# PART III: ANALYTICAL FLAME SPECTROSCOPY AND ASSOCIATED NON-FLAME PROCEDURES

## (Recommendations 1975)

## 1. INTRODUCTION

Part III is a sequel to Parts I and II of the Nomenclature for Spectrochemical Analysis. Whereas Parts I and II are mainly concerned with some general recommendations, Part III deals specifically with analytical flame spectroscopy and associated procedures.

The purpose of this nomenclature, as well as its adaptation to the documents developed by IUPAC and IUPAP in more general fields of chemistry and physics, has already been explained in the Foreword of Part I. In the development of Part III, the recommendations of IUPAC, IUPAP and the International Commission on Illumination (CIE), and of the foregoing Parts I and II were taken as a starting point. Deviations from these recommendations occur only in some exceptional cases and mainly concern the choice of a consistent set of symbols within the restricted field of analytical flame spectroscopy. Deviations may also be found in a few cases where previous international documents are not in agreement among themselves. Such deviations are explicitly identified in the *Notes* added to this document.

In those instances of specific usage in flame spectroscopy which are not already established by international conventions, compromises often had to be made between the historically developed terminology and nomenclature and those based on more logical considerations. Some expressions which have found their way into the language of practical analysts, but which could be misleading, have been abandoned. The use of alternative terms for the same item was considered undesirable and, as a rule, only one term has been recommended for each item. Some differences in terminology that developed historically among the practitioners of emission and atomic absorption methods have been reconciled.

During the period in which this document was in preparation, several national organizations developed their own nomenclature for atomic absorption spectroscopy. Through mutual deliberations, serious conflicts between national documents of restricted scope and the IUPAC nomenclature were significantly reduced. The simultaneous emergence of these national initiatives clearly proves the general need for a well defined terminology in this field and calls for international cooperation.

Part III is concerned with the analytical application of flame spectroscopy by emission, absorption, and fluorescence methods. These three branches of analysis have many terms in common and a uniform terminology seems mandatory. In the context of this document, an "ordinary" *flame* may be defined as a continuously flowing gas mixture at atmospheric pressure, which emerges from a burner and is heated by combustion. Although this document is primarily concerned with systems that comprise such ordinary flames, burners, and nebulizers, attention is also paid to similar procedures comprising other sampling, atomizing, and/or exciting devices (see Section 3.1.3). These procedures bear some resemblance to ordinary flame spectroscopy with regard to the methods of measuring emission, absorption, or fluorescence signals, as well as to the rather simple nature of the devices involved and the simplicity of the spectra obtained. Arc and spark spectroscopy involving more elaborate and expensive instrumentation are not discussed in this document.

As can be seen from the Table of Contents, this document is subdivided into several sections corresponding to the different aspects of analytical flame spectroscopy. A general classification and consistent terminology of the different branches of flame spectroscopy are presented in Table III.1. For some terms, abbreviations are suggested for practical usage. To comply with the internationally agreed restricted meaning of "photometer" (see I 4.5), the term "flame photometry" had to be abandoned,[1] although it was realized that many of the older practitioners of flame emission spectroscopy may have difficulty in giving up this long-cherished term. On the other hand, the abandonment of this term removes the illogical juxtaposition of terms such as "emission flame photometry," and "atomic absorption spectroscopy," which are often found in the literature. The more uniform terminology presented in Table III.1 should help to bridge the gap between emission and absorption methods.

*Table III.1*. Classification of methods and instruments

|  | Absorption | Emission | Fluorescence |
|---|---|---|---|
| Methods:<br>  General classification | Absorption spectroscopy[2] | Emission spectroscopy | Fluorescence spectroscopy |
| Instruments:<br>  General classification | Absorption spectrometer[3] | Emission spectrometer | Fluorescence spectrometer |
| When atomic lines are observed[4] | Atomic absorption spectroscopy (AAS)<br>Atomic absorption spectrometer | Atomic emission spectroscopy (AES)<br>Atomic emission spectrometer | Atomic fluorescence spectroscopy (AFS)<br>Atomic fluorescence spectrometer |
| When a flame is used as a means for vaporization, atomization and/or excitation[5] | Flame absorption spectroscopy (FAS)<br>Flame absorption spectrometer | Flame emission spectroscopy (FES)<br>Flame emission spectrometer | Flame fluorescence spectroscopy (FFS)<br>Flame fluorescence spectrometer |
| When both a flame is used and atomic lines are observed | Flame atomic absorption spectroscopy (FAAS)<br>Flame atomic absorption spectrometer | Flame atomic emission spectroscopy (FAES)<br>Flame atomic emission spectrometer | Flame atomic fluorescence spectroscopy (FAFS)<br>Flame atomic fluorescence spectrometer |

Descriptive terms denoting processes or instrumental components and terms for measurable quantities are presented separately. The descriptive terms and some of the most important quantitative terms are explained in a narrative form. To facilitate reference. all quantitative terms are presented in tables. together with their symbols and practical units. Notes have been added to

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[1] *Note:* The term flame photometry (flame photometer) has been abandoned (see also I 4.5).

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

[3] 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.

[4] When molecular species are observed, "molecular" is substituted for "atomic".

[5] Alternative, but presently less common means of vaporization, atomization and/or excitation are, for example, furnaces, flame-like (electrical) plasmas. and cathodic sputtering tubes (see Sec. 3.1.3). The appropriate adjective should replace the term flame.

the text as well as to the tables in order to provide additional explanation or justification, or to warn against improper usage of terms. These notes may readily be passed over on first reading, as all specifically recommended terms are incorporated in the text or the tables themselves. Such terms, when first met and defined in the text, are printed in italics for easy recognition.

This nomenclature is not intended to provide a comprehensive set of terms. Definitions and explanations of specific terms are only given when this is required to make their meaning unambiguous. General physical or chemical concepts and quantities are presented in most cases without further elucidation. To facilitate the use of this document, terms and symbols employed in flame spectroscopy which were presented in the foregoing Parts I and II have been recapitulated. This applies in particular to the general quantitative terms listed in Tables III.2 and III.5. Important terms such as "concentration," "analytical curve," "sensitivity," etc. are briefly explained in Section 4 with explicit reference to Parts I and II for a more complete explanation.

In view of the limited number of letters in the alphabet, symbols have been selected carefully, while making allowance for existing international recommendations as well as for long usage. In some cases, alternative symbols have been added, which allows the user to select a set of symbols that is most consistent in a particular context. Alternative symbols that are recommended without preference are listed after each other and separated by commas. When a particular symbol is preferred, it is listed first while the alternative symbols are separated from it by a row of dots. The printing of symbols and indices should conform to the general international rules recapitulated in I 2.3.

## 2. TERMS AND SYMBOLS FOR GENERAL QUANTITIES AND CONSTANTS

Table III.2 lists terms and symbols for some general physical and chemical quantities which are commonly used in analytical spectroscopy. This Table is partly an abstract from, and partly forms a supplement to, I 3.1 and I 7.2.

## 3. TERMS, SYMBOLS. AND UNITS FOR THE DESCRIPTION OF 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 (see Section 4) 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.

Terms for the description of component parts of a flame spectrometer (and similar systems) and of processes occurring therein are discussed below. Terms for the description of processes and properties related in particular to the gaseous state of matter in flames are discussed in Section 5.

3.1 Transformation of sample into vapour

3.1.1 Descriptive terms concerning nebulizer-flame systems

3.1.1.1 Nebulization, desolvation, volatilization, and atomization. With a *pneumatic nebulizer* driven under the action of a compressed gas stream, the solution is *aspirated* from the sample container and *nebulized* into a *mist* or *aerosol* of fine droplets. The term *sprayer*

denotes that particular part of a nebulizer where the aspirated liquid is disrupted by the gas-jet into a spray.

*By desolvation,* i.e. evaporation of the solvent from the droplets, this mist is converted into a *dry aerosol* consisting of a suspension of solid or molten particles of the solute. In the high-temperature environment of the flame, *volatilization* of these particles follows.

*Table III.2.* Terms and symbols for general quantities and constants

| Terms | Symbol | Note |
|---|---|---|
| Mass | $m$ | |
| Atomic weight ($A_r = 12$ for carbon C) of species X | $(A_r)_X$, $A_r(X)$ | |
| Atomic mass of species X | $m_X$, $m(X)$ | |
| Volume | $V$ | |
| Solid angle | $\boldsymbol{W, w}$ | |
| Time | $t$ | |
| Frequency (in optical spectroscopy) | $\boldsymbol{n}$ | |
| Frequency (in electronics | $f$ | |
| Wavelength | $\boldsymbol{l}$ | |
| Wavenumber ( $1/\boldsymbol{l}$ ) | $\boldsymbol{s}$, $\tilde{\boldsymbol{n}}$ | |
| Gas pressure | $p$ | |
| Total pressure of gas mixture | $p_t$ | |
| Partial pressure of species X | $p_X$, $p(X)$ | |
| Number of particles | $N$ | |
| (Number) density of particles (number per unit volume) | $n$ | |
| (Number) density of species X | $n_X$, $n(X)$, $[X]$ | |
| Thermodynamic (or absolute) temperature | $T$ | The unit for T is the Kelvin (K) |
| Velocity of light (in vacuum) | $c$ | |
| Gas constant | $R$ | |
| Avogadro constant | $N_A$ | |
| Boltzmann constant | $k$ | |
| Planck constant | $h$ | |
| Elementary charge | e | The symbol for electron is e and should not be printed in italics. |

In atomic flame spectroscopy, the *atomization,* i.e. the conversion of volatilized analyte into free atoms, should be as complete as possible in order to obtain a maximum signal. Any system which is capable of converting the analyte into an atomic vapour is called an *atomizer* (see also Sec. 3.1.3).

3.1.1.2 Nebulizers. In the *chamber-type nebulizer,* the nebulizing gas-jet stream emerges from the sprayer into a *spray chamber.* In such a chamber, the gas-jet stream is homogeneously mixed with the mist droplets. Some of these droplets may evaporate, coalesce, or deposit on the chamber walls and subsequently drain as waste.

Nebulizers can be described as follows:

• According to the source of energy used for nebulization, as, for example, *pneumatic* or *ultrasonic nebulizer.*
• 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.*

Special devices are the *nebulizer with heated spray chamber,* the *twin nebulizer,* and the *drop generator.*[6]

3.1.1.3 Burners and flames. Flames are produced by means of a *burner* to which *fuel* and *oxidant* are supplied, usually 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 functions of nebulizer and burner. Here oxidant and fuel emerge from separate ports and are mixed above the burner orifices through their turbulent motion. The flame produced by such a burner is *turbulent.* 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.[7]

Premix burners are distinguished as *Bunsen-, Méker-,* or *slot-burners* according to whether they have- one large hole, a number of small holes, or a slot as outlet port(s) 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 Méker burner or the narrowness of the slot in the slot-burner usually 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 the metal oxides.

3.1.2 Terms, symbols and units for measurable quantities relating to nebulizer-flame systems

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[6] *Note:* Nebulizers by themselves should not be called atomizers.

[7] *Nole:* The term total-consumption burner, which is often used, is not recommended.

An easily measurable quantity is the *rate of liquid consumption* by the nebulizing system, defined as the volume of liquid sample that is consumed per unit of time (symbol: $F_l$: see Table III.3). In the particular, but common case of a pneumatic nebulizer, the term *rate of liquid aspiration* is more specific.

*Table III.3*. Transformation of sample into vapour. Terms, symbols, and units for measurable quantities

| Term | Symbol | Practical Unit | Note |
|---|---|---|---|
| Rate of liquid consumption | $F_l$ | cm$^3$ s$^{-1}$ | For definition, see the text of Sec. 3.1.2. In the usual case of a pneumatic nebulizer $F_l$ is called the rate of liquid aspiration. |
| Efficiency of nebulization | $e_n$ | | For definition, see the text of Sec. 3.1.2. |
| Fraction desolvated | $b_s$ | | For definition, see the text of Sec. 3.1.2. |
| Fraction volatilized | $b_v$ | | For definition, see the text of Sec. 3.1.2. |
| Fraction atomized | $b_a$ | | For definition, see the text of Sec. 3.1.2. |
| Efficiency of atomization | $e_a$ | | For definition, see the text of Sec. 3.1.2. |
| 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). | $t_s$ | s | |
| (Vertical) rise velocity of flame gas | $v_r$ | cm s$^{-1}$ | |
| Burning velocity (of flame front) | $v_b$ | cm s$^{-1}$ | |
| Flow rate of unburned gas mixture | $F_u$ | cm$^3$ s$^{-1}$ | Measured at atmospheric pressure and at room temperature. |
| Flow rate of X, e.g. air, O$_2$, etc. | $F_X$ | cm$^3$ s$^{-1}$ | Measured at atmospheric pressure and at room temperature. |

Often only a fraction of the analyte solution that is aspirated passes through the flame cross-section at the observation height (see Table III.4) in a form that is accessible for spectroscopic observation. There are losses of different kinds that limit this fraction and consequently the sensitivity of the method. Examples of such losses with premix burners are the waste of solution in the spray chamber, the burner and the tubes between them, because of deposition of mist droplets on the walls. With direct-injection burners, there may be losses of droplets that are ejected from the flame because of the turbulent motion of the gases leaving the burner. Moreover, the residence time of the larger droplets in the flame may be insufficient for complete desolvation (see Sec. 3.1.1.1). Similarly, the particles formed after desolvation may not be completely volatilized (see Sec. 3.1.1.1 ) at the observation height. Finally it should be recognized that only part of the vapour produced by the analyte may consist of free atoms.

To describe these losses quantitatively, the following terms are recommended. These terms relate to the amount of analyte aspirated per second and entering the flame per second or passing through the total horizontal flame cross-section per second at the observation height in different states.

The *efficiency of nebulization,* $e_n$, is the ratio of the amount of analyte entering the flame to the amount of analyte aspirated.[8]

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. When this fraction varies with height, due to progressive evaporation of the aerosol droplets in the flame, it is appropriate to speak of the local fraction desolvated.[9]

The (local) *fraction volatilized,* $b_v$, is the ratio of the 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.[10]

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 $F_l \, e_a$. It is noted that $e_a$ may depend on $F_l$.

In Table III.3, the above quantitative terms and some further terms for measurable quantities belonging to this section are listed, together with their symbols and units.

### 3.1.3 Terms concerning special sampling, atomizing and exciting devices

3.1.3.1 Special sampling devices for flames. Samples may be introduced into flames by means other than nebulizers. The samples may be deposited on a *sampling loop, sampling boat,* or *sampling cup* made from platinum, tungsten, or other high melting point materials. and subsequently thermally vaporized.[11]

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[8] *Notes:* 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 solution, respectively, due to the partial evaporation 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.

[9] *Notes:* 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.

When this ratio varies markedly with height over the volume of flame observed, the amount of analyte found in this volume in the considered state is related to the average value of this ratio over this volume.

[10] *Note:* This fraction is determined by chemical reactions in the gaseous state. The bond strengths of the molecular compounds which the analyte may form in the flame play an important part as well as the composition and the temperature of the flame.

[11] *Note:* These devices are heated only by the flame and not by an additional source of energy.

In atomic absorption spectroscopy a *long tube device* is sometimes used with a nebulizer-flame system to increase the sensitivity. The increase in sensitivity is achieved by "retaining" the combustion gases with the atomized analyte over an extended path length by means of a tube coaxial with the optical axis. The tube is made from material capable of withstanding the flame temperature. The flame gases enter the tube at one end and leave at the other, or when a T-shaped tube arrangement is used, the gases enter at the centre and flow toward the two open ends. T-shaped tubes are called *T-tubes.*[12]

3.1.3.2 Electrical flame-like plasmas for atomization and excitation. Electrical flame-like plasmas may be current-carrying plasmas or current-free plasmas. Plasmas may be formed by an arc discharge in a chamber and transferred through an appropriate opening to form a *plasma jet.* Flame-like plasmas can also be generated by high-frequency fields with or without the use of electrodes. With the *electrodeless plasma,* the electromagnetic field is usually inductively coupled to the plasma *(inductively -coupled plasma ).* The *single-electrode plasma* is formed on a metallic tip that is connected to a high-frequency generator.[13]

3.1.3.3 Non-flame atomizing devices

3.1.3.3.1 Resistance-heated devices. When small amounts of liquid are to be analysed or if the sample is to be atomized directly from the solid state, different types of atomizing devices with electrical resistance heating can be used. The sample can be introduced on, or into, an electrically conductive support made of a material with high melting point and heated by an electrical current. The device may be specified according to the material and shape, such as a *carbon* or *metal filament, loop, ribbon* or *braid atomizer.* Atomizing devices using heated carbon or graphite tubes are called *carbon-* or *graphite-tube furnaces.* If a rod is used with a hole drilled perpendicularly to its axis, such furnaces are referred to as *carbon or graphite-rod furnaces.* Cup shaped atomizers used most often in AFS are called *carbon-* or *graphite-cup* atomizers.

Normally an electrical current flowing through the walls of the support causes the temperature to rise by resistance heating. Other less often used types have a separate resistance wire wound around the walls of the tubes or rods. Another type of resistance-heated graphite-tube furnace is used with a d.c. arc discharge to accelerate the atomizing process. In this case, the sample is not placed directly into the tube but on the tip of an anode electrode and evaporated by the arc into the heated tube.[14]

3.1.3.3.2 Hollow-cathode devices. In AAS, a *hollow cathode discharge* can also be used as an atomizer when the sample is used either as the cathode or placed in the hollow cathode in a low-pressure discharge chamber. In a *cooled hollow cathode* the cathode cylinder is cooled by water, liquid nitrogen, or other means. Under such conditions samples are atomized by *cathodic sputtering* even at high current densities. In a *hot hollow cathode* samples are atomized primarily by thermal evaporation.

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[12] *Note:* The long tube has often been referred to as an absorption cell. However, the term absorption cell should be reserved for devices closed by optical windows.

[13] *Notes:* Both chamber-type nebulizer systems and nebulizers which spray the aerosol directly into the plasma are used to introduce the sample.

The term "plasma flame," often used for flame-like plasmas is not recommended. The term "flame" should be reserved for hot gases which are produced by combustion. Similarly, the term "plasma burner" is discouraged. As a general descriptive term, "plasma torch" is often used.

[14] *Note:* The terms "graphite cell" or "graphite cuvette" should be reserved for devices with closed ends.

3.l.3.3.3 Radiation-heated devices. Solid samples can be evaporated and atomized by radiation sources, such as *pulsed-discharge lamps* and *lasers.* Because a laser beam can be brought to a sharp focal point on the sample surface, a *local analysis* can be made with this device.

3.2 Light sources in atomic absorption and atomic fluorescence spectroscopy

In AAS and AFS an auxiliary *light source* is required to produce the radiation which is to be absorbed (and partly re-emitted as fluorescence) by the analyte in the atomizer (see Sec. 3.1.1.1).[15]

Light sources are conveniently distinguished as *(spectral) continuum sources* or *(spectral) line sources.* Examples of spectral continuum sources used in AAS or AFS are the *tungsten-filament lamp* and the *high-pressure xenon lamp.* These lamps radiate light as a result of the high temperature of the filament or as a result of a gas discharge. They belong to the class of *thermal radiators* (see also the definition of thermal radiation in Sec. 5.1.1).[16]

Spectral line sources can be realized by an electrical discharge through a gas, a metal vapour, or a mixture of both at a low total pressure (the so-called *low-pressure discharge lamps* ). The following types have found application in AAS and AFS as light sources.

In the *hollow cathode lamp* accelerated electrons generate positive ions upon collisions with atoms of the *carrier gas* (usually a noble gas). These ions gain energy in the electric field and collide with the cathode which usually has a hollow cylindrical form. Atoms of the cathode material are released by these collisions *(cathodic sputtering).* These atoms are excited in the discharge and radiate their spectral lines. These lamps can be made either with the cathode sealed within the same enclosure *(sealed lamp)* or the cathode element can be changed by dismantling the lamp *(demountable lamp).* The cathode material may be composed of only one element *(single element lamp )* or of several elements *(multi-element lamp).*[17]

Another common type of spectral line source is the *metal-vapour lamp* operated at low vapour pressures. The lamp is filled with a noble gas while the metal vapour is produced from the volatile element by the thermal effect of the discharge.

The *(high -frequency excited ) electrodeless -discharge lamp* contains a noble gas at low pressure and some volatile metal or metal salt (such as an iodide or chloride). A discharge produced in the

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[15] *Notes:* The traditional term "light" here also includes other than visible radiation, although according to the International Commission on Illumination (C.l.E. Publication No. 17, E-l.l., 1970), this term should be restricted to visible radiation (see footnotes in III.1 and I.4.5).

The general term "source" includes not only lamps but also the use of an auxiliary flame into which a constant amount of analyte vapour is introduced to produee the (primary) radiation.

[16] *Notes:* Usually a spectral line source is employed containing atoms of the same element as the analyte. The line speclrum may be often superimposed upon a background that may be both discrete and/or a continuum.

The International Commission on Illumination (C.l.E. Publication No. 17 E-l.l. 1970) calls a spectral line source a "spectroscopic lamp."

Planck's law describes the spectral radiance $B_l{}^b$ (see Table III.5) of a so-called full radiator (or black body) as a function of wavelength $l$ and temperature $T$. A black body is a thermal radiator having an absorption factor $a(l)$ (see Table III.5) equal to unity at all wavelengths. In thermal equilibrium, according to Kirchhoff s law, the spectral radiance $B_l$ of any radiator with $a(l) < 1$ is given by

$$B_l = a(l)\, B_l{}^b$$

where $B_l{}^b$ is to be taken at the temperature of the radiator.

[17] *Note:* Carrier gas has also been called *fill-gas,* but this term is usually limited to sealed lamps.

noble gas by high-frequency fields generates electrons which by collisions excite the analyte atoms.

### 3.3 Optical systems

The functions of the optical system are to transfer, to select (spectrally, spatially. and temporally), and, possibly, to encode (by modulation) the radiation flux to be received by the photodetector. In addition, in AAS and AFS, the optical system should provide for the efficient conduction of the light beam through the analyte vapour contained in the atomizer (e.g. flame). In this Section, optical components, special systems, and their properties which are of interest in analytical flame spectroscopy will be considered. In I 5, general terms applicable to optical systems and spectroscopic instruments were considered. Those definitions will not be repeated here, but some of these terms are included in Table III.4 for convenience, together with the recommended symbols.

The general term *spectrometer,* as it is used in this document (see Table III.1), implies that quantitative measurements of intensities at one or more wavelengths are performed with a photoelectric detector. Spectral isolation of the desired radiation may be performed by means of *(optical) filters* (absorption filter, interference filter, etc.) or by a dispersing system. When the spectrometer is able to isolate only one narrow wavelength region, the instrument is called a *monochromator. A polychromator* is a multichannel spectrometer that allows spectral isolation of a number of narrow wavelength regions.

*A resonance spectrometer* consists of a "reservoir" of analyte atoms, which is irradiated by an external radiation beam containing among others, the resonance frequencies of the analyte atoms. The vapour in the reservoir is excited specifically by this resonance radiation. The resulting fluorescence radiation which is related to the intensity of the analyte resonance radiation in the original radiation beam, is measured.

In *AAS,* the sensitivity (see Section 4.2) may be improved by means of a *multipass system,* which allows the radiation beam from the light source to pass several times through the analyte vapour before it reaches the detector.

Most optical systems in use in flame spectroscopy are *single-beam systems.* For *double-beam systems* used in *AAS,* the radiation from the light source is split into the *sample beam* and the *reference beam.*

The optical signal can be modulated or pulsed by the periodic interruption or intensity variation of the light beam of interest. *Light modulation* when combined with an a.c. measuring system provides some advantages. For example in FES, the electrical signal arising from the flame emission may thus be distinguished from the d.c. dark current (see Section 3.4) of the photodetector. In AAS and AFS, modulation of the primary radiation beam (prior to its entrance into the flame), provides for the discrimination between the absorption or fluorescence signal and the thermal emission of the flame. Light modulation can be achieved by means of a mechanical *chopper,* or by modulating the electrical current through the lamp.

Table III.4 contains some further terms and their symbols for measurable quantities connected with the optical system.

*Table III.4.* Selection, detection. and readout of the analytical signal. Terms, symbols, and units for measurable quantities

| Terms | Symbol | Practical unit | Note |
|---|---|---|---|
| Entrance-slit width of monochromator | $s$ | mm | See Part I |
| Entrance-slit height of monochromator | $h$ | mm | See Part I |
| Spectral bandwidth of monochromator | $\Delta l_m$ | nm | See I 2.8 and I 5.2.2, respectively, for the use of Å and choice of symbol |
| 10%- or l%-width of optical filter (measured between points of 10% or or l% of maximum transmission factor) | $\Delta l_{0.1}$ or $\Delta l_{0.01}$ | | See I 2.8 and I 5.2.2, respectively, for the use of Å and choice of symbol |
| Wavelength for maximum transmission of optical filter or monochromator | $l_m$ | nm | See I 2.8 and I 5.2.2, respectively, for the use of Å and choice of symbol |
| Optical conductance | $G$ | $cm^2$ sr | For definition, see I 5.3.2. |
| Half-intensity width of line source | $\delta l_s$ | nm | See I 2.8 and I 5.2.2, respectively, for the use of Å and choice of symbol See Table III.5 for definition of half-intensity width. |
| Half-intensity width of absorption line | $\delta l_a$ | nm | |
| Response time of a system (time needed to reach the reading that is a specified fraction, e.g. 99 %, of the final value) | $t_r,\ t_{0.99}$ | s | |
| Observation height (above top of burner) | $h_{obs}$ | cm | |
| Frequency of light-modulation | $f_{mod}$ | Hz | |
| Electrical current for operating light source | $i_s$ | A | The official symbol $I$ for current may give confusion with $I$ for intensity |
| Dark current (of photodetector) | $i_d$ | A | For definition see Sec. 3.4. The official symbol $I$ for current may give confusion with $I$ for intensity. |
| Photocurrent | $i_f$ | A | For definition see Sec. 3.4. The official symbol $I$ for current may give confusion with $I$ for intensity. |
| Solid angle over which emission is measured | $W_E$ | sr | |
| Solid angle over which fluorescence is measured | $W_F$ | sr | |
| Solid angle over which radiation is absorbed by flame from light source | $W_A$ | sr | |

### 3.4 Photodetectors

The most commonly applied *photodetectors* are the *vacuum phototube* (without internal amplification), the *photomultiplier tube* (with internal amplification by secondary emission of

electrons) and the *photovoltaic cell* (a semiconductor device producing an electromotive force upon irradiation).[18]

There are two components in the output current of a photodetector. One component, the *photocurrent, $i_f$*, is that portion induced by the radiation. The detector is said to be *linear* if the photocurrent is proportional to the radiant flux. The other component is called the *dark current, $i_d$*, because it continues to exist when the radiation flux is blocked.

The *responsivity* of a photodetector (or in more general terms the sensitivity) is the change in output current per unit change in radiant flux. The responsivity is wavelength dependent; the curve describing this dependence is called the *spectral response curve.*

Table III.4 lists the quantitative terms and symbols related to photodetectors.

### 3.5 The electrical measuring system

In the electrical measuring system the electrical signal delivered by the photodetector (see Sec. 3.4) is processed and converted to a *reading* on an appropriate readout device. The reading provides a measure (see Sec. 4.1) of the radiant flux emitted, absorbed or fluoresced in the flame. In the absence of analyte, the signal trace recorded as a function of time or of wavelength is called the *baseline.* In order to speed up the evaluation of an analysis, the readout is sometimes directly calibrated in terms of concentration or amount of analyte. A non-linear analytical curve (see Sec. 4.2) may be linearized by means of a *curve corrector.* The background (see Sec. 4.1) can be compensated electronically by means of a *background corrector.*

Readings of small differences in two relatively large signals may often be made more readily by *scale expansion* of a segment of the reading range. When *zero suppression* is used, one of the signals is suppressed by displacing the zero of the meter, usually by electronic means, and the difference signal is increased by increasing the amplifier gain.

The *response time* (see also Table 3.2) is the time needed for the readout to reach a specified fraction (which must be stated) of its final value if the photodetector is suddenly exposed to the radiation flux. If this fraction is chosen to be $(1- 1/e) = 0.63$, then the response time is called the *time constant.*

Scatter and drift will be discussed in Sec. 4.3.1.

### 3.6 Survey of terms, symbols, and units for measurable quantities in the optical and measuring systems (See Table III.4).

## 4. TERMS AND SYMBOLS RELATING TO THE ANALYTICAL PROCEDURE AND THE PERFORMANCE OF AN ANALYSIS

### 4.1 General analytical terminology in flame spectroscopy

In analytical flame spectroscopy, the *sample* may be a *solution* or is brought into solution. We distinguish between the *solvent* (e.g. an alcohol-water mixture), the *analyte,* i.e. the element sought, and the *concomitants,* i.e. any species other than the analyte and the solvent. Some concomitants may be present in known and constant concentrations through having been added during chemical pretreatment of the sample, and are called *additives.* Others, which were in the original sample, may have variable and/or unknown concentrations.

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[18] *Note:* The photovoltaic cell is often called a barrier-layer cell or photodiode.

The border line between the solvent and the concomitant cannot always be sharply drawn. For example, when alcohol is added to the solution in constant known proportions (in order to improve nebulization or to produce chemiluminescence), it is regarded as a part of the solvent; when present in the original sample, in unknown or varying concentration, it may be regarded as a concomitant.

A *reference solution* is a solution with the same solvent as the sample. and contains the analyte. and possibly some concomitants, in known concentrations.

A *blank solution* is a solution that does not intentionally contain the analyte, but in other respects has, as far as possible, the same composition as the sample solution. A *solvent blank* consists only of the solvent.

The *analytical result* is the final value of *concentration, c*, or *quantity*, *q*, of the element sought, after all subprocedures and evaluations have been performed. For example, the analytical result may be obtained from a meter reading which provides a *measure, x,* of some physical quantity, such as analyte emission intensity, absorbance, or fluorescence intensity measured at the wavelength of an analytical line. The physical quantity carrying the information on the analyte concentration, is called the *(analyte) signal.*[19]

The measure obtained when a blank solution is nebulized into the flame. is called the *blank measure, $x_{bl}$* The measure obtained when the (reference) solution is nebulized can be corrected for the blank measure either instrumentally or numerically. The difference, $x - x_{bl}$, is called the *net measure.* The signal that is observed when no solution or solvent is nebulized into the flame, is called the *blank background (emission* or *absorption ).* The background observed when a blank solution is nebulized in FES, FAS or FFS, is called the *blank background (emission, absorption,* or *scattering,* respectively).[20]

### 4.2 Analytical calibration

The relationship between the measure of the signal and the solution concentration of the analyte is given by the *analytical curve*. This curve is generally established by making measurements on a series of reference solutions.

The derivative of the function $x = g(c)$, $dx/dc$, is the *sensitivity* of the analytical procedure. When the analytical curve is non-linear, the sensitivity is a function of concentration.

In AAS, it is often desirable to compare slopes of analytical curves at low analyte concentration values for different lines and/or elements. This is often done by reporting concentration values of the analyte corresponding to 1% net absorption or 0 0044 absorbance. The term *characteristic concentration* is recommended for this particular concentration value.[21]

Different techniques may be used for obtaining the analytical result. When the *analytical-curve technique* is used, the analytical result is read from an analytical curve covering the concentration range of interest.

When the *bracketing technique* is applied, the analytical result is found by graphical or numerical (usually linear) interpolation between measures of two reference solutions, one having a slightly lower, and the other a slightly higher analyte concentration than the unknown sample solution.

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[19] *Note*: If the position of the sensitivity knob of the instrument is changed, the reading, but not the measure, is changed.

[20] *Note:* See also I 6 for a further explanation of some general terms.

[21] *Note:* In the past the term 'sensitivity' has been incorrectly used for this concentration value.

When the *(analyte) addition technique* is applied, successive known quantities of the analyte are added to aliquots of the sample solution. The net measures of the solutions thus obtained are plotted against the added concentrations. This plot is extrapolated to intercept the negative concentration axis. The analytical result is found from the corresponding concentration value.

*Direct methods,* i.e. those where the analyte produces the measured signal, are generally used in flame spectrometry. For some elements, *indirect methods* have been applied. A given amount of another element, whose measured signal depends on the analyte concentration present, is added to the sample solution. If the change in the signal of the latter element is measured, a measure of the analyte concentration is obtained (e.g. the determination of phosphate by the addition and measurement of strontium). In some cases, the added element reacts with the analyte in the solution before nebulization, the resulting compound being separated. The remainder of the added element, or the amount of added element that is separated because of the compound formation, is then measured (e.g. the chloride content may be determined by the addition and measurement of silver).[22]

### 4.3 Assessment of an analytical procedure

#### 4.3.1 Measurement scatter

The measure observed when a sample solution is analyzed is, in general, composed of two portions: the blank measure and the net measure (see Sec. 4.1). The net measure refers to the (analyte) signal (see Sec. 4.1) and is thus the useful, informative portion. The blank measure can be isolated and observed when a blank solution is treated in exactly the same way as the sample solution. Because the analyte should not be present in the blank solution, the blank measure contains no information about the analyte.

When replicate determinations are made on a given sample or blank, the measured values will not be constant. but will show *scatter.* If the causes of the scatter are not known (or considered), they cannot be controlled and therefore appear accidental. Blank scatter and signal scatter both contribute to the uncertainty of the analytical result.

The numerical value for the scatter may be taken as the *standard derivation,* which is determined from a sufficiently large series of repeated determinations. For a set of $n$ measured values $x_j$ the standard deviation, $s$, is, in general, defined and calculated by the formula:

$$s = \left[ \sum_{j=1}^{n} \left( x_j - \bar{x} \right)^2 \Big/ (n-1) \right]^2$$

where

$$\bar{x} = \frac{1}{n} \sum_{j=1}^{n} x_j$$

is the average.

The scatter in general is a composite quantity produced by random fluctuations from different sources. If these random fluctuations in the measure are independent, the formula for the propagation of *variance* (square of the standard deviation) can be applied to this case in the following symbolic form:

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[22] *Note:* See also II for a further explanation of some general terms.

$$s_{bl}^2 = s_I^2 + s_{II}^2 + s_{III}^2 + \cdots$$

Typical sources of scatter in the blank and net measure are the following: (not all independent)

• Preparation of solution (accidental differences in weighing, adsorption etc.);
• Accidental external contaminations of solution; Variation of impurities in reagents;
• Random fluctuations of nebulization and transport;
• Random fluctuations of desolvation, atomization, and excitation;
• Random fluctuation in the background;
• Random fluctuations from the light source;
• Uncontrolled variations in the optical system;
• Random fluctuations in the photodetector, such as shot noise in the photocurrent and dark current, and low frequency flicker noise arising from instabilities in a photocathode;
• Electronic noise in the electrical measuring device, such as shot noise and thermal or Johnson noise which is due to the thermal agitation of charge carriers in resistors;
• Drift in amplifiers;
• Reading errors, accumulated rounding errors in calculations, calibration errors, etc.

In a complicated measuring system the contribution of these different sources can rarely be predicted theoretically. *Blank scatter,* $s_{bl}$, can only be determined by making blank analyses and then treating the measures statistically. It is therefore highly important that such a series of blank analyses be planned carefully. All causes for random fluctuations involved in the original analytical procedure must play their full part, except those which are directly bound to the presence of the analyte.

### 4.3.2 Limit of detection, precision, and accuracy

The merits of an analytical procedure may be characterized by its limit of detection, precision, and accuracy.

The *limit of detection* expressed as concentration, $c_L$, or quantity, $q_L$, is derived from the smallest measure, $x_L$, that can be accepted with confidence as genuine and is not suspected to be only an accidentally high value of the blank measure. The value of $x_L$ is given by the equation:

$$x_L = \bar{x}_{bl} + k s_{bl}$$

where $\bar{x}_{bl}$ is the mean and $s_{bl}$ the standard deviation of the blank measures, and k a numerical factor chosen according to the specified confidence level. The limit of detection is obtained directly from the analytical curve. A value of k = 3 is strongly recommended for the reasons given in II 4.1. Although a value of 2 has often been used, this value is not recommended. To avoid ambiguity, the k-value should be indicated as follows: $x_{L(k=3)}$. The time constant of the measuring device should be stated specifically, so that meaningful comparison between the limits of detection for different instruments may be made.

The *precision* of an analytical procedure can be conveniently expressed by the standard deviation or by the *relative standard deviation* $s_r = s/c$ in the analytical result (see II 2.4).

The *accuracy* relates to the difference between the analytical result obtained by a given analytical procedure and the (known or assumed) true analyte concentration in the sample.

The *bias* characterizes the systematic error in a given analytical procedure and is the (positive or negative) deviation of the mean analytical result from the (known or assumed) true value.

If materials with certified analyte concentration values (i.e. the best estimates of the true values) are not available, and the results cannot be compared with those obtained by other reliable

methods, several test experiments may be used to check the accuracy of the procedure. The *recovery test* is based on the addition of a known amount of the analyte to the sample at an early stage of the analytical procedure. This amount should be found when the analytical result for the sample solution without addition is subtracted from the result for the sample solution with addition. In the *dilution test,* different known dilutions of the sample are made and the results obtained are compared.

The correct outcome of these tests is a necessary but not sufficient proof of the absence of systematic errors in a given analytical procedure.[23]

### 4.4 Interferences by concomitants

#### 4.4.1 General

The presence of concomitants in the sample can cause *interferences,* i.e. systematic errors in the measure of the signal. An interference may be due to a particular concomitant or to the combined effect of several concomitants. A concomitant causing an interference is called an *interferent.* When C is an interferent and A the analyte, there is an interference of C on A. When an element X acts as an interferent on an analysis element Y, and Y acts as an interferent on the analysis element X, a *mutual interference* is said to exist.[24]

An interference will cause an error in the analytical result only if the interference is not adequately accounted for in the evaluation procedure. The analyte concentration determined when the interference is not accounted for is called the *apparent concentration.* If the apparent concentration is larger than the true concentration, an *enhancement* occurs or, if smaller, a *depression.* The *interference curve* relates the measure, or apparent concentration of the analyte, to the concentration of interferent, at fixed analyte concentration.

#### 4.4.2 Classification of interferences

##### 4.4.2.1 Spectral interferences

*Spectral interferences* are due to incomplete isolation of the radiation emitted or absorbed by the analyte from other radiation detected by the instrument. Their occurrence may be established by comparing the measures of the analyte-free blank solution and the solvent blank.[25]

Spectral interferences are usually strongly dependent on the spectral bandwidth of the monochromator. Spectral interference may arise:

• In 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 light or spectral ghosts that reach the detector;
—by the indirect effect of the concomitants on flame background (which is sometimes difficult to distinguish from their direct contribution to the background).

• In FAS and/or FFS—by absorption or fluorescence of radiation by overlapping molecular or atomic lines of concomitants;

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[23] *Note:* For a further explanation, see also Part II and *Pure Appl. Chem.* **18**, 439 (1969).

[24] *Note:* The influence of the solvent or of the flame background (without nebulization) on the measure is not called an interference. This is logical, because the sample and the reference solutions presumably contain the same solvent (see Sec. 4.1).

[25] *Note :* The spectral interference found when a blank solution is nebulized need not be identical with the true spectral interference, since the presence of analyte in the sample might, in turn influence the emission or absorption of the concomitants through one of the effects to be discussed in this Section.

—by thermal emission of concomitants transmitted by the monochromator, or received by the photodetector as stray light, when the light 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.

### 4.4.2.2 Non-spectral interferences.

For interferences other than spectral, the analyte signal itself is directly affected. The *non-spectral interferences* may be classified according to the following viewpoints:

(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;

(c) To the properties which are decisive for the mechanism of the interference, i.e. *physical* and *chemical* interferences.[26]

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 of the concomitants, except for the additives (see I 6.1); the *anion, cation* or *organic effect* includes all interferences caused by the presence of different anions, cations or organic constituents of the sample. When a particular solvent other than water is used, its effect on the signal (as compared with an aqueous solution) is not to be considered as an interference (see *Note* 24).

*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, $F_l$, the efficiency of nebulization, $e_n$ and the fraction desolvated, $b_s$. They may be classified as non-specific (and physical).

*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 be either 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 $ThO_2$. If the interferent has a high boiling point this latter case is sometimes referred to as blocking interference. It is often difficult to make sharp distinctions between the specific and non-specific solute-volatilization interferences.[27]

*Vapour-phase interferences* are caused by a change in the fraction of analyte dissociated,[28] ionized, or excited in the gaseous phase. 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

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[26] *Note:* The latter classification is discouraged since it can easily lead to confusion. Some physical processes (e.g. volatilization) determined by physical properties of the particles formed by the analyte in the presence of an interferent depend on the chemical properties of the analyte and interferent.

[27] *Note* 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.

[28] Here "dissociation" means the formation of free neutral atoms from free molecules in the gaseous phase (see also Sec. 6.1). The term atomization is here not appropriate because the latter also covers the formation of free atomic ions (see Sec. 3.1.1.1).

recognized because they take place even when twin nebulizers are used for aspirating the analyte and the interferent separately. All interferences of this type are specific.

*Spatial-distribution interference* may occur when changes in concentration of concomitants 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.

### 4.4.3 Reduction of errors due to interferences for given instrumental conditions

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 *baseline technique* (see Sec. 3.5), background spectral interference is corrected. The background is interpolated from background readings on both sides of the analytical line and the value thus found is subtracted from the reading at the peak of the line.

In the *reference-element technique,* the measure of the analyte is compared with the measure of a *reference element* (see I 6.2.2). This technique is used mainly for minimizing non-specific interferences.

In the *(analyte) addition technique* (see Sec. 4.2), 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* reduce emission, absorption or light scattering by an interferent, thus removing or lowering spectral interference.
• *Releasers* reduce solute-volatilization interferences by forming a compound preferentially with the interferent, thus preventing the analyte from entering a thermally stable compound.
• *Protective agents* combine chemically with the analyte or the interferent in such a way as to reduce the type of interferences discussed under 4.4.2.2.
• *Ionization buffers* are added to increase the free-electron concentration in the flame gases thus repressing and stabilizing the degree of ionization (see Sec. 6.2).
• *Volatilizers* increase the fraction volatilized (see Sec. 3.1.2) 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).
• *Saturators* are interferents added in sufficiently high concentration to the sample solution to reach the *saturation (plateau)* of the interference curve (see Sec. 4.4.1).

# 5. TERMS, SYMBOLS, AND UNITS RELATING TO RADIANT ENERGY AND ITS INTERACTION WITH MATTER

Relevant descriptive terms relating to the emission, absorption, and fluorescence of optical radiation are discussed in this section. Terms for measurable quantities are listed separately in a table, together with their recommended symbols and practical units.

### 5.1. Descriptive terms relating to the emission, absorption, and fluorescence of radiation

#### 5.1.1. Emission

The emission spectrum of a light source may consist of separate *spectral lines* (see I 7.6.1) and/or a *spectral continuum* with a continuous distribution of frequencies or wavelengths. Spectral lines emitted by free neutral atoms and ions are called *atomic lines* and *ionic lines,* respectively (see I 7.6.1). The spectral lines emitted by free molecules are grouped together in *spectral bands.* When the resolution of the monochromator (see I 5.2.2) is insufficient, some bands may appear as a (quasi-)continuum in the recorded spectrum.

The emission of an atomic line is the result of a transition of the atom from a state of higher excitation to a state of lower excitation. When the lower state of the transition is the ground state, the line is called a *resonance line.* When the ground state is a multiplet, only transitions to the lowest multiplet component should be called a resonance line.[29]

The radiation originating from a source where all particles are in a state of thermal equilibrium (see Sec. 6.1), is called *thermal radiation.* This term applies for the radiation of a spectral continuum as well as of isolated spectral lines or bands.

When the excited state from which the transition originates is mainly populated as a direct result of a chemical reaction, the radiation process is called *chemiluminescence.*[30]

#### 5.1.2 Absorption and self-absorption

When a light beam traverses a flame or other hot gases into which a sample is nebulized, its intensity (in the beam direction) may be attenuated by several processes.[31] First, radiation may be lost due to (real) *absorption,* whereby photon energy is indirectly converted into heat.[32]

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[29] *Note:* Some handbooks define a resonance line as the line that originates from the lowest excitation state for which an optical transition to the ground state is allowed. Other handbooks adopt the wider definition presented in the text (compare, e.g. *Lexicon der Physik,* edited by H. Franke, Stuttgart, with the *Handbook of the American Institute of Physics).* The broader definition conforms to common usage in analytical flame spectroscopy. If desired, the resonance line (or doublet) originating from the lowest excited level(s) may be specifically called the first resonance line (or doublet).

[30] *Note:* The adjective "thermal" as such does not indicate the kind of process (collisional, chemical or radiative) that is responsible for the excitation of the radiating substance. Note, however, that the term chemiluminescence specifies the kind of excitation process. These two concepts therefore do not necessarily exclude each other. In flames, "thermal chemiluminescence" can exist, if the chemical species involved in the chemiluminescent reaction are in chemical equilibrium. *Suprathermal chemiluminescence* results if the concentrations of the chemical species taking part in the excitation reaction are above the equilibrium value.

[31] *Note:* In atomizers (see Sec. 3.1.1) which incorporate optical windows, trivial reflection losses may also occur. Random reflections of the light beam by unevaporated droplets in the flame are for practical reasons not distinguished here from scattering effects.

[32] *Note:* Conversion of radiation into heat occurs when an atom that has been excited by photon absorption subsequently loses its excitation energy through collisional processes. The energy lost is converted to kinetic energy (see also Sec. 5.1.3). Note that the expression: "absorption of a radiation beam in a medium" means the indirect conversion of radiant energy into heat, whereas the expression: "absorption of a photon by an atom" only means the

Furthermore, *scattering* by particles in the condensed[31] or gaseous phase,[33] may change the direction (but not the energy or frequency) of the incident photons. Resonance fluorescence (see Sec. 5.1.3) is a special case of scattering by free atoms or molecules. Finally, photons may be removed from the original beam when they are transformed into photons of different frequency and direction as a result of non-resonance fluorescence (see Sec. 5.1.3).

The absorption of a photon, by which the atom is raised from a lower level to a higher one, is the reverse process of photon emission. Each atomic line appearing as an emission line, can thus in principle also occur as an absorption line. However, since the overwhelming majority of the atoms in a flame are normally in the ground state, absorption of photons (whether followed by conversion into heat or by fluorescence), is usually detectable only with resonance lines (see Sec. 5.1.1) or with lines absorbed by atoms or ions in low-lying excited states.

For a similar reason, *self-absorption* (see I 7.6.2) is usually found with the resonance lines emitted by the flame or spectral line source. There is a certain probability that the photons of the resonance line which are generated inside the light source, e.g. a flame or a hollow-cathode lamp, may be absorbed on their way out by ground-state atoms and of being partly converted into heat. This results in a loss of intensity of the total outgoing radiation. The loss will be larger, the thicker the cloud of atoms and/or the higher their concentration.[34]

*Self-reversal* of emission lines is a special case of self-absorption which occurs when the radiating core inside the light source (flame, hollow-cathode lamp) is surrounded by a mantle of atomic vapour in which little or no excitation takes place (see I 7.6.3). With a flame, this situation occurs when the temperature in the mantle is appreciably lower than at the centre. The absorption, in the mantle, of the line radiation from the core is then no longer (fully) compensated by the emission of the mantle itself. Since the absorption factor (see Table III.5) has a peak value at the centre of the line, the uncompensated loss of radiation will here be more pronounced than in the line wings. This may result in the appearance of a minimum or *reversal dip* in the centre of the line profile. In the extreme case, when practically only the line wings remain, the line may appear as two diffuse lines.

### 5.1.3 Fluorescence

The absorption of photons from a primary beam to raise an atom to a higher excited state may be followed directly or indirectly by (secondary) photon emission; this process is called *atomic fluorescence*. When the wavelengths of the absorbed radiation in the exciting beam and of the re-emitted radiation are identical, *resonance fluorescence* is said to occur. Resonance fluorescence may be considered to be a special case of scattering (see Sec. 5.1.2). When the wavelengths of the two radiations are different, several cases can be distinguished. *Direct line fluorescence* exists when the transitions in the absorption and fluorescence process have a common upper level. When the upper levels are different, *stepwise line fluorescence* occurs. *Stokes* and *anti-Stokes*

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transition of the atom to a higher excited level. When the excited atom returns to the lower level by re-emission of a photon of the same energy, no conversion of photon energy into heat results.

[33] *Note:* Scattering by free atomic or molecular species is not important in flames when the frequency of the photon does not correspond to any of the optically allowed transitions in the atom or molecule.

[34] *Note:* At high concentrations, where self-absorption becomes noticeable, the intensity of a resonance emission line will therefore increase less than proportionately with increasing atom concentration in the flame. If the emitting species occurs in a zone of the flame with a homogeneous radial temperature distribution, the relation between line intensity and atom concentraiion is described by the *curve-of-growh*. This curve has a linear branch in the range of low concentrations where self-absorption is still negligible. At high concentrations, the intensity increases as the square-root of the concentration (square-root-branch).

*fluorescence* apply when the wavelength of the fluorescence radiation is longer or shorter, respectively, than that of the absorbed radiation.[35]

*Table III.5.* Radiant energy and its interaction with matter. Terms, symbols, and units for measurable quantities

| Terms | Symbol | Practical unit | Note |
|---|---|---|---|
| (Radiant) energy | $Q$ | J | See also I 4. |
| Spectral (radiant) energy | $Q_\lambda$ | J nm$^{-1}$ | When a quantity is considered per unit of wavelength (or frequency) at a given wavelength (or frequency), it is preceded by the adjective "spectral" (see I 4.2). The appropriate symbol is obtained by adding $\lambda$ (or $\nu$) as a suffix, e.g. $Q_\lambda$. Note that the units for $Q$(J) and $Q_\lambda$ (J nm$^{-1}$) are different. The radiant energy contained in a small wavelength interval, d$\lambda$, is given by $Q_\lambda$ d$\lambda$. |
| Intensity (of radiation) | $I$ | 1 | The general term "intensity" may be used as a loose, relative expression referring to any radiant quantity without specification (see also I 6.3.1). Note, however, that "radiant intensity" has a well-defined meaning. |
| Radiant intensity | $I$ | W sr$^{-1}$ | All of above notes apply to this term. |
| Radiant flux | $F$ | W | See also I 4. When this quantity is considered per unit of wavelength (or frequency) at a given wavelength (or frequency), it is preceded by the adjective "spectral" (see I 4.2). The appropriate symbol is obtained by adding $\lambda$ (or $\nu$) as a suffix, e.g. $F_\lambda$. Note that the units for $F$(W) and $F_\lambda$(W nm$^{-1}$) are different. The radiant flux contained in a small wavelength interval, d$\lambda$, is given by $F_\lambda$ d$\lambda$. |
| Radiant flux incident on (absorbing) medium | $F_0$ | W | See also I 5. |
| Radiant flux transmitted by (absorbing) medium | $F_t$ | W | See also I 5. |
| Radiant flux absorbed by medium | $F_a$ | W | See also I 5. |
| Transmission factor ($F_t/F_0$) | $t$ | 1 | See also I 5. This quantity also includes the transmission properties of the apparatus (cell windows, etc.). The value of this quantity, for strictly monochromatic radiation with wavelength $l$, is denoted by $t(\lambda)$ (not: $t_\lambda$) |
| Internal transmission factor | $t_i$ | 1 | The value of this quantity, for strictly monochromatic radiation with wavelength $l$, is denoted by $t_i(l)$. This quantity refers to the transmission properties of the sample alone. |
| (Internal) absorbance ($-\log_{10} t_i$) | $A$ | 1 | This quantity refers to the transmission properties of the sample alone. In AAS, however, the adjective "internal" is usually dropped. |
| Peak value of $A$ (at absorption line centre $\lambda_0$) | $A(\lambda_0)$ | 1 | |
| Absorption path length | $l...b$ | cm | |

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[35] *Notes:* In resonance fluorescence the line need not be a resonance line (see Sec. 5.1. I ), although this will most often be the case.

In stepwise line fluorescence, atoms excited to an upper level by the primary beam are transferred, usually by collisions, to another excited level from which the fluorescent line is emitted.

| | | | |
|---|---|---|---|
| Integral absorption (of spectral line) $[\int\alpha(\lambda)\,d\lambda]$ | $A_t$ | nm | For the use of Å, see I 2.8. This quantity describes the energy absorbed from a continuum within the wavelength profile of a spectral line. |
| (Radiant) energy density | $u, w$ | $j\,cm^{-3}$ | See also I 4. When this quantity is considered per unit of wavelength (or frequency) at a given wavelength (or frequency), it is preceded by the adjective "spectral" (see I 4.2). The appropriate symbol is obtained by adding $\lambda$ (or $\nu$) as a suffix, e.g. $u_\lambda$ |
| Radiance | $B...L$ | $Wsr^{-1}cm^{-2}$ | See also I 4. When this quantity is considered per unit of wavelength (or frequency) at a given wavelength (or frequency), it is preceded by the adjective "spectral" (see I 4.2). The appropriate symbol is obtained by adding $\lambda$ (or $\nu$) as a suffix, e.g. $B_\lambda$ |
| (Einstein) transition probability for spontaneous photon emission (by optical transition from upper state $u$ to lower state $l$) | $A, A_{ul}$ | $s^{-1}$ | Also called (Einstein) coefficient for spontaneous emission. |
| Collisional half-intensity width (of spectral line due to collisional broadening) | $dl_C$ | nm | The term half-width is sometimes used instead of half-intensity width, but may readily be misunderstood as half of the full width. For the use of Å, see I 2.8. |
| $a$-parameter ( $\sqrt{(\ln 2)}\,(dl_C/dl_D)$ | $a$ | 1 | Also called: line-broadening parameter or damping constant. In this definition of $a$, the natural line broadening is disregarded. When natural line broadening is important, it should be included in the numerator. |

Collisions of fluorescing atoms with other atoms or molecules are said to *quench* the fluorescence when they destroy the state of excitation brought about by absorption of the primary photons. The number of secondary photons will then be smaller than the number of primary photons absorbed. The extent of quenching is determined by the competition between the rates of radiative and collisional de-excitation of the excited atoms, and quantitatively expressed by the *efficiency of fluorescence* (for definition see Table III.5).

5.2 Terms, symbols, and units for measurable quantities

Table III.5 presents terms with their symbols and practical units for some measurable quantities belonging to this Section. Sec. I 5 lists additional terms. Although practical units generally conform, alternative symbols that differ from those in Part I are occasionally recommended.

# 6. TERMS, SYMBOLS, AND UNITS RELATING TO THE GASEOUS STATE OF MATTER

Analytical flame spectroscopy and similar techniques are based on the interaction of radiation with the analyte. The strength of this interaction depends on the properties and state of the analyte in the vapour phase. In the following, we restrict ourselves to this phase (the transformation of the analyte from the condensed phase into the vapour phase has already been discussed in Sec. 3.1). A few descriptive terms will be mentioned, followed by a list of terms for measurable quantities with their symbols and practical units.

6.l Descriptive terms concerning the gaseous state of matter

In *(thermodynamic ) equilibrium,* the state of a system is generally described by the *thermodynamic* or *absolute temperature* (Table III.2) which occurs as a universal parameter in the distribution laws. These laws determine the state of *excitation, ionization,* and *dissociation* in which the analyte is found in the gaseous phase.[36]

In atomic spectroscopy, the term "dissociation" usually refers to the splitting of a free molecule into fragments, one or more of which is a free neutral analyte atom, and is thus important in connection with the atomization (see Sec. 3.1.1.1).

Strictly speaking, thermodynamic equilibrium implies that the spectral energy density obeys Planck's law (see *Note* 15 in Sec. 3.2). In flames of analytical interest, this condition is not met except at the centre of strongly self-absorbed resonance lines. However, radiative processes usually play a minor part in the population of the excited states, at least if the flame is not irradiated by an external light beam. The distribution of the particles over their various energy states and over the various forms in which they may occur (as neutral or ionized atoms, or as molecules) is then hardly affected by deviation from Planck's law. The system is then said to be in *thermal equilibrium.* This implies that there is *chemical equilibrium* between all chemical species (including ions and electrons) in the system, as well as *physical equilibrium* for the translational and internal energies of the particles. However, there need then be no *radiative equilibrium.*[37]

6.2 Terms, symbols, and units for measurable quantities

Many of the terms listed in Table III.6 are also found in I 7.3, where the terms are discussed in more detail.

*Table III.6.* Properties and state of matter. Terms, symbols, and units for measurable quantities

| Terms | Symbol | Practical unit | Note |
|---|---|---|---|
| Excitation energy | $E_{exc}$ | J. . .eV | See I 7.4. The electron volt (eV), as a practical unit for energy on an atomic scale, is still in common use. When several excited states are to be distinguished, the excitation energy of state $q$ may be written as $E4$. When several kinds of particles are also considered. the excitation energy of state $q$ of a particle X may be written as $Eq(X)$. |
| Excitation potential | $V_{exc}$ | V | See I 7.4 |
| Ionization energy | $E_{ion}, E_i$ | J. . .eV | |
| Ionization potential | $V_{ion}, V_i$ | V | |
| Dissociation energy | $E_{dis}, D_0, D_{XY}$ | J. . .eV | This is the minimum energy required to dissociate one molecule of XY at zero K in perfect gas state. The fragments must be specified when the molecule contains more than 2 atoms. The molar dissociation energy refers to one mole of substance XY. In chemistry, the symbol D,, is customarily used. |
| Dissociation potential | $V_{dis}$ | V | |

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[36] *Note:* The Maxwell-Boltzmann law describes the distribution over the translational and internal energies of the particles. Planck's law describes the distribution of the radiant energy over the spectrum. Saha's law describes the distribution of the particles over their different states of ionization. while the mass action law determines the fraction of element that is bound in molecular form.

[37] *Note:* In the absence of radiative equilibrium, it is still meaningful to define thermal radiation as it has been done in Sec. 5.1.1.

| | | | |
|---|---|---|---|
| Degree of ionization $[[M^+]/([M] + [M^+])]$ | $\beta_i\ldots g$ | 1 | M denotes an atom; [M] denotes number density of M in the flame (see also Table III.2). |
| Degree of dissociation $[[M]/([M] + [X] + [MX])]$ | $\beta_d\ldots a$ | 1 | M denotes an atom; [M] denotes number density of M in the flame (see also Table III.2). |
| Statistical weight of particle in state $q$ | $gq$ | 1 | When several kinds of particles are considered, the symbol may be extended by adding the chemical symbol X as in: $g_q(X)$. |
| Statistical weight of particle in ground state | $g0$ | 1 | When several kinds of particles are considered, the symbol may be extended by adding the chemical symbol X as in: $g_0(X)$. |
| Partition function | $Z, Q$ | 1 | When several kinds of particles are considered, the symbol may be extended by adding the chemical symbol X as in: $Z(X)$. |
| (Number) density of particles in state $q$ (see also Table III.2) | $n_q$ | cm$^{-3}$ | When several kinds of particles are considered, the symbol may be extended by adding the chemical symbol X as in: $n_q(X)$. |
| (Number) density of particles in ground state | $n0$ | cm$^{-3}$ | When several kinds of particles are considered, the symbol may be extended by adding the chemical symbol X as in: $n_0(X)$. |
| (Number) density of free atoms (M) | $n_{at}, n_a, n_M, n(M), [M]$ | cm$^{-3}$ | |
| (Number) density of free ions ($M^+$) | $n_{ion}, n_i, n_{M+}, n(M^+), [M^+]$ | cm$^{-3}$ | |
| (Number) density of free electrons | $n_e, [e^-]$ | cm$^{-3}$ | |
| (Number) density of molecules MX | $n_{MX}, [MX]$ | cm$^{-3}$ | |
| Total (number) density of element $M(n_M + n_{M+} + n_{MX})$ | $n_t, (n_t)_M, [M]_t$ | cm$^{-3}$ | |
| Ionization constant ($n_i n_e/n_a$ in equilibrium at T) | $K_i, K_i(T)$ | cm$^{-3}$ | |
| Dissociation constant ($n_M n_X/n_{MX}$ in equilibrium at T) | $K_d, K_d(T)$ | cm$^{-3}$ | |