

# 5 Inductively coupled plasma–atomic emission spectrometry

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## 5.1 Historic development and analytical capabilities

Optical emission spectrometry is a well proven analytical technique, in widespread use for the last 30 to 40 years. However, early devices available as optical emission sources (arc, spark or dc electrical discharges) had a number of disadvantages that prevented their widespread use for fully quantitative analysis of silicate samples. This situation changed dramatically during the mid-1960s with the development of inductively coupled argon plasma as an emission source for spectroscopic measurements.

Early work in establishing the formation and properties of an inductively coupled plasma that could be formed at atmospheric pressure was carried out by Babat (1947). Further important advances in techniques to form and sustain inductively coupled argon plasma discharges were reported by Reed (1961, 1962, 1963). Based on this work, two research groups, one led by Greenfield (Greenfield *et al.*, 1964) and the other by Fassel (Wendt and Fassel, 1965), demonstrated the analytical potential of this plasma as an optical emission source. By viewing the appropriate region in the argon plasma tail flame, atomic and ionic emission lines could be measured against very low background emission intensities. Very high temperatures (10 000 K maximum) are attained in modern ICP plasmas. Samples must be prepared in solution form and are introduced into the plasma by nebulization. Aerosol droplets are heated to temperatures of between 6000 and 8000 K in the plasma, and under these conditions efficient atomization occurs. Indeed, in contrast to flame atomization used in atomic absorption spectrometry, chemical interference effects in ICP plasmas are normally very small. Furthermore, ICP–atomic emission sources benefit from a very wide linear response range, often quoted to be more than six orders of magnitude. These properties give the ICP–AES source some very powerful analytical characteristics.

However, the atomic and ionic line spectra emitted by samples excited in an ICP plasma are not simple; a very large number of individual lines are present in the spectra of ‘typical’ rock samples. One of the principal concerns in the routine application of this technique, especially for the determination of trace elements, is to account adequately for all existing and potential spectrum overlap interferences. ICP–atomic emission spectrometry does not benefit from

the ‘lock and key’ effects that make spectrum overlap interferences rare in atomic absorption spectrometry (section 4.1).

However, perhaps the outstanding advantage of ICP–AES over atomic absorption methods is that instruments can be designed with direct reader spectrometers (Figure 3.46) that permit simultaneous multi-element determination. The number of elements that can be measured simultaneously is essentially limited by the number of fixed exit slits and photomultiplier assemblies fitted to the spectrometer, between 20 and 60 such channels being common. Some users prefer the flexible operation possible on instruments of alternative design incorporating sequential spectrometers, whose movement can be pre-programmed to measure selected peak and background wavelengths.

In terms of sensitivity, speed of analysis and capability for both trace and major element determinations, the inductively coupled plasma–atomic emission spectrometer has brought wet chemical schemes of analysis into the league of other established instrumental techniques such as x-ray fluorescence analysis. If there is a drawback to ICP–AES, it is that all samples must be reproducibly dissolved—compare the very simple powder pelleting procedures required for XRF trace element analysis. However, some would argue that such solution preparation procedures afford additional flexibility to ICP–AES, permitting, for example, the determination of the rare-earth elements by a procedure that incorporates an ion exchange separation.

The first commercial instrument became available in 1975, and since then ICP–AES has become the instrument of choice for routine major and trace-element determinations in many laboratories, especially those with a tradition of wet chemical analysis. Not the least attraction is the possibility of determining anything between 20 and 60 elements simultaneously in a cycle time of 2–3 minutes on a modern instrument fitted with a direct reader polychromator. The technique has become so well established that it is often referred to simply as ‘ICP analysis’; this does *not* avoid confusion with recent analytical instrumentation in which the ICP source is used to generate ions for mass spectrometric determination. The ICP–AES technique is sometimes referred to as ICP–OES (‘optical emission spectrometry’). The former terminology has been adopted here, following common usage, despite the fact that optical emission from ionic species is just as important as atomic emissions in routine analytical applications.

In parallel with the development of ICP sources, in recent years interest has increased in the direct current plasma as an optical emission source for solution analysis. Although not as versatile as the ICP, direct current plasmas have found some role in silicate rock analysis, and the analytical characteristics of this source are discussed in section 5.12.

## 5.2 The inductively coupled argon plasma

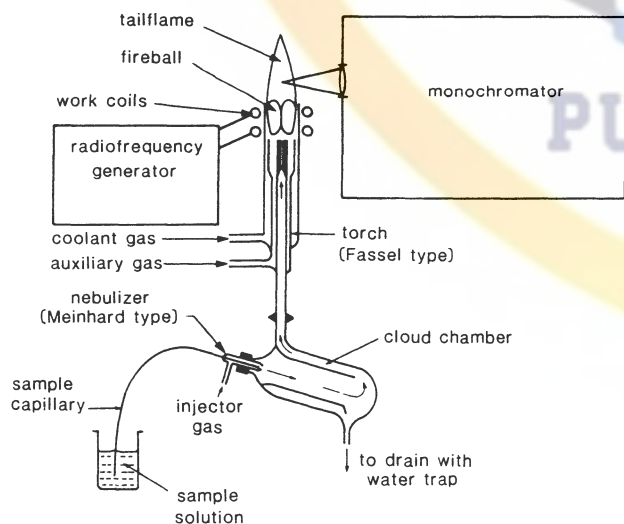
A *plasma* is any luminous volume of gas having a fraction of its atoms or molecules ionized. As indicated by Ebdon

(1982, p.36), this definition applies equally to a flame. However, in analytical spectroscopy, the term 'plasma' is normally reserved for an electrically excited discharge. A plasma source designed for emission spectrometry is shown schematically in Figure 5.1. It consists of a glass torch surrounded by a copper work coil. The functions of the components are as follows.

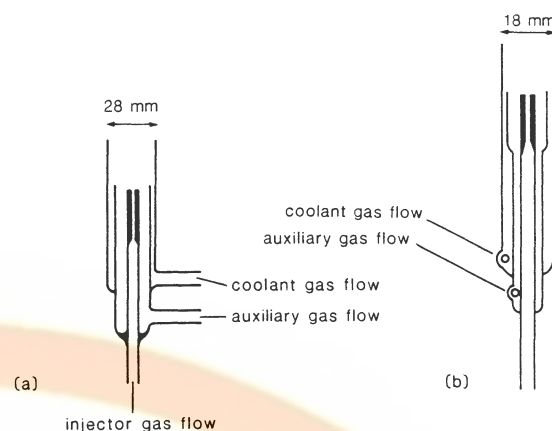
(a) *Torch assembly.* The torch is normally fabricated from glass in the form of three concentric glass tubes, the upper part of which is surrounded by the rf work coil. The torch assembly is designed to deliver gases so that a stable argon plasma is formed at the open end through which the sample aerosol can be injected. The two pioneering research groups developed separate torch designs: the Greenfield torch, which is now not widely used because of its need for a high gas flow, and the Fassel (or Scott) torch, which after progressive evolution, is now the industry standard.

The Greenfield torch (Figure 5.2a) was designed for use with conventional AA nebulizers that operate at a much higher gas flow (10L/min) than later ICP-type nebulizers (1L/min). The Greenfield torch consists of three concentric tubes, the outer one of which is 28 mm in internal diameter. Nitrogen at a flow rate of 20 to 70L/min is used as coolant gas, argon at a flow rate of 12 to 38L/min as injector and auxiliary gas (Thompson and Walsh, 1983). In order to sustain a stable plasma, relatively high power inputs are required (up to 8 kW).

The Fassel torch has evolved over a number of years to the design shown in Figure 5.2b. It is a more economical design, the outer tube having an internal diameter of 18 mm. The torch is designed to operate with nebulizers that require flow rates of only 1L/min of argon. Argon is also used as coolant gas and is supplied at a flow rate of 15 to 20L/min to the outer concentric tube. The function of the coolant gas



**Figure 5.1** Overall arrangement in an inductively coupled plasma source-atomic emission spectrometer. The plasma is shown excited at the open end of a Fassel-type quartz torch. In this diagram the sample solution is nebulized by a Meinhard-type nebulizer connected to a Scott-type spray chamber. Optical emission measurements are normally made in the plasma tail flame using a monochromator adjusted to view 15 to 20 mm above the work coils.



**Figure 5.2** Torch designs for ICP atomic emission measurements. (a) The Greenfield torch having an overall internal diameter of 28 mm, an annular gap for coolant gases of 0.5 mm and an injector tip bore of 2 mm. (b) The Fassel torch as further developed by Scott *et al.* (1974) and others. The overall internal diameter is 18 mm, the annular gap for coolant gas 1.0 mm and the injector tip bore 1.5 mm. Current design includes a tulip-shaped intermediate tube and capillary injector tube. (Thompson and Walsh, 1983.)

is to supply argon to the plasma, to stabilize the plasma centrally in the torch and to cool the outer glass jacket, preventing it from fusing or distorting. Carrier gas and sample aerosol are injected into the plasma through the axial capillary at a flow rate of 0.5 to 1.5L/min. An auxiliary supply of argon can be delivered to the plasma through the intermediate tube. In some schemes of analysis, no auxiliary supply is required. In others, a small flow of argon is used (0–1.5L/min) to lift the plasma off the injector, preventing overheating of the glass capillary and sooting of the aperture, especially if organic solvents are to be nebulized. The gas flow to the intermediate and outer tubes is supplied tangentially, the vortex created by the spiralling motion of gases improving the stability of the plasma. These outer tubes are usually made of quartz glass because of its greater heat stability. Plasmas are sustained at operating powers of about 0.7 to 2 kW. The Fassel torch is, therefore, designed to form a stable toroidal plasma, through the centre of which the sample aerosol can be injected. Design features include a tulip-shaped intermediate tube and a capillary injector tube. Manufacturing tolerances are much tighter than for the Greenfield torch in respect of both concentricity and annular spacing of torch components.

(b) *Work coil: mechanism of plasma formation.* The work coil consists of two or three turns of copper tube down the centre of which passes cooling water. This copper coil is wrapped around the outer tube of the torch, and the spacing between coil and torch, the distance between individual copper coils and the concentricity of both coil and torch are important parameters in the formation of a stable plasma.

The copper coil is connected to a radiofrequency power generator. This creates oscillating rf magnetic fields within the argon gas flowing through the torch, as shown in Figure 5.3. However, power cannot be transferred to the torch until the argon gas has been 'seeded' with a few electrons from a Tesla coil. These electrons are then subjected to intense