Overview of the ICP-MS technique

Inductively coupled plasma mass spectrometry (ICP-MS) is the most versatile and one of the most widely used mass spectrometric techniques of modern inorganic analytical chemistry. It has many practical advantages: i) multi-elemental capability, ii) inherent capability to measure isotope ratios, iii) wide dynamic range and, consequently, the possibility to analyse trace and major elements during the same measurement, iv) low detection limits for most elements, v) adaptability to the sample introduction process; vi) relatively high sample throughput and, in some cases, little sample preparation before analysis, vii) relative simplicity and limited costs of purchase of a quadrupole ICP mass spectrometer. Since the development of the prototype ICP mass spectrometer in 1976-1980 and commercialisation of this technique in 1983, it has found numerous applications in material, nuclear, forensic, earth, environmental, food and biological sciences, including fundamental research, and became a standard technique of elemental and isotopic analysis. Nowadays, after c. 40 years of development, it reached a state of maturity.

The analytical argon ICP is an efficient ion source: samples injected in the ICP flame are vaporised, atomised and ionised at temperatures of 7000-8000 K, ensuring efficient ionisation of almost all elements of the periodic table. For example, ionisation of alkaline and alkaline earth metals, rare earth elements, thorium and uranium in the ICP is almost complete. Among elements that cannot be efficiently ionised in the conventional analytical ICP, fluorine is perhaps the most cited example.

The ICP is an atmospheric pressure ion source: it is maintained by resistive heating and concomitant ionisation of argon by eddy currents induced in it by fast oscillating magnetic field - a process that cannot be realised in a high vacuum. Consequently, the ICP source can be interfaced to almost any atmospheric pressure sample introduction system that allows the sample mobilisation as an aerosol made of tiny liquid droplets or solid particles, or as a vapour. This enables analysing a wide range of samples using the same ICP mass spectrometer: liquid samples are nebulised using an ultrasonic nebuliser or a pneumatic nebuliser combined with a spray chamber to remove larger droplets before they reach the ICP. To remove the liquid matrix, increase the sensitivity, and supress spectral interferences, the nebulisation system can be coupled to a desolvator. For chemical speciation, a chromatograph can be used. Solid samples are either digested in an acid or, less frequently, an alkali to enable their analysis as solutions, or ablated – usually with little sample preparation - using a laser ablation facility that generates an aerosol made of solid particles. Samples can also be chemically treated to extract some elements (e.g., As, Se, Os) as a vapour in a process called chemical vapour generation, allowing to achieve a good sample transport efficiency to the ICP and to increase the sensitivity. This list of sample introduction techniques is not exhaustive. It is not an exaggeration to say that an appropriate sample introduction technique can be found for almost any sample, for which ICP-MS analysis is envisaged. Such adaptability is the most important reason of the versatility of ICP-MS and of a wide range of its applications.

Another reason of it is the successful experience of combining the ICP ion source with several types of mass analysers, such as the quadrupole mass filter, sector field, or time-of-flight mass analyser, to tailor the resulting ICP mass spectrometer according to the application. Quadrupole ICP mass spectrometers are employed for the single-collector, low-resolution analysis of a wide range of samples in the absence of tight restrictions regarding the data precision and elimination of spectral interferences. Collision and reaction cells used in quadrupole ICP-MS, and ultimately the triple quadrupole technology, alleviate the problem of accurate analysis in the presence of interferences. Where mass resolutions in the range of 3000-10000 are required or the possibility of multi-collection to remove the flicker noise and to improve the precision is essential – single- and multi-collector magnetic sector field ICP mass spectrometers are employed. For the analysis of short events, such as the arrival of the individual nanoparticles to the ICP and the associated outburst of ions coming from a single nanoparticle, time-of-flight ICP mass spectrometers show a promise; such spectrometers could also be more widely used in traditional trace element and isotope ratio ICP-MS applications,

especially if their ion transmission efficiency and abundance sensitivity could be improved to match the level of modern quadrupole and sector-field ICP-MS.

The versatility of ICP-MS is achieved without compromising the performance too much, although compromises do exist. Firstly, the ICP being an atmospheric pressure ion source implies that the ions have to be transferred to the vacuum part of the mass spectrometer containing ion optics, mass discriminator, and detector. Such a transfer, as well as the subsequent extraction of ions by the first lens of the ion channel of the spectrometer, are inefficient processes: most ICP-MS detect less than 0.01% of all ions formed in the ICP source. Still, for the most sensitive ICP mass spectrometers, for well-ionised, mono-isotopic elements and at low blank counts, the detected part of ions allows achieving detection limits in the order of fg/g (10^{-15} g/g) in the solution nebulisation and sub-ng/g (<10^{-9} g/g) - in the laser ablation regime. Such detection limits are low enough to ensure the detection of many isotopes without a pre-concentration in the majority of samples. Lowering the detection limit further is more concerned with cleanliness and correct definition of the blank than with improvement of the spectrometer sensitivity. Secondly, the ICP source and the process of ion extraction through the interface create interfering species: doubly charged ions and various polyatomic ions - argides, oxides, hydrides and hydroxides; the formation of polyatomic ions is facilitated by the ICP being an atmospheric pressure ion source. The usual lack of analyte pre-concentration and separation also leaves the possibility for non-spectral interferences (matrix effects). A careful optimisation of the spectrometer and sample introduction process, application of collision and reaction cells and triple quadrupole systems, or operation of the spectrometer at a higher resolution help to alleviate these issues. Thirdly, sample introduction systems, as well as the ICP/interface itself, operate so that the flow of ions entering the spectrometer interface is flickering with time: it can be denser or more diluted, the corresponding periods alternating randomly (and, in the case of a fixed-frequency noise, at a fixed frequency). The uncertainty of the resulting signal is generally higher than that predicted by the ordinary Poisson statistics, putting the ICP-MS technique at a disadvantage compared to, for example, thermal ionisation mass spectrometry. Still, the quantification of ICP-MS signals is usually based on ratios of isotope signals rather than the individual isotope signals only. Using multi-collector spectrometers allows to remove the flicker noise from the measured ratio - a remedy that is expensive and technically complex but available since long time and often employed when isotope ratio relative standard deviations <0.05% are required. For a wide range of (especially trace element) applications where such a precision is not mandatory, single-collector ICP mass spectrometers are employed.

To conclude, ICP-MS is a sensitive, rather precise, very adaptable, convenient to use and relatively affordable technique representing a workhorse of modern inorganic analytical chemistry.

****

The adaptability of the ICP ion source to the sample introduction process and the correspondingly wide range of applications, unfortunately, also have side effects. It is difficult to master the different applications equally well: usually, ICP-MS laboratories are specialised. Traditional trace element analysis of solutions, solution nebulisation analysis of semiconductors, liquid chromatography ICP-MS, high-precision multi-collector analysis of isotope ratios, laser ablation ICP-MS of geological materials and of biological materials now represent the different 'dimensions' of ICP-MS, partly overlapping but rarely explored on equal terms in a particular ICP-MS laboratory.

Our laboratory focuses on single collector laser ablation ICP-MS analysis of geological materials. We have three ICP-MS instruments: a sector-field Element XR MS (Thermo Fisher Scientific), a triple quadrupole PE5000 MS (Perkin Elmer), and a single quadrupole Agilent 7700x MS (Agilent Technologies). We also have two operational laser ablation systems: a RESOlution 193 nm excimer system equipped with a two-volume S155 ablation cell for demanding applications (suppression of flicker noise and position effect to improve precision and accuracy, respectively; fast washout; high sample throughput), and a NewWave UP-193FX excimer ablation system for general applications.