SCHEDULE 2

METHODS OF ANALYSIS

PART I

22.

DETERMINATION OF MAGNESIUM BY COMPLEXOMETRY

1 SCOPE

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

2 FIELD OF APPLICATION

2. This method applies to the determination of total magnesium and/or water-soluble magnesium in the following fertilisers:

— Straight nitrogenous fertilisers (calcium magnesium nitrate, magnesium sulphonitrate, nitrogenous fertiliser with magnesium) and straight potassic fertilisers (enriched kainite, potassium chloride containing magnesium, potassium sulfate containing magnesium salt), kieserite, magnesium sulfate, magnesium chloride solution, and kieserite with potassium sulfate.

3 PRINCIPLE

3. The magnesium is extracted by methods 15 and/or 17. First titration: with EDTA of Ca and Mg in the presence of Eriochrome black T. Second titration: with EDTA of Ca in the presence of calcein or of calcon carbonic acid. Determination of magnesium by difference.

4 REAGENTS

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4.1 Standard 0.05 M solution of magnesium:

(4.1.1) Dissolve 1.232 g of magnesium sulfate (MgSO4.7H2O) in the 0.5 M hydrochloric acid solution (4.11) and make up to 100 ml with the same acid.

or:

(4.1.2) Weigh out 2.016 g of magnesium oxide, previously calcined to remove all traces of carbonation. Place it in a beaker with 100 ml of water.

Stir in approximately 120 ml of approximately 1 M hydrochloric acid (4.12).

After dissolution, transfer quantitatively into a graduated 1 litre flask. Make up to volume and mix.

1 ml of these solutions should contain 1.216 mg of Mg (= 2.016 mg of MgO).

The laboratory is responsible for testing the strength of this standard solution.

4.2 0.05 M solution of EDTA.

Weigh out 18.61 g of the dihydrated disodium salt of ethylenediaminetetraacetic ($C_{10}H_{14}.Na_2O_82H_2O$), place it in a 1,000 ml beaker and dissolve in 600 to 800 ml of water. Transfer the solution quantitatively into a graduated 1 litre flask. Make up the volume and mix. Check this

solution with the standard solution (4.1) by taking a sample of 20 ml of the latter and by titration according to the analytical procedure described at 7.2.

4.3 0.05 molar standard solution of calcium.

Weigh out 5.004 g of dry calcium carbonate. Place it in a beaker with 100 ml of water. Progressively stir in 120 ml of approximately 1 M hydrochloric acid (4.12).

Bring to the boil in order to drive off the carbon dioxide, cool, transfer quantitatively into a graduated one-litre flask, make up the volume with water and mix. Check this solution against the EDTA solution (4.2) following analytical procedure (8.3). 1 ml of this solution should contain 2.004 mg of Ca (=2.804 mg of CaO) and should correspond to 1 ml of the 0.05 M EDTA solution (4.2).

4.4 Calcein indicator.

Carefully mix in a mortar one gram of calcein with 100 g of sodium chloride. Use 10 mg of this mixture. This indicator changes colour from green to orange. Titration must be carried out until an orange colour free from green tinges is obtained.

4.5 Calcon carbonic acid indicator.

Dissolve 400 mg of calcon carbonic acid in 100 ml of methanol. This solution may only be kept for approximately four weeks. Use three drops of this solution. The indicator changes colour from red to blue. Titration must be carried out until a blue colour free from red tinges is obtained.

4.6 Eriochrome black — T indicator.

Dissolve 300 mg of Eriochrome black-T in a mixture of 25 ml of propan-1-ol and 15 ml of triethanolamine. This solution may only be kept for approximately four weeks. Use three drops of this solution. This indicator changes colour from red to blue and titration must be carried out until a blue colour free from red tinges is obtained. It changes colour only when magnesium is present. If necessary add one millilitre of the standard solution (4.1).

When both calcium and magnesium are present the EDTA first forms a complex with the calcium and then the magnesium. In that case the two elements are determined concurrently.

4.7 Potassium cyanide solution.

Aqueous solution of KCN at 2%. (CAUTION: potassium cyanide is extremely poisonous, take suitable precautions and do not pipette by mouth. See also 10.7).

4.8 Solution of potassium hydroxide and potassium cyanide.

Dissolve 280 g of KOH and 66 g of KCN in water, make up the volume to one litre and mix.

4.9 Buffer solution, pH 10.5.

In a 500 ml graduated flask, dissolve 33 g of ammonium chloride in 200 ml of water, add 250 ml of ammonia ($\rho = 0.91$) make up the volume with water and mix. Check the pH of the solution regularly.

4.10 Diluted hydrochloric acid:

One volume of hydrochloric acid ($\rho = 1.18$ g/ml) plus one volume of water.

4.11 Hydrochloric acid solution approximately 0.5 M.

4.12 Hydrochloric acid solution approximately 1 M.

4.13 Sodium hydroxide solution 5 M.

5 APPARATUS

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5.1 Magnetic or mechanical stirrer.

5.2 pH meter.

6 CONTROL TEST

6. Carry out a determination on aliquot portions of solutions (4.1 and 4.3) such that the Ca/Mg ratio is approximately equal to that of the solutions to be analysed. To this end take (a) of standard solution (4.3) and (b – a) of standard solution (4.1). (a) and (b) are the volumes of EDTA solution in millilitres used in the two titrations performed on the solution to be analysed. This procedure is correct only if the solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make corrections.

7 PREPARATION OF THE SOLUTION TO BE ANALYSED

7. See methods 15 and 17.

8 DETERMINATION

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8.1 Aliquot portions to be taken.

Take aliquot portions of the extracts which contain between 9 and 18 mg of magnesium (= 15 to 30 mg of MgO).

8.2 Titration in the presence of Eriochrome black-T.

Pipette an aliquot portion (8.1) of the solution to be analysed into a 400 ml beaker. Neutralise the excess acid with the 5 M sodium hydroxide solution (4.12) and check the pH. Dilute with water to approximately 100 ml. Add 5 ml of the buffer solution (4.9). The pH measured by meter must be 10.5 +0.1. Add 2 ml of the potassium cyanide solution (4.7) and three drops of the Eriochrome black-T indicator (4.6). Titrate with the EDTA solution (4.2). Stirring gently with the stirrer (5.1) (see 10.2, 10.3 and 10.4). Let ‘b’ be the volume in millilitres of 0.05 molar EDTA solution used.

8.3 Titration in the presence of calcein or of calcon carbonic acid.

Pipette an aliquot portion of the solution to be analysed equal to that taken for the above titration and place it in a 400 ml beaker. Neutralise the excess acid with the 5 M sodium hydroxide solution (4.13) using the pH meter. Dilute with water to about 100 ml. Add 10 ml of KOH/KCN solution (4.8) and three drops of the indicator (4.4 or 4.5). Stirring gently with the stirrer (5.1) titrate with the EDTA solution (4.2) (see 10.2, 10.3 and 10.4). Let ‘a’ be the volume in millilitres of 0.05 M EDTA solution.

9 EXPRESSION OF RESULTS

9. For the EEC fertilisers to which the method is applicable (5 g of fertiliser in 500 ml of extract), the percentage content of the fertiliser is:

$$MgO(\%)inthefertiliser=(b\text{-}a)\times TM$$

$$Mg(\%)inthefertiliser=(b\text{-}a)\times T1M$$

Where:

a = the volume in millilitres of 0.05 M EDTA solution used for the titration in the presence of calcein or calcon carbonic acid.

b = the volume in millilitres of 0.05 M EDTA solution used for the titration in the presence of Eriochrome black-T.

M = the mass of the sample present in the aliquot taken (in grams).

T = 0.2016 × molarity of the EDTA solution/0.05 (see 4.2).

T1 = 0.1216 × molarity of the EDTA solution/0.05 (see 4.2).

10 REMARKS

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10.1. The stoichiometric EDTA-metal ratio in the complexometric analyses is always 1:1 whatever the valency of the metal and in spite of the fact that EDTA is quadrivalent. The EDTA titration solution and the standard solutions will therefore be molar and not normal.

10.2. Complexometric indicators are often sensitive to air. The solution may lose colour during titration. In this case, one or two drops of indicator must be added. This is true particularly in the case of Eriochrome black-T and calcon carbonic acid.

10.3. The metal-indicator complexes are often relatively stable and it may take some time for the colour to change. The last drops of EDTA must therefore be added slowly and a drop of 0.05 molar solution of magnesium (4.1) or calcium (4.3) added to ensure that the colour change has not already taken place. This is particularly true in the case of the Eriochrome-magnesium complex.

10.4. The colour change of the indicator must not be observed vertically, but horizontally across the solution and the beaker must be placed against a white background in a well-lit position. The colour change of the indicator may also be observed easily by placing the beaker on frosted glass lit moderately from below (25 watt lamp).

10.5. This analysis requires a certain amount of experience. The task will involve, among other things, observing the colour changes of standard solutions 4.1 and 4.3. It is recommended that the determinations be carried out by the same laboratory chemist.

10.6. If an EDTA solution of guaranteed strength is used (Titrisol, Normex, for example) this may simplify the control of the equivalence of standard solutions 4.1, 4.2 and 4.3.

10.7. The solutions containing potassium cyanide must not be poured down the sink until the cyanide has been converted into a harmless compound, for example, by oxidation with sodium hypochlorite after having been made alkaline.