METHOD 3051A

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

1.0 SCOPE AND APPLICATION

1.1 This microwave extraction method is designed to mimic extraction using conventional heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl), according to EPA Methods 200.2 and 3050. Since these methods are 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 sediments, sludges, soils, and oils 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

*Indicates elements which typically require the addition of HCl to achieve equivalent results with EPA Method 3050, as noted in reference 3.

‡Note: For matrices such as certain types of oils, this method may or may not provide total sample dissolution. For other matrices, such as soils and sediments, it should be considered an extraction method. 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. 9.0).

1.2 This method is provided as an alternative to EPA Methods 200.2 and 3050. 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 or dissolution prior to analysis so that decisions can be made about materials and site cleanup levels, the need for TCLP testing of a waste (see EPA Method 1311, Section 1.2, for further details), and whether a BDAT process is providing acceptable performance. Digests produced by the method are suitable for analysis by flame atomic absorption spectrophotometry (FLAA), graphite furnace atomic absorption spectrophotometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). 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 your manufacturer's recommended instructions for guidance on their microwave digestion system.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is extracted and/or dissolved in 10 mL concentrated nitric acid, or alternatively, 9 mL concentrated nitric acid and 3 mL concentrated hydrochloric acid for 10 minutes using microwave heating with a suitable laboratory microwave unit. The sample and acid(s) are placed in a fluorocarbon polymer (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

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

4.0 INTERFERENCES

4.1 Very reactive samples or volatile materials may create high pressures due to the evolution of gaseous digestion products. This may cause venting of the vessels with potential loss of sample and/or analytes. The complete decomposition of either carbonates, or carbon based samples, may produce enough pressure to vent the vessel if the sample size is greater than 0.25 g (depending on the pressure capability of the vessel). Variations of the method to accommodate very reactive materials are specifically addressed in Section 11.3.3.

4.2 Many types of samples will be dissolved by this method. A few refractory sample matrix compounds, such as quartz, silicates, titanium dioxide, alumina, and other oxides may not be dissolved and in some cases may sequester target analyte elements. These bound elements are considered non-mobile in the environment and are excluded from most aqueous transport mechanisms of pollution.

5.0 SAFETY

5.1 The microwave unit cavity must be corrosion resistant and well ventilated. All electronics must be 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, see reference 3 and the document of Sec. 13.2.1 for a review of safety in microwave sample preparation.

5.2 The method requires essentially microwave transparent and reagent resistant materials such as fluorocarbon polymers (examples are PFA or 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 45 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 reagent combination (9 mL nitric acid to 3 mL hydrochloric acid) results in greater pressures than those resulting from the use of only nitric acid. As demonstrated in Figures 1 and 2, pressures of approximately 12 atm have been reached during the heating of the acid mixture alone (no sample in the vessel). Pressures reached during the actual decomposition of a sediment sample (SRM 2704, a matrix with low organic content) have more than doubled when using the 9 mL nitric and 3 mL hydrochloric acid mixture. These higher pressures necessitate the use of vessels having higher pressure capabilities (30 atm or 435 psi). Matrices having large organic content, such as oils, can produce approximately 25 atm of pressure inside the vessel (as described in EPA Method 3052).

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 or 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: 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 vessel(s), or sealed vessel(s), there is the potential for any released acid vapors 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.

Users are therefore 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 reference 3 and the document listed in Sec. 13.2.1.

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 175 ± 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 3.

Alternatively, for a specific vessel type, specific set of reagent(s), and sample type, a calibration control mechanism can be developed. Through calibration of the microwave power for a specific number and type of vessels, vessel load, and heat loss characteristics of a specific vessel series, the reaction temperature profile described in Sec. 11.3.5 can be reproduced. The calibration settings are specific for the number and type of vessels 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 methods such as EPA Methods 3051, 3015, and 3052. 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. 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 (see refs. 1, 2, and 3 and the documents listed in 13.3.3 and 13.3.5).

6.1.2 The accuracy of the temperature measurement system should be periodically validated at an elevated temperature (see Section 12.2). 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 180 ± 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.

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 Volumetric 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 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 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 the document listed in Sec. 13.3.3.

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 and water, and metal-free detergents, if necessary, depending on the history of use of the container (Ref. 3). Plastic and glass containers are both suitable. For further information, see Chapter Three of SW-846.

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

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., soil, sludge, 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 reference 3 and the document listed in Sec. 13.3.5.

10.1.3 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 10.1.5. This data is clustered about the customary working power ranges. Non-linearity 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. Measure the power 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 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:

Equation 1

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

Where:

P = the apparent power absorbed by the sample in watts (W) (joule/sec)

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 °C)] 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 °C)] the calibration equation simplifies to:

Equation 2

$$P = (\Delta T)(34.86)$$

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 ± 2 V (Reference 3). 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 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 decomposition. 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 high concentration samples and low concentration 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 Weigh a well-mixed sample to the nearest 0.001 g into an appropriate vessel equipped with a controlled pressure relief mechanism. For soils, sediments, and sludges, use no more than 0.500 g. For oil or oil contaminated soils, initially use no more than 0.250 g. When large samples of oil are necessary, use of EPA Method 3052, which has sample scale-up options, is recommended. If the sample can not be well mixed and homogenized on an as received basis, then air or oven drying at 60°C or less, crushing, sieving, grinding, and mixing should be performed as necessary to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reduction in analytical variability, be aware that in certain unusual circumstances there could be loss of volatile metals (e.g., Hg, organometallics) or irreversible chemical changes (e.g., precipitation of insoluble species, change in valence state). See Chapter Three for more details.

11.3.2 Add 10 ± 0.1 mL concentrated nitric acid or, alternatively, 9 ± 0.1 mL concentrated nitric acid and 3 ± 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, iron, and silver from a variety of matrices upon addition of HCl are demonstrated in Section 17.0, in Figures 3 through 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 as a buildup 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 volatile or easily oxidized organic species. When digesting a matrix of this type, initially use no more than 0.100 g of sample. If a vigorous reaction occurs upon the addition of reagent(s), allow the sample to predigest in the uncapped digestion vessel until the reaction ceases. 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. However, if no appreciable reaction occurs, a sample mass of up to 0.250 g for oils, or 0.500 g for solids, may be used.

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 sensors 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 175 ± 5 °C in approximately 5.5 ± 0.25 minutes and remain at 175 ± 5 °C for 4.5 minutes, or for the remainder of the ten minute digestion period (see Refs. 2, 3, and 4 and the document listed in 13.3.4). The time versus temperature and pressure profile is given for a standard sediment sample in Figure 2. 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 previously in this section. (The number will depend on the power of the unit, the number of vessels, and the heat loss from the vessels (Ref. 3)).

The pressure should peak between 5 and 10 minutes for most samples (see Refs. 1 and 2 and the document listed in 13.3.4). If the pressure exceeds the pressure limits of the vessel, the pressure should be safely and controllably reduced by the pressure relief mechanism of the vessel.

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 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 (see Ref. 3 and the document listed in Sec. 13.3.3). 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 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 absorbing mass in the cavity. 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 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 (11.3.7.1), allowed to settle (11.3.7.2), or filtered (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 pre-rinsed 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 the nitric and hydrochloric 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 (Reference 3). Evaporation to near dryness 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. This

alternative may be used to alter either the acid concentration and/or acid composition prior to analysis. (For further information, see reference 3 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 weight 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 (see Ref. 3 and the document listed in Sec. 13.3.5). Interpolate the data to obtain the instrument settings needed to provide the wattage levels specified in Section 12.3.

12.5 Calculate the sample dry-weight fraction as follows:

$$\text{Dry-Wt fraction} = \frac{(W_2) - (W_3)}{(W_1) - (W_3)}$$

where: W_1 = Wt for sample + vessel, before drying, g

W_2 = Wt for sample + vessel, after drying, g

W_3 = Wt for empty, dry vessel, g

12.6 Convert the extract concentration obtained from the instrument in mg/L to mg/kg dry-weight of sample by:

$$\text{Sample concentration} = \frac{(C)\ (V)\ (D)}{(W)\ (S)}$$

where: C = Concentration in extract (mg/L)

D = Dilution factor

S = Solid dry-weight fraction for sample, g/g

V = Volume of extract, mL x 0.001

W = Weight of undried sample extracted, g x 0.001

13.0 METHOD PERFORMANCE

13.1 The fundamental chemical basis of Method 3051 with and without HCl has been compared with Method 3050 in several sources (see 13.3.4 and 13.3.5). Several papers have evaluated the leachability of NIST SRMs with this method (Ref. 1 and Sec. 13.3.5). Evaluations and optimizations of this method are being published (Ref. 5 and 6) as well as additional leaches performed on more matrices, which will be addressed in future literature papers. Method 3051 has been determined to be appropriate for enhancing recoveries of certain analytes. This data is contained in Section 17 of this method. Matrices tested include SRM 2710 (Montana Soil - Highly Elevated Concentrations), SRM 2704 (Buffalo River Sediment), and SRM 1084a (Wear Metals in Oil). Analytes demonstrating better recoveries upon addition of HCl include antimony, iron, and silver.

13.2 The following documents may provide additional guidance and insight on this method and technique:

13.2.1 Kingston, H. M. and L. B. Jassie, "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.

13.2.2 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water" ; ASTM, Philadelphia, PA, 1985, D1193-77.

13.3.3 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.

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

13.3.5 Walter, P. J. Special Publication IR4718: *Microwave Calibration Program*, 2.0 ed.; National Institutes of Standards and Technology: Gaithersburg, MD, 1991.

13.3.6 Kingston, H.M., Walter, P.J., Chalk, S.J., Lorentzen, E.M., Link, D.D., "Environmental Microwave Sample Preparation: Fundamentals, Methods, and Applications". In Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications; ACS Professional Reference Book Series; American Chemical Society: Washington, DC 1997.

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

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

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2. Binstock, D.A., Yeager, W.M., Grohse, P.M. and Gaskill, A. Validation of a Method for Determining Elements in Solid Waste by Microwave Digestion, Research Triangle Institute Technical Report Draft, RTI Project Number 321U-3579-24, November, 1989, prepared for the Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460.

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7. Link, DD., Kingston, H.M., Walter, P.J.; *Development and Validation of the EPA Microwave-assisted Methods 3015A and 3051A:* Validation Studies for Updated Microwave Leach Methods, Proceedings for the Waste Testing and Quality Assurance Symposium; July 1997.

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

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 3, Figures 1 through 7, and a flow diagram of method procedure.

TABLE 1

COMPARISON OF ANALYTE RECOVERIES FROM SRM 2704 (BUFFALO RIVER SEDIMENT) USING BOTH DIGEST OPTIONS OF METHOD 3051 (Refs. 5, 6)

Element	10 mL HNO_3 digest	9 mL HNO_3 + 3 mL HCl digest	Total Analyte Concentration
Cd	3.40 ± 0.34	3.62 ± 0.17	3.45 ± 0.22
Cr	84.7 ± 5.6	77.1 ± 12.6	135 ± 5
Ni	45.5 ± 5.9	42.2 ± 3.2	44.1 ± 3.0
Pb	163 ± 9	161 ± 17	161 ± 17

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

TABLE 2

COMPARISON OF ANALYTE RECOVERIES FROM SRM 4355 (PERUVIAN SOIL) USING BOTH DIGEST OPTIONS OF METHOD 3051 (Ref. 6).

Element	10 mL HNO_3 digest	9 mL HNO_3 + 3 mL HCl digest	Total Analyte Concentration
Cd	0.86 ± 0.16	0.85 ± 0.17	(1.50)
Cr	14.6 ± 0.47	19.0 ± 0.69	28.9 ± 2.8
Ni	9.9 ± 0.33	11.2 ± 0.44	(13)
Pb	124 ± 5.3	130 ± 3.6	129 ± 26

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.

TABLE 3

COMPARISON OF ANALYTE RECOVERIES FROM SRM 1084A (WEAR METALS IN OIL)
USING BOTH DIGEST OPTIONS OF METHOD 3051 (Ref. 6)

Element	10 mL HNO_3 digest	9 mL HNO_3 + 3 mL HCl digest	Total Analyte Concentration
Cu	91.6 ± 4.0	93.0 ± 2.6	100.0 ± 1.9
Cr	91.2 ± 3.3	94.3 ± 3.1	98.3 ± 0.8
Mg	93.2 ± 3.6	93.5 ± 2.8	99.5 ± 1.7
Ni	91.6 ± 3.9	92.9 ± 3.4	99.7 ± 1.6
Pb	104 ± 4.1	99.5 ± 5.1	101.1 ± 1.3

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

FIGURE 1

TEMPERATURE AND PRESSURE PROFILES FOR THE HEATING OF DIFFERENT RATIOS OF NITRIC ACID TO HYDROCHLORIC ACID USING METHOD 3051

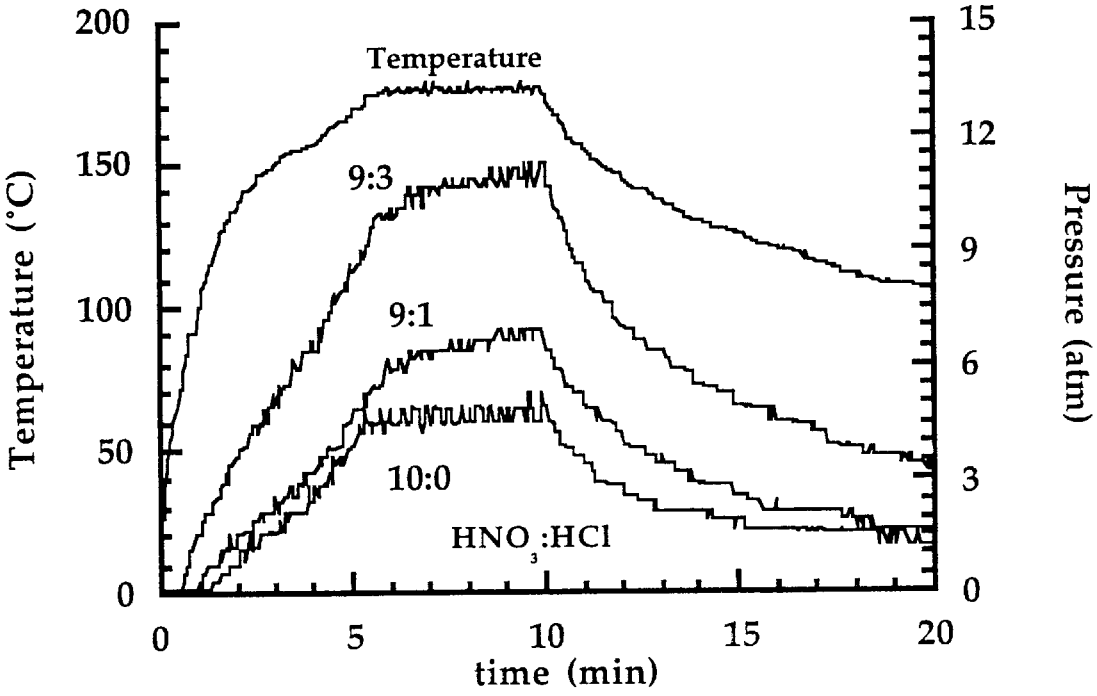


FIGURE 2

TEMPERATURE AND PRESSURE PROFILE FOR THE EXTRACTION AND DISSOLUTION OF NIST SRM 2704 (BUFFALO RIVER SEDIMENT) USING DIFFERENT RATIOS OF NITRIC ACID TO HYDROCHLORIC ACID

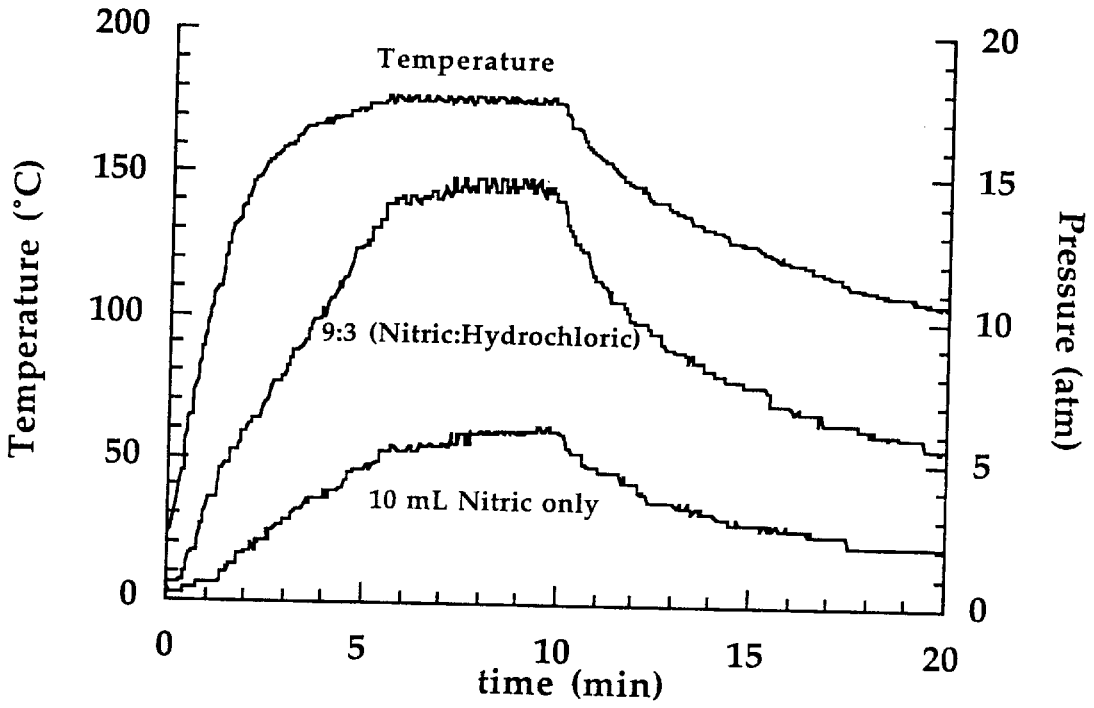


FIGURE 3

PERCENT RECOVERY OF ANTIMONY FROM NIST SRM 2710 (MONTANA SOIL) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7)

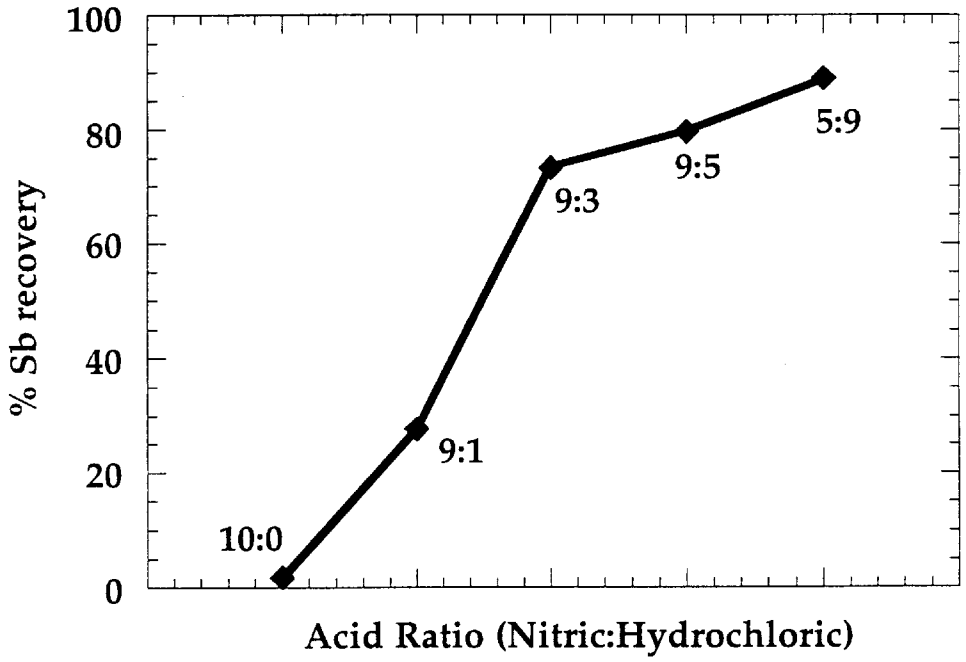


FIGURE 4

PERCENT RECOVERY OF ANTIMONY FROM NIST SRM 2704 (BUFFALO RIVER SEDIMENT) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7).

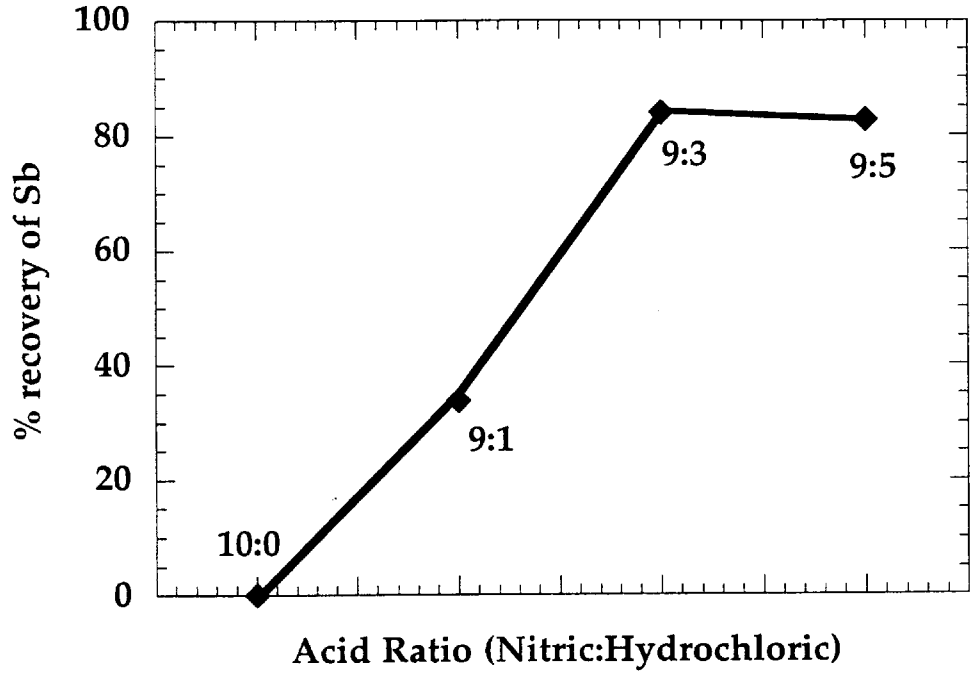


FIGURE 5

PERCENT RECOVERY OF IRON FROM NIST SRM 2704 (BUFFALO RIVER SEDIMENT) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7).

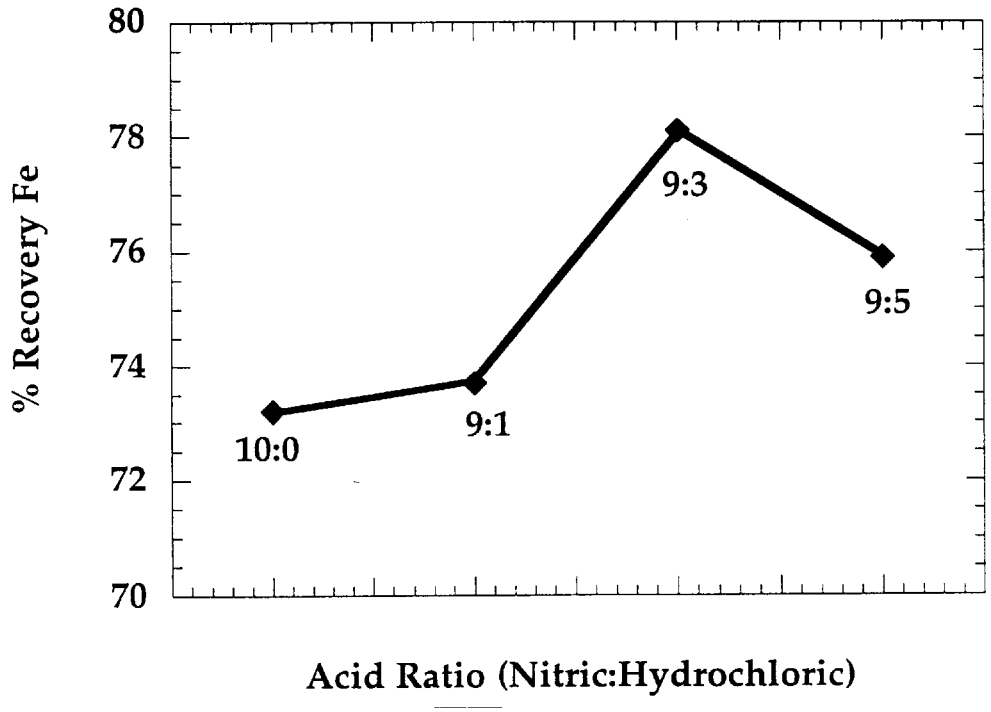


FIGURE 6

PERCENT RECOVERY OF SILVER FROM NIST SRM 2710 (MONTANA SOIL) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7)

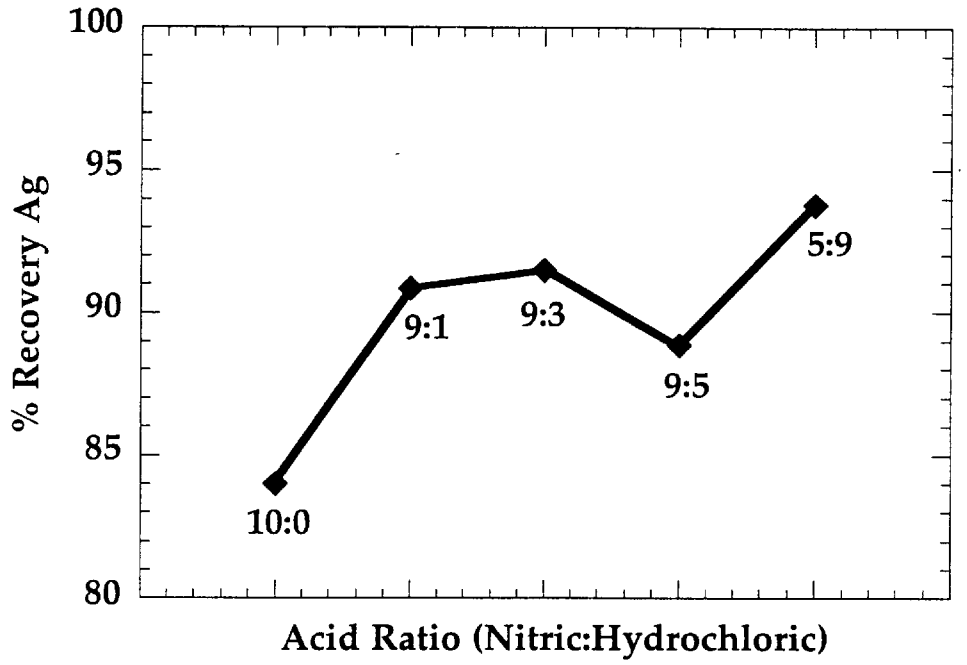
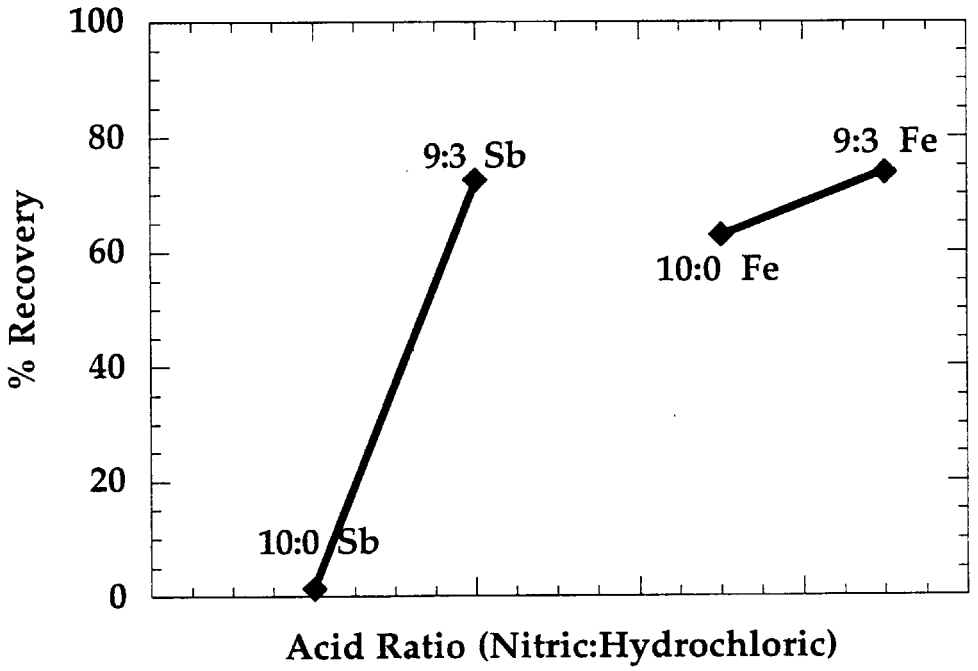


FIGURE 7

PERCENT RECOVERY OF ANTIMONY AND IRON, RESPECTIVELY, FROM SRM 4355 (PERUVIAN SOIL) USING BOTH DIGEST OPTIONS (10 ML HNO_3 AND 9 ML HNO_3 + 3 ML HCL) OF METHOD 3051 (N=6) (Refs. 6, 7)



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