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

1. Scope:

This document provides a procedure for analysis of soluble silicon in liquid and dry fertilizer products using ICP-OES.

2. Principle:

Dry samples are ground to pass a 300µm sieve (USA standard No. 50).

Clear liquid samples are extracted at room temperature using a Na_2CO_3-NH_4NO_3 extraction solution. Solid samples and liquid with particulates are extracted with the same solution but with a 5-day holding time. Sample extract is analyzed using ICP-OES. A different detection method such as visible spectroscopy with heteropoly blue analysis is used to conform violative samples.

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.

Sodium carbonate and Ammonium nitrate are toxic, cause skin and eye irritation, and shall be used under fume hood. Avoid contact with skin and breathing vapors. Ammonium nitrate is an oxidizing agent and should avoid high temperature and combustible materials.

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 calibration standard used to demonstrate ongoing instrument performance and is analyzed 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. Sodium carbonate-ammonium nitrate solution subjected to the entire analytical process to demonstrate all aspects of the analysis are free from interferences.

QC Quality Control Sample. Unspiked talc or wollastonite that is analyzed with each set to determine the amount of SiO_2 in the spiked material.

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 each matrix using this method.

RL Reporting Limit. The lowest level that can be reported accounting for variances in matrices. 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 interference 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. Shaker Table Unit (140 rpm)
- 6.1.3. Analytical Balance capable of weighing 0.1 mg

6.1.4. pH meter
6.1.5. Spectrophotometer with wavelength to 660nm.

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. FilterMate PTFE certified filter and plunger (Environmental Express Cat# SC0408)
6.2.5. Disposable funnels (Evergreen Scientific Cat# 208-5136-030)
6.2.6. Black/black tubing, 0.76mm ID (Perkin Elmer Cat# N0777043)
6.2.7. Orange/blue tubing, 0.25mm ID (Perkin Elmer Cat# N0773112)
6.2.8. Red/red tubing, 1.14mm ID (Perkin Elmer Cat# 9908585)
6.2.9. 250mL Sample bottles with caps (Thermo Scientific Cat# 2007-0008)

7. Reagents

Equivalents are acceptable

7.1. Sodium carbonate 99.95%, (ACROS Organics Cat# 207765000)
7.2. Ammonium nitrate 99% (ACROS Organics Cat# 205865000)
7.3. Nitric acid 67-70%, trace metal grade, CAS # 7697-37-2 (Fisher Scientific Cat# A509-P212)
7.4. Concentrated Sulfuric acid, 18.4 M, CAS # 7664-93-9 (Fisher Scientific Cat# A300C-212)
7.5. Ammonium molybdate, 1-0176 (J.T Baker)
7.6. Tartaric acid, A314-500 (Fisher Chemical)
7.7. Ascorbic acid, BP 351-500 (Fisher Chemical)
7.8. Scandium, 1000µg/mL in 2% nitric acid (SPEX CertiPrep Cat# PLSC2-2T)
7.9. Silicon calibration standard,1000µg/mL (SPEX CertiPrep Cat# PLS19-2Y)
7.10. Silicon ICV standard 1000µg/mL (Inorganic Ventures Cat# CGSINA1)
7.11. Sodium silicate solution,12.5% (Sigma Aldrich Cat# 338443)
7.12. Manganese 1000µg/mL (SPEX CertiPrep Cat# PLMN2-2T)
7.13. LCMS grade water

8. Standard and Extraction Solution Preparation:

8.1. Stock standards are purchased 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 1 month from preparation date. Refer to Table 2 for standard preparation.

8.3. Prepare 245 ppm SiO_2 spike solution by weighing 1.0g of 12.5% sodium silicate (w/w) in a 250mL volumetric flask and diluting with LCMS grade water.

8.4. Prepare 0.094M sodium carbonate solution by adding 20g anhydrous sodium carbonate to 2 L of water. Stir to dissolve and cap container tightly. Prepare fresh solution monthly and store at room temperature.

8.5. Prepare 0.20M ammonium nitrate solution by adding 32g ammonium nitrate to 2L of water. Stir to dissolve and cap container tightly. Prepare fresh solution monthly and store at room temperature.

8.6. Prepare sodium carbonate-ammonium nitrate extraction solution at pH 9.4 by adding 10mL each of sodium carbonate and ammonium nitrate solutions prepared in 8.3 and 8.4 to a plastic beaker. Stir and verify a pH of 9.4 ± 0.05 using a pH meter. If pH is not within the required range, dispose of solution and remake until the correct solution pH is achieved. This is only to check the pH and can be discarded.

8.7. Prepare 0.42M ammonium molybdate solution by adding 75g ammonium molybdate to 1L beaker. Add 500mL of water to dissolve. Slowly add 100mL of concentrated sulfuric acid then cool. Quantitatively transfer to a 1L volumetric flask and bring to volume using water. Store in a plastic bottle at room temperature. Prepare fresh solution weekly.

8.8. Prepare 1.33M tartaric acid solution by adding 200g tartaric acid to a 1L volumetric flask. Dilute to 1L using water. Stir to dissolve and cap container tightly. Solution expires in 3 days.

8.9. Prepare 0.017M ascorbic acid solution by adding 3g ascorbic acid to 1L volumetric flask. Dilute to 1L using water. Transfer to a plastic bottle and store in a refrigerator. Allow solution to warm to room temperature before use. Solution expires in 3 days.

8.10. Prepare standards for ICP-OES analysis (refer to Table 2).

8.11. Prepare standards for visible spectroscopy analysis (refer to Table 2A). Standards are stored in plastic bottles at room temperature.

8.12. The calibration blank solution is a 1% v/v solution prepared by adding 10mL sodium carbonate-ammonium nitrate extraction solution to a 1L of water in a volumetric flask. The calibration blank solution is also used to prepare calibration standards, the ICV, and is used as the diluent for any samples requiring a dilution.

8.13. Standards are stored at room temperature in polypropylene bottles with an expiration date of 1 month from the preparation date.

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

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

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

9. Sample Extraction for Non-Liquid (Dry) and Liquid Fertilizer Material:

9.1. Non-Liquid (Dry) Fertilizer Material (Refer to *Journal of AOAC International Vol. 96, No. 2, 2013* for extraction and detailed analysis procedure).

9.1.1. Dry the material to be used as the quality control (QC) sample for 2 hours at 105 ± 5°C. The same material will be used for the matrix spike.

9.1.2. Prepare a QC sample by weighing 0.2g ± 0.005g of material from step 9.1.1 into a tared bottle.

9.1.3. Prepare the matrix spike by weighing 0.2g ± 0.005g of material from step 9.1.1 into a tared bottle then adding 10µL of spike solution (see step 8.3) to achieve a 5ppm spike level.

9.1.4. Fertilizer samples need not be dried and should be analyzed on an as-is moisture basis.

9.1.5. Weigh 0.2g ± 0.005g of each sample into tared plastic bottles (record weight).

9.1.6. Using a plastic graduated cylinder, add 100mL each of sodium carbonate and ammonium nitrate extraction solution to the spike, QC, and each sample.

9.1.7. The reagent blank (RB) is 100mL each of sodium carbonate and ammonium nitrate extraction solution.

9.1.8. Cap bottles tightly and shake at 140 rpm at ambient temperature for 60 ± 5 minutes.

9.1.9. Remove bottles from the shaker and let stand undisturbed for 5 days. Note: 5-day timer begins at the start of shaking.

9.1.10. At the end of 5 days, filter using FilterMate filters or disposable funnel with filter paper.

9.1.11. Samples are stored at room temperature until analyzed by ICP-OES.

9.2. Liquid Fertilizer Materials

9.2.1. Follow steps 9.1.1 – 9.1.5 to prepare spike, QC, and samples.

9.2.2. Using a plastic graduated cylinder, add 50mL each of sodium carbonate and ammonium nitrate extraction solution to the spike, QC, and each sample.

9.2.3. The reagent blank (RB) is 50mL each of sodium carbonate and ammonium nitrate extraction solution.

9.2.4. Cap bottle tightly and shake at 140 rpm at ambient temperature for 60 ± 5 minutes.

9.2.5. Remove sample from shaker and filter using FilterMate filters or disposal funnel with filter paper.

9.2.6. Samples are stored at room temperature until analyzed by ICP-OES.

9.3. Confirmation of non-liquid sample results using Visible Spectroscopy with Heteropoly Blue

9.3.1. At the end of 5 days transfer 2 mL of unfiltered extract of each sample, spike, RB, QC, and standards from step 9.1.9 above without disturbing the contents of the bottles to a 200 mL polypropylene volumetric flask and dilute with water. If the sample has < 3% Si, transfer 4mL of extract instead. Stopper and mix well.

9.3.2. Pipette 20 mL of each diluted solution into a plastic test tube. Tubes may be allowed to sit overnight at this point if needed.

9.3.3. Add reagents (see steps 8.5 – 8.7) to each tube in the following order:

- Add 2 mL ammonium molybdate solution and mix well for ~10 seconds using touch agitator. Allow to rest for 10 minutes.
- Add 2mL tartaric acid solution. Stopper test tube and mix well for 10 seconds using touch agitator. Allow to rest for 5 minutes.
- Add 2mL ascorbic acid solution. Stopper test tube and mix well for 10 seconds using touch agitator.

9.3.4. Allow samples, spike, QC, blank, and standards to stand for ~60 minutes for color development. Color graduation from blue to purple shall be seen with increasing Si concentration.

9.3.5. Analyze using a spectrophotometer analysis with the wavelength to 660 nm and mode set to A.

a. Flush flow cell or cuvette three times with water between reading to prevent coating of the flow cell.

b. Read and record A data for blank, QC, standards, and samples. Determine the linear correlation equations using concentration versus A data.
c. Calculate % Si concentration in samples using equation outlined in section 13.2.

10. Instrument Calibration:

10.1. Refer to Table 1 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 is prepared and analyzed using the same method as the samples. Talc or a Magruder PT samples shall be used for solid materials and the extraction liquid shall be used for liquid samples. The spiked sample matrix result shall be within 80 to 120%. If the QC fails, the samples affected must be re-analyzed with a new QC sample.

12.4. If available, a Magruder sample with a known amount of soluble silicon may be used as a laboratory control sample. The recovery shall be within two standard deviations of the assigned value.

12.5. 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. If the IS fails, the sample is diluted and reanalyzed. If it still fails, the instrument may require maintenance or recalibration.

12.6. The MDL for soluble silicon is 0.025%. The reporting limit is 0.1%.

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.

13.2. To determine the soluble Si concentration using spectrophotometer analysis, use the equation:

$$\% \text{ Si} = \frac{((K \times A) + B)}{10{,}000} \times \frac{V_i}{W} \times \frac{V_f}{V_a}$$

K = coefficient K1, or slope factor from standard curve
A = absorbance of test sample
B= intercept from standard curve
V_i = initial volume in mL (eg., 200 mL)
V_a = aliquot taken for dilution in mL (2 mL or 4mL)
V_f = final volume in mL (eg. 200 mL)
W = test portion weight in mg (eg., 200mg)
10000 = conversion from mg/L to %.

13.3. To determine the % Si spike recovery, use the following equation:

$$\% \text{ Si spike recovery} = \frac{(C_f - C_u) \times W \times 100}{2.45}$$

C_f = Concentration of SiO_2 in spike (ppm)
C_u = Concentration of SiO_2 in QC (ppm)
W = Weight of sample (grams)
2.45 = Conc. of spike solution (245 ppm) x amount spiked (10µL)

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. Sebastian et al., Journal of AOAC International Vol. 96, No. 2, 2013. A 5-Day Method for Determination of soluble silicon concentrations in nonliquid fertilizer materials using a sodium carbonate-ammonium nitrate extractant followed by visible spectroscopy with heteropoly blue analysis.

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. Recommended Wavelengths and Calibration Conditions

Element	Primary Wavelength (nm)	Secondary Wavelength (nm)	Detection Mode
Silicon	251.611	212.412	Axial
Scandium (IS)	361.383	---	Axial/Radial

Table 2. ICP Calibration Standard Preparation for Silicon

STD ID	Final Vol. (mL)	Vol. of Si Stock - 1000 ppm (µL)	Conc. (µg/mL)
1_xxxxxx	250	12.5	0.05
2_xxxxxx	250	125	0.5
3_xxxxxx	250	250	1
4_xxxxxx	250	1250	5
5_xxxxxx	250	2500	10
6_xxxxxx	250	5000	20

Where xxxxxx is the date of preparation. Note: Standards can be made at different concentrations and volumes as necessary.

Table 2a. Visible Spectroscopy Calibration Standard Preparation

STD ID	Final Vol. (mL)	Vol. of Si Stock - 1000 mg/L (mL)	Vol. of STD A – 50 mg Si/L (mL)	Conc. (mg Si/L)
Intermediate Std A	100	5	--	50
Blank	1000	--	--	0
1_xxxxxx	1000	--	5	0.25
2_xxxxxx	1000	--	10	0.5
3_xxxxxx	1000	--	20	1
4_xxxxxx	1000	--	40	2

Note: 10 mL of extraction solution (Na_2CO_3-NH_4NO_3) is added to blank and each standard and diluted to final volume with deionized water.

Table 3. Perkin Elmer ICP-OES Avio 500 Conditions

Factor	Setting	Factor	Setting
Plasma Flow	15 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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Revision Log:

Date	What was Revised? Why?
8/18/20	Included sample extraction and holding time for non-liquid (dry) materials. Added Grinding fertilizer material and drying quality control sample. Added calculation to determine soluble silica concentration, calculation to determine spike recovery. Included procedure to determine Si using visible spectroscopy with heteropoly blue analysis.