



Designation: **D4309 – 12 D4309 – 18**

## Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water<sup>1</sup>

This standard is issued under the fixed designation D4309; 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 the general considerations for quantitative sample digestion for total metals in water using closed vessel microwave heating technique. This practice is applicable to surface, saline, domestic, and industrial wastewater.

1.2 Because of the differences among various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument.

1.3 This practice can be used with the following ASTM standards, providing the user determines precision and bias based on this digestion practice: Test Method **D857**, Test Methods **D858**, Test Methods **D1068**, Test Methods **D1687**, Test Methods **D1688**, Test Methods **D1691**, Test Methods **D1886**, Test Method **D1976**, Practices **D3370**, Test Methods **D3557**, Test Methods **D3559**, Practice **D3919**, Test Method **D4190**, Practice **D4453**, Practice **D4691**, and Test Method **D5673**.

1.4 The values stated in SI units are to be regarded as standard. ~~No other units of measurement are included in this~~ The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

1.5 *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~~ safety, health, and ~~health~~ environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

1.6 *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:<sup>2</sup>

[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 Argon Plasma Atomic Emission Spectroscopy](#)

[D3370 Practices for Sampling Water from Closed Conduits](#)

[D3557 Test Methods for Cadmium in Water](#)

[D3559 Test Methods for Lead in Water](#)

[D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water](#)

[D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry](#)

<sup>1</sup> This practice is 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 1, 2012~~ Feb. 1, 2018. Published ~~March 2012~~ May 2018. Originally approved in 1991. Last previous edition approved in ~~2007~~ 2012 as **D4309 – 02 (2007)**; **D4309 – 12**. DOI: ~~10.1520/D4309-12~~ 10.1520/D4309-18.

<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.

\*A Summary of Changes section appears at the end of this standard

[D4190 Test Method for Elements in Water by Direct-Current Plasma Atomic Emission Spectroscopy](#)

[D4453 Practice for Handling of High Purity Water Samples](#)

[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 *U.S. Code of Federal Regulations*:<sup>3</sup>

[CFR 1.030.10 Code of Federal Regulations, Volume 21](#)

2.3 *Federal Communications Commission Standard*:<sup>3</sup>

[Code of Federal Regulations, Volume 47, FCC Rule Part 18](#)

2.4 *U.S. EPA Method*:<sup>4</sup>

[U.S. EPA Method: Methods for Chemical Analysis of Water and Waste—March 1979, “Total Metals Digestion Procedure” 4.1.3, page Metals 6](#)

[U.S. EPA Method: SW 846 Method 3015 Microwave Assisted Acid Digestion of Aqueous Samples and Extracts](#)

### 3. Terminology

3.1 ~~*Definitions—Definitions:* For definitions of terms used in this practice, refer to Terminology [D1129](#).~~

3.1.1 ~~For definitions of terms used in this standard, refer to Terminology [D1129](#).~~

### 4. Summary of Practice

4.1 A representative aliquot of a homogeneous sample is digested with acid in a closed microwave transparent vessel, using microwave heating. The digestate or a filtered digestate is then analyzed by direct aspiration or injection by flame atomic absorption spectrophotometry (FAAS), inductively coupled plasma emission techniques (ICP), direct current plasma emission techniques (DCP), graphite furnace atomic absorption spectrophotometry (GFAAS), inductively coupled plasma-mass spectrometry (ICP-MS), or a combination of methods.

### 5. Significance and Use

5.1 The analysis of many types of water for metals using flame atomic absorption spectrophotometry, inductively coupled plasma emission spectrophotometry, direct current plasma emission spectrophotometry, or graphite furnace atomic absorption spectrophotometry necessitates the use of a digestion practice in order to ensure the proper statistical recovery of the metals from the sample matrix. The use of closed vessel microwave techniques will speed the complete recovery of metals from the water matrices and eliminate sample contamination from external sources.

### 6. Interferences

6.1 No interferences have been observed using microwave heating.

6.2 Precautions should be exercised to avoid those interferences normally associated with the particular analytical method for metals determination.

6.3 This practice will not totally solubilize solid silicates that are suspended in or settle out of the water sample.

### 7. Apparatus

7.1 *Laboratory Microwave Heating System*, capable of delivering 575 to 1000 W of power. The unit should be capable of 1 % power adjustment and 1 s time adjustment. The oven cavity should be fluorocarbon-coated or coated with a material that has equivalent acid resistance and microwave properties and be equipped with exhaust ventilation at 2.8 m<sup>3</sup>/min (100 ft<sup>3</sup>/min) for acid vapor protection of the unit and operator. The unit must have a rotating or alternating turntable, capable of holding 1 to 14 digestion vessels, to ensure even sample heating. Safety interlocks, to shut off magnetron power output, must be contained in the oven door opening mechanism. The unit may contain a temperature control device capable of controlling vessel temperatures to 200°C and/or a pressure control device capable of controlling vessel pressures to a minimum ~~100 psi (690 kPa)~~ 690 kPa (100 psi).

7.1.1 The unit must comply with U.S. Health and Human Services Standards under CFR Part 1030.10, sub parts (C) (1), (C) (2), and (C) (3), for microwave leakage. The unit should have FCC-type approval for operations under FCC Rule Part 18.

7.2 *Closed Vessel*, capable of holding 100 mL of solution. The vessel must be transparent to microwave energy and capable of withstanding internal pressures of ~~100 psi (690 kPa)~~ 690 kPa (100 psi) and temperatures of 200°C. The vessel must contain a safety pressure relief valve, rupture disc, pressure venting system or be connected to an external safety relief valve that will prevent possible vessel rupture or ejection of the vessel cap.

7.3 *Apparatus*, to seal the vessel system to the manufacturer’s specified requirement.

<sup>3</sup> Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401-20401-0001, <http://www.access.gpo.gov>.

<sup>4</sup> Available from National Technical Information Service (NTIS), 5301 Shawnee Rd., Alexandria, VA 22312, <http://www.ntis.gov>.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this practice. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications for 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.

8.2 *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 sufficiently high purity to permit its use without adversely affecting the bias and precision of the method. Type II water was used for the data shown in **Appendix X1**.

8.3 *Hydrochloric Acid (sp gr 1.19) (HCl)*.

8.4 *Nitric Acid (sp gr 1.42) (HNO<sub>3</sub>)*.

8.5 *Nitric Acid (1 + 1)*—Add 1 volume of HNO<sub>3</sub> (sp gr 1.42) to 1 volume of water.

## 9. Hazards

9.1 The microwave unit should be operated in accordance with the manufacturer's recommended operating and safety precautions. **Caution**—It is not recommended to place a microwave unit in a fume hood, where it is surrounded by acid fumes, which can cause corrosion of the equipment. Acid fumes generated inside the oven cavity should be air swept away from the oven cavity to a hood.

9.2 **Precaution**—The closed vessel should be operated in accordance with the manufacturer's recommended operating and safety instructions.

## 10. Procedure

10.1 *Power Temperature Control*—procedure for 7 to 12 vessel digestions:

NOTE 1—For fewer than seven samples, see **10.2**.

10.1.1 Perform an instrument power check as outlined in **Annex A1**.

10.1.2 Refer to ASTM test methods for sampling and analysis (such as Guide **D3856**) to determine any sample preservation requirements.

10.1.3 Transfer 50.0 mL of a representative aliquot of the well-mixed sample into a clean vessel (see **Note 2**). If the sample is to be analyzed by ICP, ICP-MS, ICP-AES, DCP, or FAAS, add 3 mL of HNO<sub>3</sub> (sp gr 1.42) and 2 mL of HCl (sp gr 1.19). If the sample is to be analyzed by GFAAS, add 5 mL of HNO<sub>3</sub> (sp gr 1.42) (see **Note 3**). Install a safety pressure relief valve and cap on the vessel and seal to the manufacturer's recommended torque. Weigh the vessel, record the weight, and place in the microwave instrument turntable. Attach a vent tube, if required, by the manufacturer's operating instructions.

NOTE 2—Follow the manufacturer's suggested vessel cleaning instructions to avoid possible sample contamination.

NOTE 3—Final acid concentration of this procedure is 9 %. This may shorten graphite tube lifetime, which may cause deterioration of analyte recovery. The analyst may choose to dilute the digested solution to a lower acid percentage to increase graphite tube life.

10.1.4 Repeat **10.1.3** until the turntable contains 12 vessels. A reagent blank should be digested and analyzed along with the samples. If less than 12 samples are to be digested, fill the remaining vessels with 50 mL of water and add an equal amount of acid as added to the sample. It is critical to the procedure that the total volume of solutions equals 660 mL during digestion, and that each vessel contains an equal volume of acid. This is necessary to ensure uniform heating of all vessel solutions.

NOTE 4—It is not necessary to weigh the blank vessels containing 50 mL of reagent water.

10.1.5 Turn the microwave instrument exhaust on to the maximum fan speed. Activate the turntable so that it is rotating or alternating 360°.

10.1.6 For instruments delivering a measured power of 575 to 635 W, program the instrument time for 50 min and the power to 100 %. For instruments with a measured power of 635 to 700 W, program the instrument time for 30 min and the power for 100 %. These heating parameters will allow the samples to reach a maximum temperature of 164 ± 4°C (refer to **Fig. 1**). Instruments delivering greater than 700 W must be operated at reduced powers such that the sample heating rates match the heating rates in **Fig. 1**. Depress the start key and allow the sample mixtures to heat for the programmed time.

10.1.7 At the end of the digestion period, remove the vessels from the microwave and allow the sample solutions to cool to room temperature. Shake the vessels to mix the sample solutions and vent to atmosphere any gas pressure that may be present in the vessels. (**Warning**—Shake the vessel with caution to prevent any rapid out-gassing of vapor or liquid causing acid burns of the exposed skin of the operator.)

<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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

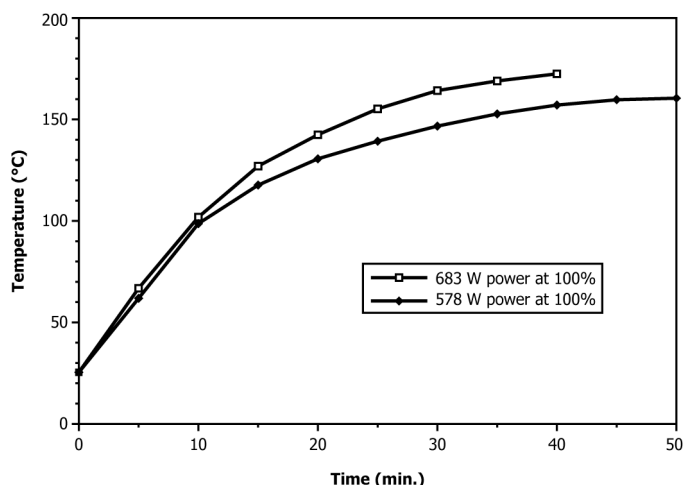


FIG. 1 Typical Heating Rates for 12 Vessels Containing 50 mL H<sub>2</sub>O, 3 mL HNO<sub>3</sub> (sp gr 1.42), 2 mL HCl (sp gr 1.19)

NOTE 5—**Warning**—Shake the vessel with caution to prevent any rapid out-gassing of vapor or liquid causing acid burns of the exposed skin of the operator.

10.1.8 Detach the vent tubing and remove the vessel assembly from the turntable. Weigh the cooled vessel system. If there is a weight loss greater than 0.5 g, open the vessel and add an amount of reagent water equal to the weight loss. Liquid loss of less than 10 % has not been found to result in any analyte loss (see Note 65). Recap the vessel and then shake the vessel to mix the sample solution.

NOTE 5—Samples containing large amounts of organics may experience excessive loss of liquid (greater than 10 %); therefore, a study may be required to determine if any analyte loss occurred.

10.1.9 Open the vessels and filter the samples, if required, to remove silicates and other insoluble materials. *Do not rinse or dilute the digested sample.* Final sample volume is 55 mL (see Note 3).

NOTE 6—In place of filtering, the sample after mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.1.10 Analyze the sample by ICP, ICP-MS, ICP-AES, DCP, FAAS, GFAAS, or ICP-MS, or a combination of methods, as required.

10.2 *Power Temperature Control*—procedure for 1 to 6 vessel digestions:

10.2.1 Perform an instrument power check as outlined in Annex A2.

10.2.2 Refer to individual ASTM test methods for sampling and analysis to determine any sample preservation requirements.

10.2.3 Transfer 50.0 mL of a representative aliquot of the well-mixed sample into a clean vessel (see Note 2). If the sample is to be analyzed by ICP, ICP-MS, ICP-AES, DCP, FAAS, or ICP-MS, add 3 mL of HNO<sub>3</sub> (sp gr 1.42) and 2 mL of HCl (sp gr 1.19). If the sample is to be analyzed by GFAAS (see Note 3) or some ICP-MS (see Note 87), add 5 mL of HNO<sub>3</sub> (sp gr 1.42). Install a safety pressure relief valve and cap on the vessel and then seal to the manufacturer's recommended torque. Weigh the vessel, record the weight, and place in the microwave instrument turntable. Attach a vent tube, if required by the manufacturer's operating instructions.

10.2.4 Repeat 10.2.3 until the turntable contains 6 evenly-spaced vessels. A reagent blank should be digested and analyzed along with the samples. If fewer than 6 samples are to be digested, fill remaining vessels with 50 mL of reagent water and add an equal amount of acid to the samples. It is critical to the procedure that the total volume of solutions equals 330 mL during digestion, and that each vessel contains an equal volume of acid. This is necessary to ensure uniform heating of all vessel solutions (see Note 4).

10.2.5 Turn the microwave instrument exhaust on to the maximum fan speed. Activate the turntable so that it is rotating or alternating 360°.

10.2.6 For instruments with a measured power of 575 to 635 W, program the instrument time for 30 min and 75 % power. For instruments with a measured power of 635 to 700 W, program the instrument time for 25 min and 75 % power. These heating parameters will allow the samples to reach a maximum temperature of 165 ± 5°C (refer to Fig. 2). Instruments delivering greater than 700 W must be operated at reduced powers such that the sample heating rates match the heating rates in Fig. 2. Follow the manufacturer's suggested procedures to measure the instrument's power. Depress the start key and allow the sample mixtures to heat for the programmed time.

10.2.7 At the end of the digestion period, remove the vessels from the microwave and allow the sample solutions to cool to room temperature. Shake the vessels to mix the sample solutions, and vent to atmosphere any gas pressure that may be present in the vessels (see Note 510.1.7).