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Development and Validation of the New EPA Microwave-Assisted Leach Method 3051A

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An updated, optimized method has been developed to minimize the chemical biases and inefficiencies between two EPA SW-846 alternative leach methods, microwave-assisted Method 3051 and open vessel Method 3050B, for the determination of metals in solid samples. The microwave method is more easily transferred and provides more reproducible leach results, mainly from more precise control of the temperature during the extraction process. Previously, reagent limitations originally placed on Method 3051 did not allow these alternative methods to yield similar results for some analytes. This work describes the development and validation of EPA Method 3051A, which includes an option to add HCl to improve the chemistry of the microwave method, making it comparable to open vessel Method 3050B. Including HCl provides complexation and stabilization of some analytes by Cl^- species, leading to improved recoveries. Optimizing the acid combination involved adding either 1, 3, or 5 mL of HCl to 9 mL of HNO_3 and performing a series of leaches on standard reference materials (SRMs). Optimum recoveries are achieved for "problem" analytes, such as Ag and Sb, by adding 3 mL of HCl. Recovery of other metals, such as Cu and Ni, are unaffected. Method validation was provided by leaching and analysis of SRMs.

Introduction

The method of expressing analyte concentrations when environmental leach methods are used poses unique quantification problems. When analyte concentrations from leach methods are compared, the precision of the measurement is used as a defacto expression of accuracy. In contrast to total decomposition methods, such as EPA SW-846 Method 3052, that provide absolute analyte concentrations, leach methods provide only relative concentrations based on the sample preparation procedure and reaction conditions achieved. Standard methods are used by a large number of different laboratories. Achieving comparable results among these laboratories depends on achieving comparable operating conditions. Control and transfer of leach methods is more difficult than for total decomposition methods. The reproducibility of the results depends on the conditions achieved during the leach process. Microwave heating with temperature feedback control has demonstrated more precise temperature control than is possible using a hot plate (*1*).

Heavy metals enter the environment as a result of industrial processes, incineration, fossil fuel production, municipal sewage processing, and dumping of metal-containing wastes. Many of these metals are potentially toxic to both humans and ecosystems, and the mobility and bioavailability of these metals must be determined. Acid leaching of solid samples is the most common method for estimating the mobility or bioavailability of toxic heavy metals in an environmental sample (*2, 3*). Leach methods for solid samples currently listed in the EPA's SW-846 manual of methods include Methods 3050B and 3051. These methods, outlined in Table 1, are used when it is more appropriate to determine the amount of analyte that may become available under worst case environmental conditions rather than either the total amount of analyte present or a TCLP evaluation (EPA Method 1311 (*4*)). EPA Method 3051, originally developed in 1988, was restricted to the exclusive use of HNO_3 to minimize potential instrumental interferences from HCl and its resulting species on some analytical detection methods, such as graphite furnace atomic absorption spectroscopy (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS).

EPA Method 3051 was developed as a microwave-enhanced alternative to leach Method 3050B and has been a promulgated SW-846 method for several years (*4, 5*). Closed vessel microwave heating offers several advantages over hot plate heating for acid leaching of environmental samples. Higher pressures attainable in closed vessels allow elevated temperatures to be reached, thus reducing reaction times from several hours to minutes. Closed fluoropolymer vessels also minimize potential losses of analytes due to volatilization (*1, 6*). In addition, use of temperature feedback control in microwave leaches typically provides much better control of the temperature than is possible on a hot plate, typically ±2.5 °C or less. This is an important advantage because leach levels are highly dependent on the reaction conditions achieved, and temperature has been proven to be one of the most important parameters in determining leach precision (*1*). Because precision is used as accuracy when comparing leach results, this precise temperature control becomes even more significant. Leachable amounts are not absolute quantities, which forces the precision of the measurement to be used as an indicator of the accuracy of the measurement. Also, using microwave energy and temperature feedback control allows for better transfer of standard methods between analysts, laboratories, and even foreign countries as compared to the wide variability and subjectivity associated with hot plate methods. Despite these advantages, Method 3051 shows a negative bias for certain analytes as compared to Method 3050B leaches (*6*−*9*). Biases on recoveries of certain RCRA-regulated metals have been demonstrated. Recently, an updated version of the microwave leach method was accepted by the EPA and is included in Update IVA of the SW-846 manual. As shown in Table 1, the new EPA Method 3051A provides the analyst with options to perform either a HNO_3-only or a HNO_3-HCl mixed-acid leach when appropriate for the recovery of the target analyte(s). This paper describes the control and transfer of elemental leach methods, presents the development and validation of EPA Method 3051A, and extends the fundamental understanding of key parameters and acid chemistry to achieve optimum leach recoveries.

Experimental Section

Sample Preparation and Analysis. Microwave leaches were performed using the MLS 1200-Mega with the microwave digestion rotor MDR-300/10 from Milestone USA (Monroe, CT) and the MDS-2100 using HDV (heavy duty vessels) from

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TABLE 1. Comparison of Three EPA SW-846 Leach Methods (*4*)

	EPA Method 3050B	EPA Method 3051	EPA Method 3051A
vessels	open vessel	closed vessel	closed vessel
heating method	hot plate heating block open vessel microwave	microwave	microwave
reagents	HNO_3 HCl H_2O_2	HNO_3	HNO_3 or HNO_3 and HCl
heating program	series of 95 °C refluxes 2−8 h or more	175 °C in 5.5 min hold at 175 °C for 4.5 min	175 °C in 5.5 min hold at 175 °C for 4.5 min

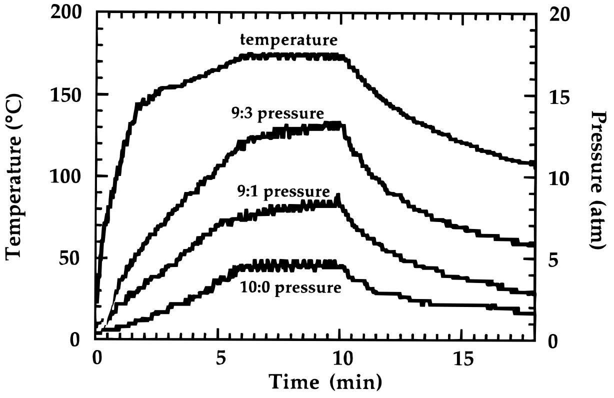

FIGURE 1. Typical temperature and pressure profiles for the heating of leaching acids using EPA Method 3051A.

TABLE 2. Recoveries of Selected RCRA-Regulated Elements from SRM 2704 (Buffalo River Sediment) Using Alternative EPA SW-846 Leach Methods 3050B and 3051 (*6*−*8*)[a]

element	Method 3050B leach	Method 3051 leach	bias at 95% CI[b]
Co	11.1 ± 1.0	10.7 ± 0.5	no
Cr	83.3 ± 5.3	81.7 ± 1.9	no
Ni	37.7 ± 2.0	36.4 ± 1.0	no
Pb	147 ± 6	143 ± 3	no
B	55.4 ± 9.7	34.6 ± 3.3	yes
Be	1.05 ± 0.10	0.69 ± 0.22	yes
Fe	3.29 ± 0.14%	2.91 ± 0.22%	yes
V	49.4 ± 5.6	25.1 ± 3.0	yes

[a] Results reported in mean μg/g analyte (or %) ±95% confidence interval. [b] Bias signifies no overlap at 95% confidence interval.

CEM (Matthews, NC). Concentrated HNO_3 and HCl were obtained (ACS reagent grade, Fisher Scientific, Pittsburgh, PA) and purified by subboiling distillation using a DuoPUR quartz still (Milestone USA, Monroe, CT) prior to use. The standard reference materials (SRMs) used in this study, SRM 2704 (Buffalo River sediment), SRM 4355 (Peruvian soil), SRM 1084a (wear-metals in lubricating oil), and SRM 1634c (trace metals in fuel oil), were obtained from the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. These SRMs were also used in the original NIST round-robin validation study evaluating Method 3051 versus Method 3050B (*7*, *8*), allowing for appropriate extension of these studies for comparison and validation of the mixed-acid option of Method 3051A. For validation of Method 3051A, appropriate masses of the solid samples were leached according to method specifications (see Table 1). After filtration and dilution, elemental analysis was performed using either flame atomic absorption spectroscopy (FAAS) (AAS 1100, Perkin-Elmer) or ICP-MS (PlasmaQuad II, VG Elemental). To minimize the potential for cross-contamination, all microwave vessels and materials coming in contact with samples were cleaned using either hot or room-temperature acid cleaning procedures prior to use and between each set of leaches. All procedures prior to and following microwave leaching were performed in a class 100 clean laboratory (*1*).

Results and Discussion

Safety. Because Method 3051A involves heating reagents in closed vessels, pressure must be considered from a safety standpoint. The reagent change causes the pressure during a typical leach to nearly triple, making certain vessels specified for use in the original EPA Method 3051 inappropriate for use in the updated Method 3051A. Prior pressure specification in Method 3051 was 10 atm (110 psi), but vessels for use in Method 3051A must be capable of withstanding pressures of at least 30 atm (435 psi). Figure 1 shows that the pressure resulting from heating the leaching acid(s) (i.e., no solid sample is present) increases as the volume of HCl is increased (*9*). Heating 10 mL of HNO_3, labeled 10:0, results in a pressure of approximately 5 atm. As HCl is added, the pressures inside the vessel increase dramatically, with the 9 mL of HNO_3: 3 mL of HCl mixture reaching approximately 12 atm. The increased pressures result from the formation of several additional species, including chlorine gas and nitrosyl chloride (NOCl), which further decomposes into Cl_2 and NO (*10*). These gaseous products increase both the pressure and the reactivity of the reagent mixture. Pressures of nearly 30 atm have been reached during the heating of 250-mg samples of oil-type matrices, which produce greater amounts of CO_2 and NO_x gas upon decomposition of the matrix (*1*). This is possible only when the reagents have sufficient oxidizing strength to provide total decomposition of the matrix, as in an HNO_3-only digestion. Typically, mixed-acid leaches of soils and sediments generate higher pressures due to heating of the acids themselves (Figure 1), while leaches of oils generate less pressure due to incomplete decomposition of the matrix. It is also important to note that internal pressures will vary somewhat depending on the vessel manufacturer due to the various heat loss characteristics of different vessel materials and designs. A more detailed evaluation and discussion of this concept is given elsewhere (*1*).

As another safeguard, when using the mixed-acid option of Method 3051A, the order of adding the acids is also specified. The analyst is cautioned that “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” (*4*).

Reagent Chemistry. Several studies have determined that alternative leach methods do not yield comparable results for some RCRA-regulated elements (*6*−*8*). As Table 2 demonstrates, the results using the microwave method in general show better precision due to more precise control of temperature. However, Method 3051 demonstrates a bias

TABLE 3. Some Possible Species Produced during Acid Leaches with Methods 3050B and 3051 (*1*, *6*)

	EPA Method 3051	EPA Method 3050B
reagents	HNO_3	HNO_3
		HCl
		H_2O_2
reactive species	H_2O	H_2O
	H_3O^+	H_3O^+
	NO_3^-	NO_3^-
	NO_2^+	NO_2^+
	NO_2	NO_2
	O_2	O_2
	digest products[a]	Cl^-
		NOCl
		Cl_2
		HO_2^-
		O_2^{2-}
		O_2 [b]
		digest products[a]

[a] Digest products may include such species as aqueous metal nitrates, carbon dioxide, water, etc. [b] Free radical oxygen species.

for some analytes as compared to Method 3050B results. This bias can be attributed to the reagents used in each method. Excluding the complexation and stabilization properties of HCl from the microwave method reduces its effectiveness for recovering certain analytes. The inclusion of HCl and H_2O_2 in Method 3050B results in the formation of several reactive species that are not found in the Method 3051 leach mixture (Table 3). The inherent drawback of the HNO_3-only microwave leach is that it does not reproduce the chemistry of the open vessel leach, which uses HNO_3, HCl, and H_2O_2. The difference between the chemistries of the leach methods is attributed to the absence of HCl in the microwave method.

H_2O_2 is included in Method 3050B as an oxidizer because of the lower temperature limitation (95 °C) of these methods. The oxidizing power of H_2O_2 increases as the acidity of the solution increases (*1*, *11*, *12*). H_2O_2 is added to the HNO_3 multiple times to increase the overall oxidizing strength of the solution. The combination of repeated additions of H_2O_2, modestly elevated temperatures, and lengthy reaction times (up to 8 h or more) provide the oxidizing ability of the open vessel leach methods. The closed vessel microwave method heats the leaching mixture to 175 °C. Because the oxidizing strength of a solution increases as the temperature increases (*13*), HNO_3 at 175 °C is a stronger oxidizer than HNO_3 at 95 °C. At these higher temperatures, the need for increasing the oxidizing strength by the addition of H_2O_2 is eliminated. Two common reactions occurring in the leaching of solid matrices are oxidation reactions, as illustrated below (*1*).

Oxidation of Most Metals into Nitrates:

$$M^0 + HNO_3 \rightarrow M(NO_3)_x(aq) + NO(g) + H_2O \qquad (1)$$

It should be noted that certain metals (high-purity iron, for example) passivate in the presence of concentrated HNO_3, and stainless steel and other alloys are resistant to decomposition in pure HNO_3 (*11*, *12*).

Oxidation of Most Organic Material:

$$(CH_2O)_x + HNO_3 \rightarrow CO_2(g) + NO_x(g) + H_2O \qquad (2)$$

The oxidation of organic material (represented by (CH_2O)) produces the gases CO_2 and NO_x as final products, which result in the increased pressures inside closed vessels when organically based matrices are digested.

Increasing the temperature of HNO_3 to 175 °C provides similar oxidizing strength as compared to the open vessel leach using both HNO_3 and H_2O_2. The key difference between Methods 3050B and 3051 and the new Method 3051A is the complexation and stabilization properties gained by adding HCl. The following equations describe specific reactions of certain metals that form stabilized chloro complexes. Additional information on the chemistry of typical mineral acid decomposition reagents with most elements is provided on the worldwide web at Duquesne University's SamplePrep website, which is coordinated with references (*14*). A recent review of acid chemistry is also available (*1*).

Antimony. Sb has been documented to be unstable and insoluble in the oxidizing environment encountered with HNO_3 leaches (*15*). This environment typically oxidizes Sb to the 5+ oxidation state. Losses of Sb in the 5+ state have been reported due to an oxidation/sorption process (*16*–*19*). Various mechanisms, shown in eqs 3 and 4, have been proposed for this process whereby Sb is oxidized in strongly oxidizing environments and subsequently adsorbs either onto undigested reactive silicate particles in the solid matrix or onto glass surfaces such as vessel walls (*20*):

$$Sb(III) + HNO_3 + HClO_4 \rightarrow Sb_2O_5 \cdot nH_2O \rightarrow Sb_2O_5 \ (18) \qquad (3)$$

$$Sb + HNO_3 \rightarrow Sb_2O_3 \text{ and/or } Sb_4O_4(OH)_2(NO_3)_2 \rightarrow Sb_2O_3 + O_2, \Delta \rightarrow Sb_2O_5 \ (10, 19) \qquad (4)$$

Sb species in the 3+ state can also be lost in the presence of HCl by complexing with chloride ions to form a volatile species that can be readily lost from solution, especially when heated (*11*, *12*). More complete recovery of Sb requires initial oxidation to the 5+ state, followed by complexation with HCl to form $SbCl_6^-$ (eq 5). This stable, aqueous anion remains soluble in solution and does not adsorb onto undigested siliceous materials (*16*, *17*):

$$Sb + HNO_3 \rightarrow Sb^{5+} + HCl \rightarrow SbCl_6^-(aq) \qquad (5)$$

Iron. High concentrations of Fe are frequently found in contaminated soils and sludges and can be stabilized in solution. In the presence of a complexing anion such as Cl^-, the Fe(II) species can form the aqueous anion $FeCl_4^{2-}$, while the Fe(III) species can form $FeCl_4^-$ (*10*). Both of these species are stable in solution:

$$Fe^{2+ \text{ or } 3+} + HCl \rightarrow FeCl_4^{2- \text{ or } -}(aq) \qquad (6)$$

Silver. Most environmental samples contain trace quantities of Cl^- as a matrix component. In the presence of these trace quantities of Cl^-, Ag precipitates out of solution as solid AgCl. The solubility of AgCl increases with increasing Cl^- concentration due to the formation of complex anions of the formula $AgCl_n^{1-n}$ (*11*). By adding HCl in Method 3051A, the Cl^- concentration is increased, and the $AgCl_n^{1-n}$ complex anions that are formed are stabilized in solution (eq 7):

$$Ag^+ + Cl^- \rightarrow AgCl(s) + Cl^- \rightarrow AgCl_2^-(aq) \qquad (7)$$

The three elements discussed above are examples of those reported to suffer recovery problems with HNO_3-only leaches. The presence of Cl^- species acts to complex and stabilize other metals as well. However, these examples give specific rationale for including HCl in the microwave method to match the chemistry of open vessel Method 3050B. These reactions are also important for achieving better recoveries using total decomposition methods. HCl should also be employed in these methods when losses or incomplete recoveries of certain analytes have been noted.

TABLE 4. Comparison of Recoveries of Analytes from SRM 2704 (Buffalo River Sediment) Using both Digest Options of EPA Method 3051A (*7*−*9*)[a]

element	10:0 leach[b]	9:1 leach[b]	9:3 leach[b]	9:5 leach[b]	3050B[c]	3051[c]	total
Co	12.2 ± 1.84	11.7 ± 2.66	11.8 ± 1.15	12.3 ± 3.78	11.1 ± 2.75	10.7 ± 1.46	14.0 ± 0.22
Cd	3.40 ± 0.34	3.60 ± 0.36	3.62 ± 0.17	3.35 ± 0.50	3.32 ± 0.43	3.19 ± 0.61	3.45 ± 0.22
Cr	84.7 ± 5.6	79.0 ± 10.1	77.7 ± 12.6	82.2 ± 12.2	83.3 ± 14.0	81.7 ± 5.33	135 ± 5
Ni	45.5 ± 5.94	36.5 ± 1.26	42.2 ± 3.17	38.9 ± 6.11	37.7 ± 5.15	36.4 ± 2.52	44.1 ± 3.0
Pb	163 ± 8.6	148 ± 6.9	161 ± 17	151 ± 8.4	147 ± 16.6	143 ± 9.46	161 ± 17
V	16.5 ± 3.00	19.5 ± 2.69	21.9 ± 3.68	22.3 ± 2.57	24.2 ± 7.21	21.0 ± 2.46	nc[d]

[a] Results reported in mean μg/g analyte ± 95% confidence interval. Total analyte concentration taken from NIST SRM certificate of analysis. [b] Results of analysis for current validation study. [c] Results of analysis from validation study of Method 3051 vs Method 3050B. [d] nc, not certified.

TABLE 5. Comparison of Recoveries of Analytes from SRM 4355 (Peruvian Soil) Using both Digest Options of EPA Method 3051A vs Validation Data for EPA Methods 3050B and 3051 (*8*, *9*)[a]

element	10:0[b]	9:3[b]	3050B[c]	3051[c]	total
Ag	1.28 ± 0.11	1.61 ± 0.16	<4	<4	(1.90)
Cd	0.86 ± 0.16	0.85 ± 0.17	1.03 ± 0.08	0.90 ± 0.09	(1.50)
Cr	14.6 ± 0.47	19.0 ± 0.69	17.1 ± 2.37	13.8 ± 1.18	28.9 ± 2.8
Ni	9.9 ± 0.33	11.2 ± 0.44	9.93 ± 1.45	9.59 ± 1.10	(13)
Pb	124 ± 5.3	130 ± 3.6	131 ± 5.4	121 ± 3.0	129 ± 26
V	64.5 ± 1.6	86.1 ± 2.0	81.4 ± 6.5	61.2 ± 2.1	(151)

[a] Results reported in mean μg/g analyte ± 95% confidence interval. Total analyte concentration taken from NIST SRM certificate of analysis. Values in parentheses indicate reference concentrations. [b] Results of analysis for current validation study. [c] Results of analysis from validation study of Method 3051 vs Method 3050B.

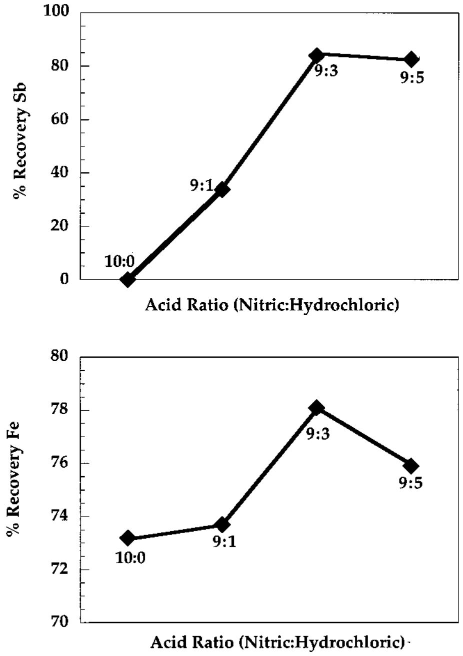

FIGURE 2. Percent recovery of antimony and iron from SRM 2704 using various mixed-acid combinations according to EPA Method 3051A.

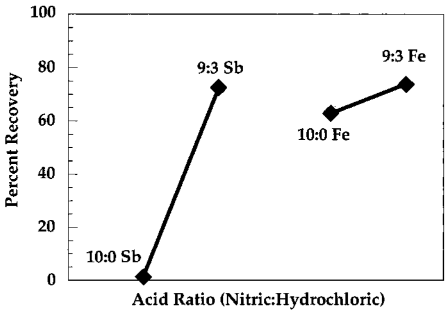

FIGURE 3. Percent recovery of antimony and iron from SRM 4355 using both digest options of EPA Method 3051A.

Reagent Optimization. The reagent combination of the method was optimized so that the oxidizing power of HNO_3 was not reduced by adding excessive amounts of HCl. Initial studies to refine the acid ratio in terms of oxidizing strength and complexation were performed using samples of SRM 2704. The ratios of HNO_3 to HCl that were tested (in mL) were 10:0, 9:1, 9:3, and 9:5. Recoveries for several of the 26 RCRA-regulated elements were determined. As shown in Figure 2, adding HCl leads to enhanced recoveries of Sb and Fe (*9*). Recoveries for Sb increase from 0% in the HNO_3-only leach to 80% in the 9 mL of HNO_3: 3 mL of HCl leach, while recoveries for Fe increase from approximately 73% to over 78%. Additional quantities of HCl (the 9:5 ratio) provided no further enhancement in recovery for either analyte, and a slight decrease was observed for Fe for the 9:5 acid ratio.

It was also important to demonstrate that the mixed-acid Method 3051A leach preserves the recoveries of those analytes that did not demonstrate any previous recovery bias between Method 3050B and Method 3051. Recoveries for additional analytes from SRM 2704, along with the results from the original validation study for Method 3051 versus Method 3050B, are shown in Table 4. Analyte recoveries are either enhanced or preserved by the mixed-acid leaches. However, the results of analysis for some of the 9:5 mixed-acid leaches demonstrate increased variability. This variability may be due in part to preparing all analytical standards and spike solutions in dilute HNO_3 (~1%) instead of matrix matching by adding HCl (*21*). Because the 9:5 mixed-acid leach either does not provide enhancement in recoveries or shows lower recoveries than the 9:3 mixed-acid leach, the 9:3 ratio is most appropriate and is specified in Method 3051A.

Method Performance. The performance of Method 3051A was evaluated on three other matrix types. Figure 3 compares the recovery of Sb and Fe from SRM 4355 for the HNO_3-only and mixed-acid leaches. Recovery of Sb increased from almost 0% in the HNO_3-only (10:0) leach to approximately 75% in the mixed-acid (9:3) leach, while the recovery of Fe increased from approximately 60% to over 75%.

TABLE 6. Comparison of Recoveries of Analytes from SRM 1084a (Wear-Metals in Lubricating Oil) Using both Digest Options of EPA Method 3051A (*9*)[a]

element	10:0 leach	9:3 leach	total
Ag	93.3 ± 2.9	98.2 ± 6.2	101.4 ± 1.5
Al	96.7 ± 4.2	99.0 ± 5.2	(104)
Cr	91.2 ± 3.3	94.3 ± 3.1	98.3 ± 0.8
Cu	91.6 ± 4.0	93.0 ± 2.6	100.0 ± 1.9
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

[a] Results reported in mean μg/g analyte ± 95% confidence interval. Total analyte concentration taken from NIST SRM certificate of analysis. Values in parentheses indicate reference concentrations.

TABLE 7. Comparison of Recoveries of Analytes from Simulated Sludge (∼0.25 g of SRM 2704 (Buffalo River Sediment) and ∼0.25 g of SRM 1634c (Trace Metals in Fuel Oil)) Using both Digest Options of EPA Method 3051A vs Validation Data for EPA Methods 3050B and 3051 (*8*, *9*)[a]

element	10:0 leach[b]	9:3 leach[b]	3050B leach[c]	3051 leach[c]
Ag	0.23 ± 0.04	0.25 ± 0.07	<4.0	<4.0
Cd	1.74 ± 0.13	1.78 ± 0.33	1.67 ± 0.09	1.50 ± 0.09
Co	6.99 ± 0.71	6.08 ± 0.95	5.89 ± 0.63	5.89 ± 0.52
Cr	49.4 ± 2.9	44.7 ± 2.4	42.3 ± 2.8	43.1 ± 2.1
Mo	1.61 ± 0.16	2.00 ± 0.51	<2.5	<2.5
Ni	29.8 ± 2.0	25.5 ± 3.6	31.4 ± 2.5	30.5 ± 2.1
Pb	84.6 ± 5.5	77.1 ± 6.9	76.4 ± 3.8	74.5 ± 3.9

[a] Results reported in mean μg/g analyte ± 95% confidence interval. [b] Results of analysis for current validation study. [c] Results of analysis from validation study of Method 3051 vs Method 3050B.

Results for other analytes from SRM 4355 are shown in Table 5. These data demonstrate that for other "problem" analytes, such as Ag and V, the 9:3 mixed-acid leach increases the recovery as compared to the HNO_3-only leach. At the same time, recoveries for other "nonbiased" analytes, such as Cd and Pb, are preserved in the 9:3 mixed-acid leach. Recoveries obtained using the 9:3 Method 3051A digest are in good agreement with those from the Method 3050B leach, which signifies that the reagent-induced bias has been minimized.

For the leaching of the oil and simulated sludge samples, the HNO_3-only leach reached a higher pressure (20 atm) than the mixed-acid leach (10 atm). This indicates that less of the organic matrix is being oxidized than in the HNO_3-only leach. Despite this difference, the effective leaching of metals from both types of matrices is quite similar, and recoveries are preserved when using the mixed-acid leaching option. Leach results are shown in Table 6 for SRM 1084a, and in Table 7 for the simulated sludge matrix. Depending on the oil matrix and the target analyte(s), it may be desirable to use only HNO_3 to maintain the highest degree of oxidizing conditions, an option given in Method 3051A contributing to its greater flexibility over the original Method 3051 protocol.

Method Control and Transfer. Because of the special conditions under which leach results are compared, the reproducibility of the reaction conditions is critical. Also, it is the practice of some testing labs and agencies in foreign countries to adopt EPA methods as their standard methods. Thus, the development of reproducible standard methods has both national and worldwide importance. This requires methods that provide reproducible control and accurate transfer. As demonstrated, use of microwave energy and temperature feedback control exceeds other methods in terms of the reproducibility of conditions and ease of method transfer from one user to another. Temperature, the parameter that controls reactions, can be maintained more accurately, resulting in more precise results.

Summary. The data presented here provide additional validation for the updated EPA Method 3051A. The effectiveness of including HCl in the leaching acid mixture for enhancing the recoveries of problem RCRA-regulated metals, such as antimony and iron, has been shown. The mixed-acid leach option also shows comparable recoveries for other nonbiased analytes. The chemistry of the open vessel methods, which include HCl and H_2O_2, is more closely reproduced by the mixed-acid option of microwave Method 3051A. The mixed-acid microwave Method 3051A provides an efficient, unified leaching chemistry for all 26 RCRA-regulated elements in a single microwave leach method.

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