SCHEDULE 2

METHODS OF ANALYSIS

PART I

20.

MANGANIMETRIC DETERMINATION OF EXTRACTED CALCIUM FOLLOWING PRECIPITATION IN THE FORM OF OXALATE

1 SCOPE

1. This method is for the determination of calcium in fertiliser extracts.

2 FIELD OF APPLICATION

2. This method applies to all fertilisers for which a declaration of the total and/or water-soluble calcium is required.

3 PRINCIPLE

3. Precipitation of the calcium contained in an aliquot portion of the extraction solution in the form of an oxalate, which is determined by titration using potassium permanganate.

4 REAGENTS

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4.1 Diluted hydrochloric acid: One volume of hydrochloric acid (ρ = 1.18 g/ml) plus one volume of water.

4.2 1:10 dilute sulfuric acid:

One volume of sulfuric acid (ρ = 1.84 g/ml) in ten volumes of water.

4.3 1:1 dilute ammonia solution: One volume of ammonia (ρ = 0.88 g/ml) and one volume of water.

4.4 Saturated solution of ammonium oxalate [$(NH_4)_2C_2O_4.H_2O$] at ambient temperature (approximately 40 g per litre).

4.5 Citric acid solution, 30% (m/v).

4.6 Ammonium chloride solution, 5% (m/v).

4.7 Solution of bromothymol blue in 95% ethanol, 0.1% (m/v).

4.8 Solution of bromocresol green in 95% ethanol, 0.04% (m/v).

4.9 Standard solution of potassium permanganate, 0.02 M.

5 APPARATUS

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5.1 Filter crucible with 5 to 20μ porosity sintered glass.

5.2 Hot water bath.

6 PREPARATION OF THE ALIQUOT PORTION TO BE ANALYSED

6. Using a pipette, take an aliquot portion of the extraction solution obtained by method 15 or 17, containing between 15 and 50 mg of Ca (= 21 to 70 mg of CaO). Let the volume of this aliquot be v_2. Pour into a 400 ml beaker. If necessary, neutralise (change of indicator (4.7) from green to blue) with a few drops of the ammonia solution (4.3).

Add 1 ml of the citric acid solution (4.5) and 5 ml of ammonium chloride solution (4.6).

PRECIPITATION OF THE CALCIUM OXALATE

7. Add approximately 100 ml of water. Bring to the boil, add 8 to 10 drops of indicator solution (4.8) and, slowly, 50 ml of the hot ammonium oxalate solution (4.4), stirring constantly. If a precipitate forms, dissolve by adding a few drops of hydrochloric acid (4.1). Neutralise very slowly with ammonia solution (4.3) while stirring continuously to a pH of 4.4 to 4.6 (change of indicator (4.8) from green to blue). Place the beaker in a boiling hot water bath (5.2) for approximately 30 minutes.

Remove the beaker from the bath, leave standing for an hour and filter through the crucible (5.1).

8 TITRATION OF THE OXALATE PRECIPITATE

8. Wash the beaker and crucible until the excess ammonium oxalate has been completely removed (this can be checked by the absence of chloride in the washing water). Place the crucible in the 400 ml beaker and dissolve the precipitate with 50 ml of hot sulfuric acid (4.2). Add water to the beaker in order to obtain a volume of approximately 100 ml. Bring to a temperature of 70 to 80° C and titrate drop by drop with the permanganate solution (4.9) until the pink colour lasts for a minute. Let this volume be n.

9 EXPRESSION OF RESULTS

9. The calcium (Ca) content of the fertiliser is as follows:

$Ca(\%)=n\times0.2004\times t0.02\times v1v2\times m$

Where:

n = the volume of 0.2 M permanganate used, in millilitres,

m = the mass of the test sample in grams,

v_2 = the aliquot volume in millilitres,

v_1 = the volume of the extraction solution in millilitres,

t = the molarity of the permanganate solution in moles per litre.

$CaO(\%) = Ca(\%) \times 1.400$.