Multi-Element Analysis of Inorganic and Organic Fertilizers by Inductive Coupled Plasma-Optical Emission Spectroscopy

1. Scope:

To provide a standardized procedure for the multi-element analysis in inorganic and organic fertilizers, and premixes using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The method is suitable for quantification of the following elements: As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, and Zn.

2. Principle:

Samples are prepared and stored according to RA-SP-SMPL-PREP. Samples are digested in acid, according to RA-SP-MINERALS-EXT and analyzed by an ICP-OES spectrometer. An ICP-OES spectrometer consists of an inductively coupled plasma (ICP) interfaced to an optical emission spectrometer (OES) and is used for simultaneous multi-elemental analysis. When the sample solution is introduced into the spray chamber, it becomes atomized into a mist-like cloud. The mist is carried into the argon plasma with a stream of argon gas. The plasma (ionized argon) produces temperatures between 6,000 and 10,000K to sequentially desolvate, vaporize, and ionize samples for elemental analysis.

As the ions produced move into the cooler region of the plasma, they return to the ground state by emitting photons of light at wavelengths characteristic of the element. Because the sample contains a mixture of elements, a spectrum of light waves is emitted simultaneously. The spectrometer uses a grating to disperse the light, separating the particular elemental emissions. The intensity of each emission line is measured by the detector. The more intense the emission, the more concentrated the element.

3. Safety:

3.1 Consult the appropriate safety data sheets (SDS) on the safe handling of all the chemicals used in this method.

3.2 Safety precautions should always be taken to avoid skin and eye contact, inhalation and digestion of materials and reagents.

3.3 Gloves, eye protection, and a lab coat shall be worn when handling hazardous materials and reagents.

3.4 Nitric acid and hydrochloric acid are very toxic, extremely corrosive, and shall be used in a fume hood.

3.5 The power unit supplies high voltage to the RF generator which is used to form the plasma. Never open the unit while the plasma is lit. Exposure to high voltage can cause serious injury.

3.6 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases from the ICP-OES are properly vented.

4. Interferences:

4.1 Contamination

4.1.1 Solvents, reagents and glassware used during sample preparation may introduce unexpected interferences or contamination to the sample prior to analysis. These materials must be demonstrated to be free from interferences and contamination by analyzing method blanks with every batch of sample.

4.1.2 The purity of nitric and hydrochloric acids should be sufficient to eliminate the introduction of contamination.

4.1.3 Distilled water with a resistivity of 18 megaohm or greater is used for sample and standard preparation. If LC/MS grade water is available, use this to prepare standard solutions and make dilutions.

4.1.4 The final dilutions of sample extracts must equal the acid content of the calibration standards to compensate for potential interference.

4.2 Spectral Interferences

4.2.1 Spectral interferences can be caused by background emissions, stray light from emission of high concentration elements, wavelength overlap between elements, or unresolved overlap of molecular band spectra.

4.2.2 To identify any potential interferences, examine the neighborhood of the spectrum of interest or the desired analytical wavelength.

4.2.3 Identification of the potential interferences is performed by the trained analyst. The need of correction that is recommended is based on the appropriate models.

4.3 Physical Interferences

4.3.1 Physical interferences are associated with the sample introduction system from the sample probe, through the nebulizer, and out of the Injector.

4.3.2 High salt concentrations can result in significant signal suppression and salt build-up on the nebulizer tip. These physical interferences can be reduced by sample dilution or compensated for by using an internal standard to monitor signal suppression.

4.4 Chemical Interferences

4.4.1 Chemical interferences are highly dependent on matrix type and the specific analyte element and can include the formation of molecular compounds, ionization effects, and solute vaporization effects.

4.4.2 These are not significant issue with this method of analysis. If observed, they can generally be minimized by proper matrix matching, dilution, and careful selection of operating conditions including RF power, torch and injector position, and plasma gas flow.

5. Apparatus and Equipment (equivalents are acceptable):

5.1 Inductively Coupled Plasma-Optical Emission Spectrometer (Agilent ICP-OES 5900, with SPS 4 autosampler and recirculating chiller G3292)
5.2 Double pass spray chamber
5.3 One-piece torch/injector assembly 5100 DV
5.4 SeaSpray glass nebulizer
5.5 Radial pre-optic window G8010-68015
5.6 Axial pre-optic window G8010-68014
5.7 Rinse solution tubing into the AVS (advanced valve system), 1.02 mm internal diameter (White-White), (Agilent 3710034400“White-White” or equivalent)
5.8 Internal standard tubing, 1.02 mm internal diameter (White-White), (Agilent 3710034400 White-White)
5.9 Autosampler rinse tubing for waste delivery out of the spray chamber into the waste container, 1.65 mm internal diameters (Blue-Blue Agilent 3710034600)
5.10 Volumetric flasks – Class A (25 mL, 50 mL, 100 mL, 250 mL, 500 mL, 1L)
5.11 Pipettes: 0.010, 0.200, 1.0, 5.0,10 mL (Eppendorf Research Plus pipettes)
5.12 Polypropylene sample vials with screw top, 50 mL (PerkinElmer B0193234)
5.13 Polypropylene beakers
5.14 Polypropylene funnels
5.15 Filter – FilterMate, PTFE (Environmental Express C0401)
5.16 Analytical balance (Mettler AE 200)

6. Reagents (equivalents are acceptable):

6.1 Stock standards used for initial calibration are obtained from Spex Certiprep; secondary standards are obtained from a variety of sources including Inorganic Ventures and Sigma-Aldrich. Stock standards are purchased from a commercial vendor and must include a Certificate of Analysis. The vendor shall be ISO 17034 accredited. Standards may also be purchased as custom multi-element mixes. Refer to Table 1 for standards preparation.
6.2 Hydrochloric acid (HCl), reagent grade (CAS # 7647-01-0) (Fisher A144C-212)
6.3 Nitric acid (HNO3), reagent grade (CAS # 7697-37-2) (Fisher A509-P212)
6.4 18 megaohm water that is free of the elements of interest at the levels of interest
6.5 Instrument rinse solution, 2% nitric acid and 0.5% hydrochloric acid

6.6 High-purity argon gas (99.996%) as the plasma gas (Argon can be used both as plasma and optical purge gas).
6.7 High-purity nitrogen as optical purge gas.

7. Standard Preparation:

7.1 All standards are stored at room temperature in polypropylene bottles or other inert containers.

7.2 If no expiration date is provided, the stocks and intermediate standards may be used for up to one year.

7.3 Primary and secondary calibration standards (also known as stock solutions) can be prepared from either single or custom mixed standards. The concentrations and the volume at which these standards are ordered can be chosen so that they suit the specific needs of the laboratory. Table 1 summarizes the logic that is used for preparing the calibration standards. If the concentration of the stock solutions changes, then the math and logic employed for the preparation of the calibrations standards needs to be adjusted accordingly.

7.4 Calibration Blank
The calibration blank is the solution used for standard and sample dilutions and is 2% HNO_3 and 0.5% HCl v/v.

7.5 Calibration Standard
Stock standards are diluted to working levels using the calibration blank solution. Refer to the standard preparation table for further information.

7.6 Initial Calibration Verification (ICV)
The ICV standard is from a different source than the calibration standards. The ICV concentrations are listed in Table 1.

7.7 Continuing Calibration Verification (CCV)
The CCV standards are prepared from the same source as the calibration standard. The CCV concentrations are listed in Table 1.

7.8 Internal Standard (IS)
Scandium is used as the IS with a concentration of 10 mg/L (10 ppm) in 2% HNO_3 and 0.5% HCl. Prepare by diluting 5 mL of the 1000 ppm scandium stock standard into a 500 mL volumetric flask and mix thoroughly.

8. Instrument Calibration:

8.1 Check that there is sufficient argon to complete the entire analytical run. The outlet gas pressure for argon should be 80-100 psi.

8.2 Check that the chiller is holding the temperature at 20°C.

8.3 Check the instrument and autosampler waste containers. Empty or replace any full waste containers.

8.4 Check that there is sufficient internal standard solution and instrument rinse solution to complete the entire analytical run.

8.5 Check the torch/injector assembly for cleanliness. If it shows signs of build-up or staining, remove and follow the cleaning procedure outlined in section 11.2.3.

8.6 Inspect the nebulizer for clogs, and the spray chamber for any evidence of build-up or other contamination. If either is dirty, remove and follow the cleaning procedure outlined in sections 11.2.5.

8.7 Inspect the sample pump tubing to ensure it is clean and in good condition.

8.8 Check the peristaltic pump tubing. The rinse solution and internal standard tubing (white-white) should last for 10-16 hours of analysis time. The autosampler rinse tubing for waste (blue-blue) only needs to be changed as a result of notable flat spots or reduction in rinse flow.

9. QA/QC:

9.1 Regression
The calibration is linear/quadratic and acceptable for this method when the correlation coefficient (r) is ≥ 0.995.

Acceptance Criteria: If the correlation coefficient (r) is at 0.995 or greater, the system is calibrated, and the analysis of the samples may proceed.

Corrective Action: Elements that do not meet these criteria are not valid, and recalibration is required.

9.2 Initial Calibration Verification (ICV)
An ICV standard is analyzed immediately after the initial calibration and must be obtained from a different vendor than the standard used for calibration.

Acceptance Criteria: The ICV percent recovery is ±10% of the true value. The % RSD shall be ≤ 10%. The ICV can be reanalyzed but must be successful twice in succession or corrective action must be taken.

Corrective Action: ICV wavelengths that do not pass these criteria are not valid to report. Continue the analysis if you don't need those wavelengths for the final

report. Prepare new ICV standard and recalibrate until results are acceptable if those wavelengths are required for report.

9.3 Calibration Blank (CB)
A CB is analyzed immediately following the ICV analysis. A CB is analyzed immediately after each continuing calibration verification standard.

Acceptance Criteria: All the analytes in the CB shall be less than the reporting limit (RL) for each element. However, the result may be greater than the Minimum Detection Limit (MDL) if the result does not adversely impact data quality.

Corrective Action: If the CB exceeds the acceptance limits, instrument contamination and carry-over from solutions are the most likely sources of contamination. Run the instrument rinse solution for at least 3-5 minutes. Reanalyze the blank. If unsuccessful, identify and resolve the contamination problem before continuing.

9.4 Continuing Calibration Verification (CCV)
A mid-level CCV standard is analyzed from the same stock as calibration standards before the first sample, after every 10 samples or less, and at the end of the analytical sequence.

Acceptance Criteria: The CCV percent recovery is ± 15% of the true value. The % RSD shall be ≤ 10%. The CCV can be reanalyzed but must be successful twice in succession or corrective action must be taken.

Corrective Action: Wavelengths in CCV that do not pass these criteria are not valid to report. Continue the analysis if you don't need those wavelengths for the final report. Prepare new CCV standard and recalibrate until results are acceptable if those wavelengths are required to be used.

9.5 Internal Standard (IS)
Scandium is used as an IS and its intensity is monitored during analysis.

Acceptance Criteria: The intensities of all internal standards are monitored in every sample and shall be within 80-120%.

Corrective Action: If the IS intensities are outside of this range, dilute and reanalyze the sample.

9.6 Quality Control Sample (QC)
A QC sample shall be run with each set of samples. Each set includes 20 samples, at least one QC sample and one method blank. If a set exceeds 20 samples, additional QC samples shall be included (one QC for every 20 samples). Both the QC and method blank are processed through the entire analytical extraction method. The QC should be a similar matrix as the samples. Acceptable QC include

reference material from a collaborative check sample such as Magruder proficiency test sample with a known mean and standard deviation.

Acceptance Criteria: QC sample results shall be within the reported mean of ±2 standard deviations.

Corrective Action: If recovery criteria are not met for one or two wavelengths, those wavelengths shall not be used but those with acceptable criteria are valid to report. If all wavelengths fail, control samples must be re-extracted and re-analyzed.

9.7 Blank Rinse
Flush the system between standards and samples with the instrument rinse solution to prevent carryover from samples with high concentrations.

9.8 Method Detection Limit and Reporting Limit
The method detection limit (MDL) is the lowest concentration of the analyte that a method can detect reliably and reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The calculated MDL and RL for all wavelengths are shown in Appendix 1.

10. Analysis:

Samples are digested according to RA-SP-MINERALS-EXT prior to analysis.

10.1 Samples may be run after the initial calibration is completed and the ICV, CB, and CCV results are within the acceptance criteria.

10.2 Report the average of at least three replicate integrations for all the QC and samples analyzed.

10.3 Flush the system with instrument rinse solution between samples and standards during the analytical run.

10.4 If the concentration of any element in the sample exceeds the linear range, as dictated by the calibration, the sample is diluted and reanalyzed.

11. Instrument:

11.1 Instrument Operation

11.1.1 Power on the chiller and ensure that the reading of the thermometer is 20°C. Then, check on the Instrument software and ensure that in the Optics category, the Peltier temperature is below -40°C and the polychromator is at 35°C.

11.1.2 In the Purges category, choose both the Boost and Snout options. The Snout purge helps with the detection of elements having a wavelength below 200 nm.

11.1.3 Turn on the autosampler and place the autosampler's rinse tubing into their respective positions. The autosampler is equipped with its own pump that delivers the rinse solution into the probe housing. Powering on the autosampler should result in self-calibration of the probe with respect to the four corners of the sampling platform. If self-calibration is not initiated, then the functionality can be manually activated.

11.1.4 Place the peristaltic tubing into their respective positions and then start the peristaltic pump and initially select the fast mode (80 rpm) to ensure that the tubing is set inside the groves in an even manner. Then, switch to normal mode (10 rpm) and close the pressure bar and engage the tensioner.

11.1.5 Ensure that the direction of the flow is correct (waste is coming out of the spray chamber's drain tubing, and the nebulizer is producing mist into the spray chamber).

11.1.6 Turn on the plasma and let the instrument to stabilize for at least half an hour before starting an analytical run.

11.2 Instrument Maintenance and Troubleshooting

11.2.1 Rinse Solution

The Agilent 5900 ICP-OES is equipped with a 7-port advanced valve system, AVS, that reduces the amount of time required for rinsing after each analysis via a constant flow of rinse solution into the system. Therefore, it is imperative to ensure that enough rinse solution is available prior to starting a run. The rinse solution, in terms of composition, matches those of the calibration standards as well as the sample digestates (2% nitric acid and 0.5% hydrochloric acid in 18 megaohm water). The rinse solution is prepared by filling a 4L glass container with 18 megaohm water to the proper level and then removing 100 mL using a graduated cylinder then adding 80mL of nitric acid and 20mL hydrochloric acid.

11.2.2 Peristaltic Pump

Sample introduction into the nebulizer is accomplished via a peristaltic pump that rotates in a counterclockwise direction. The same peristaltic pump is also responsible for the removal of waste from the spray chamber as well as the introduction of rinse solution into the AVS port. Therefore, it is important to ensure that the direction of flow with regards to the attached tubing is correct and suits the desired directionality. One simple rule of remembering how to set up the tubing in the proper direction is to consider sources and destinations. In a counterclockwise rotation, source, from which the solution is introduced, is placed at the bottom of the peristaltic

pump and the destination, to which the solution is introduced, is placed on top of the pump. Once the tubing has been set in the proper manner, start the pump, and ensure that the direction of the flow is from the injector into the nebulizer and from the spray chamber into the waste container. Initially, put the pump in the high-speed mode (80 rpm so the tubing is set and adjusted into their respective grooves) for a few seconds and then reset the pump in a normal speed mode (10 rpm). Also, note that the 7th position of the AVS is always reserved for the internal standard while sample introduction takes place via the autosampler and its own peristaltic assembly.

It is recommended that tubing should be inspected after each run and replaced after three ICP runs. This does not apply to the sample introduction tubing as it's a separate piece coming directly from the autosampler and is rinsed thoroughly so it doesn't need to be replaced as frequently.

The peristaltic pump relies on the pressure that is applied to the tubing from the tensioner onto the tension bar to direct the flow in the proper direction. It's very important for the pressure of the tensioner to be optimized on a regular basis, which ensures the proper flow throughout the system. Optimize by inspecting each tensioner one at a time and with respect to the tubing for which they're assigned to direct the flow. Place the source end of the tubing inside a small container filled with water and attach the destination end to the proper location. Turn on the peristaltic pump and quickly remove the tubing and let the air bubbles form inside. Gently adjust the tensioner to a point that air bubbles are flowing freely inside the tubing. The same optimization procedure should be repeated for all other tensioners and their respective tubing. It is strongly recommended not to change the position of tubing once tensioner optimization has been performed.

11.2.3 Torch/Injector One Piece Assembly

The torch/injector assembly, at the end of which the plasma is generated, should be inspected regularly for contamination build-up around its edges and on the side where the slit is located. If the quartz glass is discolored (which is a sign of contamination build-up), the assembly needs to be cleaned thoroughly according to the manufacturer's recommendations. The rinsing protocol for the torch/injector assembly is to let the glass side to sit in a 50 % aqua-regia solution (3:1 nitric: hydrochloric acid) overnight and then clean thoroughly with DI water. To clean the injector, pass a few drops of a 50 % aqua-regia through the injector's top opening and then rinse with enough water to ensure that all the remnants of the acid rinseate are washed out.

11.2.4 The Cone

The instrument is equipped with a pre-optic cone and its main function is to remove the plasma's tail and prevent the recombined ions from entering the

plasma. It also protects the axial pre-optic window. It is important to inspect the cone on a regular basis and ensure that it is clean and free of contamination and carbon build-up. Should there be a need to clean the cone, it can be done so using a cleaning powder, which is applied on a wet cloth and gently applied around the surface and then washed thoroughly.

11.2.5 The SeaSpray Nebulizer and Spray Chamber

The nebulizer converts liquid samples into a fine mist, which travel into the spray chamber and then onto the torch/injector assembly. The droplets that do not satisfy the size-requirement for entering the plasma (larger than 8 microns) are siphoned out into the acid waste container. The crucial role, which a nebulizer plays in sample introduction, necessitates the performance of proper maintenance. This entails regular monitoring of the back pressure to ensure that it does not exceed the normal range. The normal range is perceived as a pressure bracket within which the nebulizer operates only with acid rinseate travelling through the system without the introduction of any sample into the plasma. The instrument is also equipped with pressure warning functionality that alerts the analyst should a pressure rise exceeding the normal range occur. Pressure rise in nebulizers is usually due to the presence of a blockage somewhere in the tube and can be remedied by placing the nebulizer in a 10% nitric acid solution. Should the high rise in back pressure persist, the nebulizer can be placed inside a more concentrated acid solution for up to 24 hours and this should eradicate even the most persistent sources of blockages. The spray chamber requires less maintenance than the nebulizer and if persistent build-up is observed, a fast rinse with dilute acid should address the problem.

11.2.6 The Chiller

ICP-OES instruments require a recirculatory cooling system that can dissipate the heat generated by the coil and the detector into the surrounding environment. The chiller that works with the Agilent 5900 operates at 20°C and it needs to be turned on before powering on the instrument and the plasma. There's a built-in warning in the software that enables the analyst to monitor the temperature of the chiller to ensure that the optimum temperature is reached prior to powering on the plasma. Upon the completion of an ICP analysis, the chiller needs to be turned off. Never leave the chiller on indefinitely because with the chiller on, the instrument optics and the detector are being constantly purged using gas and should the gas supply ever get disrupted, condensation may form on the optics and the detector. This may result in irreversible damage to the instrument. It is also recommended to check on the coolant fluid level of the chiller every month to ensure that there's no leakage of coolant anywhere in the system. One last concern about the chiller is the maintenance of its air filter, which should be cleaned on a regular basis to ensure that no dust particles oversaturate its surface that may prevent air flow.

11.2.7 The Inlet Air Filter

The instrument is equipped with an inlet air filter that is located opposite to the external inlet duct adapter. This air filter is housed inside a metal bracket, which can be easily removed and dust-cleaned using a vacuum cleaner or compressed air and if needed, the filter can be washed and set to dry before being replaced back on the instrument. If the filter has collected dust so severely to a point that it is beyond being maintained, it can be replaced with a new one. Replacing the filter requires paying attention to the direction of air flow and the placement of the filter onto the metal bracket housing.

12. Discussion:

12.1 Both linear and quadratic regression can be used for constructing the calibration curves. The correlation coefficient (r^2) for the initial calibration is automatically calculated using the ICP software.

12.2 Using multiple wavelengths is encouraged for result consistency and confirmation, and so that an unusual result can be identified and corrected.

12.3 Internal standard recovery is an important factor when selecting an appropriate wavelength. The wavelength that is closest to 100% recovery is the preferred one to report.

12.4 If the IS intensities are outside of this range or the concentration of any element in the sample exceeds the linear range, the sample is diluted and reanalyzed.

12.5 Sensitivity and dynamic range of a wavelength are also considered effective components for wavelength selection.

12.6 The most appropriate wavelength in QCs can be used as a guidance tool as well. The wavelength that produces an acceptable calibration while exhibiting the least amount of percent error and the largest dynamic range is considered over its counterparts.

12.7 Interference correction is an effective way of eliminating uncertainties that may otherwise contribute to inaccurate results. Interference correction can be performed in various ways, of which the FACT (Fast Automated Curve Fitting) and IEC (Interference Element Correction) are the two methods that can be employed very effectively. There are other ways that may enable the analyst to overcome a situation where an interference is negatively impacting the analytical data, and these include manual correction on the peak in the form of peak “right-left correction”. For FACT correction, a single standard solution of the analyte is analyzed, and a model is built according to the interferent. It is advised to build a FACT model at the same intensity with respect to the analyte of interest and its interferent counterpart. With IEC correction, a single standard solution is analyzed

for the interferent at the same level to the intensity of the analyte of interest and the following mathematical formula is used to establish the corrected concentration: Correction Factor = (Intensity of the Analyte of Interest) – [(Intensity of Interferent) X (experimental concentration of the analyte/theoretical concentration of the interferent)]. For instance, if Cd 214.439 nm (cadmium) is suspected to have been interfered by Fe (iron) 273.358 nm at around 1000 ppm, then a single run with only Fe at 1000 ppm is performed. Then, the concentration for Cd for this Iron-run is checked on the instrument. Suppose the value is 0.0155 ppm. Then, right-click on the column that is represented by the wavelength under investigation, 214.439 nm. Select add a custom column. In the second line, in the equation box, initially select the Cd value with its corresponding wavelength– (Iron value at the wavelength causing interference multiplied by (0.0155 ppm divided by 1000 ppm)).

For the determination of true reporting limits, the initial weight of a sample and the final volume to which a sample is brought is considered; this value is referred to as the multiplier. The standard procedure for minerals digestion dictates taking an aliquot of 1 gram of a sample, which is then brought to a final volume of 50mL, upon the completion of digestion. This will result in a nominal value of 50 for the multiplier, which is then multiplied by the established reporting limit for a particular analyte. For instance, the established reporting limit for Mo is 0.05 ppm; however, the true reporting limit for a sample that has been subjected to minerals digestion, if the standard procedure is followed, is: 50 (multiplier) X 0.05 ppm (reporting limit) = 2.5 ppm. It must be noted that depending on the type of matrix, initial aliquots at different weights can be selected or the final volume may have to be increased for the better solubilization of the matrix. In such cases, the multiplier needs to be determined according to the initial weight and final volume and then applied to the established reporting limits.

13. References:

13.1 United States Environment Protection Agency. Inductively Coupled Plasma-Atomic Emission Spectroscopy - Method 6010C, SW846. Test Methods for Evaluating Solid Waste. https://www.epa.gov/sites/production/files/2015-07/documents/epa-6010c.pdf

13.2 Optima 2100DV, Hardware Guide. Perkin Elmer, Inc., April 2004. Official Method 2017.02 Arsenic, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Selenium, and Zinc in fertilizers

Approvals:

Written By:

Bahar Nakhjavan _____ 5/3/22
Bahar Nakhjavan — Date
Senior Environmental Scientist (Specialist)

Approved By:

Stacy Aylesworth _____ 5/3/22
Stacy Aylesworth — Date
Senior Environmental Scientist (Supervisor)

Maryam Khosravifard _____ 5/3/22
Maryam Khosravifard — Date
Environmental Program Manager I

Sarva Balachandra _____ 5/6/22
Sarva Balachandra — Date
Quality Assurance Officer

Revision Log:

Date	What was Revised? Why?

Appendix 1: **The Determination of Method Detection Limit (MDL) data and Reporting Limit (RL)**

Sample Name	Sample ID	As (188.980 nm) ppm	As (193.696 nm) ppm	B (208.889 nm) ppm	B (208.956 nm) ppm	B (249.678 nm) ppm	Ca (315.887 nm) ppm	Ca (317.933 nm) ppm	Ca (370.602 nm) ppm	Cd (214.439 nm) ppm	Cd (226.502 nm) ppm	Co (228.615 nm) ppm	Co (230.786 nm) ppm	Co (237.863 nm) ppm	Cr (205.560 nm) ppm	Cr (206.158 nm) ppm	Cr (267.716 nm) ppm
Method Blank		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
0.5 ppm 1	# 1	0.518	0.519	0.509	0.511	0.516	0.541	0.547	0.542	0.531	0.522	0.525	0.531	0.523	0.527	0.523	0.524
0.5 ppm 2	# 2	0.529	0.532	0.524	0.523	0.527	0.557	0.562	0.558	0.546	0.534	0.536	0.543	0.535	0.540	0.535	0.536
0.5 ppm 3	# 3	0.510	0.509	0.499	0.504	0.505	0.532	0.535	0.531	0.521	0.512	0.515	0.522	0.514	0.517	0.513	0.515
0.5 ppm 4	# 4	0.520	0.521	0.511	0.515	0.516	0.551	0.556	0.551	0.534	0.524	0.525	0.533	0.526	0.529	0.524	0.526
0.5 ppm 5	# 5	0.527	0.528	0.512	0.516	0.519	0.550	0.555	0.549	0.534	0.525	0.528	0.532	0.527	0.531	0.525	0.528
0.5 ppm 6	# 6	0.510	0.519	0.505	0.508	0.509	0.547	0.552	0.544	0.524	0.517	0.518	0.526	0.517	0.521	0.518	0.518
0.5 ppm 7	# 7	0.528	0.528	0.516	0.520	0.523	0.560	0.568	0.559	0.541	0.532	0.532	0.541	0.532	0.536	0.531	0.534
Mean	Average	0.520	0.522	0.511	0.514	0.516	0.548	0.554	0.548	0.533	0.524	0.525	0.533	0.525	0.529	0.524	0.526
SD	SD	0.008	0.007	0.008	0.007	0.008	0.010	0.011	0.010	0.008	0.008	0.007	0.008	0.008	0.008	0.008	0.008
MDL	SD*3.14	0.026	0.024	0.026	0.021	0.024	0.030	0.034	0.031	0.027	0.024	0.023	0.024	0.024	0.025	0.024	0.024
RL		0.051	0.047	0.051	0.042	0.047	0.060	0.067	0.061	0.053	0.047	0.047	0.047	0.047	0.050	0.047	0.047
RL		**0.05**		**0.05**			**0.06**			**0.05**		**0.05**			**0.05**		

Sample Name	Sample ID	Cu (199.970 nm) ppm	Cu (224.700 nm) ppm	Cu (327.395 nm) ppm	Fe (234.350 nm) ppm	Fe (238.204 nm) ppm	Fe (239.563 nm) ppm	K (766.491 nm) ppm	Mg (279.078 nm) ppm	Mg (285.213 nm) ppm	Mn (257.610 nm) ppm	Mn (259.372 nm) ppm	Mn (260.568 nm) ppm	Mo (201.512 nm) ppm	Mo (202.032 nm) ppm	Mo (203.846 nm) ppm	Na (589.592 nm) ppm
Method Blank		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
0.5 ppm 1	# 1	0.527	0.519	0.506	0.524	0.532	0.526	0.487	0.521	0.519	0.519	0.517	0.516	0.517	0.523	0.521	0.512
0.5 ppm 2	# 2	0.535	0.531	0.518	0.538	0.547	0.539	0.515	0.535	0.531	0.531	0.529	0.527	0.528	0.538	0.535	0.521
0.5 ppm 3	# 3	0.512	0.512	0.499	0.689	0.699	0.691	0.493	0.510	0.512	0.511	0.509	0.508	0.511	0.513	0.514	0.505
0.5 ppm 4	# 4	0.526	0.519	0.509	0.528	0.537	0.530	0.562	0.522	0.521	0.521	0.519	0.518	0.524	0.527	0.525	0.507
0.5 ppm 5	# 5	0.527	0.523	0.510	0.531	0.539	0.532	0.496	0.522	0.522	0.522	0.520	0.518	0.522	0.527	0.525	0.511
0.5 ppm 6	# 6	0.520	0.515	0.502	0.526	0.534	0.528	0.473	0.516	0.514	0.513	0.512	0.510	0.515	0.520	0.515	0.499
0.5 ppm 7	# 7	0.529	0.527	0.515	0.542	0.552	0.544	0.624	0.529	0.527	0.528	0.526	0.524	0.527	0.532	0.533	0.538
Mean	Average	0.525	0.521	0.508	0.554	0.563	0.556	0.521	0.522	0.521	0.521	0.519	0.517	0.520	0.526	0.524	0.513
SD	SD	0.007	0.006	0.007	0.060	0.060	0.060	0.053	0.008	0.007	0.007	0.007	0.007	0.007	0.008	0.008	0.013
MDL	SD*3.14	0.023	0.020	0.021	0.188	0.189	0.189	0.168	0.026	0.021	0.023	0.022	0.022	0.021	0.025	0.025	0.041
RL		0.046	0.041	0.042	0.375	0.379	0.378	0.336	0.052	0.041	0.046	0.044	0.044	0.041	0.051	0.050	0.082
		0.04			**0.38**			**0.34**	**0.05**		**0.05**			**0.05**			**0.08**

Sample Name	Sample ID	Ni (221.648 nm) ppm	Ni (230.299 nm) ppm	Ni (231.604 nm) ppm	P (178.222 nm) ppm	P (213.618 nm) ppm	P (214.914 nm) ppm	Pb (182.143 nm) ppm	Pb (217.000 nm) ppm	Pb (220.353 nm) ppm	S (180.669 nm) ppm	S (181.972 nm) ppm	S (182.562 nm) ppm	Zn (202.548 nm) ppm	Zn (206.200 nm) ppm	Zn (213.857 nm) ppm
Method Blank		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
0.5 ppm 1	# 1	0.524	0.526	0.521	0.541	0.504	0.507	0.522	0.526	0.523	0.526	0.527	0.484	0.515	0.509	0.519
0.5 ppm 2	# 2	0.537	0.536	0.534	0.575	0.524	0.520	0.556	0.535	0.533	0.531	0.547	0.506	0.527	0.520	0.532
0.5 ppm 3	# 3	0.515	0.516	0.512	0.538	0.507	0.501	0.507	0.513	0.511	0.518	0.523	0.500	0.506	0.499	0.509
0.5 ppm 4	# 4	0.526	0.525	0.525	0.562	0.520	0.518	0.522	0.520	0.522	0.511	0.528	0.489	0.518	0.512	0.521
0.5 ppm 5	# 5	0.528	0.528	0.526	0.579	0.520	0.515	0.527	0.529	0.523	0.525	0.528	0.498	0.520	0.512	0.523
0.5 ppm 6	# 6	0.519	0.519	0.516	0.572	0.512	0.502	0.521	0.508	0.517	0.519	0.540	0.479	0.510	0.504	0.514
0.5 ppm 7	# 7	0.533	0.534	0.530	0.577	0.525	0.533	0.536	0.535	0.531	0.543	0.547	0.524	0.524	0.516	0.528
Mean	Average	0.526	0.526	0.524	0.563	0.516	0.514	0.527	0.523	0.523	0.525	0.534	0.497	0.517	0.510	0.521
SD	SD	0.008	0.007	0.008	0.017	0.008	0.011	0.015	0.010	0.008	0.010	0.010	0.015	0.008	0.007	0.008
MDL	SD*3.14	0.025	0.023	0.024	0.055	0.026	0.036	0.048	0.033	0.024	0.032	0.032	0.048	0.024	0.022	0.025
RL		0.049	0.046	0.048	0.110	0.052	0.071	0.096	0.065	0.047	0.065	0.064	0.096	0.047	0.044	0.049
		0.05			**0.11**			**0.10**			**0.10**			**0.05**		

Table 1: ICP Calibration Standard Preparation

Standard ID	Vendor	Assigned ID	Stock/Intermediate	Aliquot Taken (mL)	Diluent Volume (mL)*	Final Volume (mL)	Final Concentration (µg/mL)
Primary Standards							
1000-CAL-Multi	Spex Certiprep	A	Stock 1	NA	NA	NA	1,000
10000-CAL-K	Spex Certiprep	B	Stock 2	NA	NA	NA	10,000
10000-CAL-Na	Spex Certiprep	C	Stock 3	NA	NA	NA	10,000
1000-CAL-B	Spex Certiprep	D	Stock 4	NA	NA	NA	1,000
1000-CAL-S	Spex Certiprep	E	Stock 5	NA	NA	NA	1,000
1000-CAL-P	Spex Certiprep	F	Stock 6	NA	NA	NA	1,000
500-CAL-08162021	RA*	G	I-CAL-1	2.5 mL of B + C	45 mL of U.I.S.	50	500
100-CAL-08162021	RA	H	I-CAL-2	5 mL A,E,F; 0.5 mL B,C	34 mL of U.I.S.	50	100
50-CAL-08162021	RA	I	I-CAL-3	2.5 mL A,E,F; 0.25 mL B,C	42 mL mL of U.I.S.	50	50
25-CAL-08162021	RA	J	I-CAL-4	1.25 mL A,E,F; 0.125 mL B,C	46 mL mL of U.I.S.	50	25
10-CAL-08162021	RA	K	I-CAL-5	0.5 mL A,D,E,F; 0.05 mL B,C	47.9 mL of U.I.S.	50	10
5-CAL-08162021	RA	L	I-CAL-6	0.25 mL A,D,E,F; 0.025 mL B,C	48.95 mL of U.I.S.	50	5
1-CAL-08162022	RA	M	I-CAL-7	0.5 mL H + 0.05mL D	49.7 mL of U.I.S.	50	1
0.5-CAL-08162023	RA	N	I-CAL-8	2.5 mL of K	47.45 mL of U.I.S.	50	0.5
0.1-CAL-08162024	RA	O	I-CAL-9	0.5 mL of K	49.5 mL of U.I.S.	50	0.1
0.05-CAL-08162025	RA	P	I-CAL-10	0.25 mL of K	49.75 mL of U.I.S.	50	0.05
0.025-CAL-08162026	RA	Q	I-CAL-11	0.125 mL of K	49.875 mL of U.I.S.	50	0.025
CCV Standard	RA	R	CCV	0.25 mL of A,D,E,F +0.5 mL of B,C	48.5 mL of U.I.S.		5.0 except P,S=10; K,Na=100
Secondary Standards							
100-CAL-Multi	Inorganic Ventures	S	Stock 7	NA	NA	NA	100
1000-2nd-P	Inorganic Ventures	T	Stock 8	NA	NA	NA	1,000
10000-2nd-K	Inorganic Ventures	U	Stock 9	NA	NA	NA	10,000
10000-2nd-Na	Inorganic Ventures	V	Stock 10	NA	NA	NA	10,000
1000-2nd-S	Inorganic Ventures	W	Stock 11	NA	NA	NA	1,000
ICV Standard	RA	X	ICV	5mL of S + 0.5mL of T,U,V,W	44.5 mL of U.I.S.	NA	10 except K,Na = 100
Internal Standard (IS)							
1000-IS-Sc	Spex Certiprep	Y	Stock 12	NA	NA	NA	1000
ICP-IS	RA	Z	IS	5 of Y	495 mL of U.I.S.	500	10
ICP Solutions							
Universal ICP Solution	RA	U.I.S.	U.I.S.	80 mL of HNO_3 + 20 mL of HCl	3900 mL of 18 MΩ H_2O	4000	2% HNO_3 and 0.5% HCl
HCl (hydrochloric acid)	Fisher	HNO_3	Stock-HNO_3	NA	NA	NA	NA
HNO_3 (nitric acid)	Fisher	HCl	Stock-HCl	NA	NA	NA	NA

*Diluent is the universal ICP solution: 2% HNO_3 + 0.5 % HCl in 18MΩ H_2O