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Type of mass spectrometry that uses an inductively coupled plasma to ionize the sample Inductively coupled plasma mass spectrometry ICP-MS Instrument Acronym ICP-MS Classification Mass spectrometry Analytes atomic and polyatomic species in plasma, with exceptions; usually interpreted towards concentrations of chemical elements in sample Manufacturers Skyray, Agilent, Analytik Jena, Horiba (only ICP-OES), PerkinElmer, Shimadzu, Spectro, Thermo GBC Scientific, Nu Instruments Other techniques Related inductively coupled plasma atomic emission spectroscopy Hyphenated liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS), Gas chromatography-inductively coupled plasma mass spectrometry (GC-ICP-MS), Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry that uses an inductively coupled plasma to ionize the sample. It atomizes the sample and creates atomic and small polyatomic ions, which are then detected. It is known and used for its ability to detect metals and several non-metals in liquid samples at very low concentrations. It can detect different isotopes of the same element, which makes it a versatile tool in isotopic labeling. Compared to atomic absorption spectroscopy, ICP-MS has greater speed, precision, and sensitivity. However, compared with other types of mass spectrometry, such as thermal ionization mass spectrometry (TIMS) and glow discharge mass spectrometry (GD-MS), ICP-MS introduces many interfering species: argon from the plasma, component gases of air that leak through the cone orifices, and contamination from glassware and the cones. Components Inductively coupled plasma Main article: Inductively coupled plasma An inductively coupled plasma is a plasma that is energized (ionized) by inductively heating the gas with an electromagnetic coil, and contains a sufficient concentration of ions and electrons to make the gas electrically conductive. Not all of the gas needs to be ionized for the gas to have the characteristics of a plasma; as little as 1% ionization creates a plasma.[1] The plasmas used in spectrochemical 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 numbers of ions and electrons in each unit volume of plasma. The ICPs have two operation modes, called capacitive (E) mode with low plasma density and inductive (H) mode with high plasma density, and E to H heating mode transition occurs with external inputs.[2] The Inductively Coupled Plasma Mass Spectrometry is operated in the H mode. What makes Inductively Coupled Plasma Mass Spectrometry (ICP-MS) unique to other forms of inorganic mass spectrometry is its ability to sample the analyte continuously, without interruption. This is in contrast to other forms of inorganic mass spectrometry, Glow Discharge Mass Spectrometry (GDMS) and Thermal Ionization Mass Spectrometry (TIMS), that require a two-stage process: Insert sample(s) into a vacuum chamber, seal the vacuum chamber, pump down the vacuum, energize sample, thereby sending ions into the mass analyzer. With ICP-MS the sample to be analyzed is sitting at atmospheric pressure. Through the effective use of differential pumping, multiple vacuum stages separate by differential apertures (holes), the ions created in the argon plasma are, with the aid of various electrostatic focusing techniques, transmitted through the mass analyzer to the detector(s) and counted. Not only does this enable the analyst to radically increase sample throughput (amount of samples over time), but has also made it possible to do what is called "time resolved acquisition". Hyphenated techniques like Liquid Chromatography ICP-MS (LC-ICP-MS); Laser Ablation ICP-MS (LA-ICP-MS); Flow Injection ICP-MS (FIA-ICP-MS), etc. have benefited from this relatively new technology. It has stimulated the development new tools for research including geochemistry and forensic chemistry; biochemistry and oceanography. Additionally, increases in sample throughput from dozens of samples a day to hundreds of samples a day have revolutionized environmental analysis, reducing costs. Fundamentally, this is all due to the fact that while the sample resides at environmental pressure, the analyzer and detector are at 1/10,000,000 of that same pressure during normal operation. An inductively coupled plasma (ICP) for spectrometry is sustained in a torch that consists of three concentric tubes, usually made of quartz, although the inner tube (injector) can be sapphire if hydrofluoric acid is being used. The end of this torch is placed inside an induction coil supplied with a radio-frequency electric current. A flow of argon gas (usually 13 to 18 liters per minute) is introduced between the two outermost tubes of the torch and an electric spark is applied for a short time to introduce free electrons into the gas stream. 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 million cycles per second). The accelerated electrons collide with argon atoms, and sometimes a collision causes an argon atom to part with one of its electrons. 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. The plasma also produces ultraviolet light, so for safety should not be viewed directly. 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 liter 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 liter 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. To maximise plasma temperature (and hence ionisation efficiency) and stability, the sample should be introduced through the central tube with as little liquid (solvent load) as possible, and with consistent droplet sizes. A nebuliser can be used for liquid samples, followed by a spray chamber to remove larger droplets, or a desolvating nebuliser can be used to evaporate most of the solvent before it reaches the torch. Solid samples can also be introduced using laser ablation. The sample enters the central channel of the ICP, evaporates, the molecules break apart, and then the constituent atoms ionise. At the temperatures prevailing in the plasma a significant proportion of the atoms of many chemical elements are ionised, each atom losing its most loosely bound electron to form a singly charged ion. The plasma temperature is selected to maximise ionisation efficiency for elements with a high first ionisation energy, while minimising second ionisation (double charging) for elements that have a low second ionisation energy. Mass spectrometry Main article: Mass spectrometry For coupling to mass spectrometry, the ions from the plasma are extracted through a series of cones into a mass spectrometer, usually a quadrupole. The ions are separated on the basis of their mass-to-charge ratio and a detector receives an ion signal proportional to the concentration. The concentration of a sample can be determined through calibration with certified reference material such as single or multi-element reference standards. ICP-MS also lends itself to quantitative determinations through isotope dilution, a single point method based on an isotopically enriched standard. Other mass analyzers coupled to ICP systems include double focusing magnetic-electrostatic sector systems with both single and multiple collector, as well as time of flight systems (both axial and orthogonal accelerators have been used). Applications One of the largest volume uses for ICP-MS is in the medical and forensic field, specifically, toxicology.[citation needed] A physician may order a metal assay for a number of reasons, such as suspicion of heavy metal poisoning, metabolic concerns, and even hepatological issues. Depending on the specific parameters unique to each patient's diagnostic plan, samples collected for analysis can range from whole blood, urine, plasma, serum, to even packed red blood cells. Another primary use for this instrument lies in the environmental field. Such applications include water testing for municipalities or private individuals all the way to soil, water and other material analysis for industrial purposes. In the forensic field, glass ICP-MS is popular for glass analysis.[citation needed] Trace elements on glass can be detected using the LA-ICP-MS. The trace elements from the glass can be used to match a sample found at the crime scene to a suspect. In recent years, industrial and biological monitoring has presented another major need for metal analysis via ICP-MS. Individuals working in these industries are more exposed to metals, such as a battery factory, are required by their employer to have their employees tested for exposure to hazardous materials, such as lead. Previous forensic techniques employed for the organic analysis of lipsticks by compositional comparison include thin layer chromatography (TLC), gas chromatography (GC), and high-performance liquid chromatography (HPLC). These methods provide useful information regarding the identification of lipsticks. However, they all require long sample preparation times and destroy the sample. Nondestructive techniques for the forensic analysis of lipstick smears include UV fluorescence observation combined with purge-and-trap gas chromatography, microspectrophotometry and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and Raman spectroscopy.[11] Metal speciation A growing trend in the world of elemental analysis has revolved around the speciation, or determination of oxidation state of certain metals such as chromium and arsenic. One of the primary techniques to achieve this is to separate the chemical species with high-performance liquid chromatography (HPLC) or field flow fractionation (FFF) and then measure the concentrations with ICP-MS. Quantification of proteins and biomolecules There is an increasing trend of using ICP-MS as a tool in speciation analysis, which normally involves a front end chromatograph separation and an elemental selective detector, such as AAS and ICP-MS. For example, ICP-MS may be combined with size exclusion chromatography and quantitative preparative native continuous polyacrylamide gel electrophoresis (QPN-CPAGE) for identifying and quantifying native metal cofactor containing proteins in biofluids. Also the phosphorylation status of proteins can be analyzed. In 2007, a new type of protein tagging reagents called metal-coded affinity tags (MeCAT) were introduced to label proteins quantitatively with metals, especially lanthanides.[12] The MeCAT labelling allows relative and absolute quantification of all kind of proteins or other biomolecules like peptides. MeCAT comprises a site-specific biomolecule tagging group with at least a strong chelate group which binds metals. The MeCAT labelled proteins can be accurately quantified by ICP-MS down to low attomol amount of analyte which is at least 2–3 orders of magnitude more sensitive than other mass spectrometry based quantification methods. By introducing several MeCAT labels to a biomolecule and further optimization of LC-ICP-MS detection limits in the zeptomol range are within the realm of possibility. By using different lanthanides MeCAT multiplexing can be used for pharmacokinetics of proteins and peptides or the analysis of the differential expression of proteins (proteomics) e.g. in biological fluids. Breakable PAGE SDS-PAGE (DPAGE, dissolvable PAGE), two-dimensional gel electrophoresis or chromatography is used for separation of MeCAT labelled proteins. Flow-injection ICP-MS analysis of protein bands or spots from DPAGE SDS-PAGE gels can be easily performed by dissolving the DPAGE gel after electrophoresis and staining of the gel. MeCAT labelled proteins are identified and relatively quantified on peptide level by MALDI-MS or ESI-MS. Elemental analysis The ICP-MS allows determination of elements with atomic mass ranges *r* to 250 (Li to U), and sometimes higher. Some masses are prohibited such as 40 due to the abundance of argon in the sample. Other blocked regions may include mass 80 (due to the argon dimer), and mass 56 (due to ArO), the latter of which greatly hinders Fe analysis unless the instrumentation is fitted with a reaction chamber. Such interferences can be reduced by using a high resolution ICP-MS (HR-ICP-MS) which uses two or more slits to constrict the beam and distinguish between nearby peaks. This comes at the cost of sensitivity. For example, distinguishing iron from argon requires a resolving power of about 10,000, which may reduce the iron sensitivity by around 99%. A single collector ICP-MS may use a multiplier in pulse counting mode to amplify very low signals, an attenuation grid or a multiplier in analogue mode to detect medium signals, and a Faraday cup/bucket to detect larger signals. A multi-collector ICP-MS may have more than one of any of these, normally Faraday buckets which are much less expensive. With this combination, a dynamic range of 12 orders of magnitude, from 1 ppt to 100 ppm is possible. ICP-MS is a method of choice for the determination of cadmium in biological samples.[13] Unlike atomic absorption spectroscopy, which can only measure a single element at a time, ICP-MS has the capability to scan for all elements simultaneously. This allows rapid sample processing. A simultaneous ICP-MS that can record the entire analytical spectrum from lithium to uranium in every analysis was the Silver Award at the 2010 Pittcon Editors' Awards. An ICP-MS may use multiple scan modes, each one striking a different balance between speed and precision. Using the magnet alone to scan is slow, due to hysteresis, but is precise. Electrostatic plates can be used in addition to the magnet to increase the speed, and this, combined with multiple collectors, can allow a scan of every element from Lithium 6 to Uranium Oxide 256 in less than a quarter of a second. For low detection limits, interfering species and high precision, the counting time can increase substantially. The rapid scanning, large dynamic range and large mass range is ideally suited to measuring multiple unknown concentrations and isotopic ratios in samples that have had minimal preparation (an advantage over TIMS), for example seawater, urine, and digested whole rock samples. It also lends well to laser ablated rock samples, where the scanning rate is so quick that a real time plot of any number of isotopes is possible. This also allows easy spatial mapping of mineral grains. Hardware In terms of input and output, ICP-MS instrument consumes prepared sample material and translates it into mass-spectral data. Actual analytical procedure takes some time; after that time the instrument can be switched to work on the next sample. Series of such sample measurements requires the instrument to have plasma ignited, meanwhile a number of technical parameters has to be stable in order for the results obtained to have feasibly accurate and precise interpretation. Maintaining the plasma requires a constant supply of carrier gas (usually, pure argon) and increased power consumption of the instrument. When these additional running costs are not considered justified, plasma and most of auxiliary systems can be turned off. In such standby mode only pumps are working to keep proper vacuum in mass-spectrometer. The constituents of ICP-MS instrument are designed to allow for reproducible and/or stable operation. Sample introduction The first step in analysis is the introduction of the sample. This has been achieved in ICP-MS through a variety of means. The most common method is the use of analytical nebulizers. Nebulizer converts liquids into an aerosol, and that aerosol can then be swept into the plasma to create the ions. Nebulizers work best with simple liquid samples (i.e. solutions). However, there have been instances of their use with more complex materials like a slurry. Many varieties of nebulizers have been coupled to ICP-MS, including pneumatic, cross-flow, Babington, ultrasonic, and desolvating types. The aerosol generated is often treated to limit it to only smallest droplets, commonly by means of a Peltier cooled double pass or cyclonic spray chamber. Use of autosamplers makes this easier and faster, especially for routine work and large numbers of samples. A Desolvating Nebuliser (DSN) may also be used; this uses a long heated capillary, coated with a fluoropolymer membrane, to remove most of the solvent and reduce the load on the plasma. Matrix removal introduction systems are sometimes used for samples, such as seawater, where the species of interest are at trace levels, and are surrounded by much more abundant contaminants. Laser ablation is another method. 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Electrothermal vaporization (ETV) and in torch vaporization (ITV) use hot surfaces (graphite or metal, generally) to vaporize samples for introduction. These can use very small amounts of liquids, solids, or slurries. Other methods like vapor generation are also known. Plasma torch The atomizer of an ICP The plasma used in an ICP-MS is made by partially ionizing argon gas (Ar → Ar+ + e−). The energy required for this reaction is obtained by pulsing an alternating electric current in load coil that surrounds the plasma torch with a flow of 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 → M+ + e−) so that they can be detected by the mass spectrometer. An inductively coupled plasma (ICP) for spectrometry is sustained in a torch that consists of three concentric tubes, usually made of quartz. 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If there are to be multiple ICP-MS instruments running for long periods of time, then it will most likely be beneficial for the laboratory to install a bulk or micro bulk argon tank which will be maintained by a gas supply company, thus eliminating the need to change out tanks frequently as well as minimizing loss of argon that is left over in each used tank as well as down time for tank changeover. Helium can be used either in place of, or mixed with, argon for plasma generation.[15][16] Helium's higher first ionisation energy allows greater ionisation and therefore higher sensitivity for hard-to-ionise elements. The use of pure helium also avoids argon-based interferences such as ArO.[17] However, many of the interferences can be mitigated by use of a collision cell, and the greater cost of helium has prevented its use in commercial ICP-MS.[citation needed] Transfer of ions into vacuum The carrier gas is sent through the central channel and into the very hot plasma. The sample is then exposed to radio frequency which converts the gas into a plasma. The high temperature of the plasma is sufficient to cause a very large portion of the sample to form ions. This fraction of ionization can approach 100% for some elements (e.g. sodium), but this is dependent on the ionization potential. A fraction of the formed ions passes through the plasma to create the ions. Nebulizers work best with simple liquid samples (i.e. solutions). However, there have been instances of their use with more complex materials like a slurry. Many varieties of nebulizers have been coupled to ICP-MS, including pneumatic, cross-flow, Babington, ultrasonic, and desolvating types. The aerosol generated is often treated to limit it to only smallest droplets, commonly by means of a Peltier cooled double pass or cyclonic spray chamber. Use of autosamplers makes this easier and faster, especially for routine work and large numbers of samples. 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