

AAS, GFAAS, ICP or ICP-MS? Which technique should I use?

*An elementary
overview of
elemental analysis.*

Thermo Elemental

Start here.

If your laboratory is performing elemental analysis on solutions, there are a number of mature, effective spectrometric techniques you could use, including flame and furnace AA (Atomic Absorption), ICP (Inductively Coupled Plasma), and ICP-MS (ICP Mass Spectrometry).

Selecting the most appropriate tool for the job can sometimes appear to be a daunting task, especially since there is considerable overlap of capabilities. In fact, all of the techniques may be able to perform your particular analysis at acceptable levels of accuracy and precision.

However, by evaluating the relative strengths and weaknesses of each of the techniques, particularly as they may apply to the practical and performance requirements of your analysis, it is possible to establish a rational basis for decision making. In other words, it needn't be all that difficult.

Even if you're new to elemental analysis, this booklet will get you well on your way to selecting the best technique (or techniques) to meet your lab's needs.

Understanding how each technique works.

While it isn't necessary to grasp all of the complex technological details of each of the various elemental analysis instruments, for comparison purposes it is helpful to have a general understanding of basic principles. Let's start at the beginning, with atomic absorption.

Percent Relative Standard Deviation (% RSD)

The standard deviation expressed as a percentage of the total.

ppb

An abbreviation for parts per billion. 1 part in 1,000,000,000 or one microgram per liter.

ppm

An abbreviation for parts per million. 1 part in 1,000,000 or one milligram per liter.

ppt

An abbreviation for parts per trillion. 1 part in 1,000,000,000,000 or one nanogram per liter.

Plasma

A very high-temperature ionized gas composed of electrons and positively charged ions.

Precision

A measure of the spread of a series of repeat measurements about their mean value. This is normally expressed as the standard deviation or percent relative standard deviation. It is important to note that a small spread (that is, a low standard deviation) does NOT give any information on the accuracy of the result. It is possible for a result to display excellent precision, yet be inaccurate.

Reproducibility

The ability to read back (repeat) a standard or known solution as an unknown sample and obtain the value that you specified. Reasons that you don't get the same value back as you told the instrument include: drift, calibration fit, or noise in the data.

Resolution (Optical Spectrometer)

The width of an analytical peak at half its height expressed in nanometers. A measure of the instrument's ability to separate two overlapping peaks. At the point of resolution, two peaks of equal height are said to be resolved if you can see a 1/2 height or greater dip between the tops of the two peaks.

Resolution (Mass Spectrometer)

The width of an analyte's mass peak at 5% of its peak height – for a quadrupole ICP-MS this is usually ≥ 0.8 mass units.

Sample and skimmer cone

In ICP-MS, ions are sampled from the bulk plasma initially through an orifice in the sample cone into the expansion chamber, then by a second orifice in the skimmer cone into the ion lens region of the mass spectrometer.

Sample introduction system

The apparatus used to turn the sample into an ultra-fine aerosol that can be introduced into the atomizer without overwhelming it with either too much sample or particles which are too large, either of which will extinguish the plasma or flame by taking too much thermal energy from it.

Sample throughput

The rate at which samples can be analyzed and the results printed. Usually measured as samples per hour.

Short-term stability

The ability of the instrument to read back the value you specified as the value of the standard after one hour's drift, usually around 2%.

Spectrometer

Meter = to measure. Spectro = Spectrum. For optical spectrometers this is a series of colored bands dispersed from white light by means of a refracting material (prism) or by means of a diffractive device (grating). Detectors can be placed at exact locations in the spectrum to measure the presence of the desired element.

A mass spectrometer spectrum is a series of signals registering on the detector with increasing mass-to-charge ratio, each analyte having a distinct peak at a given mass-to-charge ratio.

Spray chamber

The nebulizer sprays a fine mist of the sample into the spray chamber. The spray chamber removes the large droplets from the mist that are highly variable in supply from one moment to the next. The spray chamber, therefore, must select only the tiniest of the droplets and all the large droplets must be pumped away. Only 3% of the droplets are allowed to reach the plasma and 97% of the sample goes to the waste container.

Torch

A very hot flame. A source of bright light. The quartz or glass tubes that make up a plasma torch. The outside tube is the torch coolant tube which typically has a flow of 15 to 20 lpm of Ar gas. This flow keeps the torch below its melting point. The middle tube is the auxiliary gas tube. The gas flow through this tube is typically between 0 and 3 lpm of Ar gas. This gas pushes the plasma higher in the coil and is used to keep the plasma away from the sample injector tube. The innermost tube is the sample injector tube which injects the very small droplets of sample into the base of the plasma fireball. These droplets come from the spray chamber. The droplets rise in the torch where they are dried, and the various steps of molecular decomposition and elemental excitation take place.

Wavelength

The distance between two peaks of a wave. When Thermo Elemental refers to wavelengths we usually are speaking of wavelengths of light.

Wavelength flexibility

The ability of an instrument to "see," or measure any wavelength without having to change any hardware.



Glossary

Accuracy

The degree of agreement between the measured result and the accepted or known value. If quantified, this may be expressed as a percentage difference. It is important to note that this is NOT the same as precision. It is possible for a result to be accurate but not precise, or very precise but not accurate.

Aerosol

An extremely fine mist generated by a nebulizer. This is the form in which the sample solution is presented to the flame or plasma for volatilization and subsequent measurement.

Analyte

The element whose concentration is being determined. The atomic spectroscopy techniques discussed in this primer determine the concentration of an analyte element by comparing the instrumental response for the sample to that of a series of standard solutions containing the analyte element of interest.

Atomic absorption

A method that measures the concentration of atoms of an element by passing light, emitted by a hollow cathode lamp of that element, through a cloud of atoms from a sample. Only those atoms that are the same as those in the lamp will absorb the light from the lamp. A reduction in the amount of light reaching the detector is seen as a measure of the concentration of that element in the original sample.

Atomic emission

A method that measures the concentration of atoms or ions of an element in a sample, using the light those atoms emit when heated to very high temperatures. Since the intensity of the light that is emitted by these atoms or ions is proportional to their concentration in the original sample, this technique is capable of providing quantitative, as well as qualitative information about the sample.

Calibration

The process of analyzing a series of known concentrations as standards to determine the instrumental response to changes in concentration. Typically, a blank and one or more standard solutions of known and increasing concentration are analyzed. The instrument software then constructs an equation of response vs. concentration. This is then used to calculate the concentration of analyte elements based on the instrument response when the unknown samples are analyzed.

Detection limits

The lowest concentration that can be measured. Usually defined as a signal that is at least three times the standard deviation of the background variation. The measurement of any signal is not perfect; there is always a certain amount of noise in the signal. The magnitude of three standard deviations is a range, which, in a large number of measurements, would be expected to include 99% of all the measurements. Therefore, if a signal is three times the standard deviation of the background, we can be 99% certain that it is real and not simply a "spike" in the background noise.

Dilution

To reduce the concentration of a sample solution by the addition of an appropriate acid or organic solvent. This may be done to reduce the concentration of an analyte so that it falls within the dynamic range of the instrument or to reduce the total dissolved salt concentration of an aqueous solution or viscosity of an organic solution so that it can be nebulized.

Dynamic range

The concentration range over which the instrument continues to read a higher signal for an increase in the concentration of the measured material and can be calibrated.

Hydride generation accessory

An accessory designed to generate free hydrogen that is allowed to bubble through the sample liquid. Certain elements react with the hydrogen gas to form hydrides of those elements. Elemental hydrides are in the form of a gas so it is easy to separate them from the liquid. These gases are allowed to enter the sample cell where they are atomized. Because all of the element in the gas is exposed to the source, the signal is much larger than if it were introduced as a liquid using a nebulizer (only about 5-10% efficiency). Therefore, much lower concentrations of the element (such as As, Se, Sb and Pb) can be detected.

Ions

An atom which has lost one or more electrons becoming positively charged due to the fact that it now has more protons than it has electrons. Normally atoms are neutral in charge, electrons = protons, but if an atom loses an electron it becomes an ion and can be directed by electromagnetic fields.

Laser accessory

An accessory designed to use a UV laser to ablate (erode away) the surface of conductive or non-conductive materials. The ablated materials are in the form of a fine particulate aerosol which is carried into the plasma through the sample tube. This accessory is very good at sampling difficult to digest materials such as biological materials, rocks, glasses and ceramics.

Linear range

The range of concentrations of a sample which produces a detector signal that increases linearly (a straight line) with a corresponding linear increase in concentration. If the concentration of the sample doubles, the detector signal doubles.

Long-term stability

Usually measured as the amount of drift an instrument exhibits, per hour, as a percentage of the calibrated value. If you calibrate at a value of 10 ppm and after an hour the instrument reads back a value of 10.4 ppm the drift is 0.4 ppm /hour or 4%/hr.

Mass

In mass spectrometry (ICP-MS) "mass" refers to atomic mass-charge ratio and to the element being measured. Each element has a characteristic mass(es) in the spectrum.

Nebulizer

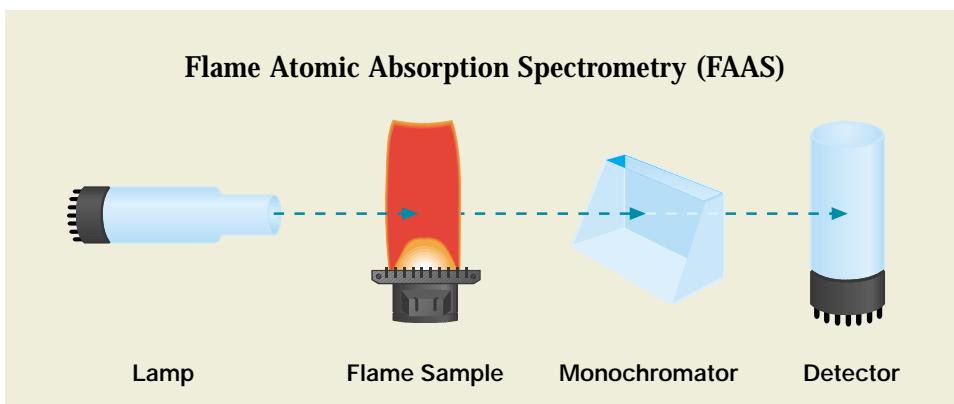
A device that is used to convert the sample solution into an aerosol or mist of tiny droplets. The nebulizer may produce this aerosol by means of gas pressure or the use of an ultrasonic transducer. This latter produces much more aerosol from a given volume of sample; so large an amount that it must be subjected to additional drying steps prior to introduction into the plasma. (Ultrasonic nebulization is not used with AAS.)

Flame Atomic Absorption Spectrometry (FAAS).

In flame atomic absorption spectrometry, either an air/acetylene or a nitrous oxide/acetylene flame is used to evaporate the solvent and dissociate the sample into its component atoms. When light from a hollow cathode lamp (selected based on the element to be determined) passes through the cloud of atoms, the atoms of interest absorb the light from the lamp. This is measured by a detector, and used to calculate the concentration of that element in the original sample.

The use of a flame limits the excitation temperature reached by a sample to a maximum of approximately 2600°C (with the N₂O/acetylene flame). For many elements this is not a problem. Compounds of the alkali metals, for example, and many of the heavy metals such as lead or cadmium and transition metals like manganese or nickel are all atomized with good efficiency with either flame type, with typical FAAS detection limits in the sub-ppt range.

However, there are a number of refractory elements like V, Zr, Mo and B which do not perform well with a flame source. This is because the maximum temperature reached, even with the N₂O/acetylene flame, is insufficient to break down compounds of these elements. As a result, flame AAS sensitivity for these elements is not as good as other elemental analysis techniques.



Strengths

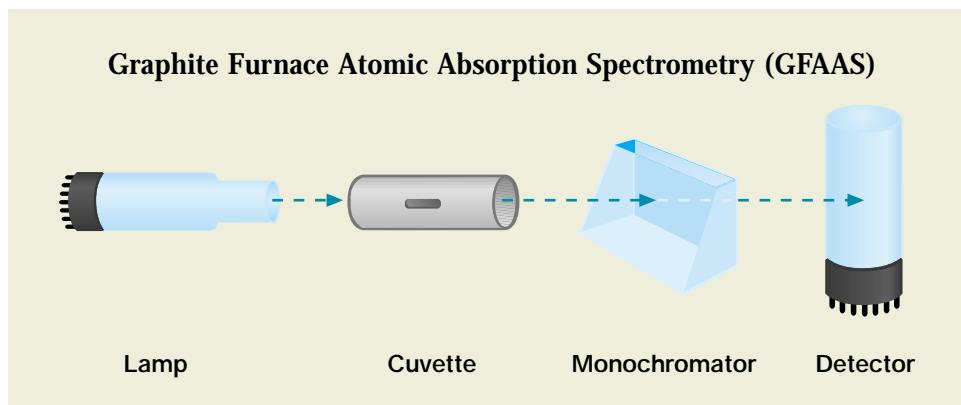
- Easy to use
- Very fast
- Lowest capital cost
- Relatively few interferences
- Very compact instrument
- Good performance
- Robust interface

Limitations

- Moderate detection limits
- Element limitations
- 1-10 elements per determination
- No screening ability

Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

This technique is essentially the same as flame AA, except the flame is replaced by a small, electrically heated graphite tube, or cuvette, which is heated to a temperature up to 3000°C to generate the cloud of atoms. The higher atom density and longer residence time in the tube improve furnace AAS detection limits by a factor of up to 1000x compared to flame AAS, down to the sub-ppb range. However, because of the temperature limitation and the use of graphite cuvettes, refractory element performance is still somewhat limited.

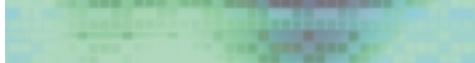


Strengths

- Very good detection limits
- Small sample size
- Moderate price
- Very compact instrument
- Few spectral interferences

Limitations

- Slower analysis time
- Chemical interferences
- Element limitations
- 1-6 elements per determination
- No screening ability
- Limited dynamic range



Element	Flame AAS (ppb)	GFAAS (ppb)	ICP AES (Radial) (ppb)	ICP AES (Axial) (ppb)	ICP-MS (ppt)
Nb	2000		4		0.01-0.1
Nd	850		2		0.01-0.1
Ni	10	0.24	6	0.4	0.1-10
Os	100		5		0.01-0.1
P	4000	100	18	13	>1,000
Pb	10	0.04	14	1	0.01-0.1
Pd	10	0.5	2		0.01-0.1
Pr	5000		0.8		0.01-0.1
Pt	75	4.5	20		0.01-0.1
Rb	5	0.06	35		0.01-0.1
Re	800		11		0.01-0.1
Rh	3	0.4	5		0.01-0.1
Ru	100	0.75	4		0.01-0.1
S			20	28	>1,000
Sb	40	0.35	18	2	0.01-0.1
Sc	30		0.2	0.05	1-10
Se	500	0.65	20	5	1-100
Si	200	0.8	5	2	>1,000
Sm	750		7		0.01-0.1
Sn	95	0.6	0.1	0.01	0.01-0.1
Sr	2	0.1	0.1	0.01	0.01-0.1
Ta	1500		9		0.01-0.1
Tb	700	0.2	5		0.01-0.1
Te	30	0.5	27		1-10
Th			17		0.01-0.1
Ti	70	1.6	0.6	0.09	0.1-1
Tl	20	0.75	16	3	0.01-0.1
Tm	20		1.5		0.01-0.1
U	40000		3.5	0.4	0.01-0.1
V	50	0.7	2	0.5	0.01-10
W	750		17		0.01-0.1
Y	350		0.2		0.01-0.1
Yb	4	0.15	0.3		0.01-0.1
Zn	1.0	0.0075	1	0.06	0.1-10
Zr	1500		0.8		0.01-0.1

* Information combined from a number of sources;
not indicative of any one instrument.

Typical detection limits of elemental analysis techniques.*

The following DL's are calculated at 3σ . The detection limits listed are representative of the technique and do not represent the performance of a particular instrument. All ICP-MS values are based upon quadrupole ICP-MS performance; lower levels of detection are available in magnetic sector ICP-MS systems.

Element	Flame AAS (ppb)	GFAAS (ppb)	ICP AES (Radial) (ppb)	ICP AES (Axial) (ppb)	ICP-MS (Quad) (ppt)
Ag	2	0.05	2	0.5	0.01-0.1
Al	30	0.25	6	1.5	0.1-10
As	300	0.33	12	2	1-10
Au	8	0.15	6	0.6	0.01-0.1
B	500	43	0.5	0.2	10-100
Ba	20	0.4	0.2	0.04	0.01-0.1
Be	1	0.025	0.2	0.06	0.1-1
Bi	50	0.3	18	2	0.01-0.1
C			50		
Ca	1	0.04	0.03	0.03	1-100
Cd	1.5	0.02	1	0.1	0.01-0.1
Ce	100,000		8		0.01-0.1
Co	5	0.5	2	0.5	0.1-1
Cr	6	0.025	2	0.4	0.1-1
Cs	4	0.3	3200		0.01-0.1
Cu	3	0.07	2	0.3	0.1-1
Dy	40	1.8	0.3		0.01-0.1
Er	35	3.8	0.7		0.01-0.1
Eu	1.5	0.8	0.3		0.01-0.1
Fe	6	0.06	1	0.3	0.1-100
Ga	65	23	7		0.1-10
Gd	2000		3		0.01-0.1
Ge	100	0.5	10		1-10
Hf	2000		4		0.01-0.1
Hg	145	18	9	1.2	1-10
Ho	60		0.5		0.01-0.1
In	40	0.3	18		0.01-0.1
Ir	500	4	4		0.01-0.1
K	2	0.02	6.5	0.5	0.1-100
La	2000		0.02		0.01-0.1
Li	2	0.1	1		0.01-1
Lu	300		0.05		0.01-0.1
Mg	0.3	0.01	0.1	0.03	0.1-1
Mn	2	0.03	0.3	0.05	0.1-1
Mo	20	0.14	4	0.5	0.01-0.1
Na	0.3	0.05	1	0.2	0.1-100

3 sigma detection limits in deionized water.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, or ICP).

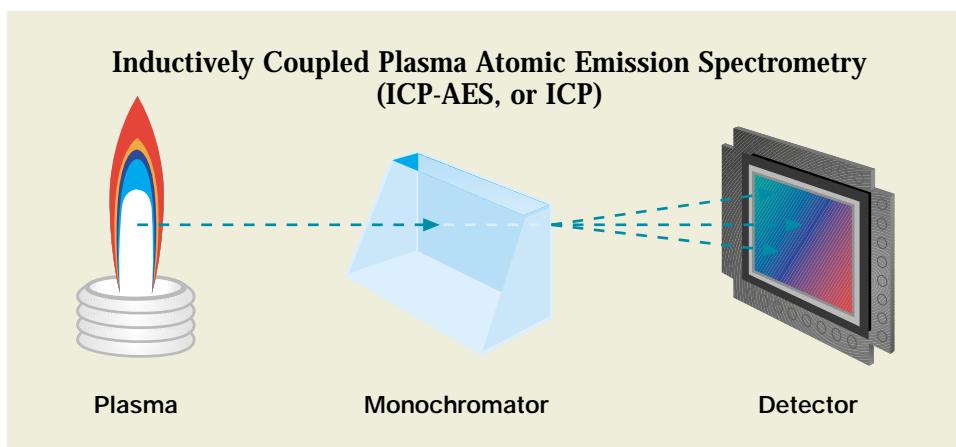
ICP-AES, often referred to simply as ICP, is a multi-element analysis technique that uses an inductively coupled plasma source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength. A detector measures the intensity of the emitted light, and calculates the concentration of that particular element in the sample.

When undergoing ICP analysis, the sample experiences temperatures as high as 10,000°C, where even the most refractory elements are atomized with high efficiency. As a result, detection limits for these elements can be orders of magnitude lower with ICP than with FAAS techniques, typically at the 1-10 parts-per-billion level.

ICP instruments come in two “flavors,” radial and axial. In the traditional radial configuration, the plasma source is viewed from the side, across the narrow emitting central channel of the plasma. Many newer systems view the emitting channel horizontally along its length; this is known as the axial method. 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.*

Simultaneous ICP instruments can screen for up to 60 elements in a single sample run of less than one minute, with no compromise of precision or detection limits. Sequential ICPs can provide analytical results for about five elements per minute.

* It should also be noted that some instruments, such as Thermo Elemental's IRIS Intrepid, can accommodate both viewing modes.



Strengths

- Easy to use
- Multi-element
- High productivity
- Very economical for many samples and/or elements
- Few chemical interferences
- Robust interface
- Excellent screening abilities
- High total dissolved solids
- Solid and organic samples

Limitations

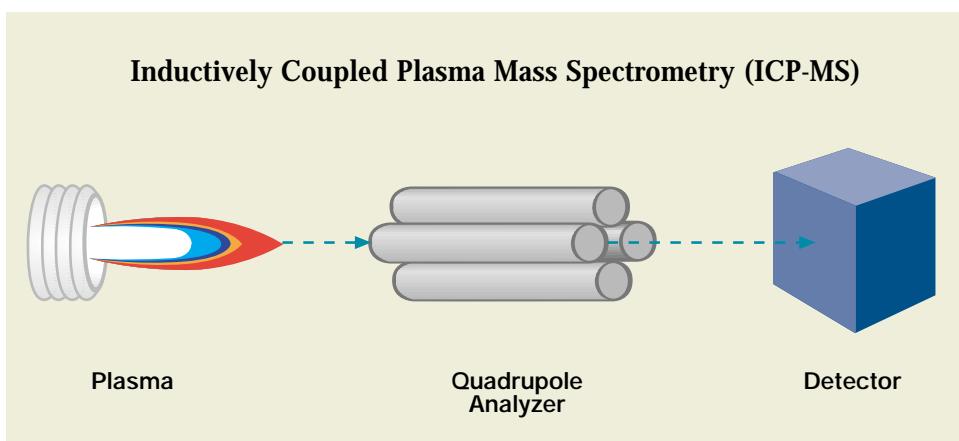
- Moderate to low detection limits (but often much better than FAAS)
- Spectral interferences possible
- Some element limitations

Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

ICP-MS is a multi-element technique that also uses an ICP plasma source to dissociate the sample into its constituent atoms or ions. However, in this case, the ions themselves are detected, rather than the light that they emit. The ions are extracted from the plasma and passed into the mass spectrometer, where they are separated based on their atomic mass-to-charge ratio by a quadrupole or magnetic sector analyzer.

The high number of ions produced, combined with very low backgrounds, provides the best detection limits available for most elements, normally in the parts-per-trillion range. It is important to remember that detection limits can be no better than lab cleanliness allows.

Quadrupole mass spectrometers are most common in ICP-MS, yet magnetic sector instrumentation fulfills exacting requirements that demand the ultimate detectability and isotope ratio measurement.



Strengths

- Excellent detection limits
- Multi-element
- High productivity
- Very economical for many samples and/or elements
- Wide dynamic range
- Isotopic measurements
- Fast semiquantitative screening
- Hybrid techniques
 - LA-ICP-MS (solids)*
 - LC-ICP-MS (speciation)*
- Easily interpreted spectra

Limitations

- Some method development skill required
- Higher initial capital cost
- Some spectral interferences, but well defined
- Limited to <0.2% dissolved solids

*LA = laser ablation LC = liquid chromatography

So, where did you come out?

It's unlikely that a single technique is going to perfectly suit all of a laboratory's needs. Unless you have unlimited space, more than enough skilled staff, and a surplus budget, you'll probably have to make some compromises.

You should also keep an eye to the future, and

try to envision what changes may occur in your analytical requirements. If possible, allow some room for system expansion.

The following table summarizes the discussion in the preceding pages, and may serve as a brief refresher as you embark on your selection process.

Summary of elemental analysis techniques

	Flame AAS	GFAAS	ICP-AES	ICP-MS
Detection limits	Very good for some elements	Excellent for some elements	Very good for most elements	Excellent for most elements
Sample throughput	10-15 secs per element	3-4 mins per element	1-60 elements/minute	All elements in <1 minute
Dynamic range	10^3	10^2	10^6	10^8
Precision short term long term	0.1-1.0% 2-beam 1-2% 1-beam < 10%	0.5-5% 1-10% (tube lifetime)	0.1-2% 1-5%	0.5-2% 2-4%
Interferences Spectral Chemical (matrix) Physical (matrix)	Very few Many Some	Very few Very many Very few	Many Very few Very few	Few Some Some
Dissolved solids in solution	0.5-5%	> 20% (slurries)	0-20%	0.1-0.4%
Elements applicable to	68+	50+	73	82
Sample volumes required	Large	Very small	Medium	Very small to medium
Semiquantitative analysis	No	No	Yes	Yes
Isotopic analysis	No	No	No	Yes
Ease of use	Very easy	Moderately easy	Easy	Moderately easy
Method development	Easy	Difficult	Moderately easy	Difficult
Unattended operation	No	Yes	Yes	Yes
Capital costs	Low	Medium to high	High	Very high
Running costs	Low	Medium	High	High
Cost per elemental analysis				
High volume – few elements	Low	High	Medium	Medium
High volume – many elements	Medium	High	Low-Medium	Low-Medium

Cost.

Finally, there's the budget – not just the initial cost of the capital equipment, but the true cost of ownership, which includes getting the lab ready for the instrument, and the actual cost of running samples. The purchase cost is very straightforward and usually well-understood, but the other two are often forgotten or underestimated.

Capital costs

Obviously, because there are many instruments available from a number of manufacturers, and because so many options and configurations are possible, it is difficult to put absolute values on capital costs. However, the table below can serve as a starting point. Remember, though, that accessories or options may add considerably to the purchase price.

Roughly, you can expect to pay from around \$15-20,000 for a base configuration flame AA system, and compute the other costs from there.

Relative System Costs

Flame AAS	1x
Furnace AAS	2x
Sequential ICP-AES	4-5x
Simultaneous ICP-AES	5-7x
ICP-MS	10-20x

Installation costs

Your laboratory may require significant changes before adding an elemental analysis instrument. For example, all these systems require fume extraction. ICP-MS or GFAAS sometimes require clean room conditions (Class 100 or better) to operate at the ppt level. ICP-based systems (ICP-AES or ICP-MS) require high-volume gas installations.

For GFAAS or ICP-MS use, your reagents may also need to be upgraded from normal analytical grade to high-purity grade. AA-grade standards, which often contain minor impurities, are suitable for AA analyses, but are not adequate for ICP-AES or ICP-MS.

You'll find considerable variations in the quantities of common supplies like argon, for instance, consumed during an analysis. GFAAS only uses about 3.0 L/min of argon; ICP-AES and ICP-MS both require around 15-20 L/min. On the other hand, the ICP techniques are much faster for a given workload and, therefore, will run for less time.

Operating costs

The following table outlines the typical consumable items and utilities required by the various techniques.

FAAS	acetylene/nitrous oxide gases (compressed air source) hollow cathode lamps reagents and standards power
GFAAS	argon gas hollow cathode lamps graphite tubes and cones reagents and standards power cooling water
ICP-AES	argon gas quartz torches reagents and standards pump tubing power cooling water
ICP-MS	argon gas quartz torches sampling and skimmer cones reagents and standards pump tubing power cooling water

Now let's narrow it down.

Before comparing the relative merits of the various analysis techniques, it's a good idea to clearly define the task at hand. What is the instrument going to measure? Where will it be located? Who's going to do the work?

Real-world questions to ask:

What is the application?

What are the sample types to be analyzed?

What elements and concentration ranges are required?

How many elements will be determined per sample?

What are the accuracy and precision requirements?

Are the analytical requirements likely to change
on a regular basis?

Are there regulatory or legal issues to take into consideration
(e.g., CRDLs*, or specific analysis protocol requirements)?

How many samples will be analyzed per day?

Who will be operating the instrument?

What level of operator expertise is available?

How much lab space is available?

And (of course) what will the budget allow?

* CRDL is an EPA-defined acronym for Contract Required Detection Limit.

Application.

Actually, all of the various techniques are used in broadly similar application areas, such as Environmental, Metallurgy and Mining, Pharmaceutical/Biotech, Semiconductor Manufacturing, Agriculture, Food & Beverage, Chemicals/Petrochemicals, Clinical and Utilities.

While there are some applications better suited to one or another of the techniques based on the elements to be analyzed (e.g., Rare Earth Element analysis is generally easier with quadrupole ICP-MS, whereas sulfur analysis is better done with ICP or with magnetic sector ICP-MS), it is generally difficult to differentiate between the techniques solely on the basis of the application.

The Periodic Table below may be of some help in narrowing down your selection. But, as you can see, there is considerable overlap for many classes of elements.

1 H 1.008													
3 Li 6.941	4 Be 1.008												5 B 10.81
11 Na 22.99	12 Mg 24.31												13 Al 26.98
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	
87 Fr (223)	88 Ra (226)	89 Ac (227)		58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	
				90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	

ICP/ICP-MS/AA

ICP-MS

ICP/ICP-MS

ICP

Speed of Measurement.

How many samples can a particular technique analyze in a given time? How many elements can be determined? For each sample, the measurement cycle consists of three steps:

An equilibration period in which sample is taken from the sample container, transported to the atom cell, and the analytical signal reaches stability.

ICP-MS and ICP-AES systems have similar new-sample delay times, which may be up to 60 seconds long. FAAS is much quicker, typically only about 5 seconds. GFAAS systems can take up to 2 minutes to dry and ash the sample prior to measurement.

A measurement period during which the signal is measured for the element(s) and, if necessary, their background points.

A rinse-out period during which the sample is removed from the source. This step may be carried out concurrently with the first; i.e. the next sample may be used to rinse out the previous one. For AAS and sequential ICP-AES systems, there is a further period while the next element line is selected.

ICP-MS and simultaneous ICP-AES systems make the fastest measurements; all analytes in a sample can be measured in about 2-5 minutes. Sequential ICP-AES systems take about 10 seconds per analyte line, including the time taken to select the line. The sequence is to measure all the analytes in a sample, one after another, then go to the next sample and measure all the lines again.

FAAS generally requires about 4 seconds per measurement, but the sequence is different. All samples are measured at a single analyte line, then the next lamp is selected and all samples are measured again.

GFAAS measurement time is less than 5 seconds for a single result at a single analyte line. However, several repeats per sample may be necessary with GFAAS to obtain satisfactory precision.

Overall the speeds are typically as follows:

ICP-MS:	All elements in 2-5 minutes
---------	--------------------------------

ICP-AES (Simultaneous):	All elements in 2-5 minutes
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ICP-AES (Sequential):	5-6 elements per minute
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FAAS:	4 seconds per element
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GFAAS:	2-3 minutes per element
--------	----------------------------

Clearly, the total analysis time taken by the different techniques will depend on the number of elements to be measured per sample. As a result, the speed parameter provides a relatively solid base for deciding on one technique over another (all other factors being equal):

- For less than 5 elements per sample, FAAS is often the quickest technique, depending on the total number of samples.
- For 5-15 elements, sequential ICP-AES is the optimum choice.
- Above 15 elements, either ICP-MS or simultaneous ICP-AES is the best choice.
- GFAAS will always be the slowest of the techniques (however, it may still be the method of choice for other reasons).



Ease of Use.

FAAS systems are usually very easy to set up and run. They are capable of some degree of automation but should not be run unattended, due to the flammable gas risk. Method development is easy and a vast library of methods exists.

GFAAS systems are somewhat more difficult to set up because of the accuracy of sample injection required to achieve the best results. Also, the limited working lifetime of the graphite tubes requires more frequent set up. Furnace method development can be difficult, and may require considerable expertise. Fortunately, a substantial methods library exists. Furnace AA systems are capable of a high degree of automation; because they only use inert argon gas, they can safely run unattended.

ICP-AES systems are easy to set up and have to be adjusted relatively infrequently. If there are major spectral interferences, method development can be complicated; however, the use of high-resolution spectrometers can minimize this problem. In general, though, method development is moderately easy, although the library of methods is less than for the AAS and GFAAS techniques. ICPs are capable of a high degree of automation, and can run unattended.

ICP-MS systems are getting easier to set up for routine analysis. Some parts of the system (e.g., the interface cones) may need regular attention to preserve performance. Method development can be more involved than with the other techniques and requires a higher level of expertise. ICP-MS systems can be fully automated, and can run unattended.

Operator Skill.

Not every technique requires a trained scientist for everyday operation. In fact, there is an increasing trend in many industries to use less skilled technicians for routine analysis tasks.

Although today's "point and click" software has greatly simplified the operation of even the most complicated equipment, software can't substitute for understanding. It is important to consider the technical level of laboratory personnel who are going to be operating the instrument, and to allow for additional training – or possibly even additional staff – if required.

Generally speaking, flame AAS is quite easy to set up and to use, and requires minimal operator skill. Furnace AA can be considerably more difficult to operate, calling for a relatively high level of knowledge and ability.

ICP-AES falls between these two, particularly for production-type applications, and is a bit easier to master than GFAAS, both in view of modern software capabilities, and the considerable body of literature available.

ICP-MS is a newer technique. Its application library, while growing rapidly, is not as complete as for the other methods. To consistently achieve superior results and reliable, high-quality data, you will probably need a somewhat more skilled person in charge of the instrument, although setting up the machine to run predesigned methods is a simple process.

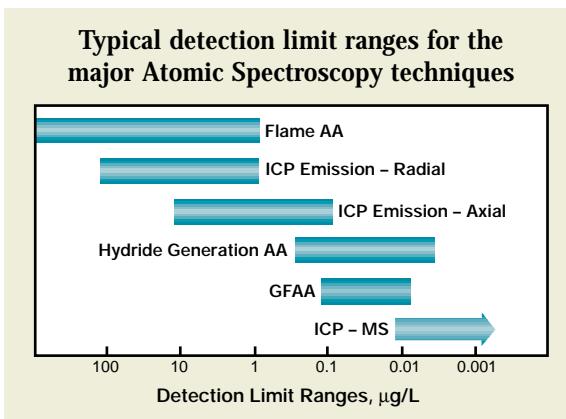
6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	2 He 4.003
14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Detection Limits.

The detection limits that can be achieved by each of the various techniques may help you decide which tool is best for the task. For example, in the field of environmental analysis, the CRDLs (Contract Required Detection Limits) specified by the USEPA for toxic metals in drinking water are considerably lower than the detection limit capabilities of FAAS, at least without some form of preconcentration.

As a rule of thumb, ICP-MS produces the best detection limits (typically 1-10 ppt), followed by GFAAS, (usually in the sub-ppb range) then ICP-AES (of the order of 1-10 ppb) and finally FAAS (in the sub-ppm range).

The table below shows typical detection limit ranges for each of the techniques, including variations such as hydride generation AA and both radial and axial ICP. A more complete, element-by-element table of detection limits appears on pages 16 and 17.



Precision.

"Precision" is a measure of the confidence you can have in your measured results. The lower the % RSD (Relative Standard Deviation) of the results, the higher the confidence.

Short-term precision generally refers to measurements made over a period of 5-10 minutes; long-term precision is generally measured over several hours of operation.

For FAAS, short-term precision is in the range of 0.1-1.0%. The long-term precision depends on the spectrometer optics; double-beam types are capable of long-term precision of 1-2%, where single-beam optics are typically in the 5% range.

Primarily because of difficulties in injecting very small volumes, GFAAS short-term precision is generally in the range of 0.5-5%. Long-term precision is highly dependent on the tube type and condition.

ICP-AES short-term precision is reasonably good, around 0.1-2%, and even over periods of several hours, should be no worse than 1-5%. Simultaneous spectrometers (where all the analyte measurements for a sample are made at the same time) generally have superior short- and long-term precision compared to sequential systems (where measurements for each analyte are made one after the other). Use of internal standardization can significantly improve precision for simultaneous instruments.

Short-term for ICP-MS is in the range 0.5-2%, with long-term precision around the 4% level. Use of internal standardization or the more costly method of isotope dilution can significantly improve precision.

Long-term precision in any of the techniques can be improved by more frequent instrument calibration or drift correction techniques.

Generally samples with higher matrix levels will exhibit worse short- and long-term precision. The use of internal standards and drift correction in ICP and ICP-MS will dramatically improve results.

Dynamic Range.

Dynamic range of the various techniques is important, because it directly affects the amount of dilution necessary in preparing solutions. A wider linear range means fewer standards are needed.

FAAS and GFAAS have limited dynamic ranges, of the order of only 10^2 - 10^3 ; therefore solutions must be held in a narrow range of concentrations.

ICP-AES has a considerably wider dynamic range, up to 10^6 , making it a more suitable technique for highly concentrated samples, or samples with widely varying concentrations of analyte elements. It can be considered a technique capable of measuring from trace to percent levels.

ICP-MS typically operates at much lower concentration levels so that linear ranges up to 10^8 can be achieved for some analytes. In standard practice, however, ICP-MS is a technique for ultra-trace to trace levels to ppm levels.

Elemental Interferences and Other Problems. All of these elemental analysis techniques suffer from various interference effects. The severity of these effects can make a big difference in results for real samples. Broadly speaking, interferences can be classed as (a) *Spectral* – due to atomic or molecular fine structure in the spectrum; (b) *Background* – due to broad features or electronic baseline; (c) *Matrix effects* – primarily due to physical or chemical influences.

Flame AAS

(a) *Spectral* – There are virtually no spectral interferences of any significance in flame AAS.
(b) *Background* – Background effects do exist and have to be compensated for by using some form of background correction. A deuterium-based lamp is commonly used for this purpose.
(c) *Matrix effects* – These are more serious, although use of the hotter N₂O/acetylene flame can minimize many of the chemical effects. Ionization becomes a problem when the hotter flames are used; ionization buffers are required. Viscosity/surface tension effects in the spray chamber/nebulizer can require the use of matched standards.

Graphite furnace AAS

(a) *Spectral* – There are virtually no spectral interferences in graphite furnace AAS.
(b) *Background* – Background effects do exist on a major scale and have to be compensated for by using deuterium or Zeeman background correction. The background usually arises from vaporized matrix components which are being atomized at the same time as the analyte.
(c) *Matrix effects* – These can be very serious and generally occur in the vapor phase; various chemical modifiers and platforms within the graphite tube are used to control these interferences. In addition, injection of samples into the tube is subject to viscosity/surface tension problems.

ICP-AES

(a) *Spectral* – Spectral interference problems are fairly common in this technique due to the line-rich spectra produced by the hot plasma source. They can be minimized by using high-resolution spectrometers or using inter-element correction factors. The simplest cure is to move to an alternative analyte line (although this may cause a loss of sensitivity).

(b) *Background* – Background effects do exist in ICP-AES and require the use of off-line background correction techniques, or, increasingly, sophisticated chemometrics. Molecular species (such as OH from the water solvent) can cause peak or band structures. It may be possible to minimize them by careful selection of plasma conditions or moving to an unaffected analyte line.
(c) *Matrix effects* – Chemical matrix effects are minimal, but physical effects such as viscosity and surface tension effects in the spray chamber/nebulizer mean that matched standards may be required. Use of an internal standard is a common way of overcoming this problem.

ICP-MS

(a) *Spectral* – Spectral interference problems in ICP-MS are relatively few and well-documented. They occur when species (which may be molecules or doubly-charged ions) have the same or very similar mass as the analyte. They are known as isobaric interferences and cannot be resolved at resolutions typically found in common quadrupole mass spectrometers.

Inter-element correction factors can be used (similar in principle to inter-element correction factors in ICP-AES) or other, lower abundance isotopes must be selected with a resulting loss of sensitivity.

Many of the interferences can now be overcome using cool plasma or collision cell technology to break up the molecules or by using high-resolution magnetic sector ICP-MS.

(b) *Background* – No broad background species exist for MS as can be found with optical techniques. Electronic background is low, but is a factor that can differentiate some ICP-MS systems. Many ICP-MS determinations are said to be “background limited,” which is a term that signifies that the contamination in the blank or memory effects which limit the detection limit. At the part-per-trillion level, this can be significant.

(c) *Matrix effects* – Chemical matrix effects can be a problem in ICP-MS, resulting in impaired accuracy if not addressed. They result from the presence of the argon plasma gas and also the solvents/acids used in preparing the samples. For this reason care should be taken when choosing the acids for dilution, nitric acid being the preferred choice.

In addition, physical effects (such as viscosity and surface tension effects in the spray chamber/nebulizer) may require the use of matched standards. As with ICP-AES, use of an internal standard can overcome this problem.

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