of only a small set of the overall research efforts. Table 2 shows some typical results from publications representative of different calibration

methods. Several authors including this group have generated more complete surveys of calibration methods [1,2,5,71].

4. Elemental fractionation during laser ablation sampling

Significant research efforts have addressed understanding and eliminating elemental fractionation, a situation in which the composition of the mass analyzed is not representative of the bulk sample [1-6]. Fractionation can occur during the laser ablation process, during transport of the ablated sample to the ICP, and within the ICP itself. Fractionation has been an area of intense investigation, and recent publications indicate that fractionation can be classified into four categories.

4.1 Intrinsic fractionation

Fractionation is element dependent; therefore, attempts have been made to correlate fractionation with elemental properties such as melting, boiling, vapor pressure, atomic or ionic radius, charge, and speciation [13-15,72-74]. Chan et al. [75] monitored KrF pulsed-laser ablated materials from Bi-Sr-Ca-Cu-O superconductors. They found that the elements with lower-melting-point oxides (Bi_2O_3 and CuO) were enriched in the vapor phase. Outridge [76,77] and co-workers examined the ablative and transport fractionation of trace elements during infrared (1064nm) laser ablation of glass, mammalian tooth, and copper samples. They related fractionation with elemental melting and boiling points. Liu et al. showed [19] an inverse logarithmic relationship between the fractionation index and oxide melting temperature during laser ablation of glass using Nd:YAG lasers with both 266 and 213 nm wavelength (figure 5). Fractionation index is defined as the change in elemental ratio with time as a crater is developed

at a single sample location (using a repetitively pulsed laser). The second half of the time signal is divided by the first half, and normalized to the Ca signal. Jeffries et al. discussed a relationship between fractionation and ionic radius, charge, and melting temperature of elements using IR and UV lasers [18]. Using IR laser ablation, the degree of fractionation in rare elements (REE) was strongly correlated to ionic radii. Chen found that fractionation depended on the sum of first and second ionization enthalpies (figure 6). More low ionization energy elements were found in the ablated mass than high ionization energy elements [59]. Fryer, et al. [78] characterized fractionation behavior for a wide range of elements and showed that a number of different chemical matrices generally followed Goldschmidt's geochemical classification of elements (figure 7). Longerich et al. [79] found that elements fell into several distinct clusters within which the elements correlated well with each other and could be determined using an internal reference element in the same cluster. Elemental speciation or chemical form may also contribute to fractionation. Mermet [80] and Winefordner [81] discussed fractionation during laser ablation of Mg and Ba compounds with different chemical forms.

Fractionation also is a function of laser beam properties (laser irradiance, pulse width, wavelength, etc). Brass was used to study the influence of laser beam properties on fractionation owing to the largely different latent heat of vaporization of Cu and Zn [55]. The influence of laser beam properties on Zn/Cu fractionation was investigated [25]. Zn/Cu fractionation showed a strong dependence on laser irradiance, but the extent was dramatically different for lasers with different pulse durations. Different mechanisms influence ps and ns laser ablation. Using a 30 ns pulse from an excimer laser (KrF, $\lambda = 248$ nm), thermal vaporization appeared to be the dominant process in low irradiance regions. The Zn/Cu ratio approached stoichiometry at higher irradiance but the ablated mass still

remained Zn rich. Using a 35 ps pulse Nd:YAG laser with wavelength $\lambda = 266, 532, \text{ and } 1064 \text{ nm}$, respectively, the Zn/Cu ratio was smaller than the stoichiometric value at low laser irradiance (figure 8). Because Zn is easier to vaporize than Cu, a small Zn/Cu ratio implies that a non-thermal mechanism **governs** the laser ablation process for ps laser ablation. When using a 3 ns Nd:YAG laser with wavelengths $\lambda = 266, 532, \text{ and } 1064 \text{ nm}$, both thermal and non-thermal processes exist. For both 3 ns and 35 ps Nd:YAG lasers, stoichiometric ablation could be achieved at high laser irradiance. Preliminary research using femtosecond lasers for analytical spectroscopy has only recently been reported [28,29].

Wavelength influence on fractionation was more significant for ns lasers (particularly in the low irradiance range) than for ps lasers, and the shorter wavelength tended to provide better stoichiometry. The laser pulse duration is a critical factor controlling fractionation of the ablated mass. A possible explanation is that for shorter laser pulse duration, less laser energy is lost through thermal dissipation, which is a function of pulse duration [82]. More laser energy can be converted to ablated mass with shorter pulses. A reduced thermal contribution is beneficial for reduced fractionation as an increasing amount of evidence indicates the elemental fractionation is thermally related.

Fractionation as a function of **laser irradiance during ablation** of NIST 610 glass using a YAG laser at 266 nm wavelength was studied; the data in the form of Pb/U ratio are shown in figure 9 [19]. The $^{206}\text{Pb}/^{238}\text{U}$ ratio initially decreased with increasing laser irradiance, but stabilized for irradiance greater than $\sim 0.6 \text{ GW/cm}^2$, at which the value was close to the reference value of 0.2249. Thermal vaporization [83] is a possible mechanism to explain the observed behavior. Laser irradiance is an important factor underlying Pb/U fractionation, and a value of

laser irradiance greater than $\sim 0.6 \text{ GW/cm}^2$ was necessary to obtain Pb/U stoichiometric ablation in this case.

The wavelength influence on elemental fractionation has been investigated extensively [13-19]. Wavelengths that have been used for laser ablation include 1064, 532, 355, 266, and 213 nm from Nd:YAG lasers, 694 nm from the ruby laser, and 308, 248, 193, and 157 nm from excimer lasers. Many investigators reported reduced fractionation with the use of UV lasers compared to the IR laser [13,18]. Gunther et al. [17] found that elemental fractionation was insignificant with the 193 nm excimer laser, whereas the Nd:YAG 266 nm produced significant time-dependent fractionation [17]. **It has not been established whether the advantages of 193 nm were related to higher photon energy or due to different beam homogenization and focusing conditions.** 266 nm may be as suitable as 248 and 213 nm for opaque samples. **Preliminary experiments by Russo et al using an F₂ laser at 157nm did not show improvement in fractionation for opaque samples [84].** However, 157 nm gave closer stoichiometry for transparent calcite samples. The fifth harmonic of a Nd:YAG laser (213 nm) was demonstrated to improve stoichiometry for a transparent calcite samples [18]. Fractionation of Pb and Bi from NIST 612 glass was reduced using the 213 nm laser compared to using 266 nm [18]. **In general, fractionation is related to the optical properties of the sample, the wavelength of the laser and significantly, the laser irradiance.**

4.2 Crater influence

The crater depth and its aspect ratio influence fractionation. Fractionation was observed with deep craters for both 266 nm Nd:YAG and 248 nm excimer lasers [85]. **Time dependent Pb/U ratios changed as the crater developed during repetitive laser pulses at a single sample**

location. The inset of figure 9 shows the time profile of three data sets with similar laser irradiance ($\sim 1.5 \text{ GW/cm}^2$) using Nd:YAG laser pulses at 266 nm, but different focusing conditions. The laser beam was focused below, above, and at the sample surface, respectively for the three data sets. The corresponding laser beam radii on the target surface was 57, 63 and 28 μm , respectively. Although the laser irradiances for the three different cases were almost the same, time-dependent Pb/U fractionation was observed to be different due to the formation of craters with different aspect ratios [19].

With a reduced laser-beam spot size and constant laser energy (increased laser irradiance), crater geometry after the same number of pulses changed from a flat-bottomed configuration, with shallow depths, to an increasingly convoluted profile. In the later case, the ablation crater deepened and the ratio of crater depth versus radius increased. As the crater aspect ratio increased, the surface area of the crater wall increased. As a consequence, the laser irradiance on the side-wall of the crater was smaller than that at the crater bottom. **Because** fractionation on the nanosecond timescale is related to the thermal properties of the sample, as the aspect ratio increased, mass removal resulting from thermal effect at low irradiance dominated the ablation process causing larger fractionation [32].

In an investigation of the effects of laser defocusing on fractionation in brass [86], laser power was unchanged while the defocus distance of the ablation laser beam was varied from 200 to 1100 μm . It was found that a significant degree of fractionation occurred with brass for defocus conditions below 400 or above 700 μm . Implemented in this study was a multivariate technique that was capable of statistically matching or differentiating solid samples analyzed by LA-ICP-MS.

Eggins et al [15] discussed the influence of crater geometry on elemental fractionation during repetitive ablation at a single spot on a glass sample. With an increase in the number of laser pulses, the geometry of the crater changed from “flat-bottom” to “cone-shape” (figure 10). At shallow ablation depths, volatile-element signals increased whereas at greater depth, refractory element signals increased. SEM examination of the ablation spot and the surrounding ejected material revealed sequential condensation of the refractory and volatile phases from the cooling plasma plume. The authors suggested that the ablation processes were primarily photo-thermal near the sample surface, but changed to a plasma-dominated mechanism at greater depth.

Mank et al. [85] reported that fractionation became significant for some elements (e.g., Zn and Pb) when the depth / diameter ratio of the ablation crater was greater than 6. Reduced elemental fractionation as well as high signal intensity was measured for craters with large initial diameters. Ingo et al. [87] found that fractionation of Pb versus U was a linear function of the pulse number (crater depth), and was inversely exponentially correlated with the crater size. Based on these measurements, an empirical method was proposed to correct elemental fractionation during laser ablation.

An exact mechanism for crater effects on fractionation is not established. One hypothesis is that a plasma confined inside a deep crater may contribute to the sampling process, leading to fractionation. Another possibility is that actual irradiance decreases as the crater deepens due to changes of effective area exposed to the laser beam. A model was developed to explain the change in irradiance with crater development [32]. This model demonstrated how actual irradiance decreased as the crater deepened due to a larger surface area of the crater. According to this model, when the actual irradiance decreased below about 0.2 – 0.3 GW/cm², fractionation became significant.

4.3 Transport process

Fractionation can occur during transport and involves selective vapor condensation on tubing walls, or selective nucleation of species on different sized particle [76,88,89]. Particle morphology as well as chemical composition governs these effects; transport efficiency and chemical composition is particle size dependent (figure 11). Figg et al. [89] demonstrated this effect by inserting a coiled Tygon tube into the transport path. Both particle size distribution and fractionation changed significantly. Large particles are believed to result from melt flushing of the heated liquid layer. The composition of molten liquid can be significantly different from the bulk. Outridge et al. [76] showed the presence of particles significantly enriched in certain elements from laser ablation of NIST 610-glass and mammal tooth, using scanning electron microscopy (SEM). Elements enriched in the particles included Pb, Bi, Zn, Au, and Ag. Recent investigations using single shot ablation showed that the particle-induced spike signal in the ICP-AES is closely related to the thermal properties of elements (figure 12).

The size distribution of particles that are transported into the ICP has been calculated to range from 2 nm to 5 μm in diameter [35]. Vapor as well as clusters smaller than 2 nm in diameter may diffuse to the walls of the chamber and transfer tube. Large particles ($>5 \mu\text{m}$) may settle out because of gravity [90]. Particle size distribution was found to change with laser irradiance. The particle entrainment efficiency as a function of laser irradiance was estimated by Jeong et al. [91] in the irradiance range of 1 ~ 13 GW/cm^2 using a Nd:YAG 266 nm laser. The entrainment efficiency was ~ 25% at lower irradiance and it decreased to ~ 5% at high irradiance. The reason for the decrease of entrainment efficiency at high irradiance could be the formation of excessively large particles ($>10 \mu\text{m}$) due to phase explosion during laser ablation.

Yoo et al. [92] found increased entrainment efficiency at even higher irradiance during laser ablation of silicon (figure 13). They proposed that strong absorption of the incident laser light by the plasma could create a high temperature and pressure region through which the particulates must traverse. The plasma temperature can reach 10,000 K, 400 ns after the laser pulse [23]. Large particulates, upon interacting with the hot plasma, can break into smaller particulates that will be **more efficiently** entrained and transported.

4.4 Fractionation and matrix effects in the ICP

The ICP also can **contribute to** elemental fractionation, dependent on the size distribution of the particles [88,89]. The largest particles that can be completely vaporized by a typical ICP are estimated to be 10-20 μm [93]. Particle transport studies by Arrowsmith et al. [35] indicated that particles greater than 5 μm could rarely be carried into the ICP. Knight et al. [94] reported incomplete **decomposition** for 3~7 μm sized particles in the ICP using time-resolved ICP-AES. The work by Figg et al. [88,89] showed that incomplete ionization in the ICP might contribute to elemental fractionation for some elements.

Matrix effects on ICP conditions were studied during laser ablation sampling [95,96]. The effects of Ca, Sr, Li, Na, K, Mg, and Al matrices on the ICP conditions (temperature and electron number densities) were investigated. **Element specific matrix effects were found**. Matrix elements with lower second ionization potential than the first ionization potential of Ar showed severe matrix effects (figure 14). Complete replacement of Ar by He as the carrier gas reduced these matrix effects significantly. Increasing the forward power however had little effect in reducing **such** matrix effects. The interference mechanism is not understood and may involve the interaction between doubly charged matrix ion and argon species [96].

5. Gas effects

The effect of carrier (or entrainment) gas on laser ablation have been investigated to improve analytical performance. Increased sensitivity and transport efficiency have been reported using helium or helium mixed with argon to flush the ablation chamber [15, 17, 97]. Eggins et al. [15] studied ablation with an ArF excimer 193 nm laser in a helium atmosphere and showed a 2 to 4- fold gain in sensitivity. **Residual deposition around the ablation crater surface was greatly reduced.** Gunther et al. **reported enhanced sensitivity in laser ablation ICP-MS using helium and argon as carrier gases [17, 97].**

The effects of five noble gases (He, Ne, Ar, Kr, and Xe) on nanosecond and picosecond laser ablation process were studied using ICP-AES [98-100]. The noble gases significantly influenced laser ablation sampling efficiency and ICP excitation. There was enhancement in the ICP emission intensity for laser ablation sampling in He and Ne, and depression for Kr and Xe relative to Ar. The extent of the gas effect on laser ablation efficiency had a direct correlation with the ionization potential and an inverse correlation with the atomic mass of the gas.

The gas enhancement or depression was found to be laser irradiance dependent **using** the 30 ns excimer laser with 248 nm wavelength. The greatest effect, a factor of approximately 2.5-fold enhancement in emission intensity occurred in He at irradiance of 0.25 GW/cm^2 . In support of the enhanced ICP-AES data, crater volumes were measured to be larger in the He atmosphere. A factor of 6-fold enhancement in emission intensity was observed using picosecond laser ablation in He. However, there was very little influence on the mass ablation behavior for other gases using picosecond laser pulses. The influence of gas and laser irradiance was different for the nanosecond and picosecond pulse cases. In the nanosecond case, the enhancement was

reduced as the irradiance increased, whereas the enhancement was improved with increasing irradiance for the picosecond case.

Mass ablated was also dependent on the gas pressure [101]. The difference in vaporized weight from a sample ablated in Ar and He atmosphere was significant in the pressure region 100~760 torr. The amount of ablated sample was much lower in the Ar atmosphere.

Plasma shielding, which reduces the laser energy coupling efficiency onto the sample, is a possible mechanism to explain **gas effects**. The degree of plasma shielding depends on the ionization potential of the gas species [102]; a plasma can form more readily in easily ionized gases. **Ambient** gas with heavy atomic mass could reduce transport efficiency due to collisions of gas species and the ablated plume. The first ionization potential is 24.58, 21.56, 15.75, 13.99, and 12.13 eV with atomic mass 4, 20, 40, 84, and 131 for He, Ne, Ar, Kr, and Xe, respectively. Helium has the highest first ionization potential and lightest mass, therefore plasma shielding in He is expected to be much less than for the other noble gases. Other than noble gases, nitrogen was also reported to improve the sensitivity during LA-ICP-MS analysis [47,103,104].

6. Applications

Because of the unique advantages of laser ablation sampling, a growing number of LA-ICP-AES/MS applications for chemical analysis have emerged. A compilation of published applications was listed in a recent review [1]. This section presents **just** a brief overview of laser-ablation applications, primarily over the past four years. Most of the applications utilize ICP-MS because of its enhanced sensitivity.

6.1 Environmental applications

Tree ring

Spatial patterns in the chemical content of **tree rings can be used to monitor changes in** atmospheric conditions, soil chemistry, and pollution history. LA-ICP-MS is an excellent approach to determine chemical content in tree samples because of **the** high spatial resolution provided by a focused laser beam. The excellent sensitivity of LA-ICP-MS allows measurements of many elements at very low detection levels [56,105-107]. Watmough et al. [56] obtained quantitative multi-element analysis of 11 elements in red maple tree rings. Significant changes in these elements were measured for trees grown in contaminated soils adjacent to a metal smelter versus trees grown in unpolluted soils (figure 15). Schongberg et al. [107] analyzed pine and birch tree rings from Norway and Russia, and discussed the elemental relationship with the pollution history of these areas.

Tree bark

Large surface area of barks from many tree species enables the effective accumulation of pollutants; the analysis of bark can provide useful information about the degree of pollution of a certain region. **Narewski et al. determined Al, Ca, Cd, Ce, Cr, Cu, Fe, Mn, P, Pb, S, Ti, and Zn in barks using LA-ICP-MS [108].** Anthropogenic sources were responsible for the higher concentrations of most of the elements under investigation. **The elemental concentrations of a sampling area were between 20 and 30% RSD.**

Seashells

Trace-element fluctuations in seashells reflect environmental change and major pollution events. Raith [109] analyzed the inner to outer walls of a shell. Elemental changes between

growth-bands of the shell showed a history of heavy-metal pollution over the years. Van der Putten et al. [110] measured spatial variations of Mg, Mn, Sr, Ba, and Pb in the calcite layer of *Mytilus edulis* seashells.

Coral

The concentration of trace elements in coral skeletons provides **data related** to changes in seawater properties. Calcification in reef-building corals is strongly affected by environmental factors such as temperature, light, water motion, as well as pollution [111]. As coral grows, it secretes a calcareous skeleton into which trace elements are partitioned. Spatial analysis of the coral skeleton allowed a detailed investigation of seasonal composition changes [112,113]. Sinclair et al. [112] analyzed corals collected from Australia and showed that elements B, Mg, Sr, and U exhibited seasonal variations (figure 16). These fluctuations coincided with the changes of sea-surface-temperature (SST). Fallon et al. [113] measured the corals taken from Japan using a similar method as used in reference [112].

Airborne particulates

The analysis of trace elements in airborne particulates may provide unique signature information for monitoring air quality and pollution. For example, arsenic, considered the major ‘marker element’ of air pollution, is one of the most hazardous anthropogenic air pollutants affecting human globally. Traditionally, membrane filters with small pore **sizes** have been used for collecting particulate samples. The entire filter is then digested and the total volume analyzed. Laser ablation is a perfect alternative for such analysis; the particulates can be ablated

directly from the filter. Tanaka et al. [114] and Wang et al. [115-117] analyzed airborne particulates for more than 20 major, minor, and trace elements using this approach.

6.2 Geological Application

Geochronology

U–Pb geochronology is one of the principal dating tools used in the earth sciences. Ages are calculated by measuring $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. The conventional method for U–Pb isotopic analysis has been thermal ionization mass spectrometry (TIMS) with chemical separation. However, very low blank values are required and the data represent the ‘average’ of the bulk grains. LA-ICP-MS has the ability to perform spatially resolved in-situ analysis of U-Pb isotopic compositions in zircons and similar minerals. Several groups [87, 104, 118-120] studied zircon and monazite samples using LA-ICP-MS. Most of these studies only show $^{207}\text{Pb}/^{206}\text{Pb}$ data and a few include the $^{206}\text{Pb}/^{238}\text{U}$ ratio, because of fractionation. Without the $^{206}\text{Pb}/^{238}\text{U}$ ratio, the analysis cannot be extended to ‘young’ (< 600 million years) zircon dating.

A laser ablation sampling multi-collector magnetic sector ICP-MS was used to determine Zr isotopic composition of grains in meteoritic minerals [121]. An array of Faraday cups allowed simultaneous static mode collection and integration of the masses. The meteoritic mineral rutile and zircon have, respectively, very high and very low Nb/Zr ratios, which are ideal for exploring the ^{92}Nb - ^{92}Zr chronometer.

Inclusion Analysis

Microscopic inclusions in minerals provide direct evidence of the composition of fluids associated with large-scale material transport in the **earth's** interior. Quantitative knowledge of the elements and isotopic composition of these fluid inclusions is a prerequisite for understanding and modeling fluid–rock interactions. Detailed chemical information is difficult to obtain because of the very small size of these inclusions (typically 10^{-11} to 10^{-9} g) [122]. Crush–leach analysis or bulk analysis of quartz containing fluid inclusions can provide concentration ratios averaged over many inclusions, but most samples contain multiple generations of fluid inclusions of different compositions. LA-ICP-MS for the analysis of individual microscopic inclusion has received considerable attention. Good quantitative results have been published mainly for synthetic fluid inclusions [123,124], where a heavy trace element of a known concentration (e.g., Sr or U) was added as an internal standard. By using a stepwise opening procedure, Günther et al. [122] reported a method of measuring complex polyphase inclusions. A series of inclusions reflecting the fluid before, during, and after the deposition of cassiterite (SnO_2) in a tin deposit in Australia were analyzed by this method. Physical and chemical mechanisms of ore precipitation were proposed based on the measured data [125]. **Trace elements** of Ca, Sr and Rb in a single fluid inclusion in halite were quantitatively measured by LA-ICP-MS using an artificial fluid inclusion in micro-capillaries as standards [126].

Precise isotope analysis

Hf, W, Sr, U, Th, Pb, Os, are of significant interest for isotope geochemistry; **they** need to be measured at trace levels with high precision. Multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with a magnetic sector is a new technology for the measurement of isotopic compositions with high precision. It is particularly suited for elements,

such as Hf, W, and Os, with high ionization potentials. Combined with laser ablation sampling, in-situ isotopic measurements at the microscopic scale are possible. Although this technology is still in its infancy, diverse applications have already led to a number of important scientific developments [127].

The initial Hf isotopic composition is more reliable than the initial Nd as a geochemical tracer due to the immobility of Hf. Thirlwall et al. and Geiffin et al. [128,129] reported Hf isotopic composition analysis in zircon samples. Godfrey et al. studied the Hf isotopic compositions in iron-manganese nodules and crusts [130]. The ^{182}Hf - ^{182}W system is a method for constraining timescales of accretion and metal/silicate differentiation in planets. The age of the Earth's core, the Moon, and Mars have been measured using this new method [127].

Sr and Pb isotopic compositions are also important for geochemistry and oceanography research. Analyses of these elements traditionally require complicated chemical separation procedures. LA-MC-ICP-MS has provided accurate and precise measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in geological materials [131]. Pb isotopic compositions in a ferro-manganese crust from the Pacific ocean were analyzed by Chrestensen et al. [132]; these authors concluded that the Pb isotopic data could be used to probe climate-driven changes in ocean circulation.

Similarly, analysis of Os isotopic ratios for iridosmine samples was reported using laser ablation with MC-ICP-MS [133]. The mineral iridosmine has been used for the definition of the Os isotopic evolution of the mantle. Stirling et al. [134] reported a method for rapid, in situ measurement of U-Th isotopic composition using laser ablation sampling in combination with MC-ICP-MS. The use of He in the ablation cell significantly improved the sensitivity of Th, and reduced the fractionation between U and Th.

Bulk analysis

Several authors [135-137] have described the application of LA-ICP-MS for the analysis of whole-rock geological samples, such as pressed power pellets and lithium metaborate fusions. In most of these studies, measurements of rare-earth elements (Zr, Hf, U, Th, Sr, Rb, Ba, Nb, and Ta) were emphasized. The determination of trace elements in zeolites by LA-ICP-MS was reported by Pickhardt et al. [137]; three geological reference materials with a matrix composition corresponding to the zeolites were employed. Both the zeolites and reference materials were fused with lithium borate to increase homogeneity. LA-ICP-MS was also used to determine the platinum group elements (Ru, Rh, Pd, Os, Ir, and Pt) and gold which have very low natural abundance, but great economic and geological importance [138].

In situ analysis

The spatially resolved analysis of elements within minerals provides crystal-growth information and the variation in the physical and chemical nature of environments in which they grew. LA-ICP-MS analysis either on a single mineral grain or on a thin section can be applied to evaluate the homogeneity with a resolution of 50 μm [139]. LA-ICP-MS analysis on minerals such as calcite, zircon, olivine, plagioclase, feldspar, titanite, apatite, amphibole, and garnet have been reported [140-142]. Spatial resolution has also been applied to a set of iron meteorites to demonstrate the laser microprobe's capability for determining platinum group elements (figure 17) [143].

6.3 Archaeology applications

An analytical method for authenticity verification of precious antiques should be either non-destructive or require an extremely small sample quantity. Using LA-ICP-MS, visible damage can be restricted to an acceptable minimum, and with high spatial resolution (figure 18). Devos et al. [144,145] used laser ablation for analysis of antique silver objects. A sample chamber was specially designed, and almost invisible 100 µm craters were produced on antique silver objects. Zn, Cd, Sn, Sb, Au, Pb, and Bi were measured, with contents used to distinguish forgery in silver antiques. Devos et al. [145], and Wanner [146] described the analysis of early-medieval archaeological iron finds such as ancient coins, various antique silver, and ancient iron. By characterizing obsidian sources using LA-ICP-MS, information on the prehistoric trade activities in Mediterranean and the Near East was obtained [147].

6.4 Waste-sample analysis

Laser ablation has many advantages when used to analyze radioactive samples. For example, organic solvents or concentrated acids that are required for conventional radiochemical analysis are not necessary for laser ablation sampling. Also laser ablation requires much less sample (< 1µg), greatly reducing the risks associated with sample handling and sample contamination. Finally, elemental and isotopic analysis can be obtained entirely within a hot cell environment, further reducing the risk of environmental contamination [148, 149]. Smith et al. studied high-level waste analysis using LA-ICP-MS [150]. Long lived radionuclides were measured in a concrete matrix [151]. Applications of laser ablation and high-resolution ICP-AES in the nuclear industry, especially the high-resolution isotopic analysis of U and the determination of lanthanide were reported by Giglio et al. [148] and Zamzow et al. [152].

6.5 Other Applications

Fingerprinting

LA-ICP-MS is ideally suited for forensic chemical analysis, for identifying physical evidence that relates a suspect to a crime scene. Walting et al. [153] examined several kinds of glass and steel samples as physical evidence of a crime. Certain plants from a specific area or geological environment characterize uniquely the source of the plant. Walting [154] showed trace element ‘fingerprint’ patterns of cannabis crops and the association of these crops to specific geological environments.

Teeth analysis

LA-ICP-MS has been used for multi-element profile analysis of human teeth [155,156]. Investigations on Hg migration [157] and Ga diffusion across the human teeth using LA-ICP-MS were also reported [158,159].

Film doping and depth profiling

Li et al reported LA-ICP-MS for quantitative analysis of the dopant dose implanted in crystalline silicon wafers [160]. The penetration depths and vertical profiles of four commonly used dopant ions in the semiconductor industry, B, As, Sb, and P, were studied. This method could eventually be utilized as an industrial standard to calibrate ion implantation and to correlate the total dose level used in different integrated circuit fabrication processes. The depth profile of various titanium based coatings [31], tungsten carbide coatings [161], and tin-coated glasses [162] was reported using laser ablation ICP-MS and ICP-AES. The measured depth profile was comparable with that measured by secondary ion mass spectrometry.

7. Conclusion

This review provides an overview of laser ablation for analytical chemistry. Standard experimental systems of LA-ICP-AES and LA-ICP-MS, along with the challenges related to laser ablation calibration and fractionation have been emphasized. With ICP as an analytical source, laser ablation has proved to be one of the most powerful analytical tools that can nearly non-destructively determine an important number of elements with very low detection limits. Because of the unique advantages of laser ablation sampling, a growing number of applications of LA-ICP-AES/MS for chemical analysis have emerged; a variety of these applications have been discussed in this review. **With continued research to overcome the challenges, it is expected that laser ablation will find additional applications in analytical chemistry. Matrix independent sampling and quantitative analysis will be forthcoming.**

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Table 1: Elements concentration in selected reference materials. Concentrations in mg/g.

References values taken from [54,70].

Reference material	CCH-1 (Crinoidal limestone) [54]	GSR-6 (Limestone) [54]	NIST-1c (Argillaceous limestone) [54]	NIST-1b (Argillaceous limestone) [54]	NIST 613 (Glass) [70]	Polymer (non certified references material) / ICP-MS [70]
Ba	6.6	120	84	86		
Fe	1189	17625	3847	5246	51	
MgO (% m/m)	2.91	5.19	0.42	0.36		
Mn	54.2	465	194	1549		
Sr	284	913	254	1180	78.4	
Cr						51.9
Mg						51.6
Co						49.2
Zn						49.3
Sb						69.8
Pb						62.6
Cu					37.7	
Ni					38.8	
U					37.38	

Table 2: Different Calibration Methods for Laser Ablation

Standard	Sample matrix	Typ. Error ^a (%)	Conc. Range (%)	Require IS?
Wet aerosol ⁶⁴	Steel	6	1-0.1	Y
		10	0.1-0.01	
Desolvated aerosol ⁶⁸	Powdered glass	10	1-0.5	N
		13	0.5-0.1	
		32	>0.1	
Geological references standards ⁵⁴	CCH-1	12	See Table 1	Y
	NIST-1c	14		
	GSR-6	18		
	NIST-1b	19		
Pressed powder pellet ⁵⁴	CCH-1	36	See Table 1	Y
	NIST-1c	31		
	GSR-6	31		
	NIST-1b	37		
Ablated liquid ⁷⁰	Polymer	18	See Table 1	N
		NIST 613		

^a Typical error represents the average error for the determinations in each concentration range as reported.

Figure Captions:

- Figure 1 Schematic of a laser ablation system, using ICP-AES and/or ICP-MS detection.
- Figure 2 **White light interferometric microscope images and cross sections of craters in NIST 610 glass. a) and c) 193 nm laser ablation, b) and D) 213nm laser. 40 shots each.**
- Figure 3 **Flow chart for calibration strategies using with laser ablation sampling.**
- Figure 4 Experimental systems for dual sample introduction, (a) using a nebulizer and spray chamber for solution introduction, (b) using a desolvation unit.
- Figure 5 **Fractionation versus wavelength. (a)** correlation between oxide melting temperature and fractionation index for 213 nm laser ablation; **(b)** relationship between fractionation index and logarithm of oxide melting temperature for 213 nm laser ablation; **(c)** correlation between oxide melting temperature and fractionation index for 266 nm laser ablation; **(d)** relationship between fractionation index and logarithm of oxide melting temperature for 266 nm laser ablation.
- Figure 6 Relationship between the **Internal Standard Normalized Fractionation Factor (ISNFF)** of elements and the sum of first and second ionization enthalpies in NIST 613 matrix. Reproduced with permission from Ref. 59.
- Figure 7 Fractionation Indices for 59 elements. The Fractionation Indices were determined from a 4 minute ablation of silicate glass and defined as the ratio of the calcium normalized signal in the second 2 min of the ablation divided by the calcium normalized signal in the first 2 min of the ablation. The Fractionation Indices were, therefore, a measure of the fractionation of each element relative to

calcium, a value of 1 indicating no relative fractionation. Reproduced with permission from Ref. 1.

Figure 8 Zn/Cu ratio as a function of laser irradiance using a Nd:YAG laser with a 35 ps pulse width and wavelength 266, 532, and 1064 nm.

Figure 9 Pb/U fractionation versus irradiance for 266 nm laser ablation. The schematics of laser irradiance change: ● laser focal point fixed, energy varies; ■ laser energy fixed, focal point varied below the sample surface; ▲ laser energy fixed, focal point varied above the sample surface. The inset shows Pb/U temporal profiles for three different cases, with the laser beam focused below, on, and above the surface. The laser irradiance was $\sim 1.5 \text{ GW/cm}^2$ for all three cases in the inset.

Figure 10 SEM images showing the development of crater morphology versus number of pulses at a constant fluence of 13 J/cm^2 . NIST 612 glass. Reproduced with permission from Ref. 15.

Figure 11 Elemental fractionation during ablation and transport for NIST C1253 Phosphorized Copper. Element concentrations normalized against Cu. Reproduced with permission from Ref. 76.

Figure 12 Relation between the particle-induced spike signals to the elemental thermal properties.

Figure 13 Ratio of ICP-MS intensity to crater volume versus laser irradiance.

Figure 14 Percentage ratio change of ZnII (206.20 nm) to ZnI (213.86 nm) emission lines in the ICP versus the amount of matrix, CaF_2 , MgO , and Li_2CO_3 .

Figure 15 Copper (A) and zinc (B) concentrations in red maple tree cores determined by LA-ICP-MS. Relationships between normalized integrated signal intensities of

^{63}Cu and ^{64}Zn , and respective Cu (mg kg^{-1}) ($r^2 = 0.999$) and Zn concentrations (mg kg^{-1}) ($r^2 = 0.999$) in wood calibration standards are included. Reproduced with permission from Ref. 56.

Figure 16 Trace element and sea-surface temperature (SST) profiles for coral from Australia's Great Barrier Reef. Data represent average of three trace element profiles measured over the same coral track. Black lines are SST data taken from a weather station. B, Mg, Sr, and U all display clear seasonal variation. Ba does not show seasonality. Reproduced with permission from Ref. 112.

Figure 17 Concentration profiles of Ru (square), Rh (diamond), and Pd (circle) across a taenite lamella in Grant IIIB iron. Reproduced with permission from Ref. 143.

Figure 18 Five rows of engraved circles on an early medieval iron tool fragment indicating the spots to be analyzed by LA-ICP-MS. Row 1: layer between welding seams; row 2: alongside a lenticular iron enclosure; row 3: lenticular iron enclosure; row 4: close to the upper sample surface; row 5: close to the lower sample surface. Reproduced with permission from Ref. 145.