Beginner's Guide to ICP-MS
Part XIII – Sampling Accessories

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Today, sampling tools — such as laser ablation, flow injection, electrothermal vaporization, desolvation systems, and chromatography devices — are considered absolutely critical to enhance the practical capabilities of inductively coupled plasma–mass spectrometry (ICP-MS) for real-world samples. Since their development more than 10 years ago, these kinds of alternate sampling accessories have proved to be invaluable for certain applications that are considered problematic for ICP-MS.

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Standard ICP-MS instrumentation using a traditional sample introduction system comprising a spray chamber and nebulizer has certain limitations, particularly when it comes to the analysis of complex samples. Some of these known limitations include

- Total dissolved solids must be kept below 0.2%
- Long washout times are required for samples with a heavy matrix
- Sample throughput is limited by the sample introduction process
- Contamination issues can occur with samples requiring multiple sample preparation steps
- Dilutions and addition of internal standards can be labor-intensive and time-consuming
- Matrix has traditionally been done off-line
- Matrix suppression can be quite severe with some samples

- Matrix components can generate severe spectral overlaps on analytes
- Organic solvents can present unique problems
- The analysis of solids, powders, and slurries is very difficult
- It is not suitable for the determination of elemental species or oxidation states.

Such were the demands of real-world users to overcome these kinds of problem areas that instrument companies devised different strategies based on the type of samples being analyzed. Some of these strategies involved parameter optimization or the modification of instrument components, but it was clear that this approach alone was not going to solve every conceivable problem. For this reason, they turned their attention to the development of sampling accessories, which were optimized for a particular application problem or sample type. During the past 10–15 years, this demand has led to the commercialization of spe-

cialized sample introduction tools — not only by the instrument manufacturers themselves, but also by companies specializing in these kinds of accessories. The most common ones used today include

- Laser ablation/sampling
- Flow injection analysis
- Electrothermal vaporization
- Desolvation systems
- Chromatography separation techniques.

Let's now take a closer look at each of these techniques to understand their basic principles and what benefits they bring to ICP-MS. In the first part of this tutorial, we will focus on laser ablation and flow injection, whereas in the next tutorial on sampling accessories, we will examine electrothermal vaporization, desolvation systems, and chromatography separation devices.

Laser Ablation/Sampling

The limitation of ICP-MS to directly analyze solid materials or powders led to the development of high-powered laser systems to ablate the surface of a solid and sweep the sample aerosol into the ICP mass spectrometer for analysis in the conventional way (1). Before we describe some typical applications suited to laser ablation ICP-MS, let's first take a brief look at the history of analytical lasers and how

they eventually became such useful sampling tools.

The use of lasers as vaporization devices was first investigated in the early 1960s. When light energy with an extremely high power density (typically 10^{12} W/cm²) interacts with a solid material, the photon-induced energy is converted into thermal energy, resulting in vaporization and removal of the material from the surface of the solid (2). Some of the early researchers used ruby lasers to induce a plasma discharge on the surface of the sample and measured the emitted light with an atomic emission spectrometer (3). Although this proved useful for certain applications, the technique suffered from low sensitivity, poor precision, and severe matrix effects caused by nonreproducible excitation characteristics. Over the years, various improvements were made to this basic design with very little success (4), because the sampling process and the ionization/excitation process (both under vacuum) were still intimately connected and highly interactive with each other.

This limitation led to the development of laser ablation as a sampling device for atomic spectroscopy instru-

Figure 1. Optical layout of the laser ablation system used in this study (courtesy of CETAC Technologies [Omaha, NE]).

mentation, where the sampling step was completely separated from the excitation or ionization step. The major benefit was that each step could be independently controlled and optimized. These early devices used a high-energy laser to ablate the surface of a solid sample, and the resulting aerosol was swept into some kind of atomic spec-

trometer for analysis. Although initially used with atomic absorption (5, 6) and plasma-based emission techniques (7, 8), it wasn't until the mid-1980s, when lasers were coupled with ICP-MS, that the analytical community stood up and took notice (9). For the first time, researchers were showing evidence that virtually any type of solid could be vaporized, irrespective of electrical characteristics, surface topography, size, or shape, and transported into the ICP for analysis by atomic emission or MS. This was an exciting breakthrough for ICP-MS, because it meant the technique could be used for the bulk sampling of solids or for the analysis of small spots or microinclusions, in addition to being used for the analysis of solutions.

The first laser ablation systems developed for ICP instrumentation were based on solid-state ruby lasers, operating at 694 nm. These were developed in the early 1980s but did not prove to be successful for a number of reasons — including poor stability, low power density, low repetition rate, and large beam diameter — which made them limited in their scope and flexibility as a sample introduction device for trace element analysis. It was at least another five years before any commercial instrumentation became available. These early commercial laser ablation systems, which were specifically developed for
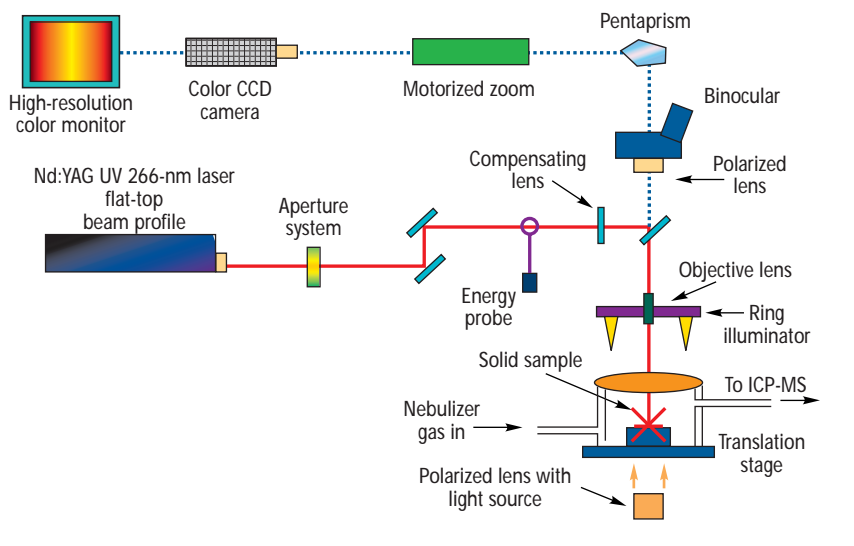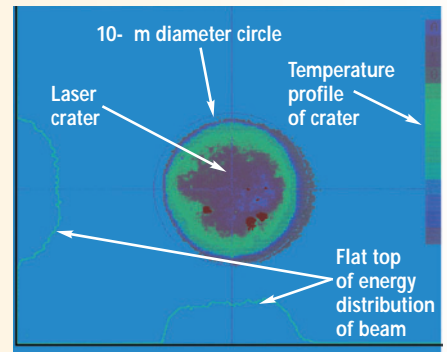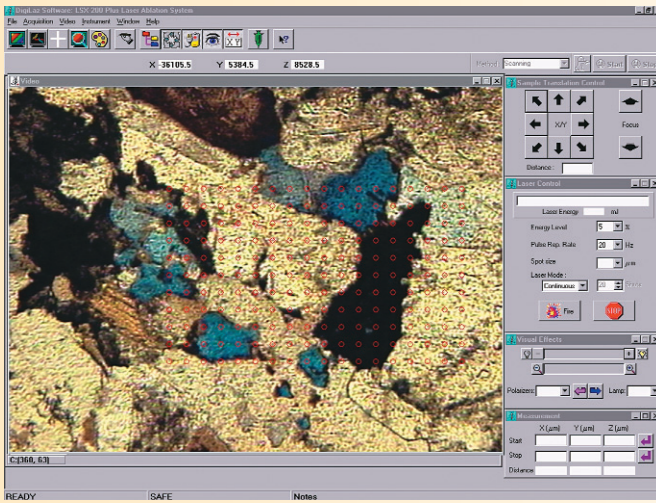
Table I. Typical detection limits (DL) and sensitivities achievable using laser ablation for NIST 612 glass (using an Agilent Technologies 4500 ICP-MS system).

Element	3σ DL (ppb)	Sensitivity (cps/ppb)	Element	3σ DL (ppb)	Sensitivity (cps/ppb)
B	3.0	293	Ce	0.053	131
Sc	3.4	135	Pr	0.047	121
Ti	9.1	5.5	Nd	0.54	12.1
V	0.40	84	Sm	0.09	44.7
Fe	13.6	5.2	Eu	0.10	46.7
Co	0.05	90.1	Gd	1.5	4.3
Ni	0.70	39.0	Dy	0.45	11.1
Ga	0.18	135.3	Ho	0.01	98.1
Rb	0.10	218	Er	0.21	13.8
Sr	0.07	90.0	Yb	0.40	10.4
Y	0.04	64.0	Lu	0.04	98.1
Zr	0.20	29.6	Hf	0.40	15.2
Nb	0.47	20.3	Ta	0.09	65.8
Cs	0.17	274.5	Th	0.02	96.0
Ba	0.036	16.0	U	0.02	294
La	0.045	185			

Energy = 5.0 mJ without beam attenuation
Pulse rate = 20 Hz
Scan rate = 10 μm/s

Figure 2. (right) Image taken by a petrographic microscope of the surface of a thin section of a garnet sample, showing 10-μm spot sizes (red circles).

Figure 3. (far right) 10-μm-diameter spot showing the flat-top energy distribution.

ICP-MS, used the Nd:YAG design, operating at the primary wavelength of 1064 nm in the infrared (10). They initially showed a great deal of promise because analysts could finally determine trace levels directly in the solid without sample dissolution. However, it soon became apparent that they didn't meet the expectations of the analytical community for many reasons, including their complex ablation characteristics, poor precision, lack of optimization for microanalysis and, because of poor laser coupling, their unsuitability for many types of solids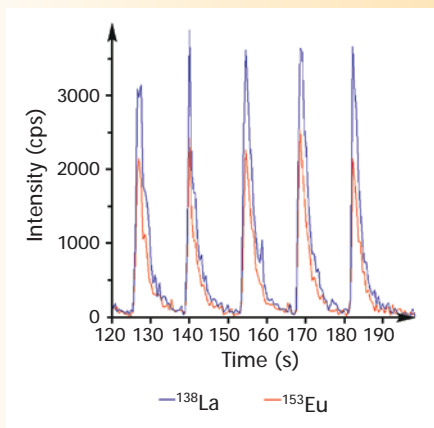. By the early 1990s, most of the laser ablation systems purchased were viewed as novel and interesting, but not suited to solve real-world application problems.

These basic limitations in IR laser technology led researchers to investigate the benefits of shorter wavelengths. Systems were developed that were based on Nd:YAG technology at the 1064-nm primary wavelength, but using optical components to double (532 nm) and quadruple (266 nm) the frequency. Innovations in lasing materials and electronic design, together with better ther-

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Figure 4. Signal response of five single-shot ablations for [138]La and [153]Eu in NIST 612 glass (using a PerkinElmer Instruments [Shelton, CT] SCIEX ELAN 6000 ICP-MS system).

sorption capabilities for UV-transparent materials like calcites, fluorites, and silicates; smaller particle size; and higher flow of ablated material. Evidence also suggested that the shorter-wavelength excimer laser exhibited better elemental fractionation characteristics (preferential ablation of some elements over others based on their

volatility) than the longer-wavelength Nd:YAG design.

Today there are a number of laser ablation designs on the market of varying wavelengths, output energy, power density, and beam profile. Even though each one has slightly different ablation characteristics, they all work extremely well depending on the types of samples
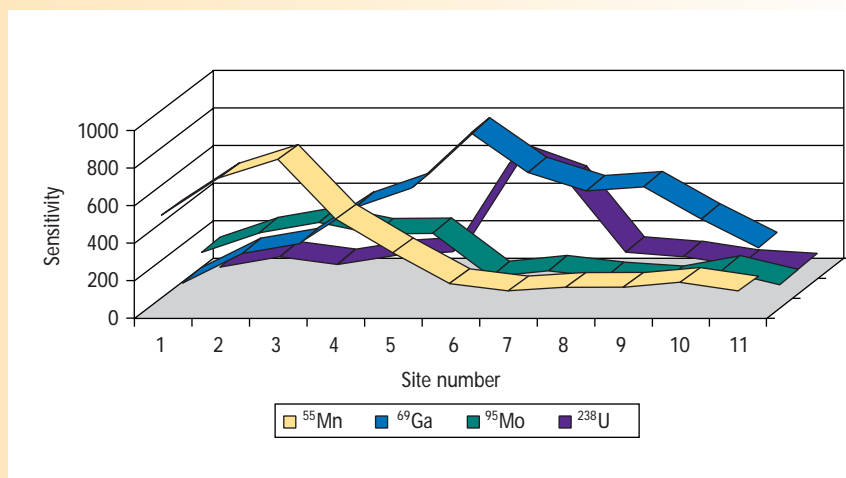
mal characteristics, produced higher energy with higher pulse-to-pulse stability. These more advanced UV lasers showed significant improvements, particularly in the area of coupling efficiency, making them more suitable for a wider array of sample types. In addition, the use of more comprehensive optics allowed for a more homogeneous laser beam profile, which provided the optimum energy density to couple with the sample matrix. This resulted in the ability to make spots much smaller and with more controlled ablations irrespective of sample material, which was critical for the analysis of surface defects, spots, and microinclusions.

The successful trend toward shorter wavelengths and the improvements in the quality of optical components also drove the development of UV gas-filled lasers, such as XeCl (308 nm), KrF (248 nm), and ArF (193 nm) excimer lasers. These showed great promise, especially the ones operated at shorter wavelengths, which were specifically designed for ICP-MS. Unfortunately, they necessitated a more sophisticated beam delivery system, which tended to make them more expensive. In addition, the complex nature of the optics and the fact that gases had to be changed on a routine basis made them a little more difficult to use and maintain and, as a result, required a more skilled operator to run them. However, their complexity was far outweighed by their better ab-

Figure 5. Elemental mapping across the surface of an andradite garnet (using Agilent Technologies [Palo Alto, CA] HP 4500 ICP-MS system).
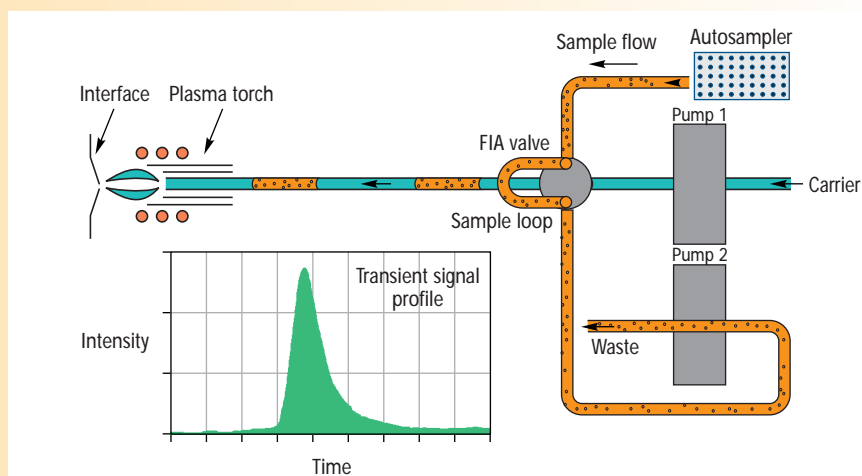

Figure 6. Schematic of a flow injection system used for the process of microsampling.

being analyzed. Laser ablation is now considered a very reliable sampling technique for ICP-MS, which is capable of producing data of the very highest quality directly on solid samples and powders. Some of the many benefits offered by this technique include

- Direct analysis of solids without dissolution
- Ability to analyze virtually any kind of solid material including rocks, minerals, metals, ceramics, polymers, plant material, and biological specimens
- Ability to analyze a wide variety of powders by pelletizing with a binding agent
- No requirement for sample to be electrically conductive
- Sensitivity in the parts-per-billion to parts-per-trillion range, directly in the solid

- Labor-intensive sample preparation steps are eliminated
- Contamination is minimized because there are no digestion/dilution steps
- Reduced polyatomic spectral interferences compared to solution nebulization

- Examination of small spots, inclusions, defects, or microfeatures on surface of sample
- Elemental mapping across the surface of a mineral
- Depth profiling to characterize thin films or coatings.

Let us now exemplify some of these benefits with some application work carried out on a commercially-available laser ablation system (LSX 200 Plus, CETAC Technologies, Omaha, NE). The optical layout of the LSX 200 system is shown in Figure 1. (Note: Since this work was carried out, CETAC Technologies has developed a more advanced laser system called the Clarus 266, which operates at the same wavelength, but includes modifications that produce a more homogeneous beam profile. The major benefit of this improved optical design is that the high-density, flat-top beam reduces elemental fractionation effects and creates more uniform and reproducible spot sizes across a wide variety of complex materials.)

There is no question that geochemists and mineralogists have driven the development of laser ablation for ICP-MS because of their desire for ultratrace analysis of optically challenging materials such as calcite, quartz, glass, and fluorite, combined with the capability to characterize small spots and microinclusions on the surface of the sample. For that reason, the ability to view the structure of a thin section of a mineral sample with a petrographic microscope is crucial to examine and select an area for analysis. Figure 2 shows the digital image of a garnet

Table II. Analytical results for NASS-4 open-ocean seawater certified reference material, using flow injection ICP-MS methodology.

Isotope	LOD (ppt)	NASS-4 (ppb) Determined	Certified
^{51}V	4.3	1.20 ± 0.04	Not certified
^{63}Cu	1.2	0.210 ± 0.008	0.228 ± 0.011
^{60}Ni	5	0.227 ± 0.027	0.228 ± 0.009
^{66}Zn	9	0.139 ± 0.017	0.115 ± 0.018
^{55}Mn	Not reported	0.338 ± 0.023	0.380 ± 0.023
^{59}Co	0.5	0.0086 ± 0.0011	0.009 ± 0.001
^{208}Pb	1.2	0.0090 ± 0.0014	0.013 ± 0.005
^{114}Cd	0.7	0.0149 ± 0.0014	0.016 ± 0.003

thin-section sample (500× magnification) using a petrographic microscope. This image was generated by illuminating the sample from the bottom with transmitted light and adjustment of the polarizers underneath the sample compartment. On closer examination of Figure 2, small red circles can be seen, which are 10 μm in diameter. The ablation sites are located in each of these red circles. Spot sizes in this range are considered optimal to characterize the elemental composition across complex grain boundaries of most minerals and still have adequate sensitivity using ICP-MS.

To achieve this, it is desirable that the laser beam have a homogenous profile that produces the optimal energy density to couple with the sample matrix. This results in small craters <10 μm in diameter with a flat-top energy distribution, as shown in Figure 3. Most applications of this type will benefit from using higher laser energy at the sample surface (5–6 mJ). Under these ideal conditions, the flat, uniform beam is imaged directly onto the sample surface providing the optimal condition for laser coupling. The primary advantage is that the energy density on the sample surface is uniform, constant, and independent of spot size, so that good precision is achieved even at a high laser energy.

When working with such small crater sizes, such as in the elemental characterization of minute inclusions, grains, or nodules, the laser system is typically used in the single-shot mode. In this mode of analysis, where the laser beam is fired just once, it is imperative to have spatial control and ablation cell stability to efficiently transport such small amounts of ablated aerosol into the plasma. This results in good shot-to-shot precision and sensitivity as illustrated in Figure 4, which shows signals from five separate single laser shots of the rare earth elements [138]La and [153]Eu in NIST 612 glass. It must be emphasized that the ICP-MS instrument must offer good sensitivity on a fast transient peak for this type of analysis. This means that, depending on the type of mass spectrometer used, the instrument scanning and settling times must be op-
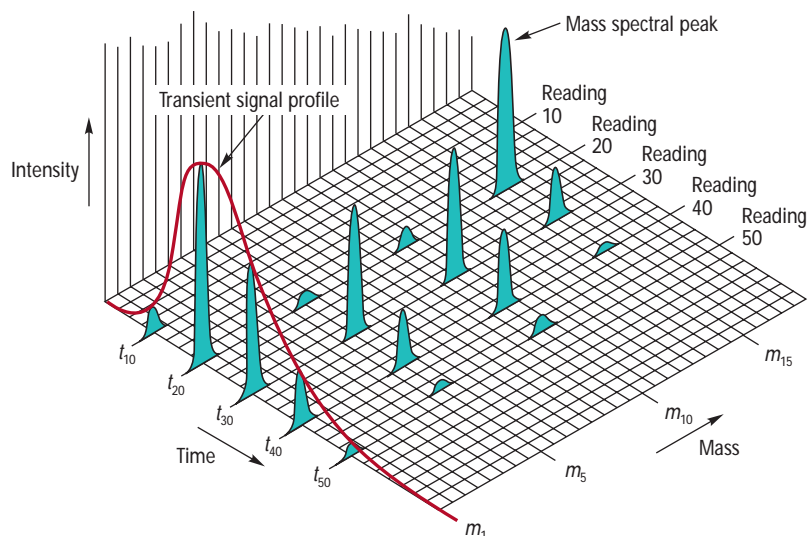

Figure 7. A 3-D plot of analyte intensity versus mass in the time domain for the determination of a group of elements in a transient peak.
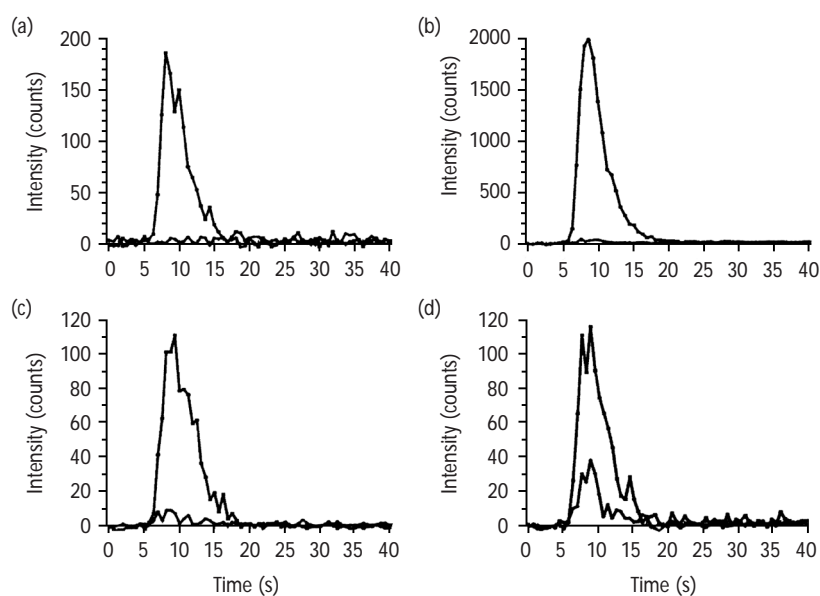

Figure 8. Analyte and blank spectral scans of (a) Co, (b) Cu, (c) Cd, and (d) Pb in NASS-4 open-ocean seawater certified reference material, using flow injection coupled to an ICP-MS system.

timized for transient peak analysis. Table I shows some typical 3σ detection limits and sensitivities achievable by laser ablation coupled to a quadrupole ICP-MS. The laser conditions for this experiment are shown at the bottom of the table.

The final example of using laser ablation as a geochemical analytical tool is in its ability to map the surface of a mineral. Figure 5 shows an elemental map of an andradite garnet, which had shown heavy zoning when viewed

through a petrographic microscope using transmitted polarized light. The garnet was sampled at 20 sites across the section, using a 20-s acquisition time per site, a laser power of 3 mJ, and a pulse repetition rate of 5 Hz. By examining data collected in this manner, differences in site mineralization behavior could be predicted and applied, to complement other geological measurements.

The applications described here are a very small subset of what is being done

in the real world. A large number of references in the public domain describe the analysis of metals, ceramics, polymer, rocks, minerals, biological tissue, paper, and many other sample types (11–15). These references should be investigated further to better understand the suitability of laser sampling ICP-MS for your application.

Flow Injection Analysis

Flow injection is a powerful front-end sampling accessory for ICP-MS that can be used for preparation, pretreatment, and delivery of the sample. Originally described by Ruzicka and Hansen (16), flow injection involves the introduction of a discrete sample aliquot into a flowing carrier stream. Using a series of automated pumps and valves, procedures can be carried out online to physically or chemically change the sample or analyte before introduction into the mass spectrometer for detection. There are many benefits of coupling flow injection procedures to ICP-MS, including

- Automation of on-line sampling procedures, including dilution and additions of reagents
- Minimum sample handling translates into less chance of sample contamination
- Ability to introduce low sample or reagent volumes
- Improved stability with harsh matrices
- Extremely high sample throughput using multiple loops.

In its simplest form, flow injection ICP-MS consists of a series of pumps and an injection valve preceding the sample introduction system of the ICP mass spectrometer. A typical manifold used for microsampling is shown in Figure 6.

In the fill position, the valve is filled with the sample (orange). In the inject position, the sample is swept from the valve and carried to the ICP by means of a carrier stream (green). The measurement is usually a transient profile of signal versus time, as shown by the green peak in Figure 6. The area of the signal profile measured is greater for larger injection volumes, but for volumes of 500 µL or greater, the signal

peak height reaches a maximum equal to that observed using continuous solution aspiration. The length of a transient peak in flow injection is typically 20–60 s, depending on the size of the loop. This means if multielement determinations are a requirement, all the data quality objectives for the analysis, including detection limits, precision, dynamic range, number of elements, and so forth, must be achieved in this time frame. Similar to laser ablation, if a sequential mass analyzer such as a quadrupole or single collector magnetic sector system is used, the electronic scanning, dwelling, and settling times must be optimized to capture the maximum amount of multielement data in the duration of the transient event (17), as seen in Figure 7, which shows a three-dimensional transient plot of intensity versus mass in the time domain for the determination of a group of elements.

Some of the many online procedures that are applicable to flow injection ICP-MS include

- Microsampling for improved stability with heavy matrices (18)
- Automatic dilution of samples and standards (19)
- Standards addition (20)
- Cold vapor and hydride generation for enhanced detection capability for elements such as Hg, As, Sb, Bi, Te, and Se (21)
- Matrix separation and analyte preconcentration using ion-exchange procedures (22)
- Elemental speciation (23).

Flow injection coupled to ICP-MS has shown itself to be very diverse and flexible in meeting the demands presented by complex samples as indicated in the above references. However, one of the most exciting areas of research at the moment is in the direct analysis of seawater by flow injection ICP-MS. Traditionally the analysis of seawater using ICP-MS is very difficult because of two major problems. First, the high NaCl content will block the sampler cone orifice over time, unless a 10–20-fold dilution of the sample is made. This isn't such a major problem with coastal waters, because the levels are high enough.

However, if the sample is open-ocean seawater, this isn't an option because the trace metals are at a much lower level. The other difficulty associated with the analysis of seawater is that ions from the water, chloride matrix, and the plasma gas can combine to generate polyatomic spectral interferences, which are a problem, particularly for the first-row transition metals.

Attempts have been made over the years to remove the NaCl matrix and to preconcentrate the analytes using various types of chromatography and ion-exchange column technology. One such early approach was to use an HPLC system coupled to an ICP mass spectrometer using a column packed with silica-immobilized 8-hydroxyquinoline (24). This worked reasonably well, but was not considered a routine method, because silica-immobilized 8-hydroxy-quinoline was not commercially available; also, spectral interferences produced by HCl and HNO_3 (pictures used to elute the analytes) precluded determination of elements such as Cu, As, and V. More recently, chelating agents based on the iminodiacetate acid functionality group have gained wider success but are still not considered truly routine for a number of reasons, including the necessity for calibration using standard additions, the requirement of large volumes of buffer to wash the column after loading the sample, and the need for conditioning between samples because some ion-exchange resins swell with changes in pH (25–27).

However, a research group at Canada's National Research Council has developed a very practical on-line approach, using a flow injection sampling system coupled to an ICP mass spectrometer (22). Using a special formulation of a commercially available imino-diacetate ion-exchange resin (with a macroporus methacrylate backbone), trace elements can be separated from the high concentrations of matrix components in the seawater with a pH 5.2 buffered solution. The trace metals are subsequently eluted into the plasma with 1 M HNO_3, after the column has been washed out with deionized water.

The column material has sufficient selectivity and capacity to allow accurate determinations at parts-per-trillion levels using simple aqueous standards, even for elements such as V and Cu, which are notoriously difficult in a chloride matrix. Figure 8 shows spectral scans for a selected group of elements in a certified reference material open-ocean seawater sample (NASS-4). Table II compares the results for this methodology with the certified values, together with the limits of detection. Using this on-line method, the turnaround time is less than 4 min per sample, which is considerably faster than other high-pressure chelation techniques reported in the literature.

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