ICP Mass Spectrometry

The 30-Minute Guide to ICP-MS

First…A Little History

ICP-MS (Inductively Coupled Plasma Mass Spectrometry) is not a new technique at all. In fact, it is over 20 years old! The first papers on ICP-MS were published in the 1980s and PerkinElmer SCIEX introduced the first commercially available ICP-MS instrument in 1983. Since that time, many improvements and refinements have been made to each generation of ICP-MS instrumentation. Today, PerkinElmer SCIEX is on its fifth generation ICP-MS and the technique is used daily by many laboratories as a routine analytical tool.

ICP-MS offers many benefits to laboratories performing trace metal determinations.

- ICP-MS offers detection limits equal to or better than those attainable using Graphite Furnace Atomic Absorption (GFAA) with much higher productivity.

- ICP-MS can easily handle both simple and complex sample matrixes.

- ICP-MS has detection limit capabilities that are superior to those obtained in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

What Can Be Measured With an ICP-MS?

For laboratories using flame or furnace AA or ICP-OES, ICP-MS offers the opportunity to achieve higher productivity and obtain lower detection limits. Let's look at what an ICP-MS instrument can do and how it does it.

The ICP-MS instrument measures most of the elements in the periodic table. The elements shown in color in Figure 1 can be analyzed by ICP-MS with detection limits[a] at or below the part per trillion (ppt)[b] range. Elements that are in white are either not measurable by ICP-MS (the upper right hand side) or do not have naturally occurring isotopes. The

[a] The detection limits are based on a 98% confidence level (3 standard deviations).
[b] Identifying a single part per trillion of an element in a solution is analogous to locating a single white raisin in a house (2,700 sq. ft) full of regular raisins.
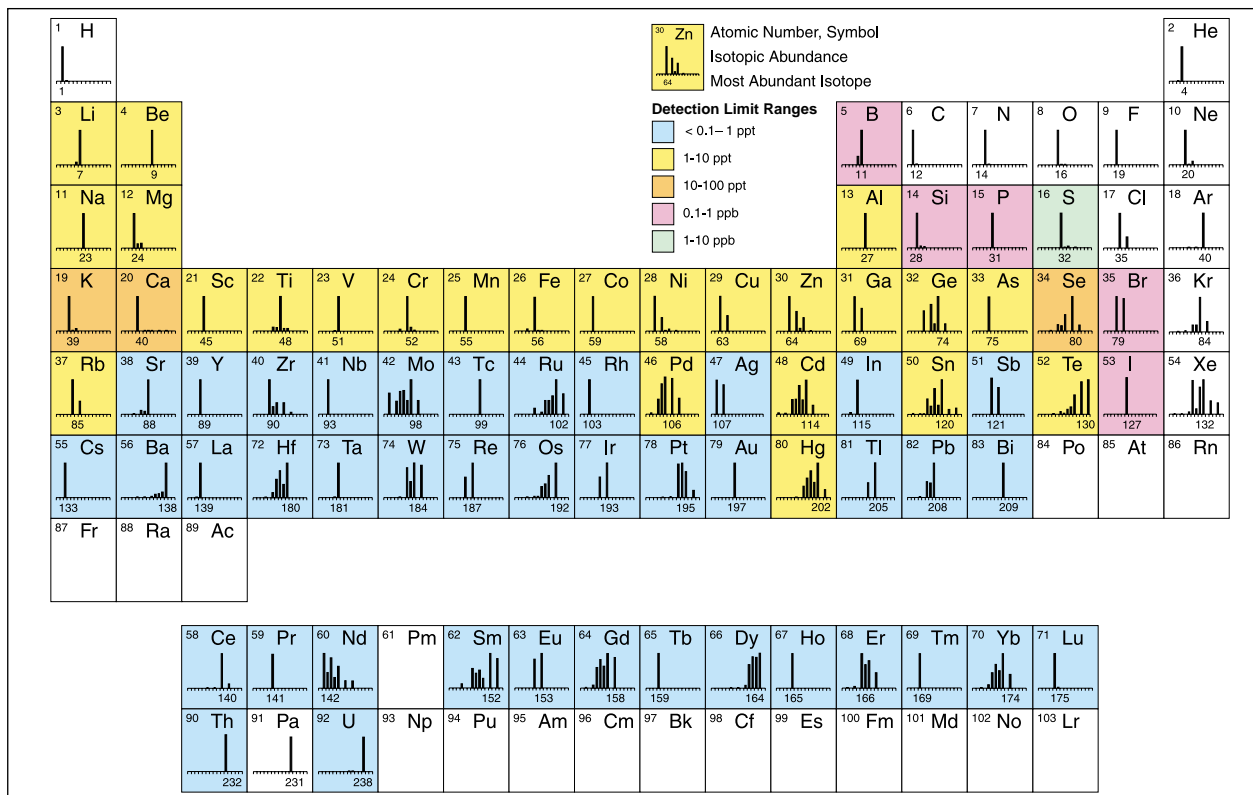

Figure 1. Elements determined by ICP-MS and approximate detection capability.

PerkinElmerSCIEX
instruments.

lines shown for each element in Figure 1 depict the number and relative abundance of the natural isotopes for that element – this is sometimes referred to as the isotopic fingerprint of the element. The naturally occurring isotopes of each element all have the same atomic number (number of protons in the nucleus), but differ by the atomic mass. This is the result of the different number of neutrons present in the nucleus of each isotope.

ICP-MS shares some components, including the quadrupole mass spectrometer, vacuum system, and detector, with other types of mass spectrometers such as LC/MS and GC/MS. However, the plasma ion source used in ICP-MS is much different than the lower-energy ion sources used in LC/MS and GC/MS instruments. The extreme high temperature of the plasma ion source completely breaks apart the molecules present in a sample. As a result, the ICP-MS detects only elemental ions. This makes ICP-MS much more comparable to other inorganic techniques, such as AAS and ICP-OES, for elemental analysis. In addition, the standard and sample preparation techniques, sample introduction systems, and potential interferences are all very similar to those in AAS and ICP-OES. One advantage of ICP-MS over

these other inorganic techniques for elemental determination is that ICP-MS can determine the individual isotopes of each element. This allows ICP-MS to perform isotope ratio and isotope dilution measurements.

A Quick Overview

An ICP-MS consists of the following components (see Figure 2):

- Sample introduction system – consists of the peristaltic pump, nebulizer, and spray chamber and provides the means of getting samples into the instrument
- ICP torch – generates the plasma which serves as the ion source of the ICP-MS, converting the analyte atoms to ions
- Interface – links the atmospheric pressure ICP ion source and the high vacuum mass spectrometer
- Vacuum system – provides high vacuum for ion optics, quadrupole, and detector
- Lens – focuses ions into a beam for transmission into the quadrupole
- Quadrupole – acts as a mass filter to sort ions by their mass-to-charge ratio (m/z)
- Detector – counts individual ions passing through the quadrupole

- Data handling and system controller – controls all aspects of instrument control and data handling to obtain final concentration results

Most samples analyzed by ICP-MS are liquids. However, solid samples can be analyzed using lasers or heated cells to vaporize the sample. Gas samples can be measured by direct introduction into the instrument. The most common sample introduction system used on an ICP-MS consists of a nebulizer and spray chamber. The nebulizer converts the liquid samples into very small droplets. These droplets are carried through the spray chamber and into the tube or injector that is the center channel of the torch and then into the plasma. The plasma ionizes the elements present in the droplets. These ions then pass through the interface and the ion lens. After being focused by the ion lens, the ions are separated by their mass-to-charge ratio in the mass spectrometer and measured by the detector. Once the detector measures the ions, the computerized data system is used to convert the measured signal intensities into concentrations of each element and generate a report of the results. The dotted blue arrow in Figure 2 shows the direction of travel of the sample
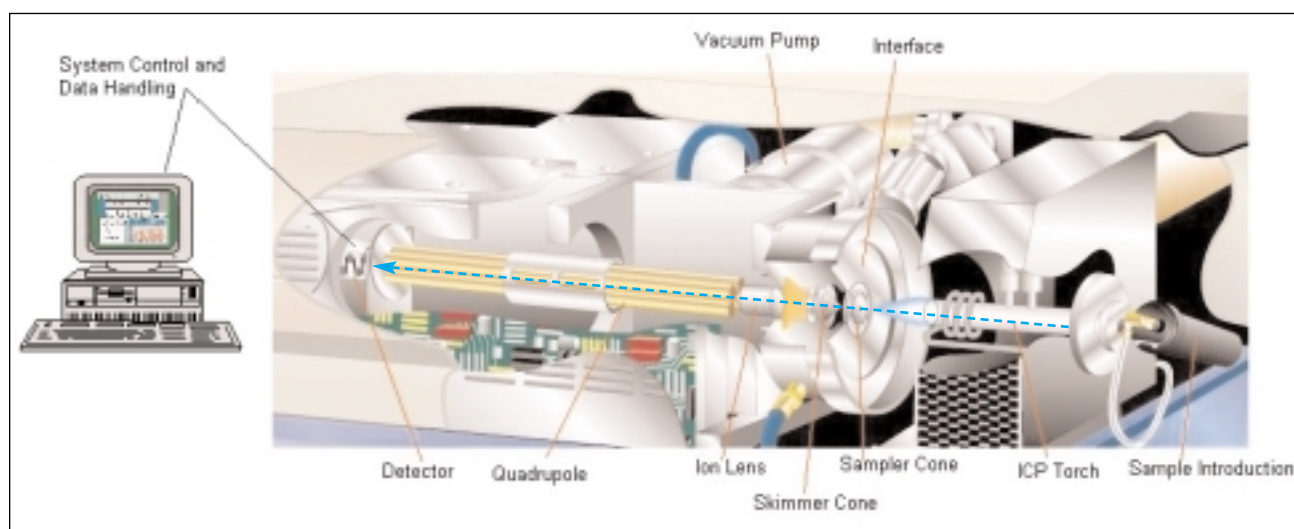

Figure 2. Components of an ICP-MS system.

through the ICP-MS. The next few pages briefly describe the function of each part of the ICP-MS in more detail.

Sample Introduction

The sample introduction system on an ICP-MS is very similar to that used on a flame AA or ICP-OES. When measuring metal content in a liquid sample, the liquid must be in a form acceptable to the instrument's plasma. This is achieved by introducing the sample to a nebulizer such as a cross-flow type shown in Figure 3. A cross-flow nebulizer works on the same principle as the old hand-pumped insecticide sprayer:

1. A flow of gas is passed at right angles over the end of a tube containing a liquid.
2. The flow of gas shears the liquid into very small droplets forming an aerosol.
3. The droplets then pass through a spray chamber that eliminates all droplets except those that are the right size[c] and velocity for introduction into the plasma.

Other types of nebulizers are also useful for introducing the liquid sample to the ICP-MS instrument. The specific type of nebulizer used can be selected based on the sample type and volume.

The ICP Torch - Making Ions

The plasma generated in the ICP torch creates a very hot zone that serves a variety of functions. At a temperature of approximately 6000°C, the plasma is about 10 times hotter than a pizza oven, three times hotter than a welding torch, and equal to the temperature at the surface of the sun. The plasma is generated by passing argon through a series of concentric quartz tubes (the ICP torch) that are wrapped at one end by a radio frequency (RF) coil. Energy supplied to the coil by the RF generator couples with the argon to produce the plasma.

During their voyage into the plasma, shown in Figure 4, the liquid droplets containing the sample matrix and the elements to be determined are dried to a solid, and then heated to a gas. As the

atoms travel through the plasma, they absorb more energy from the plasma and eventually release one electron to form a singly charged ion. The singly charged ions exit the plasma and enter the interface region.

Similar processes occur in the flame or plasma of AA and ICP instruments, respectively. The difference is that ICP-MS measures the ions themselves and the other techniques measure light instead.

The Interface – Sampling Ions

Placing a plasma, operating at 6000°C, near an ion focusing device, operating near room temperature, is like placing the Earth about a half-mile away from the sun. In addition to a large temperature difference, the plasma operates at a pressure that is much higher than the vacuum required by the ion lens and mass spectrometer portions of the instrument.

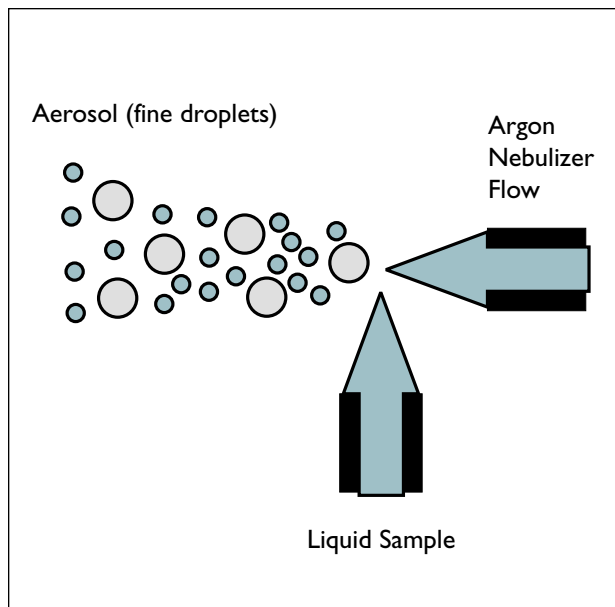The interface allows the plasma and the ion lens system to coexist and the ions generated by the
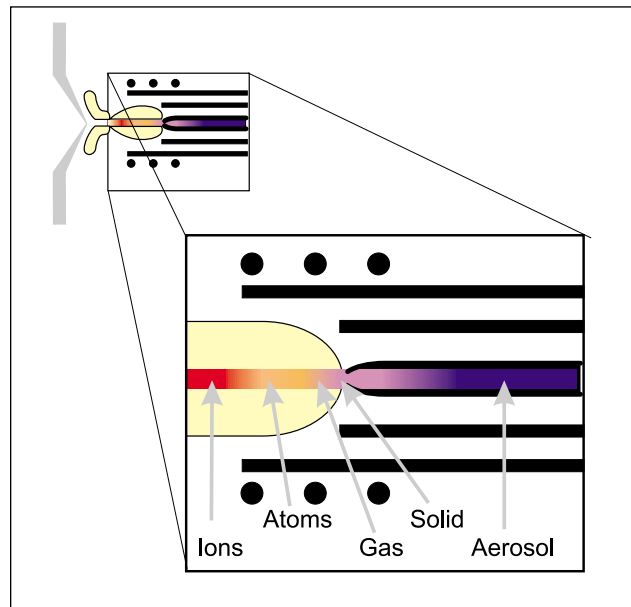

Figure 3. Cross-flow nebulizer.

Figure 4. Form of sample in ICP-MS.

[c] One micron diameter (1 X 10-6 meters) is considered an ideal diameter for introduction into the plasma.

plasma to pass into the ion lens region[d]. The interface (shown in Figure 5) consists of two inverted funnel-like devices called cones. The sampler cone is located next to the plasma and the skimmer cone is located several millimeters behind the sampler cone. Each cone has an opening of approximately one-millimeter in diameter at the apex that permits the ions to pass through. The cones are typically made of nickel or platinum and are mounted into a water-cooled metal housing to prevent damage from the heat of the plasma. The region between the two cones is evacuated to a pressure of a few Torr[e] by a mechanical roughing pump. The holes in the cones or orifices must be large enough to prevent un-vaporized materials from clogging them. The orifices must also be small enough to maintain a consistent vacuum on the other side of the interface. As samples pass through an ICP-MS instrument, materials will eventually deposit on these cones and will need to be removed by occasional cleaning. How often the cones require cleaning is an important maintenance item that must be considered when selecting an ICP-MS.

The Vacuum System – Provides Correct Operating Pressure

The distance from the interface to the detector of an ICP-MS is typically one meter or less. If an ion is to travel that distance, it cannot collide with any gas molecules. This requires removal of nearly all of the gas molecules in the space between the interface and the detector to create a vacuum. This task is accomplished using a combination of turbomolecular pumps and mechanical roughing pumps called the vacuum system. The turbomolecular pumps work like jet turbines and are capable of rapidly pumping a chamber to a pressure of 1×10^{-5} Torr. The roughing pump connected to the interface area (where the cones are located) removes most of the excess sample matrix ions and gasses. Routine maintenance on the vacuum system generally consists of changing the oil in the roughing pumps every 2 to 3 months.

The Lens System - Focusing Ions

The ion lens is positioned immediately behind the interface. It is responsible for focusing ions into the quadrupole region. Since the ions generated in the plasma are nearly all positively charged, they have a natural tendency to repel each other. In order to get as many of the ions as possible into the quadrupole for mass separation and eventual measurement, it is necessary to keep the ion beam from diverging. This is achieved by passing the ions through a charged metallic cylinder that acts as a focusing lens. Since the charge on the lens is the same as the charge on the ions, the ions are repelled (like pushing the positive poles of two magnets together) back toward each other to form a focused ion beam. The small disk located between the skimmer cone and the cylinder lens is the shadow stop. This device keeps the photons and unionized materials emitted from the plasma from moving downstream where they could have an adverse effect on the performance of the ICP-MS.

Again, focusing ions in a mass spectrometer is like focusing light in an optical spectrometer. However, the optical spectrometer uses an optical lens to bend the light beam, while the mass spectrometer uses an electrical field to focus the ion beam.

The Quadrupole - Separating Ions

The mass spectrometer separates the singly charged ions from each other by mass, serving as a mass filter. Three main types of mass spectrometers are used in commercial ICP-MS systems: quadrupole, time-of-flight, and magnetic sector. The quadrupole is the type most commonly used in routine analytical instrumentation. A quadrupole consists of 4 rods approximately 20 cm in length and 1 cm in diameter arranged as shown in Figure 6.

The quadrupole mass spectrometer works by allowing only one mass to pass through to the detector
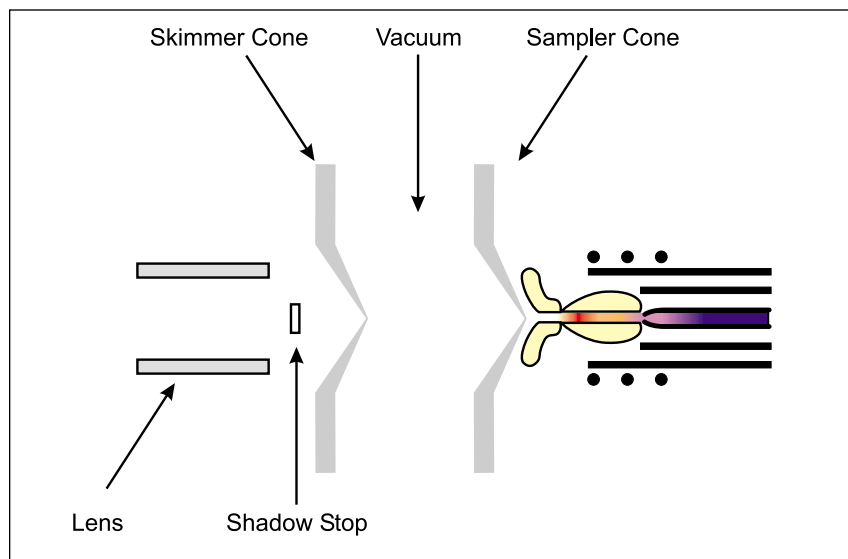

Figure 5. The ICP-MS interface.

[d] "An Improved Interface for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)", D. J. Douglas and J. B. French, Spectrochimica Acta, Vol. 41B, No 3, pp. 197-204, 1986.

[e] The Torr is a unit of pressure equal to 1-760th of an atmosphere. The Torr is named after the physicist Evangeslista Torricelli (1608-1647) who is credited with inventing the barometer.

at any given time. The quadrupole actually sorts on the mass-to-charge (often referred to as m/z) ratio of the ions. The quadrupole does this by setting up the correct combination of voltages and radio frequencies to guide the ions with the selected m/z between the four rods of the quadrupole. Ions that do not have the selected m/z pass out through the spaces between the rods and are ejected from the quadrupole. The mass spectrometer can move to any m/z needed to measure the elements of interest in the sample analyzed. For example, to measure sodium, which has a single isotope at mass 23, the mass spectrometer can be set to allow ions with m/z = 23/1 to pass. For copper, which has an isotope at mass 63, the mass spectrometer can be set to pass ions with m/z = 63/1. If a doubly charged ion were formed, for example Ba^{+2}, the mass spectrometer would need to be set for a m/z of 69[f] to allow this ion to go through.

Even though the quadrupole mass spectrometer only allows one m/z to pass through the rods at any given time, the voltage settings on the rods can be changed rapidly. The quadrupole on the ELAN® Series ICP-MS from PerkinElmer SCIEX can see from m/z = 1 to m/z = 240 in less than 0.1 seconds. This is called the scan speed of the quadrupole. This is the reason ICP-MS can determine so many different elements quickly even though

only one mass goes through the quadrupole at a time.

Another way to think of this is to compare it to AA or ICP-OES. Instead of using an optical grating in a monochromer to separate out the wavelength of light for the element being determined, the mass spectrometer separates the ions on the basis of their mass and charge.

The Detector - Counting Ions

The ions exiting the mass spectrometer strike the active surface of the detector and generate a measurable electronic signal. The active surface of the detector, known as a dynode, releases an electron each time an ion strikes it. In Figure 7, the ion exiting the quadrupole strikes the first dynode which releases electrons and starts the amplification process. The electrons released from the first dynode strike a second dynode where more electrons are released. This cascading of electrons continues until a measurable pulse is created. By counting the pulses generated by the detector, the system counts the ions that hit the first dynode. Compared with AA and ICP-OES, the detectors used in ICP-MS are not much different than the photomultiplier tubes used as the detectors in these optical instruments. Instead of detecting the light emitted by an analyte, the actual analyte ion itself is being detected.
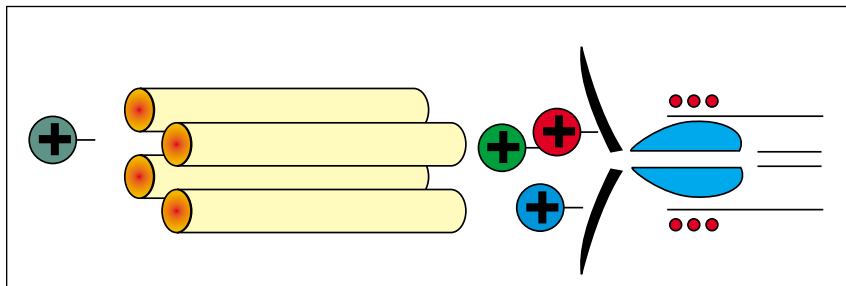
Data Handling and System Controller

All ICP instruments require computers and sophisticated software to control the plasma and mass spectrometer as well as perform calculations on the data collected. The following is an overview of the main software features provided by the ELAN software on all PerkinElmer SCIEX ICP-MS instruments.

Instrument Status and Control

All the parts of the ICP-MS discussed above are under software control. The software makes sure each part of the instrument is working properly and can provide the operator with useful information regarding the instrument status. For example, there are over 70 check points on the ELAN ICP-MS that are monitored by the system to ensure the instrument is always running in a safe and reliable manner.

Instrument Optimization

All the routine optimization procedures performed on the ELAN are controlled by the computer. Just open the optimization window for
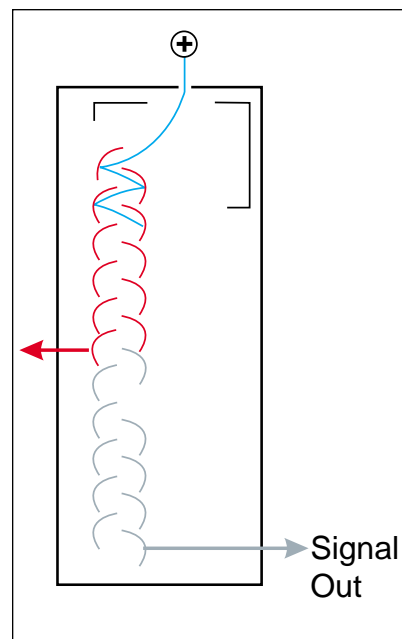

Figure 6. Quadrupole mass filter.

[f] Barium has a major isotope at mass 138 and the charge is 2, so m/z=138/2=69.

Signal Out

Figure 7. ICP-MS detector.

the parameter to be optimized and the software will do the optimization automatically.

Data Handling and Calculation

The software also translates the ion counts measured by the detector into useful information. The ICP-MS instrument can provide data in one of four ways – semi-quantitative analysis, quantitative analysis, isotope dilution analysis, and isotope ratio analysis. The ELAN software offers the user flexibility in how analytical methods, calibrations, and reports are configured. Results can be generated using customized report formats or easily transferred to a Laboratory Information Management System (LIMS) or other data handling system.

Semi-quantitative Analysis

For some analyses, it is not necessary to calibrate the ICP-MS for each element. After the instrument has been calibrated using a single solution containing as few as three elements, a high-quality semi-quantitative analysis for 82 elements can be performed in just a few minutes. Semi-quantitative analysis provides a fingerprint of the elements present in a sample and the approximate concentrations of each element. This information can help determine what standards are necessary for quantitative analysis. Additionally, semi-quantitative analysis can provide valuable information on what other elements are present in a sample that could cause interferences and potentially affect the results. In the example shown in Figure 8, the concentration of zinc has been determined to be 76 ppb. The software does this by comparing the measured spectrum of the unknown sample (in blue) to the known isotopic fingerprints for each element. When a match is obtained (shown in red), the element is identified and the concentration estimated by comparing the measured signal to a stored response file for that element.

Quantitative Analysis

The ICP-MS accurately determines how much of a specific element is in the material analyzed. In a typical quantitative analysis, the concentration of each element is determined by comparing the counts measured for a selected isotope to an external calibration curve that was generated for that element. Liquid calibration standards are prepared in the same manner as used in AA and ICP-OES analysis. These standards are analyzed to establish the calibration curve. The unknown samples are then run and the signal intensities are compared to the calibration curve to determine the concentration of the unknown. Figure 9 shows an example calibration curve for the determination of lead.
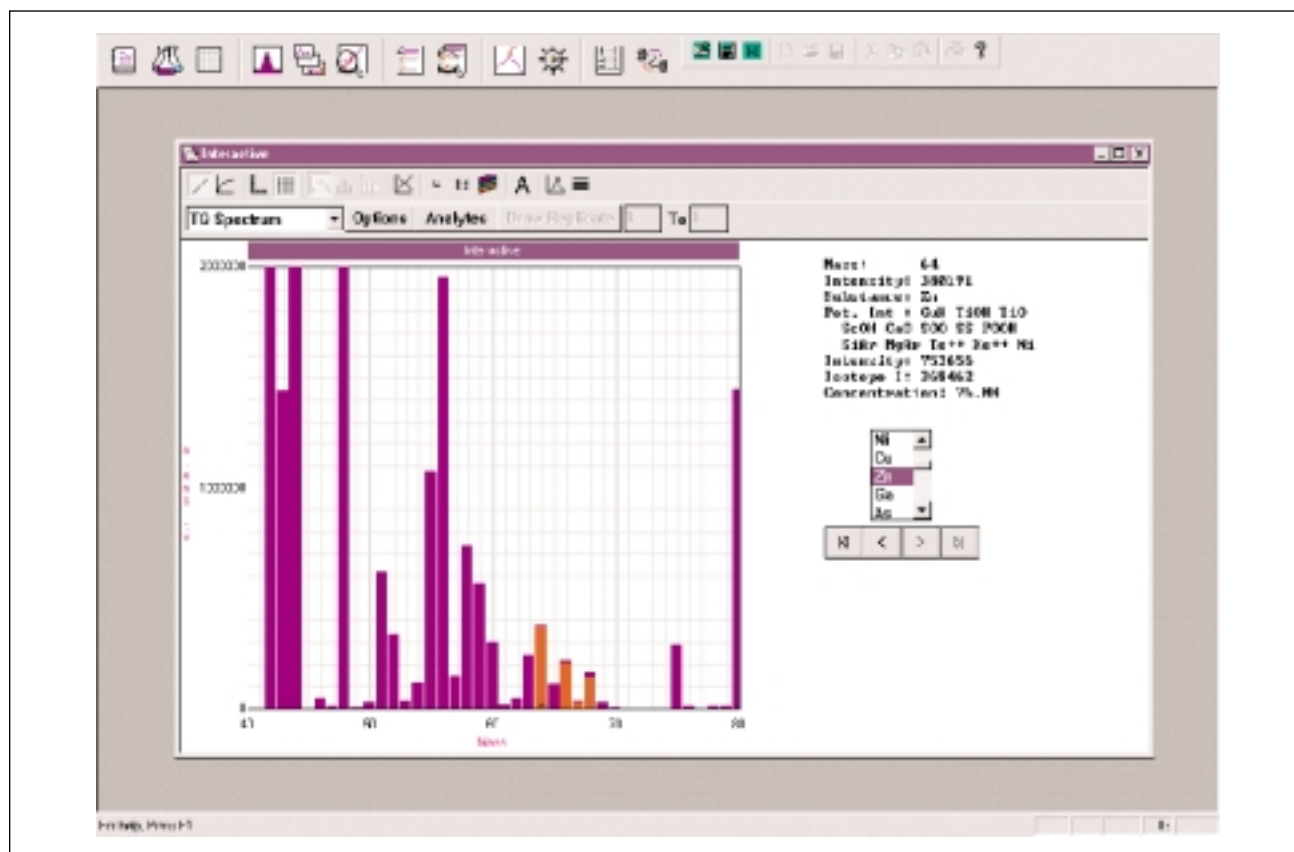

Figure 8. Semi-quantitative analysis.

Isotope Ratio

Since ICP-MS instruments measure specific isotopes of an element, the ratio of two or more isotopes can readily be determined. Isotope ratio determinations are used in a variety of applications including geological dating of rocks, nuclear applications, determining the source of a contaminant, and biological tracer studies.

Isotope Dilution

Isotope dilution experiments can also be performed by ICP-MS. In isotope dilution, the sample is spiked with an enriched isotope of the element of interest. The enriched isotope acts as both a calibration standard and an internal standard. Because the enriched isotope has the same chemical and physical properties as the analyte element, it is the best possible internal standard. For this reason, isotope dilution is recognized as being the most accurate type of all

analyses and is often used to certify standard reference materials.

Automated Quality Control Checking

The software can also monitor calibration and check standard responses and take actions to correct any problems with the analysis using the automated quality control checking feature. In addition, check standard and spike recoveries can be calculated and compared to acceptable limits. The user can specify what action to carry out for quality control samples that are outside established limits – from recalibration and re-running samples to flagging samples and continuing the analysis. The quality control software in the ELAN software adheres to the stringent U.S. EPA Quality Control Criteria. The automated quality control checking software is a key to obtaining good quality data from unattended

operation of the ICP-MS.

On-line Help and Pathfinder™

The ELAN software contains context-sensitive help to assist the analyst in using the software. There is also an operational guide called Pathfinder that walks new users through the creation of analytical methods, running samples, and reporting results.

ElanRemote™

Using ElanRemote, a service engineer or technical specialist can remotely access the instrument. This can help eliminate costly on-site service and support calls, by allowing support personnel to remotely monitor the instrument and diagnose the problem. Many times, service and technical support calls can be avoided by making adjustments via the remote connection. If a service call is necessary, ElanRemote ensures the service engineer will arrive with the correct parts to repair the instrument.
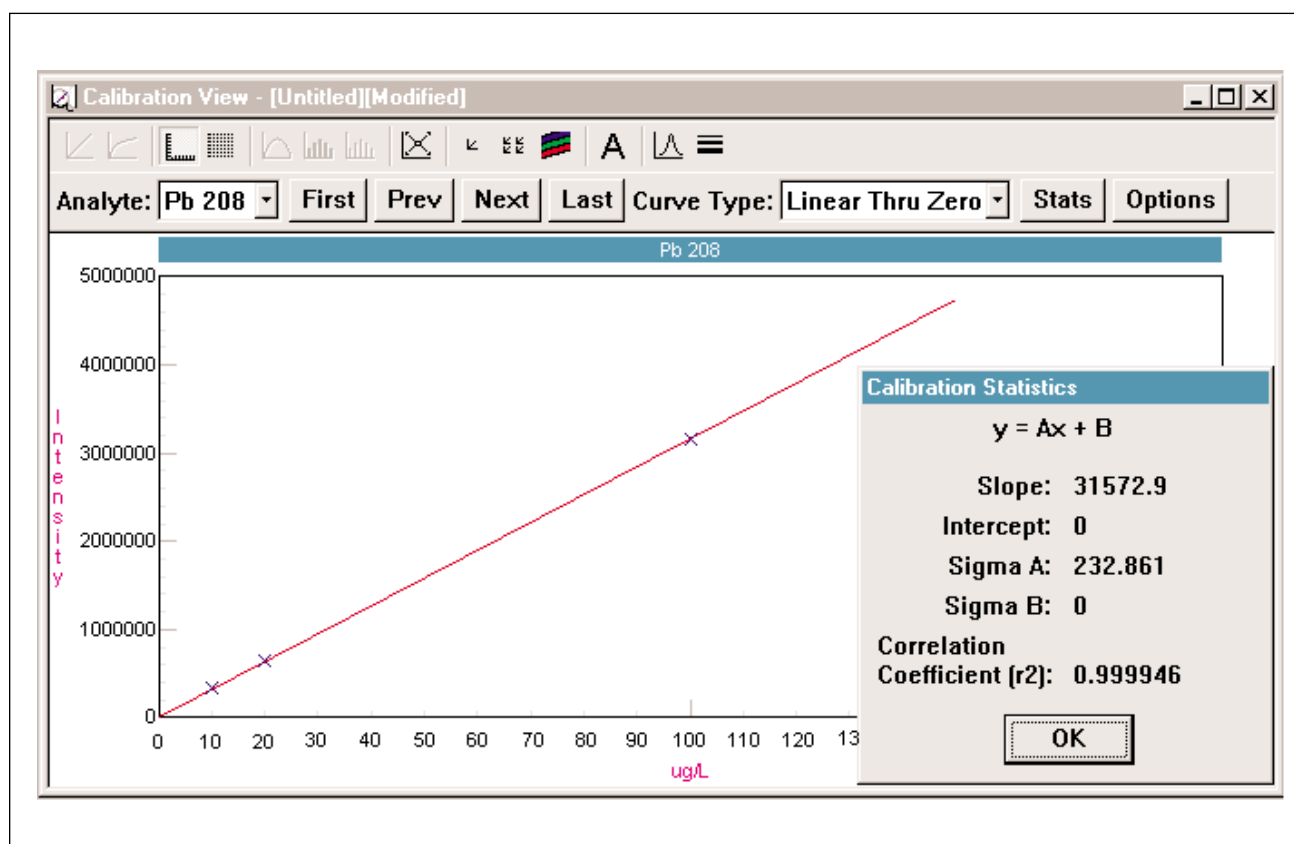

Figure 9. Quantitative calibration curve for lead at 10, 20, and 100 ppb.

Summary

There are many similarities between ICP-MS and the other analytical tools used in the laboratory, such as Atomic Absorption and ICP Optical Emission Spectrometry. The ICP-MS is another way to determine the elemental content of samples. ICP-MS accomplishes this by counting the number of ions at a certain mass of the element instead of the light emitted by the element, as in optical techniques. Sample preparation for ICP-MS is very similar to that used in AA and ICP-OES, and in many cases is identical. Standards are analyzed to generate a calibration curve and the signals from unknown samples are compared against the calibration curve to determine the concentration of each metal in the sample. The software reports data and results for quantitative, semi-quantitative, isotope ratio, or isotope dilution analyses.

ICP-MS has many advantages over other technologies, such as AA and ICP-OES, for determining the elemental composition of samples. ICP-MS generally has fewer interferences than ICP-OES and is much faster than AA and Graphite Furnace AA for the determination of multiple analytes per sample. ICP-MS detection limits are generally much lower than those that can be achieved by ICP-OES and GFAA. Quadrupole ICP-MS instruments are capable of measuring as many as 35 elements in a sample in two to three minutes. Because the spectrometer and all the accessories are under computer control, the system can literally operate 24 hours per day, 7 days per week, and analyze over 300 samples per 24-hour day. In short, no other technology can provide the low detection limits and the high productivity for elemental analysis offered by ICP-MS.

This guide is intended as a quick general overview of ICP-MS. For those interested in more details regarding the design and operation of ICP-MS instruments, additional details can be found in the scientific literature (1 - 4).

References

1. "Applications and Technology of a New ICP-MS Spectrometer," Atomic Spectroscopy, Special Issue, Vol. 16, No. 1, Jan/Feb, 1995.

2. "Method Development Strategies for ICP-MS," Ruth Wolf and Zoe Grosser, American Environmental Laboratory, February 1997.

3. "Mass Spectrometry of Inductively Coupled Plasmas," R.S. Houk, Analytical Chemistry, Vol. 58, No, 1, 1986.

4. "An Improved Interface for ICP-MS," D.J. Douglas and J. B. French, Spectrochimica Acta Part B, Vol. 41B, No.3, 1986.