



How To Choose the Right Atomic Spectroscopy Technique?

To meet your lab's needs both now and in the future



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How does atomic spectroscopy work?

Atomic spectroscopy

Atomic spectroscopy describes several analytical techniques used to determine the elemental composition of a sample by examining its electromagnetic spectrum or its mass spectrum.

Atomic spectrometry techniques can be divided into two broad categories; those techniques which identify an analyte element by its electromagnetic spectrum, and those techniques which identify an element by its mass spectrum. In the environmental laboratory, the most common electromagnetic spectrometric techniques are atomic absorption and atomic emission. X-ray-based techniques such as X-ray fluorescence (XRF) and X-ray diffraction (XRD) are technically electromagnetic spectrometric techniques as well.

Atomic absorption spectroscopy (AA)

Atomic absorption techniques rely on the fact that every element absorbs light of a characteristic wavelength, as an electron is elevated from the ground state to an excited state. The amount of light energy absorbed is proportional to the number of analyte atoms in the light path.



Figure 1. An electron is excited from the ground state to higher energy level by absorbing energy (light) at a specific wavelength. In atomic absorption spectroscopy, the wavelength of absorbed light is determined by the type of atom (which element it is) and the energy levels the electrons are moving to. How much light is absorbed is determined by the concentration of the element in the sample.

The technique is calibrated by introducing known concentrations of analyte atoms into the light path and plotting the absorption versus concentration curve. The source of light characteristic of each analyte element used is a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL). Typically each lamp is dedicated to the analysis of a single element, though sometimes a few elements can be combined into a single lamp. However, because of this limitation, atomic absorption is used for a small number of analyte elements per sample, even though it can measure 67 elements (not at the same time).

For atomic absorption to work, the analyte elements must be atomized (converted to the atomic state) using high temperature. Elements are atomized by introducing a liquid sample via a nebulizer into a high temperature acetylene flame in flame atomic absorption spectroscopy (FAAS). Elements can also be atomized by resistively heating a dried sample in a small diameter graphite cylinder – graphite furnace atomic absorption spectroscopy (GFAAS) (Figure 2).



Figure 2. Schematic diagram of flame or graphite furnace atomic absorption spectrometer system

FAAS is simple and inexpensive but has the limitation of transient and relatively diffuse atom density in the flame resulting in poor sensitivity when compared to other techniques. Typical detection limits are in the high ppb to ppm range. GFAAS has the advantage of programmable temperature control. This control allows the solvent and matrix (the components of the sample other than the elements you want to measure) to be separated from the analyte as a function of boiling point. Also, once the analyte is atomized in GFAAS, it is retained within the small volume of the graphite tube for extended measurement. As a result, detection limits using GFAAS are much lower than FAAS, typically in the sub ppb range. However, GFAAS can measure fewer analytes than FAAS, and is much slower.

Atomic emission spectroscopy

Because each element requires a dedicated HCL light source, AAS is limited in the number of elements which can be measured in a single sample. FAAS also has relatively poor sensitivity, and GFAAS is slow. Atomic emission techniques overcome these limitations and as a result have become widely used. Atomic emission techniques use the fact that once an atom of a specific element is excited (as in atomic absorption), it emits light in a characteristic pattern of wavelengths—an emission spectrum, as it returns to the ground state (see Figure 3).



Figure 3. As an electron returns from a higher energy level to its ground state, it emits light of specific wavelengths. The type of atom or ion (i.e., which element it is) and the energy levels the electron is moving between determines the wavelength of the emitted light.

While it is possible to perform atomic emission spectroscopy using a flame type instrument similar to a FAAS instrument, the flame is not an ideal excitation source for atomic emission. Typical temperatures for the acetylene flames used in AA are around 2,000 K for air-acetylene and 3,000 K for nitrous oxide-acetylene. Alternative sources for atomic emission include the microwave plasma (MP) and the inductively coupled argon plasma (ICP). Both sources are significantly hotter than a flame. The high temperatures give wider elemental coverage and higher sensitivity than FAAS.

Microwave plasma - atomic emission spectroscopy (MP-AES)

The nitrogen MP is considerably hotter than the acetylene flame, reaching temperatures nearing 5,000 K. At these temperatures, atomic emission is strong for most elements, leading to improved detection capability, and linear dynamic range over flame AA for most elements. As the MP runs on nitrogen, on-going operating costs can be significantly reduced compared to flame AA. The use of a nitrogen generator as the nitrogen source for the plasma offers further cost savings. Safety is improved compared to flame AA, as inert nitrogen is used rather than acetylene (a flammable gas). Using inert nitrogen also allows for unattended and overnight sample analysis, which is not recommended for FAAS.

Using a scanning monochromator and a solid-state detector, the MP-AES eliminates the need for individual lamps. The technique also offers faster sample to sample analysis times compared to FAAS, particularly as the number of elements (analytes) increases beyond a few elements. MP-AES can run samples up to around 3% total dissolved solids (TDS), using the appropriate sample introduction configuration.

As MP-AES is a relatively new technology, it may not be accepted for some regulated methods where a lab must use the technique specified for the analysis. If a new technique such as MP-AES can be shown to be equivalent to the established technique, other industries and regulatory bodies will accept this performance-based validation.

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

The argon ICP is hotter than the nitrogen MP and is much hotter than the acetylene flame. ICP can reach temperatures nearing 10,000 K, which allows complete atomization and significant ionization of the sample. Molecular interferences are reduced and the available atom and ion emissions for detection are maximized. Similar to the MP-AES, the ICP-OES uses an inert gas (argon) rather than flammable gas (such as acetylene for FAAS) allowing unattended and overnight sample analysis and improving safety. In addition to not requiring a lamp for each element, ICP-OES has numerous advantages over FAAS. ICP-OES is a true multi-element technique, capable of simultaneously, or near simultaneously measuring up to 74 elements at low ppb detection limits. As a result, ICP-OES – also called ICP-AES (ICP-atomic emission spectroscopy) – has become the workhorse for elemental determinations in many industries including environmental monitoring.

The high temperature of the argon plasma also means that the ICP-OES can tolerate complex matrices containing total dissolved solids (TDS) up to ~25%, depending on the specific configuration. Also, ICP-OES sensitivity falls between that of FAAS/MP-AES, and GFAAS (low ppb to percent range). ICP-OES can therefore measure all elements that were previously determined using FAAS. ICP-OES may also measure some of the elements that, because of lower required reporting limits, required the use of GFAAS.

However, ICP-OES cannot match GFAAS for detection limits in the sub-ppb and ppt range. For this reason, laboratories that use ICP-OES as their primary elemental analysis technique, will still require a more sensitive technique such as GFAAS or ICP-MS (see next section) for trace-level analysis of elements such as As, Se, Cd, Pb, etc. As sample numbers increase, GFAAS becomes the limiting factor for a laboratory's productivity. Labs with high sample numbers would therefore typically choose ICP-MS which provides multi-element analysis with low detection limits.



Figure 4. Simplified schematic diagram of ICP-OES spectrometer system

Atomic mass spectrometry

Atomic mass spectrometry (MS) – also known as inorganic mass spectrometry – refers to a technique where a mass spectrometer is used to separate and measure atoms or elements. Atomic mass spectrometry is different from "organic" MS techniques, such as LC/MS and GC/MS, which measure organic molecules or compounds.

To be able to measure the elemental composition of a sample by MS, the elements' atoms are converted to charged ions, so they can be focused and separated. The ion source can be a glow discharge (GD), a spark, a filament, an ion gun, a laser, or a plasma (as is used in ICP-MS). Some ion sources (GD, spark, laser) are used to measure solid samples, while a plasma can handle liquid samples such as aqueous solutions and acid digests.



Figure 5. The energy provided by the argon plasma removes an electron from an element atom, creating a singly charged positive ion.

The mass spectrometer used to separate the ions can be a magnetic sector, time-of-flight, ion trap, or quadrupole. A quadrupole provides a good balance between high transmission, resolution of less than 1 mass unit (u), and relatively low cost. Most ICP-MS systems use a quadrupole mass filter, either in a single quadrupole configuration or a tandem MS (MS/MS) such as a triple quadrupole (ICP-QQQ).

To provide high transmission and resolution, the mass spectrometer and detector are placed in a vacuum chamber. The ions being measured are formed inside the vacuum chamber (in the case of glow discharge, for example) or transferred into the high vacuum region from an external ion source such as a plasma. Once the different elemental ions have been separated in the mass spectrometer, they are counted, usually using an electron multiplier. The number of ions measured at each mass is compared to the signal for a known standard and converted to a concentration of each element in the material being analyzed.

Inductively coupled plasma - mass spectrometry (ICP-MS)

In the mid 1980's, the argon ICP was coupled to a quadrupole mass spectrometer resulting in the first commercial ICP-MS instruments. The development took advantage of the argon ICP as a highly efficient ion source, coupled to the quadrupole mass spectrometer for its high sensitivity, simple spectra, and fast scanning capability. The result is an instrument that combines the rapid, simultaneous, multi-element capability of ICP-OES and the sensitivity of GFAAS. In an ICP-MS instrument, the argon plasma operates as an ion source. The ions pass into the high vacuum region containing the quadrupole mass analyzer via a set of interface cones and ion lenses. Ions are separated by the quadrupole and transmitted to an electron multiplier for detection (Figure 6).



Figure 6. Simplified schematic diagram of the major components of a quadrupole ICP-MS system

While the argon plasma in an ICP-MS is similar to the plasma used in ICP-OES, the purpose is different. In ICP-MS, only ions are measured, so the plasma is optimized to ionize elemental atoms. The argon plasma is ideal for this, as argon has an ionization potential (IP)—the energy required to remove the first electron from the neutral atom—of 15.76 electron volts (eV). This IP is above the first IP of nearly every other element, but below their second IP, which means that the atoms of most elements are converted efficiently into singly charged positive ions.

Ionization efficiency – and therefore sensitivity – is better if there is a high temperature in the central channel of the plasma. A high plasma temperature is achieved using a high efficiency solid-state generator, wide internal diameter torch injector, and optimized operating conditions. The result is a "robust" plasma which delivers >95% ionization for most elements. Even poorly ionized elements such as Be, As, Se, Cd, and Hg are substantially ionized, so can be measured at trace (ppt) levels. Plasma robustness is a performance characteristic that is usually monitored by measuring the ratio of CeO⁺ to Ce⁺. CeO⁺ is a strongly bound molecular ion. An ICP-MS plasma is considered robust if it has sufficient energy to dissociate the CeO⁺ to give a CeO⁺/Ce⁺ ratio of around 1.5% or below. Operating the ICP-MS with a high plasma temperature provides better decomposition of the matrix, leading to less matrix deposition, better stability, and lower maintenance. A high plasma temperature provides more energy to dissociate other molecular ions, reducing the level of other ions that could form potential spectral interferences.

The ions are extracted from the plasma and passed into the high vacuum region for separation and detection. Photons and neutral species are rejected using an off-axis ion lens, and the remaining molecular (polyatomic) ions are removed using helium (He) cell gas with Kinetic Energy Discrimination (KED) in the collision/reaction cell (CRC). He KED mode filters out polyatomic ions, which are larger and therefore collide with the cell gas more often than the atomic ions they overlap. The polyatomic ions therefore lose more energy than the (smaller) analyte ions do, which allows the polyatomic ions to be rejected using a bias voltage at the cell exit. He KED mode has transformed the accuracy and reliability of ICP-MS analysis, particularly for multi-element analysis of the samples encountered in environmental and food laboratories.



Figure 7. This <u>short video</u> explains how helium mode works to remove ICP-MS polyatomic interferences.

The quadrupole mass spectrometer separates ions based on their massto-charge ratio (m/z). For singly charged ions, the m/z is equal to the mass, so ICP-MS measures the elements as a simple spectrum of characteristic atomic (isotopic) mass from ⁶Li to ²³⁸U. Many elements have several isotopes with different masses and for these elements the ICP-MS can also provide isotopic ratio and abundance information.

The quadrupole is a scanning mass spectrometer, but it operates at very high scan speed (more than 10 full mass scans per second). This high speed effectively measures all elements at the same time. After being separated in the mass filter, the ions are passed to an electron multiplier detector, which generates a pulse for each ion that reaches it. The pulses or "counts" are converted to concentrations by comparing the signals to a calibration created by measuring standards of known concentration.

With its wide elemental coverage (up to 70 elements can be measured routinely) and linear dynamic range from less than one ppt to thousands of ppm, ICP-MS overlaps the capabilities of both ICP-OES plus GFAAS instruments.

Continual advances in technology have addressed the fact that early ICP-MS instruments had poor tolerance of high total dissolved solids (TDS) levels. But most modern ICP MS instruments are still limited to a maximum TDS level of about 0.2% (2000 ppm), which is a factor of 100 lower than their OES cousins. To improve ICP-MS matrix tolerance and permit direct analysis of higher TDS samples, aerosol dilution is often used. Agilent ICP-MS instruments feature Ultra High Matrix Introduction (UHMI) systems. This technology uses automatically calibrated argon gas addition between the spray chamber and ICP torch to dilute the sample aerosol. The amount of aerosol reaching the plasma is reduced, allowing higher matrix levels to be analyzed without causing signal suppression, matrix deposition, and drift. UHMI eliminates the time and potential errors associated with conventional liquid sample dilution and avoids the cost and complexity of an autodilutor. Since the dilution occurs in the gas phase, no potential contamination from aqueous diluents can occur, and plasma robustness is improved by reducing the solvent (water) load on the plasma. UHMI is standard on Agilent ICP-MS systems, enabling the instruments to directly measure samples with matrix levels up to 25% TDS, close to the capability of ICP-OES.

Triple quadrupole inductively coupled plasma – mass spectrometry (ICP-QQQ)

The latest advance in atomic spectrometry is the development of an ICP-MS based on a tandem mass spectrometer – ICP-MS/MS – usually in a triple quadrupole (QQQ) configuration. The term "triple quadrupole mass spectrometer" refers to an instrument that uses two transmission quadrupole mass spectrometers in series. The two mass spectrometers are separated by a collision/reaction cell containing a multipole ion guide (see IUPAC definition Term 538).

The Agilent 8900 ICP-QQQ uses two hyperbolic profile quadrupole mass analyzers separated by an Octopole Reaction System (ORS) collision/ reaction cell. The ORS is similar to the cell used in Agilent single quadrupole ICP-MS systems, but the MS/MS configuration allows the cell to be used with highly reactive cell gases. Reaction gas modes with ICP-MS/MS can be a useful and effective approach to resolve problematic interferences that cannot be addressed using He mode with KED. The first quadrupole (Q1) of the ICP-QQQ is used to control the ions which enter the collision/reaction cell. Collisions or reactions in the cell eliminate interferences and then the analyzer quadrupole (Q2) is used to transmit the separated analyte ions to the detector. A simplified schematic diagram of the ICP-QQQ configuration is shown in Figure 8.



Figure 8. Simplified schematic diagram of triple quadrupole ICP-MS

Why ICP-QQQ?

The key difference between ICP-QQQ and single quadrupole ICP-MS is that ICP-QQQ enables MS/MS operation, where both Q1 and Q2 are operated as unit mass filters. Q1 selects the analyte ion mass that enters the cell, rejecting all other masses. This selection process ensures that the ions in the cell are consistent and independent of the sample composition, so reactive cell gas methods can be used reliably. This control of the reaction chemistry allows ICP-QQQ to resolve interference problems that cannot be addressed using conventional quadrupole ICP-MS. These include separating direct isobaric overlaps (such as 204 Hg on 204 Pb), resolving doubly charged ion overlaps (for example REE²⁺ overlaps on As and Se), and removing very intense background interferences (N₂ on 28 Si, O₂ on 32 S, etc.).

The 8900 ICP-QQQ also offers significantly higher sensitivity and much lower backgrounds than are typical for single quadrupole ICP-MS systems. Also, because it performs two mass filtering steps, the 8900 ICP-QQQ provides far superior abundance sensitivity (AS), which is a measure of the degree of overlap between adjacent peaks. MS/MS operation enables the 8900 to resolve trace peaks from major peaks at the adjacent mass (separating Mn-55 from Fe-56, for example).

How do I choose the right technique?

The atomic spectroscopy technique that is right for your lab, both now and in the future, depends on many factors. Which elements do you need to measure in which type of samples? What is your budget and how skilled are your lab technicians? We address below the main areas you need to consider when choosing a technique.

Side-by-side comparison

Let's start with a high-level comparison of the different atomic spectroscopy techniques (Table 1), relative to each other.

Table 1. A side-by-side comparison of the atomic spectroscopy techniques.

	FAAS View products	GFAAS View products	MP-AES View products	ICP-OES View products	ICP-MS View products	ICP-QQQ View products	
Relative Price	\$	\$\$	\$\$	\$\$\$	\$\$\$\$	\$\$\$\$\$	
Relative Cost per sample	\$\$	\$\$	\$	\$\$	\$\$\$	\$\$\$	
Relative Sensitivity	୦ୃ୦ୃ	dddd	QQ	QQQ	ଦ୍ୱିପ୍ପୁପ୍	ଦ୍ଦ୍ଦ୍ଦ୍ଦ୍ଦ୍ଦ୍	
Reviews	SelectScience	SelectScience	SelectScience	SelectScience	SelectScience	<u>SelectScience</u>	
Maximum samples per day ¹	100 to 200 (6 elements)	60 (four elements)	300 to 400 (10 elements)	2000 to 2500 (50+ elements)	1200 (50+ elements)	1200 (50+ elements)	
Dynamic range of measurement ²	100 ppb to 1000 ppm	10 ppt to 1000 ppb	100 ppb to 1000 ppm	10 ppb to 10,000 ppm	<1 ppt to 1000 ppm	<1 ppt to 1000 ppm	
Relative sample volume required	$\bigcirc \bigcirc \bigcirc \bigcirc$	\Diamond	$\bigcirc \bigcirc \bigcirc \bigcirc$	$\Diamond \Diamond$	$\Diamond \Diamond$	$\Diamond \Diamond$	
Relative tolerance of solids in sample	Ĩ		Ĩ		T T T		
Element measurement	Sequential	Sequential	Sequential	Simultaneous	Simultaneous	Simultaneous	
How many elements can be measured?	67	48	70	74	86	87	
Relative routine maintenance requirements	eJ	$e_{1}e_{1}$	EJ	L L L	くくくく	L L L L L	
Relative operator skill required	Ś	ଟିଟିଟି	Ś	ଟ୍ରତ	ବିବିବି	ୢୠୢୠୢୠୄୠ	
Can be left unattended	×	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	
Part 11/Annex 11 GMP compliance	(with optional software)	(with optional software)	×	(with optional software)	(with optional software)	(with optional software)	

	FAAS View products	GFAAS View products	MP-AES View products	ICP-OES View products	ICP-MS View products	ICP-QQQ View products
Specifications						
Relative operational power use	B	I I	I I	1 I	888	444
Dimensions (mm – width x depth x height)	790 x 580 x 5904 ³	1030 x 600 x 5904 ³	960 x 660 x 660	625 x 740 x 887	730 x 600 x 595	1060 x 600 x 595
Weight	75 kg	119 kg	73 kg	90 kg	100 kg	139 kg
Gas requirements	Compressed air and 99.0% pure acetylene and/or 99.5% pure N_2O (depending on elements measured), exhaust with 2.5 m ³ /min flow	99.99% Argon or 99.99% Nitrogen, exhaust with 3 m³/min flow	99.5% pure Nitrogen ⁴ , exhaust with 2.5 m³/min flow	99.95% pure Argon Optional: Nitrogen, Oxygen exhaust with 2.5 m³/min flow	99.99% ⁵ Argon, exhaust , with 5 to 7 m³/min flow	99.99% ⁵ Argon, exhaust with 5 to 7 m³/min flow
Warranty ⁶	12 months	12 months	12 months	12 months	12 months	12 months
Accessories						
Autosampler	Optional	Included	Optional	Optional	Optional	Optional
Water cooling system	Not required	Cool water supply required	Not required	Required, not included	Required, not included	Required, not included

1. The ICP-OES and ICP-MS instruments must be fitted with a switching valve to achieve these sample numbers

2. Dynamic range of the instrument only, with no sample introduction devices that enhance sensitivity

3. Height depends on the model selected

4. The MP-AES requires only nitrogen, which can be extracted from ambient air by a nitrogen generator. Alternatively, a nitrogen dewar can be used.

5. For applications where contamination must be controlled i.e. measuring impurities in semiconductor chemicals, argon purity of at least 99.999% may be required

6. Agilent has various extended warranty and support options

Which elements do you need to measure?

The first question to ask is which elements do you need to measure, as each technique can measure a different set of elements. The following color-coded periodic table is a guide to which technique can measure which elements. However, the concentrations that each technique can measure vary by element.



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Elements that are difficult to measure using atomic spectroscopy

There are some elements that either cannot be measured using any atomic spectroscopy technique, or that need a specialized approach. These elements include:

N, O, Kr, Xe

Nitrogen and oxygen are abundant in the ambient air of the laboratory environment, as well as being present in the typical aqueous solutions measured, which are usually stabilized with nitric acid (HNO₃). The resulting high background level makes it difficult to measure these elements at low levels without a specialized approach. ICP-MS offers the best detection limits for N and O but will require an alternative "dry" sample introduction approach, such as a gas sampling interface or GC-ICP-MS. Alternative techniques to atomic spectroscopy are recommended for routine analyses of these elements.

Kr and Xe are gases, so calibration is not straightforward. They are also poorly ionized and can be present at trace levels in the high purity argon used to support the ICP plasma. These elements can be measured using ICP-MS, if a suitable sample introduction system is used. For example, Xe (as a 100 ppm Xe gas standard in helium) is commonly used for tuning and as an internal standard for GC-ICP-MS applications.

F, Cl

These can be measured at relatively low levels using triple quadrupole ICP-MS, which can use reaction chemistry to convert the F or Cl ion to a measurable product ion. Cl can be measured using single quadrupole ICP-MS, but the background signal is high, so detection limits are poor.

H, He, Ne

These elements cannot be measured using any atomic spectroscopic technique. This is because these elements do not emit or absorb light in the ranges measurable by any of the optical techniques. ICP-MS does not offer a solution, as H and He are outside the mass range measured by ICP-MS, and Ne is not ionized in an argon plasma.

Ar

Argon is used as the source gas for the plasma for both ICP-OES and ICP-MS. This fact means that the background levels of Ar are very high, making it difficult to measure using those techniques.

Short lived elements

Elements such as At, Fr, Rn and those with atomic numbers greater than 99 are highly radioactive, meaning they quickly decay to another element or isotope. Some of the elements occur naturally – radon (Rn), for example – but these radioactive elements are mostly too short-lived to be measured using atomic spectroscopy techniques. A radiometric technique (radioactive decay counting) is the normal approach used to determine these elements.

Measuring isotope ratios

One of the advanced applications supported by mass spectrometric measurement (ICP-MS) is the ability to separate and measure individual isotopes of an element. This capability allows the ratio of two or more isotopes to be determined, which is useful for applications where isotope abundances vary naturally. Examples include geochronology, where the natural isotope abundance of certain elements (such as Pb, Hf, and Sr) changes depending on the age of the rock. Climate science can also use isotopic and elemental ratios in minerals incorporated in ocean sediments or corals to reconstruct historical sea temperatures.

Isotopic analysis is also used in applications such as nuclear fuel production, element fractionation studies, archaeology, and biological tracer studies. Isotope ratio measurement is also fundamental to the calibration technique known as isotope dilution mass spectrometry (IDMS). IDMS is often used in labs such as metrology institutes and for reference material certification, where traceability is required, and good accuracy and precision are essential.

How many elements and samples do you need to measure?

The number of elements and the number of samples you must measure are also important considerations when selecting an elemental analysis technique. Both ICP-OES and ICP-MS measure all the required elements in one acquisition (simultaneous analysis). Flame and graphite furnace AAS and MP-AES measure the elements one after another (sequential analysis). Simultaneous measurement is much faster than sequential measurement, as all the analytes are measured in one visit to the sample vial. If you must measure many elements (more than 10) in many samples (more than 50) the sequential techniques will be too slow.

For example, each single-element measurement using GFAAS takes around 2 or 3 minutes depending on the element measured. This means that measuring five elements with three replicates of each sample will take approximately 30 to 45 minutes per sample (5 elements x 3 replicate measurements x 2 to 3 minutes per replicate). One GFAAS instrument can therefore perform approximately 240 triplicate measurements in 24 hours. This could be 1 element in 240 samples, 4 elements in 60 samples or 10 elements in 24 samples.

By contrast, when configured with a switching valve, the ICP techniques can measure more than 50 elements in triplicate in a sample-to-sample analysis time of around 30 seconds (for ICP-OES) or 1 minute (for ICP-MS). This translates to around 60,000 triplicate determinations a day for ICP-MS and up to 125,000 for ICP-OES.

All the techniques, except flame AAS, can be left unattended, so you can load up an autosampler and let the instrument run 24 hours per day. For safety reasons, flame AAS must be continually supervised. This limits operation to working hours.



Figure 9. Using an autosampler will increase productivity and allow the instrument to run unattended.

Linear range

Each atomic spectroscopy technique can measure different concentrations of elements. The techniques can be separated into GFAAS and ICP-MS, which can measure trace levels (less than 10 ppb), and flame AAS, MP-AES, and ICP-OES, which measure higher levels – more than 10 ppb.

But that is not the whole story. Samples can contain elements at different concentrations, from trace to percentage levels. For example, you might have samples containing both 100 ppm of Na and 10 ppb of Mo.

You can always dilute or concentrate samples, but this takes time and can introduce errors. For the best productivity and accuracy, multi-element techniques such as ICP-OES and ICP-MS need to be able to measure these varied concentration levels within the same analysis. And some elements can vary a lot between samples, so the range of concentrations of each element that the technique can measure is also important. The concentration range of an analytical technique is usually described in terms of its linear dynamic range – the range over which the detector gives a linear response to a change in concentration.



Figure 10. Environmental samples such as soil, sludges, and water often contain high levels of some elements and very low levels of other elements. It's important that multi-element technique such as ICP-OES or ICP-MS can handle these concentration differences in one measurement, otherwise multiple measurements of the same sample will have to be done, with the sample preparation tasks that are part of that.

You should select a technique that can handle the concentration range of each element that is likely to be in your samples. If your lab will be receiving samples of largely unknown concentrations, then you'll need to choose a technique with a wide range, such as ICP-MS, to be sure you can do the measurements. Conversely, if you are monitoring the level of one or two elements that you know will be at 100 ppm levels, a simpler, less expensive, flame AAS system would be suitable. See Table 2 to see how the measurement ranges of each technique compare.

Table 2. The concentration range measurable by each atomic spectroscopy technique. For each technique, the bar shows the range between the typical detection limit and the upper measurement limit of the base instrument (without any enhancement of the sample introduction system).



Detection limits

The detection limits (DLs) that can be achieved by each analytical technique can be a major factor in deciding whether the technique is suitable for the intended analysis. Many regulated methods contain maximum allowable concentrations for the sample types of interest, and the chosen technique must be able to measure these concentrations reliably for that method. The method may define the approach to be used to establish the lowest concentration at which reliable analysis can be achieved, sometimes called the limit of quantitation (or quantification) – LOQ. The LOQ will typically be a factor of 3 to 10 higher than the "instrument detection limit" (IDL). A further parameter that is often quoted is the "method" detection limit (MDL), which includes the sample dilution factor and any contribution (such as contamination) from the sample preparation procedure.



Radial vs axial view ICP-OES

ICP-OES instruments come in two common configurations: radialview and axial-view. In the radial configuration, the plasma is viewed from the side (the red line in the diagram), across the width of the plasma. In the axial configuration, the plasma is viewed down its length (the blue line). Axial viewing increases the path length and reduces the plasma background signal, resulting in detection limits as much as 5-10x lower than with the radial configuration for some elements.

Radial mode is also useful when measuring Group 1 metal such as Na and K as it overcomes interference problems with these elements. The Agilent 5900 ICP-OES can measure both axial and radial views at the same time, so has the best viewing configuration for all elements. In general, the "trace element" techniques, GFAAS, and ICP-MS, have significantly lower detection limits than the other atomic spectroscopy techniques. But the story of detection limits is more complex than that. Each technique will give better performance for some elements than others, often depending on the sensitivity and the background signal for the element. For example, in ICP-OES a very intense emission line will give higher sensitivity and therefore lower DLs than a less intense emission line. Similarly, for ICP-MS, a more abundant isotope will give higher sensitivity and lower DLs than a low abundance isotope.

One of the reasons for the rapid adoption of ICP-MS in metals laboratories is that the technique generally has low DLs for the elements that are typically measured at the lowest levels. This group includes many heavy metals, such as Cr, As, Cd, Hg, and Pb. Elements with higher DLs on ICP-MS tend to be analytes that are commonly measured at higher levels, such as the mineral elements Na, K, Ca, S, Fe, etc.

The sample matrix and major element composition can also have an impact on the DL. For example, an element's DL might be severely degraded by a spectral overlap in a particular sample matrix. Laboratory environment and reagent quality will also have a big effect on the actual DLs that can be achieved routinely by each technique. It is often said that the more sensitive techniques with the lowest DLs require the cleanest chemicals and the best air quality, such as a cleanroom. But it is the achievable reporting limits that depend on these factors, rather than the technique itself. For example, poor reagent quality or sample contamination caused by a dusty lab environment may prevent an ICP-MS from achieving the ppt and sub-ppt level DLs the technique is capable of. But that doesn't matter if the minimum reporting levels are at ppb levels.

Interferences

Interferences are interactions during the sample measurement that can negatively impact the measured result. Atomic spectroscopy interferences can be divided into three groups:

- Physical interferences caused by the sample matrix or the solution it is prepared in
- Chemical interferences caused by the interaction between components of the sample and the analytes
- Spectral interferences, where the signal measured for one element is not completely separated from the signal for another element on the wavelength or mass scale

Each technique suffers from the three types of interferences to a different extent. This is illustrated in Table 3. Although atomic spectroscopy techniques have different levels of interferences, all have well-established ways to counteract the impact of those interferences. This is achieved with hardware configuration, operating conditions, and software tools, or through sample preparation and quality control procedures. The interference differences shouldn't be a major factor in choosing a technique for your lab. However, if you won't know the composition of many of the samples you will be analyzing (typically referred to as 'unknown' samples), you will need to cater for interferences during method development.

Table 3. The relative occurrence of different types of interferences for each technique (more dots indicates higher level of interferences).

		Atomic spectroscopy technique										
Interference type	Flame AAS	GFAAS	MP-AES	ICP-0ES	ICP-MS	ICP-QQQ						
Physical	••	•	••	••	••	••						
Chemical	•••	••••	••	•	••	••						
Spectral	•	•	••	•••	••	•						

Physical interferences

Physical interferences occur when variable matrix and solvent levels cause changes in the viscosity, surface tension, and evaporation rates of the solution, leading to differences in the signal levels measured. Physical interferences occur with all techniques that involve pumping liquid. These effects typically occur in the sample introduction system, although some can also affect the sample preparation step, for example during pipetting of solutions. Physical effects can be caused by:

- A different solvent used to prepare standards vs samples (e.g. HCl vs HNO₃, or aqueous solvent vs 10% alcohol)
- A different level of acid or organic solvent between standards and samples (e.g. standards prepared in 0.1% acid and samples in 10% acid)
- A different level of major elements in the samples, compared to the standards (e.g. simple synthetic standards for sample digests containing a high level of dissolved carbon, or 1% dissolved solids).

Several approaches can be used to address physical interferences, of which the most widely used are matrix matching, standard addition, and signal correction.

Matrix matching is when the user identifies the key components of the samples and prepares the standards (and blanks, QC solutions, etc.) in a similar matrix. This can be as simple as adding the same amount of acid, or a more sophisticated approach such as preparing the standards in the same solution used for sample preparation and dilution. If the standards are in the same matrix as the samples, the physical effects should be the same for both, so signal differences should be minimized.

Standard addition is an advanced form of matrix matching, where the standard solutions are added to the sample itself, eliminating any variability in the matrix composition. While attractive in principle and widely used in some industries, standard addition does have the downside that each different sample type must be calibrated using its own set of standard addition spikes.

Signal correction usually relies on the addition of a non-target element as an internal standard (ISTD). An ideal ISTD is an element that is not a required analyte, does not suffer or cause interferences on another analyte, and will not be present naturally in the samples. The ISTD element is added (often automatically using an online mixing connector) at the same level to all the solutions (standards, blanks, QCs, and unknowns). Physical interferences generally affect the total amount of solution transported to the source, so any changes to the signal should affect all elements to the same degree. After analysis, the change in the ISTD signal is used to correct the signal for the analytes. For example, if the ISTD signal was 10% lower in a sample than in the standards (90% recovery), the analyte signal would be corrected up by the same percentage. This ISTD correction compensates for the loss of signal due to the sample matrix. ISTD correction is widely used across atomic spectroscopy techniques having the benefit that it can correct for long-term drift as well as physical interferences. Multi-element techniques (ICP-OES and ICP-MS) often use several ISTD elements to give the best possible correction for all analytes.

Chemical interferences

Chemical interferences occur when the elements undergo a chemical interaction during sample introduction or measurement. Chemical interferences are more common with lower temperature atomization sources, such as flame AAS. This is because the lower temperature of the flame is less efficient at decomposing and dissociating the sample material and forming free atoms of the analytes being measured. If a matrix component combines with the analyte atoms to form another compound, there will be fewer free analyte atoms and therefore less absorbance at the analyte's characteristic atomic wavelength. The sample matrix and the specific elements present in it can therefore affect the amount of analyte signal generated compared to the signal in the standards. Chemical interferences in flame AAS can be reduced using a higher temperature flame, or by adding a chemical modifier.

Some chemical effects occur during sample aspiration, for example when an element is present in a more volatile form in the samples compared to the standards. This can lead to enhanced signal as the more volatile compound is vaporized from the surface of the aerosol droplets. Chemically stabilizing the element using an appropriate solvent or complexing agent can solve this type of chemical effect.

Ionization effects are another type of chemical interference that can affect high temperature Flame AAS analyses. Ionization effects occur when an easily ionized element is converted from the atomic form to an ion (as in ICP-MS). If ions are formed, they are not able to be quantified in atomic absorption spectroscopy.

While chemical interferences more commonly affect AAS, the higher temperature ICP atom and ion source used in ICP-OES and ICP-MS is not immune. One example that affects ICP-MS is the ionization enhancement that is seen for arsenic and selenium when measured in the presence of a high level of carbon. The presence of the carbon matrix at low % level enhances the ionization of As and Se, increasing the signal relative to the level in the low carbon standards. The effect is easily corrected by adding an excess of carbon – for example in the form of 2% butan-1-ol – to all the solutions so the signal enhancement is consistent.

Spectral interferences

Spectral interferences can affect all atomic spectroscopy techniques to different degrees. The low temperature Flame AAS source tends to suffer few spectral overlaps, while the very high temperature ICP source produces

an extremely rich and intense emission spectrum. With thousands of emission lines across the measured wavelength range of an ICP-OES (see Figure 11 as an example), there's a high chance at least two lines will be close, potentially interfering with each other. If your ICP-OES has the capability to monitor multiple emission lines per element, you can simply choose a line that is free of interferences for the analysis, which avoids the spectral interference.



Figure 11. A typical ICP-OES emission line spectrum, shown across an approximately 4 nm wavelength range.

The ICP-MS mass spectrum contains fewer than 240 natural atomic/ isotopic masses, so is much simpler that the ICP optical emission spectrum. Furthermore, every element measured by ICP-MS (except indium) has at least one mass (isotope) that is free from direct overlap by any other element. While inter-element overlaps are therefore easily avoided in ICP-MS, spectral overlaps can also be formed from combinations of elements forming molecular ions known as "polyatomic" ions. These polyatomic ions can be formed from the argon gas, elements such as N and O from the air, and components of the solution and sample matrix. Common examples of polyatomic ion overlaps include O₂⁺ which overlaps the main isotope of sulfur at m/z 32, ArO⁺ which overlaps the main isotope of iron at m/z 56, and ArCl⁺, which overlaps the only isotope of arsenic at m/z 75. The limited number of isotopes available for ICP-MS analysis can make it difficult to avoid polyatomic overlaps. Polyatomic interferences used to be a major limitation in achieving accurate results in variable and high matrix samples. Instrument manufacturers have now developed effective and automated ways to handle polyatomic interferences, but not all ICP-MS instruments have the same capability, so you should consider the differences carefully.

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Costs

Setup costs

As well as the purchase price of the instrument, you may need to invest in significant changes to your lab to accommodate an atomic spectroscopy instrument. A general list of requirements is shown, following.

- Exhaust extraction
- Gas supplies
- Fume cupboard for sample preparation (depending on your sample types)
- Sample preparation equipment such as a microwave digester (depending on your sample types)
- Laboratory benches able to accommodate the size and weight of a large analytical instrument
- Air conditioning
- Cooling water (for GFAAS, ICP-OES or ICP-MS)
- Access and lifting capabilities to get instrument into lab
- Single phase power supply (usually with the instrument on a separate circuit)
- Suitably trained or experienced analysts

If measuring elements at ppt levels

- Clean room or laminar flow hood to provide dust-free conditions
- High purity grade reagents
- High grade standards

Utilities and facilities needed for an atomic spectrometry instrument

Ongoing costs

Each atomic spectroscopy technique has different requirements for maintenance and supplies. You will need to allow for the cost of instrument supplies and servicing in your budget. Here's an overview of what is required for each technique:

Utility costs

Gases and power are the largest utility costs associated with atomic spectroscopy analyses. The quality and quantity of argon, for example, varies by technique. GFAAS uses only 3 L/min of argon (or N₂, depending on the elements being measured) whereas the plasma-based techniques of ICP-OES and ICP-MS use about 20 L/min (as the plasma is fueled by argon). ICP-MS may also require lower volume supplies of He, H₂, NH₃, and O₂ (depending on method requirements). ICP-OES can run on cheaper, lower purity 99.95% argon, whereas GFAAS and ICP-MS require high purity 99.99% argon (as a minimum). Flame AAS requires compressed air, acetylene, and nitrous oxide gases, depending on the elements you need to measure.

MP-AES offers the lowest utility costs and thus, the lowest cost-persample. It requires only an ongoing supply of nitrogen, which can be pulled from ambient air with the use of a nitrogen generator. A small supply of 99.0% pure argon (in an onboard bottle) is required to ignite the plasma. The MP-AES also has low-power requirements, requiring only a 10 A power supply.

ICP-OES and ICP-MS both consume more power than the other techniques. ICP-MS and ICP-QQQ consume the most, with both having vacuum pumps that typically operate continually. Both ICP-MS and ICP-QQQ require a separate 30 A power supply. An ICP-OES requires a 15 A power supply.

Air conditioning may be required for any of the techniques, depending on the local climate. The laboratory should be kept within 15 to 30 °C and 20 to 80% humidity.

It's important to make cost comparisons based on the cost-per-sample analysis. ICP-OES and ICP-MS are both multi-element techniques that can measure a batch of samples quickly. Although they require more gases and more power while running, they take less time than the other techniques to measure the same number of samples.

Routine maintenance

All atomic spectroscopy techniques require regular cleaning and maintenance. The more samples you measure, and the more complex the samples, the more maintenance they require. In particular, the highly sensitive techniques of GFAAS and ICP-MS (including ICP-QQQ) need to be cleaned more frequently if ultratrace level analysis is performed.

If you are using an instrument daily, you could expect to perform the following maintenance activities:

Daily

Inspect and clean the sample introduction area. This includes the nebulizer, spray chamber, torch, burner or graphite tube, pump tubing, and waste containers. These maintenance items are similar across all techniques, except for GFAAS, which has different components. Expect to spend up to 30 minutes performing these activities. Note that some instruments can automatically provide the operator with a system condition report each morning, detailing what – if any – maintenance is required.

Weekly

Inspect and clean the area where the sample is heated (e.g. the torch compartment). Expect to spend 30 to 60 minutes performing these activities.

As a rule, all the techniques have similar daily/weekly maintenance requirements. However, GFAAS, ICP-OES, and ICP-MS have more maintenance tasks that are done on an infrequent basis. These tasks include checking water levels in cooling system and vacuum pump oil levels.

Ease-of-use and analyst skill required

There is an increasing trend for analytical instruments to include high levels of automation and software functionality that reduces the analyst skill required. For common sample types, the methods and tools supplied with instruments will help ensure you report accurate results.

Flame AAS and MP-AES instruments require less skilled analysts to operate them. GFAAS requires a higher level of skill largely due to the sophisticated chemistry involved and the lower detection levels. GFAAS also typically has less automated functionality, so relies on analyst skill to develop methods and run the analyses.

Once a routine method has been setup, the day-to-day operation of any of the atomic spectroscopy techniques is relatively simple. Developing a new method takes a higher level of skill, with more complex, multi-element methods and more varied sample types increasing the level of skill required. Modern atomic spectroscopy instruments will typically include resources such as method libraries and software workflow guides to support those who are new to this potentially daunting task.

Table 4. Comparing the relative complexity of developing methods for the different atomic spectroscopy techniques.

	Flame AAS	GFAAS	MP-AES	ICP-0ES	ICP-MS	ICP-QQQ
Method development complexity	Ś	Ś	ୢୠୄୠୢୠ	\$\$	\$\$	ୢୠୢୠୢୠ

Methods - regulated and availability of pre-developed

Regulated methods

Many typical elemental analyses are government regulated in various countries. For example, measuring metals in drinking water is regulated by the US Environmental Protection Agency. The EPA has issued the following methods for drinking water:

- 200.5 Determination of Trace Elements In Drinking Water By Axially Viewed Inductively Coupled Plasma - Atomic Emission Spectrometry (2003)
- 200.7 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry (1994)
- 200.8 EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry (1994)
- 200.9 Determination of Trace Elements by Stabilized Temperature Graphic Furnace Atomic Absorption (1994)

For each of these methods, the analytical technique required is determined by the method selected. In turn, the method is likely determined by the regulations you must comply with.

There are over 1500 standard methods globally for elemental analysis. They range from the very specific, such as measuring molybdenum in workplace air (<u>GB/T 17087</u>), through to the broad, such as measuring 26 elements in water (<u>US EPA 200.8</u>).

Pre-developed methods and method development

Many instruments will be supplied with a suite of method templates that are appropriate for common analyses types, e.g., measuring elements in drinking water. Supplied methods tend to be for regulated analyses. If your analyses are out of the ordinary or you have very specific requirements then you will need to locate a published method for your instrument or develop one yourself.

Single element techniques such as flame and graphite furnace AAS have been around for a long time and tend to have well-established methods for many analytes and sample types.

The multielement methods used on ICP-OES and ICP-MS have more variables and are therefore more complex to setup. These methods may also require more modification when transferring an existing method to a new instrument.

Sample preparation

Liquid samples



Figure 12. Samples are typically introduced in liquid form for measurement using any atomic spectroscopy technique. All techniques, except GFAAS, use a nebulizer to turn the liquid sample into an aerosol mist. GFAAS injects the liquid sample using a syringe.

For conventional analysis, samples to be measured using flame, furnace, and plasma based atomic spectroscopy techniques are introduced in liquid form. Even those samples that are already liquids often need preparation before measurement. This sample preparation may include filtration, acidification, digestion, or some other form of stabilization to ensure that the analytes remain stable in the solution.

Most regulated or standard methods will specify the sample preparation process to use. There are also plenty of 'recipes' for sample preparation for different sample types online. For example, Agilent publishes <u>application</u> <u>notes that describe a wide range of analyses</u>.

Solid samples



Figure 13. Determining the elemental content of soil, rock or ore samples is a common atomic spectroscopy application.

Soil and sediment samples are often dried before processing. Samples such as rock or ore are ground into a fine powder, mixed and then subsampled to ensure you have a representative sample to analyze.

The sample of soil, sediment, or rock is then subjected to an acid treatment to extract the elements you wish to analyze (the analytes) into solution. This acid treatment process is called digestion (it is similar to the digestion process in our stomachs).

For trace-level analysis, the digestion, and any sample transfer or storage steps must be carried out in containers made of an inert material such as quartz or a polymer. Vessels made of borosilicate or soda glass must not be used for trace metal analysis as the glass material will contain elements that can be leached into the acidic solution. Glass will also adsorb trace elements from the solution, leading to instability and poor recoveries.

Digestion, dilution, and filtration



Figure 14. Samples may need to be digested with acid to release elements into solution.

Depending on which elements you want to measure and the sample type, you may need to digest samples with an acid. Digestion and other sample preparation requirements will depend on the application and the method. Regulated or standard methods will usually specify the sample preparation that should be done.

To digest a sample, it can be placed in a beaker with an acid and heated on a hot plate (inside a laboratory fume hood). You can also use microwave digestion systems or 'hot block' systems. Hot block systems can handle many samples at once and offer better temperature control than a hot plate. Microwave digesters use "closed vessels" to enable higher temperature and pressure to be used, improving digestion.

The acids you use for sample digestion depend on the sample type and elements you want to measure (a useful resource is the <u>Handbook of</u> <u>Decomposition Methods in Analytical Chemistry</u>). Challenging elements like molybdenum require a more aggressive acid such as hydrofluoric acid (HF) to get into, and stay in, solution. You may in fact need a combination of acids to break down the sample. If you need to use hydrofluoric acid during your sample preparation, you will need to use inert components as this acid attacks glass. Agilent supplies inert components for our atomic spectroscopy instruments, for example an <u>inert sample introduction</u> <u>system for ICP-OES</u>. The final steps in sample preparation will be dilution and potentially filtration. The method will normally specify what final volume to dilute samples to. You may need further dilution to get samples into the calibrated range of the instrument or to reduce the level of total dissolved solids (TDS) in the sample to a level the instrument can handle (this varies by technique and by instrument model). Samples that contain undissolved particulates will need to be filtered, otherwise the particles will cause blockages in the instrument sample introduction system.

Organic sample preparation

Organic chemicals such as oil samples can typically be analyzed with a 'dilute and shoot' approach, using a suitable organic solvent (hexane, xylene, toluene, etc.). However, if there are large particles in the samples (e.g. oil samples for wear metal analysis) they will need to be digested.

Measuring organics may require specific parts to be fitted to the instrument and specific instrument settings. With AA, MP and ICP-OES techniques, it is important to prevent carbon from the organic samples building up on the plasma torch or flame burner. When measuring organic solvents using ICP-OES or ICP-MS, oxygen gas (as a 20% mix in argon) is added to the torch to decompose the matrix and avoid carbon deposits on the injector of the torch or the ICP-MS interface cone. In ICP-MS, the addition of oxygen would lead to rapid degradation of the standard nickel cones, so the interface cones should be replaced with the platinum cones when analyzing organic solvents.

The <u>Agilent FilterMate Filtration</u> <u>System</u> allows you to digest, filter, and analyze samples using the same tube. The filter tubes are compatible with hot block digestion systems, but are not suitable foruse in microwave digestion systems.



Solvent-specific instrument components



Figure 15. Pump tubing must be compatible with the solvent you are using.

The tubing used on the peristaltic pump of the instrument must be compatible with the solvent you are using. For example, Agilent offers different types of tubing for different solvents for use with our <u>AA</u>, <u>MP-AES</u>, <u>ICP-OES</u>, and <u>ICP-MS</u> instruments.

The whole sample introduction system may need to be swapped for one that is compatible with the solvents you are using. For example, many analysts keep a separate set of components to use with organic samples.



Calibration

Atomic spectroscopy techniques measure the concentrations of the elements of interest relative to a solution of known concentration, called a standard. The process of defining the relationship between the measured value and the concentration in the known standard is called "calibration". The known standard is typically a certified calibration solution or a reference material. Calibration solutions are often available from instrument suppliers. For example, Agilent <u>offers a range of single-element</u> and <u>multi-element certified calibration standards</u>. Chemical suppliers also manufacture and supply calibration standards, while reference material producers such as the US National Institute of Standards and Technology (NIST) provide certified and standard reference materials (CRMs/SRMs) relevant to a range of industries and applications. CRMs and SRMs can be used for instrument calibration or run as quality control (QC) samples to provide an independent check of the accuracy of the calibration standards.

The usual approach to calibration in atomic spectroscopy is to prepare a series of calibration standards from a certified stock solution containing the element or elements of interest. Single element techniques such as AAS usually use a separate calibration for each element being measured. Single element standards are certified only for the concentration of the target element. Multi-element techniques such as ICP-OES and ICP-MS often use mixed calibration standards that contain all the elements of interest. ICP standards are certified not only for the correct levels of the intended elements, but are also checked and certified for the absence of other elements.

The calibration stock solutions are diluted to give standard levels covering the concentration range expected in the unknown samples. The diluted standards are then measured using the same method that will be used for the unknown samples. The signal (absorption, emission, or counts) measured for each element at each concentration level is processed by the instrument software, giving a plot of the relationship between signal and concentration. For techniques with a relatively low temperature atom source, such as Flame AAS, the linear response will only cover a small concentration range (as shown in Figure 16). This means that it will be difficult to achieve accurate results at higher concentrations, where the relationship between absorbance and concentration is not linear. This can be overcome by diluting samples to bring them into the linear part of the calibration, or using more sophisticated mathematics to establish the relationship between absorbance and concentration.



Figure 16. A linear relationship between absorbance and concentration may only cover a small concentration range for techniques such as flame AAS. This means you must dilute samples so their concentration is within the linear range of the calibration, or use more sophisticated mathematics. In the calibration graph shown here, the relationship is linear only to 100 mg/L.

On higher temperature (plasma) source instruments (ICP-OES and ICP-MS), the calibration is usually linear over several orders of magnitude. The curve fit for these linear calibrations can be expressed as y = ax + b, where a is the slope and b is the Y-axis intercept. Calibration is easier when the technique gives a linear response across a wide concentration range, as fewer standards are needed. Also, methods are more flexible, as the standards do not need to be closely matched to the sample concentrations. A linear ICP-MS calibration for Na covering five orders of magnitude is illustrated in Figure 17. This ICP-MS calibration is linear from 0.1 to 10,000 ppm.







Applications

Atomic spectroscopy is used for a wide range of measurements across a wide range of industries. Table 5 shows which techniques are most commonly used for different measurement types.

Which techniques are commonly used for different applications?

Table 5. Industries where atomic spectroscopy is used and which techniques are commonly used in each. The more dots the more commonly that technique is used.

Industry	Typical Applications	Flame AAS	GFAAS	MP-AES	ICP-0ES	ICP-MS	ICP-QQQ
Agriculture	Soil	••	•	•	•••	•••	•
	Plants	••	••	•	•••	••	•
	Fertilizer	••		••	•••		
Cannabis	Manufacturing /QC		•		••	•••	•
Clinical Research	Biological fluids		••			•••	••
Energy &	Fine chemical	•	••		•••	•••	••
Chemicals	purity						(for high purity)
	Renewable energy: Biofuels, solar panels, fuel cells	•	•	••	•••	•••	••
Environmental	Soil	•••	••	•	•••	•••	••
	Water	•••	••	•	•••	•••	••
	Air		••		••	•••	••
	Monitoring of wastes from industry and power generation	•			•••	•••	•
	Waste materials	•••	•	•	•••	••	•

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Industry	Typical Applications	Flame AAS	GFAAS	MP-AES	ICP-OE	s icp-ms	ICP-QQQ	Industry	Typical Applications	Flame AAS	GFAAS	MP-AES	ICP-OES	ICP-MS	ICP-QQQ
Food & Beverages	Food safety		•		•	•••	••	Nanomaterials	R&D and manufacturing					•••	•••
	Nutritional labeling	••	•	••	••	•			Environmental monitoring					•••	•••
	Food authenticity	•	•	•	••	•••	••		Food additives					•••	•••
Forensics	Glass, paint, ink analysis		•		••	•••	••		Consumer products					•••	•••
	Gunshot residue		••		•	•••	•	Nuclear	Fuel production					•	••
Geochemistry and Mining	Exploration	•••	•	•	•••	••	•		Decommission- ing					••	•••
	Production (final product monitoring)	•	•	•	•••	••	••		Monitoring reactor cooling water					•••	••
	Research and geochronology					••	•••	Petrochemicals	Wear metals in lubricants	••		••	•••	•	
Life Science	Single cell analysis					••	•••		Crude oil	••		••	•••	••	••
	Bio imaging					•••	•••		Process control				•••	••	••
	Proteomics					•	•••		Fuel QC	••		••	•••	••	•
	Metallomics					••	•••	Pharma/ Biopharma	Drug discovery		•			••	•••
Materials	Ceramics	•	•		•••	••	•••		Extractables and leachables		•		••	•••	•
	Batteries	•	•		•••	••	•		Manufacturing/ QC		•		••	•••	•
	Magnets	•	•		•••	•••	•••	Semiconductor	Process chemicals		•		••	••	•••
	Catalysts				•••	•••	••		purity Silicon wafer		•			••	•••
	Glass and optical fiber		•		•	••	•••		purity High purity		•		•	••	•••
Metals & Alloys	Superalloys		•		••	•••	••		metals		-		-		
,-	Precious metals		•		•••	••	•••								
	Ferrous metals				•••	••	•								

Recommendations for common measurement scenarios

Measuring trace (<10 ppb) or ultra trace (ppt) concentrations in a small number of samples

For a lab measuring a handful of elements at trace or ultratrace (ppt) levels in a small number of samples per day, there are two options: Graphite furnace atomic absorption spectroscopy (GFAAS or graphite furnace AAS) or inductively coupled plasma mass spectrometry (ICP-MS).

GFAAS can measure 48 elements, whereas ICP-MS can measure 86. The common elements that GFAAS can't measure, but ICP-MS can, are: Br, C, Ce, Cl, F, Gd, Hf, Ho, I, La, Lu, Nb, Nd, Os, Pr, Re, S, Sc, Sm, Ta, Tb, Th, Tm, U, W, Y, and Zr. Even with ICP-MS, detection limits for C are poor, and F requires a specialized ICP-QQQ approach.

GFAAS has a lower purchase price and lower running costs than ICP-MS. However, ICP-MS delivers much faster analysis, much wider linear dynamic range, and fewer interferences. For more elements or higher sample numbers, ICP-MS is faster and more cost effective as it measures all elements in a 2 to 3 minute acquisition for each sample. In contrast, GFAAS measures each element separately in the sample, with each single-element measurement taking around 2 or 3 minutes. This means that measuring five elements with three replicates of each sample will take approximately 30 to 40 minutes per sample (5 elements x 3 replicate measurements x 2 minutes per replicate) using GFAAS. One GFAAS instrument can therefore perform approximately 240 triplicate measurements in 24 hours. This could be 1 element in 240 samples, 4 elements in 60 samples or 10 elements in 24 samples.

Both techniques need a reasonable level of knowledge and skill to operate. Both can run unattended, so you can load up an autosampler and leave the instrument to complete the analysis. A typical QA/QC lab often selects GFAAS, but if the lab is expanding and needs to ensure they can cope with higher sample loads in the future, ICP-MS can provide the extra element coverage and higher sample throughput required for growth.



ICP-MS advantages

ICP-MS is ideal when you:

- Need to measure more than 10 elements per sample, or the number of elements may increase in the future
- Need to measure elements that GFAAS cannot measure
- Have more than 100 samples per day or you have sample batches of more than 200
- Measure elements that may be present at unknown levels, or the concentration of elements varies a lot from sample to sample



GFAAS advantages

GFAAS is ideal for those labs that:

- Need trace level quantitation where the sample and element load is no more than around 240 measurements per day (four elements x 60 samples in 24 hrs). This assumes three replicates on each measurement.
- Know the approximate concentration range of the analytes and that the concentration won't vary significantly from sample to sample
- Need to measure only a few elements
- Want to keep their capital expenditure low, lab setup costs minimized and operating costs down.



Agilent offers a Duo atomic absorption system, which combines a flame atomic absorption instrument and a GFAAS. Elements at low concentrations are measured on the GFAAS and elements at higher concentrations are measured using the flame AAS. Both can measure samples at the same time, which increases the sample throughput. The flame atomic absorption instrument cannot be left unattended, so analysis is limited to when an analyst can monitor the instrument.

Measuring more than ten elements at low concentrations (<10 ppb) in more than 50 samples

If your lab needs to measure ten or more elements that are present in concentrations lower than 10 ppb and you have more than 50 samples per day to measure, then inductively coupled plasma mass spectrometry (ICP-MS) is the most suitable technique. ICP-MS can also measure higher concentrations of elements, but if the number of elements and the number of samples is low, techniques such as Flame AAS or MP-AES are a lower-cost option for measuring high concentration analytes.

ICP-MS offers:

- Fast measurements of almost every element in a 3-minute sample reading (1 minute per sample if you use a switching valve)
- High sensitivity and low detection limits (down to ng/L (ppt) or sub-ppt levels) for most elements. Elemental isotope ratios can also be measured
- The ability to measure elements at concentrations of less than 0.1 ppt to more than 1000 ppm in the same measurement
- Functions that can overcome almost all measurement interferences
- The ability to measure a wide range of sample types, including organic solvents and solutions with dissolved solids levels up to 25%
- Connection to other techniques such as liquid or gas chromatography for chromatographic separations, or laser ablation (LA) for direct solid sampling
- Unattended operation, with the use of an autosampler



What type of ICP-MS do you need?

ICP-MS is available in two common configurations: single quadrupole ICP-MS or triple quadrupole ICP-MS (referred to as ICP-QQQ). ICP-QQQ is also known as tandem ICP-MS or ICP-MS/MS. Both configurations can measure 86 elements, with ICP-QQQ being able to also measure F, which a single quadrupole ICP-MS cannot.

Single quadrupole ICP-MS has a lower purchase price and slightly lower running costs than ICP-QQQ. ICP-QQQ requires a higher level of skill to setup and operate, although this depends on the methods being run. Many methods developed for a single quadrupole ICP-MS can be run without modification on ICP-QQQ.

The main advantage of ICP-QQQ is its ability to resolve spectral interferences that single quadrupole ICP-MS cannot. ICP-QQQ has much lower detection limits and more consistent results for variable sample types. For example, the elements Si, P, and S suffer intense spectral interferences when measured with single quadrupole ICP-MS, so detection limits are relatively poor. An ICP-QQQ can overcome these interferences, allowing these difficult elements to be measured at trace levels.



Single quadrupole ICP-MS

ICP-MS is ideal for those labs that:

- Run routine (often regulated) ICP-MS methods
- Measure a typical range of trace elements, not including "difficult" elements such as F, Cl, Si, P, or S
- Analyze common sample types such as environmental samples
- Do not need to measure elements at the lowest, ultra trace (less than ppt) levels



Triple quadrupole ICP-MS

ICP-QQQ is ideal for those labs that:

- Run demanding applications that include complex sample types, require analysis of F, Cl, Si, P, or S, or involve interferences that are difficult to overcome
- Need to measure ultratrace levels (less than ppt) of elements in high purity materials or semiconductor process chemicals
- Need to measure analytes that suffer direct isobaric (elemental) overlaps (such as ²⁰⁴Pb/²⁰⁴Hg, ⁸⁷Sr/⁸⁷Rb, ¹⁷⁶Hf/¹⁷⁶Lu), or radiogenic isotopes, laboratories measuring geochemical, or nuclear samples often need this capability
- Need to measure low concentrations of elements at the mass next to a major element, e.g., B in a carbon matrix, Mn in steel, Np in uranium
- Want to be able to handle the broadest range of sample types and elements, both now and in the future



Measuring a lot of elements at medium-to-high concentrations (>10 ppb) in a large number of samples

Labs with heavy workloads – needing to measure many elements in many samples will need a fast inductively coupled plasma metals analysis technique like ICP-OES or ICP-MS.

When comparing the two techniques, it's important to realize that there is an overlap of the concentration ranges that ICP-OES and ICP-MS can measure. If all elements are consistently at concentrations above 10 ppb, then ICP-OES is the best option. If you need to measure lower concentrations of some elements or you need to measure C, F, Cl, Br, or I then ICP-MS is recommended. Even with ICP-MS, detection limits for C are poor, and F requires a specialized ICP-QQQ approach. See the section, Which elements do you need to measure?, preceding.

While ICP-OES cannot measure concentrations of metals down to the parts-per-trillion levels that ICP-MS can, ICP-OES is often used for measurements that might previously have been done using flame AA.

Highly specialized applications that need to measure the radioactive elements Np, Pu, Am, or Ra or other very rare actinides elements (Ac, Bk, Cf, Cm, Pa, Po) will also require ICP-MS.

ICP-OES

ICP-OES is ideal when you:

- Have large numbers of samples (more than 1200 samples per day).
 In these situations, you'll need the speed of ICP-OES, which takes less than one minute to measure the concentration of up to 74 elements in a sample
- Need to measure samples that contain very high, percent levels of total dissolved solids (TDS) or suspended solids. ICP-MS can measure these samples, but it's easier to run them routinely on ICP-OES
- Are measuring samples that will always contain more than 10 ppb of each element

ICP-MS

ICP-MS is a better option if you need:

- Analysis at levels below 10 ppb for some elements or you are likely to need this performance in the future (because of a regulatory change for example)
- The ability to measure elemental isotope ratios
- To combine elemental analysis with other techniques such as liquid or gas chromatography for chromatographic separations, or laser ablation (LA) for direct solid sampling

Measuring fewer than 10 elements at high concentrations (>100 ppb) in fewer than 100 samples per day

When measuring a few elements at concentrations above 100 ppb in low numbers of samples, either flame atomic absorption spectroscopy (referred to as FAAS, flame AAS, or just AA) or microwave plasma atomic emission spectroscopy (MP-AES) are ideal. The MP-AES can measure 70 elements versus 67 for flame AAS. If you need to measure S, Ce or Th then MP-AES is the best choice between the two. However, there are elements that both AAS and MP-AES cannot measure.

Do you need to measure these elements?

If the list of elements you want to measure includes: Cl, I or the radioactive Tc or Pm, then ICP-OES is the best choice as neither AAS nor MP-AES can measure these elements. Note that if you need to measure low levels of those elements (<20 ppm Cl or <200 ppm I) or if the list of elements you want to measure includes Br, radioactive Np, Pu, Am, or Ra, or any of the obscure actinides elements (Ac, Bk, Cf, Cm, Pa, Po) then ICP-MS is your only choice. However, the higher cost of an ICP-MS instrument means it often cannot be justified for measuring low numbers of samples with medium to high concentrations of elements that Flame AAS, MP-AES, or ICP-OES can measure.

The difference between MP-AES vs ICP-OES vs flame AAS

Flame AAS is the lowest cost instrument to buy. Both MP-AES and flame AAS have similar sample measurement times, if the <u>Agilent Fast Sequential</u> <u>mode</u> is used for AAS. An ICP-OES instrument is more expensive to buy but measures samples much quicker than either flame AAS or MP-AES. ICP-OES would be the best choice if the number of samples or the number of elements to be measured is likely to increase.

The MP-AES has the lowest running costs and uses no flammable gases. It can operate unattended and is ideal for remote locations where it can be used with a nitrogen generator, so only requires a power supply (no gas supply).

Advantages of Flame AAS

FAAS is ideal for those labs that:

- Use regulated FAAS methods. Typically, these are in food and environmental applications
- Want to use standard methods. As FAAS has been used for a long time, there are many well-documented methods
- Want to measure a few elements only, a couple of times a week

Advantages of MP-AES

MP-AES is ideal when:

- You have a higher number of samples. It can be left unattended overnight, with an autosampler, to complete a large batch
- You want to reduce your gas supply and consumable costs compared to FAAS
- You need to measure S, Ce, or Th
- The lab is in a petrochemical plant or another site where a naked flame is not allowed
- Handling gas cylinders or using flammable gases represents an unacceptable safety risk

Advantages of ICP-OES

ICP-OES is ideal when:

- You want to use regulated ICP-OES methods. These are most often in food and environmental applications
- You need to measure Cl or I
- The number of samples or the number of elements you need to measure is likely to increase
- The concentration of elements in your sample is likely to decrease, requiring lower detection limits
- You would like to run the instrument unattended overnight, using an autosampler

Measuring a few elements at moderately low concentrations (tens of ppb to low ppm) in a small number of samples?

For a lab measuring a handful of elements at moderately low levels (more than 10 ppb) in a small number of samples per day, there are three options: Graphite furnace analysis (referred to as GFAAS or graphite furnace AAS) and the two inductively coupled plasma techniques of inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectroscopy (ICP-OES).

The choice may depend on the elements you need to measure. ICP-MS can measure 86 elements, ICP-OES can measure 74, and graphite furnace can measure 48. The common elements that GFAAS cannot measure include Br, C, Ce, Cl, F, Gd, Hf, Ho, I, La, Lu, Nb, Nd, Os, Pr, Re, S, Sc, Sm, Ta, Tb, Th, Tm, U, W, Y, and Zr. Similarly, ICP-OES can't measure C, F, Cl, Br, or I, so, if any of these elements is required, you will need ICP-MS. Even with ICP-MS, detection limits for C are poor, and F requires a specialized ICP-QQQ approach. The section <u>Which elements do you</u> need to measure?, preceding, provides the details of the elements each technique can measure.

GFAAS has the lowest purchase price and running costs of the three techniques, but GFAAS measures each element separately, with each single-element measurement taking around 2 or 3 minutes depending on the element measured. This means that measuring five elements with three replicates of each sample will take approximately 30 to 40 minutes per sample (5 elements x 3 replicate measurements x 2 minutes per replicate) using GFAAS. One GFAAS instrument can therefore perform approximately 240 triplicate measurements in 24 hours. This could be 1 element in 240 samples, 4 elements in 60 samples or 10 elements in 24 samples.

An ICP-MS instrument is more expensive to purchase and run, but delivers fast, multi-element analysis, much wider linear dynamic range, and fewer interferences. ICP-MS measures all elements in a 2 to 3 minute acquisition for each sample, so it is much faster than graphite furnace. If the number of samples and/or the number of elements is likely to increase, or the concentrations you need to measure may decrease (because of regulatory changes for example) then ICP-MS is the best option.

Of the two inductively coupled plasma techniques, an ICP-OES instrument costs less than an ICP-MS. ICP-OES also has the fastest sample measurement time, being able to measure multiple elements in up to 2500 samples per day. ICP-OES is a good choice if your sample load is likely to increase a lot or the number of elements will increase but the concentrations you need to measure will not decrease. ICP-OES cannot measure down to the same sub-ppb concentration levels as GFAAS or ICP-MS.

Both GFAAS and ICP-MS need a reasonable level of knowledge and skill to operate although standard, regulated methods can be automated. ICP-OES is easier to use. All techniques can run unattended, so you can load up an autosampler and leave the instrument to complete the analysis. A QA/QC lab that needs to measure the same elements in a few samples per day often selects GFAAS. However, if the lab is expanding and needs to ensure they can cope with higher sample loads in the future, either of the inductively coupled plasma techniques can provide the extra element coverage and higher sample throughput required for growth.

Graphite furnace advantages

GFAAS is ideal when you:

- Need trace level quantitation where the sample and element load is approximately 240 measurements per day (e.g. four elements in 60 samples). This assumes three replicates for each measurement
- Need to measure only a few elements
- Have very small sample volumes
- Know the approximate concentration range of the analytes and that the concentration won't vary significantly from sample to sample
- Have a small budget and you want to minimize both the instrument price and operating costs

ICP-MS advantages

ICP-MS is ideal when you:

- Need to analyze multiple elements at levels below 10 ppb or you are likely to need this performance in the future (because of a regulatory change for example)
- Need a combination of low detection limits, multi-element analysis, and high sample throughput
- Analyze elements that include some that can only be measured by ICP-MS (such as Br or I)
- Need to combine elemental analysis with other techniques such as liquid or gas chromatography for chromatographic separations, or laser ablation (LA) for direct solid sampling.

ICP-OES advantages

ICP-OES is ideal when you:

- Will always be measuring all analytes at high ppb levels or above
- May have a large increase in sample numbers (more than 1200 samples per day). In these situations, you'll need the speed of ICP-OES, which takes less than one minute to measure the concentration of up to 74 elements in a sample
- Need to measure samples that contain very high, percent levels of total dissolved solids (TDS) or suspended solids. ICP-MS can measure these samples, but it's easier to run them routinely on ICP-OES

Other components you may need

Other components you may need

In addition to the instrument, you may need accessories that enhance productivity or sensitivity. There are also accessories that help when measuring particular sample types or particular elements.

Autosamplers

An autosampler allows the instrument to measure a batch of samples whilst unattended. The probe of the autosampler will pull sample from each tube in turn, rinsing in between. An autosampler is recommended if you have sample batches larger than 100 samples or analysts are required to manage multiple instruments.

Sample introduction pumps

An accessory for flame AA, the Agilent Sample Introduction Pump System (SIPS) automates standard preparation, sample dilution and the addition of other solutions to each sample such as modifiers and internal standards. A SIPS accessory is ideal if you want to reduce manual sample preparation tasks, which take a lot of time and introduce errors.

Switching valves

Switching valves increase productivity and reduce gas consumption on ICP-OES or ICP-MS instruments. The valves work by preloading the next sample into the valve while the instrument is measuring the previous sample. A switching valve is recommended if you regularly measure large numbers of samples. A valve will pay for itself by reducing the amount of argon consumed.

Hydride generation

A hydride generation accessory can be used with most atomic spectroscopy techniques to measure mercury and hydride-forming elements (such as As, Bi, Ge, Pb, Sb, Se, Sn, and Te) at ppb levels. The accessory controls the chemical reaction required to form hydrides.

On Agilent ICP-OES and MP-AES instruments you can use a Multimode Sample Introduction System (MSIS) to quickly swap between vapor generation mode and standard nebulizer mode, without having to change any hardware.

Temperature-controlled spray chamber

A temperature-controlled spray chamber, like the Agilent IsoMist, is recommended when measuring viscous oil samples or those containing volatile organic solvents. Note that a temperature-controlled spray chamber is standard on all ICP-MS and ICP-QQQ instruments.

Ultrasonic nebulizer

An ultrasonic nebulizer (like the one shown here from <u>CETAC Technologies</u>) is used with an ICP-OES instrument to improve sensitivity and measurement stability for environmental applications.

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U.S. and Canada 1-800-227-9770 agilent_inquiries@agilent.com

Europe info_agilent@agilent.com

Asia Pacific inquiry_lsca@agilent.com

DE44444.6577546296

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