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PROCEDURES FOR ANALYSIS*

Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—IX

INSTRUMENTATION FOR THE SPECTRAL DISPERSION AND ISOLATION OF OPTICAL RADIATION

(IUPAC Recommendations 1995)

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Nomenclature, symbols, units and their usage in spectrochemical analysis—IX. Instrumentation for the spectral dispersion and isolation of optical radiation (IUPAC Recommendations 1995)

ABSTRACT

This document deals with nomenclature, symbols and their usage in the field of instrumentation for the dispersion and isolation of optical spectra in the wavelength region from 50 nm to 1 mm, as applied in analytical atomic and molecular emission, absorption and fluorescence spectroscopy. The whole subject is divided into 10 chapters dealing with various aspects of dispersive and non-dispersive spectral apparatus including spectral filters and interferometers. Definitions are given for spectral instruments with and without detection and measuring facilities. The properties of optical components of dispersive and non-dispersive spectral instruments are defined in detail with emphasis on such fundamental figures of merit as spectral purity, resolution, resolving power, conductance of optical systems, characteristic wavelengths and polarization. Terms closely related to the optimum use of spectral instruments, e.g., optimal slit width and height, theoretical and practical effective spectral linewidth, line-to-background radiant power ratio are given. Terms for various forms of mountings for spectral apparatus are included in the vocabulary.

CONTENTS

1 INTRODUCTION

This document is the ninth in a series dealing with nomenclature, symbols and units used in pectrochemical analysis issued by IUPAC.

Part I (Pure Appl. Chem., *30*, 653-679 (1972)) is concerned mainly with general recommentions in the field of emission spectro chemical analysis.

Part II (Pure Appl. Chem., *45*, 99-103 (1976)) covers data interpretation common to all specific fields of spectrochemical analysis.

Partrt III (Pure Appl. Chem., *45*, 105-123 (1976)) deals with the nomenclature of analytical flame spectroscopy and associated procedures.

Part IV (Pure Appl. Chem., *52*, 2541-2552 (1980)) concerns X-ray emission (and fluorescence) spectroscopy.

Part V (Pure Appl. Chem., *57*, 1453-1490 (1985)) deals with the classification and description of radiation sources.

Part VI (Pure Appl. Chem., *56*, 221-245 (1984)) covers molecular luminescence spectroscopy.

Part VII (Pure Appl. Chem., *60*, 1449-1460 (1988)) is concerned with molecular absorption spectroscopy in the wavelength region ultraviolet/visible.

Part VIII (Pure Appl. Chem., *63*, 735-746 (1991)) proposes a new nomenclature system for X-ray spectroscopy.

Part X (Pure Appl. Chem., *60*, 1461-1472 (1988)) deals with sample preparation for analytical atomic spectroscopy and other related techniques.

Part XI (Pure Appl. Chem., in preparation) deals with the detection of radiation.

Part XII (PureAppl. Chem., *64*, 253-259 (1992)) deals with the technique of electrothermal atomization (ETA) used in optical atomic spectrometry.

Part XIII (Pure Appl. Chem., *64*, 261-264 (1992)) deals with the technique of chemical vapour generation used in optical atomic spectrometry to introduce the sample into a sampling or excitation source (See Part V of this series).

Documents on Laser Based Atomic Spectroscopy and Laser-Excited Molecular Spectroscopy are in the course of preparation.

This document, Part IX deals with nomenclature, symbols and their usage in the field of instrumentation for the dispersion and isolation of optical spectra in the wavelength region of 50 nm to 1 mm, as applied in analytical atomic and molecular emission, absorption and fluorescence spectroscopy.

In this document, most terms have been described and quantities expressed in units of radiation wavelengths. Definitions can be directly or easily converted into units of frequency or wavenumber, but where this is not the case, it is indicated in the text.

2 SPECTRAL APPARATUS

An optical arrangement or an instrument which disperses *optical radiation* into a spectrum and/or isolates a specific *spectral band* is termed *spectral apparatus* or a *spectral instrument*. If the *entrance aperture*, which may be a slit, is sharply imaged in both dimensions, i.e., length and width in the same *focal plane*, it is called a *stigmatic arrangement*; when the focal planes are different in the two dimensions, *astigmatic*. When the radiation passes through the same optical components before and after being dispersed, the spectral system is *autocollimative*.

2.1 Dispersive Spectral Apparatus

Spectral separation or isolation of optical radiation may be achieved by using a *dispersive component* such as a *prism*, a *diffraction grating*, or a *multiple-beam interferometer*.

2.1.1 A *monochromator* enables a specific spectral band to be selected, e.g., by using two slits, i.e., an *entrance* and an *exit slit* (see Note [1]).

If two or more monochromators are specially constructed for simultaneous use the arrangement is termed *parallel monochromators,* e.g., two parallel monochromators.

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[1] The means whereby spectral band selection is achieved will be discussed in 8.

A *double monochromator* results when two single monochromators are arranged in series. The exit slit of the first becomes the entrance slit of the second either physically or by optical imaging, forming a common *middle slit*. Combinations of single monochromators may be repeated giving *multiple monochromators*. If, by an optical arrangement (e.g., reflection), the beam is passed twice through the same monochromator, the apparatus is called a *double-pass monochromator*.

A double monochromator, where the dispersion of the first is added to the second, is termed an *additive double monochromator* or, when the dispersions are subtracted, a *subtractive double monochromator*.

2.1.2 A *polychromator* results, when several spectral bands are isolated simultaneously, usually by a number of exit slits or some other arrangement.

2.2 *Non-dispersive Spectral Apparatus*

In such instruments isolation of a spectral band is achieved without wavelength dispersion by using *optical absorption, fluorescence, reflection* or *scattering* (see Note [2]). It is also achieved by the use of an *interference filter* based on multiple beam interference. These filters are examples of *spectral filters*. A *double-beam interferometer* may also be part of a non-dispersive spectral instrument.

3 SPECTRAL APPARATUS WITH DETECTION AND/OR MEASURING FACILITIES (see Note [2])

Dispersive or non-dispersive spectral instruments may be combined with one or more means for detecting and/or measuring the spectra. Most of the following refer to dispersive instruments.

3.1 A *spectroscope* enables visual observation and evaluation of optical spectra. It is usually confined to the visible spectral region.

3.2 A *spectrograph* is a combination of a spectral apparatus and a *camera*. This enables an image of a spectrum to be obtained. Spectra are recorded by a photographic emulsion or other means, e.g., two-dimensional electronic image sensors.

3.3 A *spectrometer* is the general term for describing a combination of spectral apparatus with one or more detectors to measure the intensity of one or more spectral bands (see Note [3]).

3.3.1 A *sequential spectrometer* enables the intensity of several spectral bands of radiation to be measured one after the other in time, i.e., sequentially.

3.3.2 A *simultaneous spectrometer* has more than one detector and enables the intensities of several spectral bands to be measured at the same time.

3.3.3 In a *multiplex spectrometer*, a single photodetector simultaneously receives signals from different spectral bands which are specifically encoded. In the case of *frequency multiplexing*, each spectral band is modulated at a specific frequency. Decoding is achieved by filtering out, by electronic means, the corresponding signals.

Frequency multiplexing may be realized e.g., with a *Michelson interferometer* (see 5.3) by changing the path difference between the two interfering beams at a uniform rate. Fourier transformation of the interferogram so obtained yields the spectrum. This method is called *Fourier Transform Spectrometry* (FTS).

3.3.4 A *filter spectrometer* has one or more spectral filters for isolating one or more spectral bands.

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[2] See also Part III, 4.3.1. Some of these terms have been described in Parts I and III.

[3] The words photometer, spectrophotometer, (also photometry, spectrophotometry) are sometimes used to describe some of those instruments and procedures related to them. These words should not be used in spectrochemical procedures related because photometry relates to radiation evaluation according to visual effects (see Part I, 4.5).

4 OPTICAL COMPONENTS OF DISPERSIVE SPECTRAL INSTRUMENTS

4.1 Entrance Collimator

An *entrance collimator* (see Fig. 1) is an optical arrangement for the production of a quasi-parallel beam of radiation of a required cross section. It consists of an objective lens or mirror, the cross section of which constitutes the *entrance aperture stop* and an *entrance field stop* at the front focal plane of the collimator. The entrance aperture stop may also form the limiting aperture stop, the *entrance pupil* of the whole apparatus.

The entrance field stop in most dispersive instruments is a *slit*. Both *curved slits* and *straight slits* are used. Distinguishing features are the *slit length h* (see Note [4]) and the slit *width s* (see Note [5]). Slits are either fixed or adjustable. They can be straight or curved depending on the optical design. An optical instrument may contain several real or virtual aperture and field stops. Those which determine the maximum throughput of radiant power are called the *limiting stops*.

Distinguishing features of the lenses or mirrors in the collimator systems are the *collimator focal length* f_{en} (see Note [6]) and the *relative aperture*. The relative aperture is defined in terms of the diameter D for circular entrance aperture stops and in terms of the effective diameter D_{eff}, where

$$D_{\mathrm{eff}} = \left(\frac{4\,B_{\mathrm{en}}H_{\mathrm{en}}}{\pi}\right)^{1/2}$$

for rectangular entrance aperture stops of width B_{en} and length H_{en}. The relative aperture k_{en} (see Note [7]) is then defined by the expression

$$k_{\mathrm{en}} = \frac{f_{\mathrm{en}}}{D}$$

for circular apertures and

$$k_{\mathrm{en}} = \frac{f_{\mathrm{en}}}{D_{\mathrm{eff}}}$$

for rectangular apertures.

Expressions for the following relative apertures

$$k_{B,\mathrm{en}} = \frac{f_{\mathrm{en}}}{B_{\mathrm{en}}} \quad \text{and} \quad k_{H,\mathrm{en}} = \frac{f_{\mathrm{en}}}{H_{\mathrm{en}}}$$

are also useful, e.g., for distinguishing diffraction properties in the plane of diffraction ("B") and perpendicular ("H") to it.

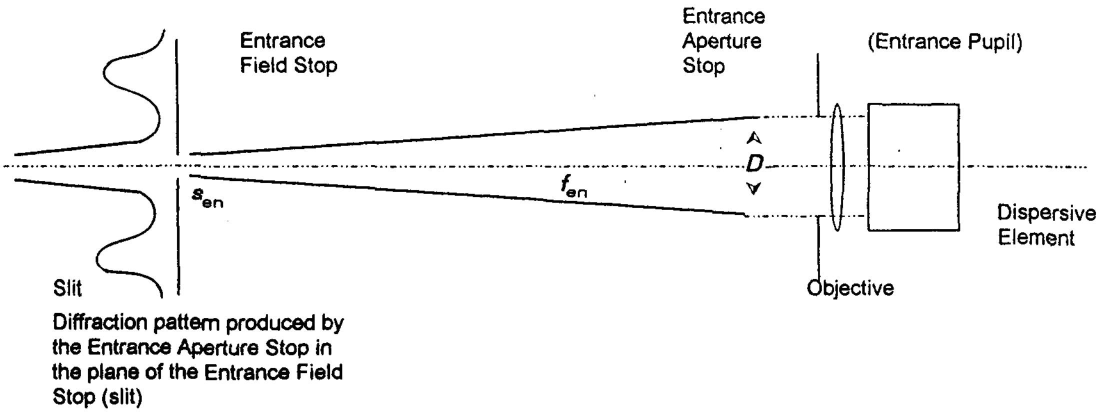

FIG. 1:- For defining the optimal slit width in units of the virtual diffraction pattern produced by the Entrance Aperture Stop in the plane of the Entrance Field Stop

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[4] The term slit height may be used when the slit is positioned vertically.

[5] The use of the word slit gap is discouraged.

[6] In this document the subscripts 'en' for entrance and 'exit' for exit will be used.

[7] The words *f*-number and optical speed are discouraged.

4.2 Dispersive Elements

Distinctive characteristics of the dispersive element components are:

- the *total angle of deviation* Θ (of the beam of radiation after refraction or diffraction);
- the *angular dispersion* $\mathrm{d}\Theta/\mathrm{d}\lambda$ with respect to the wavelength λ;
- the *theoretical resolving power*

$$R_0 = \frac{\lambda}{\delta_0\lambda} \qquad \text{(see 7.2.4);}$$

- the *upper* and *lower wavelength limits*, λ_u and λ_l between which the *transmission (or reflection) factor* exceeds a specified fraction of its maximum.

4.2.1The characteristic quantities of prisms are:

- shape and type of the prism;
- the material from which it is made and its *refractive index* n which is a function of the wavelength λ;
- the *material dispersion* $\mathrm{d}n/\mathrm{d}\lambda$, which also changes with the wavelength;
- the *linear absorption coefficient* of the material;
- the *effective base length* b_{eff}, which is the path difference between the longest and the shortest possible parallel rays closest and farthest from the base, respectively;
- the *prism angle* α;
- the *prism height* parallel to the *refractive edge*;
- the angle of minimum deviation Θ_{min}.

The following terms are derived from these quantities:

- the theoretical resolving power

$$R_0 = \beta_{\mathrm{eff}} \frac{\mathrm{d}n}{\mathrm{d}\lambda}.$$

- The angular dispersion (in radians per wavelength)

$$\frac{\mathrm{d}\Theta}{\mathrm{d}\lambda} = \frac{b_{\mathrm{eff}}}{B_W} \frac{\mathrm{d}n}{\mathrm{d}\lambda}$$

where B_W is the width of the refracted *optical beam* in the plane of refraction.

4.2.2 Diffraction gratings may be transmission or reflection types. They are dispersive optical components with *grooves* (see Note [8]) parallel to each other. *Ruled gratings* are mechanically produced by a *ruling engine* whereas *interferometric gratings* (see Note [9]) are made by interaction of an interference pattern with a photosensitive layer, e.g., a photographic emulsion. The grooves have a periodic structure in the direction of dispersion.

Replica gratings are duplications of the *master grating* (original grating). It is possible to repeat the process of the replication in several generations.

Characteristic quantities of gratings include:

- the *grating width* W of the grooved area (measured in a direction at right angles to the grooves, in the plane of the grating);
- the length of the grooved area (measured parallel to the grooves);

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[8] Grooves of mechanically ruled gratings are generally named *rulings*. With interferometric gratings, the recommended term is *lines*.

[9] The term 'holographic grating' is incorrect and should not be used.

- the total *number of grooves* N_r. We have

  $$N_r = n_r W ,$$

- where n_r is the number of grooves per unit length across W;
- the *grating constant d* which is the reciprocal of n_r;
- the *grating function* (formula) is the function relating the *angle of incidence* φ_1 to the *angle of diffraction* φ_2 ; i.e.:

  $$\sin\varphi_1 + \sin\varphi_2 = m\frac{\lambda}{d}$$

  where m is the *order of diffraction*;
- the *efficiency of the grating* $\eta(\lambda)$ is the ratio of the *diffracted* to the *incident spectral radiant power*.

  $$\eta(\lambda) = \frac{\Phi_\lambda(\text{out})}{\Phi_\lambda(\text{in})}$$

- the *usable free spectral range*, (without *order overlap*)

  $$\Delta\lambda = \frac{\lambda}{m} ;$$

- the *blaze* is the direction of optimum efficiency $\eta(\lambda)$ of the grating;
- the *blaze angle* γ. With *saw-tooth shaped grooves* γ_B represents the angle between the *grating normal* and the normal of the groove surface;
- the *blaze wavelength* λ_B is that wavelength or wavelength range at which blaze occurs. With plane gratings the blaze wavelengths are given for autocollimation.

From these quantities the following can be calculated:

- the theoretical resolving power

  $$R_0 = m N_r \quad \text{(see 7.2.4)};$$

- the angular dispersion (in radians per wavelength)

  $$\frac{d\varphi_2}{d\lambda} = \frac{R_0}{B_W}$$

  where B_W is the width of the diffracted optical beam in the plane of diffraction.

Plane gratings have lines on a flat surface. They consequently have no optical imaging properties.

Echelle gratings are *ruled plane gratings* having a comparatively large grating constant d and at least one steep blaze angle γ_W of the grooves. If used with this blaze angle as angle of incidence φ_1, a high efficiency η at high orders of diffraction can be obtained yielding high angular dispersion $d\varphi_2/d\lambda$ and theoretical resolving power R_0 at the expense of the usable free spec-spectral range $\Delta\lambda$.

Concave gratings have lines on a concave surface. The surface may be spherical, toroidal or elliptical. Concave gratings are generally used as objective components forming part of or acting fully as the collimator and/or camera of the instrument. Additional imaging characteristics may be achieved as a result of local displacement of the line or groove distance - as realized with some types of interferometric gratings.

4.2.3 A multiple-beam interferometer e.g., the *Fabry-Perot interferometer* enables high resolution measurements to be made utilizing the interference of multiple beams of monochromatic radiation at very high orders, after reflection between two surfaces. A special case of such an interferometer is the *Fabry-Perot etalon interferometer* in which the thickness of a plane parallel plate of air or of another gas between the two surfaces remains unaltered. Another, special case is the *etalon plate interferometer* basically consisting of a transparent solid plate with the reflective coating applied to the two surfaces.

Characteristic quantities are:

- the separation a between the (plane or concave) reflecting surfaces;
- the radius of curvature (with concave mirrors);
- the reflection factor ρ of the mirrors;
- the refractive index n of the medium between the reflecting surfaces which relates the wavelength λ in the medium to that in vacuum by

$$\lambda = \frac{\lambda_{\mathrm{vac}}}{n}.$$

The following properties can be expressed in these quantities:

- the *order of interference*

$$m = \frac{2a}{\lambda} = \frac{2an}{\lambda_{\mathrm{vac}}};$$

- the free spectral range

$$\Delta\lambda = \frac{\lambda}{\mathrm{m}};$$

- the *finesse*

$$F = \frac{\Delta}{\delta\lambda}$$

where $\delta\lambda$ is the resolved wavelength distance (see definition in 7.2.1).

The following distinctions can be made:

- *theoretical finesse* or *reflectivity finesse*

$$F_{\mathrm{o}} = \frac{\Delta\lambda}{\delta_{\mathrm{o}}\lambda} = \frac{\pi\,\rho^{1/2}}{1-\rho}$$

where $\delta\ \lambda$ is the theoretical resolution (see definition in 7.2.2);

- *surface defects finesse*

$$F_{\mathrm{d}} = \frac{\Delta\lambda}{\delta_{\mathrm{d}}\lambda} = \frac{\mathrm{p}}{2}$$

where λ/p denotes the maximum deviation of the plate surface from the ideal one usually measured at $\lambda = 546.1$ nm;

scanning finesse

$$F_{\mathrm{s}} = \frac{\Delta\lambda}{\delta_{\mathrm{s}}\lambda} = \frac{2\pi\ \Delta\lambda}{\Omega\ \lambda}$$

where Ω is the solid angle subtended by a scanning aperture;

- *effective instrumental finesse* F_{p} is the result of a convolution of the previous forms of finesse;
- the theoretical resolving power (see 7.2.4)

$$R_{\mathrm{o}} = mF_{\mathrm{o}} = \frac{2a}{\lambda}F_{\mathrm{o}} = \frac{2an}{\lambda_{\mathrm{vac}}}F_{\mathrm{o}};$$

the angular dispersion $\mathrm{d}\varphi/\mathrm{d}\lambda$, where φ is the angle of diffraction (see 4.2.2).

4.3 Exit Collimator

The *exit collimator* is an optical arrangement for the production of spectra as uniform adjacent images of the entrance slit. If the imaging optical system is supplemented by means for acceptance of a two-dimensional radiation detector in the focal plane, the whole system is then called a camera. Alternatively, the exit collimator may contain one or more exit slits. The objective optical system may consist of one or more lenses and mirrors. Quantities of importance are:

- the focal length f_{ex} ;
- the relative aperture k_{ex} (see 4.1);
- the usable length of the focal plane l ;
- the *inclination angle* Θ_{ex} between the normal to the focal plane and the optical axis;
- the *linear dispersion* $dx/d\lambda$ in which x is the spatial coordinate in the direction of dispersion in the focal plane;
- *reciprocal linear dispersion* is the inverse of the linear dispersion.

5 -OPTICAL COMPONENTS OF NON-DISPERSIVE SPECTRAL INSTRUMENTS

5.1 Entrance Collimators

Entrance collimators for non-dispersive spectral instruments can be described in a similar way to those described in 4.1. Not all types of apparatus require collimators.

5.2 Optical Filters

An *optical filter* attenuates radiation either in its transmission or reflection. *Neutral filters* ideally attenuate all wavelengths of radiation uniformly over the optical spectral range while spectral filters have transmissive or reflective properties which are wavelength-dependent.

In the case of spectral filters, *high-pass filters* attenuate radiation below certain *cut-off wavelengths.* The reverse holds for *low-pass filters. Band-pass filters* enable a limited spectral band to be selected. *Band-blocking filters* attenuate radiation within a specific band. Filters may be combined to achieve certain spectral characteristics (e.g., better resolution).

If the spectral characteristics of a spectral filter are independent of the direction or position of the beam of radiation, it is called a *homogeneous filter*, but if these characteristics are directionally or positionally dependent, it is called a *variable filter* (i.e. ,the central transmission wavelength changes with position or angle).

An *absorption filter* which reduces the intensities of certain portions of the spectrum may be, e.g., a solution, glass, plastic or gelatin.

An interference filter which reflects or transmits radiation in certain spectral bands as a result of optical interference may consist of partly transmissive and partly reflective *dielectric layers* with fixed separations between them.

A *Christiansen filter* reduces the intensities at those wavelengths at which the refractive index of a transmission medium differs from the refractive index of immersed particles by scattering.

5.3 Double-beam Interferometer

An example of a double-beam interferometer is the Michelson interferometer. It makes use of the interference of two beams of radiation, split by means of a semitransparent dividing plate or *beam splitter.* The beams are recombined after reflection from two separate mirrors.

A *correction plate* is used to compensate for the optical path difference between the two beams introduced by the beam splitter.

The *Twyman interferometer* is a modification of the Michelson interferometer making use of an entrance collimator.

Its characteristics are:

- The maximum shift, a_{max}, of the moveable mirror;
- the transmission factor, τ, (see 7.3.3) and the reflection factor, ρ , of the beam splitter;
- the effective beam diameter, D_{eff}.

From these the theoretical resolving power R_0 follows

$$R_0 = \frac{2a_{max}}{\lambda} .$$

6 PREDISPERSER AND POSTDISPERSER

A *predisperser* or *postdisperser* is a spectral arrangement for the additional spatial separation of radiation according to wavelength. It can be used for selecting or sorting orders in a grating or interferometric spectral instrument and/or for the reduction of stray radiation. The predispersion or postdispersion can occur in the same direction as the main dispersion or perpendicular to it. In the first case, it is an *order selector*, in the latter case an *order sorter.*

7 PROPERTIES OF SPECTRAL APPARATUS

7.1 Spectral Properties

Spectral purity depends on the ability of an instrument to isolate a wavelength region. It is characterized by the *full width at half-maximum (FWHM)*, $\delta\lambda_{0.5}$, and the *full width at hundredth-maximum*, $\delta\lambda_{0.01}$, of the spectral band.

The term *monochromatic radiation* is used only in an approximate and relative sense, depending on the particular context. In reality, strictly monochromatic radiation does not exist as it indicates radiation of infinitely narrow spectral bandwidth.

7.1.1 The instrumental profile

The *(spectral) instrumental profile* expressed by the *instrument function* describes the distortion of the registered spectrum as well as the spectral purity obtained with a spectral apparatus. Ideally, if the incident radiation were strictly monochromatic with wavelength λ_r, the outgoing intensity should be zero if λ_r differs from the wavelength λ_i to which the spectral apparatus is set. In practice, however, the outgoing radiant power decays more or less smoothly when $|\lambda_i - \lambda_r|$ is increased. This decay is described by the instrument function $\psi(\lambda_i - \lambda_r)$, which is normalized by setting $\psi(0) = 1$. For a spectral absorption filter, for example, the instrumental profile can be related directly to the transmission factor as a function of wavelength. For a prism monochromator, for example, the instrumental profile is determined by dispersion, slit widths, diffraction effects and optical imperfections. The width of the instrumental profile is a measure of the spectral purity. The *effective spectral width* may be defined by

$$\Delta\lambda_{\mathrm{eff}} = \int_0^\infty \psi(\lambda_i - \lambda)\mathrm{d}\lambda .$$

This width may be conceived as the width of an imaginary rectangular instrument profile that has the same area as the actual profile.

7.1.2 *Stray radiation* is that radiation reaching the detector and having wavelengths outside the spectral band defined by the $\delta\lambda_{0.01}$ of its spectral instrument function. This stray radiation may be *heterochromatic* (consisting of many wavelengths). The ratio of the integrated total stray radiation to the selected radiation within the spectral band is called the *stray radiation factor.*

7.1.3 The *exit spectral slit width* is the product of the exit slit width, s_{ex}, and the reciprocal linear dispersion, $\mathrm{d}\lambda/\mathrm{d}x_{\mathrm{ex}}$, i.e.,

$$\Delta\lambda_{\mathrm{ex}} = s_{\mathrm{ex}} \frac{\mathrm{d}\lambda}{\mathrm{d}x_{\mathrm{ex}}} .$$

The *entrance spectral slit width* is the product of the entrance slit width s_{en} and the reciprocal linear dispersion as measured at the entrance slit, if the radiation passes through the instrument in the reverse direction

$$\Delta\lambda_{\mathrm{en}} = s_{\mathrm{en}} \frac{\mathrm{d}\lambda}{\mathrm{d}x_{\mathrm{en}}} .$$

The *resultant spectral slit width* of a dispersive spectral instrument may be illustrated by the case of a monochromator. Here, the resultant spectral exit slit width $\Delta\lambda_s$ is the larger of the two slit widths, viz. the entrance spectral slit width, $\Delta\lambda_{en}$, and the exit spectral slit width, $\Delta\lambda_{ex}$ (see Note [10]).

7.2 Characteristics of Resolution

7.2.1 The *resolved wavelength distance* is the minimum wavelength distance between two equally intense spectral lines which can be separated clearly, and whose *FWHM* in the radiation source are small compared with their wavelength distance. They are considered *resolved lines*, when the intensity registered between the lines is $8/\pi^2$, i.e., 81 % of the intensity of two maxima.

This is the modified or *second Rayleigh criterion* (see Note [11]).

7.2.2 The *theoretical resolution* $\delta_0\lambda$ is the calculated wavelength distance between two equally intense lines where the resolution is limited only by diffraction in such a way that the centre of the *diffraction pattern* from one line coincides with the first minimum from the second (also described as the *first Rayleigh criterion* (see Notes [12], [13])). In these cases it is assumed that the widths of the slits present are sufficiently small.

7.2.3 The *practical resolution* $\delta_0\lambda$ is the wavelength distance measured under practical conditions conforming to the criterion given in 7.2.2, i.e., 81%.

Suitable emission line pairs are not always available so that the practical resolution may be obtained from the width of the instrumental profile measured at $4/\pi^2$ i.e., 40.5% of the maximum intensity. For this measurement, a line narrow with respect to the width of the instrumental profile can be used.

7.2.4 The *resolving power* is the ratio of (average) wavelength λ to the resolution $\delta_0\lambda$,i.e.,

$$R = \frac{\lambda}{\delta_0\lambda} \quad \text{(see Note } ^{14}\text{).}$$

This relationship holds for both theoretical and practical resolving powers. The theoretical resolving power may be calculated from the instrument specifications according to the appropriate formulae (see 4.2.2 and 4.2.3).

The *practical resolving power* is calculated by using the practical resolution, but with the dimensions of the entrance and exit field stops (e.g., slit widths and lengths) of the collimators being specified.

7.2.5 The *optimal slit width* or *optimal slit length* (see Note [15]) in a dispersive instrument is equal to the distance between the main (central) maximum and the first minimum of the *virtual diffraction pattern* produced by the entrance aperture stop in the entrance field stop (see Fig. 1). For a rectangular aperture the expressions are

$$s_0 = \frac{\lambda f_{en}}{B_{en}} = \lambda k_{B,en};$$

$$h_0 = \frac{\lambda f_{en}}{H_{en}} = \lambda k_{H,en}.$$

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[10] In a subtractive double monochromator the resultant spectral slit width is the smaller of the spectral slit widths of the two single monochromators. In an additive double monchromator the resultant spectral slit width is the smallest of the three spectral slit widths.

[11] If the lines do not have the same intensity, the same criterion may be applied approximately when the recorded local minimum intensity is compared with the recorded maximum of the less intense line.

[12] Under these circumstances the resolved wavelength distance is the same as the half-intensity width of the spectral profile. For this reason the same symbol $\delta_0\lambda$ is used to denote both concepts.

[13] Once the theoretical resolving power R_0 is known, $\delta_0\lambda$ may be derived from the definition of R_0, i.e., $R_0 = \lambda/\delta_0\lambda$. The calculation of the theoretical resolution of an instrument follows from the theoretical resolving power according to the relation: $\delta_0\lambda = \lambda/R_0$, or with dispersive instruments, $\delta_0\lambda = s_0(\mathrm{d}\lambda/\mathrm{d}x)$, where s_0 is the optimal slit width used.

[14] Resolution as defined in Part I, 5.2.2 (Pure Appl.Chem., *30*, 633-679 (1976)) is the practical resolving power according to the present document. Resolving power as defined in Part I, 5.2.2 is the theoretical resolving power in the present document. The present definition is the recommended term.

[15] Optimal is used in terms of theoretical resolution and optical conductance.

For a circular aperture, the *optimal diameter* is

$$s_0 = h_0 = 1.22\ \lambda \frac{f_{\mathrm{en}}}{D} = 1.22\ \lambda k_{\mathrm{en}}.$$

7.2.6 The *optimal entrance field stop* of a Fabry-Perot interferometer and of a Twyman interferometer is a circle of radius r which depends on the focal length of the entrance collimator and the theoretical resolving power

$$r_0 = \frac{2 f_{\mathrm{en}}}{R_0}.$$

From this it follows that the *optimal field angle* w_0 is obtainable from

$$\tan w_0 = \frac{r_0}{f_n}.$$

7.3 Radiation Conductance of Optical Systems

Radiation proceeds from the source to the detector through the optical system. With proper imaging, this process can be described using the *concept of optical conductance* (see Part I, Appendix B, Pure Appl.Chem., *30* (1972)).

7.3.1 In the simple case indicated in Fig. 2 the *geometrical conductance* G_0 of the entrance collimator is defined as the product of the entrance slit area A_1 and the solid angle Ω subtended by the collimator lens measured from the centre of the slit. Defining A_2 as the area of the entrance aperture stop, we have $\Omega = A_2/a_{12}^2$ and

$$G_0 = \frac{A_1 A_2}{a_{12}^2}$$

where a_{12} is the distance between A_1 and A_2. This is an approximation of the correct expression

$$G = \int_{A_1}\int_{A_2} \frac{\cos\alpha_1 \cos\alpha_2}{a_{12}^2}\, \mathrm{d}A_1\, \mathrm{d}A_2 \quad \text{(see Fig. 3)}$$

where α_1 and α_2 represent the angles between the normals of the surface elements $\mathrm{d}A_1$ and

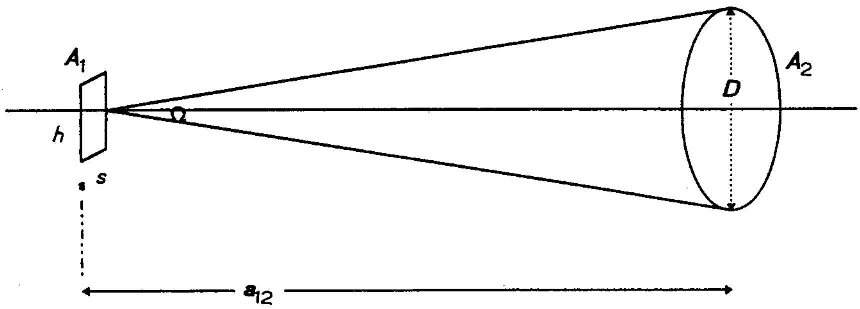

Fig. 2:- Illustrating the Approximate Geometrical Conductance of a collimator in a spectral apparatus

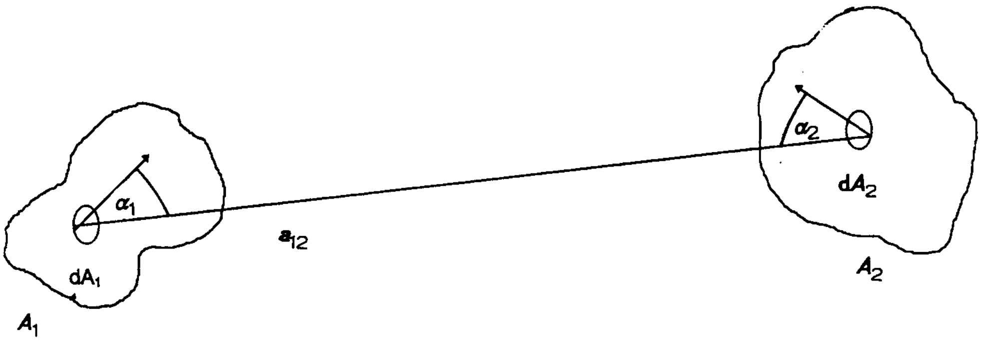

Fig. 3:- General principal of Geometrical Conductance

dA_2 to their corresponding connecting straight lines. When the apertures A are small compared to the square of the distance a_{12} and perpendicular to the connecting line, the former equation is obtained. The geometrical conductance of a spectral apparatus with a rectangular slit and entrance aperture stop can be expressed by

$$G_0 = \frac{s_{en} h_{en} B_{en} H_{en}}{f_{en}^2} = \frac{\lambda s_{en}^2 h_{en}}{s_0 h_0} .$$

7.3.2 The *optical conductance* G is the product of the geometrical conductance, G_0, and the square of the refractive index of the medium between the planes of the apertures A_1 and A_2

$$G = G_0 n^2.$$

7.3.3 The *effective optical conductance*, G_{eff}, is the product of the transmission factor, τ, taking into account losses caused by absorption and internal reflections, and the optical conductance, G:

$$G_{eff} = \tau G .$$

It determines the *radiant power*, Φ, conducted from a source having the *radiance* L through the instrument:

$$\Phi = L\, G_{eff} \quad \text{(see Note 16)}.$$

7.3.4 The *spectral optical conductance of a monochromator*, G_λ, is the quotient of the optical conductance and the resultant spectral slit width

$$G_\lambda = \frac{G}{\Delta\lambda_s} .$$

7.3.5 The *effective spectral optical conductance of a monochromator* $G_{\lambda,eff}$ is the product of the spectral optical conductance and its transmission factor

$$G_{\lambda,\, eff} = \tau\, G_\lambda$$

The radiant power Φ_U, with the proper imaging of a *continuum source*, with a spectral radiance of L_λ is given by the relationship

$$\Phi_{\lambda,U} = L_\lambda\, G_{\lambda,eff}\, (\Delta\lambda_s)^2 = L_\lambda\, G_{eff}\, \Delta\lambda.$$

The radiant power, Φ_L, with the proper imaging of a *spectral line source* with a total radiance:

$$L_0 = \int L_\lambda \mathrm{d}\lambda$$

is given by the relationship

$$\Phi_L = L_0\, G_{\lambda,eff}\, \Delta\lambda_s\, F(\lambda_L, \lambda_{eff}),$$

in which F denotes (in the plane of the exit slit) the convolution integral normalized to 1 of the instrument function ψ, and the *physical line profile function* of the *spectral line* g(x), also normalized to 1 by

$$\int_{-\infty}^{+\infty} g(x)\, \mathrm{d}x = 1 .$$

---

[16] When the various conductances depend on the wavelength, they can be written more precisely $G_0 = G_0(\lambda)$, $G = G(\lambda)$ und $G_{eff} = G_{eff}(\lambda)$, respectively.

The complete expression for F is as follows

$$F(\lambda_L, \delta\lambda_{\mathrm{eff}}) = \int_{-1/2\hat{s}_{\mathrm{ex}}}^{+1/2\hat{s}_{\mathrm{ex}}} \mathrm{d}x \int_{-\infty}^{+\infty} \psi(x'-x)\, g(x')\, \mathrm{d}x'$$

where

$$x = R_0 \frac{\lambda-\lambda_L}{\lambda_L} \quad \text{and} \quad \hat{s}_{\mathrm{ex}} = \frac{s_{\mathrm{ex}}}{s_0}$$

are reduced dimensionless variables which are useful for matching different spectral apparatus.

7.4 Terms Relating to Wavelengths of Radiation (see Note [17])

7.4.1 The *peak wavelength* λ_{max} is that wavelength at which a filter or a monochromator setting has a maximum spectral transmission.

7.4.2 The *mean wavelength* λ_{m} of a bandpass filter is the arithmetic average of those two wavelengths at which the transmission factor is half of the maximum.

7.4.3 The *weighted mean wavelength* $\bar{\lambda}$ is the mean wavelength weighted by the instrument function, i.e.,

$$\bar{\lambda} = \int_{\lambda_{\mathrm{m}}-\delta\lambda_{0.01}}^{\lambda_{\mathrm{m}}+\delta\lambda_{0.01}} \lambda_{\mathrm{m}}(\lambda)\, \mathrm{d}\lambda \Bigg/ \int_{\lambda_{\mathrm{m}}-\delta\lambda_{0.01}}^{\lambda_{\mathrm{m}}+\delta\lambda_{0.01}} \psi(\lambda)\, \mathrm{d}\lambda \,.$$

7.4.4 The *median wavelength* λ_{md} is that wavelength above and below which the instrument function contributes half the total signal

$$\int_{-\infty}^{\lambda_{\mathrm{md}}} \psi(\lambda)\mathrm{d}\lambda = \int_{\lambda_{\mathrm{md}}}^{\infty} \psi(\lambda)\, \mathrm{d}\lambda = \frac{1}{2} \int_{-\infty}^{+\infty} \psi(\lambda)\mathrm{d}\lambda.$$

7.5 Polarization

The *polarization state* of radiation is, as a rule, changed with its passage through an instrument as a result of reflection, refraction, double refraction, *dichroism* and diffraction.

To describe the polarizing properties, a 4 x 4 matrix (M) can be attributed to a spectral apparatus. The radiation entering the apparatus is described by a four-component vector $\vec{P}_1$, the *Stokes vector*. The state of polarization of the radiation leaving the apparatus can thus be given by another four-component vector $\vec{P}_2$

$$\vec{P}_2 = (\mathrm{M})\vec{P}_1$$

7.6 False Lines

Lines in the spectrum not emitted by the source are *false lines*. Depending on their origin they may be either *ghost* or *scatter lines*. They may occur in grating spectra (see Note [18]).

7.6.1 *Ghost lines*, symmetrically grouped on both sides of strong spectral lines and caused by a periodical error of a long period of the ruling engine are *Rowland ghosts*.

7.6.2 *Ghost lines* due to superposition of two unrelated periodical errors of different periods are *Lyman ghosts*.

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[17] If wavenumber or frequency is used, different relationships apply.

[18] Interferometric gratings do not show ghosts.

7.6.3 Misplaced spectral lines situated very near the parent line and caused by slight non-periodic variations in spacing of the grating lines are called *satellites.* If the satellites are numerous, they are called *near scatter.*

7.6.4 Completely random variations of the groove spacing may be the cause of *far scatter.*

7.7 The *effective spectral FWHM* of a spectral line in the plane of the exit field stop is the convolution integral of the spectral distribution functions associated with the resultant spectral slit width $\Delta\lambda_{\mathrm{en}}$, the theoretical resolution $\delta_0\lambda$, the *FWHM* of the spectral line $\Delta_{\mathrm{H}}\lambda$ and a term $\delta_{\mathrm{z}}\lambda$ due to optical imperfections. (Note [19]).

8 TERMS RELATING TO CONDUCTANCE

8.1 The *line-to-background radiant power ratio* is given by the quotient Φ_L/Φ_{U} with Φ_{U} (see 7.3.5)

$$\Phi_{\mathrm{U}} = L_{\lambda,\mathrm{U}}\Delta\lambda_{\mathrm{ex}}G_{\mathrm{eff}} \ .$$

8.2 The *irradiance, E*, is the radiant power divided by the irradiated area S:

$$E = \frac{\Phi}{S}.$$

The *irradiance at the exit slit* is

$$E_{\mathrm{ex}} = \frac{\Phi}{S_{\mathrm{ex}}} = \frac{\Phi}{h_{\mathrm{ex}}s_{\mathrm{ex}}} = \frac{\Phi}{h_{\mathrm{ex}}\Delta\lambda_{\mathrm{ex}}}\frac{\mathrm{d}\lambda}{\mathrm{d}x}$$

8.3 The *radiant exposure*, H, is the irradiance integrated over the *measuring time.*

9 MOUNTINGS Of SPECTRAL APPARATUS

9.1 *Prism Mountings*

9.1.1 An autocollimation spectral apparatus with at least one reflecting (30°) prism as dispersive element and a lens or a mirror as objective element is a *Littrow prism mounting.*

9.1.2 If a separate mirror is used, it is a *Wadsworth prism mounting.*

9.1.3 A combination of prisms can be arranged to provide a *constant deviation mounting.*

9.1.4 Mutiple prisms mountings can be used to increase the deviation and provide a larger dispersion.

9.2 *Concave Grating Mountings*

9.2.1 A mounting with a concave mirror as imaging element of the entrance collimator and a concave grating acting at the same time as dispersive element and as imaging element at normal angle of diffraction of the exit collimator is called the *Wadsworth mounting* (Fig. 4). This mounting is used because of its stigmatic imaging properties.

9.2.2 A mounting in which entrance and exit collimators are fixed at an angle of about 70° and in which wavelength variation is effected by rotation of the grating is called the *Seya-Namioka mounting* (Fig. 5). It is mainly used in the vacuum UV wavelength region.

9.2.3 A normal incidence mounting, where for wavelength adjustment the grating is rotated and transported along the bisector of the angle subtended by the entrance and exit axis is called the *Robin mounting.*

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[19] The spatial resolution (see 7.2.3) may be estimated from the effective spectral *FWHM.*

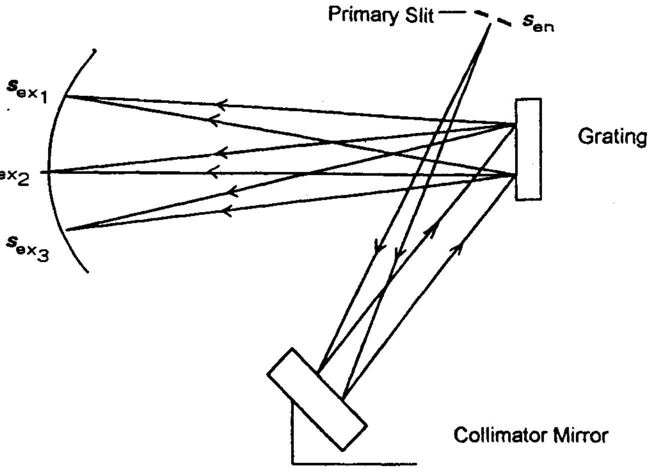

Fig. 4:- Wadsworth mounting

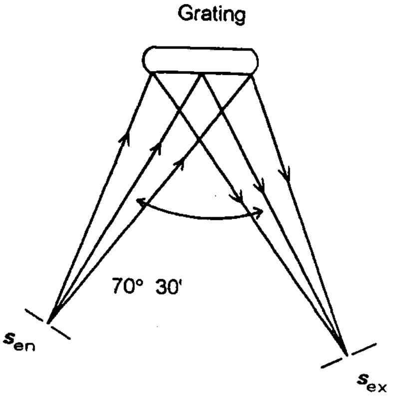

Fig. 5:- Seya-Namioka mounting

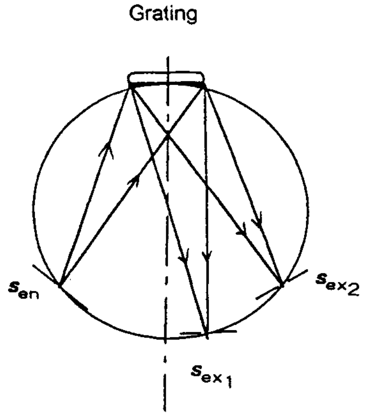

Fig. 6:- Paschen-Runge mounting

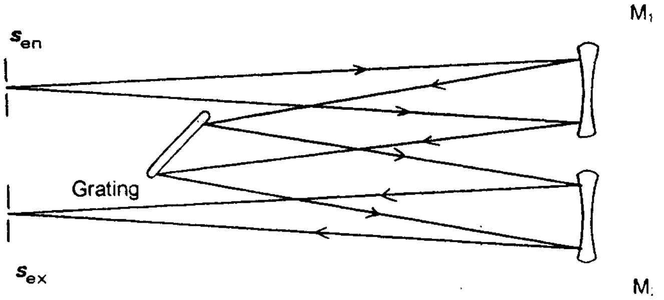

Fig. 7:- Czerny-Turner mounting

9.2.4 Flat-field mounting

A mounting of a specifically corrected interferometric grating or *flat-field grating*, where for a considerable length of the spectrum a focal plane is obtained, is called a *flat field mounting*.

9.2.5 A *Rowland circle mounting* is one where a spherical concave grating with a radius of curvature R is mounted on the perimeter of a real or imaginary circle with a diameter equal to R. The lines of the grating are normal to the plane of the circle and the radius of the grating sphere passes through the centre of the circle. An entrance slit positioned on the Rowland circle produces a focussed spectrum on the Rowland circle. The spectral lines are astigmatic.

9.2.6 A Rowland circle mounting, in which entrance slit and grating are fixed on the Rowland circle is termed the *Paschen-Runge mounting*. Photographic plates, film holders or exit slits are also attached to the circle. (Fig. 6).

9.2.7 A Rowland circle mounting near autocollimation is termed the *Eagle mounting*. It is suitable for, e.g., vacuum instruments. If the entrance slit is located side by side with the camera or exit slit, it is called the *in-plane Eagle mounting*. If they are symmetrically placed above or below the plane of the Rowland circle, it is called the *off-plane Eagle mounting*.

9.2.8 *Grazing incidence mounting* is a Rowland circle mounting for the wavelength region below 100 nm, in which use is made of the high reflection near total reflection of the incident beam. Angles of incidence and diffraction are very large and of opposite sign.

9.3 Plane Grating Mountings

9.3.1 A *plane grating mounting* with one concave mirror acting as imaging element symmetrically for both the entrance and the exit collimator is an *Ebert mounting*. It is also called an *in-plane Ebert mounting*.

9.3.2 A similar mounting, but in which entrance and exit slits or the middle of the camera are displaced symmetrically in the direction of the grating grooves, is called the *Fastie-Ebert mounting* or *off-plane Ebert mounting*.

9.3.3 A mounting similar to the in-plane Ebert mounting, but with separate mirrors for entrance and exit collimators, is called the *Czerny-Turner mounting* (Fig. 7).

9.4 Echelle Grating Spectral Apparatus

An *Echelle grating spectral apparatus* is a plane grating spectrograph, monochromator or polychromator with an Echelle grating as dispersive element. Frequently, a pre- or post-disperser for order selection or order sorting is fully integrated. According to the chosen combination and its intended use, it is called an *Echelle spectrograph, Echelle spectrometer, Echelle monochromator* or *Echelle polychromator.*

10 SPECTRAL BAND SELECTION OF A MONOCHROMATOR OR A POLYCHROMATOR

The *spectral band selection* (or settings) may be obtained by moving the dispersive component (prisms or grating), by moving either the entrance slit or the exit slit in the focal plane, by rotating a *refractor plate* located, for instance, before the exit slit, or by moving a collimating mirror.

11 LITERATURE

The following publications deal with aspects covered in this document:

IUPAC Manual of Symbols and Terminology for Physicochemical Quantities and Units, 2nd revision (Pure Appl. Chem., *51*, 1-41 (1979))

IUPAC Quantities, Units and Symbols in Physical Chemistry, 2nd Edition (Blackwell Scientific Publications, Oxford, (1993))

IUPAC Compendium of Analytical Nomenclature, Definitions, and Rules, 2nd Edition

(Blackwell Scientific Publications, Oxford, (1987))

Commission Internationale de l'Eclairage (CIE) International Lighting Vocabulary, Publ. No. 17, Paris

DIN 5030-3 Spektrale Strahlungsmessung - Spektrale Aussonderung - Auswahlkriterien, DIN Deutsches Institut für Normung, Berlin

12 INDEX OF TERMS (to sections)