METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of siliceous matrices, and organic matrices and other complex matrices. If a total decomposition analysis (relative to the target analyte list) is required, the following matrices can be digested: ashes, biological tissues, oils, oil contaminated soils, sediments, sludges, and soils. This method is applicable for the following elements:

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

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 8.0).

> Note: This technique is not appropriate for regulatory applications that require the use of leachate preparations (i.e., Method 3050, Method 3051, Method 1311, Method 1312, Method 1310, Method 1320, Method 1330, Method 3031, Method 3040). This method is appropriate for those applications requiring a total decomposition for research purposes (i.e., geological studies, mass balances, analysis of Standard Reference Materials) or in response to a regulation that requires total sample decomposition.

1.2 This method is provided as a rapid multi-element, microwave assisted acid digestion prior to analysis protocol so that decisions can be made about the site or material. Digests and alternative procedures produced by the method are suitable for analysis by flame atomic absorption spectrometry (FLAA), cold vapor atomic absorption spectrometry (CVAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and other analytical elemental analysis techniques where applicable. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to this manual's "Disclaimer" when conducting analyses using Method 3052.

1.3 The goal of this method is total sample decomposition and with judicious choice of acid combinations this is achievable for most matrices (see Sec. 3.2). Selection of reagents which give the highest recoveries for the target analytes is considered the optimum method condition.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and usually 3 mL hydrofluoric acid for 15 minutes using microwave heating with a suitable laboratory microwave system. The method has several additional alternative acid and reagent combinations including hydrochloric acid and hydrogen peroxide. The method has provisions for scaling up the sample size to a maximum of 1.0 g. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5 ºC in approximately less than 5.5 minutes and remaining at 180 ± 5 ºC for 9.5 minutes for the completion of specific reactions (Ref. 1, 2, 3, 4). After cooling, the vessel contents may be filtered, centrifuged, or allowed to settle and then decanted, diluted to volume, and analyzed by the appropriate SW-846 method.

3.0 INTERFERENCES

3.1 Gaseous digestion reaction products, very reactive, or volatile materials that may create high pressures when heated and 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. Variations of the method due to very reactive materials are specifically addressed in sections 7.3.4 and 7.3.6.1.

3.2 Most samples will be totally dissolved by this method with judicious choice of the acid combinations. A few refractory sample matrix compounds, such as TiO_2, alumina, and other oxides may not be totally dissolved and in some cases may sequester target analyte elements.

3.3 The use of several digestion reagents that are necessary to either completely decompose the matrix or to stabilize specific elements may limit the use of specific analytical instrumentation methods. Hydrochloric acid is known to interfere with some instrumental analysis methods such as flame atomic absorption (FLAA) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The presence of hydrochloric acid may be problematic for graphite furnace atomic absorption (GFAA) and inductively coupled plasma mass spectrometry (ICP-MS). Hydrofluoric acid, which is capable of dissolving silicates, may require the removal of excess hydrofluoric acid or the use of specialized non-glass components during instrumental analysis. Method 3052 enables the analyst to select other decomposition reagents that may also cause problems with instrumental analyses necessitating matrix matching of standards to account for viscosity and chemical differences.

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The temperature performance requirements necessitate the microwave decomposition system sense the temperature to within ± 2.5°C and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2°C (including the final reaction temperature of 180°C). Temperature feedback control provides the primary control performance mechanism for the method. Due to the flexibility in the reagents used to achieve total analysis, tempertuare feedback control is necessary for reproducible microwave heating.

Alternatively, for a specific set of reagent(s) combination(s), quantity, and specific vessel type, a calibration control mechanism can be developed similar to previous microwave methods (see Method 3051). Through calibration of the microwave power, vessel load and heat loss, the reaction temperature profile described in Section 7.3.6 can be reproduced. The calibration settings are specific for the number and type of vessel used and for the microwave system in addition to the variation in reagent combinations. Therefore no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of equipment and reagent combination. They may only be used if not altered as previously described in other methods such as 3051 and 3015. In this circumstance, the microwave system provides programmable power which can be programmed to within ± 12 W of the required power. Typical systems provide a nominal 600 W to 1200 W of power (Ref. 1, 2, 5). Calibration control provides backward compatibility with older laboratory microwave systems without temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older lower pressure vessels may not be compatible.

4.1.2 The temperature measurement system should be periodically calibrated at an elevated temperature. Pour silicon oil (a high temperature oil into a beaker and adequately stirred to ensure a homogeneous temperature. Place the microwave temperature sensor and a calibrated external temperature measurement sensor into the beaker. Heat the beaker to a constant temperature of 180 ± 5°C. Measure the temperature with both sensors. If the measured temperatures vary by more than 1 - 2°C, the microwave temperature measurement system needs to be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure.

> CAUTION: The use of microwave equipment with temperature feedback control is required to control the unfamiliar reactions of unique or untested reagent combinations of unknown samples. These tests may require additional vessel requirements such as increased pressure capabilities.

4.1.3 The microwave unit cavity is corrosion resistant and well ventilated. All electronics are protected against corrosion for safe operation.

> CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. A listing of these specific suggestions is 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.

4.1.4 The method requires essentially microwave transparent and reagent resistant suitably inert polymeric materials (examples are PFA or TFM suitably inert polymeric polymers) to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The vessels internal volume should be at least 45 mL, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

CAUTION: The outer layers of vessels are frequently not as acid or reagent resistant as the liner material and must not be chemically degraded or physically damaged to retain the performance and safety required. Routine examination of the vessel materials may be required to ensure their safe use.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief devices. 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 suitably inert polymerics may crack, burst, or explode in the unit under certain pressures. Only suitably inert polymeric (such as PFA or TFM and others) containers with pressure relief mechanisms or containers with suitably inert polymeric liners and pressure relief mechanisms are considered acceptable.

Users are therefore advised not to use domestic (kitchen) type microwave ovens or to use inappropriate sealed containers without pressure relief for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult Reference 3 and 6.

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within most systems (Ref. 1). The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Laboratories should not use domestic (kitchen) type microwave ovens for this method. There are several significant safety issues. First, when an acid such as nitric is used to effect sample digestion in microwave units in open vessel(s), or sealed vessels equipment, there is the potential for the acid gas vapor 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 system with isolated and corrosion resistant safety devices prevents this from occurring.

4.2 Volumetric ware, volumetric flasks, and graduated cylinders, 50 and 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, polypropylene, polyethylene or equivalent.

4.5 Analytical balance, of appropriate capacity, with a ± 0.0001 g or appropriate precision for the weighing of the sample. Optionally, the vessel with sample and reagents may be weighed, with an appropriate precision balance, before and after microwave processing to evaluate the seal integrity in some vessel types.

5.0 REAGENTS

5.1 All reagents should be of appropriate purity or high purity (acids for example, should be sub-boiling distilled where possible) to minimize the blank levels due to elemental contamination. All references to water in the method refer to reagent water (Ref. 7). Other reagent 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.

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 Refer to Chapter Three for the appropriate holding times and storage conditions.

7.0 PROCEDURE

7.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within ± 2.5 ^{o}C and permit adjustment of the microwave output power within 2 seconds.

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 (fluoropolymer liners only) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80^{o}C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80^{o}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 (not used with HF) 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 a well-mixed sample to the nearest 0.001 g into an appropriate vessel equipped with a pressure relief mechanism. For soils, ash, sediments, sludges, and siliceous wastes, initially use no more than 0.5 g. For oil or oil contaminated soils, initially use no more than 0.25 g.

7.3.2 Add 9 ± 0.1 mL concentrated nitric acid and 3 ± 0.1 mL concentrated hydrofluoric acid to the vessel in a fume hood. If the approximate silicon dioxide content of the sample is known, the quantity of hydrofluoric acid may be varied from 0 to 5 mL for stoichiometric reasons. Samples with higher concentrations of silicon dioxide (> 70%) may require higher concentrations of hydrofluoric acid (>3 mL HF). Alternatively samples with lower concentrations of silicon dioxide (< 10% to 0%) may require much less hydrofluoric acid (0.5 mL to 0 mL). Examples are presented in Table 1, 2, 3, and 6. Acid digestion reagent combinations used in the analysis of several matrices, listed in Table 7, provide guidance for the development of new matrix decomposition procedures.

7.3.3 The addition of other reagents with the original acids prior to digestion may permit more complete oxidation of organic sample constituents, address specific decomposition chemistry requirements, or address specific elemental stability and solubility problems.

The addition of 2 ± 2 mL concentrated hydrochloric acid to the nitric and hydrofluoric acids is appropriate for the stabilization of Ag, Ba, and Sb and high concentrations of Fe and Al in solution. The amount of HCl needed will vary depending on the matrix and the concentration of the analytes. The addition of hydrochloric acid may; however, limit the techniques or increase the difficulties of analysis. Examples are presented in Table 4.

The addition of hydrogen peroxide (30%) in small or catalytic quantities (such as 0.1 to 2 mL) may aid in the complete oxidation of organic matter.

The addition of water (double deionized) may (0 to 5 mL) improve the solubility of minerals and prevent temperature spikes due to exothermic reactions.

NOTE: Supporting documentation for the chemistry of this method has been prepared in chapters 2 and 3 of reference 3. It provides additional guidance and documentation of appropriate reagent, matrix and analyte combinations that can be employed in this method.

CAUTION: Only one acid mixture or quantity may be used in a single batch in the microwave to insure consistent reaction conditions between all vessels and monitored conditions. This limitation is due to the current practice of monitoring a representative vessel and applying a uniform microwave field to reproduce these reaction conditions within a group of vessels being simultaneously heated.

CAUTION: Toxic nitrogen oxide(s), hydrogen fluoride, and toxic chlorine (from the addition of hydrochloric acid) fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.

CAUTION: The analyst should wear protective gloves and face protection and must not at any time permit a solution containing hydrofluoric acid to come in contact with skin or lungs.

CAUTION: The addition of hydrochloric acid must be from concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of toxic chlorine and possibly other gases will result from a premixed acid solution. This will over pressurize the vessel due to the release of these gases from solution upon heating. The gas effect is greatly lessened by following this suggestion.

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: The addition of hydrogen peroxide should only be done when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added if the sample may contain large quantities of easily oxidizable organic constituents.

7.3.4 The analyst should be aware of the potential for a vigorous reaction. If a vigorous reaction occurs upon the initial addition of reagent or the sample is suspected of containing easily oxidizable materials, allow the sample to predigest in the uncapped digestion vessel. Heat may be added in this step for safety considerations (for example the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

7.3.5 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.

7.3.6 This method is a performance based method, designed to achieve or approach total decomposition of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 180 ± 5 ºC in approximately 5.5 minutes and remain at 180 ± 5 ºC for 9.5 minutes. The temperature-time and pressure-time profile are given for a standard soil sample in Figure 1. The number of samples simultaneously digested is dependent on the analyst. The number may range from 1 to the maximum number of vessels that the microwave units magnetron can heat according to the manufacturer's or literature specifications (the number will depend on the power of the unit, the quantity and combination of reagents, and the heat loss from the vessels).

The pressure should peak between 5 and 15 minutes for most samples (Ref. 2, 3, 5). If the pressure exceeds the pressure limits of the vessel, the pressure will be reduced by the relief mechanism of the vessel.

The total decomposition of some components of a matrix may require or the reaction kinetics are dramatically improved with higher reaction temperatures. If microwave digestion systems and/or vessels are capable of achieving higher temperatures and pressures, the minimum digestion time of 9.5 minutes at a temperature of at least 180 ± 5°C is an appropriate

alternative. This change will permit the use of pressure systems if the analysis verifies that 180°C is the minimum temperature maintained by these control systems.

7.3.6.1 For reactive substances, the heating profile may be altered for safety purposes. The decomposition is primarily controlled by maintaining the reagents at 180 ± 5°C for 9.5 minutes, therefore the time it takes to heat the samples to 180 ± 5°C is not critical. The samples may be heated at a slower rate to prevent potential uncontrollable exothermic reactions. The time to reach 180 ± 5 ºC may be increased to 10 minutes provided that 180 ± 5 ºC is subsequently maintained for 9.5 minutes. Decomposition profiles are presented in Figures 1 and 2. The extreme difference in pressure is due to the gaseous digestion products.

7.3.6.2 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in 7.3.6. The calibration settings will be specific to the quantity and combination of reagents, quantity of vessels, and heat loss characteristics of the vessels (Ref 1). If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels and when fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with the same acid mixture to achieve the full complement of vessels. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbed mass in the cavity (Ref. 1). Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed).

7.3.6.3 Pressure control for a specific matrix is applicable if instrument conditions are established using temperature control. Because each matrix will have a different reaction profile, performance using temperature control must be developed for every specific matrix type prior to use of the pressure control system.

7.3.7 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained a seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection of the disk may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or sometimes a physical sign indicates a vessel has vented.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Vent the vessels using the procedure recommended by the vessel manufacturer. 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.

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

7.3.8.2 Settling: If undissolved material remains such as TiO_2, or other refractory oxides, 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.

7.3.8.3 Filtering: If necessary, 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.

7.3.9 If the hydrofluoric acid concentration is a consideration in the analysis technique such as with ICP methods, boric acid may be added to permit the complexation of fluoride to protect the quartz plasma torch. The amount of acid added may be varied, depending on the equipment and the analysis procedure. If this option is used, alterations in the measurement procedure to adjust for the boric acid and any bias it may cause are necessary. This addition will prevent the measurement of boron as one of the elemental constituents in the sample. Alternatively, a hydrofluoric acid resistant ICP torch may be used and the addition of boric acid would be unnecessary for this analytical configuration. All major manufacturers have hydrofluoric resistant components available for the analysis of solutions containing hydrofluoric acid.

CAUTION: The traditional use of concentrated solutions of boric acid can cause problems by turning the digestion solution cloudy or result in a high salt content solution interfering with some analysis techniques. Dilute solutions of boric acid or other methods of neutralization or reagent elimination are appropriate to avoid problems with HF and the glass sample introduction devices of analytical instrumentation. Gentle heating often serves to clear cloudy solutions. Matrix matching of samples and standards will eliminate viscosity differences.

7.3.10 The removal or reduction of the quantity of the hydrochloric and hydrofluoric acids prior to analysis may be desirable. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative. Evaporation to near dryness in a controlled environment with controlled pure gas and neutralizing and collection of exhaust interactions is an alternative where appropriate. This manipulation may be performed in the microwave system, if the system is capable of this function, or external to the microwave system in more common apparatus(s). This option must be tested and validated to determine analyte retention and loss and should be accompanied by equipment validation possibly using the standard addition method and standard reference materials. This alternative may be used to alter either the acid concentration and/or acid composition. Note: The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable. Examples of analysis performed with and without removal of the hydrofluoric acid are presented in Table 5. Waste minimization techniques should be used to capture reagent

fumes. This procedure should be tested and validated in the apparatus and on standards before using on unknown samples.

7.3.11 Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques and/or SW-846 methods.

7.3.12 Sample size may be scaled-up from 0.1, 0.25, or 0.5 g to 1.0 g through a series of 0.2g sample size increments. Scale-up can produce different reaction conditions and/or produce increasing gaseous reaction products. Increases in sample size may not require alteration of the acid quantity or combination, but other reagents may be added to permit a more complete decomposition and oxidation of organic and other sample constituents where necessary (such as increasing the HF for the complete destruction of silicates). Each step of the scale-up must demonstrate safe operation before continuing.

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

7.5 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control to follow performance specifications of the method, then the calibration procedure will not be necessary.

7.5.1 Calibration is the normalization and reproduction of a microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile in section 7.3.6. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

7.5.2 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 system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems 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 (7.5.4), otherwise, the analyst must use the multiple point calibration method (7.5.3).

7.5.3 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 7.5.5. This data is clustered about the customary working power ranges. Nonlinearity has been encountered at the upper end of the calibration. If the system'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.

7.5.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.5.5. 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 7.5.3. This point should also be used to periodically verify the integrity of the calibration.

7.5.5 Equilibrate a large volume of water to room temperature (23 ± 2 ºC). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a suitably inert polymeric 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 ºC measured to ± 0.05 ºC. 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 system'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 ºC. 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 ºC. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

$$\text{Equation 1} \qquad P = \frac{K \; Cp \; m \; \Delta T}{t}$$

Where:

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

K = the conversion factor for thermochemical calories_sec^{-1} to watts (which equals 4.184)

Cp = the heat capacity, thermal capacity, or specific heat (cal g^{-1} $ºC^{-1}$) of water

m = the mass of the water sample in grams (g)
ΔT = the final temperature minus the initial temperature (ºC)
t = the time in seconds (s)

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

$$P = 34.86\ \Delta T$$

NOTE: 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 ±5 V. Electronic components in most microwave units are matched to the system's function and output. When any part of the high voltage circuit, power source, or control components in the system have been serviced or replaced, it will be necessary to recheck the system's calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period determined by all involved parties based on program or project requirements. 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 and/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.

8.4 Blank samples should be prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3052 are presented in the tables of this method. Tables 1 through 6 provide a summary of total elemental analysis.

9.2 The performance criteria are provided as an example in Figure 1. The temperature profile will be within ± 5 ºC of the mean of the temperature profile, but the pressure curve will vary depending on the acid mixture and gaseous digestion products and the thermal insulating properties of the vessel. Figure 2 provides criteria for the digestion of an oil sample.

10.0 REFERENCES

1. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M. and Jassie, L. B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.

2. Kingston, H. M., Walter, P. J., Comparison of Microwave Versus Conventional Dissolution for Environmental Applications, Spectroscopy, Vol. 7 No. 9,20-27,1992.

3. Kingston, H. M., Haswell, S, Microwave Enhanced Chemistry, ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1997.

4. Kingston, H. M.; Walter, P. J.; Lorentzen, E. M. L.; Lusnak, G. P. Report to NIST Office of Standard Reference Materials, The Performance of Leaching Studies on Soil SRMs 2710 and 2711, Duquesne University, Pittsburgh, PA, 1994.

5. Kingston, H. M. EPA IAG #DWI-393254-01-0 January 1-March 31, 1988, quarterly Report.

6. Kingston, H. M. and Jassie, L. B., "Safety Guidelines for Microwave Systems in the Analytical Laboratory". In Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H. M. and Jassie, L. B., eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.

7. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM, Philadelphia, PA, 1985, D1193-77.

8. Kingston, H. M.; Walter, P. J.; Link, D. D. Validation Study and Unpublished Data, Duquesne University, Pittsburgh, PA, 1995.

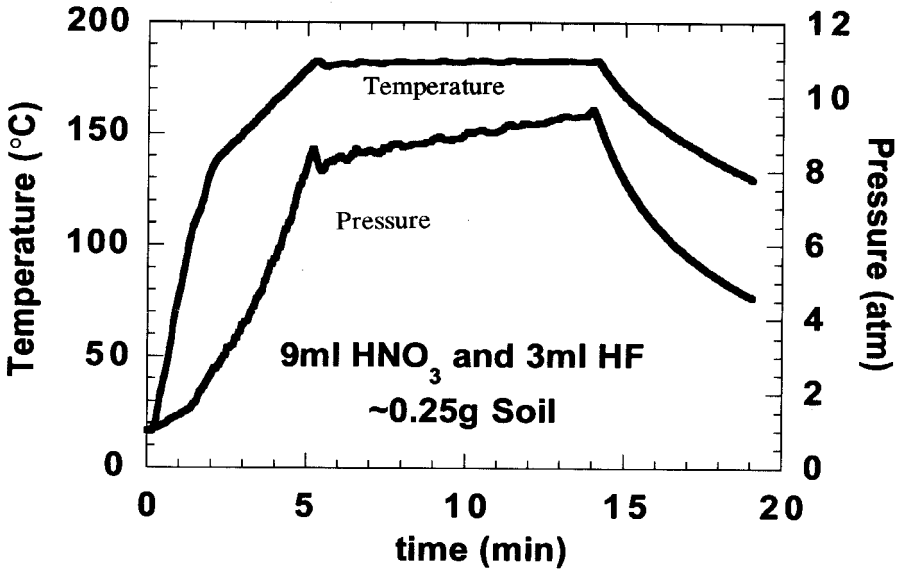


FIGURE 1. TYPICAL REACTION PROFILE FOR THE DIGESTION OF A SOIL (REF. 4 AND 8)

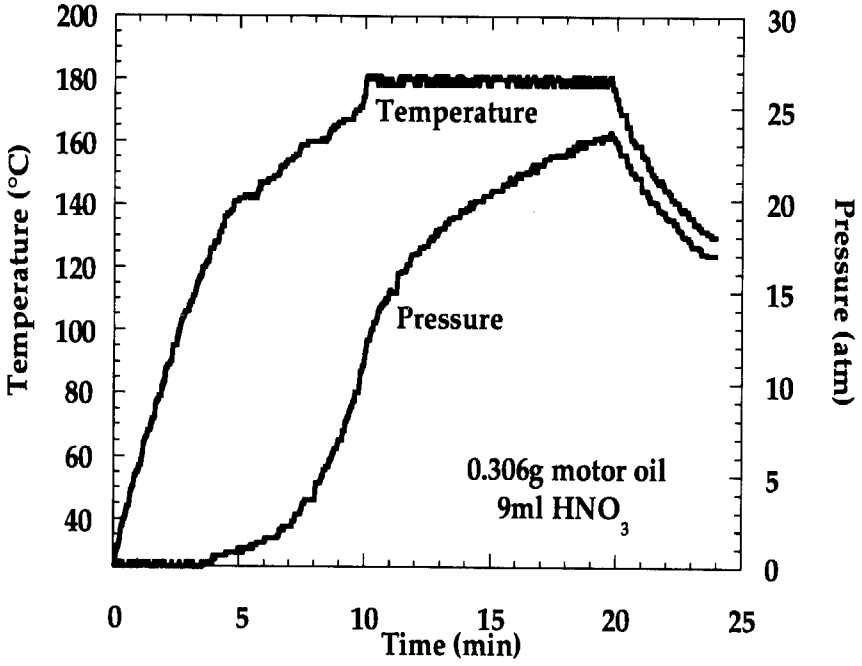


FIGURE 2. TYPICAL REACTION PROFILE FOR THE DIGESTION OF AN OIL (REF. 8)

TABLE 1
ANALYSIS OF NIST SRM 2704 (COMPILATION OF REFS. 2 AND 3)[a]
BUFFALO RIVER SEDIMENT

Element	Analyzed (µg/g)	Certified (µg/g)
Arsenic (n=4)	23.4 ± 2.6	23.4 ± 0.8
Cadmium (n=6)	3.5 ± 1.2	3.45 ± 0.22
Chromium (n=6)	132.9 ± 1.3	135 ± 5
Copper (n=6)	98.0 ± 4.2	98.6 ± 5.0
Lead (n=6)	155 ± 9.2	161 ± 17
Mercury (n=4)	1.49 ± 0.14	1.44 ± 0.07
Nickel (n=6)	43.6 ± 3.9	44.1 ± 3.0
Phosphorus (n=4)	1.016 ± 0.016 mg/g	0.998 ± 0.028 mg/g
Selenium (n=4)	1.13 ± 0.9	(1.1)
Sulfur (n=4)	3.56 ± 0.16	-----
Thallium (n=4)	1.15 ± 0.22	1.2 ± 0.2
Uranium (n=4)	2.97 ± 0.04	3.13 ± 0.13
Zinc (n=6)	441.9 ± 0.8	438 ± 12

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Section 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 2
ANALYSIS OF NIST SRM 2710 (REFS. 4 AND 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9 [b]	38.4 ± 3.0
Cadmium	21.9 ± 0.7 [a]	21.8 ± 0.2
Chromium	34.0 ± 3.2 [b]	(39)
Copper	2902 ± 83 [a]	2950 ± 130
Lead	5425 ± 251 [a]	5532 ± 80
Nickel	13.5 ± 1.0 [a]	14.3 ± 1.0
Silver	36.6 ± 0.5 [b]	35.3 ± 1.5
Zinc	7007 ± 111 [a]	6952 ± 91

[a] Digestion with either a. 9 mL HNO_3 and 4 mL HF or b. 9 mL HNO_3, 3 mL HF, & 2 mL HCl. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 3
NIST SRM 2711 (REFS. 4 AND 3)
MONTANA SOIL: MODERATELY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Cadmium	40.5 ± 1.0	41.70 ± 0.25
Chromium	45.5 ± 1.0	(47)
Copper	106.8 ± 3.4	114 ± 2
Lead	1161 ± 49	1162 ± 31
Nickel	19.6 ± 0.9	20.6 ± 1.1
Silver	4.3 ± 1.0	4.63 ± 0.39
Zinc	342 ± 9.4	350.4 ± 4.8

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 4
STABILIZATION AND RECOVERY OF ELEMENTS WITH HCl (REF. 3)[a] NIST SRM 2710
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	HNO_3 & HF (µg/g)	HNO_3, HF & HCl (µg/g)	Certified (µg/g)
Antimony	33.1 ± 2.1	39.3 ± 0.9	38.4 ± 3.0
Silver	10.6 ± 4.5	36.6 ± 0.5	35.3 ± 1.5

[a] HNO_3 and HF - Digestion used 9 mL and 3 mL, respectively.
HNO_3, HF, and HCl - Digestion used 9 mL, 3 mL, and 2 mL respectively. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 5
FUMING OFF HYDROFLUORIC ACID WITH MICROWAVE EVAPORATION SYSTEM (REF 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=4)

Element	Direct (µg/g)	Fumed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9	39.4 ± 0.9	38.4 ± 3.0
Cadmium	21.9 ± 0.7	23.3 ± 1.6	21.8 ± 0.2
Chromium	34.0 ± 3.2	32.4 ± 0.4	(39)
Copper	2902 ± 83	2870 ± 150	2950 ± 130
Lead	5425 ± 251	5502 ± 106	5532 ± 80
Nickel	13.5 ± 1.0	13.5 ± 0.8	14.3 ± 1.0
Silver	36.6 ± 0.5	38.9 ± 1.1	35.3 ± 1.5
Zinc	7007 ± 111	3992 ± 132	6952 ± 91

[a] Direct - Digestion used 9 mL HNO_3 and 3 mL HCl or 9 mL HNO_3, 3 mL HF, and 2 mL HCl
Fumed - Digestion used 9 mL HNO_3 and 3 mL HCl followed by the removal of the HF. Temperature and pressure conditions are as described in 7.3.6 of the method and similar to Figure 1. The digest solution was fumed in a microwave system under vacuum to ~1 mL and 3 mL HCl added. The digest solution was fumed to ~1 mL and 3 mL HNO_3 was added. The solution was fumed for a final step to ~1 mL and quantitatively transferred and diluted to final volume. Data reported with 95% confidence intervals.

TABLE 6
ANALYSIS OF NIST SRM 1084A (REF. 8) [a]
WEAR METALS IN OIL (100 ppm) (n=4)

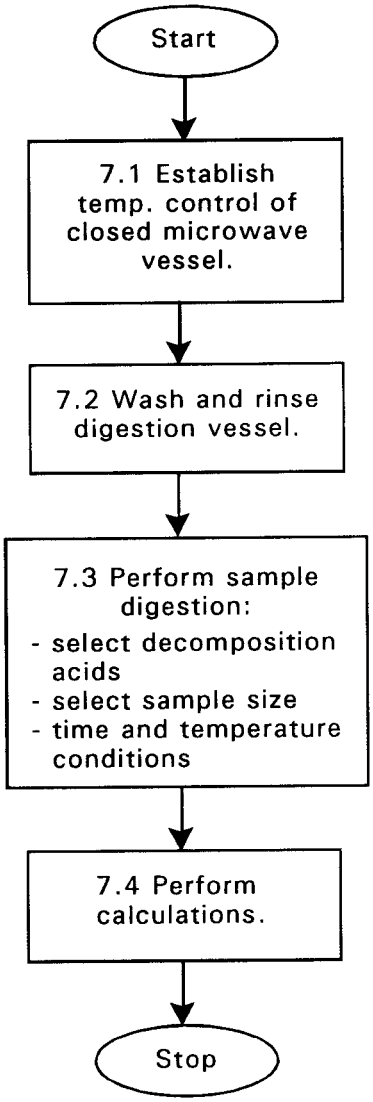
Element	Analyzed (µg/g)	Certified (µg/g)
Chromium	98.1 ± 1.1	98.3 ± 0.8
Copper	1.2.4 ± 2.4	100.0 ± 1.9
Lead	99.2 ± 2.3	101.1 ± 1.3
Nickel	99.2 ± 2.4	99.7 ± 1.6
Silver	102.7 ± 2.2	101.4 ± 1.5

[a] Digestion with 9 mL HNO_3 and 0.5 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 2. Data reported with 95% confidence intervals.

TABLE 7
DIGESTION PARAMETERS USED IN THE ANALYSIS OF SEVERAL MATRICES
BY METHOD 3052

Matrix	HNO_3	HF	HCl
Soil			
NIST SRM 2710 Highly Contaminated Montana Soil	9 mL	3 mL	0-2*mL
NIST SRM 2711 Moderately Contaminated Montana Soil	9	3	0-2*
Sediment			
NIST SRM 2704 Buffalo River Sediment	9	3	0-2*
Biological			
NIST SRM 1566a Oyster Tissue	9	0	0
NIST SRM 1577a Bovine Liver	9	0	0
Botanical			
NIST SRM 1515 Apple Leaves	9	0	0
NIST SRM 1547 Peach Leaves	9	0	0
NIST SRM 1572 Citrus Leaves	9	0.5	0
Waste Oil			
NIST SRM 1084a Wear-Metals in Lubricating Oil	9	0.5	0-2*

* HCl is added to stabilize elements such as Ag and Sb when they are analyzed.


Start
7.1 Establish temp. control of closed microwave vessel.
7.2 Wash and rinse digestion vessel.
7.3 Perform sample digestion:
- select decomposition acids
- select sample size
- time and temperature conditions
7.4 Perform calculations.
Stop