10.3.4.3 Flame emission spectrometry (FES)

10.3.4.3.1 The analytical apparatus

The functions of an analytical flame spectrometer in general are:

(a) transformation of the solution to be analyzed into a vapour containing free atoms or molecular compounds of the analyte in the flame;

(b) Selection and detection of the optical signal (arising from the analyte vapour) which carries information on the kind and concentration of the analyte;

(c) Amplification and read-out of the electrical signal.

10.3.4.3.2 Transformation of sample into vapour

With a *pneumatic nebulizer* operated by a compressed gas, the solution is *aspirated* from the sample container and nebulized into a mist or *aerosol* of fine droplets. By *desolvation*, i.e., evaporation of the solvent from the droplets, this mist is converted into a dry aerosol which is volatilized in the flame. The *atomization*, i.e., the conversion of volatilized analyte into free atoms is performed by the flame or other atomizer.

The *total consumption time* is the time required to consume the sample entirely. The *minimum consumption time* is the time for which nebulization must be carried out to perform an analysis with a given precision.

Nebulizers can be described as follows:

> According to the source of energy used for nebulization as, for example, pneumatic or *ultrasonic nebulizers*.
>
> According to the way the liquid is taken up, e.g., *suction*, *gravity-fed*, *controlled flow*, and *reflux-nebulizers*.
>
> According to the relative position of the capillaries for the nebulizing gas and the aspirated liquid, e.g., *angular* and *concentric nebulizers*.

In the *chamber-type nebulizer*, the nebulizing gas-jet stream emerges from the sprayer into a *spray chamber*. Special devices are the *nebulizer with heated spray chamber*, the *twin nebulizer*, and the *drop generator*.

Flames are produced by means of a *burner* to which *fuel* and *oxidant* are supplied in the form of gases. With the *premix burner*, fuel and oxidant are thoroughly mixed inside the burner housing before they leave the burner ports and enter the *primary combustion* or

inner zone of the flame. This type of burner usually produces an approximately *laminar flame*, and is commonly combined with a separate unit for nebulizing the sample.

In contrast, a *direct-injection burner* combines the function of nebulizer and burner. Here oxidant and fuel emerge from separate ports and are mixed above the burner orifices to produce a *turbulent flame*. Most commonly, the oxidant is also used for aspirating and nebulizing the sample. However, when the fuel is used for this purpose, the term *reversed direct-injection burner* is applied. In each case, the mist droplets enter the flame directly, without passing through a spray chamber. The term total-consumption burner, which is often used, is not recommended.

Premix burners are distinguished as *Bunsen-*, *Meker-*, or *slot-burners* according to whether they have one large hole, a number of small holes, or a slot as outlet for the gas mixture, respectively. When several parallel slots are present, they are identified as *multislot burners* (e.g., a *three-slot burner*). The small diameter of the holes in the Meker burner or the narrowness of the slot in the slot-burner prevents the unwanted *flash-back* of the flame into the burner housing. At the edge of the flame where the hot gas comes into contact with the surrounding air, secondary combustion occurs and the *secondary combustion* or *outer zone* is formed. The region of the flame confined by the inner and outer zones, where in many instances the conditions for flame analysis are optimum, is called the *interzonal region*, or, when the combustion zones have the form of a cone, the *interconal zone*.

Sometimes provision is made to screen the observed portion of the flame gases from direct contact with the surrounding air. This may be done either mechanically, by placing a tube on the top of the burner around the flame, which produces a zonal separation (*separated flame*), or aerodynamically, by surrounding the flame with a sheath of inert gas that emerges from openings at the rim of the burner top (*shielded flame*). Observations can thus be made without disturbances from the secondary-combustion zone.

To promote the atomization of elements that readily form oxides in the vapour phase in the flame, a *fuel-rich flame* is often chosen, where reducing conditions favour the dissociation of metal oxides.

10.3.4.3.3 Terms, symbols and units for measurable quantities relating to nebulizer-flame systems (Table 10.9)

An easily measurable quantity is the *rate of liquid consumption* by the nebulizing system and is defined as the volume of liquid sample consumed per unit of time (symbol: F_1, see Table 10.9). In particular, in the common case of a pneumatic nebulizer, the term *rate of liquid aspiration* is more specific. Often only a fraction of the analyte solution that is aspirated passes through the flame cross-section at the observation height in a form that is accessible for spectroscopic observation. There are losses of different kinds that limit this fraction and consequently the sensitivity.

To describe these losses quantitatively, the following terms are recommended. The *efficiency of nebulization*, e_n, is the ratio of the amount of analyte entering the flame to the amount of analyte aspirated. The quantity, e_n, is not related to the amount of solvent but to the amount of analyte. Its value cannot be determined unambiguously by simply comparing the volume of solution drained per second from the spray chamber with the aspiration rate. Correction must usually be made for the difference in analyte concentration in the drained and aspirated solutions, respectively, due to the partial evaporation of solvent from the mist droplets deposited on the walls. The quantity, e_n is not merely characteristic of the operation of the nebulizer, but of the nebulizer-burner system as a whole.

The local *fraction desolvated*, b_s, is the ratio of the amount of analyte passing in the desolvated state (i.e., either as a dry aerosol or as a vapour) to the total amount of analyte passing.

Losses due to incomplete volatilization of the dry aerosol (which depend largely on the nature and concentration of the solute), are not covered by the definition of b_s, but by the definition of b_v. The quantity b_v will usually depend on the solute whereas b_s will depend on the solvent.

TABLE 10.9 Transformation of sample into vapour.
Terms symbols and units for measurable quantities

Terms	Symbol	Practical Unit	Note
Rate of liquid consumption	F_1	cm^3s^{-1}	In the usual case of a pneumatic nebulizer F_1 is called the rate of liquid aspiration
Efficiency of nebulization	e_n	l	
Fraction desolvated	b_s	l	
Fraction volatilized	b_v	l	
Fraction atomized	b_a	l	
Efficiency of atomization	e_a	l	
Flame temperature	T_F	K	When the temperature varies locally in the flame, it is more appropriate to speak of the *local flame temperature*
Travel time (time needed for substance to be carried from base of flame to the observation volume)	t_{tv}	s	
Transit time (time needed for substance to pass through the observation volume)	t_{ts}	s	
(Vertical) rise velocity of the flame gas	v_r	$cm\ s^{-1}$	
Burning velocity (of flame front)	v_b	$cm\ s^{-1}$	
Flow rate of unburnt gas mixture	F_u	cm^3s^{-1}	Measured at atmospheric pressure and room temperature
Flow rate of species X, e.g., air, O_2, etc.	F_X	cm^3s^{-1}	Measured at atmospheric pressure and room temperature

The (local) *fraction volatilized*, b_v, is the ratio of the total amount of analyte passing in the gaseous state to the total amount of analyte passing in the desolvated state. The gaseous state includes free atoms as well as molecules observation. There are losses of different kinds that limit this fraction and consequently the sensitivity.

To describe these losses quantitatively, the following terms are recommended. The *efficiency of nebulization*, e_n, is the ratio of the amount of analyte entering the flame to the amount of analyte aspirated. The quantity, e_n, is not related to the amount of solvent but to the amount of analyte. Its value cannot be determined unambiguously by simply comparing the volume of solution drained per second from the spray chamber with the aspiration rate. Correction must usually be made for the difference in analyte concentration in the drained and aspirated solutions, respectively, due to the partial evaporation of solvent from the mist droplets deposited on the walls. The quantity, e_n is not merely characteristic of the operation of the nebulizer, but of the nebulizer-burner system as a whole.

The local *fraction desolvated*, b_s, is the ratio of the amount of analyte passing in the desolvated state (i.e., either as a dry aerosol or as a vapour) to the total amount of analyte passing.

Losses due to incomplete volatilization of the dry aerosol (which depend largely on the nature and concentration of the solute), are not covered by the definition of b_s, but by the definition of b_v. The quantity b_v will usually depend on the solute whereas b_s will depend on the solvent.

The (local) *fraction volatilized*, b_v, is the ratio of the total amount of analyte passing in the gaseous state to the total amount of analyte passing in the desolvated state. The gaseous state includes free atoms as well as molecules.

The (local) *fraction atomized*, b_a, is the ratio of the amount of analyte passing as free neutral (or ionized) atoms to the total amount of analyte passing in the gaseous state.

The overall (local) *efficiency of atomization*, e_a, is defined as the ratio of the amount of analyte that passes through the flame cross-section at the observation height, as free neutral (or ionized) atoms, to the amount of analyte aspirated. Therefore, $e_a = e_n b_s b_v b_a$. The atomic signal strength obtained for a given solution concentration is proportional to the product $F_1 e_a$. It is noted that e_a may depend on F_1.

In Table 10.9, the above quantitative terms and some further terms for measurable quantities belonging to the section are listed, together with their symbols and units.

10.3.4.3.4 Classification of interferences

Spectral interferences are due to the incomplete isolation of the radiation emitted or absorbed by the analyte from other radiation detected by the instrument. Spectral interferences are usually strongly dependent on the spectral bandwidth of the monochromator. Spectral interferences may arise:

In *flame emission spectometry* (*FES*)

> from radiation [spectral continuum, molecular bands, or atomic lines (called *interfering lines*)] emitted by the concomitants. Spectral interference may also arise from stray or scattered radiation or spectral ghosts that reach the detector or from the indirect effect of the concomitants on flame background.

In *flame atomic absorption spectromety* (*FAAS*) and/or *flame atomic fluorescence spectrometry* (*FAFS*)

> by absorption or fluorescence of radiation by overlapping molecular or atomic lines of *concomitants*;
>
> by thermal emission of concomitants transmitted by the monochromator or received by the photodetector as stray radiation, when the radiation source is not modulated;
>
> by scattering of source radiation by nonvolatilized particles formed by the concomitants;
>
> by the indirect effect of the concomitants on the blank background absorption or scattering in the flame.
>
> by foreign line absorption and/or fluorescence if the corresponding radiation happens to be emitted by the light source, in addition to the analysis line, within the spectral bandwidth of the monochromator, particularly when a *continuum source* is used.

For interferences other than spectral, the analyte signal itself is directly affected. These interferences may be attributed accordingly:

(a) to the place or stage at which the particular interference occurs, i.e., transport, solute-volatilization, vapour-phase and spatial-distribution interferences;

(b) to the effects on different elements, i.e., *specific* and *non-specific* interferences;

These different classifications do not exclude one another. If the interference cannot be specified, the term *effect* may be used. Thus, the *matrix effect* is a composite interference due to all the concomitants, except for the additives; the *anion*, *cation* or *organic effect* includes all interferences caused by the presence of different anions, cations or organic constituents of the sample. *Transport interferences* affect the amount of desolvated sample passing through the horizontal flame cross-section per unit time at the observation height. They include factors affecting the rate of liquid consumption, F_1, the efficiency of nebulization, e_n, and the fraction desolvated, b_s. They may be classified as non-specific.

Solute-volatilization interferences are due to changes in the volatilization rate of the dry aerosol particles in the case when volatilization of the analyte is incomplete in the presence and/or absence of the concomitant. These interferences can either be specific, if the analyte and interferent form a new phase of different thermostability, as when Mg and Al form $MgAl_2O_4$ in an air-acetylene flame, or non-specific, if the analyte is simply dispersed in a large excess of the interferent, as when Ag is dispersed in ThO_2. Solute-volatilization interferences do not necessarily depress the signal. Effects due to compounds causing explosive disintegration of the solid aerosol particles and consequent enhancement also belong to this group.

Vapour-phase interferences are caused by a change in the fraction of analyte dissociated, ionized, or excited in the gaseous phase. (Note: here "dissociation" means the formation of free neutral atoms from free molecules in the gaseous phase. The term atomization is here not appropriate because the latter also covers the formation of free atomic ions.) These interferences may be called *dissociation*, *ionization*, and *excitation interferences*, respectively. An excitation interference may occur when the concomitant alters the flame temperature. Experimentally these interferences may be easily recognized because they take place even when twin nebulizers are used for aspirating the analyte and interferent separately. All interferences of this type are specific.

Spatial-distribution interference may occur when changes in concentration of concomitant affect the mass flow rates or mass flow patterns of the analyte species in the flame. If they are caused by changes in the volume and rise velocity of the gases formed by combustion, in extreme cases manifesting themselves by changes in the size and/or shape of the flame, they are non-specific and are called *flame-geometry interferences*. However, if caused by changes in diffusion processes they may be specific. Thus, the *lateral diffusion interferences* arise when the presence of concomitants delays the vaporization of spray droplets or solid particles, thereby shortening the time available for lateral diffusion of the analyte gaseous species before they reach the viewing field of the spectrometer.

10.3.4.3.5 Reduction of errors due to interference

Several techniques may be used to reduce or eliminate analytical errors resulting from various types of interferences. Apart from changing the instrumental conditions, the following techniques represent some of those in current use.

In the *reference-element technique*, the measure of the analyte is compared with the measure of a *reference element*. This technique is used mainly for minimizing non-specific interferences.

In the *analyte addition technique*, errors arising from both specific and non-specific interferences, but not from spectral interferences, are minimized.

In the *simulation technique*, reference solutions sufficiently similar in quantitative composition to the sample solutions to be analyzed are used so that the interferences in the reference and sample solution are equivalent.

In the *buffer-addition technique*, an additive (called a *spectrochemical buffer*) is added to both the sample and reference solutions for the purpose of making the measure of the analyte less sensitive to variations in interferent concentration. Additives that may serve as spectrochemical buffers are:

Suppressors, which reduce emission, absorption, or light scattering by an interferent, thus removing or lowering spectral interference.

Releasers, which reduce solute-volatilization interferences by forming a compound preferentially with the interferent, thus preventing the reaction of the analyte or interferent from entering a thermally stable compound.

Ionization buffers, which are added to increase the free-electron concentration in the flame gases, thus repressing and stabilizing the degree of ionization.

Volatilizers, which increase the fraction volatilized, either by forming more volatile compounds or by increasing the total surface area of all analyte particles (e.g., by explosive disintegration or by dispersal of the analyte in a highly volatile matrix) and

Saturators, which are interferents added in sufficiently high concentration to the sample solution to reach the *saturation plateau* of the interference curve.