

# **Acid Extraction of Sediments, Sludges, and Soils**

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## 1. SCOPE, APPLICATION, AND SUMMARY OF METHOD

This method has been written to provide digestion procedure for the preparation of sediments, sludges, and soil samples for analysis by inductively coupled plasma mass spectrometry (ICP-MS). Samples prepared by this method may be analyzed by ICPAES (inductively coupled plasma atomic emission) or GFAA (graphite furnace atom absorption) for all the listed metals as long as the detection limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest.

This method will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. Availability may be different in benthic environments where benthic organism ingest sediment particles and may dissolve some elements from mineral lattice.

For the digestion of samples, a representative 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

## 2. SAMPLE PREPARATION

### *2.1 INTERFERENCES*

Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in determining whether Method 3050B is applicable to a given waste.

### *2.2. APPARATUS AND MATERIALS*

- a) Drying ovens - able to maintain temperature within  $\pm 4^\circ$  in the range of 30° to 110 °C.
- b) Digestion Vessels - 50-mL.
- c) Ribbed watch glasses (plastic)
- d) Disposable filters
- e) Centrifuge and centrifuge tubes.
- f) Analytical balance - capable of accurate weighing to 0.01 g.
- g) Mod Block adjustable and able to maintain a temperature of 90-95°C.
- h) Graduated cylinder or equivalent volume measuring device.
- i) Volumetric Flasks (PE) 100-mL.

### *2.3 REAGENTS*

Reagent with adequate purity to perform trace element analysis shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

- a) Reagent Water: For all digestion procedures, dilution of acids, and final step of cleaning procedures, water with purity higher than 18 M $\Omega$  is used. Reagent water shall be interference free.
- b) Nitric acid (concentrated): OmniTrace 69-70% HNO<sub>3</sub> (e.g. EM-NX0407-1) is used for digestion. OmniTrace Ultra 69-70% HNO<sub>3</sub> (EM-HX0628-&) is used for acidification and preparation of standards, sample dilution and blank solution.
- c) Hydrogen peroxide (30%), H<sub>2</sub>O<sub>2</sub> Extra Pure (EM1.08600.250) is used as oxidant for organic matter.

Trace metal concentration of acids as certified by supplier are listed in the Appendix.

#### 2.4. CLEANING PROCEDURE

- a) Soak in soap water (Micro ®)
- b) Rinse with tap water until all soap is removed
- c) Rinse with distilled water
- d) Fill bottles and flasks with 3% HCl, sonicate at 40 °C for 30 minutes
- e) Rinse with glass distilled water (3x)
- f) Fill bottles and flasks with 3% HNO<sub>3</sub> sonicate at 40 °C for 30 minutes
- g) Rinse with glass distilled water (3x)
- h) Rinse with 18 M $\Omega$  water (3x)
- i) Dry in drying oven at 50 °C.

#### 2.5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples must have been collected using a sampling plan that addresses the considerations discussed in sampling plans. See chapter 9 of the 3<sup>rd</sup> edition of SW 846 (<http://www.epa.gov/SW-846/main.htm#chap>).

All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. Non-aqueous samples should be refrigerated upon receipt and analyzed as soon as possible. If freezing is not possible samples should be kept cold and in darkness. It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce sub-sample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

#### 2.6 DIGESTION PROCEDURE

Pour sample into aluminum tray and dry the sample in drying oven at 105° C over night. Mix the sample thoroughly to achieve homogeneity and sieve (<2mm), if appropriate and necessary, using a USS No. 10 sieve (2 mm). All equipment used for homogenization should be clean.

Weigh 1 g of dry sample to the nearest 0.01 g and transfer to a 50 mL tube. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. See appendix for acid handling and safety.

For the digestion add 10 mL of 1:1 HNO<sub>3</sub>, mix the slurry, and cover with a watch glass (PE). Heat the sample to 90°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO<sub>3</sub>, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO<sub>3</sub>, repeat this step (addition of 5 mL of conc. HNO<sub>3</sub>) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO<sub>3</sub>. Using a ribbed watch glass heat at 90°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the tube at all times, make sure that sample does not evaporate more then down to 5 mL. Close tube and cool sample, add 2 mL of

water cover the vessel with a watch glass warm to start the peroxide reaction. Slowly add 3 mL of 30% H<sub>2</sub>O<sub>2</sub> in 0.5 mL steps to the sample. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides; cool the sample down. For high organic content more H<sub>2</sub>O<sub>2</sub> may be needed but do not add more than a total of 10 mL of H<sub>2</sub>O<sub>2</sub>. Bring all samples up to 30 mL and centrifuge for 15 minutes at 2,000-3,000 rpm. Filter samples through Whatman No. 41 filter using PE funnel and collect into 100 mL flasks, rinse filter paper thoroughly with 18 MΩ water. Fill up the 100 mL flask to mark and mix; sample is now ready for analysis by ICP-MS. The sample has a HNO<sub>3</sub> concentration of approximately 5%. Take amount of sample and dilute to appropriate concentration and adjust to 1% HNO<sub>3</sub> using *omnitrace ultra* grade acid.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

### 2.7 CALCULATIONS

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided. If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

### 2.8 QUALITY CONTROL

For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded.

NOTE: These ranges will vary with sample matrix, molecular form, and size.

## 3 METHOD PERFORMANCE

Based on EPA method 200.8, the analytical methods described here allow for the quantization of total recoverable elements in waste waters, sludges, and soils. Analysis of appropriately prepared samples is conducted by inductively coupled plasma mass spectrometry (ICP-MS). The analytes shown in Table I constitute the usual suite of trace elements included in method 200.8 analyses; however, additional non-trace elements (such as aluminum, calcium, iron, magnesium, potassium, sodium, and silica) may be determined in final digestate as appropriate.

Table I. Typical suite of elements determined by EPA Method 200.8.

	Element Name	Element Symbol	LOD ppb
<b>Trace Elements EPA 200.8 Validated</b>	Antimony	Sb	1.5
	Arsenic	As	0.5
	Barium	Ba	0.7
	Beryllium	Be	0.04
	Cadmium	Cd	0.5
	Chromium	Cr	0.8
	Cobalt	Co	2.0
	Copper	Cu	1.5
	Lead	Pb	0.4
	Manganese	Mn	1.4
	Mercury	Hg	
	Molybdenum	Mo	0.8
	Nickel	Ni	0.8
	Selenium	Se	0.8
	Silver	Ag	0.8
	Thallium	Tl	1.0
	Thorium	Th	0.8
	Uranium	U	0.8
Vanadium	V	1.0	
Zinc	Zn	0.7	
<i>NON-TRACE ELEMENTS</i>	Aluminum	Al	0.8
	Calcium	Ca	70
	Iron	Fe	20
	Magnesium	Mg	20
	Potassium	K	30
	Sodium	Na	26
	Silicium	Si	

### 3.1 SOLUTIONS AND STANDARDS

All solutions prepared for use in this method must be stored in polyethylene containers – the use of glassware is not acceptable. The useful lifetime of these solutions is no more than about one week.

- Analytical grade deionized water (DI H<sub>2</sub>O)*. Must have a resistivity of 17.5–18.5 MΩ/cm.
- Diluent solution*. Must contain 1.0 % concentrated HNO<sub>3</sub> by volume. Combine 100 mL trace metals analysis grade concentrated HNO<sub>3</sub> in several liters of DI H<sub>2</sub>O, and bring to a total final volume of 10 L with DI H<sub>2</sub>O. Mix thoroughly.
- ICP-MS tuning solution*. Contains 10 ppb Li, Y, Ce, Tl, and Co for instrument tuning and verification of performance. Mixed from single element standards of 1000 ppm concentration: *Preparation of stock solution*: Pipette 1 mL of each element solution into 100 mL volumetric flask and fill with 1% HNO<sub>3</sub> diluent. *Preparation of tuning solution*: Pipette 1 mL of stock solution in 1000 mL flask and fill with 1% HNO<sub>3</sub> diluent.
- Multi-element primary standard mixture*. Contains Fe, K, Ca, Na, and Mg at 1000 ppm and Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th, and U at 10 ppm. Available from Agilent, item number 5183-4688.
- Single-element primary standards*. If elements such as Si, Al, P in addition to those contained in the multi-element primary standard are to be determined, working standard solutions may

be supplemented with single-element standards to produce the desired concentrations. Single-element standards of suitable quality for plasma methods are available from Specs or Aldrich.

- f) *Internal standards (ISTD) primary standard mixture.* Contains Li6, Sc, Ge, Y, In, Tb, and Bi at 10 ppm for use as internal standards. Available from Agilent, item number 5183-4680.
- g) *Working ISTD solution.* To prepare the working internal standards solution (1 ppm each IS), add 10 mL IS primary standard mixture to approximately 50 mL diluent solution and dilute to a total final volume of 100 mL with diluent solution.
- h) *Erbium primary standard.* Contains Er at 1 ppm for use as a dilution standard. Available from Agilent, item number G1820-60372.
- i) *Working erbium solution.* To prepare the working dilution standard solution (50 ppb Er), add 12.5 mL 1 ppm Er to approximately 100 mL diluent solution and dilute to a total final volume of 250 mL with diluent solution.
- j) *Calibration standards.* To prepare initial calibration (ICAL) solutions, specific volumes of the multi-element primary standard mixture are diluted with diluent solution. The required volumes of multi-element primary standard mixture for preparation of a standard set of ICAL solutions is given below (Table II), followed by the resultant concentration of all analytes at each calibration level (Table III). If additional elements are desired, single-element standards must be used to supplement the preparations described below. Single standard solutions of 1000 ppm concentrations may be first diluted to 10 ppm. In order to obtain the concentrations listed in Table III, the total final volume of each solution must be 100.0 mL. If any of the elements are expected to exceed the calibration range given below, additional levels may be used in order to span the necessary range of concentrations using the multi-element or single-element standards as appropriate.

Table II. Preparation of ICAL standards.

Level	Volume, primary standard mixture (μL)	Volume, diluted single standard solutions (μL)
1	0.0	0
2	5.0	5.0
3	10.0	10.0
4	50.0	50.0
5	100.0	100.0
6	500.0	500.0
7	1000.0	1000.0

Table III. Typical ICAL Levels.

Analyte(s)	Concentration (ppb) of Analyte at ICAL Level:						
	1	2	3	4	5	6	7
Fe, K, Ca, Na, Mg, Si, Al	Blank	50	100	500.0	1,000.0	5,000.0	10,000
Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn, Th, and U	Blank	0.5	1.0	5	10.0	50.0	100.0

### 3.2 DAILY PROCEDURES FOR INSTRUMENT SETUP

Prior to operating the ICP-MS, the following steps must be performed on a daily basis. These steps assume that the instrument hardware and software is configured for the 200.8 ICP-MS application.

- a) Replace all peristaltic pump tubing. When ready for analysis, clamp the tubing in place on the pumps. Place the lines for uptake of diluent and internal standard solutions into the appropriate vessels (refer to Appendix B for a detailed diagram of the tubing configuration).
- b) Ensure that there is sufficient argon and helium supply.
- c) Verify that the hydrogen generator is functioning properly.
- d) Turn the chiller unit on prior to igniting the plasma.
- e) Verify that all waste lines are in place, and empty waste reservoirs if needed.
- f) Verify that ventilation is operating properly prior to igniting the plasma.
- g) Perform a pulse to analog (P/A) factor tuning for each tune step as follows:

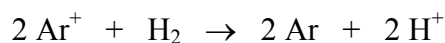
### 3.3 ANALYSIS

Sample analysis is carried out using an Agilent Technologies 7500c ICP-MS equipped with the octopole reaction system. The reaction cell allows a near-vacuum interface between the plasma and the mass spectrometer, or may alternatively be flooded with a reaction or collision gas in order to minimize various interferences. In order to minimize known possible interferences, each element is acquired in one of three segments, or tune steps, of an analysis: no reaction gas (normal mode), He collision, or H<sub>2</sub> reaction.

Elements occurring at mass to charge ratios (m/z) with no anticipated plasma-based or matrix-based interferences are acquired in normal mode. In general, these include the relatively light and relatively heavy elements.

Any element occurring at an m/z with a known matrix-based interference would be acquired in He collision mode. Polyatomic interferences occurring in the plasma as a result of matrix composition will be obstructed by the He gas to a greater degree than an analyte of the same mass owing to the smaller cross-sectional area of the analyte compared to that of the polyatomic interferent. The result is reduced interference with a relatively small reduction in analyte signal, thereby enhancing the signal to noise ratio.

Elements occurring at any m/z with a known argon-based interference are acquired in H<sub>2</sub> reaction mode. Since the plasma is composed of argon, there is inherently a tremendous abundance of Ar<sup>+</sup> ions present in the plasma. These may act as an interferent directly at m/z 40, or may participate in the formation of argon-containing polyatomic ions of the type ArM<sup>+</sup>. Flooding the reaction cell with H<sub>2</sub> results in the following:



Ar<sup>+</sup> is reduced to neutral Ar and therefore does not enter the mass spectrometer or form polyatomic ions. It should be noted that H<sub>2</sub> can act as a collision gas as well, and in fact the collisional obstruction of lighter elements by H<sub>2</sub> is considerable. However, this is far less significant when considering heavier elements. In any case, H<sub>2</sub> acts as a poorer collision gas than He due to H<sub>2</sub>'s relatively small cross-sectional area compared to that of He.

Table IV outlines the tune step in which each element is acquired, which isotope is acquired (if applicable), and internal standard element and isotope being utilized for that analyte. In addition, Tables V-IX outline the remaining acquisition parameters and instrument settings applied during this analysis.

Table IV. Tune step and internal standard m/z for each analyte m/z.

Analyte / m/z	IS / m/z	Tune Step
Be / 9	Li / 6	3 (Normal)
Na / 23	Y / 89	3 (Normal)
Mg / 24	Y / 89	3 (Normal)
Al / 27	Y / 89	3 (Normal)
Si / 29	Y / 89	3 (Normal)
K / 39	Y / 89	3 (Normal)
Ca / 40	Sc / 45	1 (H <sub>2</sub> )
V / 51	Sc / 45	2 (He)
Cr / 52	Sc / 45	1 (H <sub>2</sub> )
Mn / 55	Y / 89	3 (Normal)
Fe / 56	Y / 89	1 (H <sub>2</sub> )
Co / 59	Y / 89	3 (Normal)
Ni / 60	Y / 89	3 (Normal)
Cu / 63	Y / 89	1 (H <sub>2</sub> )
Zn / 66	Y / 89	3 (Normal)
As / 75	Y / 89	2 (He)
Se / 77	Y / 89	3 (Normal)
Se / 78	Y / 89	1 (H <sub>2</sub> )
Mo / 98	Y / 89	3 (Normal)
Ag / 107	In / 115	3 (Normal)
Cd / 114	In / 115	3 (Normal)
Sb / 121	In / 115	3 (Normal)
Ba / 137	In / 115	3 (Normal)
Tl / 205	Bi / 209	3 (Normal)
Pb / 208	Bi / 209	3 (Normal)
Th / 232	Bi / 209	3 (Normal)
U / 238	Bi / 209	3 (Normal)

Table V. Interference equations.

Mass	Equation
6	$(6)*1 - (7)*0.0813$
115	$(115)*1 - (118)*0.0149$
208	$(208)*1 + (207)*1 + (206)*1$

Table VI. Acquisition parameters.

<b>Acquisition mode</b>	Spectrum multi-tune
<b>Peak pattern</b>	Full quant
<b>Number of points per mass</b>	3
<b>Integration time per point</b>	0.10 sec
<b>Number of repetitions</b>	3
<b>Total acquisition time</b>	168 sec
<b>Detector</b>	Auto (P/A)
<b>Stabilization time, tune step 1 (tune file: mt_h2.u)</b>	30 sec
<b>Stabilization time, tune step 2 (tune file: mt_he.u)</b>	30 sec
<b>Stabilization time, tune step 3 (tune file: mt_norm.u)</b>	5 sec

Table VII. ISIS peristaltic pump program.

<b>Before Acquisition</b>	Uptake speed	0.70 rps
	Uptake time	20 sec
	Stabilization time (undiluted)	40 sec
	Stabilization time (diluted)	70 sec
<b>After Acquisition (probe rinse)</b>	Rinse speed	0.05 rps
	Rinse time (sample)	5 sec
	Rinse time (standard)	5 sec
<b>After Acquisition (rinse)</b>	Rinse vial	1
	Uptake speed	0.70
	Uptake time	60 sec
	Stabilization speed	0.02 rps
	Stabilization time	0 sec

Table VIII. ISIS autodilution settings.

<b>Dilution factor</b>	20
<b>Correction</b>	On (periodic mode)
<b>Std element</b>	166 amu
<b>Online IS element</b>	159 amu
<b>Dilute all samples</b>	Off

Table IX. Plasma conditions.

<b>RF power</b>	1500 W
<b>S/C Temperature</b>	2°C
<b>Carrier gas flow</b>	1.00 L / min
<b>Makeup gas flow</b>	0.42 L / min
<b>Peri pump speed</b>	0.10 rps
<b>Sample depth</b>	8.4 mm
<b>Torch – H</b>	x.x mm
<b>Torch – V</b>	x.x mm

### 3.4 QUALITY CONTROL

- Internal standard performance.* The response of each internal standard is monitored throughout all standard, analysis, and quality control samples. The initial response in counts per second (cps) for each IS is established when analyzing the calibration blank. All subsequent cps values for each IS must be within the range of 60% - 125% of the initial baseline value. If this condition is not satisfied, the elements quantitated using that IS may not be reported unless the sample is reanalyzed with satisfactory IS recovery.
- Continuing calibration verification (CCV).* For every ten samples, a CCV is analyzed in order to verify the integrity of the instrument calibration. The CCV may be prepared by adding 0.5 mL of the multi-element primary standard mixture and 500 µL of Si solution to 100 mL diluent solution. This results in a concentration of 5000 ppb in Fe, K, Ca, Na, and Mg and a concentration of 50 ppb in Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th, and U. The analytical result for concentration of each element in the CCV must be within 85% - 115% of the actual value. If this condition is not satisfied, the failing element(s) may not be reported in the affected samples. If reanalysis of the CCV does not produce satisfactory results, recalibration may be necessary. Once satisfactory performance of the CCV is achieved, any affected samples may be reanalyzed.
- Continuing calibration blank (CCB).* For every ten samples, a CCB consisting of unsupplemented diluent solution is analyzed in order to determine the presence or absence of unacceptable carryover. If the analytical result obtained for a CCB is greater than 0.5

ppb for trace elements or 50 ppb for non-trace elements, the affected elements may not be quantitated. Reanalysis of the CCB should be performed after rinsing the system with DI H<sub>2</sub>O. Samples may be reanalyzed after acceptable blank levels have been attained.

- d) *Overall performance verification.* An international standard for trace metals in water (NIST 1643) is measured undiluted to verify the overall performance of the trace metal analysis. This performance is tested once a month. The recovery of the standard must be between 85% to 115% for environmental analysis.

Table x: True and measured values for the NIST standard 1643

Element	concentration	Measured n=4	Dev
	µg/kg	µg/kg	%
Ag	7.6	8.4	11
Al	52.0	51.8	0
As	26.7	26.0	-3
Ba	148.0	145.2	-2
Be	34.9	34.0	-3
Cd	22.8	22.5	-1
Co	20.3	20.5	1
Cr	38.6	34.3	-11
Cu	85.2	84.3	-1
Fe	34.3	42.3	23
K	994.0	1035.1	4
Mn	121.5	123.7	2
Mo	46.8	46.8	0
Ni	27.4	27.8	1
Pb	27.9	27.7	-1
Sb	13.8	14.4	5
Se	22.0	18.8	-14
Th	Nd		
Tl	Nd		
U	Nd		
V	13.0	13.5	4
Zn	53.2	52.1	-2
	mg/kg	mg/kg	
Ca	7.0	6.8	3
Mg	5.8	5.9	2
Na	29.4	30.3	3

- d) *Spiked replicates.* Sample replicates are spiked with 50/5000 ppb calibration solution. If spike recovery is above 115% or below 85 % the element may not be reported.
- e) *Calibration range exceeded.* If any element in a sample is found to exceed the range of calibration, the sample is to be diluted into the appropriate range and reanalyzed.

### 3.5 CALCULATIONS

Recoveries for standard solutions are calculated by dividing the observed value by the expected value. The result is multiplied by 100 to give a percent recovery.

$$\% \text{ recovery} = \frac{V_0}{V_e} \times 100\%$$

$V_0 = \text{Observed Value}$

$V_e = \text{Expected Value}$

The relative percent difference between duplicate samples is calculated as the absolute difference between the sample and the duplicate, divided by the average of the sample and the duplicate, all multiplied by 100.

$$\%RPD = \frac{|S_c - D_c|}{[(S_c + D_c)/2]} \times 100\%$$

$S_c = \text{Observed Sample Concentration}$

$D_c = \text{Observed Duplicate Sample Concentration}$

The *limit of detection* (LOD) is calculated from the calibration curves using the equation

$$LOD = \frac{3.3 S_{xy}}{m}$$

where ( $S_{xy}$ ) is the standard deviation of the x-intercept and (m) is the slope. For all compounds where a peak is detected but below the limit of detection are reported as <LOD.

Recovery from *spiked samples* is calculated using

$$\% \text{ Recovery} = \frac{(C_{\text{Sample+Spike}} - C_{\text{Sample}})}{C_{\text{Spike}}} * 100$$

$C_{\text{sample+spike}}$ : measured concentration of spiked sample

$C_{\text{sample}}$ : measured concentration of sample

$C_{\text{spike}}$ : measured concentration of spike

### 3.6 CHAIN OF CUSTODY

Chain of custody form is in place in the ASET laboratory. All samples handed to ASET have to be announced in advance. Ideally an electronic sample list with running number and sample name which is unique for each sample sent to ASET lab manager (or analyst in absence). A hardcopy of this sample list is required with each sample batch handed to ASET personnel. PI, date, number and kind of samples and the required storage environment are listed in *Chain of Custody Document*. This document is signed by the person who delivers the samples and person who receives the sample (only ASET personnel is allowed to accept samples).

## 4 REFERENCES

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Kingston, H.M. Haswell, S.J. ed., Microwave Enhanced Chemistry, Professional Reference Book Series, American Chemical Society, Washington, D.C., Chapter 3, 1997.

## Appendix

Trace element certifications for acid reagents as listed by supplier VWR Scientific (<http://www.vwrsp.com/catalog/product>)

### Hydrogen Peroxide Extra Pure Grade 35-36.5%

H<sub>2</sub>O<sub>2</sub> in water

CAS: 7722-84-1

FW: 34.01

Merck Index: 13.4821

D: 1.11 kg/L

Solution. Extra Pure Grade, 35.0–36.5% (by magnetometry).

Corrosive and flammable.

Chloride (Cl)	0.005% max.
Free Acid (as H <sub>2</sub> SO <sub>4</sub> )	0.025% max.
Heavy Metals (as Pb)	0.0002% max.
Identification	Passes test
Nonvolatile Matter	0.1% max.
Residue after Ignition	0.05% max.

Nitric Acid Solution OmniTrace 69-70%HNO<sub>3</sub> in water

CAS: 7697-37-2

FW: 63.01

Merck Index: 13.6608

D: 1.49 kg/L

For elemental metal analysis via atomic absorption and ICP instruments. Actual Lot Analysis on label. Color-coded label to match acid cap.

Aluminum	10 ppb max.
Antimony	1 ppb max.
Arsenic	1 ppb max.
Barium	1 ppb max.
Beryllium	1 ppb max.
Bismuth	1 ppb max.
Boron	5 ppb max.
Cadmium	1 ppb max.
Calcium	20 ppb max.
Chloride	80 ppb max.
Chromium	5 ppb max.
Cobalt	1 ppb max.
Copper	2 ppb max.
Gallium	1 ppb max.
Germanium	5 ppb max.
Gold	5 ppb max.
Iron	40 ppb max.
Lead	1 ppb max.
Lithium	1 ppb max.
Magnesium	4 ppb max.
Manganese	1 ppb max.
Mercury	1 ppb max.
Molybdenum	1 ppb max.
Nickel	3 ppb max.
Niobium	1 ppb max.
Phosphate	200 ppb max.
Potassium	6 ppb max.
Selenium	1 ppb max.
Silicon	5 ppb max.
Silver	1 ppb max.
Sodium	20 ppb max.
Strontium	1 ppb max.
Sulfate	300 ppb max.
Tantalum	2 ppb max.
Thallium	1 ppb max.
Thorium	1 ppb max.
Tin	1 ppb max.
Titanium	1 ppb max.
Uranium	1 ppb max.
Vanadium	1 ppb max.
Zinc	5 ppb max.
Zirconium	1 ppb max.

Nitric Acid OmniTrace Ultra (EM) 67-70%HNO<sub>3</sub> in water

CAS: 7697-37-2

FW: 63.01

Merck Index: 13.6608

D: 1.49 kg/L

Clear liquid. For low level trace metal analysis. Double-distilled and packaged in ISO Class 4 (FED-STD-209E Class 10/M2.5) cleanroom conditions. Supplied in specially designed, preleached fluoropolymer resin bottles to guarantee product integrity. Certificate of Analysis supplied with each shipment.

Aluminum	100 ppt max.
Arsenic	100 ppt max.
Barium	100 ppt max.
Beryllium	100 ppt max.
Bismuth	100 ppt max.
Boron	100 ppt max.
Cadmium	100 ppt max.
Calcium	100 ppt max.
Chlorides	0.5 ppm max.
Chromium	100 ppt max.
Cobalt	100 ppt max.
Copper	100 ppt max.
Iron	100 ppt max.
Lead	10 ppt max.
Magnesium	100 ppt max.
Manganese	100 ppt max.
Mercury	100 ppt max.
Molybdenum	100 ppt max.
Nickel	100 ppt max.
Potassium	100 ppt max.
Silver	10 ppt max.
Sodium	100 ppt max.
Strontium	10 ppt max.
Sulfates	1 ppm max.
Thallium	10 ppt max.
Thorium	1 ppt max.
Tin	100 ppt max.
Titanium	100 ppt max.
Uranium	1 ppt max.
Vanadium	100 ppt max.
Zinc	100 ppt max.
Zirconium	10 ppt max.