



# Standard Practices for Identification of Crystalline Compounds in Water-Formed Deposits By X-Ray Diffraction<sup>1</sup>

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## 1. Scope

1.1 These practices provide for X-ray diffraction analysis of powdered crystalline compounds in water-formed deposits. Two are given as follows:

Practice A—Camera	Sections 12 to 21
Practice B—Diffractometer	22 to 30

1.2 Both practices yield qualitative identification of crystalline components of water-formed deposits for which X-ray diffraction data are available or can be obtained. Greater difficulty is encountered in identification when the number of crystalline components increases.

1.3 Amorphous phases cannot be identified without special treatment. Oils, greases, and most organic decomposition products are not identifiable.

1.4 The sensitivity for a given component varies with a combination of such factors as density, degree of crystallization, particle size, coincidence of strong lines of components and the kind and arrangement of the atoms of the components. Minimum percentages for identification may therefore range from 1 to 40 %.

1.5 The values stated in SI units are to be regarded as standard. The values listed in parenthesis are for information only.

1.6 *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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8 and [Note 20](#).

<sup>1</sup> These practices are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

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## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D887 Practices for Sampling Water-Formed Deposits
- D933 Practice for Reporting Results of Examination and Analysis of Water-Formed Deposits
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D2331 Practices for Preparation and Preliminary Testing of Water-Formed Deposits
- E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

## 3. Terminology

3.1 For definitions of terms used in these practices, refer to Terminology [D1129](#).

## 4. Summary of Practices

4.1 Powdered samples are irradiated with a monochromatic X-ray beam of short wavelength (from about 0.05 to 0.25 nm). The X rays interact with the atoms in the crystal and are scattered in a unique diffraction pattern which produces a fingerprint of the crystal's atomic or molecular structure. The analytical instrumentation used in X-ray diffraction includes the powder camera and the diffractometer **(1-5)**.<sup>3</sup>

## 5. Significance and Use

5.1 The identification of the crystalline structures in water-formed deposits assists in the determination of the deposit sources and mode of deposition. This information may lead to measures for the elimination or reduction of the water-formed deposits.

## 6. Purity of Reagents

6.1 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

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The boldface numbers in parentheses refer to the references listed at the end of these practices.

Reagents of the American Chemical Society, where such specifications are available.<sup>4</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.

6.2 *Purity of Water*—Reference to water that is used for reagent preparation, rinsing or dilution shall be understood to mean water that conforms to the quantitative specifications of Type I or II reagent water of Specification **D1193**.

## 7. Sampling

7.1 Collect the sample in accordance with Practices **D887**.

7.2 A suitable amount of sample should be obtained so that it is representative of the deposit under investigation.

7.3 Deposits shall be removed and protected in such a way that they remain as nearly as possible in their original states.

## 8. Safety Precautions

8.1 The potential danger of high-voltage and X-ray radiation makes it mandatory for anyone operating X-ray apparatus to be thoroughly familiar with basic safety precautions.

8.2 Place colorful signs displaying the international radiation symbol near X-ray equipment.

8.3 When X-ray equipment is producing radiation, illuminate a conspicuous light. There should be no X rays if the bulb burns out. Equipment without this feature can be modified.

8.4 Use a portable counter periodically to test for leakage of X rays from equipment. Lead or lead glass shielding is sometimes needed. X rays of shorter wavelength require more caution.

8.5 Film badges, dosimeters, or other monitoring devices shall be worn by personnel who regularly work with X-ray equipment.

## 9. Preliminary Testing of Analytical Sample

9.1 It may be advantageous and even necessary to perform other analytical investigative methods to aid in the rapid identification of crystalline components in water-formed deposits. For other testing methods refer to Practices **D2331**.

## 10. Preparation of Sample

10.1 *Apparatus*—The apparatus used for preparing the sample is as follows:

10.1.1 *Mullite or Agate Mortar*.

10.1.2 *Sieves*—A series of sieves from No. 100 mesh (150- $\mu\text{m}$ ) to No. 325 mesh (45- $\mu\text{m}$ ) as specified in Specification **E11**.

10.1.3 *Soxhlet Extractor*.

10.2 *Procedure*—The following procedure is to be used in preparing the sample:

10.2.1 Air-dry moist samples before grinding. If there is special need to preserve the nature or composition of the original deposit, special handling must be observed. Handle deliquescent deposits in a dry-box atmosphere. Handle samples subject to oxidation in an inert atmosphere.

10.2.2 If samples contain oil or grease, prepare a chloroform-insoluble fraction by first drying the specimen for 1 h at 105°C and then extracting for 2 h using chloroform in a Soxhlet extracting apparatus. Air-dry to remove solvent from specimen.

10.2.3 Grind the sample in a mullite or agate (mechanical or hand) mortar until approximately 98 % passes a No. 325 mesh (45- $\mu\text{m}$ ) sieve (see **Note 1**). Remove fragments of fiber, wood, and metal. If the specimen is not sufficiently brittle at ordinary temperatures to be ground to a fine powder or if it is suspected that certain crystallites may be plastically deformed during the grinding, the deposit can be subjected to dry-ice temperatures and then ground immediately. Grind hydrated samples under alcohol, if indicated, to prevent structural damage.

**NOTE 1**—Most materials found in water-formed deposits are sufficiently brittle to be reduced to 45  $\mu\text{m}$  and this crystallite dimension will generally give good identifiable diffraction patterns. However, it may not always be practical or possible to reduce certain materials to 45  $\mu\text{m}$ . Often good diffraction results can be obtained from larger crystallite sizes (No. 200 mesh (75- $\mu\text{m}$ ) to No. 270 mesh (53- $\mu\text{m}$ )). The only practical test for proper grain size is in reproducibility of diffraction line intensities. The ideal grain size may be in the subsieve range as small as 1  $\mu\text{m}$ , but reduction to this size may be impractical.

## 11. Selective Segregation of Analytical Sample

11.1 *Chemical and Physical Treatment of Samples*—Depending on the contents of the sample, it may or may not be necessary to concentrate or segregate components by chemical or physical treatment (see **Note 2**). Many crystalline materials produce sharp diffraction patterns and they are identifiable when present to 1 or 2 % in a mixture. Other substances that can be readily identified alone are difficult to detect in mixtures even when they are present to the extent of 50%. Separation of phases by density, acid solubility, or magnetic properties followed by diffraction analysis of the separated phase(s) may help to identify various deposit components. Separation treatment is also helpful in resolving line coincidence in complex mixtures. If concentration or segregation is not deemed necessary, disregard any treatment and proceed in accordance with Section 10. When treatment is necessary, use one or more of the following chemical or physical treatments described in **11.2** to **11.7**. It must be pointed out that the treatments provide no absolute separation, but serve only to concentrate or partially segregate specific components.

**NOTE 2**—It should be emphasized that water-formed deposits often occur in clearly defined layers and that physical separation at the time of sampling is more advantageous than later treatment.

11.2 *Water-Insoluble Fraction*—This treatment removes the water soluble from the water insoluble components. Soluble constituents would include most sodium, potassium, and lithium compounds (see **Note 3**).

<sup>4</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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

11.2.1 Weigh 0.5 g or more of sample that has been ground and passed through a No. 100 mesh (150- $\mu\text{m}$ ) sieve. Add 100 mL of water to a beaker containing the powdered specimen. Heat to boiling and then cool. Allow 30 min of reaction time, filter through a 45- $\mu\text{m}$  membrane filter, wash, and air-dry the residue. Regrind to pass through a No. 325 mesh (45- $\mu\text{m}$ ) sieve.

NOTE 3—The filtrate may be evaporated and the residue examined by diffraction. Although the crystalline structure may have changed from the original sample, it is often helpful in identifying simplified variations of the original crystals. Sodium phosphate compounds found dispersed in boiler deposits are often noncrystalline or are so complex that they are not easily identified. The water soluble residue from these deposits after evaporation is often more easily identified.

11.3 *Hydrochloric Acid-Insoluble Fraction*—This treatment removes carbonates, phosphates, and hydroxides. Partial decomposition occurs to some silicates such as serpentine, xonotlite, and analcite. Components such as anhydrite undergo only partial dissolution.

11.3.1 *Reagent*—The reagent used for this treatment is as follows:

11.3.1.1 *Hydrochloric Acid (1 + 6)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 6 volumes of water.

11.3.2 Weigh approximately 0.5 g of the sample that has been ground and passed through a No. 100 mesh (150- $\mu\text{m}$ ) sieve. Add 100 ml of HCl (1 + 6) to a beaker containing the powdered specimen. Allow 30 min of reaction time, filter through a membrane filter, wash and air-dry the residue. Regrind to pass through a No. 325 mesh (45- $\mu\text{m}$ ) sieve.

11.4 *Nitric Acid-Insoluble Fraction*—This treatment removes all the components indicated in 11.3 in addition to copper and most copper compounds.

11.4.1 *Reagent*—The reagent used for this treatment is as follows:

11.4.1.1 *Nitric Acid (1 + 13)*—Mix 1 volume of concentrated  $\text{HNO}_3$  (sp gr 1.42) with 13 volumes of water).

11.4.2 Weigh 0.5 g or more of the sample which has been ground and passed through a No. 100 mesh (150- $\mu\text{m}$ ) sieve. Add 100 ml of  $\text{HNO}_3$  (1 + 13) to a beaker containing the powdered specimen. Allow 30 min of reaction time, filter through a membrane filter, wash and air-dry the residue. Regrind to pass through a No. 325 mesh (45- $\mu\text{m}$ ) sieve.

11.5 *Density Fraction*—This treatment separates compounds in water-formed deposits which differ appreciably in density such as copper oxide and calcite.

11.5.1 Weigh 0.5 g or more of sample that has been ground and passed through a 100 mesh (150- $\mu\text{m}$ ) sieve. Add 100 mL of water to a beaker containing the powdered specimen. Stir the liquid with a mechanical stirrer, but do not use a magnetic stirrer (Note 4). The denser particles will settle to the bottom and the less dense particles will remain suspended. With continued stirring, withdraw sufficient liquid and filter through a membrane filter. Varying the speed of the stirrer will put more or less of the powdered sample into suspension. Air-dry the residue and regrind to pass through a No. 325 mesh (45- $\mu\text{m}$ ) sieve.

NOTE 4—A magnetic stirrer would attract any particle that was magnetic and might prevent segregation of particles of different densities.

11.6 *Magnetic and Nonmagnetic Fraction*—This treatment separates the magnetic components from the nonmagnetic components such as magnetite from hydroxyapatite.

11.6.1 Weigh 0.5 g or more of sample that has been ground and passed through a No. 325 mesh (45- $\mu\text{m}$ ) sieve. Add 100 mL of water to a beaker containing the powdered specimen. Stir with a mechanical stirrer for several minutes and then attach a magnet to the outside of the beaker (see Note 4). While stirring continues, magnetic components will be attracted to the area in front of the magnet, while the nonmagnetic components will remain in suspension. After 30 min, pour off the liquid while the magnet remains in place and filter. The residue should be essentially nonmagnetic. Remove the magnet from the side of the beaker, rinse the magnetic portion down the side of the beaker, swirl, and filter. Air-dry the residues and regrind to pass through a No. 325 mesh (45- $\mu\text{m}$ ) sieve.

11.7 *Brittle Fraction*—This treatment concentrates the more brittle or friable components from those that are less brittle or less friable such as calcite from silica.

11.7.1 *Apparatus*—The apparatus necessary for this treatment is as follows:

11.7.1.1 *Electrical Mechanical Sieve Shaker*.

11.7.2 Weigh 0.5 g or more of sample and hand grind in a mullite mortar until the largest particle size is approximately 1 mm in diameter. Set up the sieve-shaker apparatus with four different size sieves; No. 100 mesh (150- $\mu\text{m}$ ), No. 140 mesh (105- $\mu\text{m}$ ), No. 200 mesh (75- $\mu\text{m}$ ) and No. 325 mesh (45- $\mu\text{m}$ ). Shake the sample for several minutes and then collect the various fractions from each sieve. The most friable portion of the deposit should have passed to the bottom-most sieve. Each fraction may be examined separately after regrinding to pass a No. 325 mesh (45- $\mu\text{m}$ ) sieve.

## PRACTICE A—CAMERA

### 12. Scope

12.1 This method covers the qualitative X-ray diffraction analysis of powdered crystalline substances using photographic film as the detector. The film-camera technique has the advantage of being less expensive initially and less costly to maintain. The camera practice permits the use of smaller samples. Film cameras do not require the well-stabilized power supply as electronic detection techniques do. Often faint diffraction lines are more readily detected with film.

### 13. Summary of Practice A

13.1 Practice A utilizes the Debye-Scherrer type camera. In this method a powdered sample is placed in the center of a camera cylinder and a narrow film is wrapped around the inner wall. A monochromatic X-ray beam is directed upon the sample and the randomly oriented crystallites diffract the incident beam into a set of concentric cones in accordance with Bragg's Law ( $n\lambda = 2d \sin \theta$ ). The interceptions of the diffraction cones on the positioned film strip result in curved lines on that film. The spacings of these lines are used to identify the crystalline material.