



Standard Guide for Describing and Specifying the Spectrometer of an Optical Emission Direct-Reading Instrument¹

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1. Scope

1.1 This guide lists and discusses features of a spectrometer or polychromator used for optical emission, direct-reading, spectrochemical analysis. A polychromator in this sense consists of a spectrometer with an extended and fixed wavelength range and an array of fixed exit slits to isolate the spectral lines of the elements to be measured.

1.1.1 This guide does not apply to direct-reading systems that employ echelle spectrometers and vidicon or other detectors, where the design parameters are quite different.

1.2 This guide covers only the optical portion of the instrument, from excitation stand to photomultipliers.

1.2.1 Only general statements are made about source units.

1.2.2 Photomultipliers are included to the extent that they are mounted within the spectrometer to convert optical intensities to electrical signals, and establish the instrumental precision of each channel as a light measuring device. Readout systems are not included.

1.3 It is not the purpose of this guide to establish binding specifications or tolerances, but rather, to call attention to important parameters that manufacturers should include in their literature, to provide methods for measuring those parameters, and to assign values that are indicative of acceptably good performance. Because of the great variety of demands imposed by spectrochemical techniques, rigid performance criteria are not feasible.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.6 A partial listing of the information in this guide includes the following:

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2. Referenced Documents

2.1 ASTM Standards:

- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²
- E 172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis²
- E 356 Practices for Describing and Specifying the Spectrograph³
- E 380 Practice for Use of the International System of Units (SI) (The Modernized Metric System)⁴
- E 520 Practice for Describing Detectors in Emission and Absorption Spectroscopy³
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data³

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *background equivalent concentration (BEC)*—the concentration of an element at which the signal due to the analytical line is equal to the signal from a specimen with zero concentration of that element.

3.2.2 *channel*—the combination of exit slit and photomultiplier positioned to receive the radiation of a specific spectral line. It includes any mirror, refractor plate, filter, or other items in the exit optical path.

3.2.3 *readability*—the minimum difference between signals that can be perceived or distinguished.

NOTE 1—Readability is of concern for earlier direct-reading spectrometers that use analog or digital voltmeter displays. For direct-reading spectrometers that are interfaced with a computer, readability is replaced by standard deviation.

3.2.4 *scattered radiation*—that portion of the reading resulting from radiation at wavelengths different from the wavelength being measured, as a result of scatter by the dispersing medium or by surfaces within the spectrometer.

3.2.5 *shot noise*—the minimum deviation in the measurement of a signal due to the discreteness of the events being observed. In an optical emission spectrometer, the "events" are photons hitting a photomultiplier. Since the minimum standard deviation of the detection of photons is the square root of the total available photons, relative standard deviation is reduced as the signal intensity increases.

3.2.6 *white light precision*—the relative standard deviation of at least ten readings from a channel, either as an absolute intensity or as a ratio to an internal standard channel, when exposed to a stable radiation source.

3.2.7 *working resolution*—the ability of an exit slit to isolate the spectral line being measured from possible nearby interfering lines of other elements. Working resolution can only be measured with sharp spectral lines and may be finer than the practical resolution imposed by the source conditions required for actual determinations.

4. Significance and Use

4.1 Direct-reading polychromators are instruments commonly used for multi-element spectrochemical analysis. This guide seeks to describe those aspects of such instruments that are of significance in achieving useful spectrochemical performance. Awareness of parameters described in this practice will make manufacturers cognizant of factors they should consider in designing instruments, assist purchasers of instruments in making intelligent comparisons of competing designs, and make users aware of the compromises they must make in performing particular determinations.

4.2 Adequate description of spectrometers permits forming qualified appraisals on three important performance characteristics: accuracy of analysis, detection limits, and freedom from line interferences.

5. Fundamental Spectrochemical Objectives

5.1 The analyst is interested in three important performance characteristics of an overall direct-reading system: precision, particularly in how it affects the accuracy of a signal; detection; and freedom from or minimization of interferences.

5.2 Accuracy depends on precision and the absence of bias. In a spectrometer, accuracy depends on the precision of photometric measurement with minimal bias introduced by scattered radiation or line interference.

5.2.1 Precise photometry is the ability to closely repeat readings from the excitation of a homogeneous specimen on both short term and long term applications.

5.2.1.1 Short term, and particularly long term, precision are improved by the use of wide slits and with a marked difference between the widths of the entrance and exit slits. These conditions conflict with the requirements for sensitivity and freedom from interference.

5.2.1.2 Precision is improved by a compact, rugged spectrometer construction that remains stable despite severe mechanical vibration. Long term precision may require either a temperature-controlled spectrometer, a closely regulated temperature in the laboratory, or a spectrometer construction that adjusts or compensates for shifts in the spectrum that occur as a result of changes in ambient temperature. In an air spectrometer, atmospheric pressure can have a small effect on stability and precision.

5.2.1.3 An important factor in short term stability is the "white light precision" for each of the channels. See description of white light in 6.5 and its precision measurement in 7.6. This precision is limited by the stability of the photomultipliers. Frequently the most stable tubes are the least sensitive.

5.2.1.4 Analytical precision depends on excitation conditions and specimen homogeneity, which are outside the scope of this practice. Practice E 172 describes applicable excitation source units. See also 5.4.1 on spectral interference.

5.2.2 Bias in photometry signals can be minimized by spectrometer design and selection of spectral lines.

5.2.2.1 Scattered radiation can be reduced by having fewer components in the optical paths of radiation passing through exit slits, by dulling neutral surfaces, or by masking.

5.2.2.2 Bias is minimized when a selected analytical line shows an optimum response to changes in a concentration of

² Annual Book of ASTM Standards, Vol 03.05.

³ Annual Book of ASTM Standards, Vol 03.06.

⁴ Annual Book of ASTM Standards, Vol 14.02.

the element of interest, with little effect from other elements.

5.3 Detection and determination limits, which are discussed in Practice E 876, are favored by:

5.3.1 Improvement in the precision with which the overall signal plus background can be measured and distinguished from the background alone.

5.3.2 A higher signal-to-background ratio. Although improvement in the ratio may be realized by the use of narrow slits, this may adversely affect precision and stability.

5.3.3 Use of the most sensitive analytical line for each element.

5.3.3.1 In some cases, the most sensitive line of an element may have an interference from a strong line of another element. In these cases, the best practical detection may be obtained by using weaker emission lines that do not suffer from interference.

5.3.3.2 For some sets of elements, access to all the desirable emission lines may require an extended wavelength range, which involves either reduced dispersion, a broader focal plane, or auxiliary monochromators, or spectrometers. Reduced dispersion may impair detection.

5.4 *Minimization of Interference*—Interference in the signal of a particular element may occur due to neighboring lines of other elements or molecular species. Interference may be reduced by the use of narrow slits or higher dispersion. Narrow slits, however, may affect photometric precision and detection.

5.4.1 Different types of excitation sources can enhance or suppress certain spectral interferences on identical spectrometers. A practical evaluation of a direct-reading instrument must consider excitation conditions. See also 5.2.1.4 on analytical precision.

5.5 *Analytical Compromises*—The individual parameters of a spectrometer are closely interrelated, and there is no one best general solution. The characteristics may be modified to suite the intended application.

6. Parameters of Spectrometers and Associated Components That Affect Spectrochemical Performance

6.1 *Parameters Manufacturers Should Specify*—Since many parameters are difficult for a user to determine, but are well-known to the manufacturer, manufacturers should include them in their instrument specifications. Most of the specifications listed in Practice E 356 are germane to direct reading spectrometers. These include type of mounting, type of dispersing element, dispersion, resolution, speed, slits, wavelength coverage, illumination, and astigmatism. Some specific details on these follow:

6.2 *Dispersion*—Reciprocal linear dispersion, expressed as angstroms per millimetre ($\text{\AA}/\text{mm}$), is an important characteristic that determines the analytical performance of a polychromator, and should be specified in all analytical methods. All gratings display small changes of dispersion for different wavelengths. The calculation of dispersion is described in X1.2. Specify diffraction order as well as the reciprocal linear dispersion at a wavelength critical to an application. For example: Reciprocal linear dispersion at 3000 \AA : in the first order, 4.1 $\text{\AA}/\text{mm}$; in the second order, 2.0 $\text{\AA}/\text{mm}$.

NOTE 2—The angstrom is a depreciated unit according to Practice

E 380, but is used throughout this guide because the most common wavelength tables employ angstroms. One \AA = 0.1 nanometre.

6.3 *Working Resolution*—The resolving power of the spectrometer has little bearing on the ability of the instrument to separate an analytical line from a nearby interfering line. Frequently it will seem to indicate a performance as much as ten times better than can be achieved in practice. The more appropriate term is working resolution, expressed as the half-width of a line, as described and illustrated in 7.1. If there is a significant difference, the half-width should be specified at the center and ends of the focal curve. Parameters that affect working resolution are discussed in X1.2.2 and X1.3, and X1.4. Recommended spectral lines for measuring working resolution are given in Appendix X2.

6.3.1 A specification for working resolution might be: the half-widths listed below were obtained with a flat specimen of low alloy steel, excited by a 5 A, d-c arc in air, with entrance and exit slits of 25 and 50 μm , respectively:

Wavelength:	1930 \AA	3110 \AA	4358 \AA
Half-Width:	0.20 \AA	0.35 \AA	0.45 \AA

6.4 *Speed or Radiation Throughput*—It is a common misconception that a spectrometer with a high aperture ratio or radiation throughput will yield improved detection. Measurement precision, however, which does affect detection, requires an adequate radiation throughput. The various factors that determine the radiation throughput of a polychromator are described in Appendix X3. An interrelation of working resolution and throughput is discussed in Appendix X1.

6.4.1 Radiation throughput varies from channel to channel, due primarily to the combination of entrance and exit slit widths and the blaze of the grating, but the signal that is obtained from a channel depends more on the characteristics of an individual photomultiplier than on the optical system. For optimum detection, the selection of a photomultiplier and the voltage used to drive it must produce a signal of sufficient magnitude that the standard deviation of the background can be measured. See Note 1 on readability.

6.5 *White Light Precision*—The manufacturer should specify the guaranteed relative standard deviation in the measurement of ten or more exposures to “white light” consisting of a stabilized source of undispersed radiation or dispersed continuous radiation for all channels. In measuring these exposures, there must be sufficient signal averaging that shot noise in the source does not contribute significant variation. For example: The white light precision for all channels will be equal to or better than 0.3 % RSD.

6.6 *Scattered Light*—Radiation scattered within the spectrometer will increase an apparent reading. This will have two effects: (1) It will reduce the signal to background ratio and (2) it will give false readings for the sought element when specimens are analyzed that produce strong emission at the scattering wavelengths.

6.6.1 Scattered light may be classified as being near, from wavelengths within 100 times the working resolution, or far, from wavelengths removed from the wavelength being measured by more than 100 times the working resolution.

6.6.2 Far scattered light tends to be most severe in the extreme ultraviolet, while near scatter may be significant at all

wavelengths. The far scatter usually can be measured easily, whereas near scatter is difficult to distinguish from true spectral background.

6.6.3 Scattered light is difficult to measure without elaborate equipment such as tuneable lasers and detectors with very wide dynamic range. Therefore, it is recommended that the specification of scattered light be based on measurements of specific chemical mixtures, in which one element is present in large excess such that its emission lines give rise to detectable scattered light at the analytical wavelengths of other elements. In a practical sense, scattered light acts like a line interference, and can be defined and treated as such if it has a significant effect on the determination of an element.

6.6.3.1 For elements that exhibit a linear calibration, a simple statement of the limit of the effect of scattered light will be independent of the actual concentration. For example, with a linear calibration of arsenic, it might be stated that the scattered light at arsenic 1971 Å will not exceed the equivalent of 3 ppm arsenic when a sample containing 1000 ppm calcium is burned in a d-c arc.

6.6.3.2 When scattered light affects an element which has a non-linear calibration, the effect must be stated for a specific concentration of the element being measured. For example, for the analysis of copper in a ferrous material which can contain up to 5 % chromium, it could be stated that the effect of scattered light at copper 2136 Å will not exceed the equivalent of 0.05 % copper when the chromium is at 5 % and the concentration of copper is 0.8 %. The higher amount would have to be acknowledged even though a specimen with no copper may appear to not exceed the equivalent of 0.02 % copper for the same concentration of chromium. The difference is due to the change in the calibration slope at a higher copper concentration.

6.7 *Slits*—The combined effect of entrance slits and exit slits affects resolution and throughput as described in X1.4.

6.7.1 *Entrance Slit*—Specify whether it is fixed or adjustable, and the width or widths available. For example: A fixed slit, 20 µm wide, is standard.

6.7.2 *Exit Slits*—Specify the following:

6.7.2.1 Whether the slit directly faces the grating or is tangential to the focus circle,

6.7.2.2 Normal slit widths and special widths available, and

6.7.2.3 Limitation on the spacing between exit slits: that is, the minimum wavelength spacing, in angstroms.

6.7.3 *Accuracy of Positioning Exit Slits*:

6.7.3.1 *Concentricity*—Specify the accuracy, in angstroms, with which spectral lines will be centered on their exit slits relative to a mercury or other monitor line. For example: Exit slits will be aligned with their respective lines to within 0.03 Å of their peak obtainable setting when the mercury 4358 Å monitor line is in peak alignment.

6.7.3.2 *Parallelism*—If applicable, state the degree to which exit slits will be held parallel to spectral lines. For example: Profiles will agree within 0.02 Å when the top half, bottom half, or full slit are separately profiled.

6.7.3.3 State the mechanism provided to center the exit slits on the spectral lines. If applicable, state the mechanism provided to align the exit slits parallel to the spectral lines.

6.8 *Wavelength Coverage and Focal Curve Length*—The total wavelength range in angstroms and the useful focal curve length in millimetres in any fixed setting should be stated. For example:

Wavelength Range: 1600–5000 Å, first order, over 810 mm at 4.1 Å/mm;
1680–2500 Å, second order, over 410 mm at 2.0 Å/mm.

6.8.1 The relationship between the size of a spectrometer (diameter of the focal circle) and the reciprocal linear dispersion, and the effect on throughput is discussed in X1.3.

6.9 *Secondary Optics from Exit Slits to Photomultipliers*:

6.9.1 Specify any cylindrical or plane splitting mirrors, focusing mirrors, diffusers or filters, and physical placement of a photomultiplier in the focal plane.

6.9.2 State the maximum number of detectors and exit optical assemblies that can be installed on the focal curve.

6.9.3 List the type of photomultipliers used for specific wavelength ranges. (See Practice E 520.)

6.9.4 Describe how the photomultiplier sockets divide the voltage between the dynode stages. State if the gain change is continuous, and over what range.

6.9.5 Describe any provision to measure the total radiation from the analytical gap, through a second entrance slit, by observing the zero order reflection from the grating, or by other means.

6.10 *Optical Stability*:

6.10.1 *Design Features*—Describe the mechanism for compensating for overall shift of the spectrum, and for changes in dispersion caused by changes in ambient temperature and pressure (in an air spectrometer). For example: The design and mechanism for compensation of temperature changes consist of alignment servos, using a slit scan, or refractor plate in tilt/normal configuration.

6.10.2 *Temperature Limits*—Specify the temperature limits and rate of temperature change which must not be exceeded if the polychromator is to retain 95 % of its normal response at the extremes of the wavelength range. For example, in Fig. 1 the response drops from 910 to 865 arbitrary intensity units (95 %) for a displacement of 13 µm. If the coefficient of thermal expansion of the spectrometer is $4 \times 10^{-6} \text{ m/}^\circ\text{C}$ and the focal curve diameter is 1 m, a 1° temperature change will lengthen or shorten the focal curve by $4 \times 10^{-6} \text{ m}$ or 4 µm; then a temperature drift of $13 \text{ µm}/(4 \text{ µm/}^\circ\text{C})$ or $\approx 3^\circ\text{C}$ is allowable.

6.10.3 *Profiling Mechanism*—State the means for moving the spectrum across the array of exit slits, such as by movement of the entrance slit at right angles to the optical path or along the focal curve, by rotation of a refractor plate, or by rotation of the grating. In some early direct-reading spectrometers, sections of slit frames were able to be shifted.

6.11 *Spectrometer Illumination*—The condensing system normally supplied by the manufacturer for routine quantitative work shall be specified with respect to:

6.11.1 *Omni Illumination*—Accepting radiation from all areas of the analytical discharge.

6.11.2 *Selective Illumination*—Accepting radiation only from selected areas of the analytical discharge.

6.11.3 *Exclusive Illumination*—Accepting radiation from all

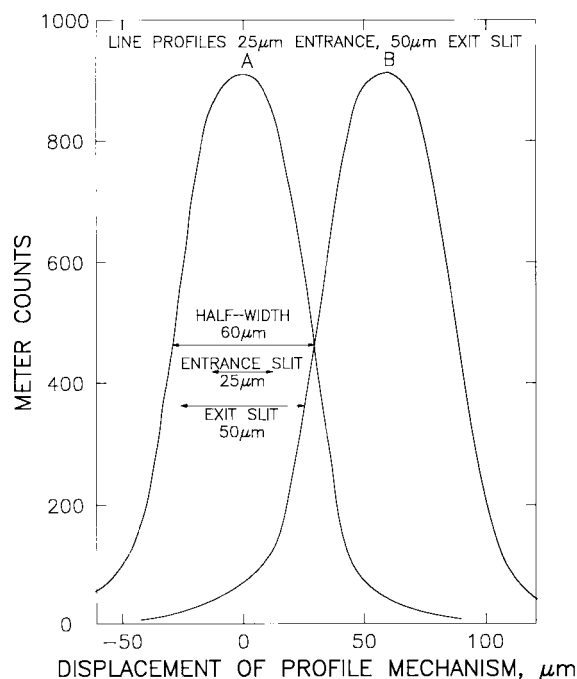


FIG. 1 Typical Line Profiles and Overlaps, Illustrating Working Resolution

parts of the analytical gap except selected areas, such as hot electrode tips.

6.11.4 *Optical Material*—Quartz or fluorite. State if there are any coatings on optics.

6.11.5 *Types of Lenses or Mirrors*—Spherical, parabolic, ellipsoidal, cylindrical or crossed cylindrical. State apertures and focal lengths at specified wavelengths. State where a lens is placed.

6.11.6 *Analytical Gap*:

6.11.6.1 State where the analytical gap is focused: on the grating, on the slit, or if there is no focus (without lens). Specify the dimensions of the illuminated area at the dispersing element. Specify the dimensions of the analytical gap sampled: at the extreme wavelength of the polychromator; and at the wavelength at which the ideal focusing is achieved, which is the smallest area of the analytical gap that can be sampled. Indicate the extent of optical aberrations and their wavelength dependence.

6.11.6.2 Indicate the axis of the analytical gap with respect to grooves of the grating.

6.11.6.3 Indicate the effect on signal of offsetting the analytical gap from the optical center line by 2 mm or other specified distance in both horizontal and vertical planes.

6.12 *Astigmatic Image*—Most direct-reading polychromators employ concave gratings in some form of Rowland circle mounting, which means that the images are astigmatic. The line images are considerably longer than the entrance slit. However, this normally is compensated for by the use of tall exit slits and photocathodes, so that little light is lost.

6.12.1 Lower detection limits may be achieved by looking at a specific level in the analytical gap. This may be done with a stigmatic polychromator by focusing the light source on the entrance slit and using an aperture at the appropriate exit slit. This is awkward to do in an astigmatic instrument, because the

Sirk's focus, that is, that position in front of the entrance slit where an aperture must be located to be in focus at the exit slits, is usually some distance in front of the entrance slit and changes with wavelength.

NOTE 3—Even though it may not be practical to work at the Sirk's focus, enhancement of line to background may be achieved in an astigmatic mount by setting the analytical gap either above or below the central optical plane.

6.12.2 If a spectrometer design achieves a stigmatic image, or if the condensing system permits a spatial resolution in the analytical gap, the arrangement should be described.

6.13 *Excitation Stands*—Describe the types of stands that are available for holding and exciting specimens, such as the following:

- 6.13.1 Flat specimen stand, for air operation,
- 6.13.2 Gas-flushed, flat specimen stand,
- 6.13.3 Gas-tight, gas-flushed, flat specimen stand,
- 6.13.4 Pin specimen stand, for air operation,
- 6.13.5 Gas-flushed, pin specimen stand, and
- 6.13.6 Rotating disk, liquid sample stand.

6.14 *Type of Vacuum System for Wavelength Coverage Below 1900 Å Only* (See 6.15 for an alternate way to work below 1900 Å.):

6.14.1 Type of pump: diffusion, mechanical, or turbomolecular.

6.14.2 Type of vacuum gages supplied and where located.

6.14.3 Protection against back-streaming.

6.14.4 Provision for shutting off high voltage on photomultipliers when the spectrometer is under partial vacuum. This safety provision is not needed if photomultiplier receptacles are not in the evacuated chamber.

6.14.5 Pump down time required.

6.14.6 Ultimate vacuum expected if no gas is bled into the vacuum chamber. Provision, if any, to allow argon or nitrogen to bleed into the chamber to keep a focusing lens clear.

6.14.7 Provisions for isolating the evacuated chamber from the pump either by choice or automatically in the event of a pump failure. This may include provision for bleeding air to the pump.

6.14.8 Safety features.

6.15 If the spectrometer can be flushed with a transparent gas, such as nitrogen, which permits an alternate way of working in the far ultra-violet region, specify how the gas flushing is controlled and how long it takes to displace air from the spectrometer.

6.16 *Physical Size and Weight*—Include overall size and weight, and distribution of weight on each foot of spectrometer.

6.17 *Service Requirements*—Electrical power, water cooling, gas supplies, etc.

6.18 *Other Features*:

6.18.1 Specify whether a fatigue light is needed or supplied.

6.18.2 Photographic capability (if any).

6.18.3 *Maintenance Features*:

6.18.3.1 *Cleaning of Entrance Optics*—In a vacuum spectrometer, either specify that the entrance optics can be cleaned without breaking the working vacuum, or indicate the pump-down time required to return to a working vacuum.

6.18.3.2 Cleaning of excitation stand.

NOTE 4—The frequency of cleaning is obviously of great interest to the user, but depends on the specific application: oil analysis with a rotating disk, analysis of zinc die castings for residual elements with an ignited arc in air, analysis of steel in an argon-flushed Petrey stand, etc. The entrance lens in a vacuum spectrometer may be vulnerable to becoming coated with polymerized oil from vacuum pump vapors.

6.18.3.3 Ease of access to, and adjustment of components.

6.18.3.4 Protection, if any, to prevent exposure of photomultipliers to room light while they are powered with high voltage.

7. Measuring Specified Polychromator Parameters

7.1 *Measuring Working Resolution*—Curve A of Fig. 1 illustrates how to interpret the plot of a dynamic profile of a spectral line of an element to obtain the line half-width that is used as a measure of working resolution. The data are easy to obtain on most direct-reading spectrometers.

7.1.1 Suitable spectral lines and the approximate concentrations appropriate for several sources are listed in Table X2.1 of Appendix X2.

7.1.2 Possible specimen-source combinations are as follows:

7.1.2.1 A pin or Petrey stand with low alloy steel, aluminum, brass or other convenient specimen, which may contain several of the elements for which the spectrometer has exit slits. To avoid broadened lines, the specimen may be excited with a unidirectional-capacitor discharge, using currents that are less than 5 r-f A, with the highest inductance and capacitance available on the source unit.

7.1.2.2 A rotating-disk, vacuum cup or porous cup solution stand, with spark or arc excitation.

7.1.2.3 A pin stand with 6 mm (0.25 in.) diameter low-alloy steel rods, excited with a stabilized d-c arc of less than 2 A, after establishing a bead on the lower, anode rod.

7.1.2.4 Hollow-cathode lamps, which typically give line widths of 0.05 Å or less, are recommended for determining working resolution that is expected to be better than 0.2 Å.

7.1.3 Procedure:

7.1.3.1 Make a conventional burn, at the setting of the adjusting mechanism at which the line is in profile.

7.1.3.2 Adjust the photomultiplier dynode or other gain adjustment or the exposure time, to keep the absolute intensity reading on scale, but at least five times what the background reading is expected to be.

7.1.3.3 Offset the adjusting mechanism to the minus side of the peak setting by two times the exit slit width (or the entrance slit width if it is wider).

7.1.3.4 Make a normal burn and note the absolute intensity reading for the line. If several lines are to be measured, note the readings for all the slits involved.

NOTE 5—Absolute intensities, rather than intensities ratioed to an internal standard, should be used in profiling to avoid changing two variables simultaneously.

7.1.3.5 Continue the process for at least the following settings in multiples of the slit width:

−2.0, −1.0, −0.6, −0.4, −0.2, 0, 0.2, 0.4, 0.6, 1.0, 2.0

7.1.3.6 Plot the readings on linear graph paper, similarly as shown for Curve A in Fig. 1.

7.1.3.7 Draw a smooth, symmetrical curve that best fits the points, even though the curve may not go through several points.

7.1.3.8 Draw a baseline between the −2.0 and +2.0 points. For a line used to specify working resolution, this baseline should be approximately horizontal.

NOTE 6—Interfering lines may lead to distortion in the baseline.

7.1.3.9 Halfway between the peak and base line reading under the peak, draw a horizontal line, intersecting the profile curve.

7.1.3.10 The length of this line between the intercepts, converted to angstroms, is the half-width that is used to specify the working resolution. In Fig. 1, the half-width measures 60 μm at a reciprocal linear dispersion of 5.6 Å/mm; therefore, after converting the half-width to millimetres, the working resolution is 0.06 mm multiplied by 5.6 Å/mm or 0.34 Å.

7.2 *Improving Working Resolution*—Working resolution is enhanced by the following factors:

7.2.1 Increased linear dispersion (a lower number for the reciprocal linear dispersion),

7.2.2 A narrower entrance slit. This will have little effect if the entrance slit is narrower than the exit slit,

7.2.3 A narrower exit slit. This will have a marked effect if the entrance slit is narrower than the exit slit. See X1.4 for a discussion of the effect of slit widths on working resolution,

7.2.4 Better focus for the line,

7.2.5 Reduced optical aberration for the line, and

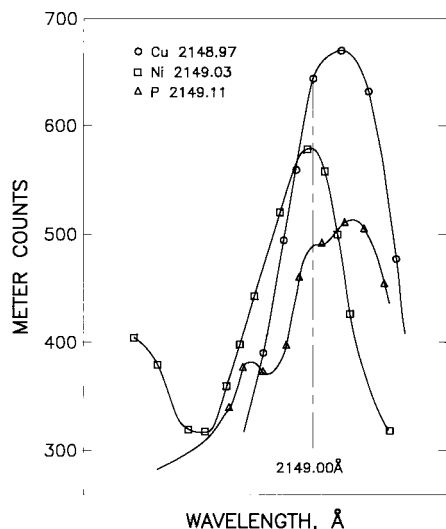
7.2.6 Improved alignment of the exit slit with the line, both for concentricity and for parallelism.

NOTE 7—Excitation conditions will affect the determination of working resolution. For example, the lithium 6707 Å line, when excited in a high current d-c arc, may have a Doppler width even greater than 1 Å; and due to Lorentz broadening, the calcium 3933 Å has a large width that contributes to stray light and background far from the line center. However, most iron lines in a d-c arc below 3 A will have line half-widths less than 0.1 Å. The latter will give a more accurate measurement of the potential working resolution.

7.3 *Importance of Working Resolution*—In general, a statement of working resolution will help to predict other element interferences. The greatest uncertainty will be due to unreliability in the tabulated relative intensities for lines of different elements, obtained with various types of excitation sources.

7.4 *Applying Working Resolution*—Curve B of Fig. 1 shows the profile reading that would be obtained at Slit A if there were a line from some other element, B, with the same intensity, displaced by the half-width of 60 μm or 0.34 Å. If there were no signal from Element A, the signal produced by Element B at the peak position for A would be about 68 counts, compared to 910 counts for A alone, or approximately 7.5 %. Although there remains a small contribution of signal from B observable on A, the lines may be considered to be resolved from each other. If Element B were 90 μm from A (that is, 1.5 times the half-width), its contribution would be about 16 counts, or less than 2 %. The actual interference from a nearby line will depend on:

7.4.1 The difference in wavelength, which usually can be determined from wavelength tables.



NOTE 1—Phosphorus 2149.11 Å is a barely perceptible shoulder on top of the copper and nickel line wings.

FIG. 2 Example of Line Interferences

7.4.2 The relative intensities of the analytical and interfering lines under the excitation conditions used. Some idea of the basic intensity of the interfering line can be obtained from the intensity rating of the line in the wavelength tables and an appraisal of how much the excitation conditions being employed are arc-like (neutral species) or spark-like (ionic species). These listings do not reflect the wide variations of excitation conditions employed and the wide variations in sample matrices encountered in practical analyses. At least for a controlled 10 A d-c arc and for a 0.1 atomic percent of an element in either copper or silver, the NBS (now NIST) values have consistency (1).⁵ For intensity measurements for select lines of the rare earths, methodology is included in Boumans (2,3) and applications are in Boumans (4-6). Formulae for calculating departures from Maxwell-Boltzman equilibrium for inductively-coupled plasmas and direct-current plasmas appear in Burton and Blades (7).

7.4.3 The concentration of the interfering element, which normally can be predicted from the nature of the unknown samples.

7.5 Line Interference:

7.5.1 Fig. 2 shows profiles obtained for phosphorus 2149.11 Å, the element to be analyzed, and two interfering lines, copper 2148.97 Å and nickel 2149.03 Å, produced using a triggered-capacitor discharge and a low alloy steel specimen. The half-width of the phosphorus line in the second order at 2.7 Å/mm, measured with a slit width of 65 μm, is 0.18 Å. Since the copper line is separated from the phosphorus line by only 0.14 Å and from the nickel line by only 0.08 Å, there is potential for interference from both lines. See Table 1 for relative intensities.

7.5.1.1 For a capacitor discharge, the spark relative intensities are more significant. The phosphorus lines in a spark-like

TABLE 1 Listed Intensities for an Analytical Line and Potential Interfering Lines

Element	Wavelength, Å	MIT Tables ^A		NBS Tables ^B
		Arc	Spark	Arc
Phosphorus	2149.11	15	[25]	2600
Copper	2148.97	15	25	unlisted
Nickel	2149.03 ^C	unlisted		unlisted

^A See Ref (8).

^B See Ref (1).

^C See Ref (9).

source have greater sensitivity than the tables indicate. The rated intensities in the MIT Tables (8) indicate that the copper line is going to present a problem, but since the nickel is unlisted, it would appear that it should be insignificant at low nickel concentration. However, in stainless steel, where nickel may run from 7 to 25 %, it may have a measurable effect. Experimentally, 1 % nickel has been found to be equivalent to 0.0020 % phosphorus.

NOTE 8—Tungsten has lines at 2149.85 Å, which make phosphorus 2149.11 Å useless in tungsten tool steels.

7.5.2 Interference from Broad Line “Wings”—Wide lines, usually identified by *h*, *R*, *r*, *W*, or *w* in tables, can have wings that extend to several angstroms on either side, producing interference or an unexpectedly high background. Such an effect is illustrated in Fig. 3, showing a profile for zinc I 2138 Å. In terms of the zinc profile contour, the background looks insignificant. However, if the tellurium 2142 Å line is profiled with a specimen of 0.2 % tellurium in a brass matrix, using a capacitor discharge in argon, the background rises continually toward lower wavelengths, which is due to the zinc 2138 Å line.

7.6 Determining White Light Precision:

7.6.1 To measure the white light precision of a channel, it is necessary to have either a line source, such as a mercury lamp, which is not dispersed by the grating, or a continuous source, such as a deuterium or tungsten filament lamp or a radioisotope-activated phosphor. Frequently the fatigue lamp, which illuminates the photomultiplier tubes between exposures, will provide a suitable light source. The source should be operated from a regulated power supply, so that it is stable to

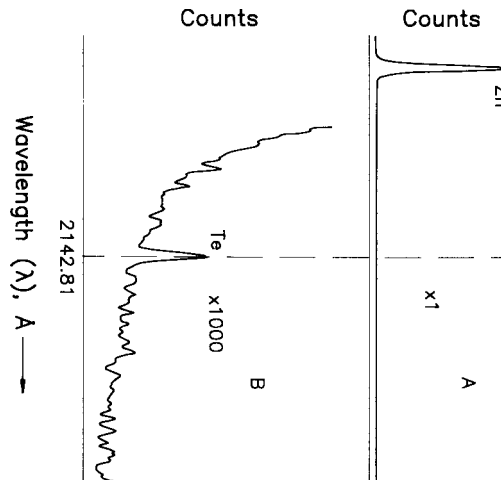


FIG. 3 Far Wing Interference of Zinc on Tellurium

⁵ The boldface numbers given in parentheses refer to a list of references at the end of the text.

0.05 %. The readout system must be wired to permit integrated exposures when the light source is substituted for a normal specimen burn. If absolute intensities are employed in the analytical procedure, they should also be used in determining the white light precision, which then is limited by the stability of the light source (and of the high-voltage supply for the photomultipliers). If intensity ratios are employed analytically, intensity ratios may be used in this test for the analytical channels. This will compensate for any slight fluctuations in lamp output.

7.6.2 Run ten or more repeat exposures, and calculate standard deviation and relative standard deviation. (See Practice E 876.)

7.6.3 The white light test is a powerful diagnostic tool since it checks the precision of each channel as a light measuring device. If the white light results are favorable, but the analytical results are poor, the problem could be: inhomogeneity of the specimens, erratic excitation by the source unit, an optical system which produces erratic illumination, or vibration in the spectrometer which affects the stability of alignment of the spectral lines with slits.

NOTE 9—A white light test is not affected by alignment of slits on analytical lines.

7.7 *Measuring Scattered Light:*

7.7.1 Scattered light can be the result of defects in the dispersing and focusing elements. With a grating, minute irregularities in the spacing of the grooves will result in scattered light.

7.7.2 Light can be scattered from various surfaces within the spectrometer, or there may be cracks in the spectrometer housing which permit some room light to enter the spectrometer.

7.7.3 Far scattered light can be measured by employing a filter that will transmit at the wavelength suspected of contributing scatter but will not transmit at the wavelength of the analytical line. Any signal that is measured must then be due to far scatter. Alternately, a photomultiplier can be used which will respond to the suspected scattering wavelengths but will not respond at the analytical wavelength. For example, if a glass filter is placed in the optical path of the photomultiplier used as the detector for the arsenic 1972 Å line, the difference in the arsenic reading obtained for a specimen with 1000 ppm of calcium and a specimen with calcium below 0.1 ppm would be due to far scatter from calcium lines and background above 3000 Å. Conversely, if a solar-blind photomultiplier, sensitive to 1650 Å, with no response above 3200 Å, shows a difference in reading the calcium 3934 Å line between specimens with calcium at 1000 ppm and 0.1 ppm, this indicates a true rise in spectral background due to unquantized recombinations between free electrons and Ca⁺ ions. In the case of calcium interference, scatter could also occur from the calcium 3968 Å line. In fact, if the arsenic 1972 Å line were being measured as a second order line (at the equivalent first order wavelength position of 3946 Å), only the calcium 3968 Å line could be considered as being far scatter, since the calcium 3934 Å line could now exhibit near scatter. See 7.7.5. (The photomultiplier will be directly sensing the background in the second order, as well as scattered light.)

7.7.4 Scattered light becomes a significant factor only when the spectral background level becomes extremely weak. With spectral background levels normally encountered with a spark or even a d-c arc or plasma, it may be difficult to detect scattered light.

7.7.5 Near scattered light is difficult to distinguish from a true increase in the spectral background due to a change in the matrix. If aluminum is being measured at 3961 Å and Specimen A, with negligible amounts of aluminum and calcium, produces a reading of 75, while Specimen B, with 1000 ppm calcium and negligible aluminum, produces a reading of 300, the increase might be due either to near scattered light or to a true increase in background at wavelengths near the calcium ion lines at 3934 Å and 3968 Å.

7.7.5.1 If available, the output from a monochromator, preferably a double monochromator with a bandpass narrower than 5 Å, can be used to irradiate the spectrometer being tested. By directing the radiation of the specimens through the monochromator set to pass 3961 Å, the signal for aluminum will certainly be reduced, but the new measurements of Specimens A and B will show whether the signal for B has been reduced relative to A. To the extent that it has not, it must be assumed that the calcium may have introduced a true increase in background, even at some distance from the interfering calcium lines.

7.7.5.2 In a given polychromator, once the best available dispersing element has been used and the greatest care has been taken to shield the photomultiplier from any light that has not passed through the exit slit, there is no other way to reduce the reading for a blank. If a specimen free of the analyte element but otherwise composed of high concentrations of typical matrix elements produces higher readings than a less complex reagent blank, it may be irrelevant whether the offset is due to true background or scattered light. Corrections as if the shift were due to an interfering line from a matrix element are required in such instances.

7.8 *Optical Alignment and Focus*—Optimum analytical results will be achieved only if the optics are well aligned and focused. All exit slits must be aligned parallel to their respective lines, and centered on them. The entrance slit must be aligned parallel to the grating rulings. Any serious departure from good focus or alignment will affect working resolution.

7.9 *Optical Stability*—Determine the time required for optical readjustment, if any, after a temperature change in the laboratory of $\pm 3^{\circ}\text{C}$. The time required for the observed intensity of a mercury pen lamp to stabilize at the new temperature is an adequate indication of adjustment time.

7.10 *Precision and Accuracy*—Test under simulated day-to-day operating conditions to determine precision and accuracy over a two day period. Standardize the instrument with homogeneous standardants, as in routine operation, except that at least four burns should be employed. Rerun these same standardants in quadruplicate at irregular intervals during the day. A plot of the average concentrations as a function of the time will measure the long-term variation in readings, as contrasted to the short-term precision. This will define the frequency at which standardization should be performed to maintain a desired accuracy of analysis. For many materials,

the required accuracy can be realized with standardization once a day. More critical specimens may require standardization every 4 or 2 h, or perhaps each hour. For very critical specimens, reference material may have to be run with each unknown.

NOTE 10—Continual running of a source can cause thermal drift. In testing for drift, the interval between burns should not be any shorter than the intervals that will be used in routine analysis.

8. Describing the Spectrometer in Analytical Methods

8.1 Each analytical method should contain the minimum characteristics required for the spectrometer, as listed in 8.2. Other information should be included which will help users to decide whether they should be able to obtain comparable results with their equipment. Performance characteristics for the spectrometer that are essential to the analytical performance described should be specified.

8.2 Essential Information:

8.2.1 Wavelength coverage and reciprocal linear dispersion are the most significant features affecting analytical performance and should be specified in all analytical methods.

8.2.2 The working resolution provides an indication of the quality of design and adjustment of the spectrometer, and provides a means for judging whether other spectrometers will provide equivalent detection limits and freedom from interferences from other elements.

8.2.3 Since the combination of entrance and exit slit widths, at a specified reciprocal linear dispersion, affects working resolution, signal to background ratio, and radiation throughput, the slit widths should be specified.

8.2.4 At low concentrations, for those channels where it is important to achieve detection, the table that shows analytical lines and concentration ranges should be supplemented with columns showing background equivalents, signal to background ratios, and achievable repeatability of measurements.

8.2.5 At high concentrations, if the precision and accuracy achieved by the method are essential, for some or all channels, the white light precision should be specified. The table of analytical lines and concentrations ranges should include a column that lists the relative standard deviations of measurements, at a specified level. If specific calibrations have been established, the white light precision may be replaced by the relative standard deviations of determined concentrations at a specified concentration.

9. Keywords

9.1 astigmatism; detection; diffraction grating; direct-reading spectrometer; line interference; optical emission spectrometer (OES); optical working resolution; radiation throughput; scattered light

APPENDIXES

(Nonmandatory Information)

X1. EFFECTS OF VARYING PARAMETERS ON WORKING RESOLUTION AND THROUGHPUT

X1.1 The physical size of the spectrometer and fineness of its grating obviously affect resolution by establishing the reciprocal linear dispersion. A finer, more closely ruled grating provides a greater angular dispersion.

X1.2 *Dispersion*—Calculate the angular dispersion for a grating as follows:

$$(d\Theta/d\lambda) = n/(b \cos \Theta) \quad (X1.1)$$

where:

- Θ = the angle of diffraction,
- λ = the wavelength of the radiation being dispersed,
- n = the order number, and
- b = a grating constant, the groove spacing in angstroms:

$$b = 10^7/g \quad (X1.2)$$

where:

- g = the grooves per millimetre in the grating.

X1.2.1 Optical design usually keeps Θ close to zero, so that $\cos \Theta$ remains near 1.0, and $d\Theta/d\lambda$ reduces to n/b . Typical values are given in Table X1.1.

X1.2.2 The effect of increased angular dispersion on radiation throughput can be illustrated by considering a spectrometer having a 1 m diameter focal curve. With a grating of 1200 grooves/mm, the reciprocal linear dispersion will be approxi-

TABLE X1.1 Values of $(d\Theta/d\lambda)$ for Gratings

Grooves/mm	600	960	1200	2400
<i>b</i> , in Å	16 666	10 410	8333	4167
Order	Radians per Angstrom			
<i>n</i> = 1	6.0×10^{-5}	9.6×10^{-5}	1.2×10^{-4}	2.4×10^{-4}
<i>n</i> = 2	1.2×10^{-4}	1.9×10^{-4}	2.4×10^{-4}	4.8×10^{-4}

mately 8.3 Å/mm, and a combination of a 25 μm entrance slit and a 50 μm exit slit will produce a working resolution of about 0.5 to 0.6 Å. If a grating of 2400 grooves/mm and the same effective aperture is substituted, the reciprocal linear dispersion becomes approximately 4.2 Å/mm. For the same combination of slits, the working resolution improves to about 0.25 to 0.3 Å, while the radiation throughput for the signals remains the same. The instrument designer or the spectroscopist who specifies the channel parameters has two contrasting options. The improved working resolution can be utilized to reduce potential interelement interferences, and to improve signal-to-background ratios in order to obtain better detection. Alternately, the entrance and exit slit widths can be increased to double the radiation throughput while retaining the original 0.5 to 0.6 Å working resolution.

X1.3 Effect of Spectrometer Size on Working Resolution

and Signal—A large spectrometer improves working resolution, but signal strength depends upon the flux of radiation that illuminates the grating. Radiation throughput is discussed in detail in Appendix X3. Following are discussions of the influence of either the focal circle diameter or the area of a grating that is illuminated.

X1.3.1 If the focal circle diameter of a spectrometer having a grating with 1200 grooves/mm is increased from 1 to 2 m, while the effective aperture and all other parameters are maintained the same, the reciprocal linear dispersion will be improved from 8.3 to 4.2 Å/mm, and the working resolution will be improved to 0.25 or 0.3 Å. The level of illumination at the exit slit, however, will be dropped to one-quarter by the inverse square law, $1/f^2$. This reduces the signal to one-quarter of what it was. The signal can be restored to its original level by doubling the height and width of the entrance slit. The exit slit height and width have to be doubled also, to accept the same proportion of the line signal and to maintain the same mechanical stability. This reduces the working resolution once more to 0.5 or 0.6 Å, resulting in no change in optical performance.

X1.3.2 If the focal circle diameter is increased from 1 to 2 m, but this time the effective aperture ratio of the grating is maintained by doubling the width and height of the ruled area that is illuminated, the illumination at the exit slit will remain at the original level. As before, assuming no higher order aberrations, the reciprocal linear dispersion becomes 4.2 Å/mm and the working resolution improves to 0.25 or 0.3 Å. There will be a real gain in line-to-background ratio, resulting in improved detection, without any loss in signal. If increased signal is more important than detection, the entrance and exit slits can be doubled in height and width, to obtain a four-fold increase in readings, at the original working resolution.

X1.4 Effect of Slit Widths:

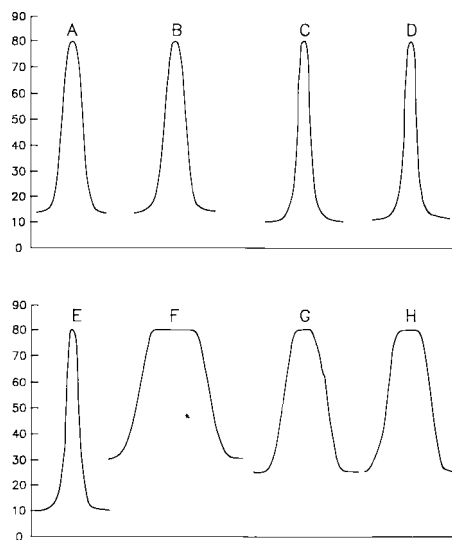
X1.4.1 *Experimental Measurements*—Fig. X1.1 shows experimental measurements obtained on a 0.5 m scanning spectrometer with a 1200 grooves/mm grating, having a reciprocal linear dispersion of 16.6 Å/mm, for a series of entrance-exit slit combinations. The mercury 4358 Å line from a tubular mercury lamp was used as a light source.

X1.4.1.1 *Intensity Normalization*—The direct measurements produced rapidly increasing signals which would reveal little information if plotted directly, either because the wider slit combinations would fall off-scale or it would be impossible to see the detail in the narrower combination. Accordingly, the data have been normalized so that the peak intensities are always plotted at 80. The performance of such slit combinations would be comparable for polychromators used for direct-reading spectrometers. The figures show how the line profile, and thus the working resolution, changes with the different slit combinations, while Table X1.2 summarizes the quantitative effect on signal to background ratio.

X1.4.2 Conclusions:

X1.4.2.1 No difference in performance can be measured if the entrance and exit slits are interchanged, as in the 10-25, 25-10 and 25-50, 50-25 μm illustrations shown in Fig. X1.1.

X1.4.2.2 The wider slit width determines the signal to



Note—

Line Profile	Entrance Slit Width, μm	Exit Slit Width, μm
A	50	25
B	25	50
C	25	10
D	10	25
E	7	7
F	50	150
G	50	100
H	10	100

FIG. X1.1 Effect of Entrance and Exit Slits on Line Profiles

TABLE X1.2 Signal/Background Ratios for Various Slit Combinations

Entrance Slit Width, μm	Exit Slit Width, μm	Signal/Background Ratio
7	7	8:1
10	25	7.6:1
25	10	7.6:1
25	50	5.9:1
50	25	5.9:1
10	100	3.2:1
50	100	3.2:1
50	150	2.7:1

background ratio or the working resolution, or both. Changing the width of the narrower slit has very little influence on signal to background ratio or working resolution. Note particularly the 50-100 and 10-100 μm examples in Fig. X1.1.

X1.4.2.3 Increasing the width of the narrower slit greatly increases the radiation throughput. If the wider slit is greater than about 50 μm, as in many direct-reading spectrometers, widening the narrower slit also narrows the flat top of the line profile, which is quite marked when there is a great difference between slit widths. Note Case E in Fig. X1.1 for both slits set at 7 μm. Not only is the half-width narrow, but there is no flat top. Even slight shifts in profile will cause a marked change in the measurement of intensity. The half-widths for Cases G and H, for an exit width of 100 μm and respective entrance slits of 50 and 10 μm, show a little more flatness for the greater disparity between slit widths in Case H. Although Case F, with both slits wide, shows a very flat top which will make the spectrometer insensitive to profile shifts, the wide half-width will show a relatively poor working resolution.

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X1.4.3 *Effects of Slit Widths on Analyses:*

X1.4.3.1 To improve detection by means of better signal to background ratios, and to reduce the possibility of interelement interferences, it is desirable to employ the narrowest practical entrance and exit slits.

X1.4.3.2 To improve stability and long term repeatability, so far as the spectrometer is concerned, it is desirable to have the greatest possible difference between entrance and exit slit widths, as in the 10 to 100 μm combination of Case H shown in Fig. X1.1. Such a combination produces a flat-topped line contour which will show relatively little change if there is a

slight drift in the spectrum with respect to the exit slits.

X1.4.3.3 The two conditions described above are mutually incompatible for a single analytical line. However, it is possible in a single polychromator to use an intermediate entrance slit width, with narrow exit slits for spectral lines of elements where the optimum detection limit is desired, and wider exit slits for lines employed to measure high concentrations with optimum precision. The channel gains will need to be adjusted to maintain adequate electrical performance as the slit widths are changed.

X2. RECOMMENDED SPECTRAL LINES AND CONCENTRATION RANGES FOR MEASURING WORKING RESOLUTION

X2.1 Table X2.1 lists 42 lines commonly employed either as analytical or internal standard lines in many direct-reading spectrometers. These may be used to find lines for measuring working resolution from 1900 \AA in the extreme ultra-violet region at the limit of transmission of air, to 5200 \AA in the green.

X2.2 Concentrations should not be too high, to avoid line broadening and self absorption. Too low a concentration, however, will not give adequate signal above background. Suggested concentration ranges are listed.

TABLE X2.1 Recommended Spectral Lines and Concentration Ranges for Measuring Working Resolution

Element	Wavelength, Å	Concentration Range, %		
		Spark	DC Arc	Solution Spark
Tin	1899.9	0.05–0.5	0.05–0.5	0.05–0.5
Carbon	1930.9	0.02–2
Arsenic	1937.0	0.02–2	0.05–0.5	0.05–0.5
Arsenic	1972.0	0.02–2	0.05–0.5	0.05–0.5
Antimony	2068.4	0.02–2	0.05–0.5	0.05–0.5
Nickel	2185.5	1–10	...	0.5–5
Copper	2247.0	1–10	0.05–0.5	0.5–5
Nickel	2253.9	1–10	...	0.5–5
Antimony	2311.5	0.02–0.2	0.05–0.5	0.05–0.5
Nickel	2316.0	0.01–0.1	...	0.05–0.5
Arsenic	2349.8	0.02–0.2	0.05–0.5	0.05–5
Iron	2382.0	0.02–0.2	0.1–1	0.05–0.5
Silicon	2516.1	0.01–0.1	0.05–0.5	0.05–0.5
Aluminum	2568.0	1–10	0.05–0.5	0.05–0.5
Manganese	2593.7	0.01–0.1	0.05–0.5	0.05–0.5
Antimony	2598.1	0.02–0.2	0.05–0.5	0.05–0.5
Iron	2599.4	0.01–0.1	0.05–0.5	0.05–0.5
Chromium	2677.2	0.05–0.5	0.05–0.5	0.05–0.5
Iron	2714.4	1–10
Chromium	2766.5	0.01–0.1	0.05–0.5	0.05–0.5
Magnesium	2798.1	0.01–0.1	0.05–0.5	0.05–0.5
Manganese	2798.3	0.01–0.1	0.01–0.5	0.05–0.5
Silicon	2881.6	0.01–0.1	0.05–0.5	0.05–0.5
Manganese	2933.1	0.01–0.1	0.05–0.5	0.05–0.5
Chromium	2989.2	1–10	...	0.5–5
Iron	3020.6	0.01–0.1	0.05–0.5	0.05–0.5
Aluminum	3082.2	0.01–0.1	0.05–0.5	0.05–0.5
Aluminum	3092.7	0.01–0.1	0.05–0.5	0.05–0.5
Copper	3247.5	0.01–0.1	0.05–0.5	0.05–0.5
Copper	3274.0	0.01–0.1	0.05–0.5	0.05–0.5
Zinc	3345.0	0.02–0.2	0.05–0.5	0.1–1
Nickel	3414.8	0.01–0.1	0.05–0.5	0.05–0.5
Iron	3719.9	0.1–1	0.05–0.5	0.05–0.5
Silicon	3905.5	1–10	0.05–0.5	0.05–0.5
Aluminum	3944.0	0.01–0.1	0.05–0.5	0.05–0.5
Aluminum	3961.5	0.01–0.1	0.05–0.5	0.05–0.5
Chromium	4254.3	0.01–0.1	0.05–0.5	0.05–0.5
Strontium	4607.3	0.05–0.5	0.05–0.5	0.05–0.5
Copper	5105.5	1–10	0.5–5	0.5–5
Magnesium	5167.3	0.1–1	0.02–2	0.01–1
Magnesium	5172.7	0.1–1	0.02–2	0.01–1
Magnesium	5183.6	0.1–1	0.02–2	0.01–1

X3. PHOTOGRAPHIC SPEED VERSUS PHOTOELECTRIC THROUGHPUT

X3.1 Photographic Speed—In a photographic spectrograph, the blackness in the developed image depends on the level of illumination at the focal curve. The light flux has to be concentrated in the image to be effective. If the slit is opened beyond the critical slit width, the line on the emulsion is broadened without a significant increase in density. If the slit height is increased, the image merely becomes longer.

X3.2 Polychromator Radiation Throughput—In a polychromator, the signal from the photomultiplier depends on the

total light flux that passes through the exit slit and falls on the cathode of a photomultiplier. If the entrance slit is opened wider than the critical slit width for an equivalent spectrograph, the photoelectric signal is increased proportionally, until the image begins to exceed the exit slit width. If the height of the entrance slit is increased, the signal increases proportionally if all of the light that passes through an appropriately high exit slit falls on the photocathode. The level of illumination at the focal curve, however, is only one of several significant factors.

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For a direct-reading spectrometer, the theoretical speed must be defined by the radiation throughput.

X3.3 Calculation of Radiation Throughput (L)—The radiation throughput is calculated as follows:

$$L = ITk_a \quad (X3.1)$$

where:

- I = the illumination of the grating by a specific radiation or narrow band of wavelengths,
- T = an overall factor affecting the transmission of radiation, and
- k_a = a factor to account for loss of radiation in an astigmatic system if the exit slit is not long enough to subtend the total focused radiation coming from the grating.

X3.3.1 Illumination (I)—The flux of radiation passing through the entrance slit is defined by the product of the area of the slit and the apparent area of the ruled portion of the grating as viewed by the slit. It is calculated as follows:

$$I = (whWH \cos \alpha) / f^2 \quad (X3.2)$$

where:

- w = the width of the entrance slit, mm (see Note X3.1),
- h = the height of the entrance slit, mm,
- W = the width of the ruled area of the grating, mm,
- H = the height of the ruled area of the grating, mm,
- α = the angle of incidence, the angle between the normal to the first surface of the dispersing element and the central ray from the entrance slit, and
- f = the focal distance from the center of the dispersing element to the entrance slit.

NOTE X3.1—If the exit slit is narrower than the entrance slit, it becomes the limiting horizontal aperture, and the narrower width should be used to calculate I . In that case, if the exit slit is tangential to the focal circle, the slit width should be reduced by multiplying by the cosine of the angle of emergence from the dispersing element.

X3.3.1.1 In a grating polychromator, with a Rowland circle mounting:

$$f = R \cos \alpha \quad (X3.3)$$

where:

- R = the radius of curvature of the grating, that is also the diameter of the Rowland circle.

Substituting f from Eq X3.3 into Eq X3.2, the illumination term becomes:

$$I = (whWH) / (R^2 \cos \alpha) \quad (X3.4)$$

X3.3.2 Transmission (T)—Transmission varies markedly with wavelength. It can be expressed as:

$$T = rtt_o i_b \quad (X3.5)$$

where:

- r = the overall reflectivity, due to the individual reflectivities of each reflecting surface,
- t = the overall transmission, due to the individual transmissions of each lens, prism, refractor plate or optical surface,
- t_o = the transmission through oxygen in an air path, and

i_b = the grating efficiency, that is, that proportion of the total light (of a particular wavelength) incident on the grating that is diffracted into the image being measured. (The remainder of the light is diffracted into other orders, into the central image, or is lost in scattering from the grooves.)

All four factors in Eq X3.5 are expressed as decimals, and are multiplied to show the total transmission, as a decimal.

NOTE X3.2—Taking into account cathode sensitivity and window transparency, variation in the response of photomultipliers with wavelength contributes to spectral response. Even though it is a function of an individual tube, not a property of the spectrometer, it must be associated with the channel. See X3.3.2.2.

X3.3.2.1 The reflection and transmission values (r and t) remain high throughout the visible and ultra-violet regions. Below 2100 Å, the reflectivity of aluminum oxide (Al_2O_3), which forms the reflecting surface of an aluminized mirror, begins to fall off rapidly unless the aluminization was performed with high-purity aluminum, under a high vacuum, with very rapid deposition, followed by overcoating with magnesium fluoride (MgF_2). The transmission of quartz lenses and windows also drops rapidly, unless highest-quality fused quartz is employed.

X3.3.2.2 Transmission (t) is also affected by optical materials that can be used in front of a photomultiplier to filter out unwanted wavelengths far from the analytical line, or to block radiation from overlapping orders. Typical transmission curves for several optical materials are shown in Fig. X3.1. Also included is a response curve for a special case of a solar-blind photomultiplier with a quartz window and a cesium telluride (CsTe) cathode which can be used to screen out long wavelengths. For practical applications, transmission depends on the combination of the cathode surface of the photomultiplier and the photomultiplier window material as well as on any optical material positioned in the radiation path. Three examples of the percent of peak sensitivity that can be expected at a specific wavelength for three different photomultipliers are shown in Fig. X3.2. Example A is for an R166 photomultiplier, a solar-blind photomultiplier. Example B is for a 1P28 photomultiplier which has a UV glass window and is commonly used for measuring signals in the near ultra-violet. When a COREX filter is used with a 1P28 photomultiplier, much of the visible radiation is not detected. Example C is for a 931A

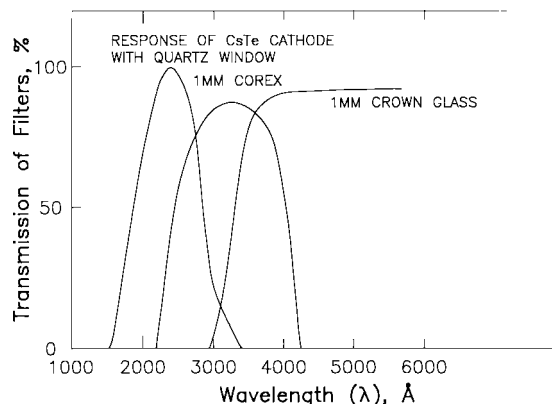
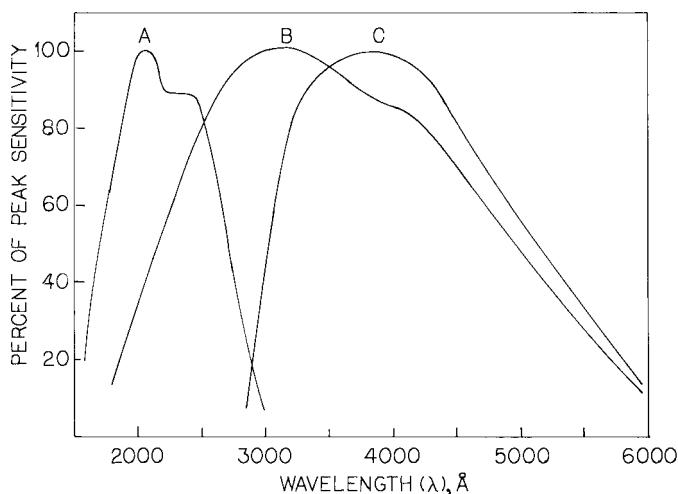


FIG. X3.1 Filter Transmission



Note—

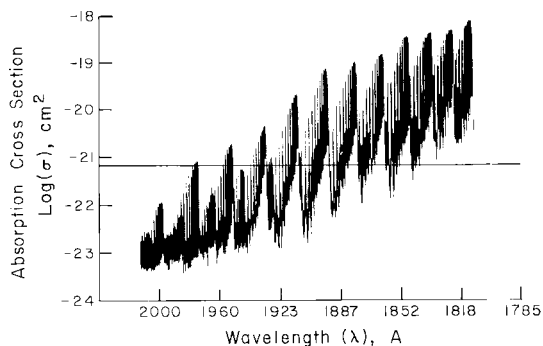
Plot	Photomultiplier
A	R166
B	1P28
C	931A

FIG. X3.2 Responses of Typical Photomultipliers

photomultiplier which has a borosilicate glass window and is used for measuring visible light. A 931A photomultiplier is effective in screening out ultra-violet radiation.

X3.3.2.3 Transmission through air (t_o) extends farther into the far ultraviolet than is commonly recognized, with useful windows down to 1890 Å. Absorption is due to the Schumann-Runge band system of oxygen, which is shown in Fig. X3.3. Note that there is very little absorption of the continuum from the hydrogen lamp until about 1965 Å, where strong absorption starts and persists to about 1945 Å. There is absorption also from 1915 Å to 1902 Å. Below 1890 Å the absorption becomes complete for practical purposes. Useful lines that can be measured in the windows of an air spectrometer with a total optical path length of three metres are listed in Table X3.1. For a vacuum spectrometer, $t_o = 1.0$.

X3.3.2.4 Grating Efficiency (i_b)—In recent direct-reading polychromators, replicas of master gratings, ruled with a diamond scribe, have been used extensively, rather than holographic gratings, because of their higher blaze efficiency.



NOTE 1—Absorption cross-section σ is in cm^2 . Horizontal line drawn for 50% transmittance through a 2 m path in air.

FIG. X3.3 Oxygen Absorption Spectrum (Adapted from Ref (11))

TABLE X3.1 Wavelength Windows in Air Polychromators, and Some of the Useful Analytical Lines

Window, Å in air	Element	Wavelength, Å in air
1890–1902	Tin	1899.26
1915–1923
1930–1945	Carbon	1930.30
	Arsenic	1936.96
Above 1953	Bismuth	1953.89
	Selenium	1960.26
	Arsenic	1971.97
	Germanium	1998.24

However, some control on blaze is now attainable with holographic gratings. Grating efficiency can be predicted for a replica from a well-ruled master grating, with less than 5% unruled surface, if wavelengths are normalized by dividing them by the blaze wavelength, λ_m . Fig. X3.4 shows such intensity distribution plots for the first, second and third orders for a typical grating. Note that the first order intensity falls off rapidly at shorter wavelengths: theoretically to zero at one-half the blaze wavelength, λ_m , where all the light should be concentrated in the second order. The intensity falls off slowly toward the long wavelength side of the peak, in the first order. In second and third orders, intensity falls theoretically to zero on both the short and long wavelength sides of the peak at the wavelengths that correspond to the peaks for the next higher or lower orders respectively.

X3.3.2.5 Since the other factors included in the T term also tend to decrease rapidly at the short wavelength, the blaze of the grating should be selected well below the center of the wavelength range of the spectrometer, somewhere between:

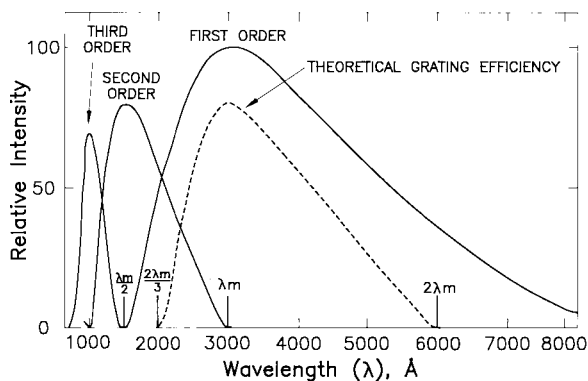
$$[\lambda_s + (\lambda_h - \lambda_s)/5] \quad \text{and} \quad [\lambda_s + (\lambda_h - \lambda_s)/3] \quad (\text{X3.6})$$

where:

λ_h = the high wavelength limit, and

λ_s = the short wavelength limit.

X3.3.2.6 Holographic gratings yield somewhat lower intensity levels, with several peaks and valleys. The relative efficiency will not vary as rapidly with wavelength as is typical for ruled gratings. The measured intensity distribution may be available from the manufacturer.



NOTE 1—The solid lines are relative efficiencies of each order, normalized to 100% for blaze wavelength (λ_m) in first order. The dashed line shows theoretical first order efficiency, normalized to incident light intensity.

FIG. X3.4 Grating Efficiency

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X3.3.3 *Astigmatism* (k_a)—The factor k_a accounts for astigmatism and becomes 1.0 in relatively stigmatic systems, such as the Wadsworth mount for concave gratings or the Ebert or Czerny-Turner mounts for plane gratings, if the exit slit is made high enough to accommodate any magnification of the image. Since a line image diverges after passing through an exit slit, it should be intercepted by the cathode of the photomultiplier before it has grown too tall or too wide, unless it is refocused on the photomultiplier.

X3.3.3.1 Fig. X3.5 shows a vertical diagram of rays in an astigmatic grating polychromator, with vertical heights greatly exaggerated. Points A_1 , C_1 , and B_1 define an entrance slit having a height of h . These points are shown focused at A_2 , C_2 , and B_2 beyond the exit slit. The exit slit is defined by the points going to S_1 in the section of the figure which shows the upper half of the grating of height H , marked as OG . The maximum illumination of the grating would be such that all points in the entrance slit would fan out to fill the grating. In fact, the usual optical arrangement is to form an image of the electrode system at the top and bottom of the grating, or just beyond those points. For simplicity, rays from Points A_1 and B_1 are shown filling only the upper half of the grating. If the exit slit is tall enough, each focus point will receive all the radiation it possibly can from the grating. By determining the intersection Points S_0 , S_1 , and S_2 , the limits imposed on throughput by the exit slit can be determined.

X3.3.3.2 In a similar way in which Eq X3.3 established the distance from the entrance slit to the grating, the distance from the grating to an exit slit is $R \cos \beta$, where β is the angle of diffraction.

X3.3.3.3 The distance from the grating to the focus of a horizontal aperture, as discussed by Beutler (10), is:

$$R/(\cos \beta - \sin \alpha \tan \alpha) \tag{X3.7}$$

This focus is shown in Fig. X3.5 by the points A_2 , C_2 , and B_2 .

X3.3.3.4 Using the height notations of Eq X3.2, the distances of the three points, S_0 , S_1 , and S_2 , from the center line along the exit slit may be calculated as follows:

$$S_0 = \frac{1}{2}h (\cos \beta) / (\cos \alpha) \tag{X3.8}$$

$$S_1 = \frac{1}{2}H (1 - F \cos \beta) + S_0 \tag{X3.9}$$

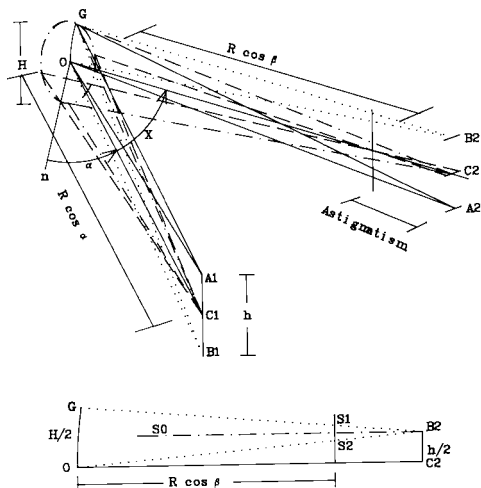


FIG. X3.5 Astigmatism of Rowland Circle Spectrometers

$$S_2 = \frac{1}{2}H (1 - F \cos \beta) - S_0 \tag{X3.10}$$

where:

$$F = \cos \beta - \sin \alpha \tan \alpha \tag{X3.11}$$

Using S_x equal to half of the height of the exit slit, and comparing S_x to the other S values, k_a factors are determined as follows:

X3.3.3.5 If S_x is $\geq S_1$, there will be no loss in throughput and k_a will equal 1.0.

X3.3.3.6 If S_x is $< S_1$ but $\geq S_0$, the reduction factor becomes:

$$k_a = 1 - (S_1 - S_x)^2 / [4S_0(S_1 - S_0)] \tag{X3.12}$$

X3.3.3.7 If S_x is $< S_0$, but $> S_2$, the reduction factor becomes:

$$k_a = [1/(2S_0)] \{ S_x + (2S_x S_0 - S_x^2 - S_2^2) / [2(S_0 + S_2)] \} \tag{X3.13}$$

X3.3.3.8 If S_x is $\leq |S_2|$, the reduction factor becomes:

$$k_a = S_x / S_0, \text{ if } S_2 \text{ is negative,} \tag{X3.14}$$

or:

$$k_a = S_x / (S_0 + S_2), \text{ if } S_2 \text{ is positive} \tag{X3.15}$$

X3.4 *Typical Radiation Throughputs*—Table X3.2 shows three combinations of typical parameters and the resultant radiation throughputs for an air polychromator.

TABLE X3.2 Typical Radiation Throughputs

Element	Example 1 Carbon	Example 2 Aluminum	Example 3 Iron
Channel			
Wavelength, Å	1930.9	2568.0	2714.7
Diffraction order, n	2	1	1
Grating			
Radius of curvature (R), mm	3000	1500	750
Grooves/mm	960	1200	2400
Groove spacing (b), Å	10416.7	8333.3	4166.7
Blaze wavelength (λ_m), Å	3000	3000	3000
Width (W), mm	60	60	40
Height (H), mm	30	40	30
Path			
Incident angle (α)	27.02°	20.66°	42.07°
Wavelength at grating normal, Å	4732.3	2940.2	2791.8
Emergent angle (β)	4.79°	2.56°	1.06°
Entrance Slit			
Width (w), mm ^A	0.020	0.025	0.025
Height (h), mm	16	2	2
Exit Slit			
Width, mm	0.075	0.075	0.050
Height, mm	20	10	15
Calculations			
Illumination (I), mm ²	7.18×10^{-5}	1.42×10^{-5}	8.98×10^{-6}
Transmission			
Reflectivity (r)	0.85	0.91	0.93
Transmission (t)	0.87	0.90	0.93
Transmission through (t_0)	0.43	0.99	0.99
Grating efficiency (i_0) ^B	0.61	0.90	0.96
Overall T	0.19	0.73	0.82
Astigmatism			
F	0.7648	0.8660	0.3950
S_0	8.95	1.07	1.35
S_1	12.52	3.77	10.42
S_2	-5.38	1.63	7.73
S_x	10	5	7.5
k_a	0.95	1.0	0.83
Overall throughput (L), mm ²	1.32×10^{-5}	1.04×10^{-5}	6.09×10^{-6}

^A 0.020 mm = 20 μ m.

^B Relative intensities read from Fig. X3.4.

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X3.4.1 The grating radius of curvature, and all slit and grating widths and heights are stated in millimetres which makes the throughput term, L , square millimetres. Although L may simply be considered to be a relative value of throughput,

if it is multiplied by a specific radiant power per millimetre squared, actual radiation throughput will be determined.

X3.4.2 For a grating instrument, there will be a considerable variation in L with wavelength, due to the T term.

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