



Designation: D5513 – 22

Standard Practice for Microwave Digestion of Industrial Furnace Feed Streams and Waste for Trace Element Analysis¹

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1. Scope

1.1 This practice describes the multi-stage microwave digestion of typical industrial furnace feed stream materials using nitric, hydrofluoric, hydrochloric, and boric acids for the subsequent determination of trace metals.

1.2 This practice has been used successfully on samples of coal, coke, cement raw feed materials, and waste-derived fuels composed primarily of waste paint-related material in preparation for measuring the following trace elements: Ag, As, Ba, Be, Cd, Cr, Hg, Pb, Sb, and Tl. This practice may be applicable to elements not listed above.

1.3 This practice is also effective for other waste materials (for example, fly ash, foundry sand, alum process residue, cement kiln dust, etc.).

1.4 The values stated in SI units are to be regarded as standard. Other units of measurement in parentheses in this standard are informational.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 8.

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:*²

D1193 Specification for Reagent Water

D5681 Terminology for Waste and Waste Management

2.2 *Other Document:*

40 CFR 266 Subpart H, Hazardous Waste Burned in Boilers and Industrial Furnaces, Latest Revision³

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology D5681.

4. Summary of Practice

4.1 A weighed portion of the feed stream material is combined with concentrated nitric acid in a polytetrafluoroethylene-lined digestion vessel, and heated in a microwave digestion unit. Following a programmed heating cycle, the vessel is vented and specified quantities of hydrofluoric and hydrochloric acids are added, and the mixture undergoes further microwave heating. Following this heating cycle, the vessel is vented and a specified quantity of boric acid solution is added, and the mixture undergoes a final microwave heating. Following this final heating cycle, the vessel is vented, the contents are quantitatively transferred to a volumetric flask, and brought to volume. Typically, the only undissolved material is particulate carbon. If particulate matter is observed, filtration or centrifugation may be needed. The digested sample is ready for analysis.

5. Significance and Use

5.1 The U.S. Environmental Protection Agency Regulations, 40 CFR 266, require that boilers, cement kilns, and other industrial furnaces utilizing waste-derived fuel adhere to specific guidelines in assessing potential metals emissions. A common approach for estimating potential emissions is performing total metals analysis on all feed stream materials.

¹ This practice is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

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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.

³ Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

This practice describes a multi-stage microwave-assisted digestion procedure that solubilizes trace elements for spectroscopic analyses.

6. Apparatus

6.1 *Microwave Digestion Unit*—Equipped with an automatic turntable, pressure and/or temperature controller, and closed perfluoroalkoxy (PFA)-lined digestion vessels equipped with pressure relief/rupture membrane fittings or equivalent pressure relief device. The unit should comply with applicable regional, federal, or state standards for microwave leakage. The user must follow specific manufacturer's instructions for system installation.

NOTE 1—The digestion unit used in developing this practice was equipped with a pressure controller, automatic turntable, exhaust fan, and programming capacity. The unit delivered 1000 W of power at 100 % output. The lined digestion vessels consisted of a high-strength polymeric vessel body and cap, inner PFA liner and rupture membrane housing, and PFA vent stem. These vessels have a maximum operating pressure of 1378.9 kPa (200 psig). There are a number of suitable lab grade microwave systems available to the user that meet these minimum specifications. The user must follow specific manufacturer's instructions for using digestion vessels.

6.2 *Analytical Balance*—Capable of weighing to 0.001 g (1 mg).

6.3 *Labware*—High-density volumetric polyethylene or polypropylene flasks/sample containers are recommended for this practice. The user should be mindful of the quality limitations associated with volumetric non-glass labware.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean meeting the numerical requirements of Type II water as defined by Specification D1193.

7.3 *Boric Acid Solution (20 g/L)*—Dissolve 20 g of boric acid (H_3BO_3) in water and dilute to 1 L. It may be necessary to place solution on a combination hot plate/magnetic stirrer and with the aid of a stir bar, allow the solution to mix under gentle heat until boric acid is fully in solution.

7.4 *Hydrochloric Acid, 37 %*, (sp. gr. 1.200), HCl.

7.5 *Hydrofluoric Acid, 48 %*, (sp. gr. 1.150), HF.

7.6 *Nitric Acid, 70 %*, (sp. gr. 1.400), HNO_3 .

⁴ *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.

8. Hazards⁵

8.1 It is recommended that all operations involving concentrated acids be performed in a laboratory fume hood.

8.2 Hydrochloric acid is a highly corrosive chemical that is reactive with metals and most alkaline chemicals. Impervious gloves and chemical goggles are required for handling. See Safety Data Sheet (SDS) for additional information.

8.3 Hydrofluoric acid is a highly corrosive chemical that is reactive with metals and water or steam. Additionally, HF specifically attacks silicate glass, making certain fume hood enclosures susceptible to damage. Impervious gloves and chemical goggles are required for handling. See SDS for additional information.

8.4 Nitric acid is a highly corrosive chemical that is reactive with metals and most organic materials. Impervious gloves and chemical goggles are required for handling. See SDS for additional information.

8.5 Some samples undergoing microwave digestion can exhibit a rapid pressure rise within the digestion vessel. The potential exists for this type of sample to rupture the rupture membrane and liberate corrosive gases. Because of this, the microwave unit must be vented to a fume hood for proper evacuation of vapors.

9. Sample

9.1 Although feed stream materials are generally pulverized powders or liquids, the homogeneity of some feed stream materials can be uncertain. The laboratory sample should be thoroughly mixed or homogenized prior to withdrawing a portion for analysis. This practice assumes that non-liquid feed streams are pulverized powders at the time of sample preparation.

NOTE 2—If a non-liquid feed stream material is not in the form of a pulverized powder, it may need to be reduced in particle size to pass through a No. 100 sieve.

10. Calibration and Standardization

10.1 Although equipment manufacturers specify general power output ratings for microwave digestion units, it is important to verify the actual power output of a specific unit. It is recommended, and may be required in some applications, that this microwave power check procedure be performed monthly.

10.1.1 *Power Check Procedure at 100 % Instrument Power:*

10.1.1.1 Remove from the instrument cavity the turntable, drive lug, and all vessels.

10.1.1.2 Adjust the instrument cavity exhaust to minimum air flow (refer to the manufacturer's instructions).

10.1.1.3 Program the instrument for 4 min time and 100 % power.

10.1.1.4 Transfer 2000 ± 2 mL of room temperature (19 to 25 °C) water into a 2 L polypropylene beaker.

10.1.1.5 Measure and record the initial water temperature (T_i) to the nearest 0.1 °C.

⁵ This information taken from the *NIOSH Guide to Chemical Hazards*, U.S. Department of Health and Human Services, June 1990.

10.1.1.6 Place the beaker in the right front corner of the instrument cavity (as you face the front of the instrument). This position closely approximates the position of a digestion vessel during processing.

10.1.1.7 Heat the water for the programmed time.

10.1.1.8 When the heating cycle is complete, immediately remove the beaker from the cavity, thoroughly stir the water to ensure even heat distribution, and measure the final temperature (T_f) to the nearest 0.1 °C.

10.1.1.9 Calculate the delivered power in accordance with the following equations:

$$\text{Power (watts)} = \Delta T \times (35 \text{ W/}^\circ\text{C}) \quad (1)$$

where:

$$\Delta T = T_f - T_i$$

$$\text{W/}^\circ\text{C} = \frac{K \times C_p \times M}{t}$$

where:

W = watts,

K = 4.2, the factor for converting thermo-chemical calories/s to joules to watts,

C_p = 1.0, the heat capacity for water, cal g⁻¹ degree⁻¹,

M = mass of water, g (1 mL H₂O = 1 g), and

t = time, s.

10.1.1.10 If the calculated power is not within the specifications of the unit, do a second test beginning at 10.1.1.1 for confirmation before contacting the manufacturer.

11. Procedure

NOTE 3—Many microwave digestion units are capable of handling up to twelve digestion vessels at a time. The number of vessels processed affects the required program settings. The microwave program examples given in Annex A1 and Annex A2 were developed to accommodate ten pressure vessels and have been proven effective in field testing. A maximum pressure of 965.27 kPa (140 psi) for a minimum time at pressure of 10 min is generally sufficient for sample digestion. A complete digestion can be verified by the user by processing reference materials and calculating analyte recoveries.

11.1 Process coal, coke, cement raw feed, and other geologic/inorganic materials as follows:

11.1.1 Weigh 0.5 g of the feed stream material directly in a PFA digestion vessel liner and record the mass to the nearest 0.01 g.

11.1.2 Place the liner with sample in the digestion vessel body and with a pipet unit or equivalent device, slowly add 8 mL HNO₃ to the PFA liner. If a chemical reaction is observed, allow the reaction to subside prior to performing 11.1.3.

11.1.3 Place the pressure controller cap assembly on the vessel body, and hand tighten to achieve a firm fit. Do not over tighten because this can damage the sealing surface and threads.

11.1.4 Be sure the pressure relief/rupture membrane screw-type fitting houses a new rupture membrane, and is tightened to finger tightness. Do not over tighten because this can potentially deform the rupture membrane and damage the threads. If a rupture membrane bursts during the digestion, stop the

digestion and remove the vessel with the ruptured membrane from the turntable and resume digestion. Discard the sample in the removed vessel.

11.1.5 Place the vessel in the microwave turntable. Insert the pressure sensing tubing from the pressure controller into the pressure controller cap assembly and tighten to finger tightness. Be sure that the pressure sensing tubing is filled with water (from the pressure controller unit to the pressure control vessel) prior to inserting this line.

11.1.6 Repeat 11.1.1 and 11.1.2 for three or five additional vessels. Cap these vessels with standard vessel cap assemblies. Be sure each vessel cap assembly is tightened to firmness. Evenly distribute the digestion vessels in the turntable to ensure uniform heating of all vessels.

11.1.7 It is recommended, and required in some applications, that a blank and a certified reference standard or a matrix spike be processed with each batch of samples of similar composition. Generally, a batch is a group of samples that are processed together by the same method, reagents, and the same manipulation. The user needs to determine the number of samples comprising a batch based on the user's quality assurance requirements.

11.1.8 The samples are ready for microwave processing. Process the samples by following the Stage 1 microwave program described in Annex A1. Be sure the instrument cavity exhaust is set to maximum air flow.

11.1.9 Following the cooling step (0 power) in Stage 1, the vessels should be cool to the touch. Additional cooling time may be necessary if vessels remain hot. Vent the vessels in a laboratory fume hood or the microwave oven cavity by slowly unscrewing the pressure relief/rupture membrane fitting. Vent the pressure control vessel in the microwave to remove the pressure sensing tubing. Remove the vessel cap assemblies.

11.1.9.1 Flush the pressure sensing tubing with water to remove any trace of acid. This is an important step, because damage will occur to the pressure controller if an acidic solution from the pressure sensing tubing is allowed to migrate to the pressure controller. The flush water should be disposed of as a waste.

11.1.9.2 Using a polyethylene syringe or other equivalent compatible device, add 4 mL of HF and 2 mL of HCl to each vessel. If a chemical reaction is observed, allow the reaction to subside prior to performing 11.1.9.3.

NOTE 4—The user may choose to vary the amounts of HF and HCl based on prior knowledge of the sample. Samples known to be low in siliceous material may require a smaller amount of HF than other samples. In no case should the user reduce the amount of HF or HCl below a 2 mL volume for each acid.

11.1.9.3 Recap the digestion vessels, making sure the pressure relief/rupture membrane fitting is tightened to finger tightness. Replace the digestion vessels in the turntable, and reconnect the pressure sensing tubing to the pressure control vessel. Be sure that the pressure sensing tubing is filled with water. Place the remaining digestion vessels in the turntable.

11.1.9.4 The samples are ready for microwave processing. Process the samples by following the Stage 2 microwave program described in Annex A1.

11.1.9.5 Following the cooling step, vent the vessels as described in 11.1.9. Remove the vessel cap assemblies, flush, and fill the pressure sensing tubing with water.

11.1.9.6 Add 35.5 mL of H₃BO₃ solution to each vessel, and recap as described in 11.1.9.1.

11.1.9.7 The samples are ready for final microwave processing. Process the samples by following the Stage 3 microwave program described in Annex A1.

11.1.9.8 Following the vessel cooling step, vent the vessels as described in 11.1.9. Remove the vessel cap assemblies, flush, and fill the pressure sensing tubing with water.

11.1.9.9 Quantitatively transfer the digested sample solution to a clean polyethylene 50 mL volumetric flask and bring to volume with water. If any particulate matter is observed, it may be removed by filtration or centrifugation.

NOTE 5—Typically, the only undissolved material is particulate carbon, which is readily removed by centrifugation. If filtration is used, the appropriate filter must be cleaned and pre-rinsed with a 1 *N* nitric acid solution.

11.1.9.10 Transfer the sample solution to a clean polyethylene sample container.

11.1.9.11 The sample is now ready for analysis.

11.2 *Waste-Derived Fuels, Oils, and Other High Organic Content Samples*—The procedure for the microwave-assisted digestion of waste-derived fuel samples or other high organic

content samples is the same as outlined in 11.1, except that (1) the user may wish to reduce the sample mass to lessen the possibility of vessel overpressurization, and (2) the Annex A2 microwave program should be followed. It should be noted that the programs in Annex A2 include a cooling step in Stage 2, and a more gradual initial temperature ramp in Stage 1. These steps are important because some waste-derived fuels can be somewhat reactive in the presence of concentrated acids and can exhibit a rapid pressure increase resulting in the venting of the digestion vessel(s). These steps will lessen the likelihood of venting the vessels.

12. Precision and Bias


12.1 *Precision*—No statement is made about the precision since this practice does not produce a specific test result.

12.2 *Bias*—No statement is made about the bias since this practice does not produce a specific test result.

12.3 Appendix X1 contains analytical results obtained following this procedure on National Institute of Standards and Technology (NIST) standard reference materials and paraffin oil-based metals standards.

13. Keywords

13.1 cement; coal; coke; microwave digestion; trace elements; trace metals; waste; waste-derived fuel


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