4.1 Introduction

The emission lines of elements in a flame was the first form of properly studied spectroscopy. It took until the 1930s before it was used commercially for elemental analysis. Since that time, atomic emission spectroscopy has been a very important analytical technique, particularly in the metals and minerals sector. The development of the hollow cathode lamp at the CSIRO labs in Melbourne in the 1950s allows atomic absorption to become a useful technique, but further developments in emission spectroscopy and other techniques have led to its gradual loss of significance.

Flame emission is known as a low temperature emission technique (2000-3000K) and essentially remains important in simple filter-based instruments – flame photometers – for the analysis of sodium and potassium. High temperature instruments (> 5000K) have now become the most important for elemental analysis. This chapter will concentrate on high temperature instruments. The difference instrumentally between the two classes of emission instruments is in the energy source.

**CLASS EXERCISE 4.1**

*What advantages would high temperature sources have over low temperature ones?*

The two main energy sources for high temperature instruments are:

- **electricity** – electrical arcs or sparks are high power and temperature bursts of electrical energy capable of generating the high temperatures required to atomise and excite even solid samples
- **plasma** - the next state of matter above a gas is a plasma, which is a cloud of ionised gas (cations and electrons)

Emission instruments, regardless of the source, will have a basic configuration as shown in Figure 4.1. The sample goes through the stages shown in Figure 4.2.

**FIGURE 4.1 Components in a generic emission instrument**

**FIGURE 4.2 Changes in the sample in an emission instrument**
4.2 Instrument configurations

There are two basic instrument configurations possible for high temperature emission instruments:

- **Sequential** – the common system for most spectroscopic instruments, where only one emission line can be measured at any one time because there is only one detector, and a scanning monochromator is used to move from one wavelength to another,

- **Simultaneous** – where multiple detectors are available, either as a number of single units or a bank of semiconductor devices; in this case, a polychromator is used which splits up the light in the normal way, but has multiple exit slits at fixed positions for different emission wavelengths; scanning is not possible in these cases (as shown in Figure 4.3)

**FIGURE 4.3 Simultaneous detection of four emission lines**

Simultaneous instruments, based on PMTs, commonly have up to 30 detectors, which are fixed in position by the manufacturer to analyse set elements. The operator then selects the elements of interest through the software. However, such an instrument cannot produce a scan or analyse an element outside the fixed set.

A new development in simultaneous instruments has a semiconductor array in two dimensions, equivalent to 50,000 + individual detectors. All the radiation from the source is directed at the detector bank, rather than selected wavelengths. This instrument is capable of scans, and doing any emission line you want.
4.3 Electrical sources
From the 1940s to the current day, analysis of metals and minerals has been dominated by arc/spark emission instruments. For metals, the technique is ideal: it is multi-component, requires no sample preparation, and standard samples are readily available for matrix matching.

Electrical arcs and sparks produce high temperatures by the passage of concentrated electrical energy between two electrodes, one of which is, or contains, the sample. The difference between the two is important for electrical engineers, but less so for chemists. **Arches** are continuous, and use relatively low voltages and high currents, while **sparks** oscillate in power at high voltages (10000 V) and currents that are low on average (but high at the peak). The temperatures produced are around 5000 K.

The arc or spark is generated between two electrodes which are generally within a few millimetres of each other. One electrode is typically iron, while the other has the sample contained in some way.

The sample conditions vary depending on the sample nature, but the technique works best for solid samples, which does provide a considerable advantage over solution-based spectroscopic techniques. If the sample is conductive (e.g. metal), it forms the second electrode by itself. If the sample is not conductive (e.g. a ore sample), then it must be held as a powder in a conductive container, which is normally a small graphite cup.

While the technique requires little sample preparation, it is not non-destructive. the powder will be completely vaporised in the 5-20 seconds of electrical discharge. A metal will have a significant scar gouged into the surface.

These instruments are not as good for solutions, or where the matrix is unknown, and hence the technique was first replaced by flame AAS and now ICP emission spectroscopy.

4.4 Plasma sources
A plasma is matter which contains a substantial proportion of free electrons and positive ions, and is generally said to the fourth state of matter, beyond gases. There is theoretically no limit to the temperatures that can be sustained in a plasma: the sun is a plasma, where temperatures reach several million degrees.

The first commercial **inductively coupled plasma (ICP)** emission instrument was available in the late 1970s, but have really only become widespread since the late 1980s, as costs came down and reliability increased. By the turn of the century, it had become the standard device for atomic analysis for solutions, replacing flame AAS. It has not replaced spark emission for metals analysis.

**Plasma generation**
Plasmas in these instruments can be formed from a number of gases, even air, but the most common gas is argon. The plasma is generated in a **torch**, which is constructed of three concentric quartz tubes, through the argon (and the aerosol sample) are carried. A copper coil surrounds the top of the torch, and is connected to a radio frequency (RF) generator. Figure 4.4 shows a typical ICP torch.

When RF energy (typically 750-1500 W) is applied through the coils, an alternating current is set up, which in turn produces electric and magnetic fields in the gas stream. A spark is applied briefly, which ionises some of the Ar atoms. The magnetic field provides energy (inductively couples) to the electrons, which then collide with, and ionise more atoms, and so the plasma forms. The plasma is a brilliant white, with temperatures ranging from 5000-10000 K. The hottest point in the plasma is in the centre of the torch surrounded by the coils.

The sample is typically held in the plasma for a few milliseconds, plenty of time to go fully through the process in Figure 4.2. Collection of the emitted radiation, which is still the same basic set of lines analysed by AAS or FES, can be done in two different ways, which will discussed in a following section.
Advantages of plasma sources

- the extreme temperatures produce almost perfect atomisation, meaning that refractory compounds, such as calcium phosphate, do not survive; this reduces matrix interference to a very minor degree
- ionisation of elements, such as sodium, should be 100% at these temperatures, but is not because of the high concentration of electrons in the plasma; ions do form, but at these temperatures, emit their own characteristic wavelengths, and in some situations, it will be the ionic emission line that is used for analysis
- the absence of matrix interference means that the linear detection range is very great; typically 10,000 times
- higher temperatures mean more elements emit, so even non-metals such as P and S are routinely analysable
- higher temperatures also mean lower detection limits, and improvements in instrument and component design have moved the measurable concentrations for many elements down to 50 ug/L; the gain in sensitivity is not as great as you might expect, because of the necessary inefficiency of the nebulisation system (this part of the system will be discussed below)

Nebuliser

A nebuliser converts the liquid sample into a fine aerosol mist that can be transported to the plasma. There are two basic processes used in ICP nebulisers to break up the liquid into fine droplets:

- pneumatic – where gas pressure directly or indirectly breaks up the liquid
- ultrasonic – oscillations from an ultrasonic generator break up the sample into the aerosol, which is then carried by the gas

Pneumatic nebulisers are used in flame AAS instruments, and in a majority of ICP instruments as well. Table 4.1 compares the major nebulisers. One important issue with plasmas that does not arise with flames is that there is a limit to how much “foreign” material (ie sample) can be delivered before the plasma fails. Therefore, the early nebulisers had to be designed to be less efficient than those in flame AAS (typically 1-3% of sample reaches the torch).

The simplest, and original, is known as a concentric nebuliser. Here the gas flows past the end of a fine capillary leading into the liquid. This creates a suction which drags the liquid through to the end of the capillary, where the passage through the small hole causes the liquid to form droplets.

To reduce the block problem, Babington and V-groove nebulisers have been developed. These create an aerosol by the gas blowing through a thin film of the solution. In the Babington design, the liquid flows over the outside of a glass sphere which has an exit hole for the argon gas, while in the V-groove, the sample flows along a “valley” in the plastic block.

Ultrasonic nebulisers are the most recent development, and have been designed to achieve greater sensitivities across a range of difficult sample types, including slurries. The sample is pumped onto the plate of a piezoelectric transducer. When the power is applied, this plate vibrates at high frequency, causing the sample to form the aerosol. This is carried towards the torch by the gas flow. However, the greater efficiency of aerosol formation would be a problem, because of
the limited ability of the plasma to cope with such a flow. Therefore, a condenser is placed in the path of the aerosol, which removes a great majority of the solvent before reaching the torch. Figure 4.5 shows the setup of an ultrasonic nebuliser.

**TABLE 4.1 Comparison of nebulisers**

<table>
<thead>
<tr>
<th>Design</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentric</td>
<td>• simple</td>
<td>• prone to blockages</td>
</tr>
<tr>
<td></td>
<td>• reliable</td>
<td>• low efficiency</td>
</tr>
<tr>
<td></td>
<td>• consistent flow</td>
<td></td>
</tr>
<tr>
<td>Babington &amp; V-groove</td>
<td>• do not block up as easily</td>
<td>• low efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• less consistent</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>• 10 x more efficient</td>
<td>• more complicated</td>
</tr>
<tr>
<td></td>
<td>• can deal with slurries and high viscosity liquids</td>
<td>• more expensive</td>
</tr>
</tbody>
</table>

**Torch**

As mentioned above, the ICP torch consists of three concentric quartz tubes, with the copper RF coils at the top, as shown in Figure 4.6. The three tubes carry three different flows of argon, for quite different purposes:

- **plasma flow** – the outer tube provides the bulk of the argon for the plasma, but also achieves cooling for the quartz; flow rates are typically 7-15 L/min
- **auxiliary flow** – argon flowing through the middle tube provides a buffer between the inner and outer flows, and helps in plasma stability; flow rates of 1-3 L/min
- **inner flow** – the argon carrying the sample comes through the central tube; flow rates of 0.5-1 L/min
Radiation collection
The first ICP instruments used collection optics for the emitted radiation on the side just above the top of the torch in a zone of the plasma which gave optimum performance (not necessarily the hottest part). This is known as a radial configuration, as in Figure 4.7(a). Recently, design improvements in the cooling of the very hot gases leaving the plasma have allowed the optics to be placed end-on, or axial, as shown in Figure 4.7(b).

FIGURE 4.7 Configuration of collection optics (a) radial (b) axial

Class Exercise 4.2
What advantages does the axial configuration bring?

Operating conditions
While the ICP technique does eliminate many problems encountered in flame AAS, it is not foolproof or problem-free. One important variation is in the change in gas flow and nebuliser settings required to run organic solvents, or solutions with more than 10% organic content (e.g. wine) (unless an ultrasonic nebuliser is used). Under standard aqueous conditions, the plasma becomes overloaded by the high sample uptake caused by the improved fluid flow of the organic solvent. Table 4.2 compares standard conditions for aqueous and organic solvents.

<table>
<thead>
<tr>
<th>Setting</th>
<th>Aqueous</th>
<th>Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power (W)</td>
<td>1000</td>
<td>1500</td>
</tr>
<tr>
<td>Plasma flow (L/min)</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Auxiliary flow (L/min)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Inner flow (L/min)</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>Nebuliser uptake (mL/min)</td>
<td>1</td>
<td>0.7</td>
</tr>
</tbody>
</table>
**Why did ICP replace FAAS?**

ICP emission instruments have the following advantages over flame AAS:

- typically 10 times better sensitivity
- the ability to measure non-metals such as P, S, N and the halogens
- low levels of chemical interferences, such as ionisation and non-atomisation
- multi-component analysis (though a new design of flame AAS by Varian allows up to six wavelengths to be measured in rapid succession without resetting the instrument)
- linear ranges of 1000 times rather than 10 times

So the question arises: does flame AAS have a future? ICP does suffer from some disadvantages:

- they still cost at least five times more, but the price difference is coming down all the time
- spectral interferences are greater, because there so many peaks, some are bound to overlap
- relative precision is higher
- very high argon use, which makes the running costs significantly higher

ICP is a relatively new technique, so the price and precision problems will become less. Flame AAS has gone the way of the dinosaurs. However, ICP cannot compete with electrothermal AAS for sensitivity for most elements (see Table 4.3). There is a non-spectroscopic technique becoming important, which uses the ICP torch but does not rely on emission of radiation. It is known as ICP-MS, and can analyse concentration below even that of the electrothermal AAS. It is very expensive, but is becoming more widely used, and this may see the end of AAS entirely within 10 years.

**TABLE 4.3 Comparison of instrument sensitivities (ug/L)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Flame AAS</th>
<th>ICP AES</th>
<th>Electrothermal AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>30</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Cd</td>
<td>2</td>
<td>1.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>6</td>
<td>4</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu</td>
<td>3</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>6</td>
<td>1.5</td>
<td>0.06</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>0.3</td>
<td>0.03</td>
</tr>
<tr>
<td>Na</td>
<td>0.2</td>
<td>1</td>
<td>0.005</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>14</td>
<td>0.3</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>0.9</td>
<td>0.008</td>
</tr>
</tbody>
</table>
Revision Questions

1. What advantages do high temperature sources have for emission spectroscopy?
2. What is the difference between sequential and simultaneous instruments?
3. What limitation is placed on ICP nebulisers by the plasma itself? How is this limitation dealt with in pneumatic and ultrasonic nebulisers?
4. What is the function of each of the three flows of argon that comprise the total gas stream to the torch?
5. What is the difference between axial and radial torch mounting?
6. What change in conditions would you make for the direct analysis of a petrol sample by ICP?
7. Explain why ICP emission spectroscopy has replaced flame AAS but not electrothermal AAS.

What You Need To Be Able To Do

- draw a schematic diagram showing the components of a general high temperature emission spectrometer, and explain the function of each component
- distinguish between simultaneous and sequential emission spectrometers
- explain how the arc/spark analysis of a powder sample is performed
- draw a schematic diagram showing the components of an ICP torch, and explain the function of each component
- compare radial and axial ICP
- list and explain the reasons for advantages of ICP compared to AAS
- list limitations of ICP analysis

Answers to these questions on following page.

Answers to class exercises can be found in the Powerpoint file provided on the website.
Answer guide for revision questions

1. Exercise 4.1
2. Page 4.2
3. Limit on the amount of sample. Pneumatics are designed to be “inefficient”, ultrasonics remove solvent
4. Page 4.5
5. Figure 4.7
6. Table 4.2 organic
7. Quicker, more sensitive and accurate than FAAS though more expensive, not sensitive enough to replace EAAS.