



Designation: E 1832 – 96<sup>ε2</sup>

# Standard Practice for Describing and Specifying a Direct-Current-Plasma Optical Emission Spectrometer<sup>1</sup>

This standard is issued under the fixed designation E 1832; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE— Figs. 1 and 2 were added editorially in August 1997.

<sup>ε2</sup> NOTE—Section 5, Theory, was deleted editorially in August 1998.

## 1. Scope

1.1 This practice describes the components of a direct-current-plasma (DCP) optical emission spectrometer. This practice does not attempt to specify component tolerances or performance criteria. This practice does, however, attempt to identify critical factors affecting bias, precision, and sensitivity. A prospective user should consult with the vendor before placing an order to design a testing protocol for demonstrating that the instrument meets all anticipated needs.

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 hazards statements are give in in Section 9.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>2</sup>
- E 158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis<sup>2</sup>
- E 172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis<sup>2</sup>
- E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis<sup>3</sup>
- E 416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory<sup>3</sup>
- E 520 Practice for Describing Detectors in Emission and Absorption Spectroscopy<sup>3</sup>
- E 528 Practices for Grounding Basic Optical Emission Spectrochemical Equipment<sup>3</sup>
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data<sup>3</sup>

<sup>1</sup> 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.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.06.

E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis<sup>3</sup>

## 3. Terminology

3.1 For terminology relating to emission spectrometry, refer to Terminology E 135.

## 4. Significance and Use

4.1 This practice describes the essential components of the DCP spectrometer. This description allows the user or potential user to gain a basic understanding of this system. It also provides a means of comparing and evaluating this system with similar systems, as well as understanding the capabilities and limitations of each instrument.

## 5. Overview

5.1 A DCP spectrometer is an instrument for determining concentration of elements in solution. It typically is comprised of several assemblies including a direct current (dc) electrical source, a sample introduction system, components to form and contain the plasma, an entrance slit, elements to disperse radiation emitted from the plasma, one or more exit slits, one or more photomultipliers for converting the emitted radiation into electrical current, one or more electrical capacitors for storing this current as electrical charge, electrical circuitry for measuring the voltage on each storage device, and a dedicated computer with printer. The liquid sample is introduced into a spray chamber at a right-angle to a stream of argon gas. The sample is broken up into a fine aerosol by this argon stream and carried into the plasma produced by a dc-arc discharge between a tungsten electrode and two or more graphite electrodes. When the sample passes through the plasma, it is vaporized and atomized, and many elements are ionized. Free atoms and ions are excited from their ground states. When electrons of excited atoms and ions fall to a lower-energy state, photons of specific wavelengths unique to each emitting species are emitted. This radiation, focussed by a lens onto the entrance slit of the spectrometer and directed to an echelle grating and quartz prism, is dispersed into higher orders of diffraction. Control on the diffraction order is accomplished by the

low-dispersion, echelle grating. Radiation of specific wavelength or wavelengths passes through exit slits and impinges on a photomultiplier or photomultipliers. The current outputs charge high-quality capacitors, and the voltages thus generated are measured and directed to the computer. Using calibration solutions, a calibration curve is generated for each element of interest. The computer compares the signals arising from the many elements in the sample to the appropriate calibration curve and then calculates the concentration of each element. Over seventy elements may be determined. Detection limits in a simple aqueous solution are less than 1 mg/L for most of these elements. Mineral acids or organic liquids also may be used as solvents, and detection limits are usually within an order of magnitude of those obtained with water. Detection limits may be improved by using preconcentration procedures. Solid samples are dissolved before analysis.

## 6. Description of Equipment

6.1 *Echelle Spectrometer*—Components of the equipment shown in Fig. 1 and described in this section are typical of a commercially available spectrometer. Although a specific spectrometer is described herein, other spectrometers having equal or better performance may be satisfactory. The spectrometer is a Czerny-Turner mount and consists of a condensing lens in front of an entrance slit, a collimating mirror, combined dispersing elements (grating and prism), focus mirror, exit slits, photomultipliers, control panel, and wavelength selector mechanism.

6.1.1 *Condensing Lens*, placed between the DCP source and the entrance slit. It should have a focal length capable of focusing an image of the source on the entrance slit and with sufficient diameter to fill the aperture of the spectrometer with radiant energy.

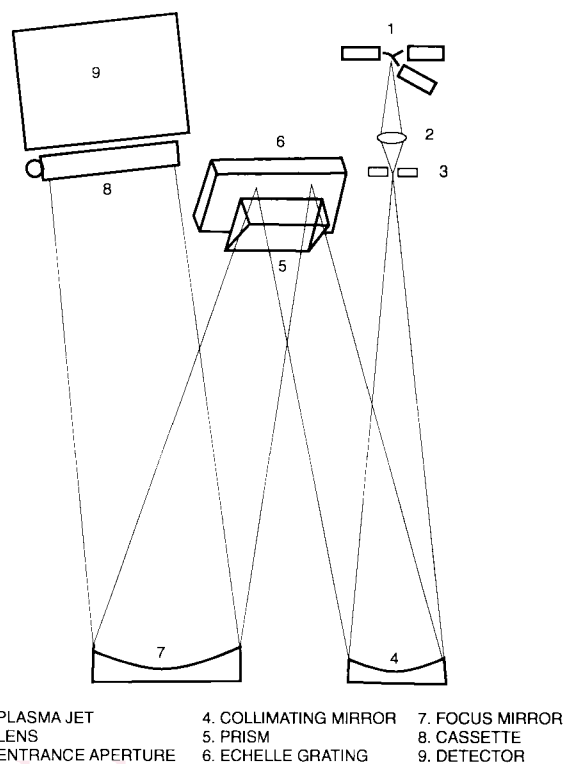
6.1.2 *Entrance Slit*, although available with fixed width and height, a slit variable in both width and height provides greater flexibility. Typical values are 0.025 to 0.500 mm in width and 0.100 to 0.500 mm in height. Adjustable slit widths and heights are useful in obtaining optimal spectral band width and radiant energy entering the spectrometer for the requirements of the analytical method.

6.1.3 *Collimating Mirror*, renders all rays parallel after entering the spectrometer. These parallel rays illuminate the combined dispersing elements. The focal length and  $f$  number should be specified. Typical focal length and  $f$  number are 750 mm and  $f/13$ .

6.1.4 *Combined Dispersing Components*, positioned so that the radiant energy from the collimating mirror passes through the prism, is refracted and reflected by a plane grating and back through the prism. Specify the ruling on the grating (for example, 79 grooves/mm).

6.1.5 *Focus Mirror*, placed to focus the radiant energy from the combined dispersing elements on a flat two-dimensional focal plane where the exit slits are located.

6.1.6 *Fixed Exit Slits*, mounted in a removable fixture called an optical cassette for multielement capability. A two-mirror periscope behind each exit slit directs the radiant energy to a corresponding photomultiplier. For single element capability, energy for one wavelength usually passes through its exit slit directly to the photomultiplier without the need for a periscope.



1. PLASMA JET 4. COLLIMATING MIRROR 7. FOCUS MIRROR  
2. LENS 5. PRISM 8. CASSETTE  
3. ENTRANCE APERTURE 6. ECHELLE GRATING 9. DETECTOR

FIG. 1 Echelle Grating Spectrometer

Select the specific exit slit width before installation. Provide a single channel cassette with one exit slit variable from 0.025 to 0.200 mm in width and from 0.100 to 0.500 mm in length.

6.1.7 *Photomultipliers*, up to twenty end-on tubes, are mounted behind the focal plane in a fixed pattern. Consider sensitivity at specific wavelength and dark current in the selection of appropriate photomultipliers. Provide variable voltage to each photomultiplier to change its response as required by the specific application. A typical range is from 550 to 1000 V in 50-V steps. A survey of the properties of photomultipliers is given in Practice E 520.

6.1.8 *Control Panels*, are provided to perform several functions and serve as input to microprocessors to control the operation of the spectrometer. Provide a numeric keyboard to enter high and low concentrations of reference materials for calibration and standardization of each channel and to display entered values for verification. Provide a switch on this panel to set the mode either to integrate during analysis or to measure instantaneous intensity. The latter mode is required to obtain the peak position for a specific channel by seeking maximum intensity by wavelength adjustment and verifying by wavelength scanning. Conduct interference and background investigations with this mode. Scanning is required if automatic background correction is to be performed. Provide other necessary switches for the following purposes: to calibrate or standardize the spectrometer, start analysis, interrupt the function being performed, set integration time and the number of replicate analyses, and direct the output to a printer, display, or storage medium. Impose a fixed time delay of 10 s before integration can begin to ensure that the solution being analyzed is aspirated into the DCP discharge. Provide digital and analog

voltmeters for displaying the instantaneous or integrated intensities during peaking, scanning, or analysis. If a computer is an integral part of the spectrometer, most of the control functions are accomplished with software.

6.1.9 *Wavelength Adjustment*, provided to adjust the wavelength range and diffraction order for peaking the spectrometer because a two-dimensional spectrum is produced. Both coarse and final control of these adjustments are required. To maintain optical alignment, the spectrometer should be thermally isolated from the DCP source or heated. A heated base on which the spectrometer rests has been satisfactory for this purpose.

6.1.10 *Dispersion and Spectral Band Pass*—Typical dispersion and spectral band pass with a 0.025-mm slit width vary from 0.061 nm/mm and 0.0015 nm at 200 nm to 0.244 nm/mm and 0.0060 nm at 800 nm, respectively.

6.2 *DCP Source*, composed of several distinct parts, namely the electrode, direct current power supply, gas flow, sample introduction, exhaust, water cooling, and safety systems. Refer to Practice E 172 for a list of the electrical source parameters that should be specified in a DCP method.

6.2.1 *Electrode System*, Fig. 2, consists of two graphite anodes fixed in a vertical plane and at a typical angle of 60° to one another, and a tungsten cathode fixed in a horizontal plane at an angle of 45° to the optic axis. In their operating position, the tips of the two anodes are separated by a distance of 1<sup>3</sup>/<sub>16</sub> in., (3.0 cm), and the tungsten cathode is 1<sup>5</sup>/<sub>8</sub> in., (4.1 cm), above the anode tips. Each electrode is recessed in a ceramic sleeve fitted into water-cooled anode and cathode blocks. Because the electrodes are of special design to fit into and be held by these blocks, the user must follow the manufacturer's recommendations for these electrodes. The electrode system shall provide mechanism to adjust the electrodes vertically and horizontally across the optic axis to properly project the image of the excitation region onto the entrance slit and obtain a maximum signal-to-noise ratio. Sometimes a visible excitation region is not produced when some specimens are aspirated into this source. Iron solutions, as well as solutions of several other elements, however, are satisfactory for this purpose.

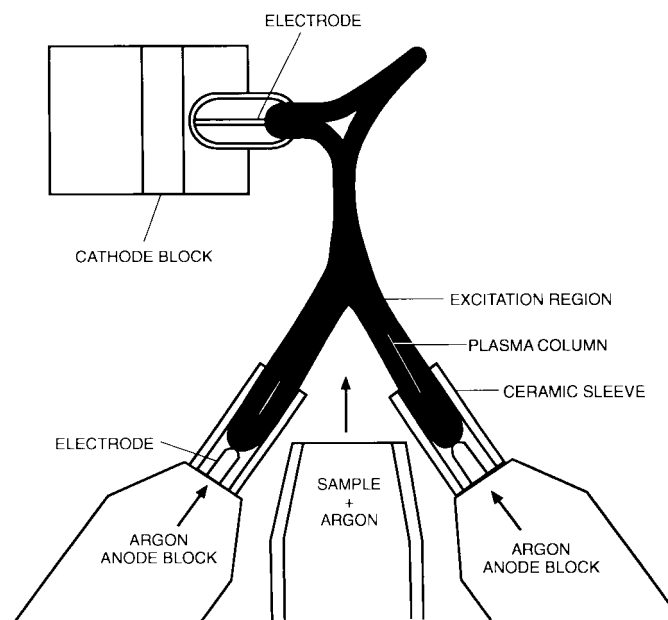
6.2.2 *Direct Current Power Supply*, capable of maintaining a constant current of 7 A dc in the discharge with a voltage of 40 to 50 V dc between the anodes and cathodes. The resulting discharge has the shape of an inverted letter Y with a luminous zone in the crotch of the Y.

6.2.3 *Gas Flow System*, (Refer to Practice E 406) shall be capable of the following:

6.2.3.1 Providing argon gas delivered at a pressure of 80 psi (5.62 kg/cm<sup>2</sup>) to the discharge sustaining gas and sample nebulization.

6.2.3.2 Providing a pneumatic system to extend the anode and cathode out of their sleeves and move the cathode block downwards so that the cathode electrode makes contact with one of the anodes and initiates the plasma.

6.2.3.3 Providing gas pressures of 15 to 30 psi (1.05 to 2.01 kg/cm<sup>2</sup>) for nebulization and 50 psi (3.52 kg/cm<sup>2</sup>) for other functions. Needle valves are used to adjust these pressures, as well as provide for division of gas flows among three electrode blocks. A balance among the gas flows through these blocks and past the electrodes is necessary to produce and maintain a



**FIG. 2 DCP Source**

symmetrical discharge and a triangular- or arrowhead-shaped excitation region where the specimen's spectrum is generated.

6.2.3.4 Providing isolation of the gas flow system from the ambient atmosphere. For good analytical performance, ensure that all tubing connections are tight and O-rings are in good condition.

6.2.4 *Sample Introduction System* is required to control the flow of sample solution. This typically involves placing a flexible tube in the sample container, which aspirates the sample solution into a nebulizer, usually a cross-flow design. A peristaltic pump is used to pump the sample solution to the nebulizer. As a specimen drop is formed at the nebulizer orifice (0.02 in. or 0.05 cm), it is removed by the argon stream and broken into several smaller drops. Most of these impinge on the walls of the spray chamber running down to collect in a waste reservoir. Typically, about 20 % of the nebulized specimen is carried by the argon stream as an aerosol into the plasma. The liquid in the waste reservoir is removed continuously by the same peristaltic pump used to feed the nebulizer, and passes through a second tube to be safely disposed. If this is not done, the volume of liquid waste in the reservoir and the spray chamber is increased, increasing the gas pressure and volume of the specimen injected into the plasma, thus extinguishing the plasma. Because this pump crushes these tubes with use, daily damage inspection is required for optimum performance.

6.2.5 *Exhaust System*—Provide a small hood connected to an exhaust fan above the plasma cabinet to remove the waste gases. The fan should have a capacity to move 100 ft<sup>3</sup>/min (47.2 L/s). The flow rate should be adjustable to efficiently remove these gases, and the hood, duct, and fan should be compatible for use with chemicals contained in typical sample solutions.

6.2.6 *Water Cooling System*—Circulate water through the electrode blocks using either the laboratory's water supply or water pumped from a reservoir located near the spectrometer.