Water-Soluble Phosphorus in Liquid Fertilizer

1. Scope:

To provide a standardized procedure for the gravimetric analysis of water-soluble (available) phosphorus in liquid fertilizer using the quinolinium molybdophosphate (QMP) method.

2. Principle:

Samples are digested with 50% nitric acid and the available phosphorus is precipitated with Quimociac reagent. The resulting precipitate is filtered, washed, dried, and weighed to calculate the amount of available phosphorus (as P_2O_5) present in the sample. Samples are prepared according to Sample Preparation, Storage, and Disposal (RA-SP-SMPL-PREP).

3. Safety:

3.1. All laboratory safety rules for chemical handling, sample preparation, and analysis shall be followed. Read the SDS for all materials before use.

3.2. Nitric acid is highly corrosive. Preparation of the Quimociac reagent and the 50% nitric acid solution shall be done in a fume hood using appropriate personal protective equipment (gloves, eye protection, etc.)

4. Definitions:

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

5. Equipment (equivalents are acceptable):

5.1. Analytical balance capable of weighing to 0.0001g
5.2. Oven capable of 250°C ± 25°C
5.3. Hot plate
5.4. Volumetric flat bottom boiling flask – 250mL
5.5. Erlenmeyer flask – 500mL
5.6. Vacuum filter flask with adapter – 2L
5.7. Gooch crucibles
5.8. Glass fiber filters – 2.4cm circles (Whatman 934-AH)
5.9. Glass fiber filters – 11cm circles (Whatman 934-AH)
5.10. Boiling chips (micro granules)
5.11. Desiccator

6. Reagents and Supplies (equivalents are acceptable):

6.1. Nitric acid, concentrated (Fisher cat# A509-P212)
6.2. Sodium molybdate dihydrate (Fisher cat# S336-3)
6.3. Citric acid (VWR cat# BDH9228)
6.4. Synthetic quinoline (Acros Organics cat# 221141000 or Sigma Aldrich cat# 241571)
6.5. Acetone (Fisher cat# A949-4)

7. Preparation of Reagents:

7.1. Prepare the 50% nitric acid by mixing 1000mL with 1000mL water.

7.2. Prepare the Quimociac reagent:

7.2.1. Dissolve 70g sodium molybdate dihydrate in 150mL water.

7.2.2. In a 1L volumetric flask, dissolve 60g citric acid in a mixture of 85mL concentrated nitric acid and 150mL water. Allow to cool.

7.2.3. Gradually add the sodium molybdate solution to the citric acid solution while stirring.

7.2.4. Dissolve 5mL synthetic quinoline in a mixture of 35mL concentrated nitric acid and 100mL water.

7.2.5. Gradually add the quinoline solution to the molybdate-citric acid solution. Mix and let stand for 24 hours.

7.2.6. Filter solution through an 11cm glass fiber filter.

7.2.7. Add 280mL acetone and fill to the mark with water.

8. Analysis

8.1. Perform the daily balance verification.

8.2. Weigh ~1g sample into a 250mL boiling flask (may need up to 2g of sample if guarantee is <1%). Record weight to nearest 0.0001g.

8.3. Add ~100mL water.

8.4. Add 10mL 50% nitric acid solution, boiling chips, and place on a hot plate in a fume hood. Gently boil for ~10 minutes. Do not let the flask boil to dryness.

8.5. Remove the flask from the hot plate, fill the flask almost to the 250mL mark with water and cool to room temperature.

8.6. Once cool, fill to the mark with water, tightly stopper, and mix. Allow particulates to settle overnight.

8.7. Pipette into a 500mL Erlenmeyer flask a suitable aliquot of the clear supernatant to form ~0.3g precipitate. If the guarantee is ≤ 5%, aliquot 50mL. If the guarantee is 5-10%, aliquot 25mL. If the guarantee is >10%, aliquot 15mL.

8.8. Add water to bring the total volume to ~100mL.

8.9. Heat on a hot plate set to 350°C for ~15 minutes. Remove from the hot plate, swirl the solution, and add 50mL of Quimociac reagent.

8.10. Swirl the solution again, return to the hot plate, and gently boil the precipitate solution for 1 minute.

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

8.12. Weigh a Gooch crucible fitted with a glass fiber filter. Record the weight to the nearest 0.0001g.

8.13. Using the vacuum flask and vacuum, filter the precipitate into the crucible.

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

8.15. Dry the crucible for 45 minutes in an oven preheated to 250°C.

8.16. Cool in a desiccator to room temperature.

8.17. Weigh the crucible and record weight to nearest 0.0001g. Subtract the weight of the crucible and filter from step 8.12 to determine the weight of the precipitate.

8.18. If the weight of the precipitate is greater than 1.0g, repeat steps 8.7 – 8.17 using a smaller aliquot of clear supernatant.

9. QA/QC:

9.1. A laboratory control sample (LCS) shall be run with each set. An acceptable LCS is a Magruder check sample with the reported mean and standard deviation for the direct available phosphate, gravimetric Quimociac (Magruder method code 041.1). An acceptable recovery is ±2 standard deviations.

9.2. The reporting limit (RL) is 0.05%.

10. Calculations:

Calculate percent available phosphoric acid (P_2O_5):

$$\% P_2O_5 = \frac{W * D * 0.03207 * 100}{S}$$

Where:

W = Weight (g) of precipitate from step 8.17
D = Dilution factor = 250mL/aliquot
S = Sample weight (g)
0.03207 = Gravimetric factor derived from
Molecular weight of P_2O_5 = 141.94
Molecular weight of QMP = 2212.71

$$\frac{P_2O_5}{2QMP} = \frac{141.94}{2 * 2212.71} = 0.03207$$

11. References:

AOAC International Official Methods of Analysis, Method 962.03 (chapter 2.3.07), 17th edition, 2000.

USDA Food Safety and Inspection Service, Chemistry Laboratory Guidebook, Method 3.009, June 1987.

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