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An overview on inductively coupled plasma mass spectrometry and its applications

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ABSTRACT

Inductively-coupled plasma mass spectrometry (ICP-MS) is a sensitive analytical technique that can be used to perform qualitative and quantitative multi-element analysis. It is able to detect elements down to the parts-per-trillion (ppt) level as well as determine the ratio of its natural-occurring isotopes. ICP-MS has been used widely over the years, finding applications in a number of different fields including drinking water, wastewater, natural water systems/hydrogeology, geology and soil science, mining/metallurgy, food sciences, pharmaceutical, and medicine.

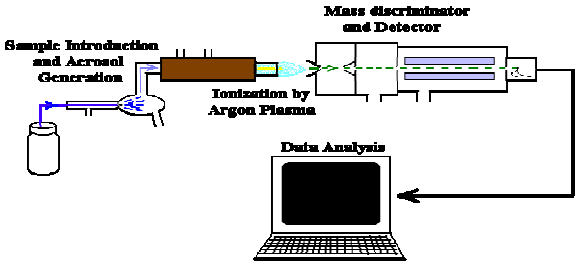
Keywords: ICP-MS, Mass spectroscopy, Mass analyser.

1. INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) was developed in the late 1980's to combine the easy sample introduction and quick analysis of ICP technology with the accurate and low detection limits of a mass spectrometer. It makes use of a plasma source as an ionizer and mass spectrometer analyzer to separate and quantify those ions. It is capable of analyzing liquid, solids or gaseous samples as well [1].

2. DESCRIPTION AND THEORY

In ICP technology all the liquid, solid, semisolid, gaseous samples can be analysed. Samples are decomposed to neutral elements in high temperature argon plasma and analyzed based on their mass to charge ratios. An ICP-MS can be thought of as four main processes, including sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination, and the detection system [7]. The schematic below illustrates this sequence of processes.



The main processes in ICP MS are:

- Plasma torch
- Sample preparation
- Sample introduction
- ICP MS interface
- Mass analyser
- Detector

3. PLASMA TORCH

Inductively coupled plasma is plasma that is energized by inductively heating the gas with an electrical coil, and contains a sufficient concentration of ions and electrons to make the gas electrically conductive [2]. Even a partially ionized gas in which as little as 1% of the particles are ionized can have the characteristics of a plasma (i.e., response to magnetic fields and high electrical conductivity).The plasmas used in petrochemical analysis are essentially electrically neutral, with each positive charge on an ion balanced by a free electron. In these plasmas the positive ions are almost all singly charged and there are few negative ions, so there are nearly equal amounts of ions and electrons in each unit volume of plasma [8].

In inductively coupled plasma (ICP) for spectrometry is sustained in a torch that consists of three concentric tubes, usually made of quartz. The end of this torch is placed inside an induction coil supplied with a radio-frequency electric

current. A flow of argon gas (usually 14 to 18 litres per minute) is introduced between the two outermost tubes of the torch and an electrical spark is applied for a short time to introduce free electrons into the gas stream [4].

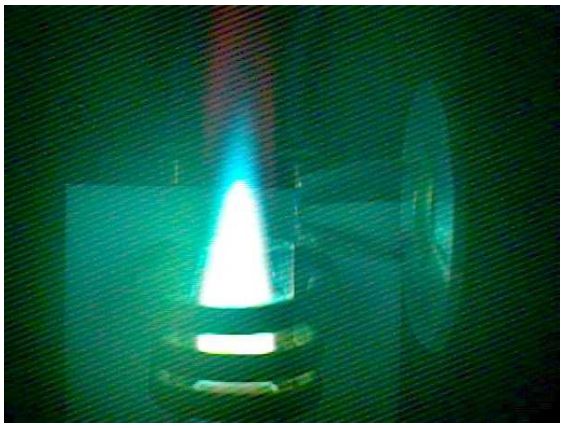
These electrons interact with the radio-frequency magnetic field of the induction coil and are accelerated first in one direction, then the other, as the field changes at high frequency (usually 27.12 MHz). The accelerated electrons collide with argon atoms, and sometimes a collision causes an argon atom to part with one of its electrons [3]. The released electron is in turn accelerated by the rapidly changing magnetic field. The process continues until the rate of release of new electrons in collisions is balanced by the rate of recombination of electrons with argon ions (atoms that have lost an electron). This produces a 'fireball' that consists mostly of argon atoms with a rather small fraction of free electrons and argon ions. The temperature of the plasma is very high, of the order of 10,000 K [5].

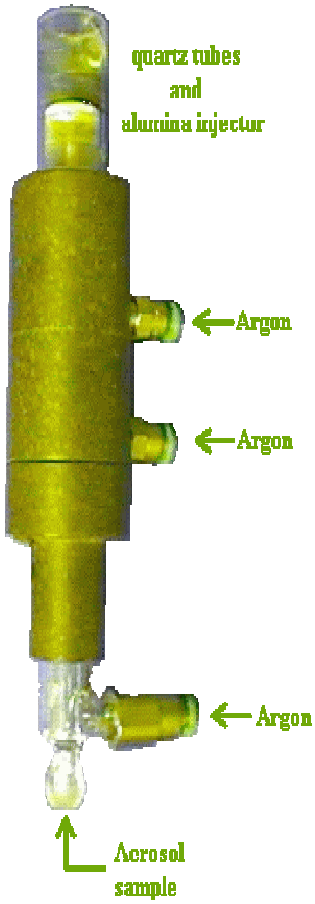
The ICP can be retained in the quartz torch because the flow of gas between the two outermost tubes keeps the plasma away from the walls of the torch. A second flow of argon (around 1 litre per minute) is usually introduced between the central tube and the intermediate tube to keep the plasma away from the end of the central tube. A third flow (again usually around 1 litre per minute) of gas is introduced into the central tube of the torch. This gas flow passes through the centre of the plasma, where it forms a channel that is cooler than the surrounding plasma but still much hotter than a chemical flame. Samples to be analyzed are introduced into this central channel, usually as a mist of liquid formed by passing the liquid sample into a nebulizer [10].

As a droplet of nebulised sample enters the central channel of the ICP, it evaporates and any solids that were dissolved in the liquid vaporize and then break down into atoms [13]. At the temperatures prevailing in the plasma a significant proportion of the atoms of many chemical elements are ionized, each atom losing its most loosely bound electron to form a singly charged ion.

The plasma used in an ICP-MS is made by partially ionizing argon gas ($Ar \rightarrow Ar^{+} + e^{-}$). The energy required for this reaction is obtained by pulsing an electrical current in wires that surround the argon gas.

After the sample is injected, the plasma's extreme temperature causes the sample to separate into individual atoms (atomization). Next, the plasma ionizes these atoms ($M \rightarrow M^{+} + e^{-}$) so that they can be detected by the mass spectrometer [15].





The advantage of using plasma over other gases is it is abundant, cheaper, has higher ionisation potential and is available either in liquid or gas form.

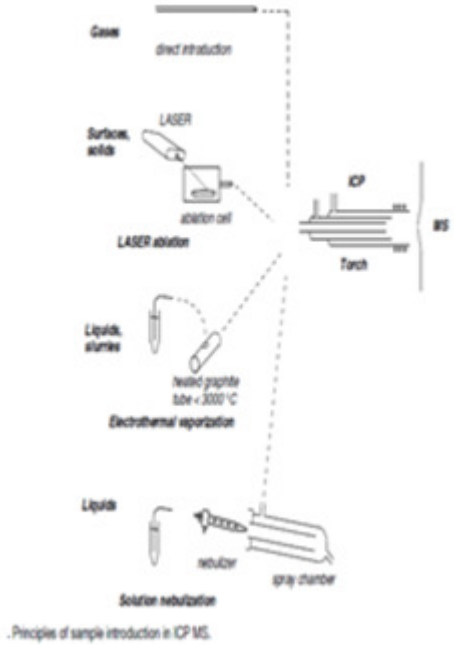
Although the ICP-MS generates essentially monatomic, positively charged analyte ions, there are still several polyatomic ions such as ArO, ArC, and ArH, which arise mainly from the combination of the argon gas used to generate the plasma with oxygen, carbon, and hydrogen from the air and the samples. So shield torch system is used which reduces interference from polyatomic atoms [18].

4. SAMPLE PREPARATION

ICP-MS, there is a relatively simple and quick sample preparation process. The main component to the sample is an internal standard, which also serves as the diluents. This internal standard consists primarily of deionised with nitric or hydrochloric acid, and Indium and/or Gallium. Depending on the sample type, usually 5 ml of the internal standard is added to a test tube along with 10–500 microliters of sample. This mixture is then vortexed for several seconds or until mixed well and then loaded onto the auto sampler tray.

5. SAMPLE INTRODUCTION

A large variety of sample introduction systems have been employed for ICP MS. Gases are introduced directly, laser ablation for solids , electro thermal vaporisation for slurries and liquids are introduced solution nebulisation [16].



. Principles of sample introduction in ICP MS.

Nebuliser - Conventional sample introduction into the ICP is still usually done using a pneumatic nebulizer combined to a spray chamber. However, using a spray chamber as a filtration device, to remove large droplets that the plasma cannot fully volatilize, desolvate the sample aerosol prior to its entry into the plasma [12]. Direct injection nebulizers, which replace the torch injector, also provide quantitative sample introduction in the plasma with lower detection limits than achieved with other types of nebulizers. Filtering the sample prior to its injection and degassing the carrier (using an ultrasonic bath) were required to stabilize the nebulising pressure [13].

Electrothermal vaporisation - here hot surfaces like graphite or metal are generally used to vaporise the sample for introduction. These can use very small amounts of liquids and slurries.

Laser ablation - LA is frequently used for direct solid analysis by ICPMS. For direct access to analytes in solids and on surfaces, laser ablation (LA) is used with a spatial resolution on the micrometer scale (31 μm), which is ideally suited for micro sampling on surfaces and in-depth profile analysis.

6. ICP MS INTERFACE

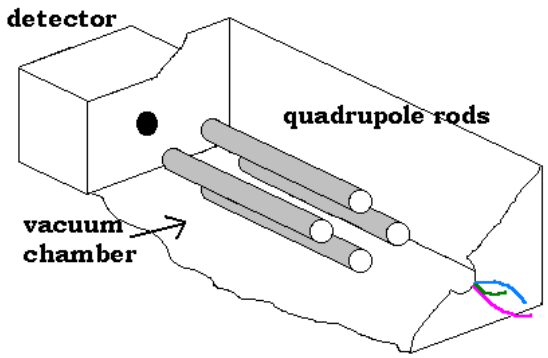
Because atomization/ionization occurs at atmospheric pressure, the interface between the ICP and MS components becomes crucial in creating a vacuum environment for the MS system. Ions flow through a small sampler and skimmer cone, approximately 1 millimetre in diameter, into a pumped vacuum system. Here 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 quadrupole. If only one pump were used, its size would be excessive to reduce the pressure immediately upon entering the mass spectrometer [16].

7. MASS ANALYSER

There are several different types of mass analyzers which can be employed to separate isotopes based on their mass to charge ratio. Quadrupole analyzers are compact and easy to use but offer lower resolution when dealing with ions of the same mass to charge (m/z) ratio. Double focussing sector analyzers offer better resolution but are larger and have higher capital cost [21].

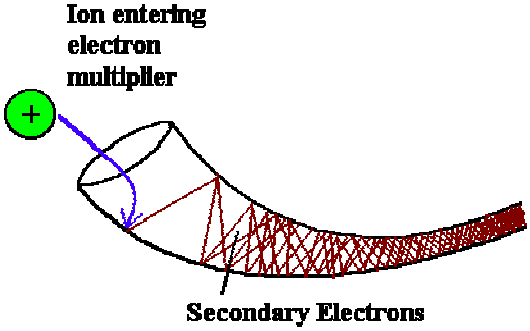
The quadrupole mass filter is made up of four metal rods aligned in a parallel diamond pattern. A combined DC and AC electrical potential is applied to the rods with opposite rods having a net negative or positive potential. Ions enter into the path between all of the rods. When the DC and AC voltages are set to certain values only one particular ion is able to continue on a path between the rods and the others are forced out of this path. This ion will have a specific m/z ratio. Many combinations of voltages are chosen which allows an array of different m/z ratio ions to be detected [19].

Three mass fragments enter into the quadrupole vacuum chamber. The voltage of the rods is set so that only the pink mass fragment passes completely through the quadrupole rod array and into the detector. The green and blue fragments are unstable at this voltage combination and their path eventually brings them into contact with the rods so that they never reach the detector [16].



8. DETECTOR

The most common type of ion detector found in an ICP-MS system is the channeltron electron multiplier. This cone or horn shaped tube has a high voltage applied to it opposite in charge to that of the ions being detected. Ions leaving the quadrupole are attracted to the interior cone surface. The electron multiplier used is discrete dynode type. When an ion enters the electron multiplier, it hits the first dynode and a shower of electrons is generated [15]. These electrons hit the next dynode, generating more electrons. Finally, the pulse generated is detected by the collector. This small signal is amplified and a measurable pulse signal is obtained When they strike the surface additional secondary electrons are emitted which move farther into the tube emitting additional secondary electrons. As the process continues even more electrons are formed, resulting in as many as 10^8 electrons at the other end of the tube after one ion strikes at the entrance of the cone. The drawing below is an illustration of electron multiplying and the photograph is an actual electron multiplier removed from a mass spectrometer [24].



11. APPLICATIONS

The ICP-MS offers high-throughput multielement analysis with ng/l (ppt) or better detection limits, very small sample volume requirements, robustness, and ease of use. Therefore, the application areas for ICP MS are very wide, from the semiconductor industry in which the concentration of analytes is extremely low, to the environmental, geological and clinical fields [25].

11.1. Environmental sample analysis

Concerns regarding safe levels of contaminants in the environment, particularly heavy metals, continue to grow. The requirement for analysis of more elements at ever-decreasing concentrations is exposing the limitations of currently used analytical techniques. ICP-MS is the only technique that offers the improvements in sensitivity that will be demanded in the near future. ICP-MS is approved for several environmental analytical methods. A large number of elements, ranging from lithium (Li) at low mass to uranium (U) at high mass can be clearly observed, even though the total analysis time was only 100 seconds [20].

11.2. Clinical sample analysis

The determination of toxic elements such as mercury (Hg), lead (Pb) and cadmium (Cd) in humans has been a critical issue in the field of clinical chemistry from the toxicology viewpoint. In addition, since recent biomedical research has shown that some elements at trace levels have specific functions in the biochemistry of living organisms, the determination of trace element concentrations in human beings has also become a major issue in the field of nutritional study. As a result, the analysis of toxic elements and also many trace elements in biological samples is required. So their blood or urine samples are analysed for metal toxicity. The analyse concentration range is large, ranging from the trace levels normally found in the body to the high levels resulting from industrial exposure. Since medical treatment regimes for hospital patients depend on the analytical results reported, the analysis of biomedical samples is critical. Therefore, the need for fast and reliable analytical methods and instrumentation is paramount [22].

11.3. Solid sample analysis

Solutions and liquids are the normal sample types measured by ICP-MS. Solid samples are normally digested using mineral acids and analyzed as solutions. However, solid samples such as glass can be analyzed directly using the laser ablation system [20]. A sample is placed in the sample cell and ablated by the beam from an

Nd:YAG laser operating at 266 nm. The fine aerosol generated is carried directly to the plasma by Ar carrier gas. Group 1 and 2 elements, transition metals, rare earth elements, and actinides can be clearly seen from a two-minute analysis, even though the concentration of most elements was at the mg/kg (ppm) level or lower in the glass [28].

11.4. Speciation analysis

Organotin compounds have been widely used for a variety of commercial applications. Trialkyltin compounds have been used for antifouling paints for ships and fish traps. Dialkyltin has been used for polymerization catalysts. Currently, there is growing concern about their effects on the environment [30]. Methods to determine the species of tin (Sn) and the total amount of Sn present are required, since the toxicity of organotin compounds varies widely with the number and types of organic groups attached to the Sn atom. The combination of ICP-MS and chromatography has the ability to perform speciation analysis with high selectivity and sensitivity. Each organotin compound was separated clearly within a total run time of 20 minutes.

11.5. Flow cytometry field

In flow cytometry a new technique uses ICP-MS to replace the traditional fluorochromes. Briefly, instead of labelling antibodies(or other biological probes) with fluorochromes, each antibody is labelled with distinct combinations of lanthanides. When the sample of interest is analysed by ICP-MS in a specialised flow cytometer, each antibody can be identified and quantitated by virtue of a distinct ICP "footprint". In theory, hundreds of different biological probes can thus be analysed in an individual cell, at a rate of ca. 1,000 cells per second. Because elements are easily distinguished in ICP-MS, the problem of compensation in multiplex flow cytometry is effectively eliminated [31].

12. CONCLUSION

ICP MS is performing extremely well and is unchallenged by other MS techniques. Increasingly, by using heteroatom's to discover and analyze molecules, ICPMS coupled to high-performance separations is expanding its role into species identification. The developments are HPLC ICP MS, GC ICP MS and even high resolution ICP MS. On the other hand, it is a unique and outstanding advantage of ICPMS 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.

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