

FERTILIZER METHODS

Chapter

PHOSPHATE ANALYSIS

Subject

Available Phosphorus (Dual Extraction) -
Segmented Flow

SCOPE: This is a double extraction, automated analytical procedure for the determination of available phosphorus in fertilizer samples that can be hydrolyzed to orthophosphate and have a range of 0 to 20% P₂O₅, the range may be increased by decreasing sample weight and/or the use of dilutions. **This method is applicable to fertilizer samples containing any amount of calcium.**

PRINCIPLE: The preparation for available phosphoric acid determinations is achieved by extracting the phosphate from the fertilizer sample with neutral ammonium citrate solution at 65° C. This procedure must be performed when triple super phosphate, super phosphate, or when greater than 10% calcium is present in the sample. The calcium is extracted from the sample with water at 65° C and prevented from forming insoluble calcium/magnesium phosphate complexes by the addition of nitric acid to the flask prior to the citrate extraction.

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 0.001 g
- Bath, Constant Temperature Circulating
- Beaker, 250 mL Conical
- Filter Paper, 7 cm Whatman No. 1 or equivalent
- Flask, 500 mL Kohlrausch (class "A")

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 6,800 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 [(NH₄)₂MoO₄] 16.5 g

Ammonium Meta-Vanadate [(NH₄)VO₃] 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 1,000 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 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 conical beaker containing sample, stopper with 1 hole stopper containing thistle tube. Place in 65° C shaker bath for 1 hour.
2. Add 10 mL of 1:1 nitric acid to Kohlrausch flasks.
3. Set up Buchner funnel – Kohlrausch flask – vacuum apparatus.
4. After one hour, remove conical beaker from shaker bath, rinse thistle tube and stopper with D. I. water at 65° C into conical beaker.
5. Transfer contents of conical beaker to wetted 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 through filter disk in bottom of Buchner Funnel. Vacuum dry filter disk.
6. Carefully remove filter disk and place in conical beaker.
7. Add 100 mL of ammonium citrate solution at 65° C to conical beaker. Try to place solution directly on the filter disk.
8. Seal with 1 hole stopper containing a thistle tube. Place in 65° C shaker bath for 1 hour.
9. Add new filter disk to Buchner funnel-Kohlrausch flask-vacuum apparatus.
10. After one hour, remove conical beaker from shaker bath, rinse thistle tube and stopper with D.I. water at 65° C into conical beaker.
11. Transfer contents of conical beaker to wetted filter disk in Buchner funnel-Kohlrausch flask – vacuum apparatus. Rinse conical beaker and sides of Buchner funnel with 100 mLs of D.I. water at 65° C through filter disk in bottom of Buckner funnel. Vacuum dry filter disk.
12. Remove top of funnel. Rinse bottom of funnel and sides of Kohlrausch flask.
13. Allow to cool to room temperature and dilute to 500 mL.
14. Shake well.

NOTE: 30-45 seconds of vigorous shaking may be required to mix sample completely.

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 off pump, 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% P₂O₅ for a 1 g 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 P₂O₅ 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:  Date: 8/26/02
Signature

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

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