

**INTERNATIONAL UNION OF  
PURE AND APPLIED CHEMISTRY**

**DIVISION OF ANALYTICAL CHEMISTRY**

**COMMISSION ON SPECTROCHEMICAL AND OTHER  
OPTICAL PROCEDURES FOR ANALYSES**

**NOMENCLATURE, SYMBOLS,  
UNITS AND THEIR USAGE IN  
SPECTROCHEMICAL ANALYSIS—I.**

**General Atomic Emission Spectroscopy**

Adopted by the IUPAC Council at Washington, DC, USA,  
during 21–23 July 1971

LONDON

BUTTERWORTHS

# ANALYTICAL CHEMISTRY DIVISION

## COMMISSION ON SPECTROCHEMICAL AND OTHER OPTICAL PROCEDURES FOR ANALYSES†

### NOMENCLATURE, SYMBOLS, UNITS AND THEIR USAGE IN SPECTROCHEMICAL ANALYSIS—I. GENERAL ATOMIC EMISSION SPECTROSCOPY

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## I. FOREWORD

The purpose of this document is to propose a consistent nomenclature for workers in spectrochemical analysis. Many of the terms have already been defined in several nomenclature documents, especially those developed by IUPAC (International Union of Pure and Applied Chemistry), IUPAP (International Union of Pure and Applied Physics) and ASTM (American Society for Testing Materials). The fact that many of the symbols, units, nomenclature and definitions previously recommended are repeated in this document demonstrates that the nomenclature of a specific field, i.e. spectrochemical analysis, is deeply rooted in the general nomenclature of chemistry and physics†. However, the adaptation of a general system to a specialized field requires a careful selection of general terms and the addition of new ones. In a few cases, it was found necessary to deviate from symbols previously recommended in order to avoid using the same symbol for different quantities. Even in a restricted field, the same symbol may have different meanings, e.g. the letter *c* may stand for the speed of light or for concentration depending on the context. In some instances, the Commission has favoured terms which have already been accepted through long usage, though logic would suggest a different terminology. Such terms were accepted only when no misunderstanding may result.

It is not the intention of this report to provide an exhaustive list of terms but rather to present a short list in the hope of securing agreement over a limited field. This report is occasionally cast in narrative form and includes brief explanatory notes. This has been done in cases where the state of the art has not yet achieved a uniform treatment of the subject in question.

The first part of this report is concerned with some general recommendations, while the remainder is concerned with more detailed aspects. A statement by ASTM (American Society for Testing Materials) on general principles of nomenclature standardization is reprinted as an appendix, with the generous permission of ASTM. The Commission endorses the general principles of this statement, while differing in detail on some of the examples.

There are several important fields of spectrochemical analysis not treated in this document but for which agreement on nomenclature is urgently required. Among these are the classification and description of the light sources‡, and nomenclature for flame atomic absorption, emission, and fluorescence spectroscopy, as well as x-ray spectroscopy. These and other items are on the programme of the Commission, but it was felt that the publication of this first set of recommendations should not be delayed by aiming at too high a degree of completeness.

Some remarks about the arrangement of the material in this document are appropriate. Some chapters start with a list of terms and symbols.

† In particular nothing in this document is in conflict with the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* prepared by IUPAC Commission I.1 for the Division of Physical Chemistry.

‡ Often it might be more accurate to speak of a 'radiation source', but the shorter traditional term 'light source' is used, it being understood to include invisible radiation.

accompanied—if necessary—by short explanatory notes. This was done for general terms and symbols to facilitate reference. Other chapters are in the form of a glossary of terms and definitions. This document is therefore not arranged in the systematic order of a textbook; it should be used as a compendium offering information at different levels and for different purposes.

## II. GENERAL RECOMMENDATIONS AND PRACTICES

2.1 For the description of general quantities used in physics and chemistry, the nomenclature and symbols adopted in the most recent official documents of international scientific unions and organizations should be followed. The most important documents are:

1. 'Symbols, Units and Nomenclature in Physics', *Document UIP 11 (SUN 65-3)*; International Union of Pure and Applied Physics [for short, IUPAP 1965]: German edition: Friedr. Vieweg und Sohn, Braunschweig.
2. 'Manual of Physicochemical Symbols and Terminology' (IUPAC), *Pure Appl. Chem.*, **21**, 1 (1970).
3. Publications of the International Organization for Standardization, Technical Committee 12 (ISO/TC 12).

2.2 The symbol for a physical quantity stands for the product of the numerical value (the measure), which is a pure number, and the unit:

$$\text{physical quantity} = \text{numerical value} \times \text{unit.}$$

Therefore in equations composed of symbols for physical quantities, units should not appear.

2.3 Symbols for physical quantities should be single letters of the Latin or Greek alphabets printed in inclined or upright type, with or without modifying signs, i.e. subscripts, superscripts and dashes.

Symbols for units of physical quantities should be printed in upright type.

Numerals should be printed in upright type.

Symbols for chemical elements should be written in upright type.

Indices that are symbols for physical quantities should be printed in inclined type.

(Rules from IUPAP 1965)

2.4 Following the recommendations of IUPAP 1965, a comma should be used in writing decimals, while in English language texts a full stop [period] is permitted. Correspondingly, a cross ( $\times$ ) should be used for the multiplication sign but only between figures or numbers—not between symbols or units—while in texts not in English a point in the middle of the line is permitted.

Quantities less than unity expressed in decimal form should be written with a zero preceding the decimal sign. To help recognition of large numbers, the figures may be grouped in threes, with a [2-unit] space separating pairs of groups. Commas or full stops should not be used for this purpose.

2.5 In this document logarithms will all be understood as logarithms to base 10 (symbol:  $\log x = \log_{10} x$ ).

2.6 Certain symbols and letters extensively employed in mathematical expressions should be reserved for this purpose. These include:  $d$ ,  $\partial$  (partial differential);  $\delta$ ,  $\Delta$  (difference);  $\Sigma$  (sum);  $f$  (function);  $\langle \rangle$ ,  $\bar{\phantom{x}}$  (average), and  $x$ ,  $y$ ,  $z$  for spatial coordinates, and for the general description of measurable quantities.

## 2.7 Usage of certain general words in connection with numerical values.

'Constant' should only be used for numerical values which really are constant, particularly for universal constants, such as the gas constant or the Boltzmann constant. 'Constant' may also be applied to unvarying material constants, such as the dielectric constant. 'Coefficient' should only be used for numerical values which occur in equations of proportionality, for example, 'coefficient of recombination'. (In English these numbers are often indicated by the termination 'ity', e.g. 'absorptivity'.)

'Index' should only be used to indicate values arising from ratios, e.g. 'refractive index'. Since quantities having the dimension unity<sup>†</sup> are concerned, it is sufficient on occasion also to use the simple expression 'number'.

2.8 The 'International System of Units (SI)', is recommended. A summary of its base<sup>‡</sup> and some supplementary and derived units is given in *Table 2.1*.

SI units for other physical quantities can be derived from the seven base units by multiplication or division without introducing numerical factors; this system is **coherent**. This recommendation is often too rigorously interpreted. For example, the exclusive use of the SI units (base or derived) is not obligatory when this leads to a unit which is inconvenient in practice [e.g. the farad is too large; microfarad ( $\mu\text{F}$ ) and picofarad ( $\text{pF}$ ) are commonly used]. Any decimal multiples and fractions of SI units may be used, provided they are clearly stated. There are officially recommended names and symbols for powers of ten in frequent use. In spectroscopy, the Ångström is widely used as unit of wavelength ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ). It is a decimal fraction of the SI unit of length, the metre. The Ångström has a convenient order of magnitude for the description of optical line spectra and atomic or molecular distances. The nanometer, however, is by one order of magnitude too large, but may be preferred for optical absorption spectroscopy, where relatively wide absorption bands must be described.

2.9 Quantitative definitions should, whenever possible, be given by means of equations.

2.10 In the nomenclature lists which follow, alternatives are occasionally recognized. If the alternative symbols are separated by a comma, then both are equally usable. Separation by a row of dots signifies that the first written symbol is preferred.

### III. TERMS AND SYMBOLS FOR PHYSICAL QUANTITIES IN GENERAL USE

(Extracted from IUPAP 1965)

#### 3.1 Basic physical quantities:

length	$l$
mass	$m$
time	$t$
electric current	$I$
thermodynamic temperature	$T$
luminous intensity	$I_v$

<sup>†</sup> Formerly called 'dimensionless'.

<sup>‡</sup> The word 'base' was chosen by the Commission Générale des Poids et Mesures with respect to non-English languages.

Table 2.1. Summary of SI base, supplementary and derived units

Physical quantity	Name of SI unit	Symbol for SI unit	Definition of units	Type
length	metre	m	—	Base
mass	kilogramme	kg	—	Base
time	second	s	—	Base
electric current	ampere	A	—	Base
thermodynamic temperature	kelvin	K	—	Base
luminous intensity	candela	cd	—	Base
amount of a substance	mole	mol	—	Base
plane angle	radian	rad	—	Supplm.
solid angle	steradian	sr	—	Supplm.
force	newton	N	$\text{kg m s}^{-2}$	Derived
pressure	pascal	Pa	$\text{kg m}^{-1} \text{s}^{-2}$ ( $= \text{N m}^{-2}$ )	Derived
energy	joule	J	$\text{kg m}^2 \text{s}^{-2}$	Derived
power	watt	W	$\text{kg m}^2 \text{s}^{-3}$ ( $= \text{J s}^{-1}$ )	Derived
electric charge	coulomb	C	A s	Derived
electric potential difference	volt	V	$\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$ ( $= \text{J A}^{-1} \text{s}^{-1}$ )	Derived
electric resistance	ohm	$\Omega$	$\text{kg m}^2 \text{s}^{-3} \text{A}^{-2}$ ( $= \text{V A}^{-1}$ )	Derived
electric conductance	siemens	G	$\text{kg}^{-1} \text{m}^{-2} \text{s}^3 \text{A}^2$ ( $= \text{A V}^{-1} = \Omega^{-1}$ )	Derived
electric capacitance	farad	F	$\text{A}^2 \text{s}^4 \text{kg}^{-1} \text{m}^{-2}$ ( $= \text{A s V}^{-1}$ )	Derived
magnetic flux	weber	Wb	$\text{kg m}^2 \text{s}^{-2} \text{A}^{-1}$ ( $= \text{V s}$ )	Derived
inductance	henry	H	$\text{kg m}^2 \text{s}^{-2} \text{A}^{-2}$ ( $= \text{V A}^{-1} \text{s}$ )	Derived
magnetic flux density	tesla	T	$\text{kg s}^{-2} \text{A}^{-1}$ ( $= \text{V s m}^{-2}$ )	Derived
luminous flux	lumen	lm	cd sr	Derived
illumination	lux	lx	cd sr m <sup>-2</sup>	Derived
frequency	hertz	Hz	s <sup>-1</sup>	Derived

## 3.2 Other physical quantities

space coordinates	$x, y, z$
breadth (width)	$b$
height	$h$
radius	$r$
area	$S, A$
volume	$V$
plane angle	$\alpha, \beta, \gamma, \delta, \theta, \varphi$
solid angle	$\omega, \Omega$
wavelength	$\lambda$
wavenumber ( $\sigma = 1/\lambda$ )	$\tilde{\nu}, \sigma^\dagger$
period	$T$
frequency ( $f = 1/T$ )	$\nu, f^\ddagger$
velocity	$v, u$
velocity (average)	$\bar{v}, \bar{u}$
speed of light (in vacuum)	$c, c_0$
relaxation time	$\tau$
radial frequency ( $2\pi f$ )	$\omega$
pressure	$p$
force	$F$
energy	$E$
power (energy divided by time)	$P$

#### IV. TERMS, SYMBOLS AND UNITS RELATED TO RADIANT ENERGY

4.1 *Table 4.1* groups together the nomenclature and symbols used to describe sources of radiant energy and their activity.

The table is restricted to a few essential terms. Items 1 and 2 are of a general nature, 3, 4, 5 and 6 refer to the source of the radiation, 7 and 8 to the receiver or irradiated object. Other radiation quantities with special names, occasionally with special units, occur in the literature, but they are superfluous.

4.2 The radiation quantities in *Table 4.1*, in particular  $\Phi$ ,  $I$ ,  $B$ ,  $J$  and  $u$  will in general be functions of the wavelength  $\lambda$  (or of the wavenumber  $\tilde{\nu}$  or the frequency  $\nu$ , as the chosen variable may be). They may also be functions of other variables, e.g. the temperature or the elements present. Thus, it may be necessary to consider the quantity of  $\Phi$ ,  $I$ ,  $B$ , etc. within a small region, for example a *bandwidth* of wavelengths. The radiance within such a bandwidth  $\Delta\lambda$  would be:  $\{dB(\lambda)/d\lambda\}/\Delta\lambda$ . For convenience, the differential quotient may be indicated by a subscript, as in  $dB/d\lambda = B_\lambda$ ;  $B_\lambda$  is called *spectral radiance*. The symbols  $\Phi_\lambda$ ,  $I_\lambda$  have corresponding meanings and the adjective spectral is used to distinguish them from the quantities treated in § 4.1.

4.3 In spectrochemical analysis, the wavelength  $\lambda$  normally describes a position within a spectrum. In other fields of spectroscopy, wavenumbers  $\tilde{\nu}$ , frequencies  $\nu$  or periods  $T$  are used as variables. Therefore, it may be useful

†  $\tilde{\nu}$  is exclusively used in molecular spectroscopy.

‡  $\nu$  in spectroscopy,  $f$  in electrotechnics.

I Name	II Symbol	III Definition	IV Dimensions	V SI unit	VI Practical unit
1. radiant flux or radiant power	$\Phi$	power in the form of radiation	power	W	W
2. (radiant) energy	$Q$	$Q = \int_0^t \Phi dt$	energy	J	$W s = J$
3. radiant intensity	$I$	$I = \Phi/\omega$	$\frac{\text{power}}{\text{solid angle}}$	$W sr^{-1}$	$W sr^{-1}$
4. radiance	$B \dots L$	$B = \frac{\Phi}{S\omega \cos \epsilon}$	$\frac{\text{power}}{\text{solid angle} \times \text{area}}$	$W sr^{-1} m^{-2}$	$W sr^{-1} cm^{-2}$
5. (radiant) emissivity	$J$	$J = \frac{\Phi}{V\omega}$	$\frac{\text{power}}{\text{solid angle} \times \text{volume}}$	$W sr^{-1} m^{-3}$	$W sr^{-1} cm^{-3}$
6. (radiant) energy density	$u$	$u = Q/V$	energy/volume	$J m^{-3}$	$J cm^{-3}$
7. irradiance	$E$	$E = \Phi/S$	power/area	$W m^{-2}$	$W cm^{-2}$
8. (radiant) exposure	$H$	$H = \int_0^t E dt$	$\frac{\text{power} \times \text{time}}{\text{area}}$	$J m^{-2}$	$W s cm^{-2} = J cm^{-2}$

Reference to 3 to 8:

It must be kept in mind that the basic quantity in this system, the radiant flux  $\Phi$ , may vary in space and direction. Therefore the area  $S$ , the solid angle  $\omega$  and the volume  $V$  in the defining equations 3 to 8 must be small enough to give meaningful local values for the derived quantities.

Reference to 4, 7 and 8:

$S$  refers to the area of the radiating element for the term radiance, and to the area of the irradiated element for the terms irradiance and (radiant) exposure;  $\epsilon$  is the angle between the normal to the surface and the direction of the radiating beam, which is assumed to be confined to a narrow solid angle.

Reference to 4:

The old symbol  $B$  is recommended for radiance in contradiction to IUPAC 1970 [*Pure Appl. Chem.* **21**, 1 (1970)], which only lists  $L$ . The letter  $L$  should not be used for radiance in atomic emission spectroscopy, since  $L$  is also the symbol for the spectrum line, for the orbital quantum number and also for self-inductance. Reference to 7 and 8:

The letter  $E$  may logically be expected as a symbol for the radiant exposure. However,  $E$  has been internationally adopted for irradiance, while  $H$  was chosen as symbol for exposure. Both quantities are important in photographic photometry, but they are seldom used in the practice of spectrochemical analysis. Reference to 2, 5, 6 and 8:

In these cases the adjective radiance may be omitted, if the meaning of the term is clear from the context. Radiant should not be dropped from radiant flux and radiance.

Reference to 4, 5, 6, 7 and 8:

For the practical units it is proposed to use the centimetre as a unit of length. (This is allowed, see para. 2.8.) The reason for this proposal is obvious: the dimensions of most radiant sources used in spectroscopy are of the order of a centimetre. The use of this unit therefore helps visualization.

to list here the relationships of bandwidths expressed in different variables and of the *spectral radiation quantities*, e.g. the spectral radiant flux  $\Phi_\lambda$ :

$$\begin{aligned}\lambda\tilde{\nu} &= 1 & \lambda\nu &= c & \lambda &= Tc \\ \Delta\lambda &= -\Delta\tilde{\nu}/\tilde{\nu}^2 = -c\Delta\nu/\nu^2 = c\Delta T \\ \Phi_\lambda &= -\tilde{\nu}^2\Phi_{\tilde{\nu}} = -\nu^2\Phi_\nu/c = \Phi_T/c\end{aligned}$$

4.4 The different radiation quantities for the *black body* play an important role in spectroscopy as natural standards because they are determined by constants of nature, temperature and wavelength. They may be distinguished by an additional superscript, the letter *b*; for example the *spectral radiance of the black body*:  $B_\lambda^b$ .

4.5 If the radiation acts as *light*, affecting the human eye, the radiation may be measured and appreciated in a different way, taking into account not only the physical but also physiological processes. The technique of measurement of light in this context is called *photometry*.

Although in modern spectroscopy visual observations and measurements have become very rare, it seems advisable to give some explanation of photometry. There has been much confusion in the past by inappropriate use of photometric terms and units in the measurement of radiation quantities.

(a) There is a set of luminous quantities, which correspond to the radiant quantities of *Table 4.1*. The same symbols are used. If confusion between luminous and radiant quantities may occur, subscripts should be added: e (energy) for radiant, v (visible) for the luminous quantities. [It has been proposed that in cases where the number of quanta has been determined instead of the energy, the subscript q might be added.]

(b) A relationship between *radiant* and *luminous* quantities has been established by the definition of the *normal eye* (*standard observer*). The normal light-adapted eye is characterized by a wavelength dependent function, the (spectral) *luminous efficacy*  $K(\lambda)$ , whose maximum  $K_m$  occurs at 555 nm and has the value  $K_m = 680$  lm/W. The function  $K(\lambda)/K_m = V(\lambda)$  is called (spectral) *luminous efficiency*. The relation between radiant flux  $\Phi_e$ , and the luminous flux  $\Phi_v$  is as follows

$$\Phi_v = K_m \int_{380 \text{ nm}}^{780 \text{ nm}} V(\lambda) \Phi_e, \lambda d\lambda$$

For the exact values of  $K_m$  and  $V(\lambda)$ , the most recent publications from the International Commission on Illumination (CIE)† should be consulted.

## V. TERMS AND SYMBOLS FOR THE DESCRIPTION OF SPECTROGRAPHIC INSTRUMENTS

5.1 *Geometrical quantities*—In this section the terms and symbols are described with a *spectrograph* in mind. The modifications necessary to consider other forms of spectral apparatus will be self-evident.

5.1.1 In the spectrograph the whole range of spectrum allowed by the design of the instrument is recorded on the photographic plate.

† CIE Publication No. 17 (E-1.1) 1970.

When in place of the photographic plate, direct means are used to measure intensities in the spectrum, the instrument is described as a *spectrometer*. For example, a thermopile or a photoelectric device may be made to scan the spectrum in the focal plane, measuring the intensity at each position.

If the focal plane is obstructed except for one slit, the instrument is called a *monochromator*. The bandwidth of the spectrum which emerges through the exit slit depends *inter alia* upon the widths of the entrance and exit slits. A monochromator is usually provided with means for altering the mean wavelength of the band transmitted, but there are also fixed monochromators, which then correspond to a filter.

The *polychromator* is an extension of the monochromator, a number of exit slits being placed in the focal plane, so allowing a number of discrete bands to pass through (for example, to fall upon a number of photomultipliers).

5.1.2 Light enters a spectrograph through a *slit* having a geometric slit-width  $s$  and height  $h$ .

5.1.3 The light strikes a collimator lens or mirror which has an *aperture stop* of diameter  $D$ , or the aperture stop may have a rectangular clear cross-sectional area  $S$  of width  $D_s$  (parallel to the width of the slit) and height  $D_h$ . The *effective diameter* for a non-circular aperture stop of area  $S$ , ( $D_{\text{eff}}$ ) is given by  $(4S/\pi)^{\frac{1}{2}}$  or  $(4D_s D_h/\pi)^{\frac{1}{2}}$ .

5.1.4 The *focal length* of the collimator lens or mirror is  $f$ , and the light-gathering power of the lens is measured by the  $f$ -number which is  $f/D_{\text{eff}}$ .

5.1.5 The light then encounters a dispersing system (see 5.1.9) and after dispersion the light enters an objective lens or mirror, where beams of different wavelengths are focused to form images of the entrance slit at different places along the focal plane.

5.1.6 In order to counteract the variation with wavelength of the *focal length*  $f'$  of the objective lens, it may be necessary to tilt the photographic plate, and the *tilt of the plate*,  $\theta$ , is the angle between the normal to the plate and the direction of the camera axis.

5.1.7 The practice of optical designers in distinguishing magnitudes in the image space from similar ones in the object space by using a prime is adopted, hence the  $f'$  used in the previous paragraph. In a monochromator, for example, the exit slit has width  $s'$  and height  $h'$ .

5.1.8 The light during passage through an instrument has a *beam* of width  $W$ , and one may distinguish at times  $W_s$  and  $W_h$ .

5.1.9 The dispersing system may be a prism or a series of prisms, and the *length of the total effective prism base* is  $b$ . The effective base is the difference between the lengths, measured within the prisms, of the extreme rays near the base and near the apices, respectively. Alternatively, the dispersing system may be a diffraction grating, having a *total number of rulings*,  $N_r$ . The *number of grating rulings per unit length* is  $n_r$ . The rulings may possess a *blaze-angle*  $\beta$ , which is the angle between the operating facet of the grooves and the overall plane of the grating. This results in the grating enhancing the intensity of wavelengths near to a blaze wavelength  $\lambda_\beta$ . (The order of the spectrum to which the blaze refers should be stated.) The *order of the spectrum* is preferably denoted by  $m$ , although  $k$  is accepted.

5.2 *Optical quantities*—5.2.1 The *refractive index* of a material is  $n$ .

5.2.2 When a spectral bandwidth is to be indicated in terms of wavelength, the symbol is  $\Delta\lambda$ . For the width of a spectral line at half-peak intensity—as it appears in a spectrum produced by an instrument—the symbol is  $\delta\lambda$ . The *width of the line itself* as it would be shown by an instrument of very high resolving power can be written as  $\delta_1\lambda$ . (This includes the natural width, Doppler and Stark effects, pressure broadening, etc). The *minimal line width* which can be produced by a spectroscopic instrument for reasons of principle (mostly limited by diffraction) is written  $\delta_0\lambda$ .

The (theoretical) *resolving power*  $R_0$  of a spectroscopic instrument is defined by  $R_0 = \lambda/\delta_0\lambda$ . Very often this resolving power  $R_0$  cannot be used or attained for practical reasons (e.g.  $\delta_1\lambda > \delta_0\lambda$ ; optical aberrations and necessity to use a wide slit). In such cases, the (*practical*) *resolution*  $R$  is defined by  $R = \lambda/\delta\lambda$ .

5.2.3 *Dispersion*  $dz/d\lambda$  is qualified in different ways according to the concept indicated by  $z$ . For example, substitution of  $z$  by  $n$  gives  $dn/d\lambda$  the *dispersion of a material*, by angle  $\varphi$ , *angular dispersion*, while substitution of  $z$  by the separation  $x$  of spectral lines gives the *linear dispersion*.

5.2.4 The reciprocal of the last named quantity is more frequently used, and referred to as the *reciprocal linear dispersion*,  $d\lambda/dx$ , and it is commonly expressed in  $\text{\AA}/\text{mm}$ .

5.3 *Quantities related to the transport of radiant energy*—5.3.1 Three expressions are used to describe how an optical system transmits, reflects or absorbs radiation. They are optically composite quantities (for example, the transmission factor of a monochromator) so to indicate this they are called factors.  $\Phi_0$  is the radiant flux entering the system. The respective terms are:

<i>transmission factor</i>	$\tau = \Phi_t/\Phi_0$
<i>reflection factor</i>	$\rho = \Phi_r/\Phi_0$ and
<i>absorption factor</i>	$\alpha = \Phi_a/\Phi_0$

5.3.2 A little known but useful quantity is the *optical conductance*  $G$  that describes the geometrical restriction of the radiant flux through an instrument (or optical system) by the apertures and the distances separating them. This quantity is discussed in detail in Appendix B.

## VI. TERMS AND SYMBOLS RELATED TO THE ANALYTICAL PROCEDURES

6.1 *Qualitative terms concerning the sample*—In analytical spectroscopy, *material* is provided, and from this is taken a *sample* that is submitted for analysis. The material has a certain composition, consisting of an aggregate of *constituents*. If the proportion of one constituent predominates, it is referred to as the *major constituent*. The latter term should be distinguished from the description of the character of the material as a whole, e.g. granite, organic tissues, solutions, which are referred to as the *base*. The element sought or determined in the sample is the *analysis element*.

Samples may be transformed into a *solution*. Here we distinguish between the *solvent* (for example, water or a mixture of water and alcohol) and *concomitants*, which include constituents other than the analysis element in the solution.

The term *matrix* refers to the sample, considered as an assemblage of

constituents, with all their individual properties. The combined effect that the various constituents of the matrix may exert on the measure of the analysis element is referred to as the *matrix effect*.

6.2 *Quantitative terms concerning the sample*—6.2.1 The *quantity* of a substance resulting from an analysis is written as  $q$ , and the unit in which it is measured must be stated explicitly (e.g. g, mg,  $\mu\text{g}$ ). The *concentration* is represented by the symbol  $c$ , in terms of mass, volume, number, or by any other means, but the units must be expressly stated. For very small concentrations, the expression *parts per million* (p.p.m.) by weight may be used without any ambiguity for impurities in solids. For trace impurities in solution, the term  $\mu\text{g/ml}$  is less ambiguous than p.p.m. and is strongly recommended. The phrase '*parts per billion*' is ambiguous and its use is discouraged.

6.2.2 Normally the *concentration* is expressed relative to the whole sample. The ratio of the concentration of a particular element to that of another one (usually present in high concentration) is called the *concentration ratio* (of X to Y) and is given the symbol  $c_r$ . In spectrochemical analysis the denominator is often the concentration of a *reference element* R, while the numerator is the concentration of the element to be determined, the *analysis element* X (see also para. 6.3.2). The *reference element* may be an important component, or it may be specially added for the purpose. If *concentration ratios* are used, the two concentrations must be expressed in the same units.

6.3 *Terms concerning the procedure*—6.3.1 In emission spectroscopy the physical quantity which is used to characterize and measure the concentration to be determined is referred to as the *intensity*. *Intensity* is one of the most frequently used words in spectroscopy in general and also in spectrochemical analysis. One speaks of the intensity of a spectrum line, of the background, of an absorption band, or of a beam of light etc. *Intensity* is a generally useful word, guiding one's thoughts in the direction of energy or power, but so far without a definite scientific meaning and therefore an offence to a nomenclature-minded scientific conscience. Therefore the use of the term *intensity* must be made respectable without sacrificing its generality. The purpose of every quantitative spectrochemical analysis is to determine a *concentration*  $c$  or a *quantity*  $q$  of a substance from the measurements. The particular physical quantity which is derived from the experimental observation (e.g. the pointer-reading of a voltmeter) is related to a radiant quantity, in photographic measurements usually a (radiant) *exposure*  $H$  and in photoelectric measurements a *radiant energy*  $Q$ . In practice it is often unnecessary to consider what radiant quantity is really measured, or to refer to the particular radiant property of the light source (*radiance* or *radiant intensity*). Then the indefinite expression *intensity*  $I$  can be used for the relative strength of a spectral line. Confusion is unlikely to happen with the *radiant intensity* which also has the symbol  $I$ ; the meaning will be clear from the context. *Intensity of a spectral line or of the background in a spectrum is then a loose relative expression referring to the radiant quantity measured by the receiver. This intensity has unit dimension.* In many cases it is not necessary to state or to determine explicitly to which reference intensity the observed value is referred. The concept of such a reference is always implicit in the use of the term *intensity*.

The relative nature of *intensity* is explicit when *internal reference lines* in

the spectrum are used. Then accidental variations in the physical conditions of the experiment (especially in the light source) are generally without harmful effect, since one measures the intensity  $I_X$  of the spectral line of the *analysis element* in relation to the intensity  $I_R$  of a line of a suitably selected *reference element* (see also 8.4.4). Ideally both the analysis element line intensity and the reference element line intensity should respond to changes in the experimental conditions in the same way and rate (Gerlach's *homologous lines*).

6.3.2 If the *analytical curve* is plotted in logarithmic coordinates for both axes, and concentration ratios are introduced, a straight line is often obtained:

$$\log c_r = \eta \log I_X/I_R + \log c_0$$

which corresponds to the Lomakin-Scheibe equation

$$c_r = c_0 (I_X/I_R)^\eta$$

In this equation,  $c_0$  is often spoken of as the *concentration index*, and from the equation will be seen to be that concentration ratio  $c_r$  for which  $I_X/I_R$  is unity and consequently  $\log I_X/I_R$  is zero. Very often, the slope  $\eta$  in the above equation is near to unity.

6.3.3 There is normally radiation present at the wavelength of the analysis element and reference element lines that does not arise from the specific electron transitions which produce the line radiation. This extra radiation, which is designated as *background*, may be part of a spectral continuum or of unresolved molecular bands. If the spectrum is photographically recorded, this *background* is to be clearly distinguished from the *fog* of the photographic plate, an overall greying of the plate due to the development process, ageing of the plate and similar processes. When it is useful to distinguish quantities concerning a line from similar quantities concerning the background, the subscripts L and U are used respectively (U is taken from the German term *Untergrund*, since B is already used for radiance).

6.3.4 In addition to background, radiation from other nearby spectral lines may perturb the measurement of intensity of the wanted line. Such lines are referred to as *interfering lines*.

6.3.5 Another type of unwanted radiation is the light which reaches the receiver in unintended ways. This radiation is identified as *stray light*.

## VII. TERMS AND SYMBOLS RELATED TO FUNDAMENTAL PROCESSES OCCURRING IN LIGHT (EXCITATION) SOURCES

7.1 *General rules*—The intensities of spectral lines emitted by a source depend on the fundamental properties of the atoms, molecules and other particles present, on their relative concentrations and on the physical conditions prevailing in the source. The system of terms and symbols must therefore be able to provide a simple means of distinguishing these properties, concentrations or conditions, when and to whatever extent it is necessary to do so. To do this with simple means, terms and symbols are employed which are already accepted by IUPAP or by IUPAC.

When, and only when, these symbols refer to different species of particles present at the same time, the correlation to the species may be given by

adding in parentheses the symbol of the particle. For example, the mass number of magnesium would be denoted by  $A(\text{Mg})$ .

The electric charge of the species may be indicated at the same time by the superscripts

$$0, +, 2 + \dots\dots\dots$$

for the neutral, singly ionized, doubly ionized  $\dots\dots\dots$  species (correspondingly for negative ions, substituting the negative sign). According to general usage, accepted by IUPAC and IUPAP, symbols relating to the electron have  $e$  as subscript, e.g.  $N_e$  denotes the number of electrons,  $P_e$  the electron pressure. The symbol  $e$  by itself represents the electron. (In the equations of equilibrium, where the symbol for the electron may occur as well as the base of the natural logarithms, the conflict of symbols may be avoided by the modern usage of 'exp' for the exponential function.)

### 7.2 Physical constants and properties of particles:

Avogadro constant	$N_A$
Boltzmann constant	$k$
Planck constant	$h$
Gas constant (molar)	$R$ (should be distinguished from Rydberg constant, $R_y$ )

Atomic mass	$m$
Atomic weight	$M$
Atomic mass of species X	$m(X), m_X$
Atomic weight of species X	$M(X), M_X$
Mass number	$A$
Atomic number	$Z$
Mass number of species X	$A(X), A_X$
Atomic number of species X	$Z(X), Z_X$
Elementary charge	$e$
Electron mass	$m_e$

### 7.3 Terms, symbols and units for measurable quantities:

Number of particles	$N$
Number of particles of species X	$N(X), N_X$
Number density of particles per unit volume	$n$
Number density of particles in state $q$	$n_q$
Number density of element as free atom	$n_{\text{at}}$
Number density of element as free ion	$n_{\text{ion}}$
Number density of electrons	$n_e$
Total number density of element in different forms (atom, ion, molecule) in the gaseous state	$n_t$
Number density of ground state species X	$[X_0]$
$n_{\text{at}}$ for atoms of X	$[X], n_{\text{at}}(X)$
$n_{\text{ion}}$ for ions of $X^+$	$[X^+], n_{\text{ion}}(X)$
$n_t$ for element X	$[X]_t, n_t(X)$
Number density of excited species $X^*$	$[X^*]$

Total gas pressure	$p, p_1$
Partial pressure of species X	$p(X), p_X$
Excitation energy	$E_{\text{exc}}$
Excitation energy of state $q$ of species X	$E_{qk}(X), (E_q)_X$
Excitation potential	$V_{\text{exc}}$
Ionization energy	$E_{\text{ion}}, E_i$
Ionization potential	$V_{\text{ion}}, V_i$
Dissociation energy (minimum energy required to dissociate one molecule, or one mole, of XY at $T = \text{zero K}$ in perfect gas state)	$D_0, D_{XY}$
Kinetic energy of particle	$E_{\text{kin}}, E_k$
Statistical weight of state $q$	$g_q$
Statistical weight of ground state	$g_0$
Statistical weight of state $q$ of species X	$g_q(X), (g_q)_X$
Partition function	$Z, Q$
Partition function of species X	$Z(X), Z_X$
Transition probability for spontaneous transition from state $q$ to state $p$	$A_{qp}$ [ $B_{pq}$ for the reverse absorption transition]
Degree of dissociation of species MX ( $[M]/[M] + [MX]$ )	$\beta_d, \alpha$
Degree of ionization of species M ( $[M^+]/[M^0] + [M^+]$ )	$\beta_i, \gamma$
Dissociation constant of MX in equilibrium at $T$ ( $[M][X]/[MX]$ )	$K_d(T)$
Ionization constant of M in equilibrium at $T$ ( $[M^+][e^-]/[M^0]$ )	$K_i, K_i(T)$
Frequency of spectral line emitted due to transition $q \rightarrow p$	$\nu_{qp}$
'Intensity' of spectral line emitted by electron transitions from states $q \rightarrow p$	$I_{qp}$
Thermodynamic temperature	$T$

7.4 *Conversion factors*—In considering the excitation of particles in a light source, certain values of energy play important roles. These require extensive explanation because the colloquial usage of nomenclature is untidy. To bring a particle into an excited state (or to a higher energy level) a certain amount of energy must be provided. This amount of energy is called the 'excitation energy' and is denoted by  $E_{\text{exc}}$ . The appropriate SI unit is the joule. To facilitate the calculation of wavelength, the energy levels of particles are often given as (*spectroscopic terms*),  $T$ , with unit  $\text{cm}^{-1}$ . The corresponding energy in joules may be obtained by multiplying the numerical value (in  $\text{cm}^{-1}$ ) by  $10^2 hc$  (in  $K_q \text{ cm}^3 \text{ s}^{-2}$ ), that is, by a factor close to  $2 \times 10^{-23}$ . Since this factor is constant, the energy may be represented by the corresponding term-values in  $\text{cm}^{-1}$ , although the dimensions are incorrect.

A similar situation arises through electron-impact experiments. The kinetic energy acquired by an electron in an electric field is given by the product of the electric charge and the difference of potential through which the electron moves.

Since the charge is constant, the kinetic energy of the electron may be represented by giving the value of the potential difference applied in volts. Referring to excitation processes, this potential difference is called *excitation-potential*,  $V_{\text{exc}}$  and is measured in volts. For the energy, a special unit has been devised which is numerically equal to the potential difference, called the electron volt† with the symbol eV. As a unit it is incoherent with the SI units :

$$\text{one eV equals } 1.6 \times 10^{-19} \text{ J}\ddagger.$$

There is a special case of excitation energy just sufficient to free an electron from the particle: this is called *ionization energy*,  $E_i$ .

### 7.5 Electrical terms:

Quantity of electricity	$Q$
Potential, potential difference	$V$
Tension	$U$ , e.g. $U = IR$
Electric current	$I$
Capacitance	$C$
Resistance	$R$
Self inductance	$L$
Mutual inductance	$M, L_{12}$
Reactance	$X$
Coupling coefficient	$k$ ; $k = M/(L_1L_2)^{\frac{1}{2}}$
Electric field strength	$E$
Current density	$j$

If the vector character of  $E$  and  $j$  is to be brought out, these letters should be printed in heavy type.

Power  $P$

7.6 *Special terms*—7.6.1 *Spectral lines*. This term originates from the appearance of an atomic spectrum observed with a spectroscope having high resolution. The individual lines are monochromatic images of the entrance slit. In atomic spectroscopy, this origin has been obscured and the term is now employed to describe a very narrow band of frequencies of electromagnetic radiation resulting from electron transitions in atoms. If the atom has its complete complement of electrons, the transition results in an *atomic line*. This type of line is indicated by the element symbol, followed by I; if one or more electrons are missing, the result is an *ionic line*. To distinguish between the different states of ionization, the type of line is indicated by the element symbol, followed by II, III, IV, etc. (These numbers should be in Roman small capitals.) Examples are: Na I, Mg II and Al III. The terms 'arc line' and 'spark line' do not distinguish them in the way intended and they should not be used.

† The use of the electron volt as an energy unit is discouraged by IUPAC, although excitation potentials given in volts fit into the International System of Units.

‡ Slightly rounded.

7.6.2 *Self-absorption* occurs in emission sources of finite thickness when radiant energy quanta emitted by atoms (or molecules) are absorbed by atoms of the same kind present in the same source. The absorbed energy is usually dissipated through collisional transfer of energy, or through emission of radiant energy of the same or other frequencies. In consequence, the observed radiant intensity of a spectral line (or band component) emitted by a source may be less than the radiant intensity would be from an optically thin source having the same number of emitting atoms. Self-absorption may occur in all emitting sources to some degree, whether they are homogeneous or not.

7.6.3 *Self-reversal* describes the effect of self-absorption on the shape of the spectral line emitted in light sources that are inhomogeneous in temperature or excitation conditions in the direction of observation. Self-reversal is manifested as a decrease in intensity at the wavelength centre of the line. In extreme cases, the intensity at the wavelength centre may become so weak that practically only the wings remain, giving the appearance of two fuzzy lines.

7.6.4 *Intensity versus time curve*. In spectrochemical analysis the study of the variation of the intensity of a spectrum line with time is very important. When the aim is to study the volatilization and excitation of a sample for spectrochemical analysis, especially to choose the optimal exposure, the plot of intensity versus time is called the *intensity time curve*. The duration of such a study may be of the order of from tens of seconds to several minutes. The time range selected for the analytical exposure is the *exposure time*. If an initial portion of the excitation cycle is rejected before the analytical exposure is made, these time intervals are designated as *pre-arc* or *pre-spark* periods, or other appropriate terms depending on the light source employed. *Time-resolved spectroscopy* refers to very short exposure periods, e.g. microseconds to milliseconds, employed when physical conditions in the light source are studied.

7.7 *Classification of additives*—7.7.1 *Additives* are substances added to samples for various purposes. There are many individual names for such substances, which have arisen historically rather than systematically. The following scheme is an attempt to frame a system in such a way that the name indicates the way the additive operates.

7.7.2 *Spectrochemical buffers* are added to samples and reference samples with the intention of making the measure of the analysis element less sensitive to changes in concentration of an interferent.

7.7.3 A *diluent* is a substance added to a sample mainly to increase its bulk for ease of handling. This addition may bring other benefits such as the suppression of undesirable effects due to the previous composition of the material (see para. 6.1 *matrix effects*).

7.7.4 Material added to a sample to increase its volatilization, or that of some component of it, is a *volatilizer*, while, if it is done for the opposite reason, it is called a *devolatilizer*. Examples of volatilizers are:  $\text{AlF}_3$ , or  $\text{NaF}$ , used with uranium, boron or silicon; also all chlorides. A typical devolatilizer is carbon, which gives rise to refractory carbides when used in the analysis of tungsten or boron.

7.7.5 A *spectrochemical carrier* is an additive which gives rise to a gas

which can help to transport the vapour of the sample material into the excitation region of the source, e.g. carbon in an air atmosphere when carbon dioxide is formed.

## VIII. PHOTOGRAPHIC INTENSITY MEASUREMENTS (PHOTOGRAPHIC PHOTOMETRY)

8.1 *Introduction*—Photographic intensity measurements play an important part in spectroscopy and spectrochemistry. This is due to the enormous information capacity of a photographic emulsion, which produces an image of an extended spectrum in one exposure, showing not only the analysis line under consideration but many other features as well.

The type of such measurements, required in spectrochemical analysis, is relatively simple: line intensities are to be compared within one spectrum only (or a few of them) where the physical conditions are known and can be kept constant. This makes calibration easy and allows a straightforward approach, which will be outlined in this section.

8.2 *Outline of the measuring procedure*—8.2.1 The aim of photographic photometry as used in spectrochemical analysis is the measurement of the comparative *intensities* of spectrum lines. (Symbols:  $I$  and in the case of logarithmic presentation  $Y = \log I$ .)

8.2.2 The physical quantity affecting the emulsion (plate, film) while it is exposed is the (*radiant*) *exposure*  $H$ . In general practice it is assumed that  $H$  is proportional to the intensity  $I$ , so usually there is no need to determine  $H$  explicitly. This step is tacitly included in the procedure of calibrating an emulsion.

8.2.3 The exposure causes a separation of silver in the developed emulsion. A measure of this effect is obtained by measuring the (photographic) *transmittance*  $T_p$  at the appropriate place on the plate. The optical instrument used to measure the transmittance  $T_p$  is commonly called a *microphotometer*. This name is slightly inappropriate, but it is unambiguous and so widespread that it can be accepted. On the other hand, the expression 'densitometer' should not be used for such an instrument.

8.2.4 The transmittance  $T_p$  is an *auxiliary* and *intermediate* quantity without independent meaning. This is indicated by the subscript  $p$ , referring to photographic plate. The particular numerical value of  $T_p$  depends not only on the exposure, the properties of the emulsion and the development, but also on the measuring arrangement [for example on the angular aperture of the light beam in the microphotometer]. There is no need to define general standard conditions for measuring  $T_p$ . It is only necessary to keep the measuring conditions constant within a series of measurements which are to be compared or correlated with each other.

8.3 *Mathematical treatment of measured values for  $T_p$  (transformations)*—

8.3.1 The exposure is generally related in a complicated way to the resulting photographic transmittance  $T_p$ , which is measured, so making further calculation inconvenient. It is therefore advisable to transform  $T_p$  into a more tractable *photographic parameter*  $P$ . Ideally such a transformation should give a linear relation between the parameter  $P$  and the logarithm of the exposure  $H$  (or instead, of the line intensity  $I$ ). But no mathematical

transformation—performed only for convenience—can ever improve poor photometric measurements.

8.3.2 The relation between the logarithm of the intensity  $I$  and the photographic parameter  $P$  is given by the *emulsion calibration function* or in graphical presentation by the *emulsion calibration curve*.

8.3.3 If—by the selection of a suitable transformation from  $T_p$  to a parameter  $P$ —the resulting emulsion calibration curve is made straight, the equation of such a straight emulsion calibration curve is

$$P = \gamma_p \log I/I_0$$

or

$$P = \gamma_p(Y - Y_0) \text{ with } Y = \log I$$

Here  $\gamma_p$  is the *slope* of the emulsion calibration curve and the index  $P$  can be retained if it is clear for what parameter it holds.

$I_0$  and  $Y_0$  respectively correspond to the value of the exposure for which  $P = 0$ .

8.3.4 One special class of transformations  $T_p \rightarrow P$  leading to (nearly) straight emulsion calibration curves is produced by generalizing the *Baker-Sampson-Seidel-transformation* (see also 8.3.6).

$$P = \kappa \log(1 - T_p) - \log T_p$$

By suitable choice of the *transformation constant*  $\kappa$ , this function is adaptable to many types of emulsions. The numerical values of the two logarithmic functions may be taken from tables or graphs. From this it can be seen that the calibration curve of a photographic emulsion can be characterized by three numbers, e.g.  $\kappa$ ,  $\gamma_p$ ,  $Y_0$  (or  $I_0$ ), all dependent on wavelength. This must essentially be true for all calibration curves having the same degree of straightness, although, by a special fixation of the transformation from  $T_p \rightarrow P$ , one of these constants may disappear from the equations, e.g. if  $\gamma_p$  is made unity.

8.3.5 The establishment of a suitable transformation can be made by different methods, for instance, by graphical methods resulting in a distortion of the coordinate network or by combining mathematical functions which are known to lead to a linear relationship.

The selection of a suitable transformation is a practical and not a theoretical matter and is irrelevant for the intensity ratios to be determined—if the procedure chosen is correctly performed. Therefore it is proposed to use the symbol  $P$  for any photographic parameter leading to a (nearly) straight 'emulsion calibration curve'. If necessary, the type of transformation may be indicated in the context. Only when the relative merits of different transformations are discussed, different suitable symbols may be used (e.g. the historic ones from the literature or subscripts).

Unfortunately and most confusingly many different symbols have been used for photographic parameters and for the respective transformations, giving a linearization of the emulsion calibration curve, e.g.  $S$ ,  $D$ ,  $W$ ,  $P$ ,  $T$ ,  $L$ ,  $l$ ,  $K$ ,  $A$  etc., hence the proposal to use only the one symbol  $P$ .

### 8.3.6 Historical note

The transformation that first served to linearize the emulsion calibration curve, although not in the lower (low intensity) range, is the simple logarithmic

transformation which turns the transmittance  $T_p$  into the *blackening*  $S$ , viz.

$$S = -\log T_p$$

In spite of the partial non-linearity just referred to, this parameter, blackening  $S$ , is still widely used (Hurter and Driffield,  $H$  and  $D$ -curve). The transformation obviously belongs to the class of transformations considered in 8.3.4, with the transformation constant  $\kappa = 0$ . In English the *blackening* is often spoken of as the 'optical density' ( $D$ ). But this may lead to misunderstanding, especially when 'optical' is omitted. In spectrochemical analysis, the use of the term 'optical density' is therefore discouraged, as well as that of the expression ' $H$  and  $D$ -curve', for the emulsion calibration curve.

The transformation that first helped to straighten the lower part of the curve was used by two astronomers, Baker and Sampson, in 1924. It was

$$P = \log(1/T_p - 1) = \log(1 - T_p) - \log T_p$$

This is the same equation as in 8.3.4 if  $\kappa = 1$ . The same transformation was rediscovered by Seidel in 1936 and subsequently was used extensively in spectrochemical analysis. Later various transformations have been proposed and investigated (see 8.3.5).

8.4 *Practical calibration of a photographic emulsion*—8.4.1 The practical calibration of a photographic emulsion is based on photometric measurements of photographic intensity marks (subscript  $m$ ) produced by intensities of known ratios. The intensity marks are made with an *intensity calibrating device*, for example, a step filter with a known *transmission ratio*  $\tau_m = I_{m,1}/I_{m,2}$ . Or one may resort to the use of a pair of spectrum lines of which the intensity ratio is known under stipulated conditions.

8.4.2 The calibration procedure is simple if the intensity ratio of two spectrum lines, close together in wavelength, is to be determined (quasi-monochromatic photometry) and if a photographic parameter  $P$ , yielding a linear emulsion calibration curve, is used. In this case all that need be measured is the slope  $\gamma_p$ . The values of  $P_1$  and  $P_2$  for the two intensity marks are measured; then the slope of the emulsion calibration curve is

$$\gamma_p = \Delta P_m / \Delta Y_m$$

where

$$\Delta P_m = P_1 - P_2$$

and

$$\Delta Y_m = \log I_{m1} - \log I_{m2} = \log \tau_m$$

8.4.3 Sometimes for convenience—especially with non-intermittent sources—a *step sector* is used as an intensity calibrating device. In this case the exposure  $H = Et$  is varied by variation of  $t$  and not by variation of the irradiance  $E$  as before. The measured values for  $\Delta P_m$  in this case may differ markedly from those obtained for the same ratio by variation of the irradiance  $E$ .

8.4.4 If the wavelengths  $\lambda_a$  and  $\lambda_b$  of the two spectrum lines to be compared differ so much that the emulsion calibration curves are different (heterochromatic photometry), then it may be necessary to use two different photo-

graphic parameters  $P_a$  and  $P_b$  produced by different transformation constants  $\kappa$ , in order to get the two emulsion calibration curves straight. The slopes  $\gamma_a$  and  $\gamma_b$  of these two curves can be determined as before if the transmission ratios  $\tau_a$  and  $\tau_b$  of the intensity calibrating device for the two wavelengths are known. In addition to this an *intensity bridge* from  $\lambda_a$  to  $\lambda_b$  is necessary in order to connect the two emulsion calibration curves and so afford the calculation of the difference in response  $Y_{a,0} - Y_{b,0}$  of the emulsion at the two wavelengths. An *intensity bridge ratio*

$$\log I_a/I_b = \Delta Y_{a,b}$$

can be derived from a spectrum with known spectral distribution of intensities. Examples are: the spectrum of a standard d.c. graphite arc or of a tungsten ribbon lamp etc. This idea of an intensity bridge is usually implicit in the term 'external standard'. But the use of this term is discouraged since it is not clearly defined and might wrongly be considered as the opposite of 'internal standard', a term that in the future should be replaced by *reference element* or *reference intensity*.

## APPENDIX A

### General Principles of Nomenclature Standardization

The following article is part of a report of the Joint Committee on Nomenclature in Applied Spectroscopy. It is reprinted here by permission of ASTM from *Methods for Emission Spectrochemical Analysis*, pp 84-86 (1957) published by the American Society for Testing Materials, 1916 Race St., Philadelphia, Pa. (This article has not been reprinted in recent editions of the book.)

The footnotes have been added by this Commission (V.4).

1. *Manuscript*. In preparing manuscripts and talks, careful attention should be given to the use of nomenclature from this and other standard lists and to the principles here given. Controversial or unusual terms should be defined clearly. When other terms are not defined, it is desirable to make reference to the standard lists from which they are taken.

2. *Units*. The same term and the same symbol should be used for a given quantity, regardless of the units employed and regardless of special values occurring for different states, molecules, times etc. Special values may be distinguished *when necessary* by subscripts or superscripts. The units used should always be stated carefully and explicitly

3. *Multiple meanings*. A given term should not have more than one technical meaning in any branch of physical science. For instance, if 'density' is accepted as the term for mass divided by volume, it should not be employed as a shortened form of optical density.

4. *Multiple terms*. A given technical concept should not have more than one name. For example, 'analytical curve' and 'working curve' should not both be standard terms.

5. *Related concepts*. If two or more concepts are closely related, this fact should be reflected in the similarity of the names assigned to them. Instruments should be named for the quantities they measure.

(a) One obvious way is to incorporate the name of the most basic of the

several concepts in the names of those subsidiary to it. Thus, in speaking of various standards, one should use, for example, internal standard†, primary standard, etc.

(b) Another exceptionally useful way to indicate such relations is to utilize the conventions regarding suffixes that are now fairly well established, especially in electricity. There are at least nine such suffixes:

-*or*, meaning a device. For example, comparator, reflector, generator and capacitor. (Other suffixes used to denote devices are -*er*, as in amplifier, and -*ment*, as in filament.)

-*ation*, meaning a process or result of a process. For example, calibration, excitation, ionization and radiation (-*ing*, as in lighting, is also used to denote a process.)

-*ance*, meaning a property of a device or body. For example resistance, capacitance, transmittance and absorbance.

-*ity*, meaning a property of a substance. For example, absorptivity, density, solubility, resistivity (which is simpler than the older term, specific‡ resistance), conductivity, and so on.

-*meter*, meaning a measuring device. For example, ammeter, spectrometer and densitometer.

-*scope*, meaning an optical or viewing device, as in electroscope, microscope and spectroscope.

-*graph*, meaning a device to produce a record of observations as in telegraph and spectrograph.

-*gram*, meaning the record produced by an instrument as in telegram and spectrogram.

-*scopy*, meaning observation, as in spectroscopy.

6. *Contrasting concepts*. The names for two diametrically opposite ideas should differ markedly in appearance and sound; for example§, microscopic and macroscopic—each consists of eleven letters, with only one of them different, and their pronunciation may lead to confusion.

7. *Self-explanatory terms*. A term should, when possible, be more or less self-explanatory and thus easy to learn and to associate with its concepts. Some terms that appear to satisfy this requirement are: buffer, carrier|| and emulsion calibration curve. On the other hand, electromotive force and the old term electric capacity not only fail to explain, but actually foster misconceptions.

8. *Simplicity*. The chosen term should be simple and euphonious, and it should have the simplest spelling that is sanctioned by dictionaries. Examples of acceptable simpler spellings are: aline, distil, focused, gage, sulfur. Terms such as quantity of heat and quantity of charge not only lack simplicity but are redundant, the *quantity* not being needed. *Sinusoidal function* should give way to *sinoidal function* and '*coefficient of linear expansion*' to '*linear expansivity*', which is not only simpler but utilizes the -*ity* convention.

† 'internal standard' to be replaced by 'internal reference' see §§ 6.2.2 and 6.3.1.

‡ The term 'specific' has now been restricted to the meaning 'divided by mass'.

§ Another unfortunate choice in our own field is *radiance* and *irradiance* (see para. 4.1).

|| See para. 7.7.5 of this document, where 'carrier' is defined in a narrower meaning than formerly.

9. *Internationality*. The name for a particular concept preferably should have essentially the same form in a number of the chief languages of the world. This is already true of various technical terms in common use as, for instance, energy, entropy and many terms having certain of the suffixes previously discussed. For the four suffixes, *-or*, *-ation*, *-ance*, *-ity*, a tabulation of 544 entries from eight different languages shows that one or the other of these suffixes is used in 96 per cent of the total. When the tabulation is confined to five of these eight languages—namely English, French, Italian, Spanish and Portuguese—there is agreement in 347 out of 355 cases, 98 per cent. Thus the proposal to achieve some degree of internationality in terminology is by no means impracticable.

10. *Faulty terms*. If a term is slightly faulty, but is too firmly established to be discarded, a brief explanatory comment should be included with its definition. If a term is faulty in some important respect, an effort should be made to change it, no matter how well established it may be. There is no better example of such a term than electromotive force.

11. *New terms*. The question arises as to the procedure to be followed in choosing a brand new term, either to replace a faulty one or to designate a new idea as yet unnamed. Obviously there are several alternative methods:

(a) Borrow a word from ordinary language. The resulting term could be ambiguous, because of inability to decide from the context in a particular case whether the technical or the everyday meaning is intended; moreover such a term will not be international, since it generally cannot be taken over directly into other languages. On the other hand, many existing terms borrowed from ordinary language have proved to be quite satisfactory. The general agreement is, however, that this method of obtaining a new term should be used with considerable restraint.

(b) Borrow a word from a living, foreign language. Gibbs did this when he took the French word 'ensemble' and gave it a new technical meaning. One objection to this general method is that the borrowed term, while good for us, may not be too satisfactory for the country from which we borrowed it. For instance, 'ensemble' in French does not convey Gibbs's idea very well.

(c) Coin a word by making an arbitrary although euphonious combination of a number of the letters of the alphabet. This method might serve on occasions, but the resulting term could be hard to learn.

(d) Adopt the name of the discoverer of the idea. If this somewhat lazy way of naming a concept is resorted to, one should at least make sure that the name selected is that of the real discoverer as established by priority of publication.

(e) Construct the new term from parts taken from a classical language, such as Greek† or Latin. The word, being a new one, is immediately recognizable as a technical term. If the component parts are properly chosen, it will also be more or less self-explanatory. Some think classical Greek is the best language for this purpose.

(f) Do not use a registered trade name of a particular company for a class of instruments.

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† For Greek words Latin transliteration has been recommended, to avoid ambiguity of spelling.

## APPENDIX B

## Application of the Concept of Optical Conductance

B.1. *General definition*—Optical conductance  $G$  is defined by the basic equation

$$\Phi = BG\tau$$

or in words: Flux = Radiance  $\times$  Optical conductance  $\times$  Transmission factor, where  $G$  embraces the geometric factors.  $B$  and  $\Phi$  are appropriately specified.

B.2.1 *Passage of flux between elements of area* of source and sink (e.g. a receiver).  $dS_1$  is an element of area of the source and  $dS_2$  of the sink.  $a_{12}$  is the intervening distance, and the normal to  $dS_1$  makes the angle  $\alpha_1$  with the direction from source to sink, and  $\alpha_2$  applies similarly to  $dS_2$ . Then, with  $dS_1$  and  $dS_2 \ll a_{12}^2$

$$\begin{aligned} d\Phi &= B(\alpha_1) \cos \alpha_1 dS_1 \cos \alpha_2 dS_2 / a_{12}^2 \\ &= B(\alpha_1) dG_{12} \end{aligned}$$

B.2.2 *Integration*. If in the above  $dS_1$  is an element of an area  $S_1$ , and  $dS_2$  of  $S_2$ , the total flux from  $S_1$  to  $S_2$  is

$$\Phi = \int_{S_1} \int_{S_2} B(x,y,z) \cos \alpha_1 \cos \alpha_2 dS_1 dS_2 / a_{12}^2$$

If the radiance may be taken as constant over the whole surface  $S_1$ , or if it may be replaced adequately by an average value, the radiance may be taken outside the integral, which then constitutes  $G$ .

B.3 *Generalization to allow for refractive index*—If the medium between  $S_1$  and  $S_2$  has the refractive index  $n$ , the optical conductance  $G_n$  is defined by

$$G_n = n^2 G_{(n=1)}$$

B.4 The practical importance of the concept of optical conductance will be realized, if one remembers that the radiance, observed within all subsequent apertures of an optical arrangement is invariant—except for losses by reflection, absorption or scattering (which are taken into account by the transmission factor  $\tau$ ).

Therefore, in a correctly designed optical arrangement, consisting of a sequence of parts or instruments (e.g. source-absorption cell-monochromator-receiver), the invariance of the calculated optical conductance between any two apertures in sequence also presupposes that all apertures are fully illuminated. (Of course, some apertures may be larger than necessary; in these cases, only the part filled with radiation must be considered.)

In consequence, the optical conductance of some part in the arrangement that cannot be enlarged for practical or technical reasons determines the effective optical conductance of all other parts and of the whole arrangement. [For example, such a limit for the effective optical conductance may be imposed by the dimensions of an absorption cell (see formula B.5.1) or those of a monochromator (B.5.6), a photometer device, or of an interference filter (B.5.2).] This fact greatly simplifies basic decisions, the choice of parts or instruments and rough calculations of the available flux.

B.5 Some examples of the use of  $G$  of interest in spectroscopy—B.5.1 Small areas  $S_1, S_2$ ; the line joining their centres having length  $a_{12}$ , constituting their common normal and  $S_1$  and  $S_2 \ll a_{12}^2$

$$G = n^2 S_1 S_2 / a_{12}^2$$

B.5.2 Radiation through a cone of vertical semi-angle  $u$ , from area  $S$ .

$$G = n^2 S \pi \sin^2 u$$

This links the optical conductance treatment with the Helmholtz theorem and the sine condition. Note  $n \sin u$  is the *numerical aperture*.

B.5.3 Sphere of radius  $r$ , radiating into space

$$G = 4\pi^2 n^2 r^2$$

This allows for the approximate treatment of arcs and sparks as small spheres.

B.5.4 Cylinder of radius  $r$  and height  $h$  radiating into space

$$G = 2n^2 \pi^2 r (h + r)$$

B.5.5 Two surfaces  $S_1$  and  $S_2$  being parts of the inside surfaces of a sphere of radius  $r$

$$G = S_1 S_2 / 4r^2$$

This shows that  $G$  is independent of the relative positions of  $S_1$  and  $S_2$ , which provides the basis for (Ulbricht's) integrating sphere.

B.5.6 Monochromator—B.5.6.1

$$G = sh D_s D_h / f^2$$

Since the resolving power  $R_0$  is  $R_0 = D_s d\phi/d\lambda = (dx/d\lambda) D_s / f$

$$G = (h D_h / f) R_0 s d\lambda / dx$$

$$G = (h D_h / f) R_0 \Delta\lambda$$

where  $\Delta\lambda$  is the range of wavelengths corresponding to the width of the entrance slit (for the other symbols see section V).

B.5.6.2 If the slit width is measured in units of the half width of the diffraction image,  $s_0 = \lambda f / D_s$ , and similarly if the slit height is measured in the unit  $h_0 = \lambda f / D_h$ ; with  $\hat{s} = s/s_0$  and  $\hat{h} = h/h_0$  then the expression for  $G$  becomes very simple

$$G = \lambda^2 \hat{s} \hat{h}$$

B.5.6.3 The value of  $G$  in 5.6.1 (with  $\Delta\lambda = 1$ ) may serve as a figure of merit for comparing monochromators, only if the assumption is made that there are no optical imperfections.

B.6. Flux through a monochromator from a continuous source of radiance, characterized by its *spectral radiance*,  $B_\lambda$ , (i.e.  $dB(\lambda)/d\lambda$ )

$$\Phi = B_\lambda \Delta\lambda \tau (h D_h / f) R_0 \Delta\lambda$$

$$\Phi = B_\lambda (\Delta\lambda)^2 \tau R_0 (h D_h / f)$$

Therefore, the square of the bandwidth is important. The monochromator itself is characterized in this equation by the product

$$Z_M = \tau R_0 (hD_n/f)$$

which obviously is a figure of merit for the transport of energy. This equation may also be written (from 5.6.1) as

$$Z_M = \tau G/\Delta\lambda$$

which is the optical conductance per unit bandwidth.