Analysis of Minerals by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

1. Scope:

This document provides a procedure for analysis of minerals in feed and fertilizer samples using ICP-OES. This method is suitable for the quantitation of the following elements: B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Se, and Zn (note: P and K analysis are only for total P & K in organic fertilizers). This replaces FEED/FERT-SM-390.0 and FEED/FERT-SP-392.0.

2. Principle:

An ICP-OES utilizes a plasma energy source to excite electrons to higher energy orbitals, which return to ground state releasing characteristic UV or visible wavelengths that can be quantified.

Refer to RA-SP-SMPL-PREP for sample preparation instructions.

3. Safety:

All laboratory safety rules for sample preparation and analysis shall be followed. Read the SDS for all materials before use.

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

Nitric acid and hydrochloric acid are very toxic, extremely corrosive, and shall be used under fume hood. Avoid contact with skin and breathing vapors.

The acidification of samples containing reactive materials may result in the release of toxic gases and can be exothermic. Acidification and digestion shall be performed in a fume hood.

Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken when handling standards and the ICP instrument shall be properly vented.

4. Definitions:

ICV	Initial Calibration Verification. A mid-level standard that is analyzed after the calibration standards that is obtained from a different vendor than calibration standards.
CCV	Continuing Calibration Verification. A mid-level standard used to demonstrate the instrument remains in calibration and is analyzed before the first sample, after every 10 samples, and at the end of the analytical sequence.

CB	Calibration Blank. Solution used to prepare calibration standards and is analyzed after the ICV and CCV standards to evaluate carryover.
IS	Internal Standard. Scandium that is mixed with the sample during sample introduction to account for matrix variations.
RB	Reagent Blank. Water subjected to the entire analytical process to demonstrate all aspects of the analysis are free from interferences.
QC	Quality Control Sample. A NIST, AAFCO, or Magruder sample that is prepared and analyzed with each set to demonstrate the accuracy of the test.
MDL	Method Detection Limit. The minimum concentration of an analyte that can be reported and measured with 99% confidence that the analyte concentration is greater than zero and is determined in a given matrix using this method.
RL	Reporting Limit. A defined or specified concentration that can be reported that accounts for variances in matrices with a reasonable degree of accuracy and precision. The RL is generally 3-5 times higher than the MDL.

5. **Interferences**:

5.1. Spectral interferences are characterized by an overlap (either partial or direct) of the analyte of interest by an interfering element. Also, the background signal for determination of an analyte signal can interfere. These interferences can lead to suppression or enhancement of signals.

5.2. Physical interferences are characterized as a difference in matrix between samples and calibration standards which affect the sample transport or nebulization.

5.3. Chemical interferences occur when there is a difference in the way that the sample and the calibration standards react in the plasma such as ionization, molecule formation and plasma loading. A special case of chemical interferences emerges when the sample contains a high concentration of easily ionized elements (alkali group elements).

6. **Equipment and Supplies**:

6.1. Equipment (equivalents are acceptable)
    6.1.1. Perkin Elmer (PE) ICP-OES Avio 500
    6.1.2. Environmental Express Hot Block (Model SC151)
    6.1.3. Analytical Balance capable of weighing 0.1 mg

6.2. Supplies (equivalents are acceptable)
    6.2.1. 100mL polypropylene sample bottles with caps (Environmental Express Cat# SC490)
    6.2.2. 15mL polypropylene sample tubes with caps (VWR Cat# 10026-076)
    6.2.3. 50mL polypropylene sample bottles (Environmental Express Cat# UC474)
    6.2.4. Disposable watch glass (Environmental Express Cat# SC610)

6.2.5. FilterMate PTFE certified filter and plunger (Environmental Express Cat# SC0408)
6.2.6. Disposable funnels (Evergreen Scientific Cat# 208-5136-030)
6.2.7. Black/black tubing, 0.76mm ID (Perkin Elmer Cat# N0777043)
6.2.8. Orange/blue tubing, 0.25mm ID (Perkin Elmer Cat# N0773112)
6.2.9. Red/red tubing, 1.14mm ID (Perkin Elmer Cat# 9908585)

7. Reagents

Equivalents are acceptable

7.1. Hydrochloric acid, CAS # 7647-01-0 (Fisher Scientific Cat# A508-P500)
7.2. Nitric acid 67-70%, Trace Metal Grade, CAS # 7697-37-2 (Fisher Scientific Cat# A509-P212)
7.3. Scandium, 1000µg/mL in 2% nitric acid (SPEX CertiPrep Cat# PLSC2-2T)
7.4. Calibration Standard Custom multi-element mix 1000µg/mL each Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Se, Zn (SPEX CertiPrep Cat# XCFAC8)
7.5. Boron 1000µg/mL, (SPEX CertiPrep Cat# PLB9-2T)
7.6. Phosphorus for ICV 100µg/mL (Inorganic Ventures Cat# MSP-100ppm)
7.7. Potassium for ICV 100µg/mL (Inorganic Ventures Cat# MSK-100PPM)
7.8. ICV Custom Standard Mix 100µg/mL each Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Se, Zn (Inorganic Ventures CAT# CDFA-1)
7.9. Manganese 1000µg/mL (SPEX CertiPrep Cat# PLMN2-2T)
7.10. Fisher Optima LC/MS Grade Water, CAS # 7732-18-5 (Fisher Scientific Cat# W6-4)

8. Standard and Extraction Solution Preparation:

8.1. Stock standards are purchased as custom standards from an ISO 17034 accredited source accompanied by a certificate of analysis. Standards are stored at room temperature.

8.2. Calibration standards are prepared by diluting stock standards to working levels using the calibration blank solution and are stored at room temperature for up to 6 months for preparation date.

8.3. The calibration blank solution is a 2% v/v solution prepared by adding 80mL of HNO_3 and 20mL HCl to 4L volumetric flask and filling to the mark with water. This solution is also used to prepare calibration standards and ICV, used as the instrument rinse solution, and is used as the diluent for any samples requiring a dilution.

8.4. The ICV is a mid-level standard prepared from a different source than the calibration standards using the CB solution.

8.5. A mid-level calibration standard is used as the CCV.

8.6. The internal standard solution (IS) is 10µg/mL scandium and is prepared by adding 5mL of 1000µg/mL scandium, 10mL of concentrated HNO_3, and 2.5mL of concentrated HCl in a 500mL volumetric flask and filling to the mark with water.

9. Sample Extraction:

9.1. Record all sample extraction information onto a sample extraction worksheet.

9.2. Turn on the hot block and set the temperature to 90°C ±10°C.

9.3. Mix each sample thoroughly before weighing. Weight 0.5 – 2.0g of sample (based on guarantee) in a labeled 100mL plastic bottle. Samples with low mineral guarantees (e.g., 0.0005%) may require sample weights of 1.5 – 2.0 g. Sample weights of 0.3 – 0.5g may be required for gypsum samples and samples with high mineral guarantees.

9.4. Add 5 mL water to each sample and soak for ~5 minutes.

9.5. In a fume hood, slowly and carefully add 9mL concentrated HNO_3 to each sample and allow acid to react with sample for ~10 minutes.

9.6. Add 3mL concentrated HCl to each sample. Place a watch glass on top of each sample and allow to digest for at least 30 minutes. Samples may be left overnight at this step.

9.7. Place samples in the hot block and reflux for ~70 minutes without boiling and avoid drying.

9.8. Remove samples from the hot block and allow to cool in fume hood.

9.9. Rinse the watch glass with water and collect the rinseate in the sample bottle. Discard the watch glass.

9.10. Transfer the sample extract into a 50mL sample vessel. Rinse each digestion bottle at least 3 times with water and transfer rinseate into the sample vessel. Add water to the 50mL mark.

9.11. Samples are filtered using FilterMate filters or disposal funnel with filter paper.

9.12. Samples are stored at room temperature until ready for analysis.

10. Instrument Calibration:

10.1. Refer to Table 2 for recommended wavelengths and Table 3 for ICP-OES conditions and settings.

10.2. Verify the argon and nitrogen outlet pressures are each is 80-100 psi.

10.3. Verify the chiller is at ~15°C and ~50 psi.

10.4. Inspect the ICP torch and injector for cleanliness. If either shows signs of build-up or staining, remove and follow the cleaning procedure outlined in Section 14.1.

10.5. Inspect the nebulizer for clogs and the spray chamber for any evidence of build-up. If either is dirty, remove and follow the cleaning procedure outlined in Section 14.2.

10.6. Inspect the sample pump and peristaltic pump tubing and fittings to ensure they are clean and in good condition (see section 14.4).

10.7. To ignite plasma, click **Plasma On/Off** tab to purge for 50 seconds before ignition. If the plasma will not ignite or ignites but will not stay lit, then perform the following:
  10.7.1. Check the sample introduction system to ensure all connections are made and are not leaking.
  10.7.2. Ensure there is enough argon and the pressure is 80-100 psi.
  10.7.3. If the torch, injector, or nebulizer were removed prior to ignition, check that all O-rings are in good condition and that all parts have been seated correctly.

10.8. Once the plasma is lit, allow the ICP to stabilize for at least 15 minutes before calibration.

10.9. The ICP-OES is calibrated each day of operation using a calibration blank and a minimum of five levels of calibration standards. The average of three replicate measurements at each wavelength is reported.

10.10. Optimization is only needed if torch was removed or replaced. A 10µg/mL manganese solution is used for radial torch alignment and a 1µg/mL manganese solution is used for axial alignment. These solutions are prepared from the 1000µg/mL manganese stock standard using CB solution.

10.11. Linearity is assessed using a linear regression that is based on the intensity counts of the target elements and the IS. The correlation coefficient (r^2) shall be ≥ 0.990. If any element fails, the instrument shall be recalibrated, and any samples analyzed using the failed curve shall be reanalyzed.

11. Analysis:

11.1. After the initial calibration is completed and the ICV and CB results are within the acceptance criteria, samples may be run. The acceptance criteria are discussed in Section 12. Report the average of at least three replicate measurements for all QC and samples.

11.2. Flush the system with instrument rinse solution between each sample and standards to prevent carryover.

11.3. Dilute samples that are out of the calibration range with CB solution and reanalyze.

12. QA/QC:

12.1. The ICV recovery shall be ±10% and CCV recovery shall be ±15% of the expected value. The %RSD of three replicate measurements at each wavelength shall be ≤10%. The ICV and CCV may be reanalyzed but must be successful twice in succession or corrective action must be taken.

12.2. The concentration of any analyte detected in the CB shall be lower than the RL.

12.3. A QC sample shall be run with each set and should be a similar matrix as the samples. It is prepared and analyzed using the same method as the samples. The results of NIST samples shall be within the certified value range. The result of Magruder and AAFCO samples shall be within three standard deviations of the assigned value.

If the QC fails for any analyte, the analyte may not be reported and the samples affected must be re-analyzed with a new QC sample for that analyte.

12.4. Scandium is used as the IS and its intensity is monitored during analysis. The IS recovery shall be within ±30% of the intensity in the CB except for samples being analyzed for selenium where the IS shall be within ±40% with an RSD<10%. If the IS fails, the sample is diluted and reanalyzed. If it still fails, the instrument may require maintenance or recalibration.

13. Calculations:

13.1. The ICP software automatically calculates the final concentration µg/mL or ppm when all the sample parameters are entered. Results > 10% shall be reported with 3 significant figures. Samples less than 10% shall be reported with 2 significant figures.

14. Maintenance and Troubleshooting:

14.1. Torch and Injector
  14.1.1. Examine the torch and injector build-up and clean periodically.
  14.1.2. To clean the torch and injector, soak in *aqua regia* (3:1 $HCl:HNO_3$) for at least 4 hours or overnight in a fume hood to remove persistent deposits. Rinse with water and dry thoroughly using clean air or nitrogen. Never touch the torch (quartz) with bare hands.

14.2. Nebulizer

14.2.1. The nebulizer should be replaced as needed, when back pressure rises dramatically, or background and/or IS intensities become suppressed.

14.2.2. To clean the nebulizer, soak in a solution of 5% nitric acid or *aqua regia* for at least 4 hours. If the deposits persist, increase the acid concentration, up to 20%, rinse with water, and dry thoroughly using clean air or nitrogen. Do not use sonication or a wire to clean, as they may damage the nebulizer.

14.3. Spray Chamber

The spray chamber contains O-rings which require periodic replacement. If the O-rings appear flattened, cracked or show signs of deposits, they should be replaced or cleaned using mild soap and water.

14.4. Tubing

Inspect sample and peristaltic pump tubing for cleanliness and flat spots and replace if needed.

- Black/Black for samples and orange/blue for internal standard - should last 10-16 hours
- Red/red for waste - only needs to be replaced if notable flat spots or reduction in rinse flow

15. References:

15.1. United Stated Environmental Protections Agency, Inductively Coupled Plasma-Atomic Emission Spectroscopy – Method 6010C, SW846.Test Methods for evaluating Solid Waste.

15.2. AOAC Official Method 2017.02 Arsenic, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Selenium, and Zinc in fertilizers

16. Tables:

Table 1. ICP Calibration Standard Preparation

STD ID	Final Vol. (mL)	Custom 1000µg/mL multi-element Mix (mL)	Boron, 1000µg/mL Standard (mL)	Standard #7 (mL)	Conc. (µg/mL)
7	50	2.5	2.5	---	50
6	50	---	---	10	10
5	50	---	---	5	5
4	50	---	---	1	1
3	50	---	---	0.5	0.5
2	50	---	---	0.25	0.25
1	50	---	---	0.05	0.05

Note: This is an example. Standards can be made at different concentrations and volumes as necessary.

Table 2. Recommended Wavelengths and Calibration Conditions

Element	Wavelength (nm)	Detection Mode	Element	Wavelength (nm)	Detection Mode
Boron	249.677	Axial	Molybdenum	202.031	Axial
Calcium	317.933	Axial	Nickel	231.604	Axial
Chromium	276.717	Axial	Phosphorus	178.227	Axial
Cobalt	228.616	Axial	Potassium	766.490	Radial
Copper	327.391	Axial	Scandium (IS)	361.383	Axial/Radial
Iron	238.204	Axial	Selenium	196.025	Axial
Magnesium	285.215	Axial	Sodium	589.592	Radial
Manganese	257.610	Radial	Zinc	206.200	Axial

Table 3. Perkin Elmer ICP-OES Avio 500 Conditions

Factor	Setting	Factor	Setting
Plasma Flow	12 L/min	Source Equilibrium Delay	15 sec
Auxiliary Flow	0.2 L/min	Read Delay	45 sec
Nebulizer Flow	0.6-0.8 L/min	Replicates	3
RF Power	1500 watts	Flush Pump Rate	1.5 L/min
View Distance	15 mm	Sample Pump Rate	1.5 L/min
Aerosol Type	Wet	Rinse Pump Rate	1.5 L/min

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5/11/20	Section 8.3. Corrected the HCl concentration