Direct analysis of solid samples by fs-LA-ICP-MS

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We review the emerging potential of femtosecond laser-ablation inductively-coupled-plasma mass spectrometry (fs-LA-ICP-MS) for the direct analysis of solid materials. Although LA-ICP-MS has been widely explored and is highly accepted for the determination of major and trace elements, as well as for the measurement of isotope ratios, it still suffers from several limitations that restrain its development as a potential alternative to other, more established techniques.

The occurrence of non-stoichiometric effects in the transient signals, defined as elemental fractionation, together with the lack of reference materials for the wide variety of samples of interest often restricts the quantitative analysis to a few elements of identical fractionation behavior. In this sense, significant improvements in the processes responsible for fractionation effects have been recently observed with the use of ultra-short laser pulses. The confinement of pulse energy guarantees better performances in spatial resolution and improves the analytical figures of merit.

This review aims to summarize the main differences between the LA mechanisms of short (>1 ps) and ultra-short (<1 ps) laser pulses based on fundamental understanding of the LA process and the most relevant parameters governing the quality of analysis. In order to show the state of the art in fs-LA-ICP-MS, we present a variety of examples for elemental and depth-profiling analysis of solid samples in biological, geological, and materials applications.

Keywords: Femtosecond; ICP-MS; Inductively-coupled-plasma mass spectrometry; Fractionation effect; LA; Laser ablation; Particle size distribution; Ultra-short laser pulse

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1. Introduction

Laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) has been widely investigated as a powerful analytical technique for the direct analysis of solid samples since 1985 [1]. The increasing need to characterize complex solid specimens, including environmental wastes, geochemical materials, coatings, and semiconductors is forcing the development of LA sampling for chemical analysis as this technique allows the characterization of solid materials both in bulk and in spatially resolved analysis [2]. In the latter case, the focused laser beam permits the spatial characterization of heterogeneities in solid materials with lateral and in-depth resolution in the low-μm and nm range, respectively (e.g., microanalysis, in-depth profiling, and surface mapping). In addition to the important advantages of ICP-MS (robust, rapid, and precise analytical technique for simultaneous element determination with very low limits of detection (LODs)), LA offers simple solid-sample introduction with rapid sample throughput, which is important for direct routine measurements on solid materials. Moreover, LA does not require complicated sample-preparation procedures, so the risk of contamination or sample loss can be avoided. These particular characteristics, as well as the reduction observed in the spectral interferences compared to conventional pneumatic nebulization, make LA-ICP-MS a very attractive alternative for the analysis of solid samples.

Conceptually, LA is a simple, straightforward process [3]. A short-pulsed, high-power laser beam is focused into the sample surface in an inert gas atmosphere (e.g., Ar) under normal pressure. The laser beam instantaneously converts a finite volume of the solid sample into a vapor-phase aerosol of the constituents, which is transferred by an Ar-gas stream into the ICP ion source of the ICP-MS instrument. The laser-generated aerosol is then vaporized, atomized, and ionized. Finally, the positively-charged ions can be analyzed using different types of mass spectrometers (e.g., quadrupole, time-of-flight (TOF), magnetic sector field, or multicollector). The analytical performances of LA-ICP-MS analysis are given by the amount and stoichiometry of the laser-generated aerosol, its degree of vaporization, atomization and ionization in the ICP, the transmission of the ions through the vacuum interface, and the ion optics of the mass spectrometer.

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The main sources of error in LA-ICP-MS analysis therefore arise from the following processes:

- the LA process itself;
- the aerosol formation;
- the aerosol transport; and,
- the atomization and ionization in the ICP.

All these factors, together with the chemical and physical properties of the samples, are important considerations for the successful use of the LA-ICP-MS technique [4].

However, one of the main limitations of LA-ICP-MS, and basically all laser-based sampling techniques, is the occurrence of non-stoichiometric effects in the transient signals, defined as elemental fractionation [5–7]. Moreover, matrix effects, non-linear calibrations, and the lack of certified reference materials (CRMs) for the majority of samples of interest are other possible limitations of LA-ICP-MS. The experimental parameters used for the LA process determine the amount, the composition, and the particle-size distribution of the aerosol released for a given sample, so the influence of such parameters has been widely investigated in recent years in order to understand better and to minimize these limitations. Most of the work carried out so far has been focused on the sampling process in terms of the laser wavelength (infrared (IR) *versus* ultraviolet (UV) wavelengths [8,9]), the pulse duration (nanosecond (ns) *versus* femtosecond (fs) LA [10–12]), the LA carrier gas (Ar *versus* He or Ne [13,14]), and the LA cell design [15,16] as significant parameters, which play important roles in the properties of the laser-generated aerosol. Although no significant changes have been made in the well-established ICP source for direct solid sampling using LA, new instrumental developments both on the MS and on the laser side always yield new insights and applications.

The developments carried out in the laser area have mainly been driven in two directions: shorter wavelengths; and, shorter pulses [17]. Both aimed at unifying the idea of better localization of the LA event and, consequently, a more efficient, defined use of the laser-pulse energy delivered. In this sense, there are undeniable reasons to investigate the ultra-short regime for LA as differences in laser-matter and laser-plasma interactions. Ultra-short (<1 picosecond (ps)) laser pulses offer very high photon intensities ($>10^{14}$ W/cm^2) with a pulse duration shorter than many fundamental time-scales (phonon vibrations), so LA on the fs time-scale is predominantly non-thermal, causes less collateral damage than longer pulses and has the potential to eliminate fractionation effects and matrix dependence. Furthermore, fs-LA provides smaller particle sizes for aerosols and no laser-plasma interactions, so that it improves the analytical figures of merit and guarantees a better spatial resolution in all dimensions [18].

This review summarizes current LA research in the field of analytical chemistry focusing on fs-LA-ICP-MS. We give a detailed description of fs-LA instrumentation, as well as its capabilities in direct analysis of solid samples. Moreover, we describe fundamental studies on laser wavelength, particle-size distribution, aerosol composition, and calibration procedures, and give several illustrative applications of fs-LA-ICP-MS to biological, geological, and metallurgical samples.

2. Femtosecond laser ablation (fs-LA)

2.1. Introduction

LA-ICP-MS is considered one of the most versatile techniques for element-selective analysis of solid materials, due to its high sensitivity and conceptual simplicity. Ideally, the sample material evaporated by the laser (which should exactly represent the bulk chemical or isotopic composition) is converted into an aerosol that must be efficiently transported to the detector and completely decomposed within the ICP source. Nevertheless, LA-ICP-MS does not generally provide accurate quantification, and it is still far from being completely accepted as a universal technique, mainly due to fractionation effects and the persistent lack of adequate reference materials [19,20]. It should be emphasized that such fractionation-related inaccuracies can largely be avoided if standard reference materials of similar composition and morphology to the sample under investigation (called matrix-matched standards) are used for calibration. However, as for many other analytical techniques, the availability of certified reference samples is also a serious restriction for LA-ICP-MS and, at present, only a few analytical problems can be solved on the basis of matrix matching.

In order to improve the analytical capabilities of LA sampling for ICP-MS, the influence of elemental and isotopic fractionation on accuracy, precision, and standardization is still under study. Fractionation is a complex process, since it can take place during aerosol formation, during transport of the aerosol into the ICP, or during digestion of the aerosol in the ICP. Moreover, three different types of laser-induced fractionation have been described for ns LA:

- fractionation through preferential evaporation of volatile elements in the carrier gas [21];
- particle-size-related elemental fractionation [5]; and,
- laser-induced isotopic fractionation [22].

There can therefore be several reasons for elemental and isotopic fractionation effects (e.g., preferential vaporization of elements (or isotopes) from the sample, failure of large particles to be transported to the ICP, or incomplete vaporization of large particles that manage to reach the ICP source). Although optical and physical properties of samples affect preferential vaporization of elements during the LA process, the total aerosol composition can represent the solid sample with the proper