



Standard Practice for Describing Atomic Absorption Spectrometric Equipment¹

This standard is issued under the fixed designation E 863; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers those features that are important for evaluating atomic absorption spectroscopy equipment. It also discusses performance characteristics and identifies parameters that should be recorded in analytical procedures.

1.2 *This standard does not purport to address all of the safety concerns, 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.* Specific warning statements are given in the Note in 5.3 and specific precautionary statements are given in Section 7.

2. Referenced Documents

2.1 ASTM Standards:

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²

E 416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory³

E 520 Practice for Describing Detectors in Emission and Absorption Spectroscopy³

E 1770 Practice for Optimization of Electrothermal Atomic Absorption Spectrometric Equipment³

E 1812 Practice for Optimization of Flame Atomic Absorption Spectrometric Equipment³

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E 135.

4. Significance and Use

4.1 This practice provides criteria for instrument selection and should be useful for setting up an atomic absorption facility.

5. Description of Equipment

5.1 *Optical System*—Both single-beam and double-beam optical systems are in use. A single-beam system employs one

optical path to measure both incident and transmitted radiation. The two measurements are separated in time. A double-beam system separates the incident radiation into two portions. One of these portions (often designated I) is measured after traversing the analytical cell; the other portion (often designated I_0) represents the radiation incident on the analytical cell. Signals from the two portions are used to compensate for baseline variability. In single-beam systems, instability of either the incident intensity or the detector-amplifier sensitivity-gain contributes to the variability of the signal. Double-beam systems can correct completely for either type of instability. Neither single-beam or double-beam systems can correct for fluctuations occurring in the flame.

5.2 *Radiation Sources*—The most widely used source of absorbing lines is the hollow cathode lamp. It emits narrow spectral lines, has low background, and is applicable to virtually all elements amenable to atomic absorption analysis. The high-frequency electrodeless discharge lamp (EDL) is also an excellent source of sharp line spectra. It provides more intensity than the hollow cathode lamp, but is not as universally applicable. EDLs require a special power supply.

5.2.1 The hollow cathode lamp shall emit stable, low-drift radiation of usable intensity, free of interfering spectral lines due to filler gas or cathode impurities.

5.2.2 *Stability*—Intensity drift shall not exceed 3 % per 15 min after a 30-min warm up. Many lamps available now are better than 1 % per 15 min after warm up.

5.2.3 *Lamp Life*—The hollow cathode lamp or EDL shall maintain the above characteristics over the manufacturer's warranted life. The expected life of hollow cathode lamps is approximately 5 Ah.

5.3 *Flames*—Flames are classified as diffusion or premixed. The characteristics of the diffusion flame are determined by the rate at which the fuel diffuses into the ambient oxygen or the oxidant supplied through a separate orifice.⁴ In the premixed flame, the characteristics are determined by the kinetics of the chemical combustion producing the flame. In general, diffusion flames are more turbulent than pre-mixed flames and the flame reactions are not spatially resolved. Premixed acetylene and air or acetylene and nitrous oxide flames are the most commonly used atomic absorption flames. Acetylene is the most common fuel. Hydrogen, natural gas, propane, and similar fuels are

¹ This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.20 on Fundamental Practices and Measurement Traceability.

Current edition approved May 10, 1998. Published July 1998. Originally published as E 863 – 82. Last Previous edition E 863 — 82 (1996).

² *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ "Guidelines for the Purity and Handling of Gases Used in Atomic Absorption Spectroscopy", *AI2.1a*, 1978, Scientific Glass Makers Association, 1140 Connecticut Ave., N.W., Washington, DC 20036.

sometimes used to produce cooler flames. Air and nitrous oxide are the normal oxidants. Oxygen has sometimes been used, but due to higher flame propagation velocities, it is not used anymore.

NOTE 1—**Warning:** Never use copper tubing for acetylene because of the possible formation of explosive copper acetylide.

5.4 *Burners*—Historically two types of burners were used in atomic absorption spectroscopy, the direct injection or total consumption burner and the pre-mix nebulizer burner. The total consumption burner ensures freedom from flashbacks and was once popular for flame spectroscopy. However, it has serious disadvantages such as high noise levels, lack of distinct flame zones, high background emission, and difficulties in obtaining flame shape suitable for absorption measurement,⁵ and, therefore is no longer being used. The most widely used burner now is the pre-mix nebulizer burner. In this burner a small fraction of the aspirated solution reaches the flame. Only the very finest droplets are used, which makes this an energy-efficient system. The burner produces a high-temperature flame with relatively low emission background or noise. The flame can be shaped to provide for a long light path through it. A serious disadvantage is that the pre-mix chamber contains an explosive gas mixture during operation. An explosive flashback is possible when the burning velocity exceeds the velocity of the burning gases passing through the burner orifice. Equipment shall be designed to minimize the probability of a flashback, protect the instrument operator and anyone nearby from injury if a flashback does occur, and minimize damage to the burner, chamber, and instrument.

5.4.1 *Nebulizers*—The nebulizer is used to aspirate the sample and convert it to a fine mist. The most common nebulizers employ oxidant gas as the source of energy for nebulization. The mist consists of a wide distribution of particle sizes but only the smallest (less than 1 μm in diameter) reach the flame and contribute to the atomic absorption signal. Some pre-mix chambers employ an impingement bead to enhance the generation of smaller particles, and mix the gases and vapors before passing through the burner slots. Other pre-mix chambers enhance particle size separation by baffles that allow only the finest particles to reach the flame. The result is a smaller but more stable absorption signal. Ultrasonic nebulizers have been used experimentally for fog generation. They provide an efficient generation of a uniform mist. In practice, however, such problems as feeding the sample uniformly, conducting the vapor to the burner, and sample memory have prevented this nebulization system from becoming popular. The nebulizer efficiency, or the fraction of the aspirated solution that actually reaches the flame, shall be specified for pre-mix nebulizer burner systems. The efficiency is a function of the rates of solution uptake and of the discharge through the drain tube.

5.4.2 *Gas Flow Controls*—Stable flame operation depends on reproducible and stable flow of fuel and oxidant gases. A minimal system shall have a two-stage regulating device at the fuel source and at the oxidant source. There shall be a pressure

meter for the nebulizing gas, a flow meter for each gas, and a flow control system for each gas line at the burner.

5.4.2.1 The manufacturer shall specify suitable gas flows. Flow meters should be calibrated in litres per minute or some comparable unit. If the burner system is to be used with a nitrous oxide acetylene flame, special precautions to avoid flashback when the flame is ignited and extinguished, shall be provided. The gas control system shall allow the oxidant to be changed from air to nitrous oxide and back again without interruption of flow to the burner. The flame shall be ignited using air and acetylene, then switched to nitrous oxide. The reverse procedure shall be followed when the flame is extinguished. Some instruments have systems which automatically provide the startup-shutdown sequence, monitor gas flows, and shut down automatically if the gas flows are outside a prescribed range.

5.5 *Electrothermal Atomizers*—Most flame atomic absorption spectrometers manufactured currently can be easily adapted for electrothermal analysis, while some atomic absorption spectrometers are dedicated to electrothermal analysis.

5.5.1 The most commonly used electrothermal atomizer is the graphite tube furnace. This atomizer consists of a graphite tube positioned in a water-cooled unit designed to be placed in the optical path of the spectrophotometer so that the light from the hollow cathode lamp passes through the center of the tube. The tubes vary in size depending upon a particular instrument manufacturer's furnace design. These tubes are available with or without pyrolytic graphic coating. However, because of increased tube life, tubes coated with pyrolytic graphite are commonly used. The water-cooled unit or atomizer head which holds the graphite tube is constructed in such a way that an inert gas, usually argon or nitrogen, is passed over, around, or through the graphite tube to protect it from atmospheric oxidation. The heating of all of these atomizers is controlled by power supplies which make it possible to heat the graphite tube to 3000°C in less than 1 s. Temperatures and drying, pyrolysis, and atomization times are controlled by these power supplies.

5.6 *Automatic Background Correction*—Automatic background correction is recommended for all atomic absorption units.

5.6.1 Automatic background correction is a necessity for all spectrophotometers used with electrothermal devices. When electrothermal atomizers, especially graphite furnaces, are heated to high temperatures, background from absorption is produced within the graphite tube. Also, small amounts of particulate matter in the furnace contribute to the background signal. Therefore, it is essential to correct or compensate for this background.

5.6.1.1 Magnetic (Zeeman type) background correction gives wider range of correction than hydrogen or deuterium background correctors and is a preferred type for spectrometers using electrothermal atomization.

5.7 *Spectrometer*—The wavelength where absorption measurements are made is isolated from the total spectrum of the primary radiation source by means of a monochromator, or by nondispersive devices.

5.7.1 *Monochromator Types*—Monochromators are primarily classified as to whether the wavelength-discriminating

⁵ Kirkbright, G. F., and Sargent, M., *Atomic Absorption and Fluorescence Spectroscopy*, Academic Press, New York, NY, 1974, p. 201.

function is performed by a grating, a prism, optical filters of various types ranging from single glass filters to multilayer interference filters⁶ (transmission or reflection types), or a combination of grating and prism such as may be used in some double monochromators.

5.7.1.1 Optical Design of Monochromators—Grating and prism monochromators are further classified by the optical configuration of the incident and dispersed beams. Such configurations include the Czerny-Turner, Ebert, Eagle, Littrow, and Littrow-Echelle mounts, used singly or in combination. The various types differ in the application or configuration of the collimating and dispersing elements, or both. The different configurations take into account optical speed, dispersion, stability, optical defects, and astigmatism. There is no overwhelmingly superior configuration.

5.7.1.2 Description of the Grating shall include the following information: (a) Type: plane or concave; (b) Size: width and height of ruled area expressed in millimetres; (c) Groove spacing: grooves per millimetre; and (d) Blaze wavelength: expressed in nanometres.

5.7.1.3 Description of the Prism shall include the following information: (a) Type: Cornu, Littrow or other type; (b) Material: specify type of quartz or other material; and (c) Dimensions: base and height expressed in millimetres, and included angle between entry and exit faces expressed in degrees.

5.7.2 Focal Length—The nominal focal length of the collimating mirror or, in the Eagle or Rowland mount, the focal length of the concave grating shall be specified.

5.7.3 Aperture Ratio—The effective ratio (commonly called *f/number*) is the focal length divided by the diameter of the circle having an area equivalent to the cross section of the beam incident on the grating. The effective area of the cross section may be limited by the diameter of the collimating mirror or by the grating face. Because the effective area of the grating face decreases as the grating is rotated to higher wavelength settings, the maximum and minimum values of *f/number* shall be given for the corresponding wavelength limits.

5.7.4 Reciprocal Linear Dispersion—This parameter is the wavelength interval per unit distance at the focal plane and is expressed in nanometres per millimetre as defined in Terminology E 135. If dispersion changes significantly with wavelength, the wavelength at which the value is given shall be specified.

5.7.5 Wavelength Range of the Spectrometer—The effective wavelength range of the spectrometer is a function of the monochromator, the detector, and the medium through which the optical path passes. The minimum and maximum wavelengths at which the monochromator optics can be set shall be specified. If this wavelength range can be varied by interchangeable gratings or prisms, it shall be so stated, and the minimum and maximum values given. The usable wavelength range of the overall system, including the detector, will usually be limited at the lower wavelength by the spectral absorption of

the ambient atmosphere and optics, and at the higher wavelength by spectral sensitivity of the detector. Descriptions of systems shall differentiate between the wavelength range of the monochromator and the usable wavelength range of the overall system.

5.7.6 Wavelength Scanning—If the monochromator provides for scanning the wavelength range at a predetermined rate, it shall be so specified. The following parameters describe the scanning functions: single speed, multiple speeds, or continuously variable scanning speeds. The minimum and maximum speeds expressed in nanometres per second or nanometres per minute should be stated, as should the specific values of scanning speeds.

5.7.7 Wavelength Accuracy—The maximum distance in nanometres between an indicated wavelength and the mean wavelength passed by the monochromator at that setting shall be specified along with the wavelength range over which the specification applies. An example might be ± 0.1 nm between 200 and 700 nm. In the case of monochromators having nonlinear dispersion, the accuracy shall be specified at the upper and lower wavelength limits.

5.7.8 Wavelength Reproducibility—The precision, expressed in nanometres, with which a given wavelength setting may be reset, is a measure of the wavelength reproducibility of the monochromator. The specification shall include the wavelength range over which the stated precision applies. In the case of monochromators having nonlinear dispersion, the wavelength precision shall be specified at the upper and lower limits of the wavelength range.

5.7.9 Slit System—The entrance and exit slit assemblies of grating and prism monochromators are of various mechanical designs. Description of the slit assemblies shall include the following functional parameters: (a) the slit jaws may be straight or curved; (b) slit widths may be fixed, step variable, or continuously variable; (c) Entrance and exit slit width settings may be gaged to a single control or may be independently adjustable; and (d) slit height may vary considerably among instruments of different optical designs. Some instruments include provision for varying slit heights.

5.8 Radiation Detectors—Most detectors used in atomic absorption spectroscopy are photomultiplier tubes, which are described in Practice E 520.

5.9 Signal Recovery Electronics—The radiation from the primary source is modulated by either pulsing the primary source electronically or by mechanically chopping its emission at a fixed frequency. The detection amplifier, being tuned to this frequency, is then immune to emission from the flame.

5.10 Output Display—The electrical output of the signal recovery electronics can be displayed by meters, recorders, digital computers, and printers.

5.11 Service Requirements—High-voltage supplies must be interlocked for operator safety. There shall be easy access to the electronics, light source, monochromator, burner system, lens and mirror mounts, and other sections requiring periodic maintenance.

6. Performance Characteristics

6.1 Stability—In general, fluctuations of the analytical signal depend on flame stability, hollow cathode or other source

⁶ Satisfactory filters can be obtained from Fisk Shurman Co., 70 Portman Rd., New Rochelle, NY 10801, or from the National Institute of Standards and Technology, Washington, DC 20234.

stability, and stability of the signal detection and processing system. The contributions of flame noise to the overall stability of the instrument can be isolated by shutting down the flame and testing the instrumental repeatability by inserting a filter of uniform optical density or transmittance in the absorption optical path.

6.2 *Linearity*—Variation in linearity is expressed in percent of the full scale reading. A successful method for determining instrumental linearity is to use special filters. These filters are stable and have a uniform optical density that is a function of thickness. A series of these filters can be used for external calibration of the instrument.

6.3 *Detection Limits* (Refer to Terminology E 135)—The detection limit is the minimum concentration, C_{\min} , that can be detected with a given degree of confidence. The detection limit is affected principally by the slope, m , of the analytical curve and by the relative standard deviation, B , of the absorbance of the blank:

$$C_{\min} = Bk/m \quad (1)$$

where: k is a factor chosen by the user. In atomic absorption spectroscopy, k commonly has a value of 2. At this value of k the signal is approximately twice the variability of the background, hence it is the concentration where 50 % precision is expected. Other k values may be used to make the quoted detection limit more or less conservative if this is desirable for a particular application.

6.3.1 The value of B actually observed depends not only on the true variability of the absorbance of the blank solution, but also on the characteristics of the detection system, that is, on the degree of damping applied to the signal or on the period of integration.

6.3.2 A parameter, B_{ni} , is the bandwidth of the spectral noise

passed by the detection system. Any measured value of C_{\min} involves B , and thus contains an implied parameter which is a function of B_{ni} . To make a valid comparison of repeatability of results obtained from various instruments and procedures, it is necessary to correct the B values obtained under different conditions to values which would have been obtained under some common, arbitrarily chosen, spectral noise bandwidth, such as 0.25 Hz. In practice this concept has been largely ignored and some arbitrary, unspecified, and variable smoothing constant (spectral noise bandwidth) has been employed in reporting analyses or detection limits.

6.4 The determination of performance characteristics under actual operating conditions is described in Practice E 1812 for flame atomic absorption spectroscopy and in Practice E 1770 for electrothermal atomic absorption spectroscopy.

7. Safety Hazards

7.1 There are hazards associated with operating atomic absorption spectroscopy equipment. The manufacturer should provide instructions on igniting and extinguishing the burner safely. The Scientific Apparatus Makers Association has published a practice which discusses safe handling of gases.⁴ Also refer to Practice E 416 for safe handling of laboratory gases.

7.2 People wearing electronic pacemakers, or other medical equipment sensitive to strong magnetic fields should not operate electrothermal atomic absorption spectrometers equipped with magnetic (Zeeman or other type) background correctors.

8. Keywords

8.1 atomic absorption; chemical analysis; flame atomic absorption; flameless atomic absorption; nebulizer

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

This standard is copyrighted by ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (<http://www.astm.org>).