METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum
Antimony
Arsenic
Boron
Barium
Beryllium
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Potassium
Selenium
Silver
Sodium
Strontium
Thallium
Vanadium
Zinc

1.2 This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3051.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5 ± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several signifant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vesselsequippedres, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mecahnisms or containers with PFA-fluorocarbon liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

<u>CAUTION</u>: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, glass or disposable polypropylene.

4.5 Analytical balance, 300 g capacity, and minimum ± 0.01 g.

5.0 REAGENTS

5.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.1.1 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, sec. 3.1.3 of this manual, for further information.

6.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section

7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using athe procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2°C). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2°C measured to ± 0.05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05°C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2°C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1 $$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W) ($W = joule \cdot sec^{-1}$)

K = the conversion factor for thermochemical $calories \cdot sec^{-1}$ to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat ($cal \cdot g^{-1} \cdot {}^{\circ}C^{-1}$) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 $cal \cdot g^{-1} \cdot {}^{\circ}C^{-1}$) the calibration equation simplifies to:

Eq. 2 $$P = (\Delta T)\ (34.86)$$

> <u>NOTE</u>: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and capassembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: All samples known or suspected of containing more than 5-10% organic material should be predigested in a hood for at least 15 minutes.

7.3.4 Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi). All vessels should be sealed according to the manufacturers recommended specifications.

7.3.4.1 Newer microwave units are capable of higher power (W) that permits digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3051, as determined by the statistical examination of interlaboratory test results, is located in Tables 1 and 2.

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206\ x$$

in the long run, where x is one result in µg/g (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303\ x$$

in the long run, where x is the average of two successive measurements in µg/g (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

10.0 REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1986; SW-846.

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TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

Element	Repeatability	Reproducibility
Ag	0.195X[a]	0.314X
Al	0.232X	0.444X
B	12.9[b]	22.6[b]
Ba	0.238X	0.421X
Be	0.082[b]	0.082[b]
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X1/2[c]	4.02X1/2
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X1/2	2.23X1/2
Zn	3.82X1/2	7.69X1/2

[a] Log transformed variable based on one-way analysis of variance.
[b] Repeatability and reproducibility were independent of concentration.
[c] Square root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD BY METHOD 3051

Average Value	Repeatability	Reproducibility
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

All results are in mg/Kg

TABLE 3.
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias (µg/g)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Mi	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

All values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.

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