

What is ICP-MS?

... and more importantly, what can it do?

Inductively Coupled Plasma Mass Spectrometry or ICP-MS is an analytical technique used for elemental determinations. The technique was commercially introduced in 1983 and has gained general acceptance in many types of laboratories. Geochemical analysis labs were early adopters of ICP-MS technology because of its superior detection capabilities, particularly for the rare-earth elements (REEs). ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICP-AES), including:

- Detection limits for most elements equal to or better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).
- Higher throughput than GFAAS
- The ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source
- Superior detection capability to ICP-AES with the same sample throughput
- The ability to obtain isotopic information

An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer.

Figure 1 shows a schematic representation of an ICP source in an ICP-MS. Argon gas flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons

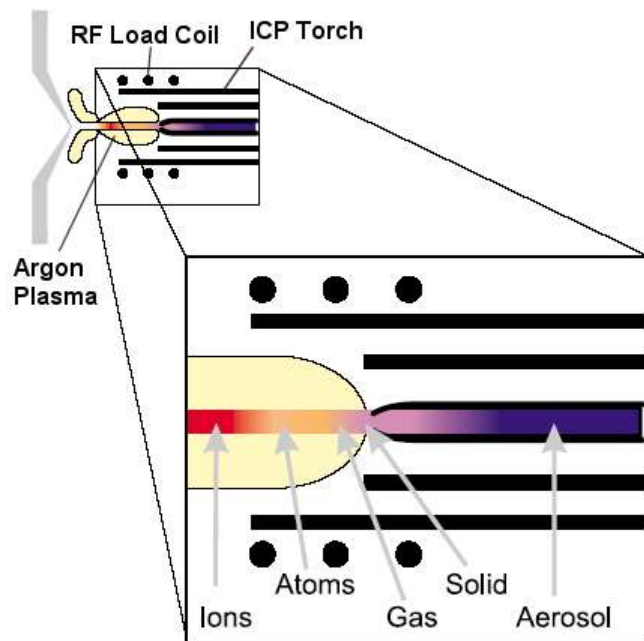


Figure 1. The ICP Torch showing fate of the sample.
(Figure reproduced with permission from PerkinElmer, Inc.)

are stripped off of the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma.

The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma.

The most important things to remember about the argon ICP plasma are:

- The argon discharge, with a temperature of around 6000-10000 K, is an excellent ion source.
- The ions formed by the ICP discharge are typically positive ions, M^+ or M^{+2} , therefore, elements that prefer to form negative ions, such as Cl, I, F, etc. are very difficult to determine via ICP-MS.
- The detection capabilities of the technique can vary with the sample introduction technique used, as different techniques will allow differing amounts of sample to reach the ICP plasma.
- Detection capabilities will vary with the sample matrix, which may affect the degree of ionization that will occur in the plasma or allow the formation of species that may interfere with the analyte determination.

Once the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones. The interface region in the ICP-MS transmits the ions traveling in the argon sample stream at atmospheric pressure (1-2 torr) into the low pressure region of the mass spectrometer ($<1 \times 10^{-5}$ torr). This is done through the intermediate vacuum region created by the two interface cones, the sampler and the skimmer (see Figure 2). The sampler and skimmer cones are metal disks with a small hole ($\sim 1\text{mm}$) in the center.

The purpose of these cones is to sample the center portion of the ion beam coming from the ICP torch. A shadow stop (see Figure 2) or similar device blocks the photons coming from the ICP torch, which is also an intense light source. Due to the small diameters of the orifices in the sampler and skimmer cones, ICP-MS has some limitations as to the amount of total dissolved solids in the samples. Generally, it is recommended that samples have

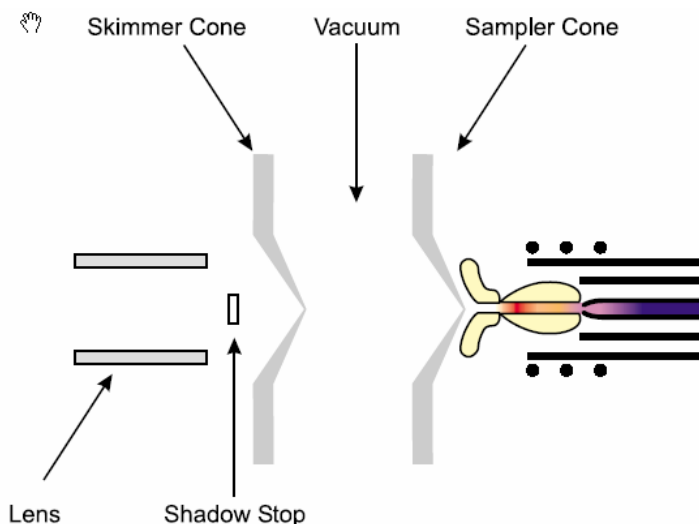


Figure 2. The interface region of an ICP-MS.
(Figure reproduced with permission from PerkinElmer, Inc.)

no more than 0.2% total dissolved solids (TDS) for best instrument performance and stability. If samples with very high TDS levels are run, the orifices in the cones will eventually become blocked, causing decreased sensitivity and detection capability and requiring the system to be shut down for maintenance. This is why many sample types, including digested soil and rock samples must be diluted before running on the ICP-MS.

The ions from the ICP source are then focused by the electrostatic lenses in the system. Remember, the ions coming from the system are positively charged, so the electrostatic lens, which also has a positive charge, serves to collimate the ion beam and focus it into the entrance aperture or slit of the mass spectrometer. Different types of ICP-MS systems have different types of lens systems. The simplest employs a single lens, while more complex systems may contain as many as 12 ion lenses. Each ion optic system is specifically designed to work with the interface and mass spectrometer design of the instrument.

Once the ions enter the mass spectrometer, they are separated by their mass-to-charge ratio. The most commonly used type of mass spectrometer is the **quadrupole mass filter**. In this type, 4 rods (approximately 1 cm in diameter and 15-20 cm long) are arranged as in Figure 3. In a quadrupole mass filter, alternating AC and DC voltages are applied to opposite pairs of the rods.

These voltages are then rapidly switched along with an RF-field. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/e) pass through the rods to the

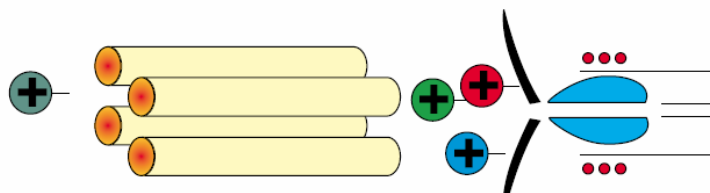


Figure 3. Schematic of quadrupole mass filter.
(Figure reproduced with permission from PerkinElmer, Inc.)

detector at a given instant in time. So, the quadrupole mass filter is really a sequential filter, with the settings being change for each specific m/e at a time. However, the voltages on the rods can be switched at a very rapid rate. The result is that the quadrupole mass filter can separate up to 2400 amu (atomic mass units) per second! This speed is why the quadrupole ICP-MS is often considered to have simultaneous multi-elemental analysis properties. The ability to filter ions on their mass-to-charge ratio allows ICP-MS to supply isotopic information, since different isotopes of the same element have different masses (see Figure 4).

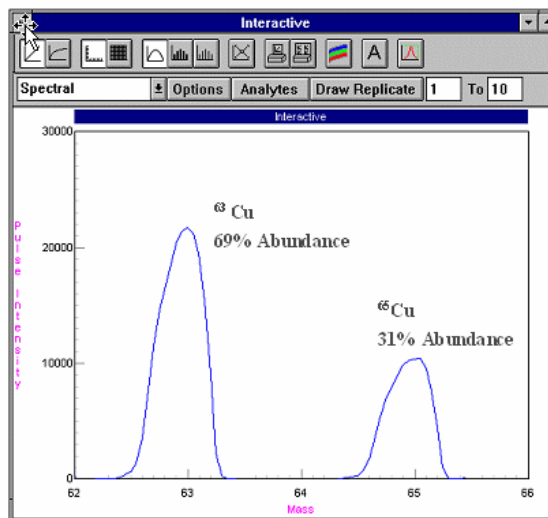


Figure 4. Spectrum showing copper isotopes by ICP-MS.

Typical quadrupole mass spectrometers used in ICP-MS have resolutions between 0.7 – 1.0 amu. This is sufficient for most routine applications. However, there are some instances where this resolution is NOT sufficient to separate overlapping molecular or isobaric interferences from the elemental isotope of interest. Table 1 below shows some commonly occurring interferences that make ultratrace determinations of several important elements difficult, particularly in specific matrices. The resolving power (R) of a mass spectrometer is calculated as $R = m/(|m_1 - m_2|) = m/\Delta m$, where m_1 is the mass of one species or isotope and m_2 is the mass of the species or isotope it must be separated from; m is the nominal mass.

Analyte	Interference	$ \Delta m $	m	R
$^{75}\text{As} = 74.92160$	$^{40}\text{Ar}^{35}\text{Cl} = 74.93123$	0.00963	75	7788
$^{52}\text{Cr} = 52.94065$	$^{37}\text{Cl}^{16}\text{O} = 52.96081$	0.02016	53	2629
$^{56}\text{Fe} = 55.93494$	$^{40}\text{Ar}^{16}\text{O} = 55.95729$	0.02235	56	2505
$^{40}\text{Ca} = 39.96259$	$^{40}\text{Ar} = 39.96238$	0.00021	40	190476
$^{87}\text{Sr} = 86.90889$	$^{87}\text{Rb} = 86.90918$	0.00029	87	300000

Table 1. Example interferences and resolving power required.

The use of high resolution or magnetic sector mass spectrometers has become more common in ICP-MS, allowing the user to eliminate or reduce the effect of interferences due to mass overlap. Figure 2 shows a typical instrumental configuration used in high resolution (HR) ICP-MS. In this type of instrument, both a magnetic sector and an electric sector are used to separate and focus the ions. The magnetic sector is dispersive with respect to both ion energy and mass and focuses all the ions with diverging angles of motion coming from the entrance slit of the spectrometer. The electric sector is dispersive only to ion energy and focuses the ions onto the exit slit. Such an arrangement is called a double-focusing high resolution mass spectrometer. In ICP-MS, reverse Nier-Johnson geometry – where the magnetic sector is before the electric sector – is commonly used in order to decouple the electric fields in the electric sector from any electric field originating by the ICP RF generator.

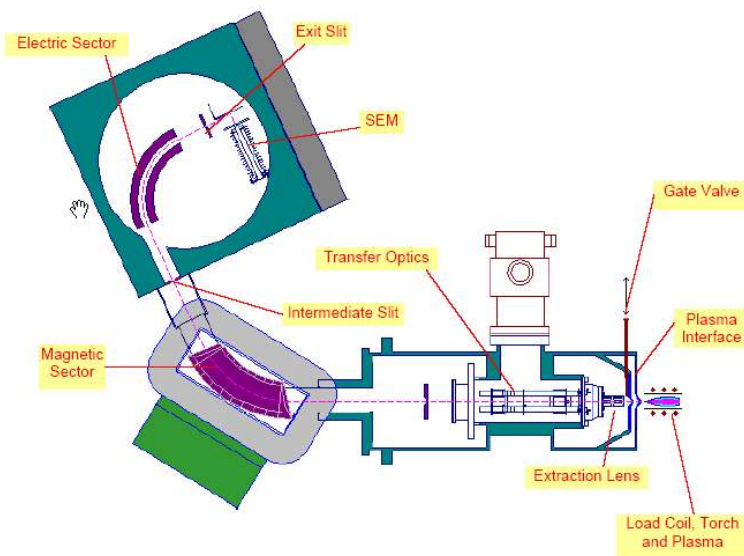


Figure 5. Reverse Nier-Johnson geometry used on the Finnigan ELEMENT HR-ICP-MS (Courtesy of Thermo Finnigan, San Jose, CA.)

The resolution of high-resolution instruments can be changed by adjusting the width of the entrance and exit slits into the spectrometer. Typical HR-ICP-MS instruments have

resolving powers up to 10,000 and are typically operated at preset resolution settings for low, medium or high-resolution to make their operation easier for the user. As we can see from Table 1, the use of HR-ICP-MS will solve many, but not all interference problems.

High resolution instruments also have several limitations. First of all, they typically cost 2-3 times that of a quadrupole ICP-MS instrument. They are also more complex to operate and maintain. In addition, for every 10-fold increase in resolving power, there is a concomitant decrease in signal intensity. This may limit the actual detection capabilities if the concentration of the analyte of interest is very low. Finally, they are much slower than a quadrupole system. Due to the longer settling times required by the magnet when the voltages are adjusted for large mass jumps, HR-ICP-MS instruments typically are 4-5 times slower than a quadrupole instrument. This makes them unsuitable for the rapid, high-throughput, multielemental analyses that are routine in production-type laboratories. They are also not the instrument of choice for transient signal analysis, including those obtained using Laser Ablation techniques for elemental profiling or chromatographic separations as their scan speeds are too slow to look at more than 1-3 elements of similar mass in an analysis. As a result, this type of instrument is generally found in research institutions and in laboratories with highly specialized needs for a low number of samples.

A second type of HR-ICP-MS instrument is also available that uses multiple detectors – this type is called a Multi-Collector HR-ICP-MS or MC-ICP-MS. These instruments are generally designed and developed for the purpose of performing high-precision isotope ratio analyses. Since an array of 5-10 detectors can be positioned around the exit slit of a double-focusing system, the isotopes of a single element can generally all be determined simultaneously, leading to the technique's high-precision. The disadvantage of this type of system is that the isotopes must all be in a narrow mass range ($\pm 15\text{-}20\%$ of the nominal mass) as the magnetic sector settings remained fixed while only the electric sector settings are scanned. This generally means that each elemental isotopic system must be measured in a separate analysis. This type of instrument is generally not suitable for routine multi-elemental analysis for major and minor constituents and is typically only used for performing isotope ratio measurements.

Once the ions have been separated by their mass-to-charge ratio, they must then be detected or counted by a suitable detector. The fundamental purpose of the detector is to translate the number of ions striking the detector into an electrical signal that can be measured and related to the number of atoms of that element in the sample via the use of calibration standards. Most detectors use a high negative voltage on the front surface of the detector to attract the positively charged ions to the detector. Once the ion hits the active surface of the detector, a number of electrons is released which then strike the next surface of the detector, amplifying the signal. In the past several years, the channel electron multiplier (CEM), which was used on earlier ICP-MS instruments, has been replaced with discrete dynode type detectors (see Figure 6). Discrete dynode detectors generally have wider linear dynamic ranges than CEMs, which is important in ICP-MS as the concentrations analyzed may vary from sub-ppb to high ppm. The discrete dynode

type detector can also be run in two modes, pulse-counting and analog, which further extends the instrument's linear range and can be used to protect the detector from excessively high signals.

MC-ICP-MS instruments tend to use simpler, less expensive Faraday Cup type detectors as they have the ability to deal with excessively high count rates common with magnetic sector instruments. However, these detectors do not have the flexibility necessary for quadrupole ICP-MS instruments.

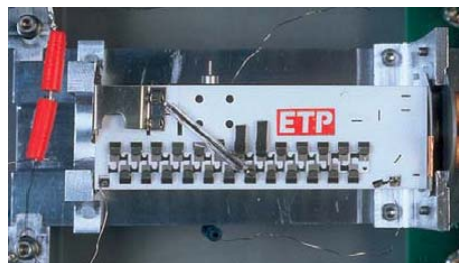


Figure 6. Discrete dynode detector used on the ELAN ICP-MS systems. (courtesy of PerkinElmer, Inc.)

A few things to remember about the ICP-MS detector:

- It is a consumable item. As ions hit the surface of the detector and are converted to electrons, the active film coating will be consumed. Depending on usage, a typical discrete dynode detector will last 6-18 months in a quadrupole ICP-MS.
- It should be protected from high signal count rates. Most manufacturers' design the detector circuitry to protect it from potentially fatal ion count rates. However, the users can further this by diluting samples with known high concentration values or choosing a less abundant isotope for their analysis.
- They are expensive. A new detector will cost on the order of \$1500-2500 depending on the specific type. Care should be taken to protect it.
- They are light sensitive. Most detectors are as sensitive to photons as they are to ions. Care should be taken to store spare detectors in the dark and never expose a detector to the light while the high voltage power supply to it is on.

Since it first became commercially available over 20 years ago, ICP-MS has become a widely used tool, for both routine analyses and for research in a variety of areas. ICP-MS is a flexible technique that offers many advantages over more traditional techniques for elemental analysis, including Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Atomic Absorption Spectroscopy (AAS). The detection limits achievable for most elements are equivalent to or below those obtained by Graphite Furnace AAS, but with several advantages. ICP-MS is a fast, multielemental technique and generally has the productivity of ICP-AES, but much lower detection capabilities.

Figure 7 shows the elements traditionally determined by ICP-MS and their approximate Instrumental Detection Limit (IDL). Care should be taken to note that IDLs are calculated as 3 times the standard deviation of a blank measurement and represent the *best* possible detection capability of the instrument. In real life, the Method Detection Limit (MDL) or Practical Quantitation Limit (PQL) will generally be 2-10 times higher than the IDL and will depend upon many factors, including: lab and instrument background levels, sample matrix, sample collection and preparation methods, and

operator skill level. However, the IDL can be used as a general guide as to the relative capabilities of the ICP-MS technique as compared to other analytical techniques.



Figure 7. Approximate detection capabilities of the ELAN 6000/6100 quadrupole ICP-MS. (Courtesy of PerkinElmer, Inc.)

It should be noted that several elements including S, Se, B, Si, P, Br, I, K, and Ca have fairly high detection limits via ICP-MS. In the case of I and Br, this is due to the fact that very few positive ions are formed in the ICP plasma for these elements. For elements such as S, Se, P, K, and Ca, isobaric and molecular interferences from either the sample matrix or plasma species interfere with the primary isotope. This means that less abundant isotopes with less interference (if available) must be used for determination of these elements, which will degrade detection capabilities for these elements.

In general it is good practice for the user of the analytical data submitting samples for ICP-MS analysis to discuss the nature of the samples and the data quality required with the ICP-MS operator so that proper isotopic selection and/or sample preparation methods can be utilized to meet the end user's needs.

[Author: Ruth E. Wolf, Ph.D., Research Chemist, USGS/CR/CICT, March 2005]