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OVERVIEW OF AN INDUCTIVELY COUPLED PLASMA (ICP) SYSTEM

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Abstract- In search for newer analytical techniques that can meet the growing trend in the world of elemental analysis, the Inductively Coupled Plasma (ICP) system is exploited. A cursory look at the driving forces behind this analytical tool and its use in series with other analytical tools with reference to some literature reports has been critically reviewed. Aspects of maintenance of the ICP system and metal speciation were also highlighted.
Keywords: plasma, metal speciation, maintenance

1.0 Introduction

An inductively coupled plasma (ICP) is a type of plasma source in which the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields [23] An inductively coupled plasma contains a sufficient concentration of ions and electrons to make the gas electrically conductive. The plasmas used in spectrochemical analysis are essentially electrically neutral, with each positive charge on an ion balanced by a free electron [35]. 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 [35]. Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples [35]. The primary goal of ICP is to get elements to emit characteristic wavelength of specific light which can then be measured [5]. The technology for the ICP method was first employed in the early 1960's with the intention of improving upon crystal growing techniques [5] Since then, ICP has been refined and used in conjunction with other procedures for quantitative analysis [5]. Following is a cursory look at the driving forces behind this analytical tool, its use in series with other analytical tools, and environmental applications of ICP [5]. Often, ICP is used in conjunction with other analytical instruments, such as the Atomic Emission Spectroscopy (AES) and the Mass Spectroscopy (MS) [5]. This is an advantageous practice, as both the AES and MS require that sample to be in an aerosol or gaseous form prior to injection into the instrument [5]. Thus, using an ICP in conjunction with either of these instruments eliminates any sample preparation time which would be required in the absence of an ICP [5]. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is one of several techniques available in analytical atomic spectroscopy [20]. ICP-AES utilizes plasma as the atomization and excitation source[20]. A plasma is an electrically neutral, highly ionized gas that consists of ions, electrons, and atoms [20].

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is one of the most common techniques for elemental analysis. Its high specificity, multi-element capability and good detection limits result in the use of the technique in a large variety of applications [22]. All kinds of dissolved samples can be analyzed, varying from solutions containing high salt concentrations to diluted acids [22].

The ICP-MS instrument employs argon plasma (ICP) as the ionization source and a mass spectrometer (MS), usually with a quadrupole mass filter, to separate the ions produced. It can simultaneously measure most elements in the periodic table and determine analyte concentrations down to the subnanogram per liter, or parts per trillion (ppt), level. It can perform qualitative, semiquantitative, and quantitative analysis, and compute isotopic ratios on water samples, and in waste extracts and digests [7, 17] ICP-MS offers detection limits in the attomolar range, regardless of the molecular environment of the target element [24].

1.1 The basic principle of ICP

ICP hardware is designed to generate plasma, which is a gas in which atoms are present in an ionized state. The basic set up of an ICP consists of three concentric tubes, most often made of silica. These tubes, termed outer loop, intermediate loop, and inner loop, collectively make up the torch of the ICP. The torch is situated within a water-cooled coil of a radio frequency (r.f.) generator. As flowing gases are introduced into the torch, the r. f. field is activated and the gas in the coil region is made

electrically conductive. This sequence of events forms the plasma [36].

The formation of the plasma is dependent upon an adequate magnetic field strength and the pattern of the gas streams follows a particular rotationally symmetrically pattern. The plasma is maintained by inductive heating of the flowing gases. The induction of a magnetic field generates a high frequency annular electric current within the conductor. The conductor, in turn, is heated as the result of its ohmic resistance [5].

In order to prevent possible short-circuiting as well as meltdown, the plasma must be insulated from the rest of the instrument. Insulation is achieved by the concurrent flow of gasses through the system. Three gases flow through the system--the outer gas, intermediate gas, and inner or carrier gas. The outer gas is typically Argon or Nitrogen. The outer gas has been demonstrated to serve several purposes including maintaining the plasma, stabilizing the position of the plasma, and thermally isolating the plasma from the outer tube. Argon is commonly used for both the intermediate gas and inner or carrier gas. The purpose of the carrier gas is to convey the sample to the plasma [5].

1.2 An ICP system
An ICP typically includes the following components:
- sample introduction system (nebulizer)
- ICP torch
- High frequency generator
- Transfer optics and spectrometer
- Computer interface [5]

An ICP requires that the elements which are to be analyzed be in solution. An aqueous solution is preferred over an organic solution, as organic solutions require special manipulation prior to injection into the ICP. Solid samples are also discouraged, as clogging of the instrumentation can occur. The nebulizer transforms the aqueous solution into an aerosol. The light emitted by the atoms of an element in the ICP must be converted to an electrical signal that can be measured quantitatively. This is accomplished by resolving the light into its component radiation (nearly always by means of a diffraction grating) and then measuring the light intensity with a photomultiplier tube at the specific wavelength for each element line. The light emitted by the atoms or ions in the ICP is converted to electrical signals by the photomultiplier in the spectrometer. The intensity of the electron signal is compared to previous measured intensities of known concentration of the element and a concentration is computed. Each element will have many specific wavelengths in the spectrum which could be used for analysis. Thus, for the selection of the best line, the analytical application in hand requires considerable experience of ICP wavelengths.

1.3 Applications of ICP
An ICP can be used in the quantitative analysis in the following areas: natural materials such as rocks, minerals, soil, sediment, air, water, plant and animal tissue; pure and applied geochemistry, mineralogy, agriculture, forestry, animal husbandry, chemical ecology, environmental sciences and food industry, including purification and distribution of water, the analysis of elements not readily identified by AAS such as Sulfur, Boron, Phosphorus, Titanium, and Zirconium [5]Other specific applications includes; analysis of glass , monitoring elements of interest in process solutions, quantitative analysis of traces of catalyst in polymers, and quantitative analysis of contaminations in thin layers [22].

1.4 Literature reports on the use of ICP
Investigated the Effects of light irradiation on etching yields of SiO_2 films by CF_3 ion beams with a low-energy mass selected ion beam system [38]. Inductively coupled plasma (ICP) from Ar gas was used as the light source. The spectrum of light emitted from the Ar ICP was measured by vacuum ultraviolet and visible monochromators [25]; reported the modification of the surface of polystyrene (PS) thin films in argon plasma to study the hydrophilicity properties. An inductively coupled plasma (ICP) system was used to generate the argon plasma. In the experiment, the effect of RF power levels, gas flow rate and treatment time was investigated. New direct injection multi-gas inductively coupled plasma (ICP) source is developed by [2] With the new ICP source, not only Ar but He, O_2, N_2, CO_2, air and their mixture gas plasma can be stably generated in the atmospheric pressure. Furthermore, aqueous solutions can be introduced directly into the plasmas using common pneumatic nebulizer.

1.5 Advantages and Disadvantages of using ICP
Advantages of using an ICP include its ability to identify and quantify all elements with the exception of Argon; since many wavelengths of varied sensitivity are available for determination of any one element, the ICP is suitable for all concentrations from ultra trace levels to major components; detection limits are generally low for most elements with a typical range of 1 - 100 g / L. Probably the largest advantage of employing an ICP when performing quantitative analysis is the fact that multi elemental analysis can be accomplished, and quite rapidly. A complete multi element analysis can be undertaken in a period as short as 30 seconds, consuming only 0.5 ml of sample solution. Although in theory, all elements except Argon can be determined using an ICP, certain unstable elements require special facilities for handling the radioactive fume of the plasma. Also, an ICP has difficulty handling halogens--special optics for the transmission of the very short wavelengths become necessary [5].

2.0 Combining ICP with MS and AES
Often, ICP is used in conjunction with other analytical instruments, such as the Atomic Emission Spectroscopy (AES) and the Mass Spectroscopy (MS). This is an advantageous practice, as both the AES and MS require that sample to be in an aerosol or gaseous form prior to injection into the instrument. Thus, using an ICP in

conjunction with either of these instruments eliminates any sample preparation time which would be required in the absence of an ICP [5].

2.1 Inductively coupled plasma mass spectroscopy (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a relatively new technique based on the hybridization of a conventional ICP optical emission source with a mass spectrometer. This system offers extremely high sensitivity for the determination of a wide range of elements, allowing a lot of information to be obtained about the examined sample. The multivariate analysis approach in its turn permits the fast characterization of a sample with the identification of particular aspects, not suspected before [4]. Inductively coupled plasma mass spectroscopy (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. The resulting instrument is capable of trace multielement analysis, often at the part per trillion levels. Precisely, the technique was commercially introduced in 1983 and has gained general acceptance in many types of laboratories. Geochemical analysis labs were early adopters of ICP-MS technology because of its superior detection capabilities, particularly for the rare-earth elements (REEs) [32].

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. The schematic below illustrates this sequence of processes [37]. An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer. ICP source is an ICP-MS. Argon gas that flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off of the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma. The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma [30].

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

- The argon discharge, with a temperature of around 6000-10000°K, is an excellent ion source.
- The ions formed by the ICP discharge are typically positive ions, $M+$ or $M+^2$, therefore, elements that prefer to form negative ions, such as Cl, I, F, etc., are very difficult to determine via ICP-MS.
- The detection capabilities of the technique can vary with the sample introduction technique used, as different techniques will allow differing amounts of sample to reach the ICP plasma.
- Detection capabilities will vary with the sample matrix, which may affect the degree of ionization that will occur in the plasma or allow the formation of species that may interfere with the analyte determination [32].

2.2 Applications of ICP-MS

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, and medicine[37].

2.3 Advantages of ICP-MS

ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICP-AES), including:

- Detection limits for most elements equal to or better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
- Higher throughput than GFAAS
- The ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source
- Superior detection capability to ICP-AES with the same sample throughput
- The ability to obtain isotopic information [32].

For archaeologists, ICP-MS has several important advantages over neutron activation and X-ray fluorescence analysis: (1) only a tiny powdered sample is required, so the technique is minimally destructive to valuable artifacts; (2) the large number of elements that can be accurately and precisely analyzed is particularly important for characterization and provenance studies; (3) isotope ratio measurements to three significant figures are possible without extensive sample preparation; and (4) the combination of small sample size and low per sample cost allows assemblages of artifacts rather than individual objects to be studied. These advantages will be illustrated by the trace element characterization and source tracing of obsidian (a jet-black volcanic glass), the compositional analysis of copper-based artifacts, and the lead isotope ratio analysis of turquoise.

2.4 Literature reports on the use of ICP-MS

The use of an inductively coupled plasma-mass spectrometer (ICP-MS) to measure isotope ratios of lead and thallium [12, 19] presented an application of inductively coupled plasma mass spectrometry (ICP-MS) to multielement analysis in fingernail and toenail as biological indices for metal exposure. The ICP-MS measurements were performed using a Thermo Elemental X7CCT series. Fingernail specimens were obtained from 130 healthy volunteers, and paired fingernail and toenail samples from 50 additional healthy volunteers of both sexes were collected as well. After warm water and acetone decontamination, 20 mg fingernails and toenails were acid mineralized after a decontamination procedure, and 32-34 elements were simultaneously quantified after acid dilution following water calibration. Li, Be, B, Al, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Ba, La, Gd, W, Pt, Hg, Tl, Pb, Bi, and U could be validated in fingernail and toenail samples. A rapid method is reported for the determination of ^{90}Sr in contaminated soil samples [10] in the vicinity of the Chernobyl Nuclear Power Plant by ICP-DRC-MS. Sample preparation and measurement procedures focus on overcoming the isobaric interference of ^{90}Zr, which is present in soils at concentrations higher by more than six orders of magnitude than ^{90}Sr. The requirement to uniquely characterise and compare physical evidence from crime scenes is a major task in forensic science. Laser ablation inductively coupled plasma mass spectrometry (LA–ICP-MS) was investigated [33] for its potential to provide data on relative trace elemental compositions to achieve this aim[29] claimed the first report of the use of ICP-MS to determine bismuth concentrations in human plasma in China [13]. Developed an inductively coupled mass spectrometric method for the direct determination of iodine in urine. The application of isotope dilution analysis with added ^{129}I offers new possibilities for automatic and accurate determinations. The application of quadrupole ICP-MS for the determination of lead isotope ratios has been evaluated [3] aiming its application on dating of monazites, using U-Pb, Th-Pb and Pb-Pb methods [18].

Reported a method for mercury speciation in seafood which was designed by on-line coupling gas chromatography (GC) to inductively coupled plasma mass spectrometry (ICP-MS) with an improved interface. Recent reports describing the presence of lead (Pb) in lipsticks have suggested that, under ordinary use, the potential amount of Pb exposure is harmful. To permit independent assessment of the Pb contamination, a method for determining total Pb in lipstick using microwave-assisted digestion and analysis employing inductively coupled plasma–mass spectrometry (ICP–MS) was developed and validated [14]. The use of inductively-coupled plasma mass spectrometry for the determination of concentrations of trace elemental constituents in water draining was reported. [15]. The potential of ablative laser technology (coupled to ICP-MS)to rapidly track the profiles of barium and strontium in side-well core sections to examine the uniformity of (sulphate) deposits linked to these elements was also explored [28].

2.5 HPLC-ICP-MS

High-performance liquid chromatography (HPLC) is used to describe any chromatographic technique where analytes dissolved in a liquid mobile phase are separated based on their interactions with the mobile phase and a stationary phase contained in a column. This would include both reverse- and normal-phase HPLC, size exclusion chromatography (SEC) and ion exchange chromatography. HPLC (or IC)-ICP-MS is used for the analysis of nonvolatile compounds or ions in solution. The solution can be aqueous, organic, or a mixture of both. It is this flexibility in the choice of both stationary and mobile phases, including gradient techniques where the mobile phase changes composition during the chromatographic run, which makes HPLC such a powerful separation technique for many applications. As an HPLC detector ICP-MS is the only universal, element-specific detector available for liquid chromatography and, as such, has many applications [1].

2.6 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is one of the most common techniques for elemental analysis. Its high specificity, multi-element capability and good detection limits result in the use of the technique in a large variety of applications. All kinds of dissolved samples can be analyzed, varying from solutions containing high salt concentrations to diluted acids. A plasma source is used to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelength depending on the element present. This light is recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample [22].

2.7 Principle of ICP-AES

In the ICP-AES a plasma source is used to make specific elements emit light, after which a spectrometer separates this light in the characteristic wavelengths.

Sample introduction

A solid sample is normally first dissolved and mixed with water. The technique is robust enough to allow direct analysis of liquids. The sample solution is transformed into an aerosol by a so-called nebuliser. The bigger droplets are separated from the smallest in a specially spraychamber. The smallest droplets (1-10 µm) are transferred by an argon flow into the heart of the ICP-AES, the argon plasma. The bigger droplets (>90%) are pumped to waste.

Plasma

To produce strong atomic emission from all chemical elements it is necessary to attain temperatures considerably above those available from simple flames. The highest amount of atomic emission is reached at temperatures in the range of 7,000 K to 10,000 K. A convenient means of obtaining these temperatures is to generate an inert-gas plasma. Plasma is a gaseous state of matter containing major concentrations of essential free electrons and highly charged ions. It is a very effective medium for volatilization and atomization (and ionization) of liquid droplets. When the aerosol droplets enter the hot area of the plasma (front page) they are converted into salt particles by desolvation. These salt particles are split into individual molecules that will subsequently fall apart to atoms and ions. Most elements get ionized very efficiently (> 90%). Almost no molecules and ground state atoms are present in plasma. In the plasma, even more energy is transferred to the atoms and ions, promoting the excitation of their electrons to higher energy levels. When these excited atoms and ions return to their ground state or to lower excitation states they will emit electromagnetic radiation in the ultra-violet/visible range of the spectrum. Each excited element emits specific wavelengths (λ), i.e. has a typical emission spectrum. The intensity of the radiation is proportional to the element concentration. Commercially available standards can be used to calibrate the ICP-AES, which makes it possible to perform highly quantitative analysis [22].

2.8 Applications of ICP-AES

ICP-AES has been widely used since the 1970's for the simultaneous multi-element analysis of environmental and biological samples after dissolution. The excellent sensitivity and wide working range for many elements-together with the low level of interferences make ICP-AES a nearly ideal method so long as sample throughput is high enough to justify the initial capital outlay. Laser sampling, in conjunction with ICP is a way to avoid dissolution procedures of solid samples prior to the determination of the elements.

ICP-AES has been approved for the determination of metals by the EPA under Method 6010. Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP-AES. This method is approved for a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis [5]. Table 1 lists the elements for which Method 6010 is applicable.

Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in the following table provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences [5].

2.9 Literature reports on the use of ICP-AES

The analysis of gold by inductively coupled plasma atomic emission spectrometry (ICP-AES) in aqueous solution in the presence of up to 50% w/v of ionic liquid [34]. The ionic liquids investigated contain the 1-butyl-3-methyl-imidazolium (bmlm) cation with the anions Cl-, BF_4^-, HSO_4^-, or $N(CN)_2^-$. A facile route to the HSO_4^- salt is also described.[26] performed Chemical analysis for rare metal Ta-Nb –Sn –Li-Be content of the pegmatite bodies using the inductively coupled plasma (ICP AES). Instrumentation technique show that these rare metals have preference for specific mineralogical zones [16]. applied Inductively coupled plasma atomic emission spectroscopy (ICP-AES) with internal standardization for the analysis of an in-house reference platinum alloy containing palladium and rhodium (approximately 5% by weight) [21]. The Screening Trace Elements and Electrolytes in Serum by Inductively-Coupled Plasma Emission Spectrometry [27]; demonstrated the use of Inductively Coupled Plasma Atomic Emission Spectrometry for Air Quality Monitoring. Inductively coupled plasma atomic emission spectrometry (ICPAES) was applied in their study for quantitative determination of traces of elements after sample extraction with aqua regia according to ISO 11466:1995. The accuracy is ensured by the following ICP–AES methodology: (a) quantification of spectral interferences in the presence of Al, Ca, Mg, Fe and Ti as a complex environmental matrix around the prominent lines of the analytes, and (b) line selection for trace analysis. The content of some pollutants (As, Ba, Cu, Mn, Pb, Zn, Al, Ca, Mg, Fe and Ti) was compared to the corresponding threshold concentration levels and to the results from the chemical analysis of hundreds of individual particles by using Electron Probe X–ray Micro-Analyses (EPXMA). A methodology based on inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave-assisted acid digestion was developed to determine the content of trace elements in curry samples from the Spanish market [11].

3.0 Metal speciation

Metal speciation is the determination of the form(s) of an element in a sample. This might be limited to speciation by valence of an inorganic form (e.g. hexavalent chromium vs. trivalent chromium vs. total chromium), or it might include speciation by valence and/or combined form(s) (e.g. elemental mercury vs. mercuric ion vs. methyl mercuric ion) [8].

A growing trend in the world of elemental analysis has revolved around the speciation of certain metals such as chromium and arsenic. One of the primary techniques to achieve this is to use an ICP-MS in combination with an HPLC. There are many advantages, from a clinical standpoint, in knowing the specific species present within a patient's body. For example, one species of chromium, known as Chromium III or Trivalent Chromium, is needed by the body and causes no ill effects; however, Chromium VI or Hexavalent Chromium, is very toxic to the body. Chromium VI can cause mutations that may

lead to cancer if not repaired by the body.[35] It is also beneficial for a clinician to utilize speciation analysis from a preventative standpoint. Many patients, who suffer from elevated levels of certain metals, do not know when or where the exposure incident(s) are occurring. By identifying the exact species, a physician can better narrow the search for possible exposure sites, therefore helping the patient to avoid certain areas in the future [35].

Metal Speciation Capabilities

- **Trace-metals speciation** - The various procedures commonly used include mercury speciation, arsenic speciation, chromium speciation, and/or tin speciation. Other applications are evaluated on a case to case basis.
- **Ultra-low level quantification** - Aqueous measurements are in pg/L to ng/L range, solid phase measurements in the pg/g and ng/g range.
- **Analysis of difficult matrices** - Preparation of hydrocarbons, coal, polymers, biota, and other complex matrices are given special consideration relative to complete dissolution and/or digestion, as well as preserving the metal species during the preparation process.
- **Analytical methods development** - Several procedures have been developed or refined by CAS staff. Evaluation and development of procedures to meet the requirements of specific applications is available.
- **Types of Metal Speciation**
- **Chemical Speciation**
  - Molecular (combined) forms (CH_3Hg^{+1}, Bu_3Sn^{+1}, etc.)
  - Oxidation State (valence) species [As(III), As(V), etc.]
  - Ionic-ligand Complexes [$HgCl^{+1}$, $HgCl_2^0$, $HgCl_3^{-1}$, etc.]
- **Physical Speciation**
  - Gaseous species [Hg^0, $(CH_3)_2Hg$, AsH_3, etc.]
  - Dissolved species [Hg^{+2}, $HgCl^{+1}$, $HgCl_2$, etc.] [8]

CE-ICP-MS for speciation analysis

The complexity of many environmental and biological matrices and the need to discriminate among analytes that have very close physicochemical properties prompted the development of high-resolution separation techniques prior to sensitive element- or molecule-specific detection. One of these techniques based on the separation in an electric field is capillary electrophoresis (CE).

CE has certain advantages in comparison to chromatographic techniques, such as:

- simplicity,
- low running costs,
- high spead of analysis,

- unique selectivity and high degree of matrix tolerance (due to high theoretical plate numbers, i.e. normally ranging from 70,000 to 200,000).

The mechanism of separation of metal ions in CE is based on the difference in electrophoretic mobility of the metal ions. Separation can be achieved by several modes of CE, namely capillary zone electrophoresis (CZE), micellar electrokinetic capillary electrophoresis (MECE) or micellar electrokinetic capillary electrophoresis (MECC), capillary isotachophoresis (CI), capillary gel electrophoresis (CGE), ion-exchange electrokinetic chromatography (IEEC), capillary isolectric focusing (CIEF), affinity capillary electrophoresis (ACE), capillary electrochromatography (CEC). While commonly based on the application of a high voltage, their separation principles are quite different, providing completely different mechanisms of characterization and identification for element species. While CE supplements conventional HPLC methods, it shows unique promise for separation purpose because it causes only a minor disturbance to the existing equilibrium between different species. There is no stationary phase, which has a huge surface area and gives various possibilities for undesired interactions. Therefore, species transformations are thought to be less frequent than with HPLC. To achieve maximum separation by CE, optimization of CE parameters is critical. The independent parameters under the control of the analysts are:

- selection of the buffer
- pH of the buffer,
- ion strength of the buffer,
- applied voltage,
- temperature of the capillary,
- dimensions of the capillary,
- additives to the background electrolyte.The coupling of CE as the separation module with ICP-MS as the element-selective detector is much less straightforward in comparison to the coupling with HPLC or GC. The main problems are the low flow rate of CE that limit the choice of a nebulizer and the necessity to apply a high voltage accross the capillary and keeping the electrode grounded. Also any dead-volumes created by the interface would lead to band-broadening that has to be kept as low as possible. One possible design of an interface is using a make-up flow that both is reducing the influence of the nebulizer (suction effect) on the separation and also allows for easy grounding of the capillary[6].

3.1 Routine maintenance

As with any piece of instrumentation or equipment, there are many aspects of maintenance that need to be encompassed by daily, weekly and annual procedures. The frequency of maintenance is typically determined by the sample volume and cumulative run time that the instrument is subjected to.

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One of the first things that should be carried out before the calibration of the ICP-MS is a sensitivity check and optimization. This ensures that the operator is aware of any possible issues with the instrument and if so, may address them before beginning a calibration. Typical indicators of sensitivity are Rhodium levels, Cerium/Oxide ratios and DI water blanks [35].

One of the most frequent forms of routine maintenance is changing out sample and waste tubing on the peristaltic pump, as these tubes can get worn fairly quickly resulting in holes and clogs in the sample line, resulting in skewed results. Other parts that will need regular cleaning and/or replacing are sample tips, nebulizer tips, sample cones, skimmer cones, injector tubes, torches and lenses. It may also be necessary to change the oil in the interface roughing pump as well as the vacuum backing pump, depending on the workload put on the instrument [35].

Instrument Calibration and Quality Control

- Incorporation of an external calibration series encompassing the elements to be analyzed is routine. This is designed to cover a range of concentrations that will completely bracket the concentration of analyte in the sample. In the event the sample is found to fall significantly outside the bracketed range, it can then be diluted and run again so that it falls within the desired range.

- Internal standards can be incorporated for each sample at known concentrations for the desired element(s) to compensate for any variation in the intensity of the element signal, which can then be corrected to the known concentration. By applying this same correction to other elements in the matrix solution, the correct element concentration can then readily be calculated.

- For potentially difficult matrices, the chemists can incorporate the use of spiked samples. This procedure involves the preparation of duplicate sample(s) spiked with each element of interest, which can then be utilized to measure the recovery efficiency of each element so that obvious discrepancies can be determined and investigate in more detail.

- Fortified laboratory blanks, typically consisting of ultrapure water, can be run to check for instrument background. Blanks may also be spiked as a further means to ensure accuracy, analyte recovery, and instrument response [9].

Conclusion

ICP appears to be a powerful technique for determination of elements and isotopes in solutions. It can be applied in a broad range of research areas, with strong ICP capabilities; analytical laboratories can provide accurate measurement with fast turn-round time to meet current research needs.

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