



Designation: E 1507 – 98

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 $\text{\AA}$: 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 $\text{\AA}$ = 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 $\text{\AA}$	3110 $\text{\AA}$	4358 $\text{\AA}$
Half-Width:	0.20 $\text{\AA}$	0.35 $\text{\AA}$	0.45 $\text{\AA}$

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

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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 4×10^{-6} m/°C and the focal curve diameter is 1 m, a 1° temperature change will lengthen or shorten the focal curve by 4×10^{-6} m or 4 µm; then a temperature drift of 13 µm/(4 µm/°C) or ≈3°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

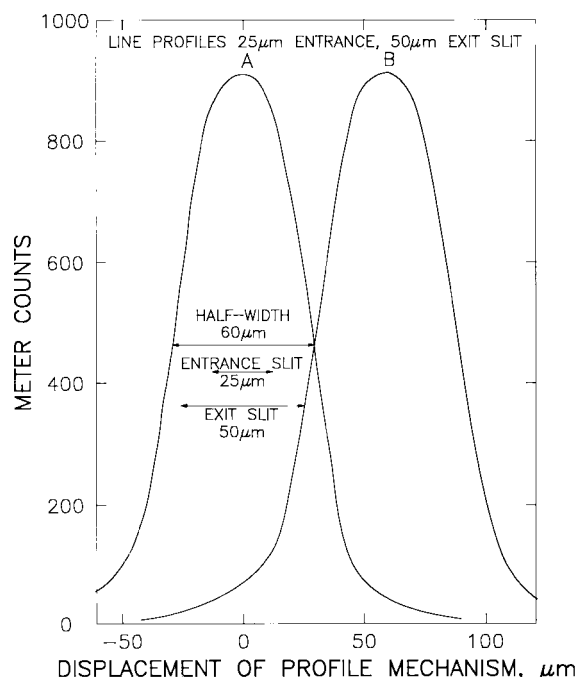


FIG. 1 Typical Line Profiles and Overlaps, Illustrating Working Resolution

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.