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#### SCHEDULE 2

# METHODS OF ANALYSIS

# PART I

# 26i.

## DETERMINATION OF MANGANESE IN FERTILISER EXTRACTS BY TITRATION

### **1 SCOPE**

1. This method describes a procedure for determining manganese in fertiliser extracts.

# **2 FIELD OF APPLICATION**

**2.** This procedure is applicable to extracts from samples of fertilisers obtained by Methods 26a and 26b for which a declaration of manganese is required.

# **3 PRINCIPLE**

**3.** If chloride ions are present in the extract, they are driven off by boiling with sulfuric acid. The manganese is oxidized by sodium bismuthate in a nitric acid medium. The permanganate formed is reduced by an excess of ferrous sulfate. This excess is titrated with a potassium permanganate solution.

# **4 REAGENTS**

4

**4.1.** Concentrated sulfuric acid ( $H_2SO_4$ ,  $\rho = 1.84$  g/ml).

4.2. Sulfuric acid, about 9 M

Carefully mix 1 volume of concentrated sulfuric acid (4.1) with 1 volume of water.

4.3. Nitric acid, 6 M

Mix 3 volumes of nitric acid (HNO<sub>3</sub>,  $\rho = 1.40$  g/ml) with 4 volumes of water.

**4.4.** Nitric acid, 0.3 M

Mix 1 volume of 6 M nitric acid with 19 volumes of water.

- **4.5.** Sodium bismuthate (NaBiO<sub>3</sub>) (85 %).
- 4.6. Kieselguhr.
- **4.7.** Orthophosphoric acid, 15 M ( $H_3PO_4$ ,  $\rho = 1.71$  g/ml).
- **4.8.** Ferrous sulfate solution, 0.15 M

Dissolve 41.6 g of ferrous sulfate heptahydrate (FeSO<sub>4</sub>. 7 H<sub>2</sub>O) in a 1-litre volumetric flask.

Add 25 ml of concentrated sulfuric acid (4.1) and 25 ml phosphoric acid (4.7). Make up to 1000 ml. Mix.

4.9. Potassium permanganate solution, 0.02 M

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Weigh out 3.160 g of potassium permanganate ( $KMnO_4$ ) to within 0.1 mg. Dissolve and make up 1000 ml with water.

4.10. Silver nitrate solution, 0.1 M

Dissolve 1.7 g of silver nitrate (AgNO<sub>3</sub>) in water and make up to 100 ml.

# **5 APPARATUS**

5

- 5.1. Filter crucible P<sub>1</sub>6/ISO 4793, porosity 4, capacity 50 ml, mounted on a 500 ml filtration flask.
- 5.2. Magnetic stirrer.

## **6 PREPARATION OF THE SOLUTION TO BE ANALYSED**

6

**6.1.** Manganese extract solution

See Methods 26a and 26b. If it is not known whether chloride ions are present, perform a test on the solution with one drop of the silver nitrate solution (4.10).

**6.2.** In the absence of chloride ions, place an aliquot portion of the extract containing 10 to 20 mg of manganese in a tall form 400 ml beaker. Bring to a volume of about 25 ml either by evaporation or by adding water. Add 2 ml of concentrated sulfuric acid (4.1).

**6.3.** If chloride ions are present, it is necessary to remove them as follows:

Place an aliquot portion of the extract containing 10 to 20 mg of manganese in a tall form 400 ml beaker. Add 5 ml of 9 M sulfuric acid (4.2). Under a fume hood, bring to boiling on a hotplate and allow to boil until copious white fumes are released. Continue until the volume is reduced to about 2 ml (thin film of syrupy liquid at the bottom of the beaker). Allow to cool to ambient temperature.

Carefully add 25 ml of water and once again test for the presence of chlorides with one drop of the silver nitrate solution (4.10). If chlorides still remain, repeat the operation after adding 5 ml of 9 M sulfuric acid (4.2).

# **7 PROCEDURE**

7. Add 25 ml of 6 M nitric acid (4.3) and 2.5 g of sodium bismuthate (4.5) to the 400 ml beaker containing the test solution. Stir vigorously for three minutes on the magnetic stirrer (5.2).

Add 50 ml of 0.3 M nitric acid (4.4) and stir again. Filter in vacuo through a crucible (5.1), the bottom of which is covered with Keiselguhr (4.6). Wash the crucible several times with the 0.3 M nitric acid (4.4) until a colourless filtrate is obtained.

Transfer the filtrate and the washing solution into a 500 ml beaker. Mix and add 25 ml of 0.15 M ferrous sulfate solution (4.8). If the filtrate turns yellow after the addition of ferrous sulfate, add 3 ml of 15 M orthophosphoric acid (4.7).

Using a burette, titrate the excess ferrous sulfate with 0.02 M potassium permanganate solution (4.9) until the mixture turns pink, the colour remaining stable for one minute. Perform a blank test under the same conditions, omitting only the test sample.

(Note) The oxidized solution must not come into contact with rubber.

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# **8 EXPRESSION OF RESULTS**

**8.** 1 ml of 0.02 M potassium permanganate solution corresponds to 1.099 mg of manganese (Mn). The percentage of manganese in the fertiliser is given by:

 $Mn(\%)=(xbxs)\times 0.1099xVa\times M$ 

where:

x<sub>b</sub> is the volume in ml of the permanganate used for the blank;

x<sub>s</sub> is the volume in ml of the permanganate used for the test sample;

V is the volume in ml of the extract solution in accordance with Methods 26a and 26b;

a is the volume in ml of the aliquot portion taken from the extract (6.2) or (6.3);

M is the mass in g of the test sample.