



Designation: D 2332 – 84 (Reapproved 1999)

## Standard Practice for Analysis of Water-Formed Deposits by Wavelength- Dispersive X-Ray Fluorescence<sup>1</sup>

This standard is issued under the fixed designation D 2332; 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.

### 1. Scope

1.1 This practice covers X-ray spectrochemical analysis of water-formed deposits.

1.2 The practice is applicable to the determination of elements of atomic number 11 or higher that are present in significant quantity in the sample (usually above 0.1 %).

1.3 *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.*

### 2. Referenced Documents

2.1 *ASTM Standards:*

D 887 Practices for Sampling Water-Formed Deposits<sup>2</sup>

D 1129 Terminology Relating to Water<sup>3</sup>

E 11 Specification for Wire-Cloth Sieves for Testing Purposes<sup>4</sup>

### 3. Terminology

3.1 *Definitions*— For definitions of terms used in this practice, refer to Terminology D 1129.

### 4. Summary of Practice

4.1 The sample or its fusion with a suitable flux is powdered and the powder is compacted (mounted). The mount is then irradiated by an X-ray beam of short wavelength (high energy). The characteristic X rays of the atom that are emitted or fluoresced upon absorption of the primary or incident X rays are dispersed, and intensities at selected wavelengths are measured by sensitive detectors. Detector output is related to concentration by calibration curves or charts.

4.2 The K spectral lines are used for elements of atomic numbers 11 to 50. Whether the K or L lines are used for the elements numbered 51 or higher depends on the available instrumentation.

### 5. Significance and Use

5.1 Certain elements present in water-formed deposits are identified. Concentration levels of the elements are estimated.

5.2 Deposit analysis assists in providing proper water conditioning.

5.3 Deposits formed from or by water in all its phases may be further classified as scale, sludge, corrosion products, or biological deposits. The overall composition of a deposit or some part of a deposit may be determined by chemical or spectrographic analysis; the constituents actually present as chemical substances may be identified by microscope or X-ray diffraction studies. Organisms may be identified by microscopical or biological methods.

### 6. Apparatus

6.1 *Sample Preparation Equipment:*

6.1.1 *Fusion Crucibles*, prepared from 25-mm (1-in.) commercial-grade graphite rods. The dimensions shall be 29 mm (1 $\frac{1}{8}$  in.) high, an inside diameter of 19 mm ( $\frac{3}{4}$  in.), and a cavity 22 mm ( $\frac{7}{8}$  in.) deep.

6.1.2 *Pulverizers*, including an agate or mullite mortar and pestle, minimum capacity 25 ml.

6.1.3 *Sieves*—No. 100 (150- $\mu$ m) and No. 270 (53- $\mu$ m) as specified in Specification E 11.

6.1.4 *Compactors*—A press, equipped with a gage enabling reproducible pressure, is recommended.

6.2 *Excitation Source (X-ray Tube):*

6.2.1 *Stable Electrical Power Supply* ( $\pm 1$  %).

6.2.2 Source of high-intensity, short-wave-length X rays.

6.3 *Sample Housing (Turret).*

6.4 *Spectrometer*—Best resolution of the spectrometer and best sensitivity are not simultaneously attainable; a compromise is effected to give adequate values for each.

6.4.1 *Collimating System.*

6.4.2 *Spectrogoniometer.*

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water and Flow Measurement of Water.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

6.4.3 *Analyzing Crystal and Holder*—The choice of the analyzing crystal is made on the basis of what elements must be determined; for example, a gypsum or an ammonium dihydrogen phosphate crystal can be used for determining magnesium but lithium fluoride is much superior for copper and iron (high-intensity diffracted secondary rays and consequently greater sensitivity and potential precision). A salt, sodium chloride (NaCl), crystal is frequently employed for general use, being applicable over a broad range and producing intense lines and medium broadening.

6.4.4 *Counter-Tube Support*.

6.5 *Evacuating or Flushing System*.

6.6 *Measuring System*:

6.6.1 *Detector* (of which the principal types are the Geiger counter, scintillation counter, and flow-proportional counter).

6.6.2 *Amplifiers (Including Preamplifier), Rate Meter, Recorder, Scaler, and Printout*.

6.6.3 *Zeroing, Gain, and Sequence Controls*.

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193 Type II.

7.3 *Detector Gas*, usual composition 90 % argon, 10 % methane (other compositions are used); usually used with flow-proportional counter for lines of longer wavelength (0.2 nm or greater).

7.4 *Gallium Oxide*, spectrographic grade (frequently used as a convenient internal standard).

7.5 *Helium Gas*, commercial grade, for the spectrometer flushing system, when vacuum or air paths are not used.

7.6 *Sodium and Lithium Borates*—( $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{Li}_2\text{B}_4\text{O}_7$ ), commonly used as fluxes for the sample.

## 8. Sampling

8.1 Collect the sample in accordance with Practices D 887.

## 9. Preparation of Sample

9.1 Reduce the entire sample of deposits to about 100 g (drying, degreasing, and crushing if necessary) and grind this subsample to a powder that will pass a No. 100 (150- $\mu\text{m}$ ) sieve.

9.2 Mix the powdered sample thoroughly and remove about 10 g for X-ray fluorescence testing (Note 1). Fuse a weighed

amount with a weighed amount of a suitable flux (2 to 10 g of flux/g of sample) to present a reproducible surface composition to the X-ray beam.

NOTE 1—At least semiquantitative results can be obtained more quickly by compacting (mounting) the test portion (9.3 and 9.4) and proceeding in accordance with Sections 10, 11, and 12. The decrease in sample preparation will actually result in improved accuracy in some instances.

9.3 Grind not more than 10 g of the material prepared for X-ray analysis (sample or fusion) to pass a No. 270 (53- $\mu\text{m}$  sieve).

9.4 Make duplicate wafers (or suitable mounts for the particular equipment that will be used) by compacting the powdered sample (precision and accuracy are improved by briquetting). An internal standard is frequently added by fusion to the material to be compacted. Some samples may require a binder (generally organic and added in minimum concentration) for reproducible packing and a smooth surface.

## 10. Preparation of Apparatus

10.1 Follow the manufacturer's instructions for the initial assembly, conditioning, and preparation of the fluorescent X-ray apparatus.

10.2 Follow the manufacturer's instructions with respect to control settings.

## 11. Excitation and Exposure

11.1 Position the mounted sample in the special chamber provided for this purpose; avoid touching or otherwise contaminating the sample surface. Produce and record the spectrum at the setting or settings recommended for the instrument. Prepare and analyze duplicate mounts for all samples (make duplicate readings on each mount).

11.2 *Radiation Measurements*—Make radiation measurements for each component of concern using Table 1 as a guide to the frequencies of interest.

NOTE 2—See also Bureau of Mines Information Circular No. 7725, which lists the 2-theta values for characteristic spectral lines when using the analyzing crystals NaCl, lithium fluoride (LiF), and quartz.

## 12. Calibration and Standardization

12.1 Semiquantitative evaluations of the concentration of each component may be obtained directly by reference to

**TABLE 1 Emission Spectra and Recommended Crystals**

Element	Recommended Crystal <sup>A</sup>	Wave-length <sup>B</sup>
Aluminum	gypsum	8.320
Calcium	lithium fluoride	3.353
Copper	lithium fluoride	1.539
Iron	lithium fluoride	1.934
Lead	lithium fluoride	1.172 <sup>B</sup>
Magnesium	gypsum	9.869
Phosphorus	pentaerythritol tetraacetate	6.142
Potassium	lithium fluoride	3.735
Silicon	pentaerythritol tetraacetate	7.111
Sodium	potassium acid phthalate	11.885
Sulfur	pentaerythritol tetraacetate	5.362
Zinc	lithium fluoride	1.434

<sup>A</sup> Updated to June, 1964; a production instrument, equipped with mounted crystals, might conveniently use lithium fluoride, pentaerythritol tetraacetate, and potassium acid phthalate.

<sup>B</sup> Emission wavelengths in kX units (1 kX unit = 1.002 Å); the wavelength for lead is the L alpha-1 line and the others are averages of the K alpha-1 and -2 lines.

<sup>5</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.



standardization curves prepared from data obtained by exposing samples containing known quantities of these components.

12.2 More accurate evaluations can be made by preparing special standards containing the same components as the sample in the ratios indicated by the semiquantitative determinations. These special standards can frequently be used to calculate correction factors for the calibration curves to minimize interference effects of the other components of the sample.

12.3 Internal standards may be used to provide direct comparison.

### **13. Analytical Values**

13.1 Average the results obtained for each component from at least two exposures of each mounted sample. Use these averaged values to read estimated concentrations from prepared calibration curves, charts, or tables.

### **14. Statistical Values**

14.1 *Precision of Instrument*—The precision of the instrument shall be determined from replicate measurements (10 to 20) on a single prepared sample without moving the sample.

This precision shall be reported as the standard deviation of the instrument and is obtained as the usual square root of the summated deviations squared divided by 1 less than the number of replicate measurements.

14.2 *Precision of Technique*—Calculate the standard deviation of the method from duplicate measurements on 10 to 20 samples over at least 3 days, removing and resetting the sample before each new series of measurements. The standard deviation of this technique is the square root of the summated deviations squared divided by 4 times the number of analyses.

14.3 Coefficient of variation of the practice is obtained by multiplying the standard deviation by 100 and dividing by the average concentration in percent.

### **15. Precision and Bias**

15.1 A precision and bias statement is not applicable. Refer to Sections 12 and 14 for estimation of element concentration and evaluation of instrument-specific precision.

### **16. Keywords**

16.1 deposits; elemental analysis; scale; X-ray fluorescence

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