Laser ablation-ICP-mass spectrometry: from a micro-analytical tool for direct bulk analysis to a fast elemental mapping technique

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Inductively coupled plasma-mass spectrometry (ICP-MS) is considered a well-established and robust analytical technique for trace elemental and isotopic analysis. It is characterized by its low limits of detection (down to the pg/L level), multi-elemental capabilities, a wide linear dynamic range and high sample throughput. The standard sample introduction system is composed of a peristaltic pump to transport the sample solution to the nebulizer and spray chamber, to generate a fine aerosol that can be introduced into the ICP ion source. When coupling a laser ablation (LA) unit to an ICP-mass spectrometer as alternative sample introduction system, direct solid sample analysis is enabled. A highly energetic pulsed laser beam is used to irradiate the solid sample surface and upon ablation, a dry aerosol (particle plume) is generated and transported away from the ablation chamber into the ICP ion source using a carrier gas. Apart from advantages such as low sample consumption and no requirement for sample dissolution, the main advantage is that spatially resolved information can be obtained.

Since the first application of LA-ICP-MS in 1985 by Gray *et al*. [1], many fundamental studies were focused on evaluating different types of lasers in terms of wavelength to improve the analytical performance, resulting in a clear shift towards deep-UV lasers [2]. In 2002, Russo *et al.* [3] demonstrated the first use of femtosecond lasers for LA-ICP-MS. After that, the main focus was on improving the aerosol transport by designing new ablation chambers of the 'two-volume type'. Since the introduction of 3rd generation low-dispersion ablation cells by Wang *et al.* [4] in 2013, many different ablation cell designs have been developed and elemental mapping via LA-ICP-MS has gained significant momentum and is being applied in many research fields ranging from geo- and cosmochemistry to biomedicine and the pharmaceutical sciences. Minimizing the aerosol dispersion maximizes the temporal analyte concentration spike in the ICP, which creates an enhancement of the signal-to-noise (S/N) ratios. Recent hardware developments are pushing the limits towards kHz pixel acquisition rates and time-of-flight (TOF) based ICP-mass spectrometers are considered the go-to instruments for dealing with these short transient signal profiles given their quasi-simultaneous monitoring capabilities across the entire elemental mass range.

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