A Review on Inductively Coupled Plasma: Mass Spectrometry with Laser Ablation

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Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) is a kind of mass spectroscopy which is used in many diverse research fields such as earth, environmental, life and forensic sciences and in food, material, chemical, semiconductor and nuclear industries. In this sort of MS, Laser ablation (LA) ICP-MS is widely used to determine elements directly in virtually all types of solid samples with minimal sample preparation. UV lasers are widely used with ICP-MS because of their highly controllable spatial resolution (spot size) and relatively low cost. This technique is used to determine low-concentrations and even ultra-low-concentrations of elements. Atomic elements are lead through a plasma source where they become ionized. The high ion density and the high temperature in plasma provide an ideal atomizer and element ionizer for all types of samples and matrices introduced by a variety of specialized devices. Then, these ions are sorted on account of their mass. ICP-MS holds a distinctive position by virtue of its speed, sensitivity, dynamic range and elemental coverage. It can be considered as a viable alternative to ICP-Optical Emission Spectroscopy (OES) (also known as Atomic Emission Spectroscopy or AES) for fast measurement of higher concentration elements. At the same time, ICP-MS in many cases exceeds the detection capability of Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) for the determination of trace and ultra-trace elements (ng/L or ppt concentrations). One of the fastest growing areas of ICP-MS is in speciation measurement: the combination of chromatographic techniques with ICP-MS as a detector to determine the chemical form of elements in the sample. This review provides an overview of recent developments and abilities of inductively coupled plasma mass spectrometry (ICPMS) coupled with different separation techniques for applications in the field of analysis and also highlighted numerous technical improvements, over the past few years which helped to promote the evolution of ICP-MS to one of the most versatile tools for elemental quantification as Laser ablation (LA) ICP-MS. In particular, the benefits and possibilities of using state-of-the-art hyphenated ICP-MS approaches for quantitative analysis applications.

Keywords: Inductively couple plasma mass spectrometry; ICP-MS; Laser ablation; Hyphenated techniques; Quantification and Trace elements.

Introduction

Inductively coupled plasma mass spectrometry[1] (ICP-MS) is a type of mass spectroscopy which is used in many diverse research fields. This technique is used to determine low-concentrations and even ultra-low-concentrations of elements. While many sampling methods have been investigated for use with ICP-MS, some have become outdated, or remain of academic interest, such as spark ablation and slurry nebulization for solids analysis, and electro thermal vaporization (ETV) as a sample introduction device.

The most commonly used sample introduction devices in practical analytical applications include:

a. Integrated sampling systems

- Constant flow nebulization
- Autodilution
- Discrete sampling
- Hydride generation
- On-line matrix removal
- Low-pressure chromatography

b. Laser ablation (LA)
c. Desolvation systems
d. Chromatography techniques

Laser ablation (LA) ICP-MS is commonly used to determine elements directly in nearly all types of solid samples with nominal sample preparation. It is a highly sensitive technique with a wide analytical dynamic range from the single figure part per billion (ppb) to the percent (%) level in the solid. UV lasers are widely used with ICP-MS because of their highly controllable spatial resolution (spot size) and fairly low cost. Systems with different wavelengths and beam profiles are available depending on the types of samples to be analyzed.

This technique is greatly recognized for:

- Direct analysis of solids and powders
- It's suitable for all kinds of solid materials including geological sample types, ceramics, metals and alloys, biological and forensic samples.

Main Applications include:

- Surface mapping studies of rocks, minerals and glasses to establish elemental distribution and migration.
- Bulk sampling of metals, alloys, nonconductive polymers and ceramics for elemental content.
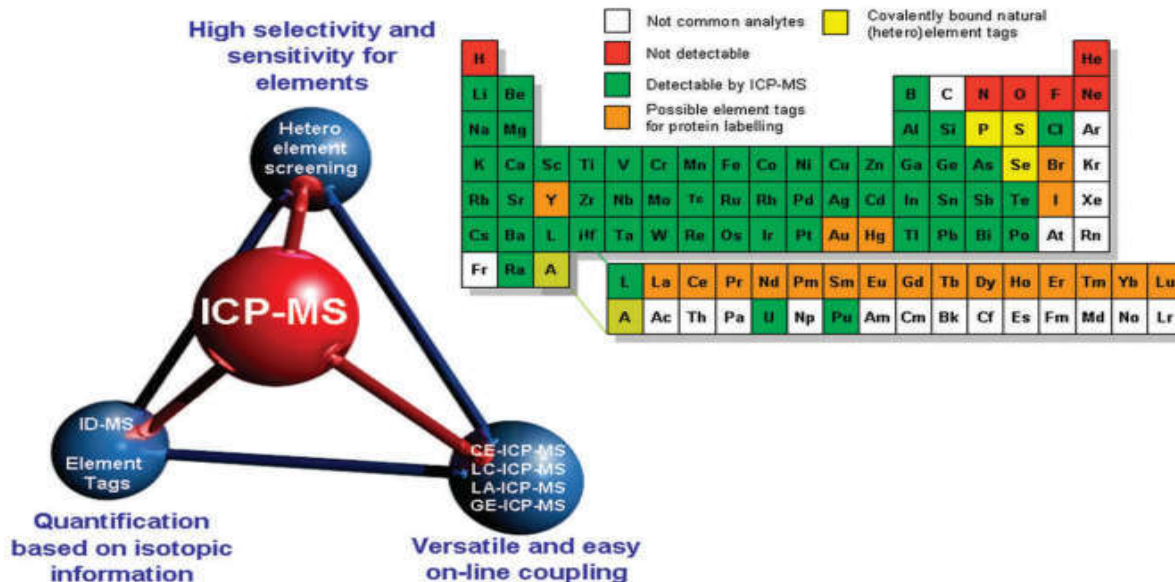- Feature analysis of micro-inclusions and small spots.

Fig. 1: Specific Features of ICP-MS[2]

History

Dr. Alan Gray of Applied Research Laboratories in Luton, UK, performed much of the early research work that led to the commercial development of ICP-MS instrumentation. Initially he worked with capillary direct current (DC) arc plasma coupled to a quadrupole mass spectrometer, he published early results and the first mass spectra acquired from plasma, in a paper in 1975[3]. This work inspired research into the use of inductively coupled radio frequency (RF) plasmas (ICP's), with some of the key developments taking place in the lab of Velmer Fassel at Iowa State University in collaboration with Dr. Gray in 1978. That leads to the development of first commercial instruments in the early 1980's based on the publication by Houk *et al*.[4] which demonstrated the possibilities offered by the ICP-MS technique. These systems were derived from parts of two existing technologies – the argon ICP, already in use in ICP-OES, and the quadrupole mass spectrometer, then being applied in fields such as Gas Chromatography Mass Spectrometry (GC-MS) and residual gas analysis. Some changes were necessary to allow the ICP to operate in physical contact with the grounded spectrometer interface, but the characteristics of these existing technologies were well matched and the performance of the first systems was impressive. Although the early ICP-MS systems were expensive, large, complex, had limited automation and tended to suffer from significant signal drift, the obvious benefits of a multi-element technique with low limits of detection and a simple mass spectrometric data output (including isotope ratio information) led to acceptance of the fledgling technique, particularly among those involved in research and geological applications. Application of the technique in laboratories where reliability, stability and automation were a high priority, led to rapid improvement of the commercial instruments and ultimately to the small, reliable, stable and highly automated systems available today. ICP-MS systems with magnetic sector and time-offlight mass analyzers have also been commercialized, but the quadrupole-based systems remain the

configuration of choice by a very wide margin. Since the first commercial ICP-MS systems were launched, major developments have occurred in sample introduction, plasma efficiency, ion transmission, interference removal and dynamic range. Even so, the major components of a modern ICP-MS instrument can be traced directly back to the earliest systems, illustrating how brilliant the original concept was.

Principle[5,6]

The general schematic representation of processes in ICP-MS from sample introduction to mass analysis is shown in Fig. 2. Distinct techniques used for the sample introduction based on physical state of the sample like for Nebulizers for liquids and Laser for Solids. Among all the Laser ablation is one technique for sample introduction for solids. For all most all laser ablation systems used with ICP-MS utilize a neodymium doped yttrium aluminum garnet crystal laser to generate a high intensity pulsed light beam at a fundamental frequency of 1064 nm. This is frequency quadrupled or quintupled to the analytically useful ultraviolet wavelengths of 266 nm or 213 nm respectively. The beam is focused onto the sample surface in an ablation chamber or cell, which is purged with argon or helium. The beam diameter can be precisely set by software-controlled apertures to generate variable "spot" sizes typically from <5 μm to 750 μm based on the application and laser being used for the analysis. The laser light couples to the surface of the sample, creating a very rapid heat, which leads to volatilization or ablation of the matrix. The laser induced aerosol which is created is then move to the ICP in an argon carrier gas stream where it get decomposed, atomized and ionized, before sending into the mass spectrometer vacuum system for analysis.
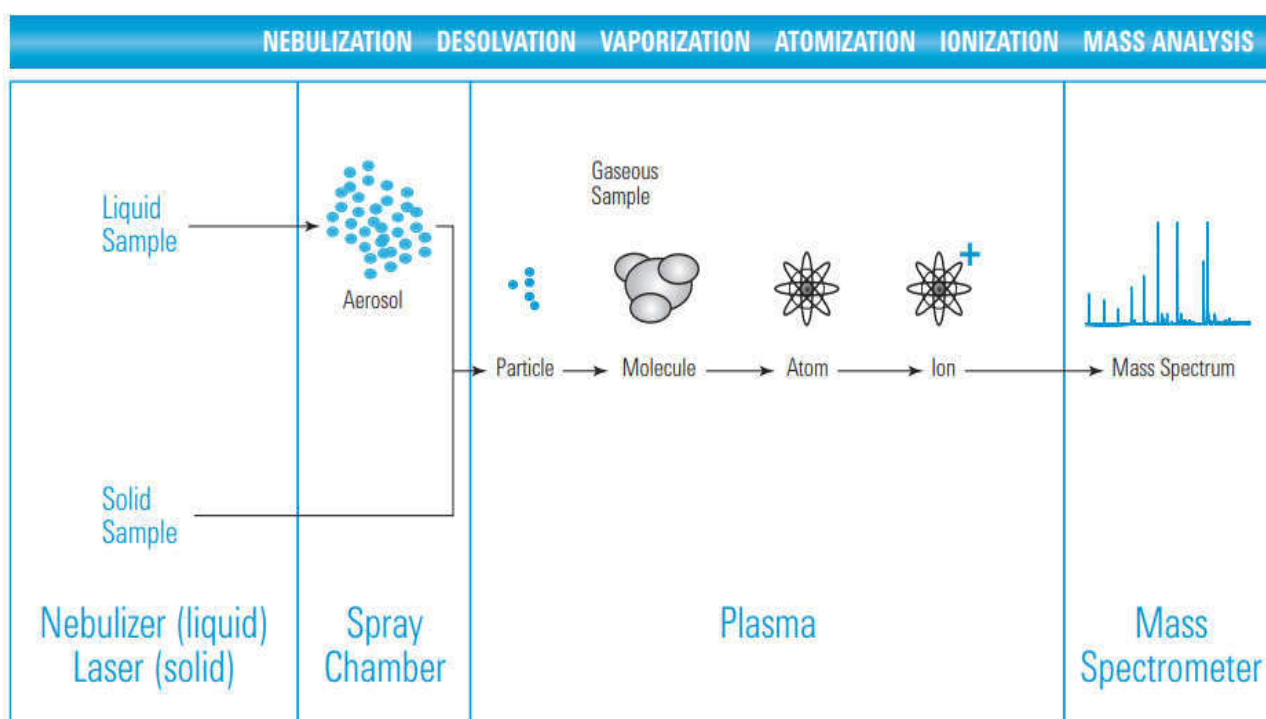

Fig. 2: Schematic representation of processes in ICP-MS from sample introduction to mass analysis.

Theory[7]

Laser ablation (LA) ICP-MS is extensively used to quantify elements directly in almost all types of solid samples with least sample preparation. It is a extremely sensitive technique with a broad analytical dynamic range from the single figure part per billion (ppb) to the percent (%) level in the solid.

The sample solution is introduced through a peristaltic pump into the device, where it becomes nebulized in a spray chamber. From there, it enters into an argon-plasma, which has a temperature of 6000-8000 K. Inside the plasma torch, solution is removed from the sample and also atomization and ionization occur. Only a small amount of the ions produced into the plasma and further infiltrate to the mass-spectrometer part.

The mass-spectrometer part consists of: An interface, in which a small amount of the free ions generated by the plasma are transmitted. During this process, the ions transfer from an environment with extremely high temperature and atmospheric pressure to a compartment at room temperature and high vacuum (< 0,001 Pa). After which the process continued with electrostatic lenses, which focus (positive) ions onto the entry to the true mass-spectrometer. The true mass-spectrometer in the GI device has a quadrupole, composed of 4 metal rods which separate the ions on basis of their mass by a kind of resonance principle. Then it reaches, electro-multiplier (a special type of detector) containing active surfaces, which enhances the signal from one colliding ion so that a measurable pulse is generated and finally, the electronics counts and sorts the pulses and relates them to the corresponding mass. This selection can be accomplished in milliseconds, so that a complete spectrum can be acquired within one second.
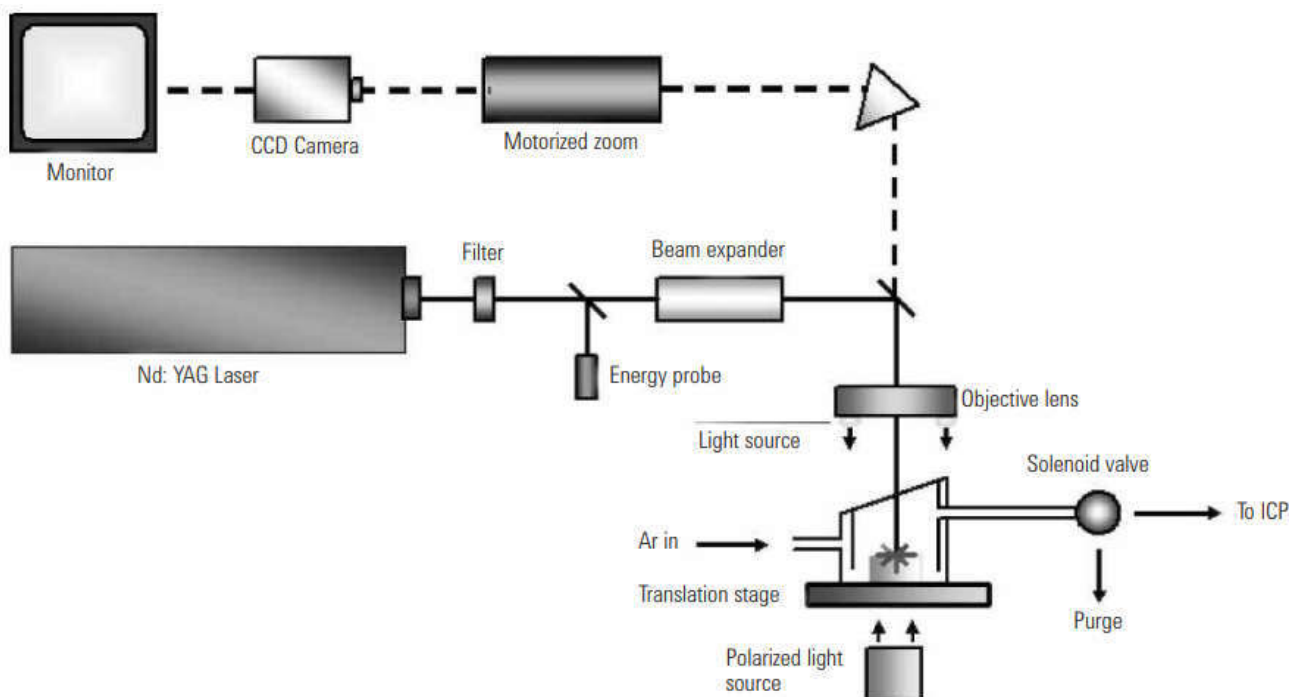
Instrumentation[8-15]

Fig. 3: Instrumentation of neodymium doped yttrium aluminum garnet crystal Laser Ablation system.

Parts

- Sample Introduction
- Argon Plasma
- ICP-MS Interface
- Vacuum System
- Ion Focusing
- Collision/Reaction Cells
- Mass Analyzer
    - Quadrupole
    - Magnetic Sector
    - Time-of-flight (TOF)
- Detector

ICP technology was built upon the same principles used in atomic emission spectrometry. Samples are decomposed to neutral elements in high temperature argon plasma and analyzed based on their mass to charge ratios.

Sample Introduction:

The sample introduction system is one of the most important components of the entire ICP-MS system and the first step in analysis. A well-designed sample introduction system will reduce routine maintenance and enhance analytical performance. This has been achieved in ICP-MS through a distinct means. ICP-MS spectrometers can accept solid as well as liquid samples. Solid samples are introduced into the ICP by way of a laser ablation system, which is shown in Fig. 4. In this method, a laser is focused on the sample and creates a plume of ablated material which can be swept into the plasma.
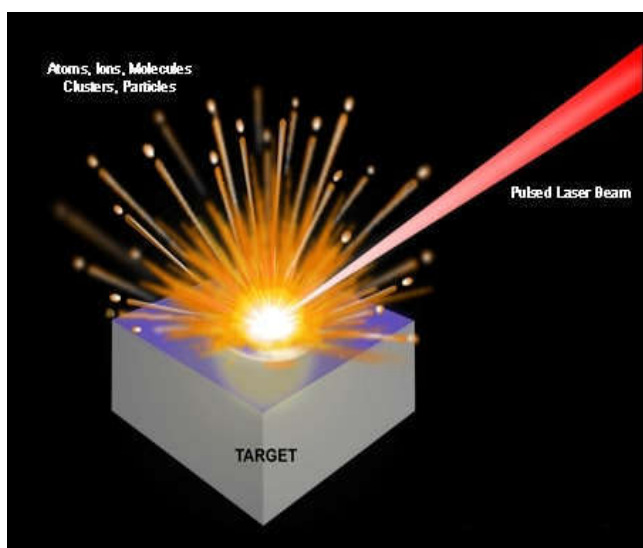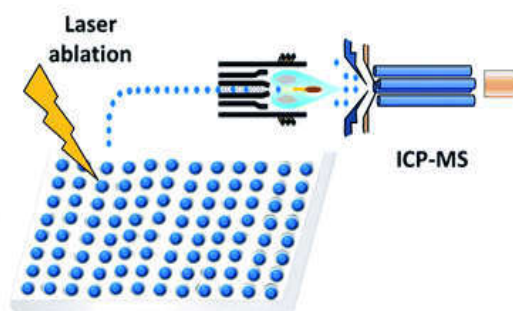

Fig. 4: Laser Ablation in ICP-MS.

Argon Plasma/Sample Ionization:

In the simplest terms, the purpose of the plasma is to form positively charged ions from the sample aerosol. To ensure good results from samples with high or varying matrices, plasma loading should be optimized to maintain high ionization temperatures while retaining good sensitivity. The goal is to achieve as high a degree of matrix decomposition and analyte ionization as possible. The sample aerosol is passed into the plasma, which is generated in a stream of argon (Ar) contained in a coupling coil and that is used to transmit radio frequency to the heated argon gas, producing an argon

plasma "flame" located at the torch. The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. In addition to being ionized, sample atoms are excited in the hot plasma, a phenomenon which is used in ICP-atomic emission spectroscopy. Shown to the right is an ICP torch. The aerosol moves into the bottom of the torch body. The green ports on the right side of the body are where more argon is introduced to the flow. At the top are two high quality quartz tubes and an inner alumina injector tube shown in Fig. 5.

Fig. 5: Argon Plasma in Operation.
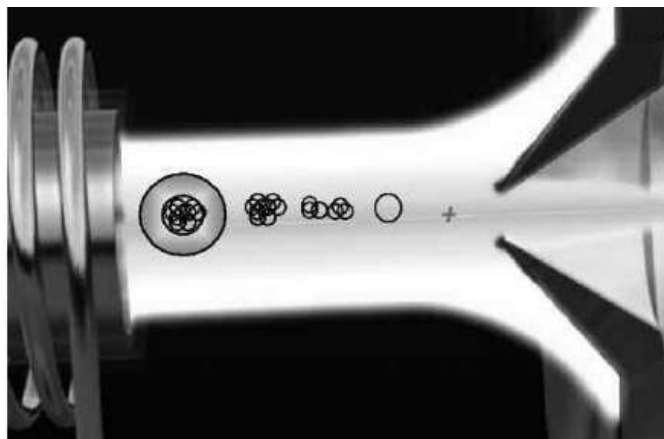
The basic steps of ion production in an ICP are:

- Sample droplets move toward the plasma and are dried
- The dried sample particles are decomposed by the plasma to form atoms (atomization)
- At this point (atomization stage), the process is optimized for ICP-OES. In ICP-OES, emitted light is determined from excited atoms as these lines are typically more stable.
- ICP-MS measurement requires an extra step: the atoms must be ionized, since the mass analyzer can only separate ions.

Thus the ICP in ICP-MS is an ion source - this requires more energy. The formation of ions from the sample atoms is achieved by the removal of a single electron. This occurs with varying ease and efficiency for different elements. This variation is usually quoted as the "Ionization Efficiency" for each element, which is a function of the first ionization potential of the element, together with estimated values for plasma electron temperature and density.

ICP-MS Interface:

The positively charged ions that are produced in the plasma are extracted into the vacuum system, via a pair of interface "cones". The cones are essentially metal plates with central orifices through which the ions pass which is shown in Fig. 6. Generally, atomization/ionization occurs at atmospheric pressure, the interface between the ICP and MS components becomes crucial in creating a vacuum environment for the MS system. Ions flow through a small orifice, approximately 1 millimeter in diameter, into a pumped

vacuum system. Here a supersonic jet forms and the sample ions are passed into the MS system at high speeds, expanding in the vacuum system. The entire mass spectrometer must be kept in a vacuum so that the ions are free to move without collisions with air molecules. Since the ICP is maintained at atmospheric pressure, a pumping system is needed to continuously pull a vacuum inside the spectrometer. In order to most efficiently reduce the pressure several pumps are typically used to gradually reduce pressure to 10-5 mbar before the ion stream reaches the quadruple. If only one pump were used, its size would be excessive to reduce the pressure immediately upon entering the mass spectrometer.
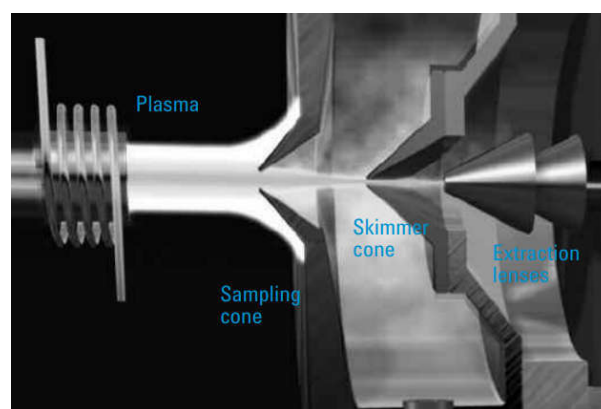

Fig. 6: ICP-MS Interface.

Vacuum System:

Mass spectrometers work most efficiently at low pressure (high vacuum). The maintenance of a high vacuum in the

analyzer region is essential, in order to reduce the background and scattering effects that a high level of residual gas molecules would cause. The preferred configuration in both early and current commercial instruments is for a 3 stage differentially pumped vacuum system comprising the interface, intermediate and analyzer stages at progressively lower pressures. The typical vacuum configuration for commercial ICP-MS instruments is for the interface stage to be evacuated using a rotary vane pump, which is switched off when the ICP-MS is in "standby" mode, to allow access to the interface cones and ion lenses for maintenance. The intermediate and analyzer vacuum stages are typically pumped by two separate turbo-molecular pumps or by a single, dual-stage pump. A "backing" rotary pump removes exhaust from the turbo-molecular system. The intermediate and analyzer vacuum stages are typically isolated from the interface region by a gate valve, which seals the high vacuum region when the interface pump is switched off.

This allows routine maintenance without requiring the high vacuum pumps to be switched off, so the vacuum is maintained and start-up times are minimized. The gate valve is under pneumatic or solenoid switch control, such that any power, coolant or gas failure or plasma shutdown causes the valve to shut automatically, avoiding sudden loss of vacuum.

Ion Focusing:

Electrostatic plates, known as ion "lenses", keep the ions focused in a compact "ion beam" as they pass through the vacuum system to the final chamber, where the mass spectrometer (MS) and detector are housed which is shown in Fig. 7. The ion lenses perform a second essential function of separating the ions from the photons and residual neutral material, which is achieved by using the electrostatic fields in the lenses to deflect the ions thus separating them from the photons and neutrals. It has a high transmission off-axis or Omega lens arrangement that separates the positively charged ions from the photons and neutral particles, which would otherwise reach the detector and increase random background noise.

In order to prevent the loss of ions from the beam, the ion lenses are used to focus and transfer charged species efficiently to the mass spectrometer entrance aperture. While several different ion lens designs have been used in ICP-MS, the typical arrangement is to use one or more cylindrical lenses, to which a voltage can be applied. When the positive ions generated by the plasma pass through the electrostatic field in the lens system, they are attracted to negative and repelled from positive fields, so can be manipulated in the required trajectory.

The ion lens system may consist of a simple, single cylindrical electrostatic lens, which has the virtue of low cost and simple operation, but has limited flexibility. Alternatively, a multi-component ion lens design may be used, which increases cost but allows greater flexibility of optimization. Early designs of lens systems utilized a grounded metal disc, known as a "photon" or "shadow" stop, on the axis of the instrument, to block the direct line from plasma to detector.
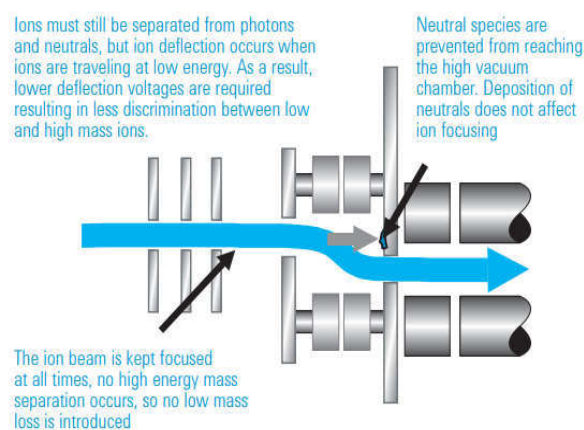

Fig. 7: Schematic of off-axis ion lens design.

Collision/Reaction Cell:

Collision/Reaction cells (CRC's) are helps to remove spectral. There are various configurations of CRC but fundamentally the device consists of an ion guide, which is enclosed in a cell that can be pressurized with a gas and is positioned after the main ion lenses. The gas interacts with the ion beam to remove polyatomic interferences in any of these two ways like Reaction Mode, where the gas reacts with an interference to convert it to a different species or Collision Mode, where the gas collides with the polyatomic interference, causing it to lose energy. Since polyatomic species are large, they undergo more collisions than do analytes, and so lose more energy. The lower energy interference is then separated from the higher energy analyte by energy discrimination (ED).

Mass Analyzer:

Finally, Ions pass from the ion lens system into the analyzer vacuum stage, where they are separated by the quadrupole, according to their mass to charge ratio. The most widely used mass analyzer in ICP-MS is the quadrupole because of its ease of use, robustness, mass range, high scanning speed and relatively low cost. The other analyzers that have been used in ICP-MS are magnetic sector or double focusing and time of flight (TOF).

Quadrupole: It is a sequential mass filter, which separates ions based on their mass to charge ratio (m/z). It consists of two pairs of parallel cylindrical rods, arranged in a square, on the axis of the ion beam which is shown in Fig. 8. A varying or AC voltage, operating at high frequency, plus a DC voltage is applied to the two pairs of rods. The AC (same voltage but out of phase between the 2 pairs of rods) and DC (positive on one pair and negative on the other) voltages give a dynamic hyperbolic electric field, in which any ion above or below the set mass of the quadrupole enters an unstable trajectory and is lost from the ion beam.

Combining the AC and DC components produces a narrow band pass filter that allows only a narrow range of masses to be transmitted. By varying the AC and DC fields, but keeping the ratio between them constant, different masses can be selectively allowed to pass through the filter. Since these voltages can be adjusted very rapidly, the elemental mass range from 2 to 260amu

can be scanned very quickly, giving a mass spectrum for all elements and their isotopes (Li to U), which is acquired virtually simultaneously.
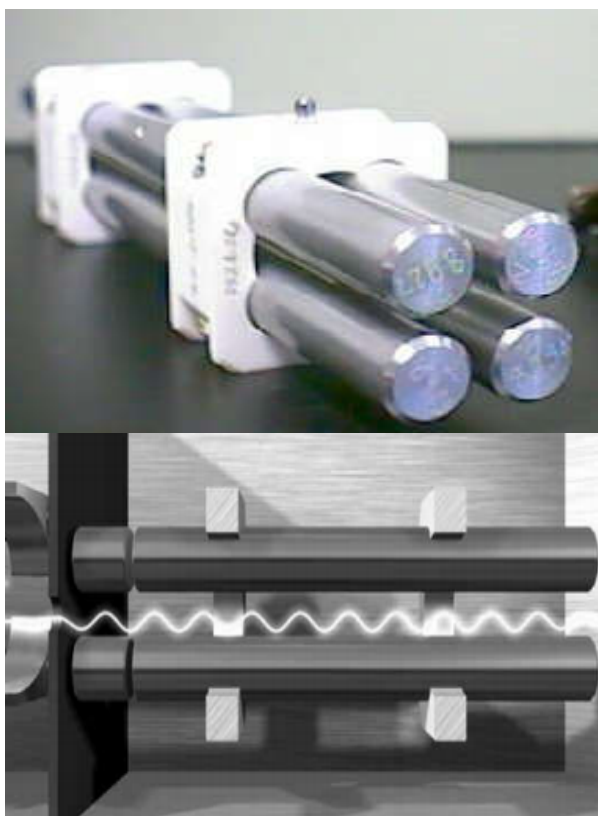

Fig. 8: Schematic of Quadrupole Analyzer.

Magnetic Sector or Sector Field Analyzers: These types of analyzers are typically employed where mass resolution significantly higher than unit resolution is required. The systematic of this type of analyzer is shown in Fig. 9.

The principles can be explained as follows:

- Ions sampled from the plasma are first accelerated in the ion optic region before being focused into the variable entrance slits – this stage determines resolution.
- The ions then enter an electromagnet induced magnetic field which deflects different masses through different angles.
- The next step is often referred to as "energy filtering": - Ions enter an electrostatic sector, where they are filtered or resolved according to their kinetic energy (energy resolution).
- Ion detection done by using multiple Faraday cups are used in multi collector systems. Multi collector systems are optimized for high-precision isotope ratio analysis of a large range of elements. They operate at a maximum resolution of around 3500. These systems are not well suited to making trace concentration measurements because of poor signal to noise on the Faraday cup detectors.

Fig. 9: Schematic of Magnetic Sector Analyzer.

Time of Flight Mass Analyzer: In a time of flight mass analyzer which is shown in Fig. 10, a uniform electrostatic pulse is applied to all ions at the same time, causing them to accelerate down a flight tube. Lighter ions get higher velocities and reach the detector first, so the mass-to-charge ratios of the ions are determined by their arrival times. These analyzers have also been used in ICP-MS for applications where many masses are determined in short lived transient signals e.g. laser ablation studies. This is because the time of flight mass spectrometer separates the ions and delivers all masses to the detector with a very short time delay, allowing many thousands of full mass scans to be acquired per second, giving a virtually simultaneous measurement.
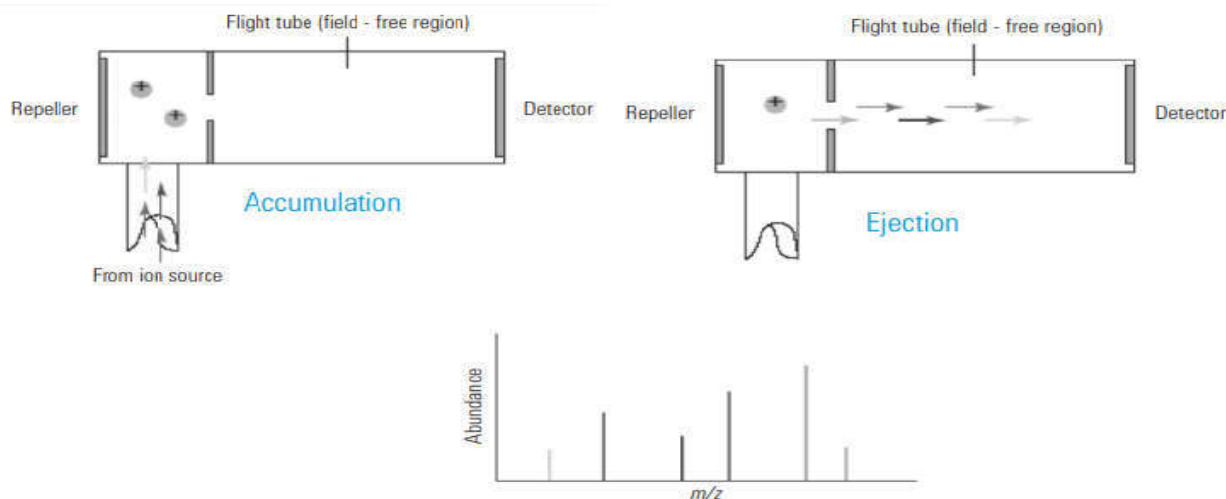

Fig. 10: Schematic of Time of Flight Mass Analyzer.

Detector:

The detector is responsible for the distinctiveness of very high sensitivity and low random background, for which the technique is famous. The reason for the high sensitivity is that the detector used in virtually all modern ICP-MS instruments is a so-called "electron multiplier" device, which means that it can generate a measurable signal pulse from the impact of a single ion which is shown in Fig. 11. To make best use of this sensitivity, it is essential that the arrival of an ion can be reliably distinguished from any random background noise arising either from the vacuum and spectrometer system or from the electronics.

The basic principle involved in these detectors is at the first, a positive ion arrives at the mouth of the detector, and it is deflected onto the first dynode, which is held at a high negative voltage. The impact of the ion releases several free electrons from the dynode surface, which are repelled from the high negative voltage at the front and strike the next dynode. Each electron which strikes the second dynode releases several electrons from that surface and so on down the many stages of the detector – hence the name "electron multiplier". By the time the electron cascade reaches the final dynode, the multiplication factor has built up a pulse large enough to be measured reliably as an ion "count".
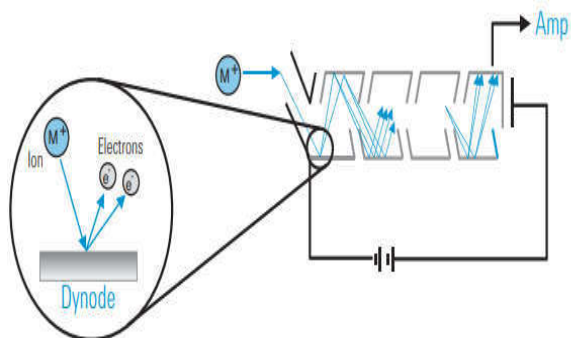

Fig. 11: Schematic of Electronic Multiplier.

Detection Limits[16]

One of the great advantages to ICP-MS is extremely low detection limits for a wide diversity of elements. Some elements can be measured down to part per quadrillion ranges while most can be detected at part per trillion levels. The Table 1 shows some common detection limits by element.

Table 1: Detection Limit of Some Elements.

Element	Detection Limit (PPT)
U, Cs, Bi	less than 10
Ag, Be, Cd, Rb, Sn, Sb, Au	10-50
Ba, Pb, Se, Sr, Co, W, Mo, Mg	50-100
Cr, Cu, Mn	100-200
Zn, As, Ti	400-500
Li, P	1-3 ppb
Ca	less than 20 ppb

Advantages[17]

- Wide elemental coverage – nearly all elements can be measured by ICP-MS, including alkali and alkaline earth elements, transition and other metals, metalloids, rare earth elements, most of the halogens and some of the non-metals.
- Performance - high sensitivity and low background signals combine to give very low detection limits (sub-ng/L – parts-per-trillion (ppt) in most cases)
- Rapid analysis times – with a high speed scanning quadrupole analyzer, measurement of a full suite of elements takes only about 4 minutes per sample
- Extensive analytical operational range – up to 9 orders in a single acquisition
- Isotopic information
- Excellent chromatographic detector

Applications of Laser Ablation (LA) ICP-MS[17-21]

- *Environmental*
  - The identification of trace elements in "clean" samples such as drinking water, rain water and air samples.
  - The quantification of elements over a wide concentration range in wastewater, sewage sludge, trade effluents, landfill leachates, soil and sediment digests and biota.
  - The identification of trace and ultratrace elements in high matrix samples such as open ocean seawater.
- *Food and Agriculture*
  - Trace element monitoring at almost every stage of food production.
  - Measuring isotope ratios in elements provided as trace element supplements.
  - Quantifying metals in proteins to monitor elemental absorption from the diet.
  - Semiconductor
  - Analysis of ultra-pure water (UPW) and process chemicals used in semiconductor manufacture.
  - Quality control of semiconductor devices.
- *Clinical and Pharmaceutical*
  - The identifying of trace elements in urine, blood and serum.
  - Quantification of heavy metals and/or metal species in drug product.
- *Geological*
  - Categorization of rocks and minerals.
  - Broadcast samples in mining exploration, product quality and ore processing.
  - Isotope ratio determination for geochronology.
- *Nuclear*
  - Nuclear fuel production: impurity analysis of fuels intermediate compounds and fuel cladding materials.
  - Nuclear power plants: monitoring of primary cooling water for corrosion and monitoring of moderator (boron) isotope ratio.
  - Effluent discharge monitoring.
  - Monitoring of workforce – clinical sampling and workplace monitoring.

- *Forensic*
  - Accurate measurement of elemental "fingerprint" in crime scene evidence to characterize and identify materials.
  - Discriminating elemental and isotopic differences of solid samples directly at the part per billion level using laser ablation LA-ICP-MS.
- *Chemical, Petrochemical*
  - Analysis of trace metal concentrations in petrochemical samples.
  - Trace element levels in printer ink.
  - Speciation measurement of petrochemical samples.

Improvements Required For ICP-MS

When compared to all the other available methods of elemental analysis, ICP-MS comes closer to being the ideal method, but still need some improvements in.

- Speciation approaches must be devised or refined.
- Matrix interferences must be better understood and controlled.
- Less expensive instruments for the elimination of spectral interferences must be developed.
- Alternative sources and mass spectrometers should be considered and evaluated.
- Sample-introduction efficiency must be improved.
- Sample-utilization efficiency ought to be raised.
- Precision must be increased.
- Instrumentation should be reduced in price and made simpler to use.

Conclusion

The outstanding instrumental developments for the period of the last decade in the field of elemental mass spectrometry and its application as a (hetero)element specific detector, as well as the continuous progress in the development of new hyphenated techniques, has resulted in a growing interest in such technologies and their unique analytical properties. As indicated by the broad range of examples ranging from environmental analysis of emerging compounds to proteomics related topics, such as protein phosphorylation studies or absolute protein quantification, ICP-MS has the potential to become a key technology for quantification, especially because of its unique characteristics, such as compound-independent ionization behavior, sensitivity, and robustness, which represent the main strengths of ICP-MS. With respect to most of these criteria, determination of trace elements by ICP MS is performing enormously and is uncontested by other MS techniques. On the other hand, it is a unique and outstanding advantage of ICP MS to use inexpensive, unspecific, certified element standards, allowing a quantitative control on elemental losses, species decomposition or contamination in each single step of an experiment. Whereas molecular fragmentation is used to determine the structure of unknown compounds, in plasma, atomized elements provide convenient and efficient access to high sensitivity for target-element orientated quantitation and the discovery of relevant unknown compounds and in the same process quantifying their relative mass contribution to the total content. Among all, Laser ablation (LA) ICP-MS is commonly used to determine elements directly in nearly all types of solid samples with nominal sample preparation. It is a highly sensitive technique with a wide analytical dynamic range from the single figure part per billion (ppb) to the percent (%) level in the solid. UV lasers are widely used with ICP-MS because of their highly controllable spatial resolution (spot size) and fairly low cost. It is probable that in the future, offsprings of today's instruments will contain both types of ion sources, allowing researchers to work with only one combined analytical system and still satisfying the research needs.

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