METHOD 3015A

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This microwave method is designed to perform extraction using microwave heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl). Since this method is not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution of available metals in aqueous samples, drinking water, mobility-procedure extracts, and wastes that contain suspended solids for the following elements:

Element		CASRN[a]
Aluminum	(Al)	7429-90-5*
Antimony	(Sb)	7440-36-0*
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3*
Beryllium	(Be)	7440-41-7*
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3*
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6*
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4*
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4*
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2*
Zinc	(Zn)	7440-66-6

---

[a] Chemical Abstract Service Registry Number

*Elements which typically require the addition of HCl for optimum recoveries. Other elements and matrices may be analyzed by this method if performance <u>is demonstrated</u> for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 9.0).

1.2 This method provides options for improving the performance for certain analytes, such as antimony, iron, aluminum, and silver by the addition of hydrochloric acid, when necessary. It is intended to provide a rapid multi-element acid extraction prior to analysis so that decisions can be made about materials and site clean-up levels, and as an estimate of metal toxicity. Digests produced by the method are suitable for analysis by inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrophotometry (FLAA), and graphite furnace atomic absorption spectrophotometry (GFAA). However, the addition of HCl may limit the methods of detection, or increase the difficulties of detection with some techniques.

Due to the rapid advances in microwave technology, consult the manufacturer's recommended instructions for guidance on their microwave digestion system. This method is generic and may be implemented using a wide variety of laboratory microwave equipment.

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is extracted in 5 mL concentrated nitric acid or, optionally, 4 mL concentrated nitric acid and 1 mL concentrated hydrochloric acid, for 20 minutes using microwave heating with a suitable laboratory microwave unit. The temperature of the acid-sample mixture is brought to 170 ± 5 °C in 10 minutes, and maintained at 170 ± 5 °C for 10 minutes to accelerate the leaching process. The sample and acid(s) are placed in a fluorocarbon polymer (such as PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed 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 determinative method.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 Digestion of samples which contain organics will create high pressures due to the evolution of gaseous digestion products. This may cause venting of the vessels with potential loss of sample components and/or analytes. When warranted by the potential reactivity of the sample, a smaller sample size may be used, and the concentration for final calculations adjusted, but the final water volume prior to addition of acid(s) is recommended to be 45 mL. This is recommended in order to retain the heat characteristics of the calibration procedure if used. Variations of the method, due to very reactive materials, are specifically addressed in Section 11.3.3. Limits of quantitation will change with sample quantity (dilution) and with instrumentation.

4.2 Many samples can be dissolved by this method. However, when the sample contains suspended solids which are made up of refractory compounds, such as silicon dioxide, titanium dioxide, alumina, and other oxides, they will not be dissolved and in some cases may sequester target analyte elements. These bound elements are considered nonmobile in the environment and are excluded from most aqueous pollutant transport mechanisms.

5.0 SAFETY

5.1 The microwave unit cavity must be corrosion resistant and well ventilated. All electronics must be well 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. The analyst is advised to consult the equipment manual, the equipment manufacturer, and other appropriate literature for proper and safe operation of the microwave equipment and vessels. For further details and safety literature, references 1, 7 and 8 review methods and safety in microwave sample preparation.

5.2 The method requires microwave transparent and reagent resistant materials such as fluorocarbon polymers (examples are PFA and TFM) or quartz 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 internal volume of the vessel should be at least 100 mL, and the vessel must be capable of withstanding pressures of at least 30 atm (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. In order to retain the specified performance and safety requirements, these outer layers must not be chemically degraded or physically damaged. Routine examination of the vessel materials is necessary to ensure their safe use.

> CAUTION: Another 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. Some digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only fluorocarbon (such as PFA, TFM, and others) or quartz containers with pressure relief mechanisms or containers with fluorocarbon or quartz liners and pressure relief mechanisms are considered acceptable.

> CAUTION: An aqueous sample must contain no more than 1% (V/V or g/V) oxidizable organic material. Upon oxidation, organic material, whether liquid or solid, contributes to gaseous digestion products. Pressure build-up above the pressure limit will result in venting of the closed digestion vessel.

> CAUTION: Laboratories should not use domestic (kitchen) type microwave ovens for this method because of significant safety issues. When acids such as nitric and hydrochloric are used to effect sample digestion in microwave units in open or sealed vessel(s), there is the potential for acid vapors 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 instrument components and safety devices prevents this from occurring.

Users are advised not to use domestic (kitchen) type microwave ovens or sealed containers which are not equipped with controlled pressure relief mechanisms for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult references 1, 7, and 8.

6.0 EQUIPMENT AND SUPPLIES

6.1 Microwave apparatus requirements

6.1.1 The temperature performance requirements necessitate the microwave decomposition system to 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 170 ± 5 °C). Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e., different vessel types and microwave oven designs), temperature feedback control is preferred for reproducible microwave heating. For further details, consult reference 7.

Alternatively, for a specific vessel type, specific set of reagent(s), and sample type, a calibration control mechanism can be developed similar to those described in previous microwave methods (See EPA Method 3051). Through calibration of the microwave power for a specific number and type of vessel, vessel load, and heat loss characteristics of a specific vessel series, the reaction temperature profile described in Section 11.3.5 can be reproduced (Reference 7). The calibration settings are specific for the number and type of vessel and microwave system being used, in addition to the specific reagent combination being used. 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 microwave equipment and vessel type. They may be used as previously described in EPA Methods 3052 and 3051. In this circumstance, the microwave system provides programmable power, which can be programmed to within ± 12 W of the required power. Typical systems provide 600 W - 1200 W of power. Calibration control provides backward compatibility with older laboratory microwave systems which may not be equipped for temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older vessels with lower pressure capabilities may not be compatible (References 4 - 8).

6.1.2 The accuracy of the temperature measurement system should be periodically validated at an elevated temperature. This can be done using a container of silicon oil (a high temperature oil) and an external, calibrated temperature measurement system. The oil should be adequately stirred to ensure a homogeneous temperature, and both the microwave temperature sensor and the external temperature sensor placed into the oil. After heating the oil to a constant temperature of 170 ± 5°C, the temperature should be measured using both sensors. If the measured temperatures vary by more than 1 to 2°C, the microwave temperature measurement system should be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure (see EPA Method 3052).

6.1.3 A rotating turntable is employed to ensure the homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm. Other types of equipment that are used to assist in achieving uniformity of the microwave field may also be appropriate.

6.2 Class A or appropriate mechanical pipette, volumetric flask, or graduated cylinder, 50 or 100 mL capacity or equivalent.

6.3 Filter paper, qualitative or equivalent.

6.4 Filter funnel, glass, polypropylene, or other appropriate material.

6.5 Analytical balance, of appropriate capacity and resolution, meeting data quality objectives.

7.0 REAGENTS

7.1 All acids should be sub-boiling distilled and/or high purity where possible to minimize 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 decreasing the accuracy of the determination. If the purity of a reagent is questionable, the reagent should be analyzed to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

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

7.1.2 Concentrated hydrochloric acid (HCl). The acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

7.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. For further details, consult Reference 2.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of SW-846. Refer to that chapter, as updated, for guidance.

8.2 All sample containers must be prewashed with acids, water, and metal-free detergents, if necessary, depending on the use history of the container (Reference 7). Plastic and glass containers are both suitable. For further information, see Chapter Three.

8.3 Aqueous waste waters must be acidified to a $pH < 2$ with HNO_3.

9.0 QUALITY CONTROL

9.1 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.

9.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analysis 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., wastewaters, extracts, etc.).

9.3 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.

9.4 Periodically, the accuracy of the temperature measurement system used to control the microwave equipment should be validated per Section 6.1.2.

9.5 (Not necessary if using temperature feedback control.) Each day that samples are extracted, the microwave-power calibration should be verified by heating 1 kg of ASTM Type II water (at 22 ± 3 °C) in a covered, microwave-transparent vessel for 2 min at the setting for 490 W and measuring the water temperature after heating per Section 10.1.5. If the power calculated (per Section 12) differs from 490 W by more than ± 10 W, the microwave settings should be recalibrated per Section 10.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration of Microwave Equipment

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

10.1.1 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 given in section 11.3.5. 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.

10.1.2 For cavity type microwave equipment, calibration 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 (see Section 10.1.4). Otherwise, the analyst must use the multiple point calibration method (see Section 10.1.3). Assistance in calibration and software guidance of calibration are available in References 7 and 8.

10.1.3 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 10.1.5. 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 re-evaluated.

10.1.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Power is measured at 100% and 50% using the procedure described in Section 10.1.5. From this 2-point line, determine the partial power setting that corresponds to the power, in watts, specified in the procedure to reproduce the heating profile specified in Section 11.3.6. 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 Section 10.1.3. This point should also be used to periodically verify the integrity of the calibration.

10.1.5 Equilibrate a large volume of water to room temperature (22 ± 3 °C). One kg of reagent water is weighed (1,000.0 ± 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 22 ± 3 °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 system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water is vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation (irradiating with the stir bar in the vessel could cause electrical arcing) 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 (after making adjustments for any loss of weight due to heating), both the water and the beaker must have returned to 22 ± 3 °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) (joule $\sec^{-1}$)

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

C_p = the heat capacity, thermal capacity, or specific heat (cal $g^{-1}\,°C^{-1}$) 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 (120 sec) and 1 kg (1000 g) of distilled water (heat capacity at 25 °C is 0.9997 cal $g^{-1}\,°C^{-1}$), 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. During measurement and

operation the line voltage should not vary by more than ± 2 V (Reference 7). 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 re-evaluated.

11.0 SAMPLE PROCEDURE

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

11.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between highly concentrated samples and low concentrated samples, all digestion vessels (fluoropolymer or quartz liners) 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 by hot (1:1) nitric acid (greater than 80 °C, but less than boiling) for a minimum of two hours. The vessels should then be 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 prior sample digestions in 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 material used and then rinsed with reagent water and dried in a clean environment.

11.3 Sample Digestion

11.3.1 Measure a 45 mL aliquot of a well-shaken, homogenized sample using an appropriate volumetric measurement and delivery device, and quantitatively transfer the aliquot to an appropriate vessel equipped with a controlled pressure relief mechanism.

11.3.2 Add 5 ± 0.1 mL concentrated nitric acid or, alternatively, 4 ± 0.1 mL concentrated nitric acid and 1 ± 0.1 mL concentrated hydrochloric acid to the vessel in a fume hood (or fume exhausted enclosure). The addition of concentrated hydrochloric acid to the nitric acid is appropriate for the stabilization of certain analytes, such as Ag, Ba, and Sb and high concentrations of Fe and Al in solution. Improvements and optimal recoveries of antimony and silver upon addition of HCl have been described in the literature (Reference 7). The addition of hydrochloric acid may, however, limit the detection techniques or increase the difficulties of analysis for some detection systems.

CAUTION: The addition of hydrochloric acid must be in the form of concentrated hydrochloric acid and not from a premixed combination of acids. A build-up of chlorine gas, as well as other gases, will result from a premixed acid solution. These gases may be violently released upon heating. This is avoided by adding the acid in the described manner.

CAUTION: Toxic nitrogen oxide(s) and chlorine 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.

CAUTION: The use of microwave equipment with temperature feedback control is required to control any unfamiliar reactions that may occur during the leaching of samples of unknown composition. The leaching of these samples may require additional vessel requirements such as increased pressure capabilities.

11.3.3 The analyst should be aware of the potential for a vigorous reaction, especially with samples containing suspended solids composed of volatile or easily oxidized organic species. When digesting a matrix of this type, if a vigorous reaction occurs upon the addition of reagent(s), this sample represents a safety hazard. Do not leach the sample as described in this method due to the high potential for unsafe and uncontrollable reactions.

11.3.4 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, when applicable, connect appropriate temperature and pressure monitoring equipment to vessels according to manufacturer’s specifications.

11.3.5 This method is a performance based method, designed to achieve or approach consistent leaching of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 170 ± 5 °C in approximately 10 minutes and remain at 170 ± 5 °C for 10 minutes, or for the remainder of the twenty-minute digestion period (References 3, 4, 6, and 7). The time vs. temperature and pressure profiles for the leaching of three simulated wastewater samples using Method 3015 are shown in Figure 1. The samples are composed of approximately 0.35 g SRM 2704 (Buffalo River Sediment) mixed in 45 mL double-deionized water. The figure demonstrates the temperature and pressure profiles for both the all-nitric digest (5 mL concentrated nitric acid), and the nitric and hydrochloric mixed-acid digest (4 mL concentrated nitric acid and 1 mL concentrated hydrochloric acid). Also shown is the profile for the heating of the wastewater sample without addition of acids. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of vessels that can be heated by the magnetron of the microwave unit according to the heating profile specified in this section. (The number will depend on the power of the unit, the number of vessels, and the heat loss characteristics of the vessels (Reference 7)).

11.3.5.1 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in Section 11.3.5. The calibration settings will be specific to the quantity of reagents, the number of vessels, and the heat loss characteristics of the vessels (Reference 7). If calibration control is being used, any vessels containing acids 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 45 mL water, and the acid mixture added, so that the full complement of vessels is achieved. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity (Reference 7). Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed.)

11.3.6 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. Cooling of the vessels may be accelerated by internal or external cooling devices. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained their 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 the 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, in addition to weighing, may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or a physical sign that can indicate whether a vessel has vented is appropriate.

11.3.7 Complete the preparation of the sample by carefully uncapping and venting each vessel in a chemical fume hood (or fume exhausted enclosure). Vent the vessels using the procedure recommended by the vessel manufacturer. Quantitatively 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 (Section 11.3.7.1), allowed to settle (Section 11.3.7.2), or filtered (Section 11.3.7.3).

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

11.3.7.2 Settling: If undissolved material, such as SiO_2, TiO_2, or other refractory oxides, remains, 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.

11.3.7.3 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.

11.3.8 The removal or reduction of the quantity of sample may be desirable for concentration of analytes prior to analysis. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative (Reference 7, 8). Sample evaporation in a controlled environment with controlled purge 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. For further information, see References 7 and 8 and Method 3052.

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. 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.

11.3.9 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.

12.0 DATA ANALYSIS AND CALCULATIONS

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

12.2 Prior to use of the method, verify that the temperature sensing equipment is properly reading temperature. A procedure for verification is given in Section 6.1.2. This will establish the accuracy and precision of the temperature sensing equipment, which should be carried throughout the statistical treatment of the quality assurance data.

12.3 In calibrating the microwave unit (Section 10.0), the power absorbed (for each power setting) by 1 kg of reagent water exposed to 120 seconds of microwave energy is determined by the expression:

$$\text{Power (in watts)} = (T_1 - T_2)\,(34.86)$$

where: T_1 = Initial temperature of water (between 21 and 25 °C to nearest 0.1 °C)

T_2 = Final temperature of water (to nearest 0.1 °C)

12.4 Plot the power settings against the absorbed power (calculated in Section 12.3) to obtain a calibration relationship. Alternatively, use a microwave calibration program to analyze the calibration data (References 7 and 8). Interpolate the data to obtain the instrument settings needed to provide the wattage levels specified in Section 12.3.

13.0 METHOD PERFORMANCE

13.1 The fundamental analytical validation of Method 3015 with nitric acid has been performed (Reference 6). The results are shown in Table 1. Variations of 3015 including nitric acid and hydrochloric acid have also been published in the literature (References 5, 7, 9). The method has also been tested on a variety of matrices, including two simulated wastewater matrices, one consisting of ~ 0.35 g sediment (SRM 2704) mixed with 45 mL double-deionized water, and the other consisting of ~ 0.35 g soil (SRM 4355) mixed with 45 mL double-deionized water. The results are shown in Tables 2 and 3, and are published in the literature (Reference 9).

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

16.0 REFERENCES

1. Kingston, H.M.; Jassie, L.B. In 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; Chapters 6 and 11.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM, Philadelphia, PA, 1985, D1193-77.

3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.

4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

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

6. Sosinski, P., and Sze, C., “Absolute Accuracy Study, Microwave Digestion Method 3015 (nitric acid only)”; EPA Region III Central Regional Laboratory, 1991.

7. Kingston, H. M., Haswell, S. J., Eds. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications; ACS Professional Reference Book Series; American Chemical Society: Washington, DC 1997.

8. Duquesne University. Analytical Sample Preparation and Microwave Chemistry Center. *SamplePrep Web*. Access http://www.sampleprep.duq.edu/

9. Link, D.D., Kingston, H.M., Walter, P.J., “Development and Validation of the New EPA Microwave-Assisted Leach Methods 3051A and 3015A.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 3, Figure 1, and a flow diagram of method procedure.

TABLE 1

RESULTS OF VALIDATION STUDY FOR METHOD 3015 (NITRIC ONLY)
(REFERENCE 6)

Element	TM-11		TM-12		T-95		T-107		T-109	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Al	480	26	2800	88.			210	19	120	31
As							13	1	90	11
Ba	140	23	2400	70			200	16		
Be							11.3	0.5	26	1
Ca							12000	783	59000	999
Cd	45	2	240	8			12	1	10	2
Co	240	14	1150	36						
Cr	64	4	350	10			23	1	30	6
Cu	78	4	320	9			42	4	34	4
Fe	290	16	1180	43			60	9	130	7
K					5000	784			2600	383
Mg					35000	1922	2200	110	10200	218
Mn	61	3	300	9			53	3	47	3
Na					20000	10690	2300	1056	13800	516
Ni	280	16	1290	39					61	2
Pb	280	32	1360	35			30.1	0.2	39	1
Se					65.97	2.65	13	1		
V	530	26	2400	61						
Zn	56	3	520	9			31	3	70	4

Element	WP980 #1		WP980 #2		WS378 #4		WS378 #12	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Sb	18.0	0.5	110	34				
Tl	55	2	7.0	0.5				
Ag					ND		19	5

TABLE 2

COMPARISON OF ANALYTE RECOVERIES FROM “SIMULATED WASTEWATER” MIXTURE OF ~ 0.35 G SRM 2704 (BUFFALO RIVER SEDIMENT) AND 45 ML DOUBLE-DEIONIZED WATER USING BOTH DIGEST OPTIONS OF METHOD 3015

(REFERENCE 9)

Element	**5 mL HNO_3 digest**	**4 mL HNO_3 + 1 mL HCl digest**	**Total Analyte Concentration**
Ag	0.31 ± 0.05	0.41 ± 0.09	<4
B	23.8 ± 3.1	30.6 ± 8.3	---*
Be	0.81 ± 0.13	0.91 ± 0.19	---*
Co	12.0 ± 0.30	11.5 ± 0.98	14.0 ± 0.6
Hg	----	1.49 ± 0.03	1.44 ± 0.07
Mo	2.97 ± 0.72	3.15 ± 0.28	---*
Ni	39.6 ± 2.5	41.3 ± 1.7	44.1 ± 3.0
Sr	41.9 ± 1.3	49.0 ± 1.6	(130)
V	6.18 ± 2.5	14.6 ± 2.4	95 ± 4
Zn	418 ± 12	412 ± 31	438 ± 12

Results reported in µg/g analyte (mean ± 95% confidence limit).
Total concentrations are taken from NIST SRM Certificate of Analysis.
Values in parenthesis are reference concentrations.
* The total concentration of this analyte in SRM 2704 is not certified.

TABLE 3

COMPARISON OF ANALYTE RECOVERIES FROM “SIMULATED WASTEWATER” MIXTURE OF ~0.35 G SRM 4355 (PERUVIAN SOIL) AND 45 ML DOUBLE-DEIONIZED WATER USING BOTH DIGEST OPTIONS OF METHOD 3015

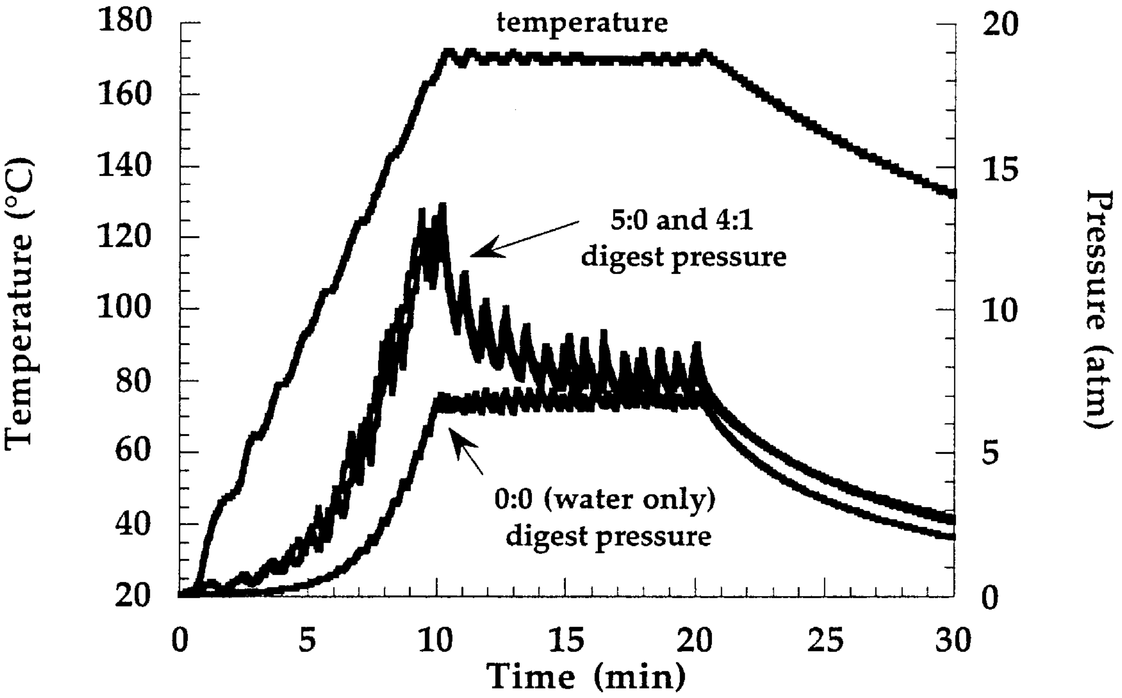
(REFERENCE 9)

Element	**5 mL HNO_3 digest**	**4 mL HNO_3 + 1 mL HCl digest**	**Total Analyte Concentration**
Ag	1.31 ± 0.12	1.62 ± 0.11	(1.9)*
B	32.9 ± 2.1	31.8 ± 2.7	(63)*
Co	10.5 ± 0.34	10.4 ± 0.41	14.8 ± 0.76
Mo	0.99 ± 0.06	1.1 ± 0.11	(1.7)*
Ni	12.2 ± 1.2	13.1 ± 1.9	(13)*
Pb	135 ± 4	136 ± 4	129 ± 26
Sb	3.7 ± 0.30	5.2 ± 0.53	14.3 ± 2.2
Sr	140 ± 6	143 ± 7	(330)

Results reported in µg/g analyte (mean ± 95% confidence limit).
Total concentrations are taken from NIST SRM Certificate of Analysis.
* Values in parenthesis are reference concentrations.

FIGURE 1

THE TYPICAL TEMPERATURE AND PRESSURE PROFILE FOR THE HEATING OF A SIMULATED WASTEWATER SAMPLE (~ 0.35 G SRM 2704 + 45 ML DOUBLE-DEIONIZED WATER) USING BOTH DIGEST OPTIONS (5 ML HNO_3 AND 4 ML HNO_3 + 1 ML HCL) OF METHOD 3015.



METHOD 3015A

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS