



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 Spectrometry¹

This standard is issued under the fixed designation D 1971; 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 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
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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 D 3856 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 for information only.

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

2. Referenced Documents

2.1 ASTM Standards:

- D 511 Test Methods for Calcium and Magnesium in Water²
- D 857 Test Methods for Aluminum in Water²
- D 858 Test Methods for Manganese in Water²
- D 1068 Test Methods for Iron in Water²
- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 1687 Test Methods for Chromium in Water²
- D 1688 Test Methods for Copper in Water²
- D 1691 Test Methods for Zinc in Water²
- D 1886 Test Methods for Nickel in Water²
- D 1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 3372 Test Method for Molybdenum in Water²
- D 3557 Test Methods for Cadmium in Water
- D 3558 Test Methods for Cobalt in Water²
- D 3559 Test Method for Lead in Water²
- D 3645 Test Method for Beryllium in Water²
- D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water²
- D 3866 Test Methods for Silver in Water²
- D 3919 Practices for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²
- D 4190 Test Method for Elements in Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy²
- D 4191 Test Method for Sodium in Water by Atomic

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

Current edition approved March 10, 2002. Published June 2002. Originally published as D 1971 – 91. Last previous edition D 1971 – 95.

² *Annual Book of ASTM Standards*, Vol 11.01.

Absorption Spectrophotometry²

D 4192 Test Method for Potassium in Water by Atomic Absorption Spectrophotometry²

D 4309 Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for Determination of Total Recoverable Metals in Water²

D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry²

D 5673 Test Method for Elements in Water by Inductively Coupled Plasma-Mass Spectrometry³

2.2 *U.S. EPA Method:*

EPA-600/4-79-020 Methods for Chemical Analysis of Water and Wastes⁴

EPA-600/R-94/111 Methods for the Determination of Metals in Environmental Samples—Supplement 1⁴

2.3 *U.S. Geological Survey Method:*

U.S. Geological Survey 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 Samples⁵

Quality Laboratory—In-Bottle Acid Digestion of Whole Water Samples⁵

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *digestion*—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*—the amount of 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. 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 Methods D 1976, D 3919, D 4691, and D 4190) or plasma-mass spectrometry (See Test Method D 5673) 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 D 4309.

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.⁶ 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 D 1193, Type I. Other reagent water types may be used, provided it is first ascertained that the water is of 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 Specification D 1192 and Practices D 3370.

³ *Annual Book of ASTM Standards*, Vol 11.02.

⁴ Revised March 1983. Published by the United States Environmental Protection Agency. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

⁵ Available from USGS National Center, 12201 Sunrise Valley Dr., Reston, VA 20192, USA.

⁶ *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.

**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 acid-resistant containers with selected reagents and subjected to 121°C and 15 psig (103 kPa gage) 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 15 psig (103 kPa gage) 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

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

12.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO₃).

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 HNO₃ (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 15 psig (103 kPa gage).

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 HNO₃ (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 the appendix. References to specific test methods are included in the appendix. The metals digestion procedure of the USEPA⁴ 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 HNO₃ and HCl and heated on a hot plate or steam bath to reduce the volume to a defined level. After filtration, 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.

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 (HNO₃).

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 HNO₃(sp gr 1.42).

NOTE 6—If the sample has been preserved at the recommended level of 5 mL of HNO₃ 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 HNO₃(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.

19.5 Cool and remove solids (see Note 4). Quantitatively transfer sample to 100 mL volumetric flask (or other suitable size). Adjust to volume.

19.6 Proceed with assay of digested sample by atomic absorption spectrophotometry, plasma emission spectroscopy, or plasma mass spectrometry.

PRACTICE C—IN-BOTTLE DIGESTION WITH ACIDS MINERAL ACIDS

20. Scope

20.1 This practice presents a digestion technique used for water samples that gives what is defined as whole-water recoverable metals. The term “whole-water 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. The user of the practice is responsible to ensure that the practice is appropriate for a given element and/or a given analytical technique.

21. Summary of Practice

21.1 Samples are acidified with HNO₃ and HCl and heated in an oven for a specified time period. After digestion, the samples are filtered to stop the dissolution of particulate or colloidal material that may be present in the sample. After filtration, the samples are ready for analysis by flame atomic absorption spectrophotometry, graphite furnace atomic absorption spectroscopy, plasma emission spectroscopy, or plasma-mass spectrometry.

22. Interferences

22.1 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.

22.2 *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.

22.3 *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.

22.4 *Instrumental Interferences*—The use of hydrochloric acid in this practice may cause difficulties because chloride is an interfering ion in the analysis of metals by ICP-MS and GFAA.

NOTE 7—Practice D 3919 for GFAA uses 5% argon/hydrogen as a carrier gas.

23. Apparatus

23.1 Temperature controlled drying oven capable of being programmed to hold 65° C for 8 hours, then cooling to below 40° C.

23.2 Laminar flow hood.

23.3 Analytical balance, capable of accurately weighing to 0.01 grams.

24. Reagents and Materials

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

24.2 *Nitric Acid (sp. gr 1.42)*—Concentrated nitric acid (HNO₃).

24.3 *Precleaned polyethylene bottles, or equivalent*

24.4 *Disposable filter funnels*—type 41, polypropylene, Whatman #1920-1441 or equivalent.

25. Procedure

25.1 If samples have not already been preserved with HNO₃, add 4 mL HNO₃ per liter of sample to each sample bottle.

25.2 Weigh the sample bottle with cap, to determine the gross weight for each bottle being digested.

25.3 Subtract the appropriate tare weight for the capped bottle from the gross weight to determine the sample weight.

25.4 Add 1.0 mL of concentrated HCl for each 50 mL of sample, based on the measured sample weight. Any size

sample is appropriate for digestion, just maintain the ratio of 1 mL of hydrochloric acid per 50 mL of sample.

25.5 Recap the bottle and shake vigorously.

25.6 Place the bottle in the oven. If there are multiple samples, arrange the bottles so that they are evenly spaced throughout the oven, with open area around each bottle.

25.7 The oven is preprogrammed to 65°C; set oven timer to 8 hours.

25.8 Digest the samples for 8 hours in the oven. Allow the samples to cool to room temperature prior to filtration.

25.9 Carry out all filtration steps in a laminar flow hood.

25.10 To pre-clean the filter assembly, rinse the filter funnel twice using 500 mL of 0.1 N HNO₃ solution. Follow the acid rinses with three rinses of water.

25.11 Shake the sample bottle after digestion. Allow the sediment to settle for 1-2 hours before filtering.

25.12 Place the filter funnel into a pre-cleaned polyethylene bottle. Pour the contents of the digested sample into the filter funnel. Do not introduce any solution other than the sample into the filter funnel. If the filter becomes plugged with sediment, replace it with a new filter and decant the solution from the first filter into the second one.

25.13 Proceed with the assay of digested sample by atomic absorption spectrophotometry (flame atomization or graphite furnace atomization), plasma emission spectroscopy or plasma-mass spectrometry.

NOTE 8—Experience with this practice indicates that with sample and acid volumes in the ranges specified, the final volume after digestion will approximate the original sample volume within 2%. 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 digestion is not sufficiently close to the original sample volume, a dilution factor can be calculated and applied to the analytical results.

26. Keywords

26.1 digestion; flame atomic absorption spectroscopy; graphite furnace atomic absorption spectroscopy; inductively coupled plasma (ICP); metals; plasma-mass spectrometry; waste water; water

APPENDIX

(Nonmandatory Information)

X1. ASTM TEST METHODS FOR METALS BY FLAME ATOMIZATION ATOMIC ABSORPTION

X1.1 Table X1.1 lists the ASTM test methods for metals by flame atomization atomic absorption.

TABLE X1.1 Metals by Flame AAS

D 511	Test Methods for Calcium and Magnesium in Water
D 857	Test Methods for Aluminum in Water
D 858	Test Methods for Manganese in Water
D 1068	Test Methods for Iron in Water
D 1687	Test Methods for Chromium in Water
D 1688	Test Methods for Copper in Water
D 1691	Test Methods for Zinc in Water
D 1886	Test Methods for Nickel in Water
D 3372	Test Method for Molybdenum in Water
D 3557	Test Methods for Cadmium in Water
D 3558	Test Methods for Cobalt in Water
D 3559	Test Methods for Lead in Water
D 3645	Test Methods for Beryllium in Water
D 3866	Test Methods for Silver in Water
D 4191	Test Method for Sodium in Water by Atomic Absorption Spectrophotometry
D 4192	Test Method for Potassium in Water by Atomic Absorption Spectrophotometry

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