application note

AAS or ICP-OES—Are They Competing Techniques?

Introduction

The analyst today is faced with a bewildering choice of techniques when deciding to enter the field of elemental analysis. Should it be Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Arc Spark (ICP-AS)?

One of the areas where the choice is supposedly most difficult to resolve concerns AAS and ICP-OES. When ICP-OES was developed in the mid-1970's, the scientific press read 'ICP is going to sweep AAS away and take over as the only analytical technique worth considering for liquid samples'. Today, whilst there has been a significant move by analysts away from AAS towards ICP-OES, it is important to remember that in fact the techniques are complimentary rather than competitive.

Applications

AAS and ICP-OES are solution-based analytical techniques, although solid sampling has been pursued in both types of equipment with varying degrees of success. Due to commonality of sample type and sample preparation, it is understandable that both techniques serve the same analytical needs. The following sample types can be analysed by either technique without the need for any major pre-treatments:

- Metals and alloys
- Ores, rocks and minerals
- Petroleum products
- Water and effluents
- Agricultural products
- Foods and beverages
- Horticultural research
- Environmental
- Clinical and pharmaceutical
- Cements, glasses and ceramics

It is difficult, therefore, to differentiate between them on the basis of application area, although some applications are better suited to one technique for particular reasons. Those reasons are summarized as ***element type*** and ***detection limit.***

Element Type and Detection Limit

Using these two criteria, it is possible to highlight areas in which the techniques offer different performance capabilities, thus simplifying the choice.

Considering AAS first, particularly flame analysis, the atom source is either an air/acetylene or a nitrous oxide/acetylene flame. This limits the excitation temperature reached by the sample to 2600K for an air/acetylene flame and 3000K for a nitrous oxide/acetylene flame. The residence time of an atom within the optical beam of the spectrometer, which determines the absorption, is extremely short, approximately 10^{-3} seconds, depending on the velocity of the flame gases. For many elements this is not a problem; compounds of the alkali metals, many of the heavy metals (lead, cadmium) and transition metals (manganese, nickel) are all atomized at high efficiency with either flame type.

However, there are a number of refractory elements like vanadium, zirconium and molybdenum which cause problems in flame AAS. The maximum temperature reached by the nitrous oxide/acetylene flame is insufficient to break down compounds of these elements and therefore sensitivity is poor.

With an inductively-coupled plasma source, the sample experiences temperatures estimated to be in the vicinity of 10000K. This results in atomization and excitation of even the most refractory elements with high efficiency so that detection limits for these elements with ICP-OES can be well over an order of magnitude better than the corresponding values for flame atomic absorption. For approximately half of the transition elements, the detection limits are within a factor of two for either flame AAS or ICP-OES.

Of the other transition elements, the higher temperature of the plasma produces superior detection limits. The lanthanides and phosphorus have significantly better detection limits for ICP-OES than flame AAS. Sulphur can only be measured by ICP-OES. A comparison of flame AAS detection limits in mg/L (ppm) with the corresponding ICP-OES detection limits is shown in Table 1 for GBC products.

From Table 1, many examples can be chosen which confirm the above statements when comparing detection limits. For example, detection limits for cadmium, copper and zinc are approximately the same by either technique, but for sodium and potassium, detection limits are much better with flame AAS. However vanadium, zirconium and boron detection limits using ICP-OES are respectively factors of 70, 500 and 500 better than the flame AAS detection limit.

When an AAS is fitted with a graphite furnace electrothermal atomizer the comparison changes dramatically. Although the graphite furnace is restricted to a similar maximum temperature to that of the nitrous oxide/acetylene flame, i.e., 3300K, the atom residence time is markedly greater (up to 1000 ms) and this results in sensitivities up to 100 times better than flame AAS values for many elements.

Table 2 lists GBC ICP-OES and graphite furnace AAS detection limits in µg/L. The values indicate that the improvement in performance of the graphite furnace accessory against ICP-OES is similar to the ICP-OES improvement over flame AAS. Thus most elements including refractory elements like vanadium and molybdenum are better analysed by the graphite furnace accessory. Nonetheless, ICP-OES maintains an analytical advantage when compared to graphite furnace AAS for elements such as boron and phosphorus.

For the geological sciences, rare earth elements are now becoming more important industrially, but their analysis has been very difficult because of their chemical similarity. There is also a wide variation in the concentration levels of individual rare earth elements in most geological materials. Some of the light rare earths such as lanthanum, cerium and neodymium are present at relatively high concentrations. Others may be present at levels 100 times lower, even in the same sample. Normal geological practice is to normalize sample results to the chondritic abundances (i.e., typical of levels found in chondritic meteorites, which are indicative of the element's cosmic abundance).

Comparison of the flame AAS and ICP-OES detection limits (Table 1) for rare earth elements indicates that flame AAS detection limits are unacceptable for analysis. Similarly graphite furnace AAS (Table 2) shows poor sensitivity because of the very refractory, carbide-forming nature of the rare earths. Cerium cannot be determined by AAS at all. As a result, ICP-OES is the obvious choice for solution-based analysis of these elements.

The analysis of metals in biological samples is another important requirement. Table 3 lists reference range concentrations for several toxic metals in serum (or whole blood for lead and cadmium) and urine samples. All the values are quoted in µg/L (ppb). Due to the viscous nature and high dissolved salts in these fluids, they are normally analyzed after a degree of dilution to reduce these two effects.

Comparison of these reference range values (without dilution) with the ICP-OES detection limits given in Table 2 indicates that ICP-OES cannot analyze these samples. For biological analysis with these types of samples and concentration levels, graphite furnace analysis is suitable. Therefore, as a technique, graphite furnace AAS is the primary method of analysis for body fluids as well as biological tissue samples. Most published methodology for biological materials involving ICP-OES is for tissue analysis where analyte levels may be concentrated during the sample dissolution stage of analysis.

These two cases represent a situation where decision-making is reasonably clear cut. In some situations neither technique can adequately cover all eventualities, so that a combination of ICP-OES and AAS would be the best choice.

When considering element type and detection limits, the following conclusions can be made:

1. In some cases there are no significant differences between detection limits for flame AAS and ICP-OES. In general, differences of up to a factor of two to three are not considered significant as they are within the normal day-to-day variation in most laboratories.
2. The more refractory the element, the more ICP-OES will be the favoured technique over flame AAS.
3. Graphite furnace AAS will always hold an absolute performance advantage over ICP-OES, except for the most refractory and carbide-forming elements.
4. ICP-OES offers significantly better sensitivity for the non-metal elements such as S, P and B.

These conclusions can be used by an analyst when deciding which type of instrument technique is suitable for their sample types.

Speed of Analysis

In a number of analytical applications, for example environmental analysis, speed can be an important factor. Those advocating simultaneous ICP-OES regard it is the only method worth considering for this task because it is so much quicker in operation. An instrument which analyses samples in minutes is only fast enough if the sample preparation time takes only a few minutes.

For each sample the analytical cycle consists of an equilibration period (where the sample is taken from the sample container into the spray chamber, then into the atomizer where it reaches stability), a measurement period (during which the emission or absorption signal is measured at the element wavelength, and background correction performed), followed by the wash through (as the previous sample is being removed from the atomizer and spray chamber; this may be carried out concurrently with equilibration by using the next sample to wash through the previous sample). For AAS and sequential ICP-OES the measurement period also incorporates a period of time as the next wavelength is selected.

To assess speed of analysis, assume the requirement is to analyse 10 elements per sample. Hence the techniques can be assessed in terms of the number of elements determined per hour.

1. Simultaneous ICP-OES

(a) A typical equilibration time for an ICP-OES system employing a peristaltic pump feed is relatively lengthy because of the low uptake rates (typically 1.5 mL/min) used for sample introduction. If the equilibration period is also used for the wash-through phase then a 25 second period may be required.

(b) Measurement with a simultaneous system does not involve any delays as the different wavelengths have previously been selected. Therefore only the actual measurement time is involved. Usually this is a total of 35 seconds for the integration and the background correction time period. This then gives a cycle time per sample of 60 seconds and a resulting sampling rate of 60 samples per hour. Therefore the system can measure at a rate of 600 element determinations per hour.

2. Sequential ICP-OES—Single and Dual Mono

(a) Equilibration times for sequential systems are identical to those for simultaneous systems, i.e., 25 seconds overall.

(b) Total slewing time between ten discrete wavelengths for sequential systems is typically 15 seconds. The computer software selects the order of analysis to reduce the time spent changing wavelength. Measurement times for 3 replicates at 2 seconds integration time including any background correction is of the order of 10 seconds. Cycle time is therefore 140 seconds per sample, (25+15+[10x10]), and the sampling rate is 25 samples per hour. Therefore the sequential system can measure at a rate of 250 element determinations per hour.

(c) With the option to increase sample throughput by the addition of a second monochromator, 10 elements per sample can be split into five elements for each monochromator, effectively halving the cycle time. The sample throughput of a dual monochromator instrument is therefore (25+7.5+[5x10]), providing a sampling rate of 44 samples per hour, or 440 element determinations per hour.

3. Flame AAS

(a) Due to the much higher uptake rates in AAS, equilibration times are short, typically 3 seconds. Wash through in most cases is done by using the next sample.

(b) Measurement time for any element is of the order of 6 seconds (2 second read, 3 replicates, which includes any background correction measurement). Sample changeover time is in the order of 3 seconds. Therefore the cycle time per sample is 12 seconds provided there is no change of element involved i.e., a rate of 300 determinations per hour.

(c) To determine 10 elements, AAS methodology involves 10 changes of hollow cathode lamps with the appropriate re-tuning of wavelength. Assuming the lamps have been pre-warmed before they are moved into their operational position, the average operator should take 1–2 minutes to achieve this. Therefore approximately 15 minutes will be required per hour for an operator to change conditions for 10 elements. Under these conditions an AA instrument measures at a rate of 225 determinations per hour.

4. Graphite Furnace AAS

In terms of speed, graphite furnace AAS is not competitive due to the long cycle time required for this technique. To obtain a single result requires a cycle time of up to 2 minutes, with a statistically valid result (3 replicates) taking about 5–6 minutes.

Therefore as speed of analysis becomes important, simultaneous ICP-OES is more likely to become the technique of choice, provided that several elements are to be determined in each sample.

Number of Elements per Sample

Table 4 shows the determinations per hour for the various techniques related to the number of elements analysed per sample. The rates are calculated on the basis of the times used in the previous section.

When less than 5 elements per sample are being analysed, flame AAS is competitive with either ICP-OES system on a throughput and cost per analysis basis. A simultaneous ICP-OES is approximately three times as fast as flame AAS for determinations of 10 elements per sample. If the number of elements per sample to be determined increases, the speed differential is even more favourable to simultaneous ICP-OES systems.

In contrast, sequential ICP-OES systems perform determinations at approximately the same rate as flame AAS systems. A sequential ICP-OES will be faster only when determinations of more than 10 elements per sample are required. The addition of a second monochromator to a sequential ICP-OES will provide a speed advantage of five elements per sample over flame AA. Further, the dual monochromator sequential ICP will be almost as fast as a simultaneous ICP when determining up to 10 elements per sample, providing a cost effective alternative.

In most laboratories, the average number of elements to be analyzed per sample typically lies between 5–20 and rarely exceeds 20. Therefore, under these conditions either AAS or sequential ICP-OES (single or dual monochromator) will be competitive with or faster than a simultaneous system. Only where a large analytical workload exists will simultaneous ICP-OES provide the fastest rate of analysis.

A further consideration when choosing between an AAS or ICP-OES system regards the type of element to be analyzed. Sequential ICP-OES instruments offer virtually unlimited element choice (although vacuum capability may be required to reach certain analytical wavelengths in the vacuum UV, below 200 nm). AAS does not offer such flexibility as the technique is limited by the requirement for element-specific hollow cathode lamps. However to increase the capability of an AAS instrument, additional hollow cathode lamps can be purchased at relatively low costs (on average US$200–$300).

Costs of Instrumentation

The final important consideration is the cost of the instrument, incorporating both the initial purchase and day-to-day running costs. In terms of purchase cost, flame AAS remains the least expensive technique and simultaneous (or simultaneous/sequential) ICP-OES the most expensive in approximately the following ratios:

Flame AAS	$ x
Flame and Furnace AAS	$ 2x
Single Mono Sequential ICP-OES	$ 3x
Dual Mono Sequential ICP-OES	$ 4x
Simultaneous ICP-OES	$ 6x

Clearly many analysts have switched from flame AAS to sequential ICP-OES because of the productivity enhancements, particularly when analyzing typically more than 10 elements per sample and because of the narrowing price differential. For analysts requiring an even greater sample throughput, a dual mono sequential ICP-OES offers great value, achieving the productivity of two ICPs for only a third of the extra cost.

TABLE 1
Detection Limits of ICP-OES versus Flame AAS for GBC Instrumentation

Element	ICP-OES	FLAME AAS	Element	ICP-OES	FLAME AAS
Ag	0.0008	0.002	Os	0.0002	0.1
Al	0.002	0.03	P	0.007	40
As	0.007	0.2	Pb	0.01	0.01
Au	0.002	0.01	Pd	0.004	0.01
B	0.001	0.5	Pr	0.009	6.0
Ba	0.0006	0.01	Pt	0.007	0.1
Be	0.00007	0.001	Rb	0.001	0.007
Bi	0.007	0.04	Re	0.003	0.6
C	0.01	-	Rh	0.02	0.004
Ca	0.00007	0.0005	Ru	0.01	0.06
Cd	0.0005	0.0004	S	0.003	-
Ce	0.02	-	Sb	0.009	0.04
Co	0.001	0.004	Sc	0.0003	0.04
Cr	0.002	0.003	Se	0.01	0.25
Cs	40	0.004	Si	0.005	0.1
Cu	0.0009	0.001	Sm	0.01	1.0
Dy	0.002	0.03	Sn	0.009	0.03
Er	0.0007	0.03	Sr	0.0002	0.002
Eu	0.0009	0.02	Ta	0.01	2.0
Fe	0.0007	0.005	Tb	0.006	0.5
Ga	0.01	0.06	Te	0.004	0.03
Gd	0.005	2.0	Th	0.007	-
Ge	0.02	0.2	Ti	0.0004	0.07
Hf	0.004	2.0	Tl	0.01	0.02
Hg	0.007	0.15	Tm	0.002	0.9
Ho	0.002	0.04	U	0.06	40
In	0.02	0.04	V	0.0007	0.05
Ir	0.007	0.4	W	0.008	1.0
K	0.02	0.003	Y	0.0006	0.2
La	0.001	2.0	Yb	0.0003	0.004
Li	0.0007	0.002	Zn	0.0006	0.0005
Lu	0.0003	0.3	Zr	0.002	1.0
Mg	0.00008	0.0003			
Mn	0.0002	0.002			
Mo	0.003	0.02			
Na	0.003	0.0002			
Nb	0.005	2.0			
Nd	0.01	1.0			
Ni	0.003	0.09			

NOTE
All values shown as mg/L (ppm). Detection limits are given as 2 sigma values (other manufacturers may report ICP-OES detection limits as 3 sigma values).

TABLE 2
Detection Limits of ICP-OES versus Graphite Furnace AAS for GBC Instrumentation.

Element	ICP-OES	FURNACE AAS	Element	ICP-OES	FURNACE AAS
Ag	0.8	0.005	Mn	0.2	0.01
Al	2	0.01	Mo	3	0.02
As	7	0.2	Na	3	0.005
Au	2	0.1	Ni	3	0.1
B	1	15	P	7	30
Ba	0.6	0.04	Pb	10	0.05
Be	0.07	0.02	Pd	4	0.3
Bi	7	0.1	Pt	7	0.2
Ca	0.07	0.01	Rb	1.4	0.05
Cd	0.5	0.003	Ru	10	1
Co	1	0.02	Sb	9	0.15
Cr	2	0.01	Se	10	0.5
Cs	40,000	0.2	Si	5	0.1
Cu	0.9	0.02	Sn	9	0.2
Dy	2	1	Sr	0.2	0.1
Er	0.7	2	Tb	6	0.1
Eu	0.9	0.5	Te	4	0.1
Fe	0.7	0.02	Ti	0.4	0.5
Ga	10	0.5	Tl	10	0.1
Hg	7	2	V	0.7	0.2
In	20	1	Zn	0.6	0.001
K	20	0.1			
Li	0.7	0.1			
Mg	0.08	0.004			

NOTE

All values shown as μg/L (ppb). Detection limits are given as 2 sigma values (other manufacturers may report ICP-OES detection limits as 3 sigma values).

TABLE 3
Reference range for elements determined in serum (whole blood) and urine by Graphite Furnace Analysis.

	Pb[3]	Cd[3]	As	Se	Cr	Ni
Serum[1]	90–140	<1	0.5–1.7	0.05–0.14	0.04–0.35	<5
Urine[2]	6.3–13.0	0.5–4.7	10–30	7–160	0.2–1.8	2.2–2.7

Note: All values in µg/L *(ppb)*

1. Taken from Subramanian, K.S., *Progress in Analytical Spectroscopy*, *9*,237-334,1986.
2. Taken from Iyenger, V. and Woittiez, J., *Clin Chem, 34*,474,1988.
3. Cadmium and lead values are for whole human blood.

TABLE 4
Number of determinations per hour for the analysis of 2, 5, 10 and 15 elements per sample.

Instrumentation	Elements per Sample			
	2	5	10	15
Simultaneous ICP-OES	120	300	600	900
Single Mono Sequential ICP-OES	120	200	250	290
Dual Mono Sequential ICP-OES	170	350	440	510
Flame Atomic Absorption	280	260	225	175

GBC Scientific Equipment Pty Ltd
A.C.N. 005 472 686

12 Monterey Road, Dandenong, Victoria, 3175, Australia
Phone: (03) 9213 3666 Fax: (03) 9213 3677
E-mail: gbc@gbcsci.com URL: www.gbcsci.com