Designation: D1971 − 16 (Reapproved 2021)$^{\varepsilon 1}$

Standard Practices for Digestion of Water Samples for Determination of Metals by Flame Atomic Absorption, Graphite Furnace Atomic Absorption, Plasma Emission Spectroscopy, or Plasma Mass Spectrometry[1]

This standard is issued under the fixed designation D1971; 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.

ε[1] NOTE—The WTO caveat was editorially added in November 2021.

1. Scope

1.1 Most atomic absorption and plasma emission spectroscopy, and plasma-mass spectrometric test methods require that the metals of interest be dissolved in a liquid phase before being introduced into the spectrophotometer. These practices describe digestion or dissolution procedures whereby analyte metals associated with the solid fraction of a sample can be brought into solution for subsequent analysis. The following practices are included:

	Sections
Practice A—Digestion with Mineral Acids and Elevated Pressure	8 through 13
Practice B—Digestion with Mineral Acids and Heating at Atmospheric Pressure	14 through 19
Practice C—In-Bottle Digestion with Mineral Acids	20 through 25

1.2 These practices have been demonstrated to be applicable to a wide variety of sample types and sample matrices, and in many cases, will give complete dissolution of the analyte metals of interest. They are by no means the only digestion procedures available.

1.3 The user of these practices should be cautioned that these practices may not completely dissolve all portions of a sample's solid phase and may not give complete recovery of the desired analyte metals. In these cases, other digestion techniques are available that will effect complete dissolution of a sample. It is the user's responsibility to ensure the validity of these practices for use on their particular sample matrix, for their metals of interest.

1.4 This practice assumes that the criteria established in Guide D3856 can be met.

1.5 These digestion procedures have been selected for their wide application, low cost, and ease of use.

1.6 The values stated in SI units are to be regarded as the standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 6.

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D511 Test Methods for Calcium and Magnesium In Water
D857 Test Method for Aluminum in Water
D858 Test Methods for Manganese in Water
D1068 Test Methods for Iron in Water
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1687 Test Methods for Chromium in Water
D1688 Test Methods for Copper in Water
D1691 Test Methods for Zinc in Water
D1886 Test Methods for Nickel in Water
D1976 Test Method for Elements in Water by Inductively-Coupled Plasma Atomic Emission Spectroscopy
D2972 Test Methods for Arsenic in Water
D3082 Test Method for Boron in Water

[1] These practices are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Nov. 1, 2021. Published December 2021. Originally approved in 1991. Last previous edition approved in 2016 as D1971 – 16. DOI: 10.1520/D1971-16R21E01.

[2] 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.

D3370 Practices for Sampling Water from Flowing Process Streams
D3372 Test Method for Molybdenum in Water
D3373 Test Method for Vanadium in Water
D3557 Test Methods for Cadmium in Water
D3558 Test Methods for Cobalt in Water
D3559 Test Methods for Lead in Water
D3645 Test Methods for Beryllium in Water
D3697 Test Method for Antimony in Water
D3859 Test Methods for Selenium in Water
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D3866 Test Methods for Silver in Water
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D3920 Test Method for Strontium in Water
D4190 Test Method for Elements in Water by Direct-Current Plasma Atomic Emission Spectroscopy
D4191 Test Method for Sodium in Water by Atomic Absorption Spectrophotometry
D4192 Test Method for Potassium in Water by Atomic Absorption Spectrophotometry
D4309 Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water
D4382 Test Method for Barium in Water, Atomic Absorption Spectrophotometry, Graphite Furnace
D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry

2.2 *EPA Method:*[3]

EPA-600/4-79-020 Methods for Chemical Analysis of Water and Wastes, Revised March 1983
EPA-600/R-94/111 Methods for the Determination of Metals in Environmental Samples—Supplement 1[3]

2.3 *USGS Method:*[4]

USGS Open File Report 96–225 Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—In-Bottle Acid Digestion of Whole Water Samples

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *digestion, n*—treating a sample with the use of heat or elevated pressures, or both, usually in the presence of chemical additives, to bring analytes of interest into solution or to remove interfering matrix components, or both.

3.2.2 *total recoverable, n*—a descriptive term relating to the metal forms recovered in the acid-digestion procedures resulting in a metal analyte measurable by atomic absorption spectrophotometry, plasma emission spectroscopy or plasma mass spectrometry after applying the digestion procedure in either Practice A, Practice B, or Practice C.

3.2.2.1 *Discussion*—The choice of Practice A, B, or C shall be noted in reporting resultant data.

4. Significance and Use

4.1 The determination of metals in water often requires the measurement of total (suspended and dissolved) metals as well as soluble (dissolved) metals. In such cases, consistent and dependable digestion procedures must be used so that data derived for the total metals content is reliable.

4.2 The practices given are applicable to a wide variety of sample types for the purpose of preparing a sample for metals analyses by atomic absorption spectrophotometry or plasma emission spectroscopy (see Test Method D1976, Practice D3919, Practice D4691, and Test Method D4190) or plasma-mass spectrometry (see Test Method D5673) and have been shown to give good recovery in the following matrices: industrial effluents; waste water treatment plant influents, sludges, dewatered sludges, and effluents; river and lake waters; and plant and animal tissues. Elements which have shown good recovery include: copper, nickel, lead, zinc, cadmium, iron, manganese, magnesium, and calcium.

4.2.1 Good recovery for the indicated sample types and metals may not be achieved at all times due to each sample's unique characteristics. Users must always validate the practice for their particular samples.

4.3 The analytical results achieved after applying these practices cannot necessarily be deemed as a measure of bioavailable or environmentally available elements.

4.4 These three practices may not give the same recovery when applied to the same sample, nor will they necessarily give the same results as achieved using other digestion techniques. An alternate digestion technique is Practice D4309.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used throughout. Acids shall have a low-metal content or should be doubly distilled and checked for purity. 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.[5] 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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Other reagent water types may be used, provided it is first ascertained that the water is of

[3] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[4] Available from U.S. Geological Survey (USGS) National Center, 12201 Sunrise Valley Dr., Reston, VA 20192, https://www.usgs.gov.

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

sufficiently high purity to permit its use without lessening the bias and precision of the determination.

6. Hazards

6.1 These practices involve the heating of solutions of mineral acids. Appropriate precautions shall be taken to protect the analyst from these acids and heated containers. Heated samples and acids may splatter or boil unexpectedly.

7. Sampling

7.1 As with all chemical assay procedures, the user of this practice shall ensure that all sample aliquot used are adequately representative of the environmental situation being monitored.

7.2 Appropriate sampling and subsampling techniques for particular environmental samples can be found in other references.

7.3 Collect the sample in accordance with Practices D3370.

PRACTICE A—DIGESTION WITH MINERAL ACIDS AND ELEVATED PRESSURE

8. Scope

8.1 This practice presents a digestion technique that has broad application and can be performed inexpensively with minimal labor, equipment, and space. In addition, this practice allows for many samples to be processed quickly and simultaneously under the same conditions.

9. Summary of Practice

9.1 Samples are placed in loosely capped, heat-, and acidresistant containers with selected reagents and subjected to 121°C and 103 kPa (15 psi) for 30 min. After removing any particulate matter remaining, the digestate is ready for analysis by atomic absorption spectrophotometry, plasma emission spectroscopy, or plasma-mass spectrometry.

9.2 The practice may be found to be more applicable to a particular sample or analytical scheme after appropriate modifications of reagent addition, temperature, pressure, digestion time, or container selection. Any such modifications to this practice must be validated by the user.

10. Apparatus

10.1 *Digestion Containers*—50 mL disposable polypropylene centrifuge tubes and 125 mL polypropylene reagent bottles with screw caps have been used successfully. Any container that is not attacked by the digestion conditions, is sufficiently free of the analyte(s) of interest, and can be loosely capped, may be used.

10.2 *Digestion Container Rack*—Any rack that will fit inside the autoclave, will hold the digestion containers securely, and is not attacked by the conditions in the autoclave, may be used.

10.3 *Autoclave*—Any autoclave or similar apparatus with a pressure chamber large enough to hold the desired number of samples and capable of achieving and holding 121°C and 103 kPa (15 psi) for 30 min., may be employed. An autoclave with automatic cycling is desirable. As the digesting samples release acidic fumes, the portions of the autoclave coming in contact with these fumes should be constructed of acid resistant materials.

NOTE 1—Prolonged use of an autoclave with a stainless steel interior for this practice may result in discoloration of the autoclave walls. This discoloration has not been shown to cause any problems with autoclave operation. A commercially available autoclave with a stainless steel interior has been in daily use for this practice, as well as for routine sterilization purposes, for ten years without any degradation of the autoclave or its performance.

11. Interferences

11.1 The interferences of this practice relate to the inability of the described procedure to quantitatively dissolve the analyte metals of interest in certain situations. These interferences can be either physical or chemical.

11.2 *Physical Interferences*—In some samples, the metals of interest are bound or occluded in a matrix that is impervious to dissolution by the acids. This is most frequently encountered in geological and boiler water samples.

11.3 *Chemical Interferences*—The complete dissolution of a metal of interest may not occur due to the digestion conditions being insufficiently rigorous for that particular metal. In other instances, the chemical makeup of the sample may render the digestion acids ineffective.

12. Reagents and Materials

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

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

12.3 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method

13. Procedures

13.1 In this section two types of digestion procedures are described: one for liquid samples (see 13.2) and one for solid and semi-solid samples (see 13.3).

13.2 *Liquid Samples:*

13.2.1 Using a sample volume from 40 to 100 mL, pipet an aliquot of sample, hydrochloric acid, and nitric acid into a digestion container in the following ratio: 100 volumes sample to 5 volumes HCl (sp gr 1.19) to 1 volume HNO_3 (sp gr 1.42).

13.2.2 Swirl digestion container gently to mix contents.

13.2.3 Loosely place caps on digestion containers and place digestion containers in rack.

NOTE 2—Caps should be attached securely enough so that they are not thrown off during autoclaving, but not so securely that gas is unable to move freely in and out of the container.

13.2.4 Place rack of digestion containers in autoclave and process for 30 min. at 121°C and 103 kPa (15 psi).

13.2.5 Remove digestion containers from autoclave; allow to cool to room temperature.

13.2.6 Proceed with assay of digested sample.

NOTE 3—Experience with this practice indicated that with sample and acid volumes in the ranges specified in 13.2.1 final volume after autoclaving will approximate the original sample volume within 1 %. If, after verifying this observation and determining if this degree of volumetric uncertainty is acceptable, the user may proceed to use the digestate without any volume correction. In cases where the final volume after autoclaving is not sufficiently close to the original sample volume, experience indicates that the final volume will still be very reproducible. In these cases and where the final digestate volume is less than the original volume of sample, a fixed volume of water can be added to the digestate to make its volume closely approximate the original sample volume. Conversely, a sufficient volume of water can be added prior to autoclaving, such that the final volume of digestate is close enough to the original sample volume.

NOTE 4—Any solids remaining after digestion must be removed from the liquid portion to be analyzed, by filtration, centrifugation, or settling.

13.3 *Solid and Semi-Solid Samples:*

13.3.1 Place an accurately weighed portion of sample, less than or equal to 1 g, in a digestion container. It is the analyst's responsibility to note if the sample weight was determined after drying at a specific temperature.

13.3.2 Add 10 mL of water, 5 mL of HCl (sp gr 1.19), and 1 mL of HNO_3 (sp gr 1.42) to the digestion container. Swirl gently to mix. Loosely cap the container (see Note 2).

13.3.3 Place digestion containers in rack and place rack in autoclave. Process samples for 30 min. at 121°C and 15 psig (103 kPa gage).

13.3.4 Remove digestion containers from autoclave and allow to cool to room temperature.

13.3.5 Quantitatively transfer the contents of the digestion container to a 100 mL volumetric flask (or other suitable size) and make up to volume with water.

13.3.6 Proceed with assay of digested sample by atomic absorption, plasma-mass spectrometry, or plasma emission spectroscopy (see Note 4).

PRACTICE B—DIGESTION WITH MINERAL ACIDS AND HEATING AT ATMOSPHERIC PRESSURE

14. Scope

14.1 This practice presents a digestion technique widely used for wastewater samples to give what is defined as total recoverable metals. The term "total recoverable metals" is utilized in some regulatory requirements. The user of this practice bears the responsibility of verifying the appropriateness of the practice for regulatory compliance work.

NOTE 5—This practice corresponds to that utilized in the ASTM test methods listed in Appendix X1. References to specific test methods are included in Appendix X1. The metals digestion procedure of the USEPA [3] for "total recoverable" metals is similar, but uses one-half the amount of HCl that is specified in this practice.

15. Summary of Practice

15.1 Samples are acidified with HNO_3 and HCl and heated on a hot plate or steam bath to reduce the volume to a defined level. After filtration (12.3), the samples are ready for analysis by atomic absorption spectrophotometry, plasma emission spectroscopy, or plasma-mass spectrometry.

16. Interferences

16.1 The interferences of this practice relate to the inability of the described procedures to quantitatively dissolve the analyte metals of interest in certain situations. These interferences can be either physical or chemical.

16.2 *Physical Interferences*—In some samples, the metals of interest are bound or occluded in a matrix that is impervious to dissolution by the acids. This is most frequently encountered in geological samples.

16.3 *Chemical Interferences*—The complete dissolution of a metal of interest may not occur due to the digestion conditions being insufficiently rigorous for that particular metal. In other instances, the chemical makeup of the sample may render the digestion acids ineffective.

17. Apparatus

17.1 *Steam Bath* or Hot Plate.

NOTE 6—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature (65°C to 85°C) across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

18. Reagents and Materials

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

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

18.3 *Filter Paper*—Fine textured, acid washed, ashless, No. 19.

19. Procedure

19.1 Measure 100 mL of a well-mixed sample into a 125 mL beaker or flask. Add 0.5 mL of HNO_3 (sp gr 1.42).

NOTE 7—If the sample has been preserved at the recommended level of 5 mL of HNO_3 per litre of sample, the addition of acid at this step can be omitted.

19.2 For a solid or semi-solid sample, weigh out accurately to the nearest milligram, 0.5 g or less and place in a 125 mL (or larger) beaker or flask. Add 100 mL of water and 0.5 mL of HNO_3 (sp gr 1.42). Samples should be homogeneous. Solid samples should be finely ground.

19.3 Add 5 mL of HCl (sp gr 1.19) to the beaker or flask.

19.4 Heat the samples on a steam bath or hot plate in a well-ventilated hood until the volume has been reduced to 15 to 20 mL, making certain that the sample does not boil. When analyzing samples containing appreciable amounts of solid matter, the actual amount of reduction in volume is left to the discretion of the analyst.