## 1.8 Atomic spectrometry: emission and absorption

Atomic emission spectrometry, flame photometry, and atomic absorption spectrometry are analytical techniques that measure the concentration of chemical elements in a sample. When elements are transformed into atomic vapour at high temperatures, emission or absorption of light may occur and this can be accurately measured at a unique resonant wavelength, which is characteristic of the emission/ absorption lines of the elements concerned.

Using this basic process, the concentrations of most elements may be estimated by measuring the amount of radiation either emitted by the sample (emission spectrometry) or absorbed by the sample following production by a primary radiation source (absorption spectrometry).

In emission spectrometry/flame photometry, a small proportion of the atoms undergo excitation with a subsequent and characteristic emission of radiation, at wavelengths in the ultraviolet or visible regions, which is proportional to the number of excited atoms.

Thus under controlled conditions, it is possible with either technique to relate the measured light intensity (emission or absorption) to the concentration of individual elements in the sample.

The major advantage of emission spectrometry is the relatively low cost and simplicity of instrumentation, since it requires no additional source of primary radiation. The fraction of excited atoms produced by most elements at normal flame temperatures is small and hence, in practice, emission spectrometry is limited to a few elements such as sodium, potassium, lithium, and calcium. Sensitivity may be increased, however, by using higher flame temperatures or other more effective means of excitation.

In comparison, absorption spectrometry offers greater sensitivity, since absorption is proportional to the concentration of ground state atoms, which are produced in sufficient numbers by most elements at normal operating flame temperatures. The disadvantage of this technique is the high initial cost of instrumentation, because of the requirement for a primary source of radiation (an individual hollow cathode lamp, one for each element to be determined).

Both techniques are comparative in nature and require the concomitant preparation and use of standard reference solutions of all elements to be determined.

### Apparatus

The emission spectrometer consists essentially of a burner - an atomic generator of the element to be determined (flame, furnace, plasma, arc, etc.), a suitable filter or monochromator, and a detector. The absorption spectrometer also includes a source of radiation (a hollow cathode tube) where the cathode consists of the same element as that to be determined.

### Use of solvents

For flame spectrometry, the ideal solvent is one that produces neutral atoms and interferes the least with the emission or absorption processes. Differences in surface tension or viscosity between the test and reference solutions may cause difficulties in the aspiration or atomization rates and significant changes in the signals generated. The solvent of choice for the preparation of test and reference solutions should, therefore, be water, although organic solvents, such as flammable solvents, either alone or mixed with water, may also be used if precautions are taken to ensure that they do not interfere with the stability of the flame. When mineral acids are necessary for the dissolution of the element, care should be taken to avoid interference from the acidic anion. A dilute solution of hydrochloric acid is the preferred solvent for this purpose.

### Calibration

To calibrate the instrument, introduce water or the blank solution into the atomic vapour generator (flame) and adjust the reading of the instrument, either to zero for *emission spectrometers* or to indicate maximum transmission for *absorption spectrometers.* For emission measurements, introduce the most concentrated standard solution into the flame and adjust the sensitivity to full-scale deflection. Refer to the manufacturer's instructions for instruments with an absorbance scale.

### Recommended procedure

Follow the manufacturer's instructions for the operation of the spectrometer, and use the wavelength indicated in the individual monograph. Use Method 1, unless otherwise specified in the monograph.

### Method 1: External standard method

Prepare the solution of the substance to be tested as specified in the monograph. Prepare concurrently, adding any reagents in the same concentration as for the solution above, not fewer than three reference solutions of the element to be determined that cover the expected concentration range of the solution under test. Similarly, prepare a blank solution.

After calibration, introduce each reference solution into the instrument three times, recording the steady reading obtained. If the generator is a flame, wash the apparatus after each introduction with water or the blank solution to check that the reading returns to its initial setting. If the generator is a furnace, fire it after each introduction. Prepare a curve by plotting the mean of each group of three readings against the concentration.

Introduce the solution to be tested into the instrument three times, and record the readings. Determine the concentration of the element using the mean of the readings and interpolating from the curve.

### Method 2: Standard addition method

Prepare in at least three similar volumetric flasks a series of solutions containing equal quantities of the substance to be tested as specified in the monograph and increasing volumes of the reference solution containing known concentrations of the element to be determined. The concentrations chosen should be expected to give responses in the linear part of the curve. One of the solutions of the substance to be tested should contain no added reference solution.

After calibration, introduce each solution into the instrument three times, recording the steady reading obtained. If the generator is a flame, wash the apparatus after each introduction with water or the blank solution to check that the reading returns to its initial setting. If the generator is a furnace, fire it after each introduction.

By using a least-squares fit, calculate the linear equation of the graph and derive from it the concentration of the element determined in the test solution. Alternatively, plot the mean of the readings on a graph against the added quantity of the element and determine the concentration of the element in the test solution by extrapolating the straight line joining the points on the graph to an extended concentration axis.