Designation: D 2331 – 80 (Reapproved 1999)

Standard Practices for Preparation and Preliminary Testing of Water-Formed Deposits[1]

This standard is issued under the fixed designation D 2331; 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 These practices provide directions for the preparation of the sample for analysis, the preliminary examination of the sample, and methods for dissolving the analytical sample or selectively separating constituents of concern.

1.2 The general practices given here can be applied to analysis of samples from a variety of surfaces that are subject to water-formed deposits. However, the investigator must resort to individual experience and judgement in applying these procedures to specific problems.

1.3 The practices include the following:

	Sections
Preparation of the Analytical Sample	8
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Dissolving the Analytical Sample	10

1.4 *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.* For a specific warning statement, see Note 2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 887 Practices for Sampling Water-Formed Deposits[2]

D 932 Test Method for Iron Bacteria in Water and Water-Formed Deposits[2]

D 933 Practice for Reporting Results of Examination and Analysis of Water-Formed Deposits[2]

D 934 Practices for Identification of Crystalline Compounds in Water-Formed Deposits by X-Ray Diffraction[2]

D 993 Test Method for Sulfate-Reducing Bacteria in Water and Water-Formed Deposits[3]

D 1128 Method for Identification of Types of Microorganisms and Microscopic Matter in Water and Waste Water[4]

D 1129 Terminology Relating to Water[5]

D 1193 Specification for Reagent Water[5]

D 1245 Practice for Examination of Water-Formed Deposits by Chemical Microscopy[2]

D 2332 Practice for Analysis of Water-Formed Deposits by Wavelength-Dispersive X-Ray Fluorescence[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

3. Terminology

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

4. Significance and Use

4.1 Deposits in piping from aqueous process streams serve as an indicator of fouling, corrosion or scaling. Rapid techniques of analysis are useful in identifying the nature of the deposit so that the reason for deposition can be ascertained.

4.2 Possible treatment schemes can be devised to prevent deposition from reoccurring.

4.3 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.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. [7] Other grades may be used, provided it is first ascertained that the reagent is of

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[1] These practices are under the jurisdiction of ASTM Committee D-19 on Water and are 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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[2] *Annual Book of ASTM Standards*, Vol 11.02.

[3] Discontinued—see 1987 *Annual Book of ASTM Standards*, Vol 11.01.

[4] Discontinued—see 1981 *Annual Book of ASTM Standards*, Part 31.

[5] *Annual Book of ASTM Standards*, Vol 11.01.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] *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.

sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

6. Sampling

6.1 Collect and preserve the sample in accordance with Practices D 887.

7. Preparation of Analytical Sample

7.1 *Preliminary Examination*—Examine the sample as collected, using a microscope if available, for structure, color, odor, oily matter, appearance of mother liquor if any, and other characteristics of note (for example, attraction to magnet). Record results for future reference.

7.1.1 Filtration and other steps in the preparation of the analytical sample may frequently be bypassed; for example, a moist sample that contains no separated water shall be started in accordance with 7.3.1, and a dry sample shall be started in accordance with 7.4, 7.5, or 7.6. Partitioning, 7.4, is not always practical or even desirable. Solvent extraction, 7.5, is unnecessary if the sample contains no oily or greasy matter.

7.2 *Filtration of Sample* (see Note 1)—If the sample includes an appreciable quantity of separated water, remove the solid material by filtration. Save the filtrate, undiluted, pending decision as to whether or not its chemical examination is required. Transfer all of the solid portion to the filter, using the filtrate to rinse the sample container if necessary. Air-drying or partial air-drying of the filter is frequently helpful toward effecting a clean separation of the deposit.

NOTE 1—If the sample obviously contains oily matter, its extraction with a suitable solvent (see 7.5) is essential before filtration or air-drying is attempted. Likewise, if the sample is suspected to contain easily oxidizable materials, such as sulfide, analysis for these materials should be completed before air-drying.

7.3 *Air-Drying*—Remove the drained solid sample from the filter, being careful to avoid gross contamination with filter paper.

7.3.1 Air-dry the entire quantity of solid, spread in a thin layer on a nonreactive, impervious surface. A record of the loss of weight during air-drying is often used.

7.4 *Partitioning the Sample*—Many samples are obviously heterogeneous. If useful to explain the occurrence of the water-formed deposit, separate clearly defined layers or components, and approximate the relative percentages.

7.4.1 Retain the individual air-dried fractions for separate analysis, preferably storing over an effective desiccant such as anhydrite.

7.5 *Solvent Extraction*—This step is essential only if the air-dried sample smears or agglomerates when tested for pulverization (smears caused by graphite are possible but rare with water-formed deposits).

7.5.1 Weigh no more than 10 g of air-dried sample and place this, wrapped in fine-textured filter paper, in a prepared (extracted and dried) Soxhlet thimble. Paper clips are useful for preventing unfolding of the paper. Weigh the thimble and its contents and extract in a Soxhlet apparatus until the solvent (chloroform) in the extraction chamber is colorless. Record the loss in weight of the thimble and contents, dried at 105°C, as chloroform-extracted matter. If important to the solution of the problem, evaporate the solvent, and examine the residue.

7.5.2 The extraction may be repeated with other volatile organic solvents if exploratory tests warrant such procedure.

7.6 *Pulverizing*—Whether the sample is dry as received, air-dried or air-dried extracted, it must be pulverized to adequate homogeneity. Grind the entire sample, or enough of it to be representative of the whole, to pass a No. 100 (150-μm) sieve, as specified in Specification E 11. Continue the grinding until all the material passes through the sieve, except for fragments such as splinters of fiber, wood, and metal.

7.6.1 Identify fragments separated from the sample during grinding by standard methods if this information is valuable.

7.6.2 Mix the sieved material thoroughly by tumbling in a closed dry container that is no more than two thirds full.

7.6.3 Transfer 5 to 10 g of the thoroughly mixed material to a weighing bottle. This is the analytical sample. Unless the determinations are to be made on an air-dried basis, dry at 105°C and store in a desiccator.

8. Preliminary Testing of Analytical Sample

8.1 This section outlines methods for the preliminary examination of samples of water-formed deposits. Use one or more of these methods to disclose the component elements of the sample and whether the concentrations are major, minor, or trace, an essential guide to planning the analysis. This preliminary testing frequently also provides important guidance toward defining technological problems associated with the occurrence of the deposits. The methods include spectrography, atomic absorption spectrophotometry, X-ray diffraction, X-ray fluorescence, microscopy, and ordinary qualitative analysis.

8.2 *Spectrography*—Make the spectrographic analysis by a suitable method, for example, as outlined in 8.2.2 to 8.2.7.

8.2.1 Although superior results are obtainable with a spectrograph and associated equipment, data of lesser degree of accuracy can frequently be obtained with less formal equipment such as a visual-arc spectroscope.

8.2.2 For best results use a spectrograph having a suitable reciprocal linear dispersion, associated adjuncts and optics, a microphotometer for measuring the transmittances of spectra-line images, and associated equipment for determining intensity ratios.

8.2.3 Mix 50 mg of the pulverized sample, obtained in accordance with 7.6.2, with 900 mg of graphite powder and 250 mg of lithium carbonate. Pack the mixture into graphite-cup electrodes.

8.2.4 Record the spectra obtained upon excitation with a d-c arc.

8.2.5 Measure the transmittances of the analytical and lithium lines (internal standards other than lithium are preferred by some operators). Determine intensity ratios from these data.

8.2.6 Use the intensity ratios to estimate concentrations from standard analytical curves.

8.2.7 The metallic constituents can frequently be determined within 20 % of their content in the deposit, which is sufficiently close for classification as major, minor, or trace.

8.3 *Atomic Absorption*—Make the atomic absorption analysis in accordance with appropriate method.

8.3.1 The required apparatus shall include an atomizer and burner, suitable pressure-regulating devices, a multielement hollow-cathode lamp (alternatively, a hollow-cathode lamp for each metal to be tested), an optical system capable of isolating the desired wavelengths of radiation as lines, and adjuncts for obtaining amplified measurements and readout.

8.3.2 Prepare standards as in the selected or multiple standards if a multielement is used. Follow the manufacturer's recommendations for instrument start-up and optimization of test conditions. Calibrate the instrument for each element to be determined by aspirating prepared standard solutions and noting the corresponding instrument read out. Aspirate a blank solution between each standard to assure instrument stability. Each element absorbs energy from the line source at a characteristic wavelength which results in a decrease in energy noted at the detector. Record the instrument readings, and plot against the occurrence of the absorbing atom in milligrams per litre of the aspirated solution.

8.3.3 Prepare the solubilized sample (9.2, 9.3, or 9.4, depending on the solubility of the water-formed deposit). Using volumetric flasks, make 100 mL each of the two dilutions, 1 + 9 and 1 + 99, by adding enough water to 10 and 1 mL of the solubilized sample, respectively.

8.3.4 Aspirate the solubilized sample and the two dilutions prepared from it, aspirating water before going from one dilution to another. Record the instrument readings for the wavelengths of interest.

8.3.5 Determine the concentration of each metal tested in each dilution of the solubilized sample by referring the absorbance obtained to a prepared calibration curve that relates the concentration of prepared standard solutions and their corresponding absorbances. Alternatively, when direct readout in terms of concentration is possible, note the concentration of metal for each sample aspirated. Correct the sample readings for baseline drift or contaminants, or both, in the reagents used to solubilize the sample by subtracting the blank reading from the sample reading.

8.3.6 Calculate the concentration of each element determined in the original sample as follows:

$$\text{Concentration, mg/L} = \frac{C \times F}{D} \times 10^{6}$$

where:

C = concentration of element in the solubilized sample, mg/L,
F = dilution of the solubilized test sample, if required, and
D = weight of the original deposit sample diluted to a 1-L volume, mg.

8.3.7 Atomic absorption may be increased or decreased by chemical interferences. For example, calcium absorbance is lowered in the presence of phosphate, silica can interfere with iron, and aluminum interferes with the determination of magnesium. If these constituents are suspected to be present and more quantitative results are desired, refer to the methods provided by the manufacturers of the equipment for suppressing these interferences.

8.4 *X-Ray Diffraction*—Perform the X-ray diffraction analysis in accordance with Practices D 934.

8.4.1 The required apparatus shall include a radiation source, of which more than one may be needed, a camera or other device for sensing or recording radiation intensity, and adjuncts for interpreting the recorded data.

8.4.2 Regrind a portion of the pulverized sample, obtained in accordance with 7.6.2, to pass a No. 270 (53-μm) sieve (or as directed by a specific manufacturer). Mount the powdered material in the shape or form required for the sensing device that is used.

8.4.3 Record the diffraction pattern on photographic film, or its equivalent while the mounted sample is exposed to the X-ray beam for the required interval.

8.4.4 The radiation pattern shall be translated into lines and intensities, using the adjuncts available for this purpose, and these shall be compared with standard diffraction patterns for known compounds.

8.4.5 Identification of a substance is made when sufficient characteristic lines of a standard pattern occur in the pattern derived from the sample, in essentially the same relative intensity. However, owing to the poor crystallization characteristic of many water-formed deposits, the sensitivity of this evaluation is often much poorer than the 1 percent usually cited.

8.5 *X-Ray Fluorescence*—Perform the X-ray fluorescence analysis in accordance with Practice D 2332.

8.5.1 The required apparatus shall include sample preparation equipment, excitation source, devices for housing the sample, a spectrometer assembly, and adjuncts for obtaining and interpreting data.

8.5.2 Regrind the pulverized sample obtained in accordance with 7.6.2 to pass a No. 270 (53-μm) sieve. For order of magnitude determinations the ground sample shall be briquetted to form a wafer (alternatively, the powdered sample may be tamped into a specimen holder that is supplied with the apparatus).

8.5.3 For more accurate evaluations, fuse the sample with a flux to improve homogeneity. Even higher degrees of precision are often obtainable through chemical pretreatment to segregate or isolate the constituents of major concern.

8.5.4 Radiate the mount with an X-ray beam of short wavelength (high energy). Use sensitive detectors to measure intensities at selected wavelengths of the dispersed characteristic X rays of each constituent emitted or fluoresced upon absorption of the primary or incident X rays.

8.5.5 Use the K spectral lines to identify elements of atomic number 11 to 50. Use either the K or L lines for elements with an atomic number of 54 or higher, depending on the available instrumentation.

8.5.6 Relate detector output (radiation pattern) to constituent concentration by reference to calibration curves or charts, as appropriate.

8.6 *Microscopy*—Perform the microscopical examinations in accordance with Practice D 1245, Method D 1128, Test Method D 932, and Test Method D 993.

8.6.1 Perform these microscopical tests on the sample as received to ensure that the selection of sample portions for examination is made competently.

8.6.2 The microscopical examination shall include observations relating to sample description, as required in Practices D 887. Describe outstanding characteristics such as structure and homogeneity as seen through the microscope.

8.6.3 Follow the directions and technique given in Practice D 1245 to test selected components of the deposit on microscope slides.

8.6.3.1 Add the reagents recommended for qualitative testing. Observe and interpret the test results obtained.

8.6.3.2 Use polarized light and refractive index standards to identify selected crystals from optical characteristics. Amorphous materials may also have optical characteristics that provide a basis for identification under a microscope.

8.6.4 Identify microorganisms as one of the types tabulated in Method D 1128, using stains where applicable to differentiate the organisms from the background. Specific identification of each species of bacteria, molds, and other organisms can be made by experienced personnel, but this identification is not usually required.

8.6.5 Test for iron bacteria in corrosion deposits formed at temperatures below 55°C, consulting Test Method D 932 for the identification of the bacteria. Where required, apply the chemical microscopy in this method to verify identification.

8.6.6 Test for sulfate-reducing bacteria in corrosion deposits formed below 40°C, following the procedures in Test Method D 993. Use preferred or less precise methods for detecting the presence of such bacteria in the deposits. Estimate their relative number by the process of incubation and determination of the amount of hydrogen sulfide formed in the culture.

8.7 *Qualitative Testing*—Use qualitative testing, either on a macro or a micro scale, when optical instrumentation is not readily available.

8.7.1 Use qualitative testing as an adjunct to testing by optical methods. For example, effervescence of the air-dried sample with acids suggests the presence of carbonate, and the deposit probably contains iron if it is attracted by a magnet.

8.7.2 Include under qualitative testing the metals more commonly found in water-formed deposits; also, carbonate, sulfate, and phosphate.

9. Dissolving the Analytical Sample

9.1 *Selective Isolation or Segregation of Constituents*—The preliminary examination (8.1 to 8.6) will disclose which constituents comprise the deposit and provide an estimate of the content of each. A considerable number of quantitative determinations can be made directly on the analytical sample, obtained in accordance with 7.6.3, utilizing special methods of extraction. These solubilizing procedures are usually specific to a particular determination and are included with that determination.

9.2 *Solution in Hydrochloric Acid*— This treatment will dissolve water-formed deposits that do not contain a substantial percentage of stubborn components, including calcium sulfate, various silicates, and some of the more refractory spinels. The use of this solvent is advantageous in that it is not oxidizing, and possible interference from sulfate or nitrate is not introduced.

9.2.1 *Reagents*—The reagents for this solubilizing method are as follows:

9.2.1.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

9.2.1.2 *Hydrochloric Acid* (1 + 4)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 4 volumes of water.

9.2.1.3 *Hydrochloric Acid* (1 + 9)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 9 volumes of water.

9.2.2 Weigh approximately 0.5 g of the analytical sample obtained in accordance with 7.6.3, into a 250-mL beaker. Add 50 mL of HCl (1 + 4) and evaporate to dryness on a hot plate contained in a hood. Add 10 mL of concentrated HCl (sp gr 1.19) and again evaporate to dryness. Add 10 mL of HCl (1 + 9), bring to a boil, and separate the solution by filtration through a medium-texture, ashless filter paper. Wash the residue and dilute with water the combined filtrate and washings to a measured volume. Aliquots of this solution shall be used for the analysis of the constituents to be determined.

9.2.3 The residue may be retained for further examination.

9.3 *Solution in Mixed Hydrochloric Acid-Nitric Acid*—This solvent is more effective in eliminating traces of organic material and in dissolving more refractory components which resist hydrochloric acid alone. The nitric acid, however, may interfere with some analytical procedures unless it is thoroughly removed during the dehydration step.

9.3.1 *Reagents*—The reagents for this solubilizing method are as follows:

9.3.1.1 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

9.3.1.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

9.3.2 Add 5 mL of HNO_3(sp gr 1.42) to approximately 0.5 g of the analytical sample that has been weighed into a 250-mL beaker, and evaporate to near dryness on a hot plate contained in a hood.

9.3.3 Add 50 mL of HCl (1 + 1) and 5 mL of HNO_3(sp gr 1.42). Evaporate to dryness on a hot plate in a hood.

9.3.4 Cool and add 10 mL of HCl (1 + 1) acid and 1 mL of HNO_3(sp gr 1.42) and repeat the evaporation.

9.3.5 Allow the beaker to cool and then add 50 mL of HCl (1 + 1). Boil until the volume is decreased to approximately 25 mL and filter through a medium-texture, ashless filter paper.

9.3.6 Wash the residue and dilute with water the combined filtrate and washings to a measured volume. Aliquots of this solution shall be used for the analysis of the constituents to be determined.

9.4 *Solution in Mixed Sulfuric Acid*— The reagents listed in 9.4.1 are considered good universal solvents for water-formed deposits containing silica, but sulfate and silica must be determined on a different portion of the sample.

9.4.1 *Reagents*—The reagents for this solubilizing method are as follows:

9.4.1.1 *Hydrofluoric Acid* (48 to 51 %) (HF).

NOTE 2—**Warning:** HF causes rapid and severe burns. Use face shield, rubber gloves, and aprons.

9.4.1.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (NHO_3).

9.4.1.3 *Sulfuric Acid* (1 + 1)—Mix carefully 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 1 volume of water.

9.4.2 Add 3 mL of H_2SO_4(1 + 1) and 10 mL of HF to approximately 0.5 g of the analytical sample, as described in 7.6.3, in a 30-mL platinum crucible; perform these operations in a hood.

9.4.3 Evaporate until most of the hydrofluoric acid has been volatilized, then add 1 mL of HNO_3(sp gr 1.42) and continue heating until strong fumes of sulfur trioxide are evolved. Cool the crucible and contents.

9.4.4 Slowly and cautiously add 15 mL of water and digest for ½ h.

9.4.5 Transfer the contents of the crucible quantitatively to a 250-mL volumetric flask and adjust to volume when cool. Unless the quantity of insoluble matter (for example, barium, if present, will form barium sulfate) in the flask is appreciable, it may be ignored.

9.4.6 If alkali metals are to be determined on this solubilized portion, a suitable aliquot for these determinations should be withdrawn from the volumetric flask and stored in a plastic bottle.

9.5 *Alkali Fusion*—This method of dissolving the sample is especially useful for the rapid determinations of silica and aluminum.

9.5.1 *Reagents*—The reagents for this solubilizing method are as follows:

9.5.1.1 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

9.5.1.2 *Sodium Hydroxide* (NaOH), pellets (do not store in glass bottle).

9.5.2 Add nine sodium hydroxide pellets (approximately 1.5 g) to a 75-mL nickel crucible. Slowly heat the crucible over a Meker burner until the pellets are molten. Allow the crucible and its contents to cool to room temperature.

9.5.3 Weigh 0.5 g of the analytical sample, as described in 7.6.3, and transfer to the crucible containing the NaOH.

9.5.4 Reheat the crucible to remelt the hydroxide and swirl to mix in the weighed material. Use a nickel wire or rod to complete the mixing.

9.5.5 Continue heating for 3 min after mixing, then allow the melt to cool.

9.5.6 Add 50 mL of water to the crucible and stir the contents of the crucible occasionally until the melt is disintegrated completely (about 1 h).

9.5.7 Transfer the contents to a 1-L-volumetric flask (previously rinsed with HCl (1 + 1) containing about 400 mL of water and 20 mL of HCl (1 + 1) (a plastic funnel with a stem at least 152 mm (6 in.) long should be used so that the strong alkaline extract will not contact the glass). Use a policeman to wash the crucible and to ensure complete transfer.

9.5.8 Dilute to volume with water, and transfer the solution to a plastic bottle for storage.

10. Report

10.1 Methods for reporting analytical results should follow those described in Practice D 933, when applicable.

11. Keywords

11.1 crystallographic examination; deposits; sample preparation; scale; spectrographic analysis