Designation: D 5513 – 99

Standard Practice for
Microwave Digestion of Industrial Furnace Feedstreams and Waste for Trace Element Analysis[1]

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1. Scope

1.1 This practice describes the multi-stage microwave digestion of typical industrial furnace feedstream 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 previously listed.

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

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.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specifications for Reagent Water[2]

2.2 *Other Document:*

40 CFR 266, Subpart H, Hazardous Waste Burned in Boilers and Industrial Furnaces, Latest Revision[3]

3. Summary of Practice

3.1 A weighed portion of the feedstream 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.

4. Significance and Use

4.1 The U.S. Environmental Protection Agency Regulations, 40 CFR, 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 feedstream materials. This practice describes a multi-stage microwave-assisted digestion procedure that solubilizes trace elements for spectroscopic analyses.

5. Apparatus

5.1 *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 federal or state standards, or both, 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 delivers 1000 W of power at 100 % output. The lined digestion vessels consist 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 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.

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

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

5.2 *Analytical Balance*—Capable of weighing to 0.001 g.

5.3 *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.

6. Reagents and Materials

6.1 *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.

6.2 *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 Specifications D 1193.

6.3 *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.

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

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

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

7. Hazards [5]

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

7.2 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 material safety data sheet (MSDS) for additional information.

7.3 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 MSDS for additional information.

7.4 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 MSDS for additional information.

7.5 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.

8. Sample

8.1 Although feedstream materials are generally pulverized powders or liquids, the homogeneity of some feedstream 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 feedstreams are pulverized powders at the time of sample preparation.

NOTE 2—If a non-liquid feedstream 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.

9. Calibration and Standardization

9.1 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 that this microwave power check procedure be performed monthly.

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

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

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

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

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

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

9.1.1.6 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.

9.1.1.7 Heat the water for the programmed time.

9.1.1.8 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.

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

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

where:
ΔT = $T_f - T_i$.
W/°C = $\dfrac{K \times Cp \times M}{t}$

where:
W = watts,
K = 4.2, the factor for converting thermo-chemical calories/s to joules to watts.
Cp = 1.0, the heat capacity for water, cal g^{-1} $degree^{-1}$,
M = mass of water, g (1 mL H_2O = 1 g), and
t = time, s.

9.1.1.10 If the calculated power is not within the specifications of the unit, do a second test beginning at 9.1.1.1 for confirmation before contacting the manufacturer.

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[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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

10. Procedure

NOTE 3—Many microwave digestion units are capable of handling up to 12 digestion vessels at a time. The number of vessels processed affects the required program settings. The microwave program examples given in Annexes A1 and A2 were developed to accommodate 10 pressure vessels have been proven effective in field testing. A maximum pressure of 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.

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

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

10.1.2 Place the liner with sample in the digestion vessel body and with a pipet unit, or equivalent device, slowly add 8 mL HNO_3 to the PFA liner. If a chemical reaction is observed, allow the reaction to subside prior to performing 10.1.3.

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

10.1.4 Be sure the pressure relief/rupture membrane screw-type fitting houses a new rupture membrane, and is tightened to finger-tightness. Do not overtighten 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.

10.1.5 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 completely filled with water (from the pressure controller unit to the pressure control vessel) prior to inserting this line.

10.1.6 Repeat 10.1.1 and 10.1.2 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.

10.1.7 It is recommended 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 considered to be samples that are processed together by the same method, reagents, and the same manipulation. The user will need to determine the number of samples comprising a batch based on the user's quality assurance requirements.

10.1.8 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.

10.1.9 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 in order to remove the pressure sensing tubing. Remove the vessel cap assemblies.

10.1.9.1 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.

10.1.9.2 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 10.1.9.3.

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 lesser amount of HF. In no case should the user reduce the amount of HF or HCl below a 2-mL volume for each acid.

10.1.9.3 Recap the digestion vessels, making sure the pressure relief/rupture membrane fitting is tightened to finger-tighteness. 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 completely filled with water. Place the remaining digestion vessels in the turntable.

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

10.1.9.5 Following the vessel cooling step, vent the vessels as described in 10.1.9. Remove the vessel cap assemblies, flush and fill the pressure sensing tubing with water.

10.1.9.6 Add 35.5 mL of H_3BO_3 solution to each vessel, and recap as described in 10.1.9.1.

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

10.1.9.8 Following the vessel cooling step, vent the vessels as described in 10.1.9. Remove the vessel cap assemblies, flush and fill the pressure sensing tubing with water.

10.1.9.9 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.

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

10.1.9.11 The sample is now ready for analysis.

10.2 *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 10.1, 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.

11. Precision and Bias

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

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

11.3 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.

12. Keywords

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

ANNEXES

(Mandatory Information)

A1. DIGESTION PROGRAM FOR COAL, COKE, RAW FEED, AND FLY ASH

STAGE 1 – Add: sample, HNO_3	(1)	(2)	(3)
Power	65 %	60 %	0 %
PSI	140	140	0
Time	30.0	30.0	10.0
TAP^A	7.00	10.00	10.00

STAGE 2 – Add: HC1, HF	(1)	(2)	(3)
Power	60 %	45 %	0 %
PSI	140	140	0
Time	30.0	30.0	10.0
TAP^A	6.00	10.00	10.00

STAGE 3 – Add: H_3BO_3 solution	(1)	(2)	(3)
Power	65 %	58 %	0 %
PSI	50	50	0
Time	30.0	30.0	10.0
TAP^A	4.00	5.00	10.00

[A] TAP = time at pressure.

A2. DIGESTION PROGRAM FOR HIGH ORGANIC CONTENT SAMPLES

STAGE 1 – Add: sample, HNO_3	(1)	(2)	(3)
Power	65 %	60 %	0 %
PSI	140	140	0
Time	30.0	30.0	10.0
TAP[A]	7.00	10.00	10.00

STAGE 2 – Add: HC1, HF	(1)	(2)	(3)	(3)
Power	60 %	0	45 %	0 %
PSI	140	140	140	0
Time	30.0	10.0	30.0	10.0
TAP[A]	6.00	3.00	10.00	10.00

STAGE 3 – Add: H_3BO_3 solution	(1)	(2)	(3)
Power	65 %	58 %	0 %
PSI	50	50	0
Time	30.0	30.0	10.0
TAP[A]	4.00	5.00	10.00

[A] TAP = time at pressure.

APPENDIX

(Nonmandatory Information)

X1. ANALYTICAL RESULTS OF NIST PARAFFINIC OIL-BASED STANDARDS

Element[A]	SRM 1632b Bituminous Coal Value, mg/kg	Digestion Result, mg/kg	Recovery, %	SRM 2704 Buffalo River Sediment Value, mg/kg	Digestion Result, mg/kg	Recovery, %	SRM 1633a Coal Fly Ash Value, mg/kg	Digestion Result, mg/kg	Recovery, %	Oil-based Metals Standards Value, mg/kg	Digestion Result, mg/kg	Recovery, %
Ag	...	1.6	...	...	1.9	...	...	1.12	...	500	484.6	96.9
As	3.72	4.1	110.2	23.4	21.0	89.7	145	140.9	97.2	100	97.5	97.5
Ba	67.5	58	85.9	414	319	77.1	1500	1253	83.5	500	465	93
Be	...	1.2	...	...	1.9	...	(12)	24.8	...	5000	4830	96.6
Cd	0.0573	<2.0	...	3.45	<2.0	...	1	1.1	110.0	500	489	97.8
Cr	(11)	13	118.2	135	113	83.7	196	182	92.9	500	502	100.4
Hg	...	...	...	1.44	1.55	107.6	0.16	0.12	75.0	100	91.8	91.8
Pb	3.67	<5.0	...	161	155	96.3	72.4	73	100.8	500	492	98.4
Sb	(0.24)	<0.5	...	3.79	3.7	97.6	6.8	6.2	91.2	5000	4900	98
Tl	...	...	...	1.2	1.5	125.0	5.7	5.9	103.5	...	...	...

[A] Elemental analysis by flame and graphic furnace atomic absorption. Mercury analysis by cold vapor atomic absorption.

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