

FERTILIZER METHODS

Chapter

PHOSPHATE ANALYSIS

Subject

Total Phosphorus - Segmented Flow

SCOPE: This is an automated analytical procedure for the determination of total phosphorus in fertilizer samples having a range of 0 to 20% P₂O₅.

PRINCIPLE: The preparation for total phosphoric acid determinations is achieved by digesting the fertilizer sample with HNO₃ and HCl and reacting this digestate with neutral ammonium citrate solution.

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")
- 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

- 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 [(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 q.s.		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

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

For bonemeal and other materials containing small amounts of organic matter;

1. Add 15 mL of D.I. water, 30 mL of HNO_3 and 5 mL of HCl to sample, boil until clear (about 15 minutes). Cool.
2. Add 100 mL of ammonium citrate solution at 65°C to conical beaker. Stir and let stand for 10 – 15 minutes.
3. Set up Buchner funnel – Kohlrausch flask – vacuum apparatus.
4. 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.
5. Remove top of funnel. Rinse bottom of funnel and sides of Kohlrausch flask.
6. Allow to cool to room temperature and dilute to 500 mL.
7. Shake well.

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

Skip to sample analysis.

For basic slag and fertilizers containing iron (Fe) or aluminum (Al) phosphate;

1. Add 15 mL of D.I. water, 30 mL of HCl , and 10 mL of HNO_3 to sample. Boil until clear (about 15 minutes).
2. Cool, add 100 mL of ammonium citrate solution at 65°C to conical beaker. Stir and let stand for 10-15 minutes.
3. Set up Buchner funnel – Kohlrausch flask – vacuum apparatus.
4. 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.
5. Remove top of funnel. Rinse bottom of funnel and sides of Kohlrausch flask.
6. Allow to cool and dilute to 500 mL.

7. 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 rinse 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% P_2O_5 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 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:  Date: 8/23/02
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

REFERENCE:

AOAC 15th Edition, *Method 958.01, 978.01*

