Available Phosphorus in Solid Fertilizer – Direct Extraction

1. Scope:

To provide a standardized procedure for the gravimetric analysis of water-soluble (available) phosphorus (as P_2O_5) in solid fertilizers using direct extraction.

2. Principle:

Samples are prepared according to Sample Preparation, Storage, and Disposal (RA-SP-SMPL-PREP). Samples are extracted with ammonium citrate at pH 7.0 in the presence of disodium EDTA (ethylenedinitrilotetraacetic acid) to complex the calcium and magnesium. The available phosphorus is precipitated with Quimociac reagent and the resulting precipitate is filtered, washed, dried, and weighed to calculate the amount of available phosphorus (as P_2O_5) present in the sample.

3. Safety:

3.1 Read all SDS on the safe handling of chemicals used in this method.

3.2 Nitric acid is highly corrosive. Preparation of the Quimociac reagent and the nitric acid (1+1) should be done in a fume hood using the appropriate protective clothing, eye protection, and gloves.

3.3 Aqueous ammonium hydroxide is toxic and produces vapors that are very irritating to the skin and respiratory tract. Preparation of the (1+1) aqueous ammonium hydroxide and the ammonium citrate/EDTA solution shall be done in a fume hood using the appropriate protective clothing, eye protection, and gloves.

4. Definitions:

QMP = quinolinium molybdophosphate = $(C_9H_7N)_3H_3PO_4 \cdot 12MoO_3$

5. Equipment & Supplies (equivalents are acceptable):

5.1 Analytical balance (Mettler Toledo XS204)
5.2 Laboratory oven (Fisher Scientific ISOTEMP Oven 725F)
5.3 Water bath with shaker (capable of maintaining temperature of 65°C ± 3°C)
5.4 Hot plate (Thermo Scientific HPA2235MQ)
5.5 Volumetric flat bottom boiling flask – 250 mL
5.6 Erlenmeyer flask – 500 mL
5.7 Vacuum filter flask with adapter – 2 Liter
5.8 Gooch crucibles – Coors #4 dried at ~250°C

5.9 Glass fiber filter paper – 2.4 cm circles (Whatman 934-AH)
5.10 Desiccator
5.11 pH meter

6. Reagents (equivalents are acceptable):

6.1 Nitric acid (HNO_3), concentrated (Fisher A509-P212)
6.2 30% Aqueous ammonium hydroxide (NH_4OH)
6.3 Disodium EDTA (ethylenedinitrilotetraacetic acid) (Fisher S311-500)
6.4 Dibasic ammonium citrate (Fisher A663-500)
6.5 Sodium molybdate dihydrate (Fisher S336-3)
6.6 Citric acid (VWR BDH9228)
6.7 Synthetic quinoline (Acros organics 221141000 or Sigma Aldrich 241571)
6.8 Acetone (Fisher A949-4)

7. Preparation of Reagents:

7.1 Prepare (1+1) nitric acid by mixing 1L concentrated nitric acid and 1L DI water.

7.2 Prepare the ammonium citrate EDTA solution:
- 7.2.1 Dissolve 25g disodium EDTA and 50g dibasic ammonium citrate in 1.5L DI water.
- 7.2.2 Add 30mL aqueous ammonium hydroxide.
- 7.2.3 Adjust the pH to 7.00 by adding (1+1) aqueous ammonium hydroxide.
- 7.2.4 Dilute to 2L with water.

7.3 Prepare the Quimociac reagent:
- 7.3.1 Dissolve 70g sodium molybdate dihydrate in 150mL water.
- 7.3.2 Dissolve 60g citric acid in a mixture of 85mL concentrated HNO_3 and 150mL DI water. Allow to cool.
- 7.3.3 Gradually add the sodium molybdate solution to the citric acid HNO_3 mixture with stirring.
- 7.3.4 Dissolve 5mL synthetic quinoline in a mixture of 35mL HNO_3 and 100mL DI water.
- 7.3.5 Gradually add the quinoline solution to the molybdate-citric acid- HNO_3 solution, mix, and let stand for 24 hours.
- 7.3.6 Filter then add 280mL acetone, dilute to 1L with DI water, and mix.

8. Analysis:

8.1 Perform daily balance and oven temperature verification.

8.2 Thoroughly mix the sample before weighing by rotating and shaking the bottle. Weigh approximately 0.5g sample into a 250mL boiling flask. Record this weight to the nearest 0.0001g.

8.3 Add ~100mL ammonium citrate/EDTA solution to the flask and gently swirl to mix.

8.4 Secure the flask on the shaker rack in the 65°C ± 3°C water bath. Allow the flask to sit in the water bath for ~15 minutes to warm the solution to approximately 65°C.

8.5 Close the flask tightly with a rubber stopper and set the shaker to gently shake the flask for ~60 minutes.

8.6 Remove the flask from the water bath, fill the flask almost to the 250mL mark with DI water, and cool to room temperature.

8.7 Dilute the flask to volume with DI water, tightly stopper, and mix. Allow the particulates to settle overnight or filter the solution to remove the particulates.

8.8 Pipet a suitable aliquot of the clear supernatant to form ~0.3g of precipitate into a 500mL Erlenmeyer flask.

Guarantee	Suggested Amount
<9.7%	50mL
9.7 – 19%	25mL
>19%	15mL

8.9 Add DI water to bring the total volume to ~100mL.

8.10 Add ~10mL HNO_3 (1+1), place on a hot plate in a fume hood, and gently heat to boiling or near boiling for ~30 minutes. **Carefully swirl the flask several times during the heating process to prevent the solution from super heating.**

8.11 Remove from the hot plate and add ~50mL Quimociac reagent.

8.12 Place back on the hot plate, and gently boil the precipitate solution for ~1 minute.

8.13 Remove from the hot plate and allow to cool to room temperature. Carefully swirl the flask 3-4 times during cooling.

8.14 Weigh a Gooch crucible which has been fitted with a glass fiber filter paper. Record this weight to the nearest 0.0001g.

8.15 Using the vacuum flask and vacuum, filter the precipitate into the Gooch crucible.

8.16 Wash the precipitate with five ~5mL portions of DI water, allowing each portion to drain thoroughly before adding the next portion.

8.17 Dry the crucible containing precipitate for ~45 minutes in a ~250°C oven.

8.18 Cool to room temperature in a desiccator (~1 hour).

8.19 Weigh the crucible and precipitate. Record this weight to the nearest 0.0001g.

8.20 If the weight of the precipitate is greater than 1.0g, repeat steps 8.8 – 8.19 using a smaller aliquot.

9. QA/QC:

A Laboratory Control Sample (LCS) should be run with each set (12 samples or less). An acceptable LCS is a Magruder check sample with the reported mean and standard deviation for the direct available phosphorus as P_2O_5 (Magruder method code 041). An acceptable recovery for the LCS is to be within the Magruder mean ±2 Magruder standard deviations. The minimum reportable result is 0.1%.

10. Calculations:

$$\%\ \text{Avail}\ P_2O_5 = \frac{\text{Weight of precipitate x DF x 0.03207 x 100}}{\text{Sample weight (g)}}$$

Where:

DF = dilution factor = 250mL/aliquot

0.03207 = Gravimetric factor derived from:

Molecular weight of P_2O_5 = 141.90

Molecular weight of QMP = $(C_9H_7N)_3H_3PO_4 \cdot 12MoO_3$ = 2212.71

P_2O_5	=		141.90	=	0.03207
2QMP			2 x 2212.71		

11. References:

Official Methods of Analysis of AOAC International, Methods 993.31 (2.3.14) and 962.02 (2.3.03), 19th Edition, 2012.

U.S.D.A. Food Safety and Inspection Service, Chemistry Laboratory Guidebook, Method 3.009, June 1987.

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