Elemental Analysis of Bio-Oils by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Laboratory Analytical Procedure (LAP)

Issue Date: May 13, 2022

Earl D. Christensen, Steve Deutch, Cheyenne Paeper, and Jack R. Ferrell III

National Renewable Energy Laboratory

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1. Introduction

1.1 Concentrations of inorganic elements are key quality metrics for bio-oils, as certain elements impact upgrading processes and product quality. Unless reduced or removed during production and processing, alkali and alkaline metals native to lignocellulosic biomass can carry over into bio-oils, contributing to ash content and degraded catalyst performance during upgrading to hydrocarbon fuels or chemical products. Non-metallic elements such as sulfur and phosphorus can also negatively impact upgrading catalysts and product quality.

1.2 Inductively coupled plasma optical emission spectroscopy (ICP-OES) can be used to measure elements of interest in bio-oils. This procedure covers the preparation and analysis of fast pyrolysis and catalytic fast pyrolysis bio-oils.

1.3 This laboratory analytical procedure provides two approaches for analysis of bio-oils: microwave-assisted acid digestion with aqueous/acidic ICP and solvent dilution with organic ICP.

2. Scope

2.1 These procedures have been developed to measure the concentrations of inorganic elements in bio-oils (fast pyrolysis bio-oils and catalytic fast pyrolysis bio-oils) listed in the procedures below. Other elements may be measured by these procedure as required; however, further considerations regarding sample preparation, instrument parameters, and calibration should be evaluated prior to measurement of additional elements.

2.2 Microwave-assisted digestion with concentrated nitric acid has been utilized in Procedure A to ensure elements of interest are fully solubilized. Other digestion methods may be applicable but have not been evaluated as part of this procedure. The use of hydrofluoric acid (HF) is not in the scope of this method, and therefore elements requiring HF such as Si and Ti may not be applicable to this procedure.

2.3 Organic ICP via dissolving oils in a polar and non-volatile solvent has been utilized in Procedure B. Alternative solvents to diglyme utilized here may be applicable but have not been evaluated as part of this procedure.

2.4 Hydrocarbon products derived from bio-oils via deoxygenation can be analyzed for residual elements following ASTM D7111 (or similar) written for fuels and oils. Analysis of fuel products is not included in the scope of these procedures for bio-oils. Consult relevant fuel specifications for guidance on analysis of hydrocarbon products.

3. Terminology

3.1 *Bio-oil* – The crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.

3.2 *Pyrolysis* – Chemical decomposition of organic materials by heating in the absence of oxygen.

3.3 *Fast pyrolysis* – Pyrolysis conducted with rapid heating and short residence time; typically less than 10 seconds.

3.4 *Catalytic fast pyrolysis* – Fast pyrolysis conducted in the presence of a catalyst designed to perform partial deoxygenation.

4. Significance and Use

4.1 These procedures are used to determine the concentration of selected elements in bio-oils by ICP-OES. The concentrations of these elements can indicate potential bio-oil quality from the perspective of deoxygenation processes. The implications of elemental composition will depend on process parameters such as upgrading catalyst sensitivities.

5. Interferences

5.1 Elemental wavelengths provided in this procedure have been found to be free of significant interferences with all other elements specified. Additional elements not specified in this procedure may have interferences with the wavelengths provided. If spectral interference is found or suspected, selecting wavelengths other than those provided is recommended. Alternative wavelengths may not yield the same sensitivity as the ones provided in this procedure; therefore, alternative selections should be evaluated to ensure adequate sensitivity.

6. Apparatus

6.1 Analytical balance accurate to 1 mg.

6.2 ICP-OES instrument capable of operating under the conditions provided (Agilent 5110 ICP-OES or equivalent).

6.3 Procedure A: Microwave-assisted digester capable of achieving the parameters provided (CEM Mars 5 or equivalent).

6.4 Procedure A: Microwave digestion vessels (CEM XP-1500 Plus, 100 mL or equivalent).

6.5 Procedure A: Peristaltic pump tubing for aqueous/acidic: PVC; for sample, 1.02 × 450 mm; for waste, 1.65 × 450 mm (Agilent part numbers 370034400 and 3710034600, respectively, or equivalent).

6.6 Procedure B: ICP-OES equipped with oxygen introduction and torch designed for ICP of semi-volatile organics.

6.7 Procedure B: Peristaltic pump tubing for organic: Marprene; for sample, 1.02 × 450 mm; for waste, 1.65 × 450 mm (Agilent part numbers 3710044200 and 3710044400, respectively, or equivalent).

6.8 Class A volumetric flasks; 50 mL and 25 mL recommended.

6.9 Adjustable pipets in the range of 1–10 mL, 0.2–1 mL, and 0.01–0.1 mL.

7. Reagents and Materials

7.1 Reagents:

7.1.1 Deionized (DI) water, 18.2 MΩ.

7.1.2 Yttrium internal standard stock solution: 1,000 µg/mL. AccuStandard Cat # ICP-69N-1 or equivalent.

7.1.3 Procedure A: Concentrated nitric acid: 69%–70%

7.1.4 Procedure A: Calibration standards: Individual aqueous/acidic elemental standards or a multiple element standard is acceptable. A stock standard concentration of 1,000 µg/mL is recommended. AccuStandard MES-04-01, 23 element solution was used for method development along with AccuStandard ICP-56W-1 sulfur standard and ICP-41W-1 phosphorus standard.

7.1.5 Procedure B: Diethylene glycol dimethyl ether (diglyme), 99%. Sigma Cat # M14102, or equivalent.

7.1.6 Procedure B: Calibration standards: Individual elemental standards or a multiple element standard is acceptable. A stock standard concentration of 1,000 µg/mL is recommended. AccuStandard MES-04-01, 23 element solution was used for method development. Sulfur and phosphorus standards prepared from salts were found to be insoluble in diglyme at the recommended concentration; therefore, stock solutions were prepared from thiophene for S and tributyl phosphate for P (Sigma Cat # T31801 and 240494, respectively). Si and Ti can be added to the calibration if desired; AccuStandard ICP-64W-1 and ICP-52W-1, respectively, have been used successfully with this procedure.

7.2 Materials:

7.2.1 50-mL polypropylene conical centrifuge tubes suitable for ICP autosampler.

7.2.2 Filters suitable for ICP sample prep. Consult with ICP or microwave digester manufacturer for filter selection with appropriate pore size and material.

8. Environmental Safety and Health Considerations and Hazards

8.1 Nitric acid is highly corrosive and an oxidizer.

8.2 Diglyme is combustible and a peroxide former.

8.3 Follow all applicable chemical handling procedures.

8.4 Microwave-assisted digestion presents additional hazards regarding pressurized and heated vessels. Extra care should be taken in this process, along with closely following the manufacturer's instructions for safe operation. Consult instrument manual for further safety guidance or discuss with instrument supplier.

9. Sampling, Test Specimens, and Test Units

9.1 Bio-oil should be allowed to reach room temperature and thoroughly homogenized to obtain a representative sample.

9.2 Exposure to oxygen and heat should be minimized to prevent sample degradation prior to analysis.

10. Procedure A: Microwave-Assisted Digestion and Aqueous/Acidic ICP

10.1 Preparation of samples for microwave digestion:

10.1.1 Weigh 0.5 g ± 0.05 g of bio-oil sample into a digestion vessel. Preparing all samples in triplicate is recommended.

10.1.1.1 This sample size assumes a digestion vessel of 100-mL volume. Sample sizes larger than 0.5 g may result in over-pressurization of 100-mL digestion vessels. Smaller sample sizes may be required if using smaller-volume digestion vessels to prevent over-pressurization. Follow manufacturer's instructions regarding maximum sample sizes and minimum digestion volumes.

10.1.2 Place digestion vessels in a fume hood and accurately add 0.25 mL of 1,000-µg/mL Y standard stock solution.

10.1.3 Carefully add 10 mL of concentrated nitric acid to each vessel. Allow sample to react with the acid in the open vessel in the fume hood for approximately 5 minutes to allow the most volatile components to subside.

10.1.4 Seal digestion vessel following the manufacturer's instructions.

10.1.5 Digest samples with the following parameters: Ramp to temperature, 200°C in 15 minutes, hold temperature for 15 minutes, maximum pressure 500 psi, power setting per manufacturer's instructions for the number of vessels.

10.1.6 After digestion is complete, allow samples to cool to below 50°C before opening vessels. Open digestion vessels in a fume hood, carefully venting vapors.

10.1.7 Quantitatively transfer digested sample to a 50-mL centrifuge tube by transferring sample and rinsing vessel a minimum of three times with 3–5 mL of DI water. Rinse vessel cap with minimal DI water and add to centrifuge tube to ensure any sample on lid is also transferred.

10.1.8 Dilute the sample to a final volume of 50 mL with DI water and invert several times to mix. Filter sample using an appropriate filter for ICP analysis. Avoid filtration media that can result in background contamination such as glass fiber.

10.2 Aqueous/acidic calibration standards:

10.2.1 Stock standard concentrations of 1,000 µg/mL of each individual element are recommended. Mixed standards containing Na, K, Mg, Ca, Al, and Fe, as well as other elements, are commonly available at 1,000 µg/mL. The use of individual standards and individual element calibrations is also acceptable. Individual standards for S and P in water were used for method development in conjunction with a 23-element mixture in 1-M nitric acid containing Na, K, Mg, Ca, Al, and Fe. Concentrations and volumes provided in this procedure are suggestions that will result in an acceptable calibration range. Alternate standard concentrations and calibration standard volumes can be used as long as the calibration range generated is applicable to samples being analyzed.
Note: Some standard solutions and elements are not compatible at high concentrations (e.g., Ca and S as SO_4). If so, individual standard dilutions may be required. Consider solubility constant (K_{sp}) limits when evaluating alternative standard preparation procedures.

10.2.2 Prepare a working stock solution at a concentration of 50 µg/mL containing elements of interest. In a 50-mL volumetric flask, add 10–20 mL DI water. Carefully add 10 mL of concentrated nitric acid. Add 2.5 mL of each 1,000-µg/mL stock standard. For example, 2.5 mL of 1,000-µg/mL standard containing mixed elements, 2.5 mL of 1,000-µg/mL S standard, and 2.5 mL of 1,000-µg/mL P standard. Combine solutions, fill to the line with DI water, and invert to mix. Prevent pressure buildup in the flask by removing the stopper after each inversion. Invert several times to ensure the solution is homogenous.

10.2.3 Prepare individual curve points from the 50-µg/mL working stock. In individual 50-mL volumetric flasks, add 10–20 mL of DI water. Carefully add 10 mL of concentrated nitric acid to each solution. Table 1 provides suggested standard solution volumes to be added to each calibration level. After adding standard solutions, carefully dilute each flask to the line with

DI water and invert to mix. Prevent pressure buildup in the flask by removing the stopper after each inversion. Invert several times to ensure the solution is homogenous.
Note: The volume of acid should match that used in the digestion step to ensure samples and standards have matching matrixes. If using alternative volumes, keep the concentration of acid consistent to ensure consistent nebulizer performance.

Table 1. Suggested calibration curve volumes and concentrations prepared in 50-mL volumetric flasks for aqueous/acidic ICP

Curve Point	Blank	1	2	3	4	5
Working stock standard, mL	0	0.05	0.5	2	3	5
Y internal standard, mL	0.25	0.25	0.25	0.25	0.25	0.25
Concentrated nitric acid, mL	10	10	10	10	10	10
Nominal µg/mL	0	0.05	0.5	2.0	3.0	5.0

10.2.4 Transfer each calibration standard into an appropriate centrifuge tube for ICP analysis.

10.3 Aqueous/acidic ICP method parameters:

10.3.1 Table 2 provides the wavelengths used to monitor each element in argon plasma along with instrument settings. Table 3 provides common conditions used for the ICP method. Consult with the instrument manufacturer to ensure appropriate settings for the instrument being utilized.

Table 2. Elements, suggested wavelengths, and method settings for aqueous/acidic ICP

Element	Suggested wavelengths, nm	Viewing mode	RF power, kW	Stabilization time, s	Read time, s	Nebulizer flow, L/min	Plasma flow, L/min
Al	308.215, 396.152	Axial	1.40	15	20	0.60	13.0
Ca	315.887, 396.847	Radial	1.10	3	5	0.85	12.0
Co	228.615, 230.786	Axial	1.40	15	20	0.60	13.0
Cr	267.716, 283.563	Axial	1.40	15	20	0.60	13.0
Cu	324.754, 327.395	Axial	1.40	15	20	0.60	13.0
Fe	238.204, 259.940	Axial	1.40	15	20	0.60	13.0
K	766.491, 769.897	Radial	1.10	3	5	0.85	12.0
Li	670.783	Axial	1.40	15	20	0.60	13.0
Mg	279.533, 285.213	Radial	1.10	3	5	0.85	12.0
Mn	257.610, 293.305	Axial	1.40	15	20	0.60	13.0

Element	Suggested wavelengths, nm	Viewing mode	RF power, kW	Stabilization time, s	Read time, s	Nebulizer flow, L/min	Plasma flow, L/min
Na	589.592	Radial	1.10	3	5	0.85	12.0
Ni	216.555, 221.648	Axial	1.40	15	20	0.60	13.0
P	213.618	Axial	1.40	15	20	0.60	13.0
S	180.669	Axial	1.40	15	20	0.60	13.0
Sr	407.771	Radial	1.10	3	5	0.85	12.0
Zn	206.200	Axial	1.40	15	20	0.60	13.0
Y	371.029	Axial	1.40	15	20	0.60	13.0

Table 3. Recommended common measurement conditions for aqueous/acidic ICP

Replicates	3
Pump speed, rpm	13
Uptake delay, s	20
Intelligent rinse, maximum rinse time, s	90
Viewing height, nm	10
Auxiliary flow, L/min	1.00

10.4 Aqueous/acidic ICP calibration and analysis:

10.4.1 Infuse standards from lowest to highest (blank followed by levels 1 through 5). Reanalyze the mid-curve point after infusing the calibration standards and at the end of the sequence to evaluate stability of the instrument during analysis. When analyzing a large batch of samples, a blank and a calibration standard should be analyzed every 10 samples to monitor instrument stability. It is recommended that calibration standards analyzed to monitor the instrument be varied across the curve throughout the sequence as much as reasonable.

10.4.2 A solution of 2% nitric acid is recommended as the rinse solvent on the ICP instrument for rinsing the autosampler, tubing, and spray chamber between samples.

10.4.3 Suggested background correction is “fitted.” Evaluate calibration curves as a linear fit. Acceptable calibrations have $R^2 \geq 0.995$ and calibration error <15%.

10.4.4 If a calibration check differs from the known value by greater than 10%, the instrument response may have drifted during analysis, and recalibration should be conducted to correct response.

10.4.5 Infuse samples using the same parameters as the standards.

10.4.6 If samples are found to be highly concentrated in any element resulting in a reading >20% above the calibration range, the sample should be diluted and reanalyzed within the appropriate range in intensity for accurate measurement.

11. Procedure B: Organic ICP

11.1 Sample preparation for organic ICP:

11.1.1 Prepare Y internal standard working stock solution: Dilute 1,000-µg/mL stock standard to a concentration of 40 µg/mL in diglyme. This solution will be added to each standard and sample. Be sure to prepare adequate volume. Suggested dilution: Add 2.0 mL of 1,000-µg/mL Y stock standard to a 50-mL volumetric flask and fill to line with diglyme. Invert several times to mix.

11.1.2 Weigh 0.5 g ± 0.05 g of bio-oil sample into a 50-mL centrifuge tube. Preparing all samples in triplicate is recommended.

11.1.3 Add 0.5 mL of 40-µg/mL Y solution.

11.1.4 Add 1.0 mL of DI water.
Note: Addition of water at this concentration has been found to be necessary to maintain consistent argon plasma during sample infusion.

11.1.5 Fill to a final volume of 25 mL with diglyme.

11.1.6 Cap the 50-mL tube and invert several times to dissolve and homogenize. If the oil does not readily dissolve, the use of a vortex mixer or sonicating bath has been found to assist in dissolution. Vigorous mixing may be necessary to dissolve high-viscosity oils.

11.2 Organic ICP calibration standards:

11.2.1 Stock standard concentrations of 1,000 µg/mL of each individual element are recommended. Mixed standards containing Na, K, Mg, Ca, Al, and Fe, as well as other elements, are commonly available at 1,000 µg/mL. The use of individual standards and individual element calibrations is also acceptable. A 23-element mixture in 1-M nitric acid containing Na, K, Mg, Ca, Al, and Fe was used for method development. Concentrations and volumes provided are suggestions that will result in an acceptable calibration range. Alternate standard concentrations and calibration standard volumes can be used as long as the calibration range generated is applicable to samples being analyzed.
Note: Elements such as Si and Ti requiring HF for aqueous/acidic analysis can used for calibration of organic ICP as long as the standards are soluble

in diglyme. Solutions of aqueous Ti and Si were used during development of this method and found to work well with diglyme for organic ICP. The same dilution strategies provided can be used for Si, Ti, and other elements as needed.

11.2.2 Prepare 1,000-µg/mL sulfur stock standard from thiophene. Weigh 0.066 g of thiophene in a 50-mL centrifuge tube (or other appropriate vial) and record weight. Add 25.0 mL of diglyme and record weight. Cap tube and invert several times to mix. Calculate actual µg/mL concentration of sulfur in stock solution for use in calibration.

11.2.3 Prepare 1,000-µg/mL phosphorus stock standard from tributyl phosphate. Weigh 0.215 g tributyl phosphate into a 50-mL centrifuge tube (or other appropriate vial) and record weight. Add 25.0 mL diglyme and record weight. Cap tube and invert several times to mix. Calculate actual µg/mL concentration of phosphorus in stock solution for use in calibration.

11.2.4 Prepare a 50-µg/mL working stock solution of multi-element mixture from 11.2.1 or individual elements if not using a mixed standard. Add 1.25 mL of 1,000-µg/mL stock standard to a 25-mL volumetric flask and fill to line with diglyme. Cap and invert several times to mix.

11.2.5 Prepare individual curve points of mixed element standard in 25-mL volumetric flasks. Table 4 provides suggested standard solution volumes to be added to each calibration standard and concentrations, assuming a nominal working stock concentration of 50 µg/mL. After adding solutions, fill to volume with diglyme and invert several times to mix.

Table 4. Suggested calibration curve volumes and concentrations prepared in 25-mL volumetric flasks for organic ICP

Curve Point	Blank	1	2	3	4	5
Working stock, mL	0	0.05	0.25	0.5	1.0	1.5
Y internal standard, mL	0.5	0.5	0.5	0.5	0.5	0.5
DI water, mL	1	1	1	1	1	1
Nominal µg/mL	0	0.1	0.5	1.0	2.0	3.0

11.2.6 Prepare working stock of S, P, Si, and Ti at 50 µg/mL each. Add 1.25 mL of each 1,000-µg/mL stock standard for S and P to a 25-mL volumetric flask. Fill to 25 mL with diglyme and invert several times to mix.

11.2.7 Prepare individual curve points of the S, P, Si, and Ti standard in 25-mL volumetric flasks. Table 5 provides suggested standard solution volumes to be added to each calibration standard and concentrations, assuming a nominal working stock concentration of 50 µg/mL. After adding solutions, fill to volume with diglyme and invert several times to mix.

Note: S and P have higher limits of detection than other elements and are therefore recommended at somewhat higher concentrations than the mixed standard provided in Table 4.

Table 5. Suggested calibration curve volumes and concentrations for sulfur and phosphorus prepared in 25-mL volumetric flasks for organic ICP

Curve Point	Blank	1	2	3	4	5
S+P working stock, mL	0	0.25	0.5	1.0	1.5	2.0
Y internal standard, mL	0.5	0.5	0.5	0.5	0.5	0.5
DI water, mL	1	1	1	1	1	1
Nominal µg/mL	0	0.5	1.0	2.0	3.0	4.0

11.2.8 Transfer each calibration standard into an appropriate centrifuge tube for ICP analysis.

11.3 ICP method parameters for organic solvent analysis:

11.3.1 Table 6 provides the wavelengths used to monitor each element along with instrument settings. Table 7 provides common conditions used for the organic ICP method. Consult with the instrument manufacturer to ensure appropriate settings for the instrument being utilized.

Table 6. Elements, suggested wavelengths, and method settings for organic ICP

Element	Suggested wavelengths, nm	Viewing mode	RF power, kW	Stabilization time, s	Read time, s	Nebulizer flow, L/min	Plasma flow, L/min
Ag	328.068, 338.289	Axial	1.40	15	20	0.60	13.0
Al	308.215, 396.152	Axial	1.40	15	20	0.60	13.0
B	208.956, 249.678	Axial	1.40	15	20	0.60	13.0
Ba	455.403, 493.408	Radial	1.10	3	5	0.85	12.0
Ca	315.887, 396.847	Radial	1.10	3	5	0.85	12.0
Cd	214.439, 226.502	Axial	1.40	15	20	0.60	13.0
Co	228.615, 230.786	Axial	1.40	15	20	0.60	13.0
Cr	267.716, 283.563	Axial	1.40	15	20	0.60	13.0
Cu	324.754, 327.395	Axial	1.40	15	20	0.60	13.0
Fe	238.204, 259.940	Axial	1.40	15	20	0.60	13.0
Ga	287.423, 294.363	Axial	1.40	15	20	0.60	13.0
K	766.491, 769.897	Radial	1.10	3	5	0.85	12.0
Li	670.783	Axial	1.40	15	20	0.60	13.0

Element	Suggested wavelengths, nm	Viewing mode	RF power, kW	Stabilization time, s	Read time, s	Nebulizer flow, L/min	Plasma flow, L/min
Mg	279.533, 279.800	Radial	1.10	3	5	0.85	12.0
Mn	257.610, 293.305	Axial	1.40	15	20	0.60	13.0
Na	589.592	Radial	1.10	3	5	0.85	12.0
Ni	216.555, 221.648	Axial	1.40	15	20	0.60	13.0
P	213.618	Axial	1.40	15	20	0.60	13.0
Pb	220.353, 283.305	Axial	1.40	15	20	0.60	13.0
Pt	273.396, 306.471	Axial	1.40	15	20	0.60	13.0
S	180.669	Axial	1.40	15	20	0.60	13.0
Si	251.611, 288.158	Axial	1.40	15	20	0.60	13.0
Sr	407.771	Radial	1.10	3	5	0.85	12.0
Ti	334.941, 336.122	Axial	1.40	15	20	0.60	13.0
Zn	206.200	Axial	1.40	15	20	0.60	13.0
Y	371.029	Axial	1.40	15	20	0.60	13.0

Table 7. Common measurement conditions for organic ICP

Replicates	3
Pump speed, rpm	10
Uptake delay, s	20
Intelligent rinse, maximum rinse time, s	90
Viewing height, nm	10
Auxiliary flow, L/min	1.00
Oxygen %	25

11.4 Organic ICP calibration and analysis:

11.4.1 Infuse standards from lowest to highest (blank followed by levels 1 through 5). Reanalyze the mid-curve point after infusing the calibration standards and at the end of the sequence to evaluate stability of the instrument during analysis. When analyzing a large batch of samples, a blank and a calibration standard should be analyzed every 10 samples to monitor instrument stability. It is recommended that calibration standards analyzed to monitor the instrument be varied across the curve throughout the sequence as much as reasonable.

11.4.2 A solution of 20% diglyme in DI water is recommended as the rinse solvent on the ICP instrument for rinsing the autosampler, tubing, and spray chamber between samples.

11.4.3 Suggested background correction is "fitted." Evaluate calibration curves as a linear fit. Acceptable calibrations have $R^2 \geq 0.995$ and calibration error <15%.

11.4.4 If a calibration check differs from the known value by greater than 10%, the instrument response may have drifted during analysis, and recalibration should be conducted to correct response.

11.4.5 Infuse samples using the same parameters as the standards.

11.4.6 If samples are found to be highly concentrated in any element resulting in a reading above the calibration range, the sample should be diluted and reanalyzed within the appropriate range in intensity for accurate measurement.

12. Calculations

12.1 Using the calibration generated in Procedure A or B for each element, quantify the concentration of individual elements detected in samples:

$$C_s = [(A_i/A_{IS}) - b]/m * vol/mass$$

Where:
C_s = concentration in sample, µg/g
A_i = average (of three replicates) intensity of the element being measured
A_{IS} = average intensity of Y 371.029
b = intercept of the calibration curve
m = slope of the calibration curve
vol = final volume of sample, mL
mass = mass of sample recorded, g.

12.2 Percent relative standard deviation (RSD):

$$\%RSD = \left(\frac{\sigma}{mean}\right) * 100$$

Where:
σ = standard deviation of concentration from replicate analyses
mean = average concentration determined from replicate analyses.

13. Report Format

13.1 Report concentrations rounded to the nearest 1 µg/g.

14. Precision and Bias

14.1 To be determined by an interlaboratory study.

15. Quality Control

15.1 It is recommended that a spike analysis be performed with bio-oil to establish method accuracy by adding a known concentration of elements of interest to representative samples. An accuracy/spike recovery of 85%–110% indicates adequate performance of either Procedure A or Procedure B.

15.2 Evaluate the percent RSD of triplicate sample preparations. If triplicate analyses result in an RSD >10%, this may indicate poor homogeneity of the sample, inaccurate dilution, or an error during weighing. Reanalysis of the sample is suggested to determine whether an error occurred during sample preparation. If poor homogeneity of samples is suspected, it is recommended that each sample be prepared in triplicate and an average value be taken.