

10.3.4.1 Arc emission spectrometry

If the sample is electrically conductive, it may be used directly as one (or both) of the electrodes (*self-electrode*). For electrically non-conductive samples, powders or liquids, the sample is introduced into the different types of discharge in a *sample electrode*, generally of graphite or amorphous carbon. The non-sample-carrying electrode is called the *counter electrode* and may be of carbon, graphite or metal. Graphite and carbon electrodes differ in their *electrical and thermal conductivity*. The characteristics and operation of the arc depend on the material and shape of the electrodes and on the *analytical gap (arc gap)* as well as on the *polarity* of the sample electrode. If the sample electrode is positive, *anodic vaporization* takes place. If the sample electrode is negative, *cathodic vaporization* ensues. If radiation from only a thin layer near the cathode is utilized, the technique is known as the *cathode layer arc*.

10.3.4.1.1 Discontinuous procedures

During a given arcing period, a given amount of the sample is evaporated completely or partially, and the vapour products enter the plasma where they are excited as atoms or ions. The different vapour pressures of volatile components of a sample influence the time sequence of their evaporation and this *fractional distillation* or *burning off effect* may cause systematic errors in the results of an analysis. While evaporation of the sample takes place, different *thermo-chemical reactions* occur.

It is sometimes possible to form the conductive sample into a small molten sphere on the tip of a supporting electrode (usually carbon) in a dc arc. This type of arc is known as the *globule arc*.

Table 10.8 Classification of Methods and Instruments

	Absorption	Emission	Fluorescence
Methods	Absorption	Emission	Fluorescence
General classification	spectroscopy*	spectroscopy*	spectroscopy*
Instruments	Absorption	Emission	Fluorescence
General classification	spectrometer**	spectrometer**	spectrometer**
When atomic lines are observed ⁺	Atomic absorption spectroscopy (AAS)	Atomic emission spectroscopy (AES)	Atomic fluorescence spectroscopy (AFS)
	Atomic absorption spectrometer	Atomic emission spectrometer	Atomic fluorescence spectrometer
When a flame is used as a means for vapourization, atomization and/or excitation ⁺⁺	Flame absorption spectroscopy (FAS)	Flame emission spectroscopy (FES)	Flame fluorescence spectroscopy (FFS)
	Flame absorption spectrometer	Flame emission spectrometer	Flame fluorescence spectrometer
When both a flame is used and atomic lines are observed	Flame atomic absorption spectroscopy (FAAS)	Flame atomic emission spectroscopy (FAES)	Flame atomic fluorescence spectroscopy (FAFS)
	Flame atomic absorption spectrometer	Flame atomic emission spectrometer	Flame atomic fluorescence spectrometer

Note: The term flame photometry (flame photometer) has been abandoned.

*Spectroscopy may be replaced by the more restrictive term *spectrometry* when quantitative measurements of intensities at one or more wavelengths are performed with a spectrometer (see below).

**The term *spectrometer* as it is used here implies that quantitative measurements of intensities at one or more wavelengths are performed with a photoelectric detector. Wavelength selection may be accomplished, e.g., with a monochromator or optical filter.

⁺When molecular species are observed, "molecular" is substituted for "atomic".

⁺⁺Alternative methods of vaporization, atomization and/or excitation are, for example, arc, sparks, furnaces, plasmas, and cathodic sputtering tubes. The appropriate adjective should then replace the term flame.

Metallic filings or drillings may be analyzed by compacting them into pellets which may be used as *self-electrodes* or contained in a supporting electrode. *Non-conducting powder* samples have to be mixed with a conductive metal powder or graphite and placed directly, or in the form of a pellet, into hollow or *cup electrodes*.

Liquid samples (solutions) may be analyzed as evaporated residues on the top surface of plane flat *carrier electrodes*. Metal samples are sometimes dissolved and analyzed as liquids. *Liquid sample injection* enables a limited volume of a solution to be converted into an *aerosol* by means of a *nebulizer* and introduced into one of the various plasmas for analysis.

10.3.4.1.2 Continuous procedures

The continuous supply of fresh quantities of sample ensures uniform or *stationary radiation conditions* in the arc plasma over a relatively long arcing period. The influence of fractional distillation of various constituents is thus reduced.

For the continuous supply of a powdered sample into the discharge, a hollow *sifter electrode* may be used. The acoustical shock-wave at the beginning of each discharge of an ac arc causes a small portion of the sample powder to fall from an upper sifter electrode through small holes in its base into the plasma where vaporization, dissociation, atomization and excitation occur. This is called the *acoustical shock-wave sifter system*. In a similar fashion, powdered samples may be introduced into the arc plasma between two horizontal electrodes by means of a *gravity-fed powder sifter system*. For the transport of a sample into the discharge from below the arc, different *blow-in procedures* are possible. A high frequency discharge may be used to prevent *agglomeration* of the powder.

The sample can be mixed with a binding medium, e.g., cellulose, and pressed to form a rod. The rod is then continuously fed into the discharge through an electrode bored to the diameter of the rod to give a *piston electrode*.

Liquid samples or solutions can be injected directly into the arc discharge through a *drilled electrode*. In *capillary electrodes* the sample is supplied from a reservoir and drawn into the discharge by capillary action. The whole capillary electrode can be made from graphite and the reservoirs from a non-reactive material, e.g., polytetrafluoroethylene (PTFE). An example of this is the *vacuum-cup electrode*.

Porous cup electrodes (*porodes*) are hollow electrodes with porous bases. They are filled with the solution which penetrates through the bottom into the discharge. *Rotating disc electrodes* (*rotrodes*) can be used to provide a continuous supply of liquid sample into the discharge. The vertical disc electrode rotates continuously and is partially immersed in the sample solution. The discs can be made from metal, but normally crystalline graphite discs are used. Arcing takes place between the rotating analytical electrode and a counter electrode.

Liquid samples or solutions can be dried to leave a residue on the upper surface of a *rotating platform (platrode)*. In the latter case fresh material is continuously brought into the discharge, provided that the total exposure time is less than the time taken for one complete rotation of the platform.

Liquid samples or solutions may also be analyzed by first creating an *aerosol* which can be introduced into various types of current-carrying or non-current-carrying arc plasmas. This technique enables a constant and uniform supply of the sample to be maintained.

10.3.4.1.3 Erosion techniques

Erosion techniques are the generation of aerosols by means of *laser erosion* or by *electro-erosion*, e.g., by arcs or sparks. The aerosol so formed may be conducted to an analyzing plasma. An example of this type of source is the capillary arc which is essentially a wall-stabilized arc.

10.3.4.1.4 Operation - electrical parameters

Many of the properties of an arc which make it suitable for spectrochemical analysis depend on the *electrical source parameters*.

A dc arc maybe energized by a *rectified source* operating from the mains. In this case a *load resistor* is used to establish the current at a predetermined value, and an *inductor* may be used to smooth it.

In other instances a power supply, also operating from the mains, may provide an output of *constant voltage*. Electronic circuits may provide *constant current* to the arc under widely varying conditions. Sources of this type are called electronically *stabilized voltage-* or *stabilized current supplies*.

As with dc arcs, ac arc circuits must have a load resistor to limit current. Other means, such as *thyristor control*, are also used to stabilize the supply voltage and the current. Sometimes additional current is supplied to the arc by means of a repeatedly charged capacitor, thus giving a *condensed arc*. Where a low voltage arc must be ignited, an *ignitor circuit* is used consisting of a high voltage pulse operating through a *Tesla coil*. A *high frequency shorting capacitor* prevents high voltage from feeding back and damaging components in the lower voltage arc circuit.

10.3.4.1.5 Spectrochemical properties and applications

The arc has a relatively high operating temperature and as such is suitable for the evaporation, dissociation, atomization, ionization and excitation of a wide variety of

materials. The radiation thus consists of *molecular bands*, *atomic* and *ionic spectra* and also continuous radiation due to *radiant particles*. Samples may be mixed with or introduced together with additives for controlling volatilization, transport into the discharge region, excitation, background reduction, etc. These techniques include *buffered arcs*, *constant temperature arcs*, *carrier distillation arcs*, *seeded arcs*, etc.

The free-burning dc arc consumes relatively large amounts of electrode material. It is suited to determination of trace elements in conductive samples and in non-conductive powder samples. For larger quantities of sample or for the determination of traces of volatile elements, the *double arc* is useful. With this method, the sample is heated by one arc and the evaporated material excited by a second arc.

The ac arc is used mainly for metallic samples, pelleted powder samples and solutions. Various *dc arc plasmas* are also successfully used for the analysis of solutions (see sections 10.3.1.2.5).

10.3.4.1.6 Classification of spectrochemical additives

Spectrochemical additives are substances added to samples for various purposes. *Spectrochemical buffers* are added to samples and reference samples with the intention of making the measure of the analytical element less sensitive to changes in concentration of an interferent. A (*spectrochemical*) *diluent* is a substance added to the sample to increase its bulk for ease of handling or for the suppression of undesirable matrix effects. Material added to a sample to increase its volatilization, or that of some component of it, is a *volatilizer*; if it is done for the opposite reason, it is called a *devolatilizer*. Examples of volatilizers are AlF_3 or NaF , used with uranium, boron or silicon. A typical devolatilizer is carbon, which gives rise to refractory carbides when used in the analysis of tungsten or boron. A *spectrochemical carrier* is an additive which gives rise to a gas which can help to transport the vapour of the sample material into the excitation region of the source.