

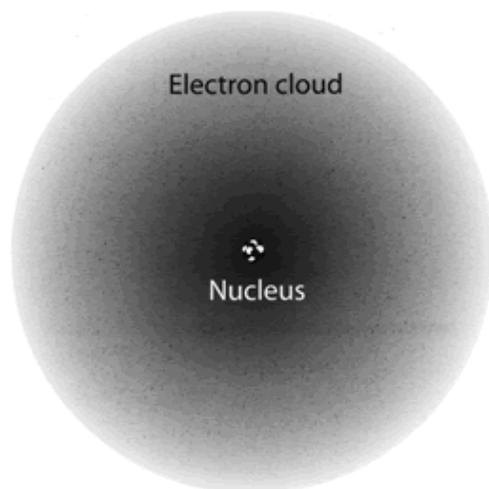
Plasma Chemistry

Analytical Background:

Elements, Atoms & Isotopes

Every object on earth is made of atoms, from the sand in the Sahara to the snow in the Antarctic. An atom is the smallest unit of **ordinary matter** that retains all the properties of a **chemical element**. Although atoms are very small, they are composed of three basic components: **protons, neutrons** and electrons. The neutrons and protons are located in the nucleus of an atom, while the electrons form an electromagnetic cloud around the nucleus.

A model of an atom illustrating the nucleus and the electron cloud.

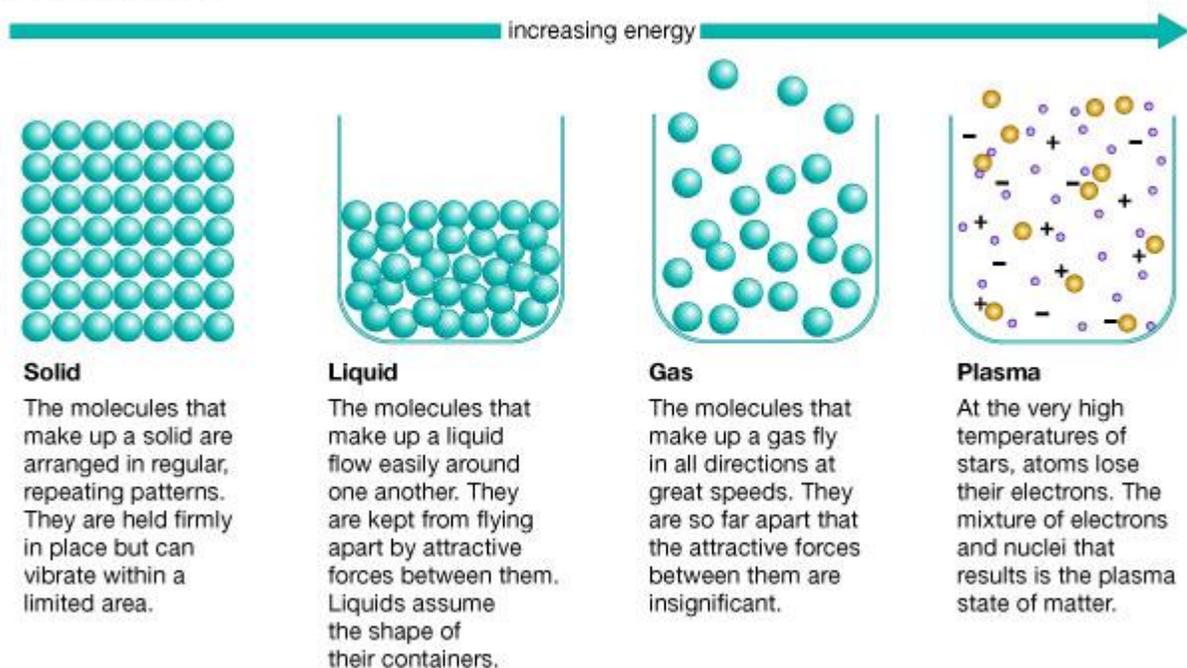


An element is a group of atoms that share the same number of protons in their nucleus. Atoms of the same element can have different number of electrons. These atoms are **ions** of the element, retaining all the properties of the element, but having different electromagnetic charges. Similarly, atoms of the same element can

have a different number of neutrons in their nuclei. These atoms are referred to as **isotopes**, retaining all the properties of the element, but have different masses.

The difference in atomic mass between isotope species of an element is extremely useful for many areas of research. It is what enables scientists to identify and measure radiocarbon for biobased content testing or radiocarbon dating and it is also what is used by inductively coupled plasma (ICP) spectrometers to quantitatively and qualitatively determine the element present in a given sample.

Physical states



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Plasma

A major component of ICP spectrometry is the plasma. Plasma is considered a fourth state of **matter**, distinct from **liquid**, **solid** and **gas** phases. The four states of matter are distinguished by the properties of **volume** and **shape**. Matter in the solid state, has both a fixed volume and shape. Atoms in a solid are tightly ordered and arranged so that they maintain that shape and volume. Matter in the liquid state has a fixed volume but no fixed

shape, and will take the shape of any container it is placed into. Atoms in the liquid state are still close together and ordered, but they move freely and thus cannot maintain a fixed shape. Matter in the gaseous state has neither a fixed volume nor shape and adapts both to fit its container. Atoms in the gaseous state are not close together, ordered or fixed in place. Matter in the plasma state also has no fixed volume or shape, adapting to fit its container. What differentiates plasma from gas is that atoms in the plasma state have been split into ions and free electrons, both of which are able to move independently and freely.

States of matter are not fixed: the introduction of energy, usually as heat, facilitates the transition of matter between these states. To create plasma a substantial amount of energy is introduced, which is sufficient for electrons to detach from atomic nuclei producing a cloud of positively charged ions (cations) and electrons.

Mass Spectrometry

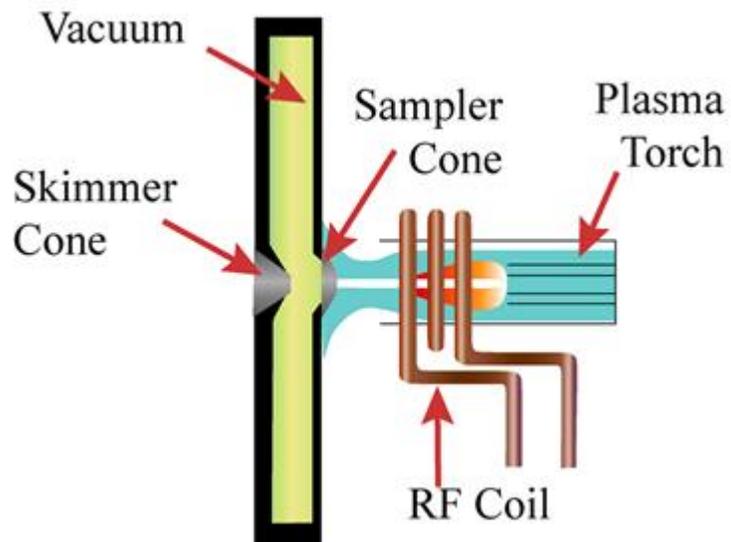
ICP-MS is an analytical technique that enables multi-element analysis of **trace** elements. This method is optimal for sub-part-per-million analysis, with ideal elemental concentrations ranging in the hundreds part-per-billion (ppb) to parts-per-trillion range. The major components of an ICP-MS are: the sample introduction system and ionization source, an interface for transferring analytes from a high-temperature and atmospheric pressure system to a low-temperature vacuum, a mass filter (called a mass analyzer), and ultimately a detector.

Elements Measureable by ICP-MS

Hydrogen 1 H 1.0079																	Helium 2 He 4.0026															
Lithium 3 Li 6.941		Beryllium 4 Be 9.0122																		Boron 5 B 10.811	Carbon 6 C 12.011	Nitrogen 7 N 14.007	Oxygen 8 O 15.999	Fluorine 9 F 18.998	Neon 10 Ne 20.180							
Sodium 11 Na 22.990		Magnesium 12 Mg 24.305																		Aluminum 13 Al 26.982	Silicon 14 Si 28.086	Phosphorus 15 P 30.974	Sulfur 16 S 32.065	Chlorine 17 Cl 35.453	Argon 18 Ar 39.948							
Potassium 19 K 39.098	Calcium 20 Ca 40.078	Scandium 21 Sc 44.956	Titanium 22 Ti 47.867	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.845	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546	Zinc 30 Zn 65.38	Gallium 31 Ga 69.723	Germanium 32 Ge 72.63	Arsenic 33 As 74.922	Selenium 34 Se 78.96	Bromine 35 Br 79.904	Krypton 36 Kr 83.798															
Rubidium 37 Rb 85.468	Strontium 38 Sr 87.62	Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906	Molybdenum 42 Mo 95.94	Technetium 43 Tc 98	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 102.91	Palladium 46 Pd 106.42	Silver 47 Ag 107.87	Cadmium 48 Cd 112.41	Indium 49 In 114.82	Tin 50 Sn 118.71	Antimony 51 Sb 121.76	Tellurium 52 Te 127.60	Iodine 53 I 126.90	Xenon 54 Xe 131.29															
Cesium 55 Cs 132.91	Barium 56 Ba 137.33																	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.95	Tungsten 74 W 183.85	Rhenium 75 Re 186.21	Osmium 76 Os 190.23	Iridium 77 Ir 192.22	Platinum 78 Pt 195.08	Gold 79 Au 196.97	Mercury 80 Hg 200.59	Thallium 81 Tl 204.38	Lead 82 Pb 207.2	Bismuth 83 Bi 208.98	Polonium 84 Po (209)	Astatine 85 At (210)	Radon 86 Rn (222)
Francium 87 Fr (223)	Radium 88 Ra (226)	Rutherfordium 104 Rf (261)	Dubnium 105 Db (262)	Seaborgium 106 Sg (266)	Bohrium 107 Bh (264)	Hassium 108 Hs (277)	Meitnerium 109 Mt (288)	Darmstadtium 110 Ds (271)	Roentgenium 111 Rg (272)																							
Lanthanum 57 La 138.905	Cerium 58 Ce 140.12	Praseodymium 59 Pr 140.908	Neodymium 60 Nd 144.24	Promethium 61 Pm (145)	Samarium 62 Sm 150.36	Europium 63 Eu 151.96	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.925	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.93	Erbium 68 Er 167.26	Thulium 69 Tm 168.934	Ytterbium 70 Yb 173.054	Lutetium 71 Lu 174.967																		
Actinium 89 Ac (227)	Thorium 90 Th 232.038	Protactinium 91 Pa 231.04	Uranium 92 U 238.03	Neptunium 93 Np (237)	Plutonium 94 Pu (244)	Americium 95 Am (243)	Curium 96 Cm (247)	Berkelium 97 Bk (247)	Californium 98 Cf (251)	Einsteinium 99 Es (252)	Fermium 100 Fm (257)	Mendelevium 101 Md (288)	Nobelium 102 No (286)	Lawrencium 103 Lr (260)																		

The basic principle of ICP-MS involves the introduction of a sample into inductively coupled plasma—where temperatures range from 6,000 to 10,000 K. When the sample is introduced into the plasma, its molecules are broken down into gaseous atoms that are then ionized into, predominately, cations (ions with a positive charge). The ions are then transferred into an interface region designed to put the ions under vacuum. The interface region in an ICP-MS consists of two (or more) metal cone-shaped disks with a single hole in the center of each. The small diameter of the hole allows for sampling of ions concentrated at the center of the plasma—herein lies one of the limitations of ICP-MS as the small diameter of the cones inherently requires samples to be free of particulates, which may not be completely atomized and further ionized, that can clog the cones. Once the ions have traversed the interface, electrostatic lenses then focus the ions from the plasma source into a small beam. Because most ions formed in the plasma have a positive charge, and therefore will be repelled by an electrostatic field of the same polarity (i.e. positive charge), the electrostatic lenses (small, positively charged

tubes through which the ions traverse) collimate the ions into a narrow, focused beam. The ion beam is focused into the entrance of the mass spectrometer where the ions are then separated by their mass-to-charge ratio (m/z). The majority of ions produced in the plasma have a single-charge (i.e. +1), so the m/z is effectively equivalent to the mass of each ion. In other words, a copper-63 (^{63}Cu) atom will be ionized to $^{63}\text{Cu}^+$; the mass (63) to charge (1) ratio is then 63. Ions with a m/z of 63 will be separated from other ions with a differing mass in the mass analyzer. Once separated, the ions with a defined mass are directed to a detector where they are counted.



ICP-MS Fundamentals

- *Quadrupole Mass Analyzer*

There are several different mass analyzer techniques, each with a distinct method for separating ions. One of the most popular techniques in ICP-MS technology is the quadrupole mass spectrometer. The quadrupole mass analyzer works by filtering out everything except ions with a specific m/z . This separation is achieved by employing electrostatic forces of attraction and repulsion as well as inertia. The electrostatic forces at play in the quadrupole are explained by Coulomb's law, which tells us that particles with a different charge attract and particles with the same charge repel. The

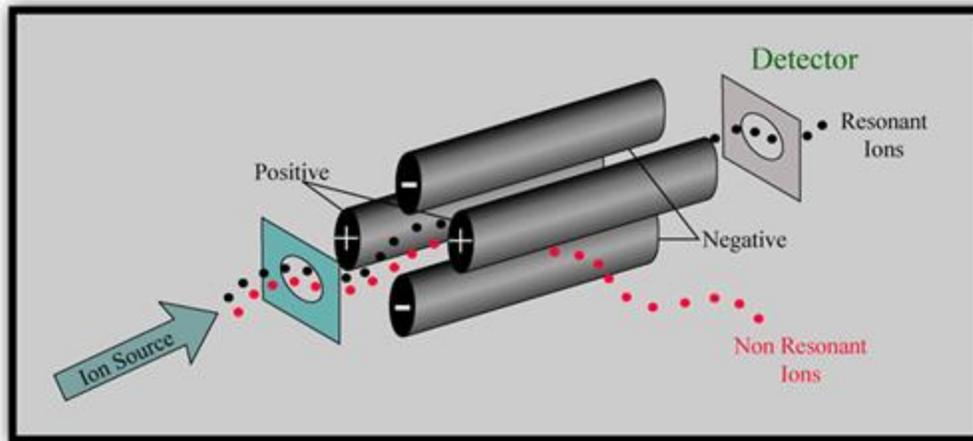
tendencies of the particles to react to the attractive or repulsive forces, however, are also governed by inertia. The laws of inertia dictate that the more massive an object, the greater its tendency to resist changes in its state of motion. Within the quadrupole region, these forces are used in combination to transfer only those ions with the desired m/z .

In the quadrupole region, 4 rods are arranged in a diamond-like orientation with a space in the middle. Each rod is paired with the rod to its diametric opposite. One rod-pair has positive direct current (DC) and an alternating current (AC) potential applied to the rods, while the other rod-pair has a negative DC as well as an AC potential applied. The magnitude of the AC and DC voltages controls the trajectory of ions as they travel through the quadrupoles, allowing only ions with a specific mass/ z through to the detector at any given time.

To better understand the theory behind the quadrupole, envision the rods aligned along a Cartesian coordinate, where one rod-pair is aligned along the x-axis and the other is aligned along the y-axis. Imagine the rods paired in the x-direction have a positive DC and AC voltage applied, while the rods paired in the y-direction have a negative DC and an AC voltage applied.

Consider for the moment only AC voltage is applied to the rods. When an alternating current is applied to the rods, the voltage switches polarity over time. The AC potential applied to both sets of rods is offset by 180° such that the voltage on one pair is positive and negative on the other pair. As a result, ions oscillate in a corkscrew pattern as they are attracted and repelled by the rod-pairs. Because lighter ions are more readily affected by electrostatic variations, these ions will readily respond to changes in alternating current. When the alternating current on a rod-pair is positive, the rods will repel these smaller cations. When the AC is negative, the rods will attract the smaller cations. A balance must be maintained between the attractive

and repulsive forces to promote further oscillation of the ions. If either force is too strong, the cations will make contact with the rods, at which time it will be neutralized and disposed from the system. The factors governing whether the particle will oscillate or collide with a rod include the magnitude of the voltage, the AC frequency, and the mass and charge of the ions. At a given AC voltage, then, all cations with a mass less than the mass of interest will have an unstable trajectory, eventually colliding with a rod, and will not be detected. Meanwhile, the more massive cations, with greater inertia, will resist the forces resulting from the AC potential.



Now consider that each rod-pair has a DC potential of opposite sign. Suppose the rod-pair in the x-direction has a positive DC potential and the rod-pair in the y-direction has a negative DC potential. The positive DC potential will focus the cations towards the center of the rods, but the negative DC potential will attract the more massive ions, and any cation with a mass greater than the mass of interest will collide with the negative DC rod pair.

With these factors (AC and DC potentials) combined, the quadrupole selectively allows cations with a single m/z through the mass filter. The magnitudes of the AC and DC potentials are adjusted to allow ions to be detected sequentially. At this point, the ions are converted to an electronic signal at the detector and measured.

- *Mass Interferences*

Because quadrupoles have low resolution and filter ions based on m/z , distinct species with similar m/z will not be distinguishable. This leads to interferences during analysis. There are two major types of interferences in ICP-MS: isobaric and polyatomic.

Isobaric interferences occur when two isotopes have the same mass. For instance, indium (In) and tin (Sn) both have isotopes of mass 115. ^{115}Sn has a mass of 114.9033 and ^{115}In has a mass of 114.9038. Discrimination of these two isotopes requires a mass analyzer with a resolving power greater than 200,000. Since quadrupole ICP-MS generally has a resolving power of 1,000 the quadrupole ICP-MS is incapable of distinguishing these two species. In such a case, both isotopes would be measured at the same time and the concentration of either would not be ascertainable if both were appreciably present in the sample.

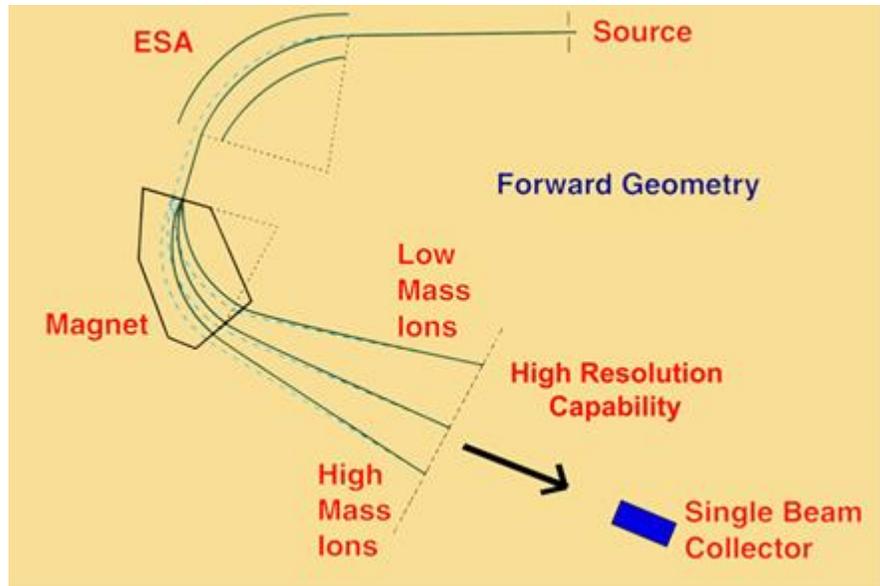
The second major type of interference is polyatomic interference. Polyatomic interferences occur when molecules recombine with argon or other matrix components. When these polyatomic (molecular) species have the same mass as an isotope of the element of interest, the two species may be indistinguishable. For example, argon and oxygen recombine in the plasma to form a molecular species with a mass similar to that of the dominant iron isotope. In this example, ^{40}Ar and ^{16}O recombine to form $^{40}\text{Ar}^{16}\text{O}^+$ with a m/z of 56, which is similar to $^{56}\text{Fe}^+$.

These mass interferences can be overcome through planning and foresight. Techniques such as the use of cool plasma, reaction or collision cells, or chromatographic separation can be employed to correct or eliminate many of the interferences. Additionally, selecting an alternate isotope, if possible, can help avoid these interferences.

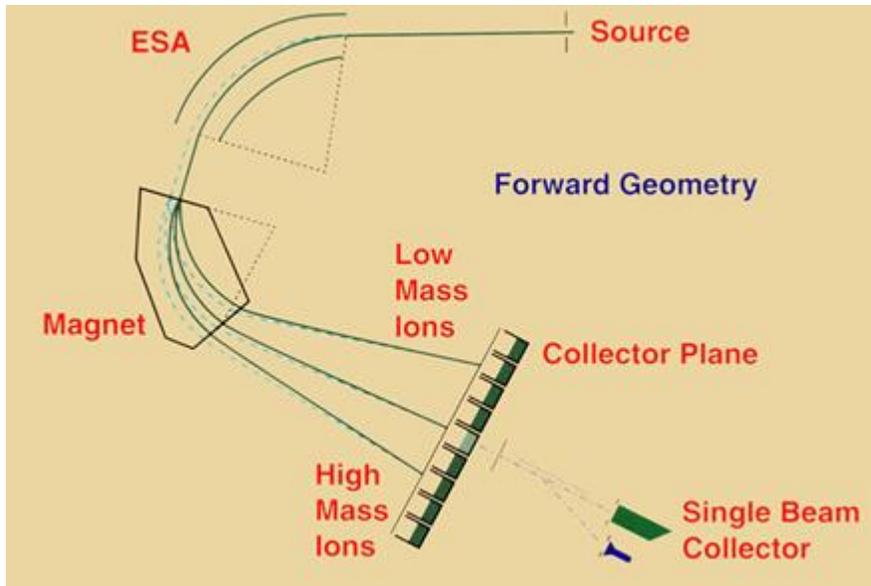
- *The Magnetic Sector and MC-ICP-MS Theory*

Unlike the quadrupole, wherein the ions oscillate through the quadrupole and are removed by collision with one of the quadrupoles, in the magnetic sector analyzer ions are accelerated through a flight tube and the path traveled is influenced by a magnetic field. Although the geometry of the flight tube can vary between different types of magnetic sectors, all magnetic sectors deflect the ions in an angular path. The specific angle the ions acquire is dependent on two forces, centripetal and magnetic field, experienced by the ions. These forces are proportional to mass, and as a result, all ions with a specific m/z will have a unique path radius determined by the magnetic field and voltage difference applied. In other words, the deflection of ions through the flight tube is dependent on kinetic energy.

When a constant magnetic field and voltage differential is applied to the flight tube, ions too heavy to be deflected at the corresponding angle of the flight tube will collide with one side of the flight tube. On the other end of the spectrum, light ions experience a greater degree of curvature. When the degree of curvature experienced by lighter ions is greater than the angle of the flight tube, these ions will also collide into the walls of the flight tube. Within the flight tube, ions that have the ideal curvature (as dictated by the magnetic field), relative to the flight tube, will travel unobstructed and experience unique trajectories based on their m/z . Each of these trajectories, or ion beams, can then be focused into a series of detectors. This is the basis of both single and multiple collector -ICP-MS.



In MC-ICP-MS, the ion beams of various isotopes are focused into one of numerous detectors (i.e. multiple collectors)--oftentimes Faraday Cup style detectors. As a result, within certain limitations (e.g. similar mass), various isotopes can be measured simultaneously. This differs from the quadrupole mass analyzer and other single-collector mass spectrometers, which only measure different isotopic species sequentially. The inherent lower precision of sequential analysis limits the applicability of single-collectors. The simultaneous detection and measurement of isotopes, on the other hand, offers an efficient and precise method for measuring and calculating isotopic ratios.



Optical Emission Spectrometry

Atomic Emission Spectroscopy (AES) is also known as Optical Emission Spectroscopy (OES) and is a technique wherein elements in a mixture are identified and quantified by observing the interactions of atoms with electromagnetic radiation (e.g. light). In OES a sample is ionized, at which time electrons are excited. Upon relaxation of the excited species, energy is emitted in the form of light. A detector measures the wavelength of this light.

OES is based on two important principles guiding the behavior of atoms. The first principle is that atoms can only exist in discrete states, also known as levels, which are characterized by distinct amounts of energy (this is referred to as quantized energy). One way to think about this is by comparing it to living in a two-story building. Your home may be on the ground floor or it may be on the second floor, and you can live on either floor, but you cannot live in the space between. This is the same principle for atoms, and when the atom changes from one level to the next, it can either absorb or emit a photon (def.: a photon is a small packet of energy that can carry electromagnetic radiation) with energy that is equivalent to the

difference in energy between the two levels. The second principle is that the frequency, ν , or wavelength, λ , of the radiation emitted or absorbed as the atom transitions from one energy level to the next is defined by the equation:

$$E_f - E_i = \frac{hc}{\lambda}$$

where E represents the energy of the atom at its initial (i) and final (f) state, h and c are constants, and λ represents the wavelength of the photon released. In other words, the greater the amount energy released, the shorter the wavelength of the electromagnetic radiation.

Tying these two principles together, we can see that at low temperatures the atoms of a sample of matter are essentially at their most relaxed levels, known as ground state, but these atoms can be excited to a higher energy level with heat from a flame, a plasma, or an electric arc or spark. When the atom relaxes from the excited energy level to a lower energy level, energy is released in the form of electromagnetic radiation and the wavelength of that light is inversely related to the difference in energy.

In an OES, atoms are excited in the inductively couple plasma and upon relaxation, photons are emitted. The emitted electromagnetic radiation then passes through an optical spectrometer where each wavelength is separated in space (this is the same process by which a prism separates white light into the various, distinct wavelengths and produces rainbows). The wavelengths emitted are characteristic of the atoms present, much like fingerprints. In this way, OES is used qualitatively to identify the atoms present in a sample. The intensity of the radiation can also be quantified to infer the concentration of each element.

Elements Measureable by ICP-OES

hydrogen 1 H 1.0079																	helium 2 He 4.0026												
lithium 3 Li 6.941	beryllium 4 Be 9.0122													boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180										
sodium 11 Na 22.990	magnesium 12 Mg 24.305													aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948										
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798												
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cesium 55 Cs 132.91	barium 56 Ba 137.33													hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po (209)	astatine 85 At (210)	radon 86 Rn (222)	
francium 87 Fr (223)	radium 88 Ra (226)													rutherfordium 104 Rf (261)	dubnium 105 Db (262)	seaborgium 106 Sg (266)	bohrium 107 Bh (264)	hassium 108 Hs (277)	meitnerium 109 Mt (288)	darmstadtium 110 Ds (271)	roentgenium 111 Rg (272)								
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm (141)	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05	lutetium 71 Lu 174.97															
actinium 89 Ac (227)	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np (237)	plutonium 94 Pu (244)	americium 95 Am (243)	curium 96 Cm (247)	berkelium 97 Bk (247)	californium 98 Cf (251)	einsteinium 99 Es (252)	fermium 100 Fm (257)	mendelevium 101 Md (288)	nobelium 102 No (286)	lawrencium 103 Lr (260)															

ICP-OES Fundamentals

- *Plasma*

An argon plasma is utilized for ICP-OES. Here, the argon ions maintain temperatures as great as 10,000 K. The energy of the plasma is capable of atomization (the conversion of a sample into atoms) and excitation of the atoms. Upon excitation, an electron from each atom transitions from the ground state to a state of higher energy. An atom in the excited state is not stable and will decay back to a less excited state. As the atom decays back to a less excited state, energy is lost by the emission of a photon. The magnitude of the photon's energy is equivalent to the amount of energy initially required to excite the atom.

- *Obtaining Information*

Because every element has a unique and characteristic set of energy levels, the wavelengths produced by the atoms can be used for identification purposes. In OES, a sample is introduced into the

plasma where the sample is atomized and the atoms are excited. The emitted wavelengths are then analyzed with a detector for qualitative determination and the intensity of the wavelength is compared to that of standards of known concentration to determine the concentration of elements in the sample.

- *Instrumental Interferences*

Several types of interference occur in ICP-OES, and these can be broadly divided into non-spectral and spectral interferences. A major non-spectral interference in ICP-OES is due to easily ionizable elements, particularly group I and group II elements. In ICP-OES the goal is to provide sufficient energy to excite an electron. If more energy is supplied, however, the electron may be completely dislodged, resulting in a cation. As there is no emission of electromagnetic radiation during this process, each atom that is ionized is lost from detection. The net result is a decrease in the intensity of emission lines for that element, resulting in an observed concentration lower than actual.

Another major type of non-spectral interference occurs when there is a shift in the equilibrium of the system. This equilibrium exists between the ground state atoms, excited atoms, and ions. The overabundance of an element may shift this equilibrium, affecting the intensity of emission. For example, an overabundance of potassium (K) may cause an increase in the apparent concentration of sodium (Na). The large number of K atoms may collide with the Na atoms and upon collision the Na atoms will be excited and emit light. This excitation augments the excitation of the atoms in the plasma and results in an increased signal-intensity for Na when compared to a standard solution with a considerably lower concentration of K atoms.

The two types of spectral interferences that occur in ICP-OES are background emission interferences and the overlap of lines emitted from other elements. Background emission results from the emission

of excited molecules in the plasma. Molecules that are formed during the rearrangement of atoms in the plasma can absorb energy and emit light. However, unlike the discrete bands emitted from atoms, broad bands are produced when molecules emit light. The broad bands may then overlap with lines of interest. The best method for dealing with this interference is to analyze a reagent blank and subtract the signal of interferences from the sample.

The other major source of spectral interference occurs when another element in the sample matrix emits light at a similar wavelength as the element of interest. In this case, identification and quantification are not possible. One work-around is to select a different emission wavelength, one that lacks interference.