

Trace elemental analysis

Finding the right technique for seamless elemental analysis in your laboratory

Chemical elements constitute all the ordinary matter in the universe. Of the 118 elements that have been identified, 94 are found naturally on Earth, having either stable or unstable isotopes.

Knowing the compositions or concentrations of elements in each material is essential to ensure no hazards may originate from it, for example, that drinking water is free from toxic metals like lead, food supplies do not contain potentially harmful amounts of arsenic, or pharmaceutical products are free of mercury.

However, the elemental composition can also unveil other qualities about a material, such as geographic origin, product quality, or process operation. Laboratories performing elemental (or inorganic) analysis determine small amounts of chemical elements in a wide range of samples; these small amounts often span a wide concentration range (e.g., high mg·L⁻¹ or even % range in wastewater, soils or materials; µg·L⁻¹ and lower levels for contaminants in food; parts per trillion in semiconductor-grade chemicals).

Finding the right technique for elemental analysis depends strongly on the specific requirements that a laboratory may have. This guide is intended to provide an overview of the most used techniques, inductively coupled plasma-optical emission spectroscopy (ICP-OES) and -mass spectrometry (ICP-MS).

Inductively coupled plasma

Inductively coupled plasma (ICP) is an excitation and/or ionization source commonly used for atomic spectroscopy since the 1970s. The plasma itself can be best described as matter in gaseous form, which has been significantly ionized inside an oscillating radio frequency (RF) field, "coupled" using an induction coil to form inside a torch. The RF field causes the gaseous ions to oscillate with the field, resulting in extreme heat.

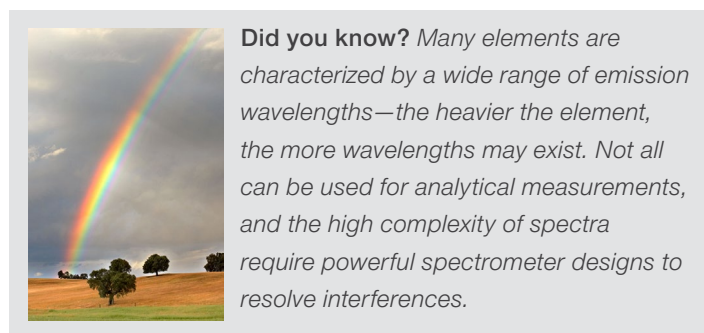


Did you know? Plasmas can achieve temperatures of up to 10,000 K and remain stable as long as energy is provided. Lightning is a good example of a plasma formed through an electrical discharge between sky and ground.

In the plasma, the fine mist generated from a sample in the sample inlet is completely vaporized and atomized, and individual atoms transition to excited states. In ICP-MS, temperatures are usually higher, so most elements easily make the transition from atoms to ions. A very useful characteristic of the argon plasma is that most of the formed ions are singly charged positive ions, so mass spectra are relatively simple to generate and interpret. Whereas interferences can be more easily recognized in optical emission spectra due to deformed peaks or increased baselines, they are more difficult to unveil in mass spectrometry.

Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

ICP-OES derives its analytical data from the emission spectra of elements following excitation in a high-temperature plasma. Like the emissions seen in fireworks, caused by the addition of strontium or barium, for example, to the mixture, all elements emit light of specific wavelengths upon excitation, both in the visible range of the spectrum and in the UV range.



Modern ICP-OES systems, like the Thermo Scientific™ iCAP™ PRO Series ICP-OES (Figure 1), combine fast and sensitive analysis with the well-known robustness that has made ICP-OES an established technique in environmental testing laboratories and in industrial applications. Wavelengths with different relative intensities can be utilized to calibrate across wider calibration ranges.

The sample (typically a liquid) is introduced into the plasma, and the optical system (spectrometer) is used to separate element-specific wavelengths of light and to focus the resolved light onto the detector as efficiently as possible.

In ICP-OES, the plasma can usually be observed in two ways. Radial observation monitors a cross-section of the plasma, whereas axial observation captures the entire length of the plasma along its axis. The radial plasma view is slightly less sensitive compared to the axial view; however, it is preferable when analyzing difficult samples such as organics or very high amounts of dissolved solid matrices. Axial observation is selected for best detection limits, as the quantity of light observed is increased. However, it is more susceptible to interferences.

For the analysis of elements with emission in the UV range, for example lead (220.353 nm), arsenic (193.759 nm), or phosphorous (177.495 nm), it is imperative that optical pathways leading into the spectrometer are free from air, otherwise absorption of light could occur. The iCAP PRO Series ICP-OES spectrometer can be purged with argon or nitrogen, and analysis can be started within 5 minutes after switching on the instrument from standby (model dependent).

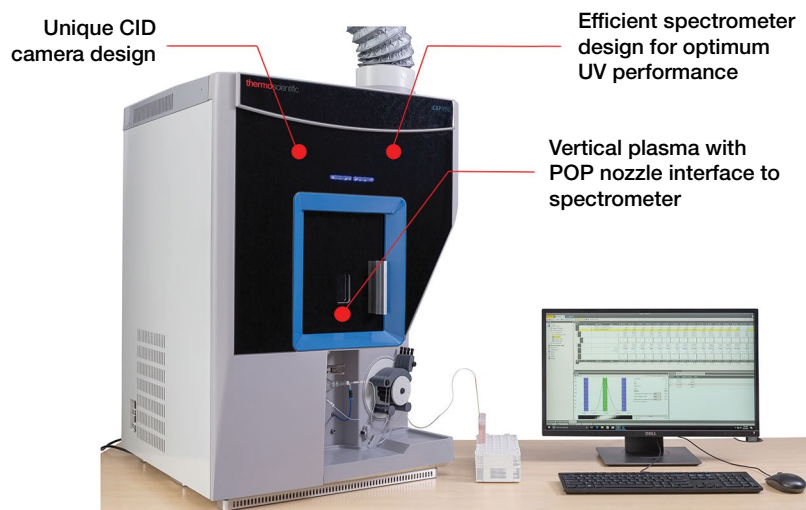



Figure 1. Overview of ICP-OES with the Thermo Scientific™ iCAP™ PRO XP ICP-OES

Most commonly, echelle-based optical designs are applied to produce the typical emission spectrum of an ICP-OES. These consist of an echelle grating, a prism, and a focusing mirror. This creates a high-resolution, two-dimensional spectrum, which is then transferred onto the detector to record intensity of a given wavelength. The iCAP PRO Series ICP-OES uses a unique solid-state detection system based on charge injection devices (CIDs) for detection.

CIDs allow for individual, random access, and pixel-by-pixel integration as readout electrodes are available for every pixel. The read-out process is non-destructive, and the CID has excellent anti-blooming capability. This allows for an optimum signal-to-noise ratio at each integration, enabling both intense and weak light emissions to be recorded simultaneously. The CID chip used in the iCAP PRO Series ICP-OES allows for full wavelength coverage between 167 nm to 852 nm (intelligent Full Range or iFR mode) and allows Full Frame image capture of all incoming signals on the chip, regardless of the method elements specified. This Full Frame is then stored and can be used for retrospective analysis. Figure 2 shows a Full Frame image of a soil sample.

As an alternative to CIDs, charge coupled devices (CCDs) are also used in ICP-OES. However, there are some disadvantages of this technology: a CCD sequentially transfers the charge from each pixel to a buffer and then to an output register. Pixels may be processed either by rows or segments. During the process of reading a CCD, the charge in a pixel is destroyed. This may lead to poor readings for low-intensity signals if more intense signals are recorded simultaneously, as they would determine the overall reading for a row or segment.



Did you know? *The CID chip used in the iCAP PRO Series ICP-OES offers more than 4 million individual pixels. Combined with the powerful optics design, this allows read out of the full spectrum (UV and visible range) in a single exposure—ideal for fast multi-elemental analysis!*

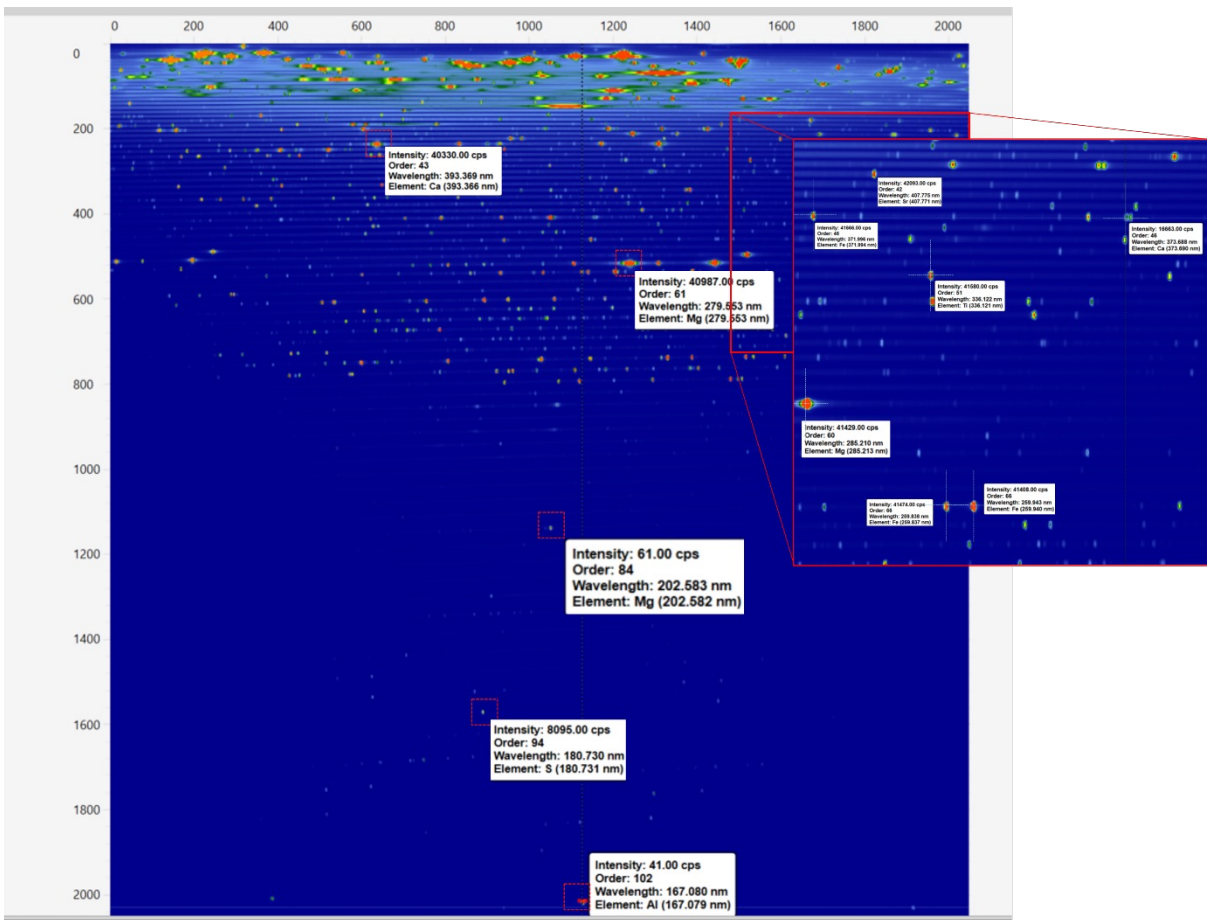


Figure 2. A Full Frame image of an unknown sample viewing the full spectrum between 167–852 nm simultaneously in a single exposure

Inductively coupled plasma mass spectrometry (ICP-MS)

The use of mass spectrometry in conjunction with an ICP as an ion source was commercialized almost immediately after its first publication. Since then, ICP-MS is the technique of choice for the lowest detection limits and has seen a growing number of applications, including speciation analysis, targeted and spatially resolved analysis, size- and number concentration of nanoparticles, and even microplastic characterization. State-of-the-art instruments like the Thermo Scientific™ iCAP™ MX Series ICP-MS allow sub ng·L⁻¹ detection limits to be achieved, while at the same time being able to cope with samples containing several thousand mg·L⁻¹ of matrix load.

An ICP-MS system comprises five basic parts: the sample introduction system, plasma, vacuum interface, collision/reaction cell, ion optics with mass analyzer (Figure 3).

A long-standing limitation in ICP-MS has been a restriction in the amount of total dissolved solids (TDS) that can be introduced to the system without affecting data quality. For previous generations of ICP-MS instruments, 0.2% (m/m) of solids has often been the upper limit. However, recent innovations, like the use of automatic dilution of the sample using argon gas prior to the plasma (easyAGD) in combination with intelligent control of the interface region, have enabled the extension of accessible samples.

Following ionization in the plasma, newly generated ions are transferred to the mass analyzer via a vacuum interface. This is a crucial part of ICP-MS and involves a pair of water-cooled cones with an intermediate vacuum stage between atmospheric pressure and the high vacuum of the mass spectrometer. The design and parameters applied here influence the system's sensitivity, its ability to be unaffected by matrix effects, and, last but not least, most of the typical interferences observed in ICP-MS originate from the interface region.

Ions generated in the plasma will be separated according to their mass to charge ratio (m/z) using a mass analyzer. Quadrupole instruments are typically used in routine labs since they are relatively easy to operate and maintain.

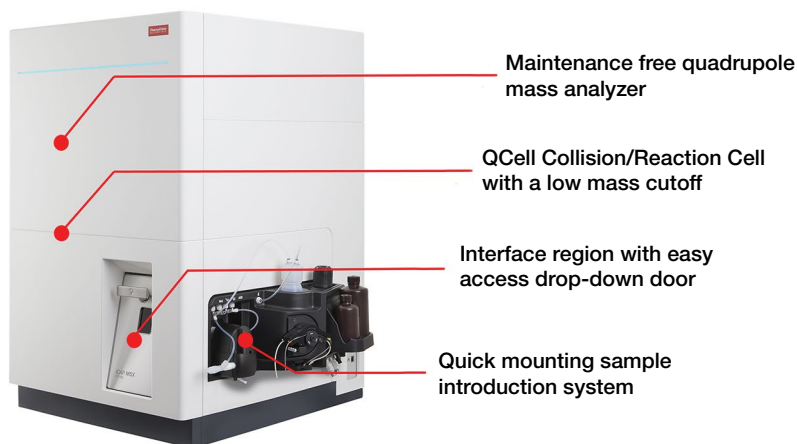


Figure 3. General setup of an ICP-MS system, here a Thermo Scientific™ iCAP™ MSX ICP-MS

Analyte signals may overlap with other isotopes of the same mass or polyatomic species, causing interference. Quadrupole-based mass analyzers cannot distinguish small mass differences, leading to biased signals. Reducing these interferences is crucial for accurate ICP-MS analysis and can be done during or after data acquisition.

Kinetic energy discrimination (KED), commonly used in single quadrupole ICP-MS, applies helium in the collision/reaction cell to remove interferences. Collisions of analyte ions with helium slow down all ions. The application of a positive bias potential at the exit of the cell ensures only ions with sufficient kinetic energy can enter the analyzing quadrupole so that polyatomic interferences are effectively removed. In combination with an automatic low mass cut off, removing lower mass precursor ions from the ion beam, and inhibiting formation of new interferences, nearly all sample matrices can be run in one mode only, meaning that analysis time per sample can be reduced.

Triple quadrupole ICP-MS systems, like the Thermo Scientific™ iCAP™ MTX ICP-MS, further enhance data quality by allowing reactive gases to selectively eliminate interferences. After an initial mass filtration before the collision/reaction cell, target ions are once again filtered from interferences in the analyzing quadrupole.



Did you know? The QCell collision/reaction cell used on the iCAP MX Series ICP-MS offers more effective interference removal due to its automatically adjusted low mass cut off—a secondary interference removal mechanism to further reduce backgrounds compared to KED alone.

Triple quadrupole ICP-MS systems can also remove isobaric interferences— isotopes from different elements having the same nominal mass. A good example is ^{204}Hg interfering on ^{204}Pb , commonly used to correct for naturally present Pb in dating applications.

Summary and conclusion

Both technologies share many powerful advantages for elemental analysis, but there are also differences. Figure 4 provides an overview.

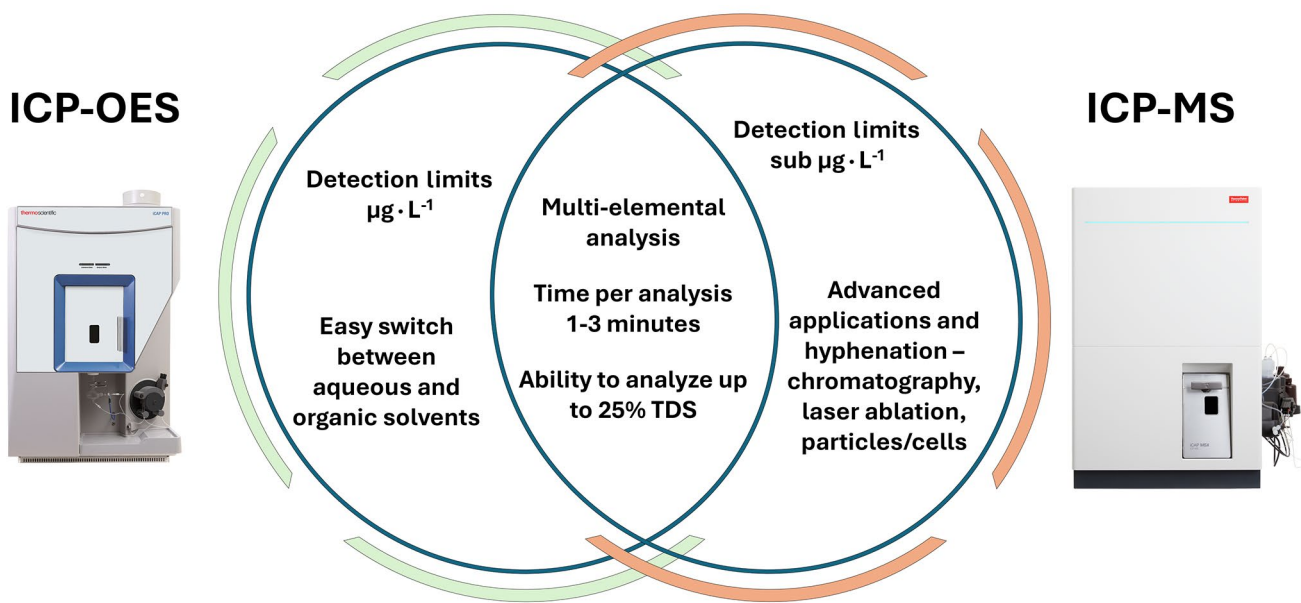
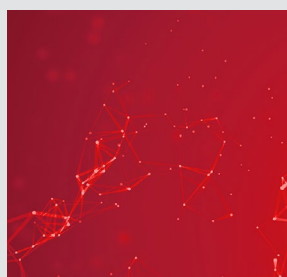


Figure 4. Overview of ICP-OES and ICP-MS technologies

For a laboratory seeking a reliable workhorse to tackle a wide range of possible sample types with detection limits in the $\mu\text{g}\cdot\text{L}^{-1}$ range, ICP-OES is the perfect choice. Because of its ability to perform multi-elemental analysis, it is becoming an attractive alternative for laboratories looking at increasing the number of analytes and lowering achievable detection limits from atomic absorption. ICP-OES can be flexibly set up to analyze aqueous samples with variable amounts of total dissolved solids as well as organic solvents like fuels or lubricants. Because of its unique optical and detection system design, the iCAP PRO Series ICP-OES can allow highly sensitive analysis but also offer sample turnover times well below 60 s for high throughput testing of soils or fertilizers.

ICP-MS is the right choice for laboratories seeking to future-proof their abilities in terms of detection limits. With modern ICP-MS systems, detection power can be combined with matrix robustness, so that samples that used to be predominantly run on GF-AAS and ICP-OES are within reach for ICP-MS. Recent innovations in the iCAP MX Series ICP-MS will allow laboratories to increase productivity by reducing the need for maintenance and improved overall laboratory workflows. Laboratories seeking flexibility and readiness for advanced applications, such as speciation analysis, laser ablation, or nanoparticle analysis, will find a powerful solution to fulfill their needs with the iCAP MTX ICP-MS.



Did you know? *The iCAP PRO Series ICP-OES leverages an innovative AI/ML toolset for background and drift correction, as well as semiquantitative analysis without the need for calibrating the instrument!*

The iCAP MX Series ICP-MS comes with easyAGD and Intelligent Matrix Handling (IMH), two features that help to greatly reduce the need for maintenance on your ICP-MS!

Using the Thermo Scientific™ Hawk™ Consumables and Maintenance Assistant, it has never been easier to perform the right maintenance at the right time for maximized system uptime!

Learn more at thermofisher.com/tea