

**FERTILIZER
METHODS**

Chapter

PHOSPHATE ANALYSIS

Subject

Citrate Insoluble Phosphorus - Segmented Flow

SCOPE: This is a double extraction, automated analytical procedure for the determination of citrate insoluble phosphorus in fertilizer samples that have a range of 0 to 20% P₂O₅, the range may be increased by decreasing sample weight and/or the use of dilutions.

PRINCIPLE: The preparation for citrate insoluble phosphorus is achieved by extracting the phosphate from the fertilizer sample with D.I. water at 65° C and neutral ammonium citrate solution at 65° C. The sample residue is then ignited and digested with HCl. The automated colorimetric determination of phosphorus in fertilizer samples is achieved by using two 10.6 mL time delay heating coils [93-95° C] and perchloric acid to destroy ammonium citrate, to destroy other colored materials, and for the hydrolysis of phosphates to orthophosphate. The orthophosphate/molybdovanadate color complex is read at 420 nm.

SAFETY: Each laboratory is responsible for maintaining a current file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis.

**APPARATUS &
EQUIPMENT:**

- Balance, accuracy to .001 g
- Bath, Constant Temperature Circulating
- Beaker, 250 mL Conical
- Boiling Chips
- Filter Paper, 7 cm Whatman No. 1 or equivalent
- Filter Paper, 7 cm Whatman No. 5 or equivalent
- Flask, 500 mL Kohlrausch (class "A")
- Funnel, Buchner 7 cm
- Glass jar, 7½ gallon

- Heater, for Ammonium Citrate Solution
- Stopper, Two Hole, for 500 mL Kohlrausch Flask
- Stopper, One Hole, for 250 mL Conical Beaker
- Thistle Tube, Polyethylene
- Segmented Flow Autoanalyzer
- Automated continuous segmented flow analyzer
- Automatic Sampler – with adjustable sample and wash periods
- Proportioning Pump
- Analytical Manifold with heater
- Colorimeter equipped with filter and flow cell
- Chart Recorder, compatible with colorimeter output
- Pump tubes, tubing, and sample cups as needed
- Porcelain Crucible

**REAGENTS &
CHEMICALS:**

- Citric Acid Monohydrate Certified A.C.S. grade or equivalent
- Ammonium Hydroxide Certified A.C.S. grade or equivalent
- Ammonium Molybdate [(NH₄)₂MoO₄] Certified A.C.S. grade or equivalent
- Ammonium Meta-Vanadate [(NH₄)VO₃] Certified A.C.S. grade or equivalent
- Deionized Water (D.I.) q.s.
- Hydrochloric Acid Certified A.C.S. grade or equivalent
- Nitric Acid Certified A.C.S. grade or equivalent
- Perchloric Acid A.C.S. Reagent grade or equivalent
- Potassium Phosphate [KH₂PO₄], Primary Standard
- Sodium Lauryl Sulfate (Sodium Dodecyl Sulfate)

- Concentrated Wetting Agent – “SLS”

Sodium Lauryl Sulfate 15 g

Deionized Water 87 mL

Add 15 g of sodium lauryl sulfate to 87 mL of D.I. water, stir until mixed.
Shelf life 90 days.

- Dilute Wetting Agent – “SLS”

Concentrated Wetting Agent	20	drops
Deionized Water	50	mL

Add 20 drops of concentrated wetting agent to 50 mL of D.I. water, stir until mixed. Make up weekly.

- Neutral Ammonium Citrate Solution

Citrate Acid Monohydrate	6,800	g
Deionized Water	24	L
Ammonium Hydroxide	6,250	mL

Add 6800 g of Citric Acid Monohydrate to a 7½ gallon jar. Add 24 L of deionized water to dissolve Citric Acid Monohydrate with constant stirring. When completely dissolved, add 6,250 mL of ammonium hydroxide (with constant stirring) to citrate solution, allow to cool. Adjust pH to 7.00 by adding small increments of ammonium hydroxide or Citric Acid Monohydrate. Adjust specific gravity to 1.09 by addition of D.I. water.

- Molybdovanadate Reagent

Ammonium Molybdate [(NH ₄) ₂ MoO ₄]	16.5	g
Ammonium Meta-Vanadate [(NH ₄)VO ₃]	0.6	g

Dissolve 16.5 g of ammonium molybdate in 400 mL of hot D.I. water. Allow to cool.

Dissolve 0.6 g of ammonium meta-vanadate in 250 mL of hot D.I. water. Cool and add 60 mL of perchloric acid.

Gradually add ammonium molybdate solution with constant stirring to ammonium vanadate solution. Add 2 mL of dilute wetting agent and dilute to 2 L.

- System Wash Solution

Deionized Water	800	mL
Dilute Wetting Agent – “SLS”	4	drops

- Perchloric Acid, Stock Reagent

Perchloric Acid	342	mL
Deionized Water	Final Volume 1000 mL	

Add 342 mL perchloric acid to 400 mL D.I. water and dilute to 1 L.

- Perchloric Acid, Daily Reagent

Perchloric Acid 250 mL

Dilute Wetting Agent – “SLS” 4-5 drops

Add 4-5 drops of dilute wetting agent to 250 mL of perchloric acid reagent, shake well.

NOTE: This reagent must be made fresh daily.

STANDARDS:

- KH_2PO_4 Stock Standard 5,000 ppm
Potassium Phosphate Primary Std. 4.7938 gm
Deionized Water, q.s. Final Volume 500 mL
Dissolve 4.7938 g of Potassium Phosphate Primary Standard (dried for 2 hours at 105°C) in deionized water. Dilute to 500 mL.
- Working Standard High Range 400 ppm
Pipet 20 mL of KH_2PO_4 stock standard and dilute with D.I. water to 250 mL.
- Working Standard Low Range 80 ppm
Pipet 4 mL of KH_2PO_4 stock standard and dilute with D.I. water to 250 mL.
- Working Standard Mid Range 200 ppm
Pipet 10 mL of KH_2PO_4 stock standard and dilute with D.I. water to 250 mL.
- An internal standard is weighed and analyzed with each set to check for completeness of reaction and the precision and accuracy of technique.
- Class “A” glassware is used throughout method.

**SAMPLE
PREPARATION:**

Weigh sample directly into 250 mL conical beaker.

NOTE ON WEIGHING SAMPLE:

For 0-5% Guarantees, weigh $\approx 3.00 \text{ g} \pm 0.10 \text{ g}$

For 5-10% Guarantees, weigh $\approx 1.00 \text{ g} \pm 0.10 \text{ g}$

For 10-20% Guarantees, weigh $\approx 0.5 \text{ g} \pm 0.10 \text{ g}$

For Guarantees $\geq 20\%$, weigh $\approx 0.5 \text{ g} \pm 0.10 \text{ g}$, + a 1:2 dilution

1. Add 100 mL of D.I. water at 65° C to 250 mL conical beaker containing sample, seal with 1 hole stopper containing a thistle tube. Place in shaker bath at 65° C for 15 minutes.
2. Set up Whatman No. 1 filter disk - Buchner funnel – Kohlrausch flask – vacuum apparatus.
3. After 15 minutes remove conical beaker from shaker bath, wash thistle tube and stopper with D.I. water, at 65° C.
4. Transfer contents of conical beaker to wetted Whatman No. 1 filter disk in Buchner funnel – Kohlrausch flask – vacuum apparatus. Rinse conical beaker and Buchner funnel with 100 mLs of D.I. water at 65° C in 10 mL increments. Allow each portion of the water to pass through the filter paper before adding the next portion. Vacuum dry filter disk.
5. Carefully remove filter disk and place in conical beaker.
6. Add 100 mL of ammonium citrate solution at 65° C to conical beaker, try to place solution directly on the filter disk.
7. Stopper with 1 hole stopper containing a thistle tube. Place in 65° C shaker bath for 1 hour.
8. Add a Whatman No. 5 filter disk to Buchner funnel – Kohlrausch flask – vacuum apparatus.
9. After one hour remove conical beaker from shaker bath, rinse thistle tube and stopper with D.I. water at 65° C.
10. Transfer contents of conical beaker to wetted Whatman No. 5 filter disk in Buchner funnel – Kohlrausch flask – vacuum apparatus. Rinse conical beaker and Buchner funnel with 100 mL of D.I. water at 65° C in 10 mL increments. Allow each portion of the water to pass through the filter paper before adding the next portion. Vacuum dry filter disk.
11. Remove filter disk and transfer it to a porcelain crucible.
12. Ignite filter disk at 600° C until all organic matter has been destroyed.
13. Cool crucible and contents.

14. Transfer contents to 250 mL conical beaker and digest with 15 mL of HCl until all phosphate dissolves.
15. Dilute to appropriate volume.

**SAMPLE
ANALYSIS:**

System Start-up:

1. Check the level of all the reagents to insure an adequate supply.
2. Place the reagent lines in the system wash solution, place the platen on the pump, and start the pump. Pump system wash solution until the system is clear of irregular air bubbles.
3. Shut the pump off; place all the reagent lines in their respective containers. Restart the pump.
4. While the reagents are being pumped, adjust the baseline, zero and full scale readings of the colorimeter and recorder.
5. Pour samples into sample cups and place in Automatic Sampler.
(See Figure 1)

NOTE: This procedure has a phosphate range of 0 to 20% P_2O_5 for a 1g sample diluted to 500 mL. Different ranges are possible by varying the sample weight and/or dilution volume.

6. Once the baselines have stabilized and been adjusted, turn the sampler on. Adjust standards readings to full scale using the STD CAL (standard calibration knob).
7. Analyze the samples at 420 nm. Check the 100 ppm P_2O_5 standard after every 10 to 12 samples.

System Shutdown:

1. Once all samples and standards have been analyzed, allow reagents to pump for 20 minutes.
2. Shut the pump off. Place all of the reagent lines into the system wash solutions. Restart the pump and flush for thirty minutes.
3. Shut the pump off. Remove all reagent lines from system wash solutions, restart pump and pump all lines dry. Stop pump. Remove the pump platen. Make sure the recorder, colorimeters, pump, and sampler are turned off.

CALCULATIONS:

Drift Corrected Readings:

Where:

- R = sample reading between standards S_{m1} ... and S_{m2}
- S_{m1} = reading of mid-range standard preceding the sample
- S_{m2} = reading of second mid-range standard following the sample
- T(R) = set position number of the sample
- T(S_{m1}) = set position number of the mid-range standard preceding the sample
- T(S_{m2}) = set position number of the second mid-range standard following the sample
- S.W. = sample weight
- 500 = Flask size in mL
- 200 = ppm of the Mid Range Standard
- 50 = Chart reading of the Mid Range Standard

$$\text{Corrected Reading} = [R - (S_{m1}) - (50)] - \frac{(S_{m2}) - (S_{m1})}{T(S_{m2}) - T(S_{m1})} \times [T(R) - T(S_{m1})]$$

$$\%P_2O_5 = \text{Corrected Reading} \times \frac{200}{50} \times \frac{500}{S.W.} \times 10^{-6} \times 100 \times \text{extra dilutions}$$

$$\%P_2O_5 = \text{Corrected Reading} \times \frac{0.20}{S.W.} \times \text{extra dilutions}$$

APPROVAL:

Approved by: _____


Signature

Date: 8/26/02

Bureau Chief

Title

METHOD REVISION HISTORY:

Version	Date	Description	Author
Original	02/10/94	Replaces P-100.00	W. M. Bell
Original	08/22/02	Replaces FM-501	W. M. Bell

REFERENCE:AOAC 15th Edition, *Method 963.03*

PHOSPHATE SYSTEM SCHEMATIC

