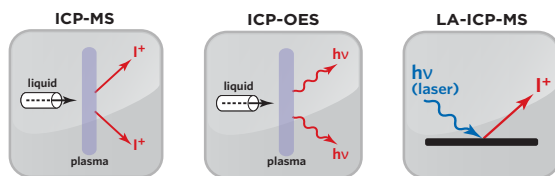


Inductively Coupled Plasma (ICP) Services

Eurofins EAG Laboratories (EAG) offers comprehensive compositional analysis services, including “full scan” measurements of up to 69 elements, through its suite of Inductively Coupled Plasma (ICP) Analytical Techniques.

Inductively Coupled Plasma (ICP) comprises a family of widely used instrumental analytical chemistry techniques spanning both atomic spectroscopy and mass spectrometry. EAG offers Optical Emission Spectroscopy (ICP-OES), Mass Spectrometry (ICP-MS), and Laser Ablation-Mass Spectrometry (LA-ICP-MS). This diverse array of techniques is unified by its common method of sample ionization: the Inductively Coupled Plasma.

The ICP is created by passing an inert gas, typically argon, through a radiofrequency (RF) coil that generates a high frequency alternating magnetic field. The interaction of the gas with the RF field induces the formation of a high-temperature plasma consisting of ionized atoms. The plasma electron temperature of an argon ICP ranges from ~6,000 K to ~10,000 K, comparable to the surface of the sun at the low end of that range. When a sample is introduced to the plasma as liquid droplets from a nebulizer or solid nanoparticles generated by laser ablation, its atoms collide with the electrons and charged particles of the argon plasma and eject electrons, becoming ionized themselves. The steps that follow sample ionization diverge between Optical Emission Spectroscopy and Mass Spectrometry.



ICP Suite Strengths

- Able to analyze a diverse range of matrices (organic and inorganic) for up to 69 elements.

- Bulk analysis by solution OES or MS overcomes sample heterogeneity challenges, while microanalysis by LA-ICP-MS yields spatially resolved data for solid samples.
- Provides sample statistics (e.g., mean concentration and relative standard deviation) through replicate analyses with minimal additional time needed.
- Fully quantitative concentrations calculable from NIST-traceable reference materials.
- Used across industry, academia, and government with ASTM, EPA, and other standard test methods well-developed and widely accepted.

ICP Suite Limitations

- Samples not readily digestible in mineral acid cannot be measured by solution ICP-OES or MS; LA-ICP-MS or a non-ICP technique is required.
- Labor-intensive mechanical and chemical preparation of digested samples can lead to extended turnaround time for results.
- Reagents used for digestion and dilution can introduce interferences and/or contamination, requiring careful monitoring and mitigation.
- Hard ionization limits analytes to elements and not molecular species.

ICP-MS

In solution ICP-MS, and LA-ICP-MS, the positively charged particles of the ionized sample are separated into the different elements being

measured according to their mass to charge ratio (m/z). The sample intensities are compared with the intensities measured in calibration reference materials with known concentrations of each element of interest, thus permitting the calculation of fully quantitative concentrations for the sample. The linear dynamic range (LDR) for a modern ICP-MS can be up to 10 orders of magnitude for a single isotope, facilitating the measurement of a vast breadth of concentrations by a single technique. The high sensitivity and wide LDR of ICP-MS are complemented by the lower sensitivity and great robustness of ICP-OES, with which it can be paired to routinely measure elements occurring at weight percent concentrations.

ICP-MS Ideal Uses

- Quantitative analysis of minor ($\mu\text{g/g}$ in solids; mg/L in liquids) and trace (ng/g in solids; ng/L - $\mu\text{g/L}$ in liquids) elements.
- Purity certification, cleaning validation, and contamination identification for a broad range of materials and processes of industrial significance.
- Supply chain support, ranging from raw materials/feedstock qualification, traceability (provenience) analysis, and production control to failure analysis.
- Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS) testing for lead, mercury, chromium, and cadmium.
- Heavy metal testing in pharmaceuticals, medical devices, and personal care and hygiene products.
- Development of reference materials for quality control and calibration: metals, alloys, ceramics, rocks and minerals, polymers, and more.

ICP-MS Strengths

- Many elements can be measured in one analysis due to the steady-state signal of solution ICP-MS.

- High sensitivity yields low detection limits.
- Dynamic Reaction Cell (DRC), Kinetic Energy Discrimination (KED), and Triple Quadrupole (TQ, or MS/MS) technology mitigate most isobaric, polyatomic, and double-charged interferences.

ICP-MS Limitations

- Destructive and potentially time-consuming sample preparation.
- Limited to $< 0.2\%$ dissolved solids in dilute sample.
- Not measurable: Hydrogen and helium (below mass range of detector), carbon, nitrogen, oxygen, and argon (present at high background levels), fluorine and neon (not ionizable in argon plasma), sulfur, chlorine, bromine, and iodine (doable but other techniques preferred).

Case Study: Mitigation of argon interference for trace analysis of potassium in nickel superalloys



Potassium is the 20th most abundant element in the solar system and the 17th most abundant by weight on Earth, so it should be no surprise that it is a commonly requested analyte by the clients of EAG. At weight % concentrations, potassium is readily measurable by ICP-OES. However, at trace levels measurement of potassium requires the more sensitive ICP-MS technique. A ubiquitous obstacle to using ICP-MS for potassium analysis, regardless of the sample matrix, derives from the very nature of ICP – it is almost always an argon plasma. The most abundant isotope of argon occurs at mass 40. The most abundant, and typically measured, isotope

of potassium occurs at mass 39. Unlike an isobaric interference, in which the measured isotope of an analyte overlaps with an isotope of a different element (e.g., $^{40}\text{Ar}^+$ interfering $^{40}\text{Ca}^+$), the ^{40}Ar interference on potassium occurs through two different phenomena: peak tailing and polyatomic interference.

Peak tailing interference occurs when attempting to measure a lower intensity peak that occurs at an m/z ratio adjacent to a very high intensity peak. Commercial quadrupole ICP-MS instruments are not able to fully resolve, or distinguish between, the two adjacent peaks. Signal from the high intensity $^{40}\text{Ar}^+$ peak can “spill over” onto the adjacent lower intensity $^{39}\text{K}^+$ peak, leading to erroneously high measurements for that analyte. Additionally, potassium at mass 40 can be interfered by the polyatomic argide $^{38}\text{Ar}^1\text{H}^+$. ICP-MS instrument manufacturers have typically recommended using “cold plasma” conditions for trace measurement of potassium with an argon plasma. In cold plasma conditions, the temperature of the plasma is reduced such that it is sufficient to ionize the analytes of interest (especially low ionization potential elements like potassium), while minimizing formation of interfering argides like $^{38}\text{Ar}^1\text{H}^+$ and $^{40}\text{Ar}^+$. However, this is only an effective approach for high-purity samples like deionized water.

EAG scientists need to routinely measure potassium at low concentrations in matrices like nickel superalloys that require a high temperature plasma. To achieve reliable measurement of trace potassium in concentrated, high matrix samples that induce plasma loading effects, ammonia gas (NH_3) is introduced to the reaction cell of the ICP-MS. Ammonia is effective at both mitigating $^{38}\text{Ar}^1\text{H}^+$ interference and suppressing the otherwise intense signal of $^{40}\text{Ar}^+$ from the ICP that can result in peak tailing. This occurs primarily through ammonia inducing a charge exchange reaction with $^{40}\text{Ar}^+$ (yielding a charge-free ^{40}Ar atom and an ammonia ion) and a proton exchange reaction with $^{38}\text{Ar}^1\text{H}^+$ (yielding a charge-free ^{38}Ar atom and an ammonium ion). These mechanisms reduce the intensity of the signal from the argon beam, mitigating peak tailing, and remove the polyatomic interference on mass 39.

An alternative to ammonia Dynamic Reaction Cell mode is helium Kinetic Energy Discrimination mode. While also modestly effective at mitigating argide interferences on potassium, EAG scientists have found that the background equivalent concentration of potassium measured in ammonia DRC mode is up to 80% lower than when measured in KED mode and the calibration curve can exhibit improved linearity. Through its commitment to experimentation and innovation, EAG can offer trace analysis of potassium in nickel superalloys with reporting limits as low as 5 ppm.

ICP-OES

ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) measures the light emitted at element-specific characteristic wavelengths from excited and ionized atoms. A detector measures the intensity of the emitted light, which is then used to evaluate the concentration of that particular element in the sample by comparison with calibration reference materials.

ICP-OES Ideal Uses

- Precise and accurate bulk quantitative analysis of major (i.e., matrix) and minor trace elements in solids, liquids, and suspensions.
- Development of reference materials for quality control and calibration: metals, alloys, ceramics, rocks and minerals, polymers, and more.
- Supply chain support, ranging from raw materials/feedstock qualification, traceability (provenience) analysis, and production control to failure analysis.
- Determination of major elements in metal alloys to test compliance with alloy grade specifications.

ICP-OES Strengths

- A hydrofluoric acid-resistant sample introduction system enables determination of low levels of silicon and boron in HF-containing digestions.

- The analysis can be automated, enhancing accuracy, precision, and sample throughput.
- The combination of ICP-OES and ICP-MS is very powerful for determining a wide range of elemental concentrations, from major components to trace level components with high accuracy and precision.

ICP-OES Limitations

- The sample to be analyzed must be digested or dissolved prior to analysis.
- Emission spectra can be complex, and spectral interferences are possible if the wavelength of the element of interest is very close to or overlaps that of another element.
- Matrix-related effects can create challenges in quantification.
- Carbon, nitrogen, hydrogen, oxygen, and halogens cannot be determined using this technique.

Case Study: Overcoming titanium argide interference to measure strontium in barium titanate



Barium titanate (BaTiO_3) is a ferroelectric, pyroelectric, and piezoelectric ceramic used in capacitors, nonlinear optics, and electromechanical transducers. Although it occurs rarely in nature as the mineral barioferroperovskite, for industrial applications barium titanate is produced by hydrothermal synthesis or a solid-state reaction of barium carbonate and titanium dioxide. A client submitted samples of synthetic barium titanate for “full survey” elemental analysis including all majors and trace level impurities. It should be noted here

that determination of strontium in titanium based samples by mass spectrometric techniques, when argon is used as a discharge gas, is challenging because of very strong polyatomic interferences caused by titanium argides. Strontium is typically measured using $^{88}\text{Sr}^+$ but $^{48}\text{Ti}^{40}\text{Ar}^+$ interferes with that mass. The minor isotope ^{86}Sr is an alternative, but its lower abundance coupled with interferences from $^{46}\text{Ti}^{40}\text{Ar}^+$ and $^{48}\text{Ti}^{38}\text{Ar}^+$ do not make it a favorable option relative to ^{88}Sr .

To resolve these issues, solid sampling mass spectrometry analysis was complemented with solution ICP-OES. Barium titanate was subjected to microwave assisted digestion using hydrofluoric and nitric acids as reagents. Boric acid was also added to the samples prior to digestion to ensure that any excess hydrofluoric acid did not cause barium and strontium to precipitate out of solution after the digestion was complete. ICP-OES is known to be a highly effective technique for measuring weight % (i.e., matrix) elements in a digested sample, such as barium and titanium in this case. However, it can also measure much lower concentrations, sometimes overlapping with the trace element range of ICP-MS depending on the analyte and the matrix.

To demonstrate the effectiveness of this digestion and instrumental technique for measuring trace strontium in barium titanate, a spike recovery study was conducted. A known amount of strontium from a single element, NIST-traceable, reference solution was spiked into replicate preparations of the actual client samples prior to digestion. The subsequent measurement of the digested samples by ICP-OES yielded strontium spike recovery in the range of 95% - 105%, illustrating the viability of this method. For the barium titanate samples without spikes (i.e., for reporting values to the client), ICP-OES measured strontium between 6 ppm and 9000 ppm. Because ICP-OES measurements are based on the emission of electromagnetic radiation at wavelengths characteristic of the elements present in a sample, this technique is unaffected by the titanium argide interferences that can bias strontium measurement even by high resolution mass spectrometry.

LA-ICP-MS

In LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry), the sample is analyzed by ablating a solid sample with a pulsed laser beam. This creates a plume of ions and atoms which condense into aerosolized nanoparticles that are transported by a gas stream into the core of the inductively coupled argon plasma. The plasma in ICP-MS is used to generate ions that are then introduced to the mass analyzer, the same as in solution ICP-MS. The constituents of an unknown sample can then be identified and measured in comparison to a calibration reference material.

For laser ablation, any type of solid sample can be ablated for analysis; there are few sample-size restrictions and typically no chemical preparation. Chemical analysis using laser ablation requires a smaller amount of sample (micrograms) than that required for solution ICP-MS (milligrams). Depending on the analytical measurement system, very small amounts of sample may be sufficient for this technique. In addition, a focused laser beam permits spatial characterization of heterogeneity in solid samples, with single micron resolution both in terms of lateral (x, y) and depth (z) dimensions.

LA-ICP-MS Ideal Uses

- Survey elemental analysis of solids.
- Traceability/provenience analysis.
- Elemental distribution analysis and mapping.
- Local inclusion and defect analysis.
- Depth specific multi-element chemical assay.

LA-ICP-MS Strengths

- Qualitative (uncalibrated), semi-quantitative, or fully quantitative data as needed.
- Spatially resolved microanalysis with laser spot sizes of 10-200 μm .
- Sample type not limited by electrical conductivity, vacuum stability, inorganic/organic composition, or optical transparency/opacity.

- Fast – no chemical preparation, clean – fewer opportunities for contamination, and green – no hazardous waste generated and minimal consumables used.
- Interferences caused by acid reagents and issues caused by the instability of some elements in dilute acid solution are avoided.

LA-ICP-MS Limitations

- Matrix-matched reference materials must be analyzed to obtain fully quantitative results.
- Internal standard element for data normalization cannot be added to most samples.
- Large and/or irregular samples may need mechanical preparation to fit in the sample cell.
- Requires samples stable at room temperature and free of liquids for most applications.
- Typically, the same analyte limitations as solution ICP-MS; may vary on a case-by-case basis.

Case Study: Measuring phosphorous and sulfur in lithium ore by LA-ICP-MS/MS



The lithium-ion battery life cycle is complex, beginning with lithium production from hard rock spodumene ore or lithium-rich brines and ending with the nascent battery recycling industry. The major element composition of raw ore and post-beneficiation concentrate destined for lithium carbonate and lithium hydroxide production facilities can be determined using techniques such as XRF, ICP-OES, ICP-MS, and LA-ICP-MS. Relative to raw ore, concentrates are enriched in the lithium-bearing mineral spodumene and depleted in the

unwanted gangue minerals. ICP-OES can provide empirically calibrated concentrations with NIST-traceability for most major and minor elements in these materials; however, in lithium ore concentrates phosphorous and sulfur can fall below the quantification limit of ICP-OES but are still important to measure.

ICP-MS is much more sensitive than ICP-OES but has a technique-specific challenge to overcome for measuring phosphorous and sulfur. The element phosphorous is monoisotopic, with an atomic mass of 31, and has a high ionization potential of 10.49 eV. A polyatomic interference on mass 31 caused by the molecule $^{14}\text{N}^{16}\text{O}^1\text{H}^+$, coupled with poor ion yield for ^{31}P , makes measurement with low detection limits difficult. Sulfur suffers from a similar problem. Although it has four isotopes to choose from for measurement, the most abundant isotope, ^{32}S , is strongly interfered by the dimer $^{16}\text{O}_2^+$. Sulfur also has a high ionization potential of 10.36 eV. To make trace-level measurement of these elements viable, EAG uses the latest tandem mass spectrometry (MS/MS) instrumentation coupled to a state-of-the-art 193 nm Excimer laser ablation system. Triple quadrupole ICP-MS adds additional collision/reaction and mass filtration options beyond the interference mitigation capabilities of single quadrupole ICP-MS. To measure ^{31}P and ^{32}S in lithium concentrate, the two elements are measured "off mass" following an oxidation reaction. Phosphorous is measured at mass 47 as $^{31}\text{P}^{16}\text{O}^+$ and sulfur is measured at mass 48 as $^{32}\text{S}^{16}\text{O}^+$. The element titanium occurs at masses 47 and 48 but any titanium present in the sample would have been filtered out by the first quadrupole prior to the oxidation reaction, leaving only mass-shifted phosphorous and sulfur remaining for measurement at low detection limits and with excellent calibration linearity.

Notably, all the Triple Quadrupole ICP-MS advantages described above are applicable to both solution ICP-MS on digested samples and solid sampling analysis by laser ablation. EAG recommends LA-ICP-MS for this application because lithium ore and ore concentrate samples

will only require milling to powder and pressing into a pellet for preparation. In contrast, solution ICP-OES and/or ICP-MS requires milling followed by acid digestion (or milling, sodium hydroxide fusion, and then digestion), leading to additional prep time, opportunity for contamination, and potentially new interferences caused by the digestion and dilution reagents. A lack of matrix-matched, certified reference materials is a limitation of LA-ICP-MS, but EAG has acquired a series of spodumene ore reference materials that permit fully quantitative LA-ICP-MS of lithium ores and concentrates in support of the battery supply chain.

ICP Services at EAG

EAG has been a trusted, long-standing partner with applications spanning fields as diverse as semiconductor manufacturing, green energy generation and climate change mitigation, implantable medical devices and wearable technology, aerospace and defense, and earth science, paleontology, and archaeology. Over the past three decades EAG has established a suite of ICP-based elemental analysis services that feature advanced instrumentation, a comprehensive reference material collection, highly educated staff capable of leveraging scientific expertise for problem solving, and a rigorous data security and IP confidentiality practice. The capabilities highlighted here feature both direct solid sampling and digestion/solution sampling techniques which provide full survey major, minor, and trace element analysis and purity certification for up to 69 measurable elements.