



Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water¹

This standard is issued under the fixed designation D 4309; 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 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 Methods D 857, Test Methods D 858, Test Methods D 1068, Specification D 1192, Test Methods D 1687, Test Methods D 1688, Test Methods D 1691, Test Methods D 1886, Practices D 3370, Test Methods D 3557, Test Methods D 3559, Practice D 3919, Test Methods D 4190, Practice D 4453, and Practice D 4691.

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.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:

- 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 3370 Practices for Sampling Water from Closed Conduits²

D 3557 Test Methods for Cadmium in Water²

D 3559 Test Methods for Lead in Water²

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water²

D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²

D 4190 Test Methods for Elements in Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy²

D 4453 Practice for Handling of Ultra-Pure Water Samples²

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

2.2 U.S. Code of Federal Regulations:

CFR 1.030.10 Code of Federal Regulations, Volume 21³

2.3 Federal Communications Commission Standard:

Code of Federal Regulations, Volume 47, FCC Rule Part 18³

2.4 U.S. EPA Method:

U.S. EPA Method: Methods for Chemical Analysis of Water and Waste—March 1979, “Total Metals Digestion Procedure” 4.1.3, page Metals 6⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D 1129.

4. Summary of Practices

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), or graphite furnace atomic absorption spectrophotometry (GFAAS), or a combination of methods.

¹ This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² Annual Book of ASTM Standards, Vol 11.01.

³ Available from Office of the Federal Register, National Archives Records Administration, Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20401.

⁴ Available from National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161.

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 m³/min (100 ft³/min) for acid vapor protection of the unit and operator. The unit must have a rotating or alternating turntable, capable of holding 1 to 12 digestion vessels, to ensure even sample heating. Safety interlocks, to shut off magnetron power output, must be contained in the oven door opening mechanism.

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 psig and temperatures of 200°C. The vessel must contain a safety pressure relief valve, rupture disc, 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 tighten the vessel system cap to the manufacturer's specified torque.

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.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.

8.2 *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 adversely affecting the bias and precision of the method. Type II water was used for the data shown in Appendix 1.

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

8.4 *Nitric Acid (sp gr 1.42) (HNO₃)*.

8.5 *Nitric Acid (1 + 1)*—Add 1 volume of HNO₃(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 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 D 3856) 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, DCP, or FAAS, add 3 mL of HNO₃ (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 HNO₃(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.

⁵ *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.

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 $164 \pm 4^\circ\text{C}$ (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.

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 6). Recap the vessel and then shake the vessel to mix the sample solution.

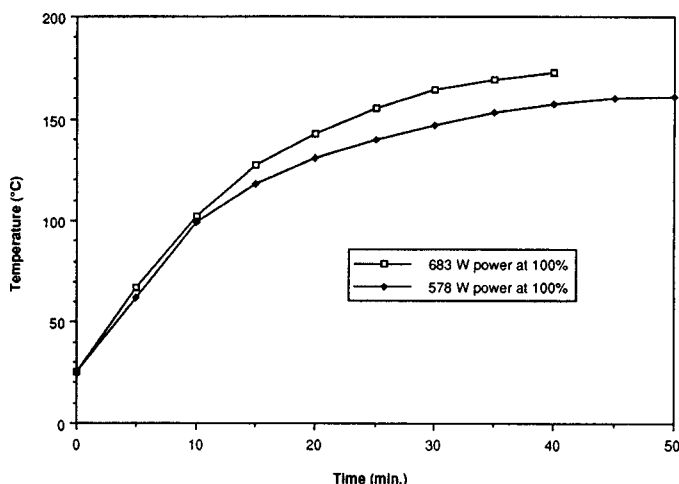


FIG. 1 Typical Heating Rates for 12 Vessels Containing 50 mL H_2O , 3 mL HNO_3 (sp gr 1.42), 2 mL HCl (sp gr 1.19)

NOTE 6—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 7—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, DCP, FAAS or GFAAS, or a combination of methods, as required.

10.2 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, DCP, or FAAS, add 3 mL of HNO_3 (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_3 (sp gr 1.42) (see Note 3). 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 $165 \pm 5^\circ\text{C}$ (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 5).

10.2.8 Detach the vent tubing and remove the vessel assembly from the turntable. Weigh the cooled vessel system. If there

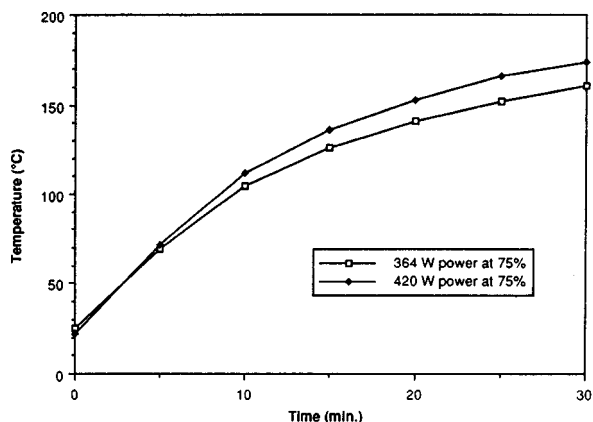


FIG. 2 Typical Heating Rates for 6 Vessels Containing 50 mL H₂O, 3 mL HNO₃(sp gr 1.42), 2 mL HCl (sp gr 1.19)

is a weight loss greater than 0.5 g, open the vessel and add an amount of reagent water equal to the weight loss (see Note 6). Recap the vessel and then shake the vessel to mix the sample solution. Liquid loss of less than 10 % has not been found to result in any analyte loss.

10.2.9 Open the vessels and filter the samples, if required, to remove silicates and other insoluble material. *Do not rinse or dilute the digested sample.* Final sample volume is 55 mL (see Note 3 and Note 7).

10.2.10 Analyze the sample by ICP, DCP, FAAS, or

GFAAS, or a combination of methods, as required.

11. Calculation

11.1 The analyst is to refer to the specific standard test method for either ICP, DCP, FAAS, or GFAAS, or combination of methods. The standard test methods contain all the information for constructing calibration curves and calculations necessary for the determination of the metal concentrations in the water matrices under which they were tested.

12. Precision and Bias

12.1 *Precision*—This practice was tested by digesting different samples of NPDES effluent water by one laboratory. Table X1.1 contains element concentration recovery conducted on four portions of the samples digested by this practice and by EPA Digestion Procedure 4.1.3. All element concentrations were determined by inductively coupled plasma spectroscopy techniques.

12.2 Precision and bias for the standards listed in 1.3 were determined using the total recoverable metals digestion procedures included in those standards and are not applicable to this practice. It is the responsibility of the user to establish the precision and bias of the digestion practice in conjunction with the analytical measuring method.

13. Keywords

13.1 digestion; metals; microwave; vessel

ANNEXES

(Mandatory Information)

A1. POWER CHECK AT 100% INSTRUMENT POWER

A1.1 Procedure:

A1.1.1 Remove from the instrument cavity the turntable, drive lug, and all vessels.

A1.1.2 Adjust the instrument cavity exhaust to minimum air flow.

A1.1.3 Program the instrument for 4 min time and 100 % power.

A1.1.4 Transfer 2000 mL \pm 2 mL of room temperature (19 to 25°C) water into a 2-L polypropylene beaker.

A1.1.5 Measure and record the initial water temperature (T_i) to the nearest 0.1°C.

A1.1.6 Place the beaker in the right front corner of the instrument cavity (as you face the front of the instrument).

A1.1.7 Heat the water for the programmed time.

A1.1.8 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.

A1.1.9 Calculate the delivered power according to Eq. 1:

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

where:

ΔT = $T_f - T_i$, where

T_f = final water temperature, °C, and

T_i = initial water temperature, °C,

35 = $K \times C_p \times M/t$, where

K = 4.2, the conversion factor for thermochemical calories to Watts,

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

M = mass of water, g,

t = time, s.

A2. POWER CHECK AT 75% INSTRUMENT POWER

A2.1 Procedure:

A2.1.1 Remove from the instrument cavity the turntable, drive lug and all vessels.

A2.1.2 Adjust the instrument cavity exhaust to minimum air flow.

A2.1.3 Program the instrument for 4 min time and 75 % power.

A2.1.4 Transfer 2000 mL \pm 2 mL of room temperature (19 to 25°C) water in a 2-L polypropylene beaker.

A2.1.5 Measure and record the initial water temperature (T_i) to the nearest 0.1°C.

A2.1.6 Place the beaker in the right front corner of the instrument cavity (as you face the front of the instrument).

A2.1.7 Heat the water for the programmed time.

A2.1.8 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.

A2.1.9 Calculate the delivered power according to Eq. 1.

APPENDIX

(Nonmandatory Information)

X1. Table X1.1

X1.1 Table X1.1

TABLE X1.1 Comparison of Element Recovery for EPA Digested versus Microwave Digested NPDES Waste Water Samples

Aluminum								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3483	0.453	0.433	0.395	0.396	0.450	0.432	0.410	0.506
3721	0.470	0.454	0.470	0.463	0.468	0.464	0.461	0.462
3728	0.235	0.208	0.240	0.241	0.228	0.206	0.196	0.230
Arsenic								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
1094	0.445	0.472	0.456	0.464	0.444	0.432	0.444	0.460
3331	0.366	0.371	0.365	0.380	0.370	0.360	0.351	0.358
4952	0.450	0.459	0.434	0.407	0.434	0.448	0.439	0.434
Barium								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3351	0.035	0.035	0.035	0.037	0.036	0.036	0.035	0.036
3469	0.014	0.015	0.016	0.016	0.016	0.016	0.015	0.015
4911	0.072	0.076	0.070	0.071	0.072	0.071	0.073	0.072
Cadmium								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3331	0.039	0.041	0.039	0.039	0.042	0.036	0.042	0.039
3471	0.051	0.049	0.043	0.048	0.050	0.052	0.048	0.052
4952	0.051	0.052	0.050	0.047	0.053	0.053	0.055	0.055
Antimony								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3312	0.452	0.429	0.372	0.350	0.486	0.481	0.492	0.476
3313	0.425	0.506	0.438	0.452	0.440	0.438	0.450	0.414
3331	0.218	0.373	0.390	0.272	0.408	0.392	0.395	0.412
Chromium								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
2911	0.047	0.050	0.043	0.043	0.044	0.044	0.045	0.042
3479	0.053	0.054	0.051	0.050	0.054	0.058	0.052	0.054
3312	0.073	0.080	0.082	0.076	0.078	0.075	0.074	0.076

Copper								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3331	0.106	0.106	0.103	0.107	0.104	0.101	0.105	0.106
3351	0.153	0.190	0.182	0.158	0.167	0.166	0.164	0.161
4952	0.036	0.036	0.037	0.033	0.035	0.036	0.037	0.035
Iron								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
1211	2.48	2.49	2.42	2.54	2.50	2.53	2.52	2.49
3479	6.12	5.96	5.92	5.97	6.51	6.27	6.21	6.12
4911	0.452	0.442	0.444	0.442	0.426	0.419	0.432	0.424
Manganese								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
1061	0.212	0.213	0.243	0.246	0.238	0.237	0.233	0.233
1094	0.030	0.032	0.029	0.034	0.032	0.030	0.030	0.033
4911	0.113	0.110	0.112	0.110	0.110	0.109	0.113	0.108
Nickel								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3441	0.397	0.402	0.401	0.411	0.402	0.399	0.401	0.404
3661	0.103	0.102	0.099	0.098	0.106	0.105	0.107	0.102
4952	0.436	0.440	0.433	0.394	0.424	0.426	0.424	0.432
Lead								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
1031	0.375	0.412	0.362	0.366	0.369	0.371	0.368	0.362
3312	0.209	0.206	0.212	0.206	0.199	0.202	0.190	0.198
3351	0.976	1.08	1.09	1.06	1.02	1.03	1.05	1.03
Silver								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3861	0.070	0.074	0.060	0.066	0.082	0.077	0.077	0.071
4952	0.014	0.009	0.012	0.013	0.013	0.011	0.012	0.014
7395	0.312	0.139	0.148	0.135	0.449	0.456	0.440	0.431
Selenium								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
3351	0.836	0.834	0.850	0.825	0.825	0.826	0.842	0.809
4911	0.753	0.748	0.752	0.728	0.758	0.709	0.773	0.765
4952	0.662	0.654	0.638	0.656	0.634	0.623	0.674	0.648
Zinc								
Sample No.	EPA Digested, mg/L					Microwave Digested, mg/L		
2621	0.332	0.340	0.354	0.342	0.320	0.322	0.326	0.333
3471	1.71	1.74	1.71	1.69	1.75	1.79	1.75	1.75
4911	0.025	0.019	0.021	0.021	0.022	0.020	0.023	0.023

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