Flame Emission Spectroscopy (FES)

In flame emission spectrometry, the sample solution is nebulized (converted into a fine aerosol) and introduced into the flame where it is desolvated, vaporized, and atomized, all in rapid succession. Subsequently, atoms and molecules are raised to excited states via thermal collisions with the constituents of the partially burned flame gases. Upon their return to a lower or ground electronic state, the excited atoms and molecules emit radiation characteristic of the sample components. The emitted radiation passes through a monochromator that isolates the specific wavelength for the desired analysis. A photodetector measures the radiant power of the selected radiation, which is then amplified and sent to a readout device, meter, recorder, or microcomputer system.

Combustion .flames provide a means of converting analytes in solution to atoms in the vapor phase freed of their chemical surroundings. These free atoms are then transformed into excited electronic states by one of two methods: absorption of additional thermal energy from the flame or absorption of radiant energy from an external source of radiation.
In the first method, known as flame emission spectroscopy {FES), the energy from the flame also supplies the energy necessary to move the electrons of the free atoms from the ground state to excited states. The intensity of radiation emitted by these excited atoms returning to the ground state provides the basis for analytical determinations in FES.

INSTRUMENTATION FOR FLAME SPECTROMETRIC METHODS The basic components of flame spectrometric instruments are discussed in this section. These components provide the following functions required in each method: (1) deliver the analyte to the flame, (2) induce the spectral transitions (absorption or emission) necessary for the determination of the analyte, (3) isolate the spectral lines required for the analysis, (4) detect the increase or decrease in intensity of radiation at the isolated lines(s), and (5) record these intensity data.

Pretreatment of Sample

Flame FES requires that the analy1e be dissolved in a solution in order to undergo nebulization (see the next section). The wet chemistry necessary to dissolve the sample in a matrix suitable for either flame method is often an important component of the analytical process. The analyst must be aware of substances that interfere with the emission measurement. When these substances are in the sample, they must be removed or masked (complexed). Reagents used to dissolve samples must not contain substances that lead to interference problems.

Sample Delivery

The device that introduces the sample into the flame or plasma plays a major role in determining the accuracy of the analysis. The most popular sampling method is nebulization of a liquid sample to provide a steady flow of aerosol into a flame. An introduction system for liquid samples consists of three components: (1) a nebulizer that breaks up the liquid into small' droplets, (2) an aerosol. modifier that removes large droplets from the stream, allowing only droplets smaller than a certain size to pass, and (3) the flame or atomizer that converts the analyte into free atoms.

Nebulization

Pneumatic nebulization is the technique used in most atomic spectroscopy determinations. The sample solution is introduced through an orifice into a high- velocity gas jet, usually the oxidant. The sample stream may intersect the gas stream in either a parallel or perpendicular manner (Figure 9.1a). Liquid is drawn through the sample capillary by the pressure differential generated by the high-velocity gas stream passing over the sample orifice. The liquid stream begins to oscillate, producing filaments. Finally, these filaments collapse to form a cloud of droplets in the aerosol modifier or spray chamber.

In the spray chamber the larger droplets are removed from the sample stream by mixer paddles or broken up into smaller droplets by impact beads (Figure 9.1 b) or wall surfaces. The final aerosol, now a fine mist, is combined with the oxidizer/fuel mixture and carried into the burner (Figure 9.2).

A typical distribution range of droplet diameters is shown in Figure 9.3. Droplets larger than about 20 μm are trapped in the spray chamber and flow to waste. The distribution of drop sizes is a function of the solvent as well as the components of the sampling system. In AAS only a small percentage (usually 2% or 3%) of the nebulized analyte solution reaches the burner.

Atomization

The atomization step must convert the analyte within the aerosol into free analyte atoms in the ground state for FES analysis. Very small sample volumes (5-100 ILL) or solid samples can be handled by flameless electrothermal methods.

Flame Atomizers. The sequence of events involved in converting a metallic element, M, from a dissolved salt, MX, in the sample solution to free M atoms in the flame is depicted in Figure 9.4. After the aerosol droplets containing 1v.IX enter the flame, the solvent is evaporated, leaving small particles of dry, solid 1v.IX. Next, solid 1v.IX is converted to *NIX* vapor. Finally, a portion of the MX molecules are dissociated to give neutral free atoms. The efficiency with which the flame produces neutral analyte atoms is of equal importance in all the flame techniques.

If the events proceed vertically from the top down in Figure 9.4, the efficiency of free- atom production is high. Processes that branch horizontally interfere with the production of free analyte atoms. These processes include: (1) excitation and emission of radiation by *MX(g)* molecules, (2) reaction of *M(g)* atoms with flame components at high temperatures to produce molecules and ions that also absorb and emit radiation, and (3) formation of M^{+x} ions, which, in addition to reducing the efficiency of free-atom production,. complicate the analysis by adding lines to the spectrum. The flame remains the most generally useful atomizer for atomic spectroscopy despite the developments in electrothermal atomization. A satisfactory flame source must provide the temperature and fuel/oxidant ratio required for a given analysis. The maximum operating temperature of the flame is determined by the identities of the fuel and oxidant, whereas the exact flame temperature is fixed by the fuel/oxidant ratio. In addition, the spectrum of the flame itself should not interfere with the emission or absorption lines of the analytes. Components of the flame gases limit the usable range to wavelengths longer than 210 nm.

Ionization Interference

At elevated flame and furnace temperatures, atoms with low ionization potentials become ionized. Any ionization reduces the population of both the ground state and the excited state of neutral free atoms, thus lowering the sensitivity of the determination. This problem is readily overcome by adding an excess (ca. 100- fold) of a more easily ionized element such as K, Cs, or Sr to suppress ionization in both sample and calibration solutions. The more easily ionized atoms produce a large concentration of electrons in the vapor. These electrons, by mass action, suppress the ionization of analyte atoms. Thus, suppressant should be added to samples that contain variable amounts of alkali metals analyzed by acetylene/air flames to stabilize free-electron concentrations. The addition of suppressants is even more important in analyses that require the hotter acetylene/nitrous oxide flames.

APPLICATIONS

Most applications of FES have been the determination of trace metals, especially in liquid samples. It shoul dbe remembered that FES offers a simple, inexpensive, and sensitive method for detecting common metals, including the alkali and alkaline earths, as well as several transition metals such as Fe, Mn, Cu, and Zn. FES has been extended to include a number of nonmetals: H, B, C, N, P, As, O, S, Se, Te, halogens, and noble gases. FES detectors for P and S are commercially available for use in gas chromatography.

FES has found wide application in agricultural and environmental analysis, industrial analyses of ferrous metals and alloys as well as glasses and ceramic materials, and clinical analyses of body fluids. FES can be easily automated to handle a large number of samples. Array detectors interfaced to a microcomputer system permit simultaneous analyses of several elements in a single sample.

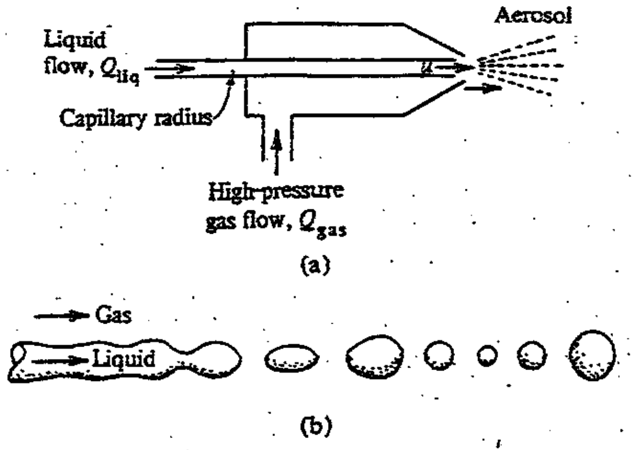

FIGURE 9.1
(a) Construction of pneumatic nebulizer and (b) breakdown of liquid filament into droplets.

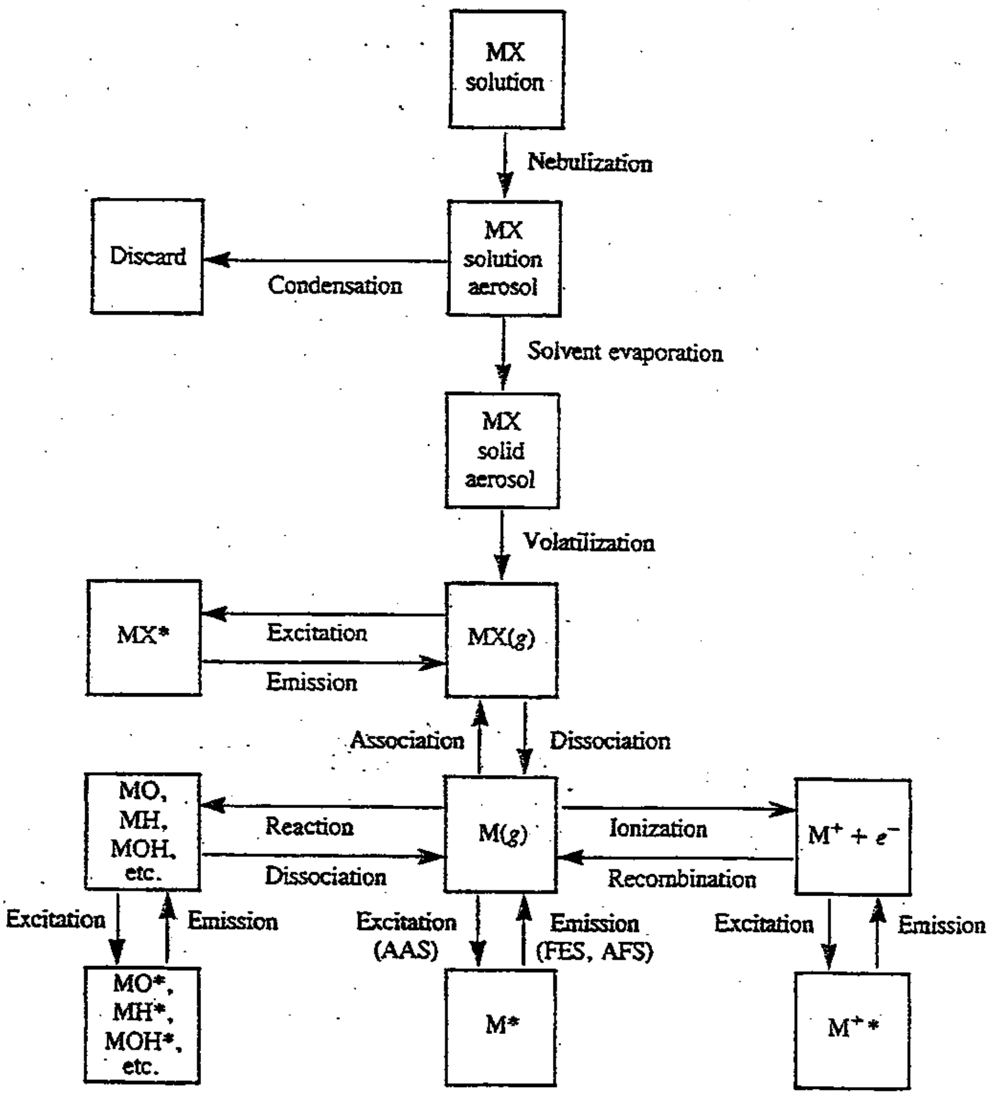

FIGURE 9.4
Flame atomization processes for the salt MX. Asterisk (*) indicates excited state.