TUTORIAL

Beginner's Guide to ICP-MS

Part XIV – Sampling Accessories, Part II

Robert Thomas

Sampling accessories are considered critical to enhance the practical capabilities of inductively coupled plasma–mass spectrometry (ICP-MS); since their development more than 10 years ago, they have proved to be invaluable for difficult, real-world applications. In the first part of the tutorial on sampling accessories (1), we looked at laser ablation and flow injection techniques. In this second installment, we will focus on three other important sampling approaches: electrothermal vaporization, desolvation systems, and chromatographic separation devices.

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Electrothermal atomization (ETA) for use with atomic absorption (AA) has proven to be a very sensitive technique for trace element analysis during the previous three decades; however, the possibility of using the atomization/heating device for electrothermal vaporization (ETV) sample introduction into an ICP mass spectrometer was identified in the late 1980s (2). The ETV sampling process relies on the basic principle that a carbon furnace or metal filament can be used to thermally separate the analytes from the matrix components and then sweep them into the ICP mass spectrometer for analysis. This is achieved by injecting a small amount of the sample (usually 20–50 µL via an autosampler) into a graphite tube or onto a metal filament. After the sample is introduced, drying, charring, and vaporization are achieved by slowly heating the graphite tube/metal filament. The sample material is vaporized into a flowing stream of carrier gas, which passes through the furnace or over the filament during the heating cycle. The analyte vapor recondenses in the carrier gas and is then swept into the plasma for ionization.

One of the attractive characteristics of ETV for ICP-MS is that the vaporization and ionization steps are carried out separately, which allows for the optimization of each process. This is particularly true when a heated graphite tube is used as the vaporization device, because the analyst typically has more control of the heating process and, as a result, can modify the sample by means of a very precise thermal program before it is introduced to the ICP for ionization. By boiling off and sweeping the solvent and volatile matrix components out of the graphite tube, spectral interferences arising from the sample matrix can be reduced or eliminated. The ETV sampling process consists of six discrete stages: sample introduction, drying, charring (matrix removal), vaporization, condensation, and transport. Once the sample has been introduced, the graphite tube is slowly heated to drive off the solvent. Opposed gas flows, entering from each end of the graphite tube, then purge the sample cell by forcing the evolving vapors out the dosing hole. As the temperature increases, volatile matrix components are vented during the charring steps. Just before vaporization, the gas flows within the sample cell are changed. The central channel (nebulizer) gas then enters from one end of the furnace, passes through the tube, and exits out the other end. The sample-dosing hole is then automatically closed, usually by means of a graphite tip, to ensure no analyte vapors escape. After this gas flow pattern has been established, the temperature of the graphite tube is ramped up very quickly, vaporizing the residual components of the sample. The vaporized analytes either recondense in the rapidly moving gas stream or remain in the vapor phase. These particulates and vapors

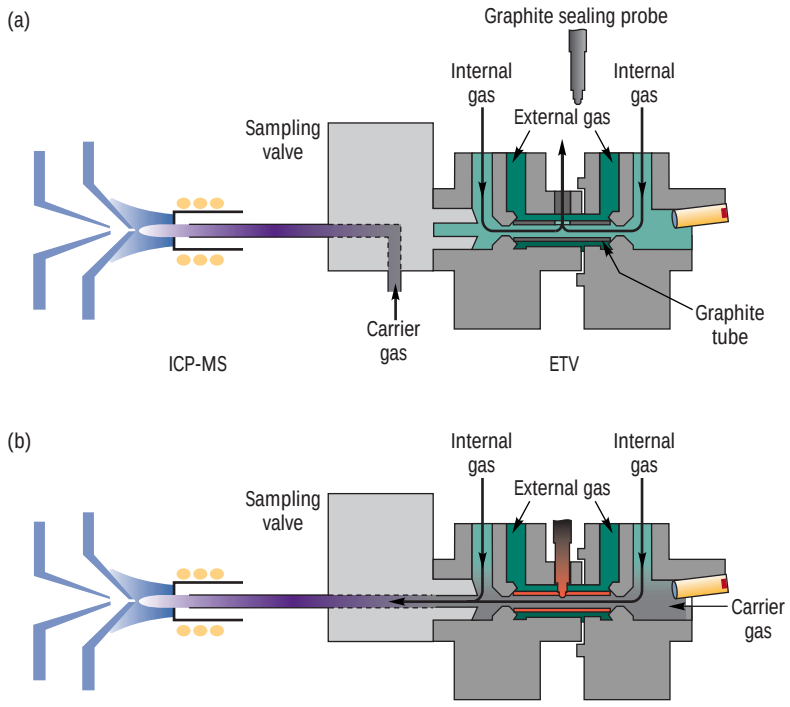

Figure 1. A graphite furnace ETV sampling device for ICP-MS, showing the two distinct steps of (a) sample pretreatment and (b) vaporization into the plasma. (Courtesy of PerkinElmer Instruments, Shelton, CT.)

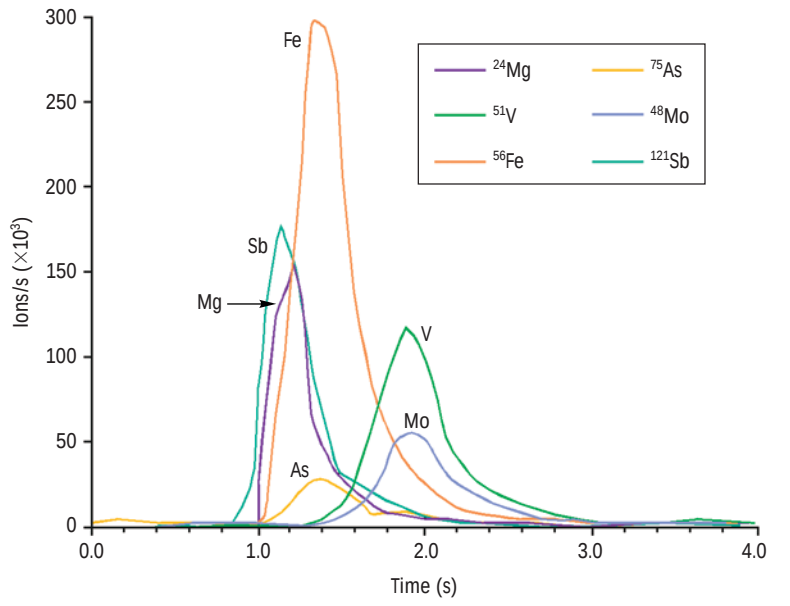

Figure 2. A temporal display of 50 pg of magnesium, antimony, arsenic, iron, vanadium, and molybdenum in 37% hydrochloric acid by ETV-ICP-MS (8).

are then transported to the ICP in the carrier gas where they are ionized by the ICP for analysis in the mass spectrometer.

Another benefit of decoupling the sampling and ionization processes is the opportunity for chemical modification of the sample. The graphite furnace itself can serve as a high-temperature reaction vessel where the chemical nature of compounds within it can be altered. In a manner similar to that used in AA, chemical modifiers can change the volatility of species to enhance matrix removal and increase elemental sensitivity (3). An alternate gas such as oxygen may also be introduced into the sample cell to aid in the charring of the carbon in organic matrices such as biological or petrochemical samples. Here the organically bound carbon reacts with the oxygen gas to produce carbon dioxide, which is then vented from the system. A typical ETV sampling device, showing the two major steps of sample pretreatment (drying and ashing) and vaporization into the plasma, is shown schematically in Figure 1.

During the past 15 years, ETV sampling for ICP-MS has mainly been used for the analysis of complex matrices including geological materials (4), biological fluids (5), seawater (6), and coal slurries (7), which have proven difficult or impossible to analyze by conventional nebulization. By removal of the matrix components, the potential for severe spectral and matrix-induced interferences is dramatically reduced. Even though ETV-ICP-MS was initially applied to the analysis of very small sample volumes, the advent of low-flow nebulizers has mainly precluded its use for this type of work.

An example of the benefits of ETV sampling is the analysis of samples containing high concentrations of mineral acids such as hydrochloric, nitric, and sulfuric acids. Besides physically suppressing analyte signals, these acids generate massive polyatomic spectral overlaps that interfere with many analytes, including arsenic, vanadium, iron, potassium, silicon, zinc, and titanium. By carefully removing the matrix components with the ETV device, the deter-

Table I. Detection limits for vanadium, iron, and arsenic in 37% hydrochloric acid by ETV-ICP-MS.

Element	DL (ppt)
^{51}V	50
^{56}Fe	20
^{75}As	40

mination of these elements becomes relatively straightforward. Figure 2 shows a spectral display in the time domain for 50-pg spikes of a selected group of elements in concentrated hydrochloric acid (37% w/w) using a graphite furnace–based ETV-ICP-MS system (8). It can be seen in particular that good sensitivity is obtained for ^{51}V, ^{56}Fe, and ^{75}As, which would have been virtually impossible by direct aspiration because of spectral overlaps from $^{35}Cl^{16}O$, $^{40}Ar^{16}O$, and $^{40}Ar^{35}Cl$, respectively. The removal of the chloride and water from the matrix translates into parts-per-trillion detection limits directly in 37% hydrochloric acid, as shown in Table I.

Figure 2 also shows that the elements are vaporized off the graphite tube in the order of their boiling points. In other words, magnesium, which is the most volatile, is driven off first, while vanadium and molybdenum, which are the most refractory, come off last. However, even though they emerge at different times, the complete transient event lasts <3 s. This physical time limitation, imposed by the duration of the transient signal, makes it imperative that all isotopes of interest be measured under the highest signal-to-noise conditions throughout the entire event. The rapid nature of the transient also limits the usefulness of ETV sampling for routine multielement analysis because realistically only a small number of elements can be quantified with good accuracy and precision in <3 s. In addition, the development of low-flow nebulizers, desolvation devices, and collision cell technology means that rapid multielement analysis can now be carried out on difficult samples without the need for ETV sample introduction.

Desolvation Devices

Desolvation devices are mainly used in ICP-MS to reduce the amount of solvent entering the plasma. With organic samples, desolvation is absolutely critical because most volatile solvents would extinguish the plasma if they weren't removed or at least significantly reduced. However, desolvation of all types of samples can be very useful because it reduces the severity of the solvent-induced spectral interferences like oxides, hydroxides, and argon/solvent-based polyatomics that are common in ICP-MS. The most common desolvation systems used today include:

- Water-cooled spray chambers
- Peltier-cooled spray chambers
- Ultrasonic nebulizers (USNs) with water/Peltier coolers
- USNs with membrane desolvation
- Microconcentric nebulizers (MCNs) with membrane desolvation.

Water- and/or Peltier- (thermo electric) cooled spray chambers are standard on a number of commercial instruments. They are usually used with conventional or low-flow pneumatic nebulizers to reduce the amount of solvent entering the plasma. This has the effect of minimizing solvent-based spectral interferences formed in the plasma, and can also help to reduce the effects of a nebulizer-flow–induced secondary discharge at the interface of the plasma with the sampler cone. With some organic samples, it has proved to be very beneficial to cool the spray chamber to −10 to −20 °C (with an ethylene glycol mix) in addition to adding a small amount of oxygen into the nebulizer gas flow. This has the effect of reducing the amount of organic solvent entering the interface, which is beneficial in eliminating the build-up of carbon deposits on the sampler cone orifice and also minimizing the problematic carbon-based spectral interferences (9).

Ultrasonic nebulization was first developed for use with ICP–optical emission spectroscopy (OES) (10). Its major benefit was that it offered an approximately 10–20-fold improvement in detection limits because of its more efficient aerosol generation. However, this was not such an obvious benefit for ICP-MS because more matrix was entering the system compared with a conventional nebulizer, increasing the potential for signal drift, matrix suppression, and spectral interferences. This was not a problem with simple aqueous samples, but was problematic for real-world matrices. The elements that showed the most improvement were the ones that benefited from lower solvent-based spectral interferences. Unfortunately, many of the other elements exhibited higher background levels and, as a result, showed no significant improvement in detection limit. In addition, because of the increased amount of matrix entering the mass spectrometer, it usually necessitated the need for larger dilutions of the sample, which again negated the benefit of using a USN with ICP-MS. This limitation led to the development of an ultrasonic nebulizer fitted with a membrane desolvator — in addition to the conventional desolvation system. This design removed virtually all the solvent from the sample, which dramatically improved detection limits for a large number of the problematic elements and also lowered oxide levels by at least an order of magnitude (11).

The principle of aerosol generation using an ultrasonic nebulizer is based on a sample being pumped onto a quartz plate of a piezo-electric transducer. Electrical energy of 1–2 MHz frequency is coupled to the transducer, which causes it to vibrate at high frequency. These vibrations disperse the sample into a fine droplet aerosol, which is carried in a stream of argon. With a conventional ultrasonic nebulizer, the aerosol is passed through a heating tube and a cooling chamber, where most of the sample solvent is removed as a condensate before it enters the plasma. If a membrane desolvation system is fitted to the ultrasonic nebulizer, it is positioned after the cooling unit. The sample aerosol enters the membrane desolvator, where the remaining solvent vapor passes through the walls of a tubular microporous PTFE membrane. A flow of argon gas removes the volatile vapor from the exterior of the membrane, while the ana-

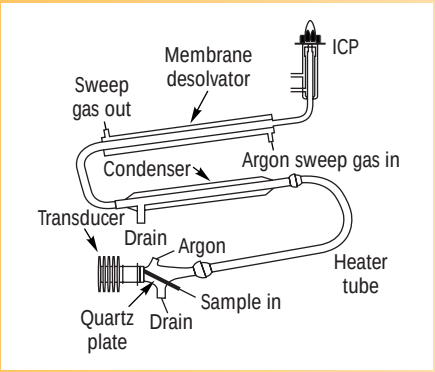

Figure 3. Schematic of an ultrasonic nebulizer fitted with a membrane desolvation system.

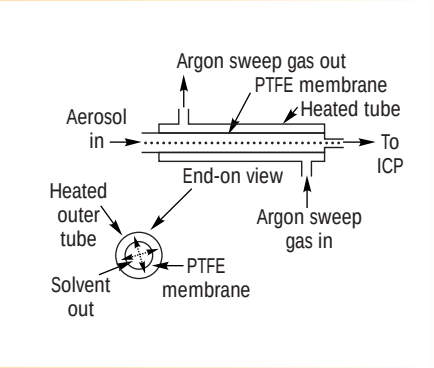

Figure 4. Principles of membrane desolvation.

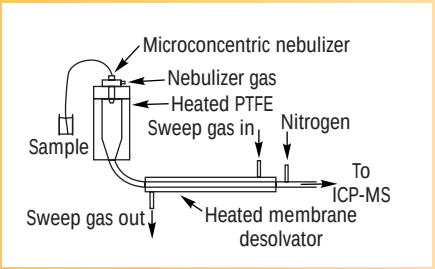

Figure 5. Schematic of a microconcentric nebulizer fitted with a membrane desolvation system. (Figures 3, 4, and 5 are courtesy of CETAC Technologies, Omaha, NE.)

lyte aerosol remains inside the tube and is carried into the plasma for ionization. Figure 3 shows a schematic of a USN, and Figure 4 shows the principles of membrane desolvation.

For ICP-MS, the system is best operated with both desolvation stages working, although for less demanding ICP-OES analysis, the membrane stage can be bypassed if required. The power of the system when coupled to an ICP mass spectrometer can be seen in Table II, which compares the sensitivity (counts per second [cps]) and signal-to-background of a membrane desolvation USN with a conventional crossflow nebulizer for three classic solvent-based polyatomic interferences — $^{12}C^{16}O_2$ on ^{44}Ca, $^{40}Ar^{16}O$ on ^{56}Fe, and $^{40}Ar^{16}OH$ on ^{57}Fe — using a quadrupole ICP-MS system. The sensitivity for the analyte isotopes are all background subtracted.

It can be seen that for all three analyte isotopes, the net signal-to-background ratio is significantly better with the membrane ultrasonic nebulizer than with the crossflow design, which is a direct impact of the reduction of the solvent-related spectral background levels. Even though this approach works equally well and sometimes better when analyzing organic samples, it does not work for analytes that are bound to an organic molecule. The high volatility of certain types of organometallic species means that they stand a very good chance of passing through the microporous PTFE membrane and never making it into the ICP-MS. For this reason, caution must be used when using a membrane desolvation system for the analysis of organic samples.

A variation of the membrane desolvation system uses a microconcentric nebulizer in place of the ultrasonic nebulizer. A schematic of this design is shown in Figure 5.

The benefit of this approach is not only the reduction in solvent-related spectral interferences with the membrane desolvation system, but also advantage can be taken of the microconcentric nebulizer's ability to aspirate very low sample volumes (typically 20–100 µL). This can be particularly useful when sample volume is limited, as in vapor phase decomposition (VPD) analysis of silicon wafers. The problem with this kind of demanding work is that there is typically only 500 µL of sample available, which makes it extremely difficult using a traditional low-flow nebulizer because it requires the use of both cool and normal plasma conditions to carry out a complete multielement analysis. By using an MCN with a membrane desolvation system, the full suite of elements — including the notoriously difficult iron, potassium, and calcium — can be determined on 500 µL of sample using one set of normal plasma conditions (12).

Low-flow nebulizers were described in greater detail in Part II of this series. The most common ones used in ICP-MS are based on the microconcentric design and operate at 20–100µL/min. Besides being ideal for small sample

Table II. Comparison of sensitivity and signal/background ratios for three isotopes (courtesy of Cetac Technologies)

Isotope/ interference	Mass (amu)	Crossflow nebulizer (cps)	Net signal/ BG	Membrane Desolvation USN (cps)	Net signal/ BG
^{44}Ca (25 ppb)		2300		20,800	
$^{12}C^{16}O_2$ (BG)	44	7640	0.3	1730	12
^{56}Fe (10 ppb)		95,400		262,000	
$^{40}Ar^{16}O$ (BG)	56	868,000	0.1	8200	32
^{57}Fe (10 ppb)		2590		6400	32
$^{40}Ar^{16}OH$ (BG)	57	5300	0.5	200	

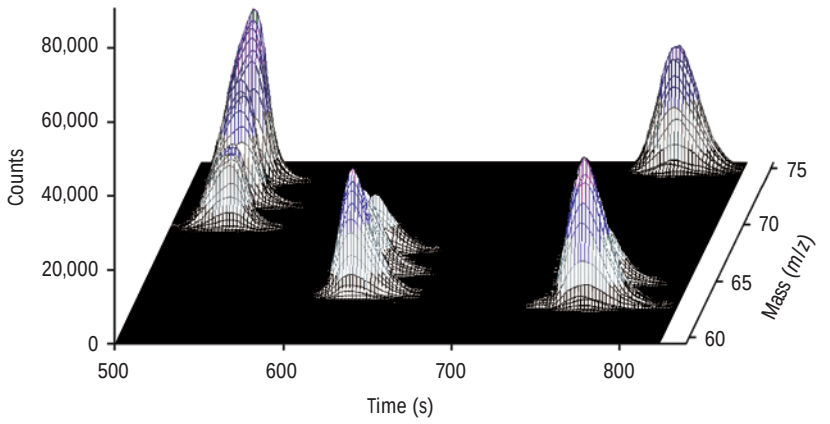

Figure 6. A typical chromatogram generated by a liquid chromatograph coupled to an ICP mass spectrometer, showing a temporal display of intensity against mass. (Courtesy of PerkinElmer Instruments.)

volumes, the major benefit is that less matrix is entering the mass spectrometer, which means that there is less chance of sample-induced long-term drift. In addition, most low-flow nebulizers use chemically inert plastic capillaries, which make them well suited for the analysis of highly corrosive chemicals. This kind of flexibility has made low-flow nebulizers very popular, particularly in the semiconductor industry where it is essential to analyze high-purity acids using sample introduction systems free of sources of contamination (13).

Chromatographic Separation Devices

ICP-MS has gained in popularity, mainly because of its ability to rapidly quantitate ultratrace metal contamination levels. However, in its basic design, ICP-MS cannot reveal anything about the metal's oxidation state, alkylated form, or how it is bound to a biomolecule. The desire to understand in what form or species an element exists led researchers to investigate the combination of chromatographic separation devices with ICP-MS. The ICP mass spectrometer becomes a very sensitive detector for trace element speciation studies when coupled with a chromatographic technique like high performance liquid chromatography (HPLC), ion chromatography (IC), gas chromatography (GC), or capillary electrophoresis (CE). In these hybrid techniques, element species are separated based on their chromatographic retention/mobility times and then eluted/passed into the ICP mass spectrometer for detection (14). The intensity of the eluted peaks are then displayed for each isotopic mass of interest in the time domain as shown in Figure 6, which shows a typical chromatogram for a selected group of masses between 60 and 75 amu.

There is no question that the extremely low detection capability of ICP-MS has allowed researchers in the environmental, biomedical, geochemical, and nutritional fields to gain a much better insight into the impact of different elemental species on us and our environment — something that would not have been possible 10–15 years ago. The majority of trace element speciation studies being carried out today can be broken down into three major categories:

- Those involving redox systems, where the oxidation state of a metal can change. For example, hexavalent chromium, Cr(VI), is a powerful oxidant and extremely toxic, but in soils and water systems, it reacts with organic matter to form trivalent chromium, Cr(III), which is the more common form of the element and is an essential micronutrient for plants and animals (15).
- Another important class is alkylated forms of the metal. Very often the natural form of an element can be toxic, while its alkylated form is relatively harmless — or vice versa. A good example of this is the element arsenic. Inorganic forms of the element such as As(III) and As(V) are toxic, whereas many of its alkylated forms, such as monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA), are relatively innocuous (16).
- An area being investigated more and more is biomolecules. For example, in animal studies, activity and mobility of an innocuous arsenic-based growth promoter is determined by studying its metabolic impact and excretion characteristics. Measurement of the biochemical form of arsenic is crucial to know its growth potential (17).

Table III represents a small cross section of speciation work that has been carried out by chromatography techniques coupled to ICP-MS in these three major categories.

As mentioned previously, there is a large body of application work in the public domain that has investigated the use of different chromatographic separation devices, such as LC (18,19), IC (20), GC (21,22), and CE (23,24) with ICP-MS. The area that is probably getting the most attention is the coupling of HPLC with ICP-MS. By using either adsorption, ion-exchange, gel perme-

Table III. Some elemental species that have been studied by researchers using chromatographic separation devices coupled to ICP-MS

Redox systems	Alkylated forms	Biomolecules
Se(IV)/Se(VI)	Methyl — Hg, Ge, Sn, Pb, As, Sb, Se, Te, Zn, Cd, Cr	Organo — As, Se, Cd
As(III)/As(V)	Ethyl — Pb, Hg	Metallo-porphyrines
Sn(II)/Sn(IV)	Butyl — Sn	Metallo-proteins
Cr(III)/Cr(VI)	Phenyl — Sn	Metallo-drugs
Fe(II)/Fe(III)	Cyclohexyl — Sn	Metallo-enzymes

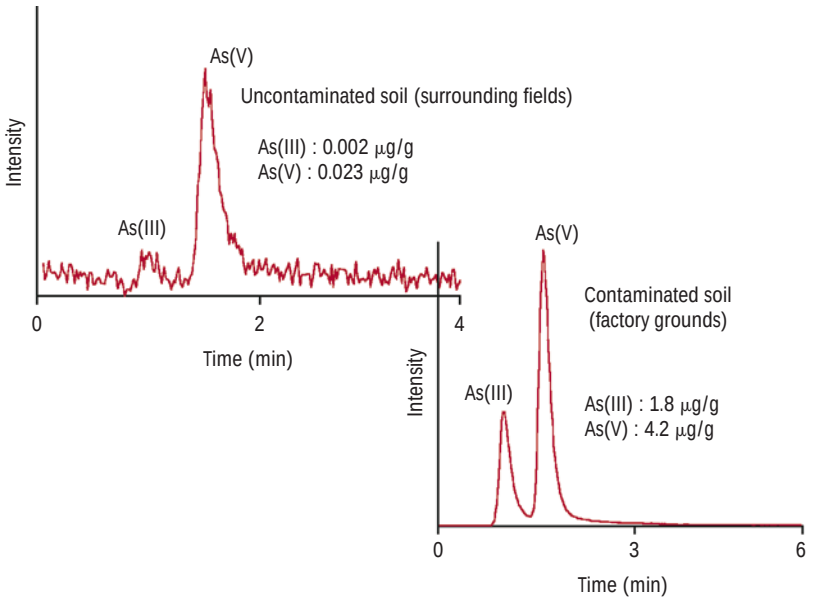

Figure 7. HPLC-ICP-MS chromatogram showing comparison of As(III) and As(V) levels in two different soil samples in and around an industrial site. (Courtesy of CETAC Technologies.)

ation, or normal- or reversed-phase chromatography configurations, valuable elemental speciation information can be derived from a sample. Let's take a look at one of these applications — the determination of different forms of inorganic arsenic in soil, using ion-exchange HPLC coupled to ICP-MS, to get a better understanding of how the technique works.

Arsenic toxicity depends directly on the chemical form of the arsenic. In its inorganic form, arsenic is highly toxic, while many of its organic forms are relatively harmless. Inorganic species of arsenic that are of toxicological interest are the trivalent form (As[III]), such as arsenious acid, H_3AsO_3 and its arsenite salts; the pentavalent form (As[V]), such as arsenic acid, H_3AsO_5, and its arsenate salts; and arsine (AsH_3), a poisonous, unstable gas used in the manufacture of semiconductor devices. Arsenic is introduced into the environment and ecosystems from natural sources by volcanic activity and the weathering of minerals, and also from anthropogenic sources, such as ore smelting, coal burning, industrial discharge, and pesticide use. The ratio of natural arsenic to anthropogenic arsenic is approximately 60:40.

A recent study investigated a potential arsenic contamination of the soil in and around an industrial site in Europe. Soil in a field near the factory in question was sampled, as was soil inside the factory grounds. The soil was dried, weighed, extracted with water, and filtered. This careful, gentle extraction procedure was used to avoid disturbing the distribution of arsenic species originally present in the sample — an important consideration in speciation studies. A 10-mL sample was injected onto an amine-based, anion-exchange resin, where the different oxidation states of arsenic in soil were chromatographically extracted from the matrix and separated using a standard LC pump. The matrix components passed straight through the column, whereas the arsenic species were retained and then isocratically eluted into the nebulizer of the ICP mass spectrometer using 5 mM ammonium malonate. The arsenic species were then detected and quantified by running the instrument in the single-ion monitoring mode, set at mass 75 — the only isotope for arsenic. Figure 7 shows that both As(III) and As(V) were eluted off the column in less than three minutes using this HPLC-ICP-MS setup. The chromatogram also shows that both species are approximately three orders of magnitude lower in the soil sample from the surrounding field, compared with the soil sample inside the factory grounds. Although the arsenic does not exceed average global soil levels, it is a clear indication that the factory is a source of arsenic contamination.

It is worth mentioning that for some reversed-phase HPLC separations, gradient elution of the analyte species with mixtures of organic solvents like methanol might have to be used (25). If this is a requirement, consideration must be given to the fact that large amounts of organic solvent will extinguish the plasma, so introduction of the eluent into the ICP mass spectrometer cannot be carried out using a conventional nebulization. For this reason, special sample introduction systems like refrigerated spray chambers (26) or desolvation systems (27) have to be used, in addition to small amounts of oxygen in the sample aerosol flow to stop the build-up of carbon deposits on the sampler cone. Other approaches, such as direct injection nebulization (DIN) (28), have been used to introduce the sample eluent into the ICP-MS, but unfortunately have not gained widespread acceptance because of usability issues. DIN was very popular when first developed in the early 1990s because of its ability to handle small sample volumes and its low memory characteristics. However, it has been replaced by other sampling techniques and, as a result, appears to have limited commercial viability.

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