

⟨1730⟩ PLASMA SPECTROCHEMISTRY—THEORY AND PRACTICE

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1. INTRODUCTION

The purpose of this general chapter is to provide a general overview of fundamental principles, instrumentation and application of inductively coupled plasma optical emission spectroscopy (ICP–OES) and inductively coupled plasma mass spectrometry (ICP–MS). It is the companion chapter to *Plasma Spectrochemistry* (730). A glossary of terms is located at the end of this general chapter.

2. SAMPLE PREPARATION

Sample preparation is critical to the success of plasma-based analysis and is the first step in performing any analysis via ICP–OES or ICP–MS. Plasma-based techniques are heavily dependent on sample transport into the plasma, and because ICP–OES and ICP–MS share the same sample introduction system, the means by which samples are prepared may be applicable to either technique. The most conventional means by which samples are introduced into the plasma is via solution nebulization. If solution nebulization is employed, solid samples must be dissolved in order to be presented into the plasma for analysis. These samples may be dissolved in any appropriate solvent. There is a strong preference for the use of aqueous or dilute nitric acid solutions, because there are minimal interferences with these solvents compared to other solvent choices. Hydrogen peroxide, hydrochloric acid, sulfuric acid, perchloric acid, combinations of acids, or various concentrations of acids can all be used to dissolve the sample for analysis. Dilute hydrofluoric acid can be used, but great care must be taken when using this acid to ensure the safety of the analyst, and to protect the components of the sample introduction system, specifically: peristaltic pump tubing, the nebulizer, spray chamber, and inner torch tube should be manufactured from hydrofluoric acid-tolerant materials. Proper safety procedures must be followed to protect the analyst, as well. Additionally, alternative means of dissolving the sample can be employed. These include, but are not limited to: the use of dilute bases, straight or diluted organic solvents, combinations of acids or bases, and combinations of organic solvents, or any solvent that is compatible with the instrumentation.

When samples are introduced into the plasma via solution nebulization, it is important to consider the potential matrix effects and interferences that might arise from the solvent. The use of an appropriate internal standard and/or matching the standard matrix with samples should be applied for ICP–OES and ICP–MS analyses in cases where accuracy and precision are not adequate. The use of an internal standard should be considered the rule, rather than the exception, in the case of ICP–MS analyses. In either event, the selection of an appropriate internal standard should consider the analyte in question, ionization energy, wavelengths or masses, and the nature of the sample matrix.

Where a sample is found not to be soluble in any acceptable solvent, a variety of digestion techniques can be employed. These include hot-plate digestion and microwave-assisted digestions, including open-vessel and closed-vessel approaches. The decision regarding the type of digestion technique to use depends on the nature of the sample being digested, as well as on the analytes of interest.

Use acids, bases, and hydrogen peroxide of ultra-high purity, especially when ICP–MS is employed. Deionized water must be at least 18 MΩ. Check diluents for interferences before they are used in an analysis. Because it is not always possible to obtain organic solvents that are free of metals, use organic solvents of the highest quality possible with regard to metal contaminants. Open-vessel digestion is generally not recommended for the analysis of volatile metals, e.g., selenium and mercury. The suitability of a digestion technique, whether open-vessel or closed-vessel, should be supported by spike recovery experiments in order to verify that, within an acceptable tolerance, volatile metals have not been lost during sample preparation. Additionally, it may be necessary to extract the analyte(s) of interest, should a sample not completely dissolve. In such an instance, the validity of the extract must be demonstrated by means of spike and recovery studies.

It is important to consider the selection of the type, material of construction, pretreatment, and cleaning of analytical lab ware used in ICP–OES and ICP–MS analyses. The material must be inert and, depending on the specific application, resistant to caustics, acids, and/or organic solvents. For some analyses, diligence must be exercised to prevent the absorption of analytes onto the surface of a vessel, particularly in ultra-trace analyses. Contamination of the sample solutions from metal and ions present in the container can lead to inaccurate results.

The use of lab ware that is not certified to meet Class A tolerances for volumetric flasks is acceptable if the linearity, accuracy, and precision of the method have been experimentally demonstrated to be suitable for the purpose at hand.

3. SAMPLE INTRODUCTION

There are two ways to introduce the sample into the nebulizer: by means of a peristaltic pump, and by self-aspiration. The peristaltic pump is preferred and serves to ensure that the flow rate of sample and standard solution to the nebulizer is the same irrespective of sample viscosity. The speed setting of the peristaltic pump should remain constant throughout an analysis during the time period when readings are being taken by the instrument. In some cases, where a peristaltic pump is not required, self-aspiration can be used.

The purpose of a nebulizer is to generate very small droplets of the sample, with the goal of generating a fine aerosol mist. A wide variety of nebulizer types is available, including pneumatic (concentric and cross-flow), grid, and ultrasonic nebulizers. Micronebulizers, high-efficiency nebulizers, direct-injection high-efficiency nebulizers, and flow-injection nebulizers are also available. The selection of the nebulizer for a given analysis should consider the sample matrix, analyte, and desired sensitivity. Some nebulizers are better suited for use with viscous solutions or those containing a high concentration of dissolved solids, whereas others are better suited for use with organic solutions.

Note that the self-aspiration of a fluid is due to the Bernoulli, or Venturi, effect. Not all types of nebulizers will support self-aspiration. The use of a concentric nebulizer, for example, is required for self-aspiration of a solution.

Once a sample leaves the nebulizer as an aerosol, it enters the spray chamber, which is designed to permit only the smallest droplets of sample solution into the plasma; as a result, typically only 1%–2% of the sample aerosol reaches the ICP, although some special-purpose nebulizers have been designed that permit virtually all of the sample aerosol to enter the ICP.

As with nebulizers, there is more than one type of spray chamber available for use with ICP–OES or ICP–MS. Examples include the Scott double-pass spray chamber, as well as cyclonic spray chambers of various configurations. The spray chamber must be compatible with the sample and solvent and must equilibrate and wash out in as short a time as possible. When a spray chamber is selected, the nature of the sample matrix, the nebulizer, the desired sensitivity, and the analyte should all be considered. Gas and liquid chromatography systems can be interfaced with ICP–OES and ICP–MS for molecular speciation, ionic speciation, or other modes of separation chemistry, based on elemental emission or mass spectrometry.

Ultimately, the selection of sample introduction hardware should be demonstrated experimentally to provide sufficient specificity, sensitivity, linearity, accuracy, and precision for the analysis at hand.

In addition to solution nebulization, it is possible to analyze solid samples directly via laser ablation (LA). In such instances, the sample enters the torch as a solid aerosol. LA–ICP–OES and LA–ICP–MS are better suited for qualitative analyses of pharmaceutical compounds because of the difficulty in obtaining appropriate standards. Nonetheless, quantitative analyses can be performed if it can be demonstrated, through appropriate method validation, that the available standards are adequate (1).

4. STANDARD PREPARATION

Single- or multi-element standard solutions, whose concentrations are traceable to primary reference standards, such as those of the National Institute of Standards and Technology (NIST), can be purchased for use in the preparation of working standard solutions. Alternatively, standard solutions of elements can be accurately prepared from standard materials, as appropriate, and their concentrations can be determined independently. Working standard solutions, especially those used for ultra-trace analyses, may have limited shelf life, depending on the analyte in question, the type of storage container, the solution's concentration, and the storage conditions. As a general rule, working standard solutions with concentrations less than 10 ppm (w/v) should be retained for NMT 24 h unless stability is demonstrated experimentally. The selection of the standard matrix is of fundamental importance in the preparation of element standard solutions. Spike recovery experiments should be conducted with specific sample matrices in order to determine the accuracy of the method. If sample matrix effects cause excessive inaccuracies, standards, blanks, and sample solutions should be matrix matched, if possible, in order to minimize matrix interferences.

In cases where matrix matching is not possible, an appropriate internal standard or the method of standard additions should be used for ICP–OES or ICP–MS. The method of standard additions may be necessary, even with the use of matrix-matched solutions and internal standards. In any event, the selection of an appropriate internal standard should consider the analytes in question, their ionization and excitation energies, their chemical behavior, their wavelengths or masses, and the nature of the sample matrix. Ultimately, the selection of an internal standard should be demonstrated experimentally to provide sufficient specificity, sensitivity, linearity, accuracy, and precision of the analysis at hand.

The method of standard additions involves adding a known concentration of the analyte element to the sample at no fewer than two concentration levels plus an unspiked sample preparation. The instrument response is plotted against the concentration of the added analyte element, and a linear regression line is drawn through the data points. The absolute value of the x-intercept multiplied by any dilution factor is the concentration of the analyte in the sample.

Optimization of the ICP–OES or ICP–MS method is also highly dependent on the plasma parameters and means of sample introduction. Forward power, gas flow rates, and torch position may all be optimized to provide the best signal. Selection of wavelengths or isotopes must be carefully considered. The presence of dissolved carbon at concentrations of a small percentage in aqueous solutions enhances ionization of selenium and arsenic in an inductively coupled argon plasma. This phenomenon frequently results in a positive bias for ICP–OES and ICP–MS selenium and arsenic quantification measurements, which can be

remedied by using the method of standard additions or by adding a small percentage of carbon, such as analytically pure glacial acetic acid, to the linearity standards.

5. INDUCTIVELY COUPLED PLASMA (ICP)

The components that make up the ICP excitation source include the argon gas supply, torch, radio frequency (RF) induction coil, impedance-matching unit, and RF generator. Argon gas is almost universally used in the ICP. The plasma torch consists of three concentric tubes designated as the inner, the intermediate, and the outer tube. The intermediate and outer tubes are almost universally made of quartz. The inner tube can be made of quartz or alumina if the analysis is conducted with solutions containing hydrofluoric acid. The nebulizer gas flow carries the aerosol of the sample solution into and through the inner tube of the torch and into the plasma. The intermediate tube carries the intermediate (sometimes referred to as the auxiliary) gas. The intermediate gas flow helps to lift the plasma off the inner and intermediate tubes to prevent their melting and the deposition of carbon and salts on the inner tube. The outer tube carries the outer (sometimes referred to as the plasma or coolant) gas, which is used to form and sustain the toroidal plasma. The tangential flow of the coolant gas through the torch constricts the plasma and prevents the ICP from expanding to fill the outer tube, keeping the torch from melting.

An RF induction coil, also called the load coil, surrounds the torch and produces an oscillating magnetic field, which in turn sets up an oscillating current in the ions and electrons produced from the argon. The impedance-matching unit serves to efficiently couple the RF energy from the generator to the load coil. The unit can be of either the active or the passive type. An active matching unit adjusts the impedance of the RF power by means of a capacitive network, whereas the passive type adjusts the impedance directly through the generator circuitry. Within the load coil of the RF generator, the energy transfer between the coil and the argon creates a self-sustaining plasma. Collisions of the ions and electrons liberated from the argon ionize and excite the analyte atoms in the high-temperature plasma. The plasma operates at temperatures of 6,000–10,000 K, so most covalent bonds and analyte-to-analyte interactions are eliminated.

6. INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

The ICP can use either an optical or a mass spectral detection system. In the former case, ICP-OES, analyte detection is achieved at an emission wavelength of the analyte in question. Because of differences in technology, a wide variety of ICP-OES systems are available, each with different capabilities as well as different advantages and disadvantages. Simultaneous-detection systems are capable of analyzing multiple elements at the same time, thereby shortening analysis time and improving background detection and correction. Sequential systems move from one wavelength to the next (sometimes referred to as slewing) to perform analyses, and often provide a larger number of analytical lines from which to choose.

Modern instruments typically use array detectors as detection devices. Array detectors, including charge-coupled devices and charge-injection devices, have detectors assembled on a chip, making it possible to combine the advantages of both simultaneous and sequential systems. These types of detection devices are used in the most powerful spectrometers, providing rapid analysis and a wide selection of analytical lines. Some instruments may use photomultiplier tubes (PMT's) for detection. PMT's are best-suited for simultaneous analyses; however, the use of PMT's is quickly waning, and array detectors are more commonly found.

The ICP can be viewed in either axial or radial (also called lateral) mode. The torch is usually positioned horizontally in axially viewed plasmas and is viewed end on, whereas it is positioned vertically in radially viewed plasmas and is viewed from the side. Axial viewing of the plasma can provide higher signal-to-noise ratios (better detection limits and precision); however, it also incurs greater matrix and spectral interferences. Axial plasmas normally require the use of a shear gas, which effectively removes the coldest part of the plasma to help reduce self-absorption. Methods validated on an instrument with a radial configuration may not be completely transferable to an instrument with an axial configuration, and vice versa.

Additionally, dual-view instrument systems are available, making it possible for the analyst to take advantage of either torch configuration. The selection of the optimal torch configuration will depend on the sample matrix, the analyte in question, the analytical wavelength(s) used, the cost of instrumentation, the required sensitivity, and the type of instrumentation available in a given laboratory.

Regardless of torch configuration or detector technology, ICP-OES is a technique that provides a qualitative and/or quantitative measurement of the optical emission from excited atoms or ions at specific wavelengths. These measurements are then used to determine the analyte concentration in a given sample. Upon excitation, an atom or atomic ion emits an array of different frequencies of light that are characteristic of the distinct energy transition allowed for that element. The intensity of the light is generally proportional to the analyte concentration. It is necessary to correct for the background emission from the plasma. Sample concentration measurements are usually determined from a working curve of known standards over the concentration range of interest. It is, however, possible to perform a single-point calibration under certain circumstances, such as limit tests, if the method has been validated for sufficient specificity, sensitivity, linearity, accuracy, precision, ruggedness, and robustness.

Because there are distinct transitions between atomic energy levels, and because the atoms in the ICP are rather dilute, emission lines have narrow bandwidths. However, because the emission spectra from the ICP contain many lines, and because "wings" of these lines overlap to produce a nearly continuous background on top of the continuum that arises from the recombination of argon ions with electrons, a high-resolution spectrometer is required in ICP-OES.

The decision regarding which spectral line to measure should include an evaluation of potential spectral interferences. All atoms in a sample are excited simultaneously; however, the presence of multiple elements in some samples can lead to spectral overlap. Spectral interference can also be caused by background emission from the sample or plasma. Modern ICPs usually have background correction available, and a number of background correction techniques can be applied. Simple background correction typically involves measuring the background emission intensity at a baseline level away from the main peak and subtracting this value from the total signal being measured. Mathematical modeling to subtract the interfering signal as a

background correction can also be performed with certain types of ICP–OES spectrometers. One simple way to avoid spectral interferences is to select an analytical line that is free of interferences, if possible.

The selection of the analytical spectral line is critical to the success of the ICP–OES analysis, regardless of torch configuration or detector type. Though some wavelengths are preferred, the final choice must be made in the context of the sample matrix, the type of instrument being used or the sensitivity required. Analysts might choose to start with the wavelengths recommended by the manufacturer of their particular instrument and select alternative wavelengths based on manufacturer recommendations or published wavelength tables (2, 3, 4, 5, 6). Ultimately, the selection of analytical wavelengths should be demonstrated experimentally to provide sufficient specificity, sensitivity, linearity, accuracy, and precision of the analysis at hand.

Forward power, gas flow rates, viewing height, and torch position can all be optimized to provide the best signal. However, it must also be kept in mind that these same variables can influence matrix and spectral interferences.

The analysis of the Group I elements can pose some challenges. When atomic ions are formed from elements in this group, they assume a noble gas electron configuration, with correspondingly high excitation energy. Because the first excited state of these ions is extremely high, few are excited, so emission intensity is correspondingly low. This situation can be improved by reducing the fractional ionization that can in turn be achieved by using lower forward power settings in combination with adjusted viewing height or nebulizer gas flow, or by adding an ionization suppression agent to the samples and standards.

When organic solvents are used, it is often necessary to use a higher forward power setting, higher intermediate and outer gas flows, and a lower nebulizer gas flow than would be employed for aqueous solutions, as well as a reduction in the nebulizer gas flow. It could be necessary to reduce the peristaltic pump speed, and alter the selection of the spray chamber. When using organic solvents, it could be necessary to bleed small amounts of oxygen into the torch to prevent carbon buildup in the torch.

6.1 Calibration

The wavelength accuracy for ICP–OES detection must comply with the manufacturer's applicable operating procedures. Because of the inherent differences among the types of instruments available, there is no general system suitability procedure that can be employed. Calibration routines recommended by the instrument manufacturer for a given ICP–OES instrument should be followed.

6.2 Standardization

The instrument must be standardized for quantitation at time of use. Because ICP–OES is a technique generally considered to be linear over a range of 6–8 orders of magnitude, it is not always necessary to continually demonstrate linearity by the use of a standard curve composed of multiple standards. Once a method has been developed and is in routine use, it is possible to calibrate with a blank and a single standard. One-point standardizations are suitable for conducting limit tests, as well as other analyses, on production materials and final products if the method has been rigorously validated for sufficient specificity, sensitivity, linearity, accuracy, precision, ruggedness, and robustness. The use of single-point standardization is also acceptable for qualitative ICP–OES analyses, where the purpose of the experiment is to confirm the presence or absence of elements without the requirement of an accurate quantitation.

An appropriate blank solution and standards that bracket the expected range of the sample concentrations should be assayed and the detector response plotted as a function of analyte concentration, as in the case where the concentration of a known component is being determined within a specified tolerance. The plot of the analyte concentration against the known concentrations of components is usually performed automatically by the instrument.

It is not always possible to employ a bracketing standard when an analysis is performed at or near the detection limit. This lack of a bracketing standard is acceptable for analyses conducted to demonstrate the absence or removal of elements below a specified limit. The number and concentrations of standard solutions used should be based on the purpose of the quantitation, the analyte in question, the desired sensitivity, and the sample matrix. Regression analysis of the standard plot should be employed to evaluate the linearity of detector response, and individual monographs may establish other criteria.

6.3 Procedure

It is important to follow the procedure for the instrument parameters, as directed in the individual monograph. The specification of definitive parameters in a monograph does not preclude the use of other suitable operating conditions, and adjustments of operating conditions may be necessary. Because of differences in manufacturers' equipment configurations, the manufacturer's suggested default conditions could be used and modified as needed. Alternative conditions must be supported by suitable validation data, and the conditions in the monograph will take precedence for official purposes. Data collected from a single sample introduction are treated as a single result. This result might be the average of data collected from replicate sequential readings from a single solution introduction of the appropriate standard or sample solution. Sample concentrations are calculated versus the working curve generated by plotting the detector response versus the concentration of the analyte in the standard solutions, which is often calculation directly by the instrument.

7. INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP–MS)

When using the ICP–MS, analytes are detected directly at their atomic masses. Because these masses must be charged to be detected in ICP–MS, the method relies on the ability of the plasma source to both atomize and ionize sample constituents. As is the case with ICP–OES, a wide variety of ICP–MS instrumentation systems are available.

The systems most commonly in use are quadrupole-based systems. Additionally, high-resolution sector field instruments and time of flight-based instruments are available, as are multiple quadrupole systems. Regardless of instrument design or configuration, ICP–MS provides both a qualitative and a quantitative measurement of the components of the sample.

Ions are generated from the analyte atoms by the plasma, and ions are then extracted from the atmospheric-pressure plasma through a sampling cone into a lower-pressure zone, ordinarily held at a pressure near 1 Torr. In this extraction process, the sampled plasma gases, including the analyte species, form a supersonic beam, which dictates many of the properties of the resulting analyte ions. A skimmer cone, located behind the sampling cone, "skims" the supersonic beam of ions as they emerge from the sampling cone. Behind the skimmer cone is a lower-pressure zone, often held in milli Torr ranges. Lastly, the skimmed ions pass a third-stage orifice to enter a zone held near micro Torr pressures, where they encounter ion optics and are passed into the mass spectrometer. The pressure differences aid in moving the ions along and into the mass spectrometer, which separates the ions according to their mass-to-charge (m/z) ratios. The ICP-MS has a mass range up to 240 atomic mass units.

Depending on the equipment configuration, analyte adducts can form with diluents, with argon, or with their decomposition products. Also formed are oxides and multiply-charged analyte ions, which can increase the complexity of the resulting mass spectra. Interferences can be minimized by appropriate optimization of operational parameters, including gas flows (central, intermediate, and outer gas flow rates), sample-solution flow, RF power, extraction-lens voltage, etc., or by the use of collision or reaction cells, or cool plasma operation, if available on a given instrument. Unless a laboratory is generating or examining isotopes that do not naturally occur, a list of naturally occurring isotopes will provide the analyst with acceptable isotopes for analytical purposes. Isotopic patterns also serve as an aid to element identification and confirmation. Additionally, tables of commonly found interferences and polyatomic isobaric interferences and correction factors can be used, and are often pre-programmed into an instrument.

ICP-MS generally offers considerably better detection limits than ICP-OES, largely because of the extremely low background noise that it generates. This ability is a major advantage of ICP-MS for determination of very low analyte concentrations or when elimination of matrix interferences is required. In the latter case, some interferences can be avoided simply by additional dilution of the sample solution. In some applications, analytes can be detected below the parts per trillion (ppt) level using ICP-MS. As a general rule, ICP-MS as a technique requires that samples contain significantly less total dissolved solids than does ICP-OES.

The selection of the analytical mass to use is critical to the success of the ICP-MS analysis, regardless of instrument design. Though some masses are often considered to be the primary ones, because of their high natural abundance, an alternative mass for a given element is often used to avoid spectral overlaps (isobaric interferences). Selection of an analytical mass must always be considered in the context of the sample matrix, the type of instrument being used, and the concentrations to be measured. Analysts could choose to start with masses recommended by the manufacturer of their particular instrument and select alternate masses based on manufacturer's recommendations or published tables of naturally occurring isotopes (7).

Optimization of the ICP-MS method is also highly dependent on the plasma parameters and means of sample introduction. Forward power, gas flow rates, and torch position may all be optimized to provide the best signal. When organic solvents are used, it is often necessary to use a higher forward power setting and a lower nebulizer flow rate than would be used for aqueous solutions. Additionally, when organic solvents are used, it could be necessary to introduce small amounts of oxygen into the central or intermediate gas to prevent carbon buildup in the torch or on the sampler cone orifice. The use of a platinum-tipped sampling or skimmer cone may also be required in order to reduce cone degradation with some organic solvents.

7.1 Calibration

The mass spectral accuracy for ICP-MS detection must be in accordance with the applicable operating procedures. Because of the inherent differences between the types of instruments available, there is no general system suitability procedure that can be employed. Analysts should refer to the tests recommended by the instrument manufacturer for a given ICP-MS instrument.

7.2 Standardization

The instrument must be standardized for quantification at the time of use. Because the response (signal vs. concentration) of ICP-MS is generally considered to be linear over a range of 6–8 orders of magnitude, it is not always necessary to continually demonstrate linearity by the use of a working curve. Once a method has been developed and is in routine use, it is common practice to calibrate with a blank and a single standard. One-point standardizations are suitable for conducting limit tests on production materials and final products, provided that the method has been rigorously validated for sufficient specificity, sensitivity, linearity, accuracy, precision, ruggedness, and robustness. An appropriate blank solution and standards that bracket the expected range of the sample concentrations should be assayed and the detector response plotted as a function of analyte concentration, which are normally performed by the instrument. The number and concentration of standard solutions used should be based on the analyte in question, the expected concentrations, and the sample matrix, and should be left to the discretion of the analyst.

The method of standard additions should be employed in situations where matrix interferences are expected or suspected. This method involves adding a known concentration of the analyte element to the sample solution at no fewer than two concentration levels. The instrument response is plotted against the concentration of the added analyte element, and a linear regression line is drawn through the data points. The absolute value of the x-intercept multiplied by any dilution factor is the concentration of the analyte in the sample. In many instances, the instrument will perform this calculation automatically after being programmed to use the method of standard additions.

7.3 Procedure

Follow the procedure for the detection mode and instrument parameters for ICP-MS, as directed in the individual monograph. The specification of definitive parameters in a monograph does not preclude the use of other suitable operating conditions, and adjustments of operating conditions may be necessary. Alternative conditions must be supported by suitable validation data, and the conditions in the monograph will take precedence for official purposes. Because of differences in manufacturers' equipment configurations, the analyst could begin with the manufacturer's suggested default conditions and

modify them as needed. Data collected from a single sample introduction are treated as a single result. Data collected from replicate sequential readings from a single introduction of the appropriate standard or sample solutions are averaged as a single result. Sample concentrations are calculated versus the working curve generated by plotting the detector response versus the concentration of the analyte in the standard solutions. With modern instruments, this calculation is often performed by the instrument.

8. GLOSSARY

Auxiliary gas: See *Intermediate (or auxiliary) gas*.

Axial viewing: A configuration of the plasma for AES in which the plasma is directed toward the spectrometer optical path, also called "end-on viewing."

Central (or nebulizer) gas: One of three argon gas flows in an ICP torch. The central gas is used to help create a fine mist of the sample solution when solution nebulization is employed. This fine mist is then directed through the central tube of the torch and into the plasma.

Collision cell: A design feature of some ICP-MS instruments. Collision cells are used to reduce interferences from argon species or polyatomic ions and facilitate the analysis of elements that might be affected by those interferences.

Cool plasma: Plasma conditions used for ICP-MS that result in a plasma that is cooler than that normally used for an analysis. This condition is achieved by using a lower forward power setting and higher central-gas flow rate, and is used to help reduce isotopic interferences caused by argon and some polyatomic ions.

Coolant gas: See *Outer (or coolant or plasma) gas*.

Forward power: The number of watts used to ignite and sustain the plasma during an analysis. Forward power requirements may vary, depending on sample matrix and analyte.

Intermediate (or auxiliary) gas: Gas used to "lift" the plasma off the surface of the torch, thereby preventing melting of the intermediate tube and the formation of carbon and salt deposits on the inner tube.

Internal standard: An element added to or present in the same concentration in blanks, standards, and samples to act as an intensity reference for the analysis. An internal standard should be used for ICP-AES work and must always be used for quantitative ICP-MS analyses.

Lateral viewing: See *Radial viewing*.

m: The ion mass of interest.

Multiply-charged ions: Atoms that, when subjected to the high-ionization temperature of the ICP, can form doubly or triply charged ions (X^{++} , X^{+++} , etc.). When detected by MS, the apparent mass of these ions will be $\frac{1}{2}$ or $\frac{1}{3}$ that of the atomic mass.

Nebulizer: Used to form a consistent sample aerosol that mixes with the argon gas, which is subsequently sent into the ICP.

Outer (or coolant or plasma) gas: The main gas supply for the plasma.

Plasma gas: See *Outer (or coolant or plasma) gas*.

Radial viewing: A configuration of the plasma for AES in which the plasma is viewed orthogonal to the spectrometer optic path. Also called "side-on viewing." See also *Lateral viewing*.

Reaction cell: Similar to *Collision cell*, but operating on a different principle. Designed to reduce or eliminate spectral interferences. Used in ICP-MS.

Sampling cone: A metal cone (usually nickel-, aluminum-, or platinum-tipped) with a small opening, through which ionized sample material flows after leaving the plasma in ICP-MS.

Sequential: A type of detector configuration for AES or MS in which discrete emission lines or isotopic peaks are observed by scanning or hopping across the spectral range by means of a monochromator or scanning mass spectrometer.

Simultaneous: A type of detector configuration for AES or MS in which all selected emission lines or isotopic peaks are observed at the same time by using a polychromator or simultaneous mass spectrometer, offering increased analysis speed for analyses of multi-element samples.

Skimmer cone: A metal cone through which ionized sample flows after leaving the sampling cone and before entering the high-vacuum region of an ICP-MS.

Standard additions: A method used to determine the actual analyte concentration in a sample when viscosity or matrix effects might cause erroneous results.

Torch: A series of three concentric tubes, usually manufactured from quartz, in which the ICP is formed.

9. REFERENCES

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