

Analysis of Available Phosphate and Soluble Potash in Fertilizer by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

1. Scope:

This document provides a procedure for analysis of available phosphorus (P) and soluble potassium (K) in fertilizers using ICP-OES. It is not suitable for the determination of total phosphorus and potassium.

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.

Ammonium hydroxide, disodium EDTA and dibasic ammonium citrate can cause skin irritation. Use in a fume hood and avoid contact with skin.

Nitric acid is toxic and corrosive and shall be used under fume hood.

4. Definitions:

- ICV Initial Calibration Verification. A mid-level standard obtained from a different vendor, a different lot or concentration from the same vendor, or prepared by a different analyst than the calibration standards.
- CCV Continuing Calibration Verification. A mid-level standard used to demonstrate the instrument remains in calibration 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 to demonstrate that the instrument is free from interferences and to determine the background from the instrument.
- IS Internal Standard. Scandium and ionization buffer (Cesium) that is mixed with the sample during sample introduction to account for matrix variations.
- MB Method Blank. A blank (water) that is subjected to the entire analytical process to demonstrate all aspects of the analysis are free from interferences.

- QC Quality Control Sample. A NIST 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 measured and reported 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 using this method. 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. PerkinElmer (PE) ICP-OES Optima 2100 DV
 - 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 graduated polypropylene beakers (VWR Cat# 25384-150)
 - 6.2.4. Whatman No. 2 filter paper (Sigma Aldrich Cat# 1002-110)

7. Reagents

Equivalents are acceptable

- 7.1. Nitric acid 67-70%, Trace Metal Grade, CAS # 7697-37-2 (Fisher Scientific Cat# A509-P212)
- 7.2. EDTA (ethylenediamine tetra acetic acid), disodium salt, dihydrate, CAS #6381-92-6 (Fisher Scientific Cat# S311-500)
- 7.3. Ammonium citrate, dibasic, CAS # 3012-65-5 (Fisher Scientific Cat# A663-500)

- 7.4. Ammonium hydroxide 28-30% as NH₃, CAS # 1336-21-6 (VWR Cat# 470300-204)
- 7.5. Triton X-100 – Octyl phenol ethoxylate
- 7.6. Cesium chloride, CAS # 7647-17-8 (VWR Cat# BDH4124-1KG)
- 7.7. Scandium, 1000µg/mL in 2% nitric acid (SPEX CertiPrep Cat# PLSC2-2T)
- 7.8. Manganese, 1000µg/mL in 2% nitric acid (SPEX CertiPrep Cat# PLMN2-2T)
- 7.9. Phosphorus, 1000µg/mL in water (SPEX CertiPrep Cat# PLP9-2X)
- 7.10. Phosphorus, 10,000µg/mL in water (SPEX CertiPrep Cat# PLP9-3Y)
- 7.11. Potassium, 1000µg/mL in 2% HCl (SPEX CertiPrep Cat# PLK1-2X)
- 7.12. Potassium, 10,000µg/mL in 5% HNO₃ (SPEX CertiPrep Cat# PLK2-3Y)
- 7.13. 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 from an ISO 17034 accredited source and are accompanied by a certificate of analysis.
- 8.2. Working standards are stored at room temperature in polypropylene bottles with an expiration date of 6 months from the preparation date.
- 8.3. Ammonium citrate-EDTA extraction solution is prepared by adding ~1.5L of water to a 2L volumetric flask. Add 25g of disodium EDTA and 50g dibasic ammonium citrate and mix to dissolve. In a fume hood, add 30mL of 1:1 NH₄OH-H₂O (v/v) and mix well. Adjust pH to 7.00 (+/- 0.05) with additional 1:1 NH₄OH-H₂O dropwise.
- 8.4. A 40% ammonium citrate-ETDA solution is made fresh for each set by mixing 40mL of the above ammonium citrate-EDTA solution with 60mL water. This solution is used for the CB and for sample dilutions.
- 8.5. Calibration standards are made by diluting stock standards to working levels. Calibration standard preparation details and concentration levels are shown in Table 1. Calibration standards may be prepared at other concentrations, if needed.
- 8.6. Standard level 3 or another mid-level standard is used for the CCV (see Table 1).
- 8.7. 0.5% Triton X solution is prepared by diluting 1mL of Triton X-100 to 200mL water.
- 8.8. 1% HNO₃ autosampler wash solution is prepared by diluting 10mL of HNO₃ to 1000mL water.
- 8.9. The internal standard solution (IS) (10µg/mL scandium and 0.018M cesium chloride in 4% HNO₃) is prepared by dissolving 3g cesium chloride in water then mixing with 10mL of 1000µg/mL Scandium stock solution, 40mL of concentrated HNO₃, and 1mL of 0.5% Triton-X in a 1L volumetric flask and filling to mark with water.
- 8.10. The alignment solution is 0.5mg/L manganese solution prepared by diluting 0.05mL of Manganese stock solution with water to 100mL.

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 65°C.
- 9.3. Weight ~0.3g sample in a labeled 100mL plastic bottle. Weigh 0.5g for samples with guarantees < 1% P and/or K.
- 9.4. Add 40mL ammonium citrate-EDTA extraction solution to each bottle and swirl gently. Cap the bottle and place in the hot block once the hot block has reached the set temperature.
- 9.5. Warm the samples in the hot block for ~15 minutes. Check samples and shake gently or swirl to break down any solid material or to remove solid material adhered to the bottle wall. Return samples to the hot block for ~60 minutes.
- 9.6. Remove the samples from the hot block, add 60mL water to each bottle and swirl gently.
- 9.7. Allow samples to cool to room temperature.
- 9.8. Filter each sample using a Whatman No. 2 filter paper and make dilutions as needed. Transfer ~10mL prepared sample to a 15mL centrifuge tube for ICP analysis. Samples may be stored at room temperature for analysis at a later time.

10. Instrument Calibration:

- 10.1. Refer to Table 2 for recommended P and K wavelength and calibration conditions and Table 3 for ICP-OES conditions and settings.
- 10.2. Verify the outlet gas pressures are 80-100 psi for argon and 100 psi for nitrogen.
- 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. In the instrument software on the **Instrument tab**, click **Plasma Control** and perform the following:
 - 10.7.1. Activate peristaltic pump and check the solution flow through the sample introduction system.

- 10.7.2. Click on the **pump** icon to activate the peristaltic pump and allow solution to flow until it has filled rinse station.
- 10.8. 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:
 - 10.8.1. Check the sample introduction system to ensure all connections are made and are not leaking.
 - 10.8.2. Ensure there is enough Argon and the pressure is 80-120 psi.
 - 10.8.3. 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.
- 10.9. Once the plasma is lit, allow the ICP to stabilize for at least 30 minutes before calibration.
- 10.10. Optimization is only needed if the torch was removed or replaced. In **Instrument** tab, click **Spectrometer Control** and follow the steps to realign the X-Y position of the torch:
 - 10.10.1. Re-align the axial spectrometer
 - 10.10.1.1. Click the axial icon in the **Spectrometer Control** window.
 - 10.10.1.2. Place autosampler probe in 0.5mg/L Mn solution and aspirate.
 - 10.10.1.3. Click on the align view and ensure the wavelength is set for Mn 257.610 and the delay time is set to 30 seconds.
 - 10.10.2. Re-align the radial spectrometer window by.
 - 10.10.2.1. Click the radial icon in the **Spectrometer Control** window
 - 10.10.2.2. Place auto sampler probe in 0.5 mg/L Mn solution and aspirate.
 - 10.10.2.3. Click on the radial view. Ensure the wavelength is set for Mn 257.610 and the delay time is set to 30 seconds.
 - 10.10.3. Once alignment is complete, send autosampler probe to wash position by clicking "Go to Wash" in **Instrument** tab to start at proper position.
- 10.11. 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.
- 10.12. Linearity is assessed using a linear regression that is based on the intensity counts of both P and K and the IS. The correlation coefficient (r) shall be ≥ 0.995 . 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 (1% nitric acid in water) between each sample and standards to prevent carryover.
- 11.3. Dilute with the 40% ammonium citrate-EDTA solution prepared in step 8.4 and reanalyze samples that are out of the calibration range.

12. QA/QC:

- 12.1. The ICV and CCV recovery shall be $\pm 15\%$ of the expected value. The %RSD of three replicate measurements at each wavelength shall be $\leq 10\%$. 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 80% of the lowest calibration standard.
- 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. Acceptable QC samples may be a NIST reference material or a Magruder test sample with a known mean value and standard deviation. The results of NIST samples shall be within the certified value range. The result of Magruder samples shall be within three standard deviations of the assigned value. If the QC sample fails, it may be re-injected. If it still fails, the cause is investigated, and the entire set is re-extracted.
- 12.4. Scandium is used as the IS and its intensity is monitored during analysis. The IS recovery shall be within $\pm 20\%$ of the intensity in the CB.
- 12.5. Method detection limits (MDL) were determined by spiking P and K stock solutions on 0.3g samples and are as follows (P_{213} is the preferred wavelength because of the lower detection limit but P_{178} may be used if interferences are seen with P_{213}):

$P_{178} = 0.525$ ppm	$P_2O_5 (P_{178}) = 0.044\%$
$P_{213} = 0.235$ ppm	$P_2O_5 (P_{213}) = 0.024\%$
$K_{776} = 0.363$ ppm	$K_2O (K_{776}) = 0.018\%$
- 12.6. Reporting limits (RL) are defined as:

P = 2 ppm	$P_2O_5 = 0.09\%$
K = 3 ppm	$K_2O = 0.07\%$

13. Calculations:

- 13.1. The ICP software automatically calculates the concentration of P and K in % when all the sample parameters are entered. To determine % P_2O_5 in a sample, multiply the %P result by 2.29. To determine % K_2O in a sample, multiply the %K result by 1.204.
- 13.2. Two significant figures shall be reported for results $< 10\%$. Three significant figures shall be reported for results $\geq 10\%$.

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: HNO₃) 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 internal standard, 0.76 mm I.D should last 10-16 hours
- Orange/White for sample, 0.64 mm I.D should last 10-16 hours
- Yellow/Yellow for drain, 1.42 mm I.D replace only if notable flat spots or reduction in rinse flow

15. References:

- 15.1. Determination of Phosphorus and Potassium in Commercial Inorganic Fertilizers by Inductively Coupled Plasma-Optical Emission Spectrometry: Single Laboratory Validation. Bartos et al: Journal of AOAC International, Vol. 97, No 3, 2014
- 15.2. Optima 2100DV, Hardware Guide. Perkin Elmer, Inc., April 2004.

16. Tables:

Table 1. ICP Calibration Standard Preparation

<u>Standard ID</u>	<u>Calibration Concentrations</u>		<u>Volume of Stocks</u>		<u>Ammonium Citrate – EDTA Solution (mL)</u>	<u>Final Volume (mL)</u>
	<u>P (µg/mL)</u>	<u>K (µg/mL)</u>	<u>P (1000 µg/mL)</u>	<u>K (1000 µg/mL)</u>		
			<u>(mL)</u>	<u>(mL)</u>		
PK-L1 xxxxxx	<u>2.00</u>	<u>2.00</u>	<u>1.00</u>	<u>1.00</u>	<u>200</u>	<u>500</u>
PK-L2 xxxxxx	<u>10.0</u>	<u>10.0</u>	<u>1.00</u>	<u>1.00</u>	<u>40.0</u>	<u>100</u>
PK-L3 xxxxxx	<u>50.0</u>	<u>50.0</u>	<u>5.00</u>	<u>5.00</u>	<u>40.0</u>	<u>100</u>
PK-L4 xxxxxx	<u>100</u>	<u>100</u>	<u>10.0</u>	<u>10.0</u>	<u>40.0</u>	<u>100</u>
PK-L5 xxxxxx	<u>200</u>	<u>200</u>	<u>20.0</u>	<u>20.0</u>	<u>40.0</u>	<u>100</u>

Where xxxxxx is the date prepared. The ammonium citrate-EDTA solution is prepared in step 8.3 and the final concentration in the calibration standards is 40%. Water is used to bring standards to final volume.

Table 2. Recommended Wavelengths and Calibration Conditions

Element	Primary Wavelength (nm)	Calibration Range µg/mL	Curve Fit	Detection Mode	Spectral Deconvolution
P	177	2 to 1000	Linear	Radial	None
P	178	2 to 1000	Linear	Radial	None
P	213	2 to 1000	Linear	Radial	Cu 213.598
K	766	3 to 1500	Linear	Radial	None
Sc	361				

Table 3. Perkin Elmer ICP-OES 2100 Conditions

Factor	Setting	Factor	Setting
Power	1500 Watts	Spray Chamber	Baffled Furnace
Plasma Flow	15 L/min	Nebulizer Type	High Solids Gem Cone
Auxiliary Flow	0.2 L/min	Sample Pump Tube	Orange/White
Nebulizer Flow	0.65 L/min	Internal Standard	Black/Black
Sample Flow Rate	1.0 mL/min	Waste Pump Tube	Yellow/Yellow
Source Equilibration Delay	15 sec	CsCl ionic Buffer	0.018M
Read Delay	45 sec	Internal Standard	10µg/mL

Approvals:

Revised By:

Liping Nie
Liping Nie
Environmental Scientist

5/8/20
Date

Approved By:

Stacy Aylesworth
Stacy Aylesworth
Senior Environmental Scientist (Supervisor)

5/8/20
Date

Approved By:

Maryam Khosravifard
Maryam Khosravifard
Environmental Program Manager I

5/8/20
Date

Approved By:

Sarva Balachandra
Sarva Balachandra
Quality Assurance Officer

5/11/20
Date

