II

(Acts whose publication is not obligatory)

COMMISSION

COMMISSION DIRECTIVE

of 14 December 1978

amending Directive 77/535/EEC on the approximation of the laws of the Member States relating to methods of sampling and analysis for fertilizers

(79/138/EEC)

THE COMMISSION OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Economic Community,

Having regard to Council Directive 76/116/EEC of 18 December 1975 on the approximation of the laws of the Member States relating to fertilizers (1), and in particular Article 9 (2) thereof,

Whereas Commission Directive 77/535/EEC (2) provides for official controls for EEC fertilizers for the purpose of checking compliance with the requirements imposed by the Community provisions concerning the quality and composition of fertilizers; whereas that Directive should be amended by the addition of three new methods of analysis;

Whereas the measures provided for in this Directive are in accordance with the opinion of the Committee on the Adaptation to Technical Progress of the Directives for the Removal of Technical Barriers to Trade in Fertilizers,

HAS ADOPTED THIS DIRECTIVE:

Article 1

Annex II to Directive 77/535/EEC is amended by the insertion after method 5.1 of methods 5.2, 5.3 and 5.4 as annexed to this Directive.

Article 2

1. The Member States shall, not later than 1 April 1979, bring into force the laws, regulations or administrative provisions necessary to comply with this Directive. They shall forthwith notify the Commission thereof.

2. Once notification of this Directive has been effected, the Member States shall, in sufficient time to enable it to submit its comments, inform the Commission of all draft laws, regulations or administrative provisions which they intend to adopt in the field covered by this Directive.

Article 3

This Directive is addressed to the Member States.

Done at Brussels, 14 December 1978.

For the Commission

Étienne DAVIGNON

Member of the Commission

(1) OJ No L 24, 30. 1. 1976, p. 21.
(2) OJ No L 213, 22. 8. 1977, p. 1.

ANNEX

Method 5.2

DETERMINATION OF TOTAL MAGNESIUM

1. SCOPE

This document defines the procedure for the determination of total magnesium.

2. FIELD OF APPLICATION

Exclusively to the fertilizer magnesium ammonium nitrate in respect of which Annex IA to Council Directive 76/116/EEC of 18 December 1975 provides for the indication of total magnesium.

3. PRINCIPLE

Solution in boiling acid of the magnesium contained in a test sample.

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

Distilled or demineralized water.

4.1. Standard 0·05 molar solution of magnesium.

Weigh out 2·016 g of magnesium oxide for analysis, previously calcined at 600 °C for two hours. Place it in a beaker with 100 ml of water. Stir in 120 ml of approximately 1N hydrochloric acid. After dissolution, transfer quantitatively into a graduated one-litre flask, make up the volume with water and mix.

Check the strength of the solution gravimetrically as ammonium-magnesium phosphate.

1 ml of the solution should contain 1·216 mg of Mg (= 2·016 mg MgO).

4.2. 0·05 molar solution of EDTA

Weigh out 18·61 g of the dihydrated disodium salt of ethylenediaminetetraacetic acid ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$), place it in a litre beaker and dissolve in 600 to 800 ml of water. Transfer the solution quantitatively into a graduated one-litre flask. Make up the volume and mix. Check this solution with solution (4.1) by taking a sample of 20 ml of the latter and by titration according to analytical procedure 7.4.1.

1 ml of the EDTA solution should correspond to 1·216 mg of Mg or 2·016 mg of MgO and to 2·004 mg of Ca or 2·804 mg of CaO (see remarks 9.1 and 9.6).

4.3. 0·05 molar standard solution of calcium

Weigh out 5·004 g of dry pure calcium carbonate. Place it in a beaker with 100 ml of water. Progressively stir in 120 ml of approximately 1N hydrochloric acid.

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 7.4.2. 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 molar EDTA solution.

4.4. Calcein indicator

Carefully mix in a mortar 1 g of calcein with 100 g of sodium chloride. Use 10 mg of this mixture. The indicator changes from green to orange. Titration must be carried out until an orange colour is obtained which is free from green tinges.

4.5. Calcon carbonic acid indicator

Dissolve 400 mg of calcon carbonic acid in 100 ml of methanol. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue colour is obtained which is free from red tinges.

4.6. Eriochrome black-T indicator

Dissolve 300 mg eriochrome black-T in a mixture of 25 ml propanol-1 and 15 ml triethanolamine. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue colour is obtained which is free from red tinges. It changes colour only when magnesium is present. If necessary add 0·1 ml of standard solution 4.1. When both calcium and magnesium are present the EDTA first forms a complex with the calcium and then with the magnesium. In that case these two elements are determined concurrently.

4.7. Potassium cyanide

Aqueous solution of KCN at 2 %.

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. pH 10·5 buffer solution

Dissolve 33 g of ammonium chloride in 200 ml of water, add 250 ml of ammonia (d = 0·91) make up the volume to 500 ml with water and mix. Test the pH of this solution regularly.

4.10. Diluted hydrochloric acid 1 : 1

One part of hydrochloric acid (1·18 density) and one part of water.

4.11. Sodium hydroxide solution 5N

5. APPARATUS

5.1. Magnetic or mechanical stirrer.

5.2. pH meter.

5.3. Graduated 500 ml and 1 000 ml flasks.

5.4. 300 ml beakers.

6. PREPARATION OF THE SAMPLE

See method 1.

7. PROCEDURE

7.1. **Sample**

Place 5 g of the prepared sample weighed out to an accuracy of 1 mg in a graduated 500 ml flask.

7.2. **Solution**

Add about 200 ml water and 20 ml hydrochloric acid (4.10), boil for half an hour. Cool, make up the volume with water, mix and filter.

7.3. **Control test**

Carry out a determination on aliquot parts of solutions (4.1) and (4.3) such that the Ca/Mg ratio is equal to that expected from the sample.

To this end take (*a*) ml of standard solution (4.3) and (*b*—*a*) ml standard solution (4.1).

(*a*) and (*b*) are the numbers of ml EDTA solution used in the two titrations when analyzing the sample. This procedure is correct only if the standard solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make the appropriate corrections.

7.4. **Determination**

7.4.1. *Titration in the presence of eriochrome black-T*

Pipette 50 ml (1) of the solution to be analyzed into a 300 ml beaker. Neutralize the surplus acid with the 5N sodium hydroxide solution (4.11) using the pH meter. Dilute with water to 100 ml. Add 5 ml of the buffer solution (4.9). The pH measured by the 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 9.2, 9.3 and 9.4). Let 'b' be the number of ml of 0·05 molar EDTA solution.

7.4.2. *Titration in the presence of calcein or of calcon carbonic acid*

Pipette an aliquot part of the solution to be analyzed equal to that taken for the above titration and place it in a 300 ml beaker. Neutralize the surplus acid with the 5N sodium hydroxide solution (4.11) using the pH meter. Dilute with water to about 100 ml. Add 10 ml of the KOH/KCN solution (4.8) and the indicator (4.4) or (4.5). Stir gently and titrate with the EDTA solution. (See notes 9.2, 9.3 and 9.4.) Let 'a' be the number of ml of 0·05 molar EDTA solution.

8. EXPRESSION OF THE RESULT

The result is expressed as a percentage of MgO or Mg

8.1. % MgO in the fertilizer $= \frac{(b - a) \times T}{M}$

or

% Mg in the fertilizer $= \frac{(b - a) \times T'}{M}$

If the strength of EDTA solution is exactly 0·05 M, T = 0·2016 and T' Mg = 0·1216.

M = the weight of the sample, expressed in grams, present in the aliquot taken as a sample.

9. REMARKS

See method 5.1.

(1) At the time of titration 25 ml EDTA should not be greatly exceeded as otherwise the volume of the aliquot part must be reduced. However, it may also be increased.