



Standard Practice for Describing and Specifying a Wavelength-Dispersive X-Ray Spectrometer¹

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1. Scope

1.1 This practice covers the components of a wavelength-dispersive X-ray spectrometer that are basic to its operation and to the quality of its performance. It is not the intent of this practice to specify component tolerances or performance criteria, as these are unique for each instrument. The document does, however, attempt to identify which of these are critical and thus which should be specified.

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 safety hazard statements are given in 5.3.1.2 and 5.3.2.4, and in Section 7.

1.3 There are several books and publications from the National Institute of Standards and Technology² and the U.S. Government Printing Office^{3,4} which deal with the subject of X-ray safety. Refer also to Practice E416.⁵

2. Referenced Documents

2.1 ASTM Standards:⁵

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E416 Practice for Planning and Safe Operation of a Spec-

trochemical Laboratory (Withdrawn 2005)⁶

E876 Practice for Use of Statistics in the Evaluation of Spectrometric Data (Withdrawn 2003)⁶

3. Terminology

3.1 For terminology relating to X-ray spectrometry, refer to Terminology E135.

4. Significance and Use

4.1 This practice describes the essential components of a wavelength-dispersive X-ray spectrometer. This description is presented so that the user or potential user may gain a cursory understanding of the structure of an X-ray spectrometer system. It also provides a means for comparing and evaluating different systems as well as understanding the capabilities and limitations of each instrument.

5. Description of Equipment

5.1 *Types of Spectrometers*—X-ray spectrometers can be classified as sequential, simultaneous, or a combination of these two (hybrid).

5.1.1 *Sequential Spectrometers*—The sequential spectrometer disperses and detects secondary X rays by means of an adjustable monochromator called a goniometer. In flat-crystal instruments, secondary X rays are emitted from the specimen and nonparallel X rays are eliminated by means of a Soler slit (collimator). The parallel beam of X rays strikes a flat analyzing crystal which disperses the X rays according to their wavelengths. The dispersed X rays are then measured by suitable detectors. Adjusting the goniometer varies the angle between the specimen, crystal, and detector, permitting the measurement of different wavelengths and therefore different elements. Sequential instruments containing curved-crystal optics are less common. This design substitutes curved for flat crystals and entrance and exit slits for collimators.

5.1.2 *Simultaneous Spectrometers*—Simultaneous spectrometers use separate monochromators to measure each element. These instruments are for the most part of fixed configuration, although some simultaneous instruments have a

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² NBS Handbook, *X-Ray Protection*, HB76, and NBS Handbook 111, ANSI N43.2-1971, available from National Institute of Standards and Technology, Gaithersburg, MD 20899.

³ *Radiation Safety Recommendations for X-Ray Diffraction and Spectrographic Equipment*, No. MORP 68-14, 1968, available from U.S. Department of Health, Education, and Welfare, Rockville, MD 20850.

⁴ U.S. Government Handbook 93, *Safety Standards for Non-Medical X-Ray and Sealed Gamma-Ray Sources*, Part 1, General, Superintendent of Documents, available from U.S. Government Printing Office, Washington, DC 22025.

⁵ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁶ The last approved version of this historical standard is referenced on www.astm.org.

scanning channel with limited function. A typical monochromator consists of an entrance slit, a curved (focusing) analyzing crystal, an exit slit, and a suitable detector. Secondary X rays pass through the entrance slit and strike the analyzing crystal, which diffracts the wavelength of interest and focuses it through the exit slit where it is measured by the detector. Some simultaneous instruments use flat crystals, but this is less common.

5.1.3 Hybrid Spectrometers—Hybrid spectrometers combine features found in sequential and simultaneous instruments. They have both fixed channels and one or more fully functional goniometers.

5.2 Spectrometer Environment:

5.2.1 Temperature Stabilization—A means for stabilizing the temperature of the spectrometer shall be provided. The degree of temperature control shall be specified by the manufacturer. Temperature stability directly affects instrument stability.

5.2.2 Optical Path:

5.2.2.1 A vacuum path is generally preferred, especially for the analysis of light elements (long wavelengths). Instruments capable of vacuum operation shall have a vacuum gage to indicate vacuum level. An airlock mechanism shall also be provided to pump down the specimen chamber before opening it to the spectrometer. Pump down time shall be specified by the manufacturer.

5.2.2.2 A helium path is recommended when light element analysis is required and the specimen (such as a liquid) would be disturbed by a vacuum. Instruments equipped for helium operation shall have an airlock for flushing the specimen chamber with helium before introducing the specimen into the spectrometer. Helium flushing time shall be specified by the manufacturer. The manufacturer shall also provide a means for accurately controlling the pressure of the helium within the spectrometer.

5.2.2.3 An air path is an option when the instrument is not equipped for vacuum or helium operation. Light element analysis and some lower detection limits are sacrificed when operating with an air optical path.

5.3 Excitation—A specimen is excited by X rays generated by an X-ray tube which is powered by a high voltage generator and is usually cooled by circulating water. The intensity of the various wavelengths of X rays striking the specimen is varied by changing the power settings to the tube or by inserting filters into the beam path.

5.3.1 X-Ray Tube—The X-ray tube may be one of two types; end-window or side-window. Depending upon the instrument, either the anode or the cathode is grounded. Cathode grounding permits the window of the X-ray tube to be thinner and thus affords more efficient transmittance of the longer excitation wavelengths.

5.3.1.1 X-ray tubes are produced with a variety of targets. The choice of the target material depends upon the wavelengths that require excitation. X rays from certain materials excite the longer wavelengths more efficiently. Other materials are better for exciting the shorter wavelengths. Generally the choice of target material is a compromise.

5.3.1.2 X-ray tubes are rated according to maximum power, maximum current, and typical power settings. These should be specified by the manufacturer. (**Warning**—It is important that the user be protected from exposure to harmful X rays. Standard warning labels shall warn the user of the possibility of exposure to X rays. Safety interlock circuits (7.3) shall shut down power to the X-ray tube whenever protective shielding is removed.)

5.3.2 High Voltage Generator—The high voltage generator supplies power to the X-ray tube. Its stability is critical to the precision of the instrument.

5.3.2.1 The dc voltage output of the high voltage generator is typically adjustable within the range of 10 to 100 kV. Voltage stability, drift with temperature, and voltage ripple should be specified. Voltage repeatability should be specified for a programmable generator, which is frequently used in sequential systems.

5.3.2.2 The current to the X-ray tube is typically adjustable within the range of 5 to 100 mA. Current stability and thermal drift should be specified. Current repeatability should be specified for programmable generators.

5.3.2.3 Voltage and current recovery times should be specified for programmable generators. The software routines which control the generator must delay measurement until the generator recovers from voltage or current changes.

5.3.2.4 Input power requirements should be specified by the manufacturer so the proper power can be supplied when the instrument is installed. Maximum generator power output should be stated. (**Warning**—Safety is a primary concern when dealing with high voltage. Safety interlock circuits (7.3) and warning labels shall protect the user from coming in contact with high voltage. The interlock system shall shut down the generator when access to high voltage is attempted. Circuits shall be provided to protect the X-ray tube from power and current overloads.)

5.3.3 Water Cooling Requirements—The X-ray tube and some high voltage generators require cooling by either filtered tap water or a closed-loop heat exchanger system.

5.3.3.1 The manufacturer shall specify water flow and quality requirements.

5.3.3.2 To protect components from overheating, an interlock circuit that monitors either water coolant flow or temperature or both shall shut down power to the X-ray tube whenever these requirements are not met.

5.3.3.3 Water purity is especially critical in cathode-grounded systems since this requires the coolant to be nonconducting. A closed-loop heat exchanger is necessary to supply high purity cooling water. A conductivity gage shall monitor water coolant purity in these systems and shall shut down power to the X-ray tube when coolant purity is below requirements.

5.3.4 Primary Beam Filter—A primary beam filter is commonly used in sequential spectrometers to filter out the characteristic emissions from the X-ray tube's target when these emissions might interfere with the measurement of an analyte element. Primary beam filters are also useful for lowering the background in the longer wavelength portion of

the spectrum. This serves to increase the peak to background ratio and offers greater detection of those longer wavelength X rays.

5.3.4.1 Primary beam filters are made of several different metals (depending upon the X-ray tube's target) and come in various thicknesses. The manufacturer should specify the type, thickness, and location of the primary beam filter.

5.4 *Sample Positioning*—The process of positioning a specimen in a spectrometer for analysis involves several components; the specimen holder, the specimen changer, and the specimen rotation mechanism (spinner). These components contribute collectively to the reproducibility of positioning the specimen in the optical path and thus, to instrument precision. The design of these components should therefore be regarded critically.

5.4.1 Reproducibility of the distance between the face of the specimen and the window of the X-ray tube is especially critical and should be specified by the manufacturer.

5.4.2 The spinner rotates the specimen while it is being exposed to the X-ray beam and thus helps to minimize the influence of surface defects and specimen inhomogeneity on analytical results.

5.4.3 Imperfections in the surface of the specimen have the greatest effect on analytical results in spectrometers with a shallow angle of irradiation or take-off angle. The manufacturer shall specify these angles.

5.4.4 Other important specifications include maximum specimen size (thickness and diameter) and the specimen rotation speed (if the instrument is equipped with a spinner).

5.5 *Dispersion*—The analyzing crystal is the dispersive device in a wavelength-dispersive X-ray spectrometer. Various crystals having a variety of interplanar spacings are used to disperse the specimen's characteristic wavelengths.

5.5.1 Sequential spectrometers may contain several different crystals mounted on a crystal changer mechanism. Thus, the analyst is able to select a specific crystal for the wavelength being measured.

5.5.2 Each monochromator in a simultaneous instrument has a separate specified crystal. The selection is made in accordance with the expected analytical requirements. The crystal is generally bent and ground to a curve or a logarithmic spiral in order to focus the analytical line through the monochromator's exit slit.

5.5.3 The manufacturer should specify each of the crystals installed in a particular spectrometer according to composition, location (which monochromator or crystal changer position), lattice orientation (when applicable), interplanar spacing, and shape (flat or curved).

5.5.4 The manufacturer shall provide an adjustment for rotating the crystal to peak the spectrometer or monochromator.

5.6 *Beam Moderating Devices:*

5.6.1 *Soller Slits*—Soller slits are provided for systems containing flat crystals. They are composed of a series of closely-spaced, thin, parallel plates or tubes. When a Soller slit is placed in the path of a beam of X rays, only those X rays that

are parallel to the plates or tubes will pass through the slit. Therefore, the X rays that exit the slit are parallel.

5.6.1.1 Soller slits may be present in several locations. A primary Soller slit is always present in the optical path between the specimen and the analyzing crystal. Auxiliary slits may be installed at the detector windows between the detector and the analyzing crystal.

5.6.1.2 It is common for a sequential spectrometer to have both coarse and fine primary Soller slits, installed and mounted in a changer mechanism. Better resolution is achieved with a fine slit, but at the expense of a loss of intensity.

5.6.1.3 The manufacturer should specify the location and plate spacing of all Soller slits installed in a particular instrument. A means shall be provided for adjusting (peaking) each slit.

5.6.2 *Entrance and Exit Slits*—Both entrance and exit slits are required in a curved-crystal spectrometer. The curved crystal establishes a focusing circle that is similar to the Rowland circle defined by a grating in an optical emission spectrograph. In an X-ray spectrometer, however, proper focusing requires that both slits not only be on the focusing circle but also have identical chordal distances from the slits to the crystal. A detector is aimed at the crystal through the exit slit.

5.6.2.1 The manufacturer should specify the size of the entrance and exit slit for each monochromator and shall provide adjustments to peak each monochromator. Depending upon the manufacturer, peaking may involve movement of the crystal, the exit slit, or both.

5.6.3 *Apertures*—In flat-crystal spectrometers, an aperture is placed at the point in the optical path where the secondary X rays exit the specimen. The aperture limits the area of the specimen seen by the detector. In some instruments, the size of this aperture is fixed, but in most it can be varied, either by manual replacement or a mechanical changer. The manufacturer should specify the sizes of any apertures installed in the spectrometer.

5.6.4 *Attenuators*—When an element is present at a high concentration, it is sometimes desirable to decrease the intensity of its emissions to avoid exceeding the detector's linear counting range. An attenuator, positioned between the specimen and the analyzing crystal, absorbs some of the secondary X rays and thus lowers the intensity. The manufacturer should specify the location (which monochromator) and the attenuation ratio of all attenuators.

5.6.5 *Masks*—Masks must be properly positioned in the optical path to prohibit secondary X rays from bypassing the crystal and reaching the detector directly. This is particularly important at large 2θ angles.

5.7 *Detection:*

5.7.1 *Goniometer*—The goniometer in a sequential or hybrid spectrometer is an integral part of its detection system. Adjusting the goniometer varies the angle between the specimen, crystal, and detector, thus changing the wavelength seen by the detector. The spectrometer therefore can be set to measure the intensity at a specific wavelength.

5.7.1.1 It is critical that the angle indicated by the goniometer readout be an accurate and reproducible indication of the actual 2θ angle. The manufacturer should specify the reading

accuracy, reproducibility, and scanning range of the goniometer. Scanning speed should also be indicated for motor-driven goniometers.

5.7.2 Detectors—A variety of detectors is commonly used in wavelength-dispersive X-ray spectrometry. These include Geiger-Müller counters, gas-filled and gas-flow proportional counters, and scintillation counters. The detectors are powered by a high voltage power supply, capable of supplying different voltages to each detector.

5.7.2.1 A single detector is required for each monochromator in a simultaneous instrument. Sequential instruments, however, generally have several detectors in order to detect both long and short wavelengths. It is common for a gas-flow proportional and scintillation counter to be mounted in tandem on the detector arm of the sequential spectrometer. Another arrangement is to mount several detectors on a detector changer mechanism.

5.7.2.2 Gas is generally supplied to gas-flow proportional counters from a cylinder fitted with a pressure regulator. The spectrometer should have a mechanism for controlling the flow and stabilizing the pressure of the detector gas as this is critical to counting stability. Instruments having more than one gas-flow proportional counter require either multiple delivery systems or a manifold to feed all of the detectors.

5.7.2.3 A detector's wavelength sensitivity and counting linearity are limited. The manufacturer should specify the wavelength range that can be detected by each detector and the maximum intensity it can accept before its response becomes nonlinear. Detectors should be specified according to their type, location within the spectrometer, and, for gas-filled detectors, detector gas and window thickness.

5.8 Signal Processing and Display:

5.8.1 Amplification—The detector's signal is usually magnified by a preamplifier and a series of amplifiers before being processed further. Most instruments locate the preamplifier at the detector, which makes the instrument less susceptible to electronic noise.

5.8.1.1 Each detector has its own preamplifier. It is common in sequential instruments, however, to direct the output current of all of the preamplifiers into a single amplifier. Therefore, if two detectors feed current to a single amplifier simultaneously and pulse height discrimination is desired at a later stage, the height of the pulses from the two preamplifiers must be adjusted approximately equally.

5.8.1.2 Simultaneous instruments have separate preamplifiers for each monochromator. In some instruments, these preamplifiers feed current to separate amplifiers while in others, the current signal from each preamplifier is collected on separate capacitors and then read sequentially through a single amplifier.

5.8.1.3 The manufacturer should describe the spectrometer's amplification scheme. Typical amplifier gain settings should also be specified.

5.8.2 Pulse Height Discrimination—As voltage pulses pass from the amplifier through the pulse height discriminator, pulses with a voltage below a prescribed lower limit or above a prescribed upper limit are filtered out and only those pulses between the two limits are allowed to pass for further process-

ing. Pulse height discrimination is effective for removing electronic noise and interferences which are approximately at the same 2θ angle but of a different spectrum order. Sequential instruments generally have a single pulse height discriminator while simultaneous instruments have a separate one for each channel.

5.8.3 Other Circuitry—Other circuits may include those for pulse shaping and automatic dead-time correction. Automatic dead-time correction extends the linear range of the detectors.

5.8.4 Display—Display may be analog or digital, or both.

5.8.4.1 Analog display may be in the form of a chart recorder (for qualitative purposes), an analog ratemeter, or a tracing on a computer display terminal.

5.8.4.2 Digital display may be provided by a digital ratemeter or a computer. Typically the computer is interfaced and dedicated to the spectrometer. The computer controls the operations of data gathering, calculates the analytical curves, and converts the intensity data to concentrations using algorithms stored in computer memory.

5.8.4.3 Software design is a major criterion to consider when evaluating an instrument. The data gathering routine should be closely studied as this directly affects the quality of the data. Software should be fully documented.

5.8.4.4 Algorithms for converting intensity to concentration may be either fundamental or empirical and should be specified and documented by the manufacturer.

5.8.4.5 The maximum number of standards and corrections that the software can accept should be specified. The manufacturer should specify the maximum number of characters for sample identification and formatting for output.

5.8.4.6 Manufacturers should provide other software routines that are helpful to the analyst. These may include plotting, scanning, instrument diagnostics, and so forth. These ancillary routines should be specified and documented.

6. Performance Criteria

6.1 Detector Linearity—The manufacturer shall specify the maximum intensity which each detector can accept while maintaining a linear response.

6.1.1 To test a detector's linearity, first select a pure element specimen having an atomic number two to five less than the atomic number of the X-ray tube's target. Measure that element at a constant voltage while increasing the current stepwise. Prepare a plot of intensity versus current. The plot should "flatten" at the higher intensities. Extrapolate a straight line from the lower, linear portion of the plot upward. The point at which the plot appears to depart from the straight line indicates the intensity at which the detection system's response becomes nonlinear.

6.2 Precision—The precision of an X-ray spectrometer is a function of several variables. These include power stability, electronic noise, detector gas stability, counting statistics, and the reproducibility of the optical alignment. The mechanical nature of the optical alignment task for sequential spectrometers tends to make them less precise than their simultaneous counterparts.

6.2.1 To test the precision of an X-ray spectrometer, select a specimen containing an element with a concentration of at least

1000 times its detection limit and make 10 consecutive 20 s measurements. Measurement conditions should be set to ensure at least 1 000 000 total counts per measurement. The sample cup should be removed and reinserted and all mechanical settings (that is, crystal, collimator, filter, attenuator, aperture, and goniometer setting) changed between measurements. The relative standard deviation of the instrument tested in this way should be in the range of 0.1 to 0.3 %.

6.3 Detection Limit—The detection limit in X-ray spectrometry is a function of the sensitivity (the slope of the analytical curve) and the precision of the background. To determine the detection limit, refer to Paragraph 6.2 on Linearity in Practice E876.

7. Safety Features

7.1 “X Rays On” Lamp—The manufacturer shall provide a lamp that will indicate that the X-ray tube is energized. It shall be of a “fail-safe” design in which the power to the X-ray tube will be shut down if the lamp fails to operate.

7.2 Optical Alignment of the Spectrometer—A means shall be provided for safely aligning the spectrometer. The manufacturer shall provide detailed instructions to the user in order that this procedure may be carried out without harmful exposure to X rays.

7.3 Interlock System—A safety interlock system (see 5.3.1.2 and 5.3.2.4) shall be provided to protect the user from harmful exposure to X rays or high voltage. It shall shut down power to the X-ray tube or to high voltage components if unauthorized access is attempted.

7.4 Collant Interlock—See 5.3.3.2.

7.5 Emergency Shutdown System—An emergency shutdown system shall be provided to protect the spectrometer in the event of a power failure. A power outage shall deactivate the power switch to the X rays so that the switch must be reset manually. A power failure shall also deactivate a solenoid valve to seal the spectrometer chamber so that pump fluid is not pulled into the chamber. The pressure within the spectrometer chamber will then be allowed to increase gradually to atmospheric pressure, thus protecting the proportional detector windows from rupture. Return of power shall reactivate the solenoid valve and reinitiate pump down of the spectrometer.

8. Keywords

8.1 spectroscopy; X-ray emission; X-ray spectrometer

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