

COMMISSION DIRECTIVE

of 1 August 1989

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

(89/519/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⁾, as last amended by Council Directive 89/284/EEC ⁽²⁾, and in particular Article 9 (2) thereof,

Whereas Directive 89/284/EEC supplements and amends Directive 76/116/EEC in respect of the calcium, magnesium, sodium and sulphur content of fertilizers;

Whereas Commission Directive 77/535/EEC ⁽³⁾, as last amended by Directive 87/566/EEC ⁽⁴⁾, 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 supplemented so that fertilizers to which Council Directive 89/284/EEC relates can also be checked; whereas it is necessary to replace methods 5.1, 5.2, 5.3 and 5.4; whereas general provisions relating to methods for analysing fertilizers applicable to all methods should be added to the general observations of Annex II;

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,

HAD ADOPTED THIS DIRECTIVE:

Article 1

1. General provisions relating to methods for analysing fertilizers of Annex I to this Directive are added to the general observations of Annex II to Directive 77/535/EEC.

2. The methods 8.1 to 8.10 in Annex II to this Directive are added to Annex II to Directive 77/535/EEC.

3. Methods 5.1 to 5.4 set out in Annex II to Directive 77/535/EEC are deleted.

Article 2

1. Member States shall take measures necessary to comply with this Directive by 1 September 1990 and shall forthwith inform the Commission thereof.

The provisions adopted pursuant to the first indent shall make express reference to this Directive.

2. Member States shall communicate to the Commission the texts of the provisions of national law which they adopt in the field covered by this Directive.

Article 3

This Directive is addressed to the Member States.

Done at Brussels, 1 August 1989

For the Commission
Martin BANGEMANN
Vice-President

⁽¹⁾ OJ No L 24, 30. 1. 1976, p. 21.

⁽²⁾ OJ No L 111, 22. 4. 1989, p. 34.

⁽³⁾ OJ No L 213, 22. 8. 1977, p. 1.

⁽⁴⁾ OJ No L 342, 4. 12. 1987, p. 32.

ANNEX I

GENERAL PROVISIONS RELATING TO METHODS OF ANALYSING FERTILIZERS**1. Reagents**

Unless otherwise specified in the method of analysing, all of the reagents must be analysis-pure (a. p.). Where trace elements are to be analysed the purity of the reagents must be checked by means of a blank test. Depending upon the result obtained, it might be necessary to conduct a further purification.

2. Water

The dissolution, dilution, rinsing or washing operations mentioned in the methods of analysis without stating precisely what the nature of the solvent or diluent is, imply the use of water. Normally, the water will have to be demineralized or distilled. In these specific instances, as mentioned in the method of analysis, that water will have to be subjected to specific purification processes.

3. Laboratory equipment

In view of the equipment normally used in inspection laboratories, the apparatus described in the methods of analysis is restricted to special instruments and apparatus or to such demanded by any specific requirements. This equipment must be perfectly clean, above all where small quantities are to be determined. The laboratory will have to ensure the accuracy of any graduated glassware used by referring to the standards.

ANNEX II

Methods 8

SECONDARY NUTRIENTS

Method 8.1

EXTRACTION OF TOTAL CALCIUM, TOTAL MAGNESIUM, TOTAL SODIUM AND TOTAL SULPHUR
IN THE FORM OF SULPHATES

1. SCOPE

This document defines the procedure for extracting total calcium, total magnesium and total sodium, and for extracting the total sulphur present in the form of sulphates, so that the same extract may be used for the determination of each nutrient required.

2. FIELD OF APPLICATION

This method applies to EEC fertilizers, for which a declaration of the total calcium, total magnesium, total sodium, and total sulphur in the form of sulphates is provided for in Council Directive 89/284/EEC ⁽¹⁾.

3. PRINCIPLE

Solubilization by boiling in dilute hydrochloric acid.

4. REAGENTS

4.1 Diluted hydrochloric acid:

One volume of hydrochloric acid ($d = 1,18$) plus one volume of water.

5. APPARATUS

Electric hot plate with adjustable temperature.

6. PREPARATION OF THE SAMPLE

See method 1 in Commission Directive 77/535/EEC.

7. PROCEDURE

7.1 Test sample

Calcium, magnesium, sodium and sulphur in the form of sulphates are extracted from a test sample of five grams weighed to within one milligram.

However, when the fertilizer contains more than 15 % of sulphur (S) i. e. 37,5 % SO_3 , and more than 18,8 % of calcium (Ca) i. e. 26,3 % CaO, the extraction of calcium and sulphur is carried out on a test sample of one gram, weighed to within one milligram. Place the test sample in a 600 millilitre beaker.

7.2 Preparation of the solution

Add approximately 400 millilitres of water and, taking care when the sample contains a significant quantity of carbonates, 50 millilitres of dilute hydrochloric acid (4.1) a small amount at a time. Bring to the boil and maintain for 30 minutes. Allow to cool, stirring occasionally. Decant

⁽¹⁾ OJ No L 111, 22. 4. 1989, p. 34.

quantitatively into a 500 millilitre graduated flask. Make up to volume with water, and mix. Pass through a dry filter into a dry container, discarding the initial portion. The extract must be completely transparent. Stopper if the filtrate is not used immediately.

Method 8.2

EXTRACTION OF TOTAL SULPHUR PRESENT IN VARIOUS FORMS

1. SCOPE

This document defines the procedure for extracting the total sulphur contained in fertilizers in elemental form and/or in other chemical combinations.

2. FIELD OF APPLICATION

This method applies to EEC fertilizers for which a declaration of the total sulphur present in various forms (elemental, thiosulphate, sulphite, sulphate) is provided for in the Council Directive 89/284/EEC.

3. PRINCIPLE

Elemental sulphur is converted in an alkaline medium into polysulphides and thiosulphate; these, together with any sulphites which may be present, are then oxidized with hydrogen peroxide. The various forms of sulphur are thus converted into sulphate which is determined by precipitation of barium sulphate (method 8.9).

4. REAGENTS

4.1 Diluted hydrochloric acid:

One volume of hydrochloric acid ($d = 1,18$) plus one volume of water.

4.2 Sodium hydroxide solution, NaOH, 30 % minimum ($d = 1,33$).

4.3 Hydrogen peroxide solution, 30 % w/w.

4.4 Aqueous solution of barium chloride $BaCl_2 \cdot 2H_2O$, 122 gram per litre.

5. APPARATUS

Electric hot plate with adjustable temperature.

6. PREPARATION OF THE SAMPLE

See method 1.

7. PROCEDURE

7.1 Test sample

Weigh out to within one milligram a quantity of fertilizer containing between 80 and 350 milligrams of sulphur (S) or 200 and 875 milligrams of SO_3 .

As a rule (where $S < 15\%$), weigh out 2,5 grams. Place the test sample in a 400 millilitre beaker.

7.2 Oxidation.

Add 20 millilitres of sodium hydroxide solution (4.2) and 20 millilitres of water. Cover with a watch glass. Boil for five minutes on the hot plate (5.1). Remove from the hot plate. Using a jet of hot water, collect the sulphur sticking to the sides of the beaker and boil for 20 minutes. Leave to cool.

Add 2 millilitres increments of hydrogen peroxide (4.3) until no reaction is observed. Six to eight of hydrogen peroxide will be necessary. Allow oxidation to continue for one hour, then bring to the boil for half an hour. Leave to cool.

7.3 Preparation of the solution to be analysed.

Add approximately 50 millilitres of water and 50 millilitres of the hydrochloric acid solution (4.1).

— *If the level of sulphur (S) is less than 5%:*

filter into a 600 millilitre beaker. Wash the residue on the filter several times with cold water. After washing, check for the absence of sulphate in the last drops of the filtrate using a barium chloride solution (4.4). The filtrate must be perfectly clear. Sulphate is determined on the whole of the filtrate in accordance with method 8.9.

— *If the level of sulphur (S) is at above 5%:*

transfer quantitatively into a 250 millilitre volumetric flask, make up to volume with water and mix. Filter through a dry filter into a dry container; the filtrate must be completely clear. Stopper if the solution is not to be used immediately. Determine sulphates on an aliquot of this solution by precipitation in the form of barium sulphate (method 8.9).

Method 8.3

EXTRACTION OF WATER-SOLUBLE CALCIUM, MAGNESIUM, SODIUM AND SULPHUR (IN THE FORM OF SULPHATES)

1. SCOPE

This document defines the procedure for extracting water-soluble calcium, magnesium, sodium and sulphur (in the form of sulphates), so that the same extract can be used to determine each nutrient required.

2. FIELD OF APPLICATION

This method applies solely to fertilizers for which a declaration of the water soluble calcium, magnesium, sodium and sulphur (in the form of the sulphates) is provided for in Council Directive 89/284/EEC.

3. PRINCIPLE

The nutrients are solubilized in boiling water.

4. REAGENTS

Distilled or demineralized water of equivalent quality.

5. APPARATUS

Electric hot plate with adjustable temperature.

6. PREPARATION OF THE SAMPLE

See method 1.

7. PROCEDURE

7.1 Test sample.

(a) Where fertilizers contain no sulphur or where they contain, at the same time, no more than 3% of the sulphur (S) i. e. 7,5% SO₃ and no more than 4% of calcium (Ca) i. e. 5,6% CaO, weigh out five grams of fertilizer to within one milligram.

- (b) Where fertilizers contain more than 3% of sulphur (S) and more than 4% of calcium (Ca), weigh out one gram of fertilizer to within one milligram.

Place the test sample in a 600 millilitre beaker.

7.2 PREPARATION OF THE SOLUTION.

Add approximately 400 millilitres of water and boil for 30 minutes. Allow to cool, stirring occasionally, and decant quantitatively into a 500 millilitre graduated flask. Make up to volume with water and mix.

Filter through a dry filter into a dry container. Discard the initial portions of the filtrate. The filtrate must be completely transparent.

Stopper if the solution is not to be used immediately.

Method 8.4

EXTRACTION OF WATER-SOLUBLE SULPHUR WHERE THE SULPHUR IS IN VARIOUS FORMS

1. SCOPE

This document defines the procedure for extracting the water-soluble sulphur contained in fertilizers in various forms.

2. FIELD OF APPLICATION

This method applies to fertilizers for which a declaration of the water-soluble sulphur trioxide is provided for in Directive 89/284/EEC.

3. PRINCIPLE

The sulphur is dissolved in cold water and converted into sulphate by oxidation with hydrogen peroxide in an alkaline medium.

4. REAGENTS

4.1 Diluted hydrochloric acid:

One volume of hydrochloric acid ($d = 1,18$) plus one volume of water.

4.2 Sodium hydroxide solution containing at least 30% NaOH ($d = 1,33$).

4.3 Hydrogen peroxide solution, 30% w/w.

5. APPARATUS

5.1 500 millilitre graduated Stohmann flask.

5.2 Rotary shaker, 30 to 40 turns per minute.

5.3 Electric hot plate with adjustable temperature.

6. PREPARATION OF THE SAMPLE

See method 1.

7. PROCEDURE

7.1 Test sample

- (a) Where fertilizers contain a maximum of 3% of sulphur (S) i. e. 7,5% SO_3 , together with a maximum of 4% of calcium (Ca) i. e. 5,6% CaO , weigh out 5 grams of fertilizer to within one milligram.

(b) Where fertilizers contain more than 3 % of sulphur (S) together with more than 4 % of calcium (Ca), weigh out one gram of fertilizer to within one milligram.

Place the test sample in a 500 millilitre flask (5.1).

7.2 Preparation of the solution

Add approximately 400 millilitres of water. Stopper. Shake (5.2) for 30 minutes. Make up to volume with water and mix. Pass through a dry filter into a dry container. Stopper if the solution is not to be used immediately.

7.3 Oxidation of the aliquot portion to be analysed

Take an aliquot portion of the extraction solution not exceeding 50 millilitre and, if possible, containing between 20 and 100 milligrams of sulphur (S).

Make up the volume to 50 millilitres with water, if necessary. Add three millilitres of sodium hydroxide solution (4.2) and two millilitres of hydrogen peroxide solution (4.3). Cover with a watch glass and boil gently for one hour on the hot plate (5.3). Keep adding one millilitre increments of hydrogen peroxide solution for as long as the reaction continues (maximum quantity five millilitres).

Then leave to cool. Remove the watch glass and wash the underside into the beaker. Add approximately 20 millilitres of dilute hydrochloric acid (4.1). Make up to approximately 300 millilitres with water.

Determine the content of sulphates on the whole of the oxidized solution in accordance with method 8.9.

Method 8.5

EXTRACTION AND DETERMINATION OF ELEMENTAL SULPHUR

WARNING

This method of analysis involves the use of carbon disulphide (CS₂). Special safety measures must therefore be taken, in particular with regard to:

- the storage of CS₂,
- protective equipment for staff,
- occupational hygiene,
- prevention of fires and explosions,
- disposal of the reagent.

This method requires a highly skilled staff and a suitably equipped laboratory.

1. SCOPE

This defines the procedure for extracting and determining the elemental sulphur contained in fertilizers.

2. FIELD OF APPLICATION

This method applies to EEC fertilizers for which a declaration of the total sulphur in elemental form is provided for in Council Directive 89/284/EEC.

3. PRINCIPLE

After the removal of soluble compounds, elemental sulphur is extracted by using carbon disulphide, followed by gravimetric determination of the sulphur extracted.

4. REAGENTS

Carbon disulphide.

5. APPARATUS

5.1 100 millilitre extraction flask with ground glass stopper.

5.2 Soxhlet apparatus, with the appropriate filter elements.

- 5.3 Vacuum rotary evaporator.
- 5.4 Electric oven, fan assisted, set at 90 ± 2 °C.
- 5.5 Porcelain petri dishes, five to seven centimetres in diameter, not exceeding five centimetres in height.
- 5.6 Electric hot plate with adjustable temperature.

6. PRÉPARATION OF THE SAMPLE

See method 1.

7. PROCEDURE

7.1 Test sample

Weigh out five to ten grams of the sample to an accuracy of one milligram and place in the thimble of the Soxhlet apparatus (5.2).

7.2 Extraction of the sulphur

Wash thoroughly the contents with hot water to remove all soluble compounds. Dry in the oven at 90 °C (5.4) for at least one hour. Place the filter in the Soxhlet apparatus (5.2).

Place a few glass beads in the flask of the apparatus (5.1) and weigh (P_0), then add 50 millilitres of carbon disulphide (4.1).

Connect the apparatus and leave the elemental sulphur to be extracted for six hours. Switch off the heat and, after cooling, disconnect the flask. Connect the flask to the rotary evaporator (5.3) and evaporate until the contents of the flask have solidified in a spongy mass.

Dry the flask in the oven at 90 °C (5.4) (generally one hour is necessary) until a constant weight is obtained (P_1).

7.3 Determination of the purity of the elemental sulphur

Certain substances may have been extracted by the carbon disulphide at the same time as the elemental sulphur. The purity of the elemental sulphur is determined as follows:

homogenize the contents of the flask as thoroughly as possible, and remove two to three grams, weighed to an accuracy of one milligram (n). Place in the Petri dish (5.5). Weigh dish and contents together (P_2). Place on the hot plate (5.6) set at a temperature not exceeding 220 °C so as not to cause combustion of the sulphur. Continue sublimation for three or four hours until a constant weight is obtained (P_3).

NB: For some fertilizers, it may not be necessary to determine how pure the sulphur is. In this case, omit step 7.2.

8. EXPRESSION OF RESULTS

The percentage elemental sulphur (S) content of the fertilizer is as follows:

$$\text{Impure S (\% of the fertilizer)} = \frac{P_1 - P_0}{m} \times 100$$

$$\text{Purity of sulphur extracted (\%)} = \frac{P_2 - P_3}{n} \times 100$$

$$\text{Pure S (\% of the fertilizer)} = \frac{(P_1 - P_0)(P_2 - P_3)}{m \times n} \times 100$$

Where:

m = the mass of the test sample of fertilizer in grams,

P_0 = the mass of the Soxhlet flask in grams,

P_1 = the mass of the Soxhlet flask and the impure sulphur after drying,

n = the mass of the impure sulphur to be purified in grams,

P_2 = the mass of the Petri dish,

P_3 = the mass of the Petri dish after sublimation of the sulphuring.

Method 8.6

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

1. SCOPE

This document defines the procedure for determining the calcium in fertilizer extracts.

2. FIELD OF APPLICATION

This method applies to EEC fertilizers for which a declaration of the total and/or water-soluble calcium is provided for in Council Directive 89/284/EEC.

3. PRINCIPLE

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

4. REAGENTS

4.1 Diluted hydrochloric acid:

One volume of hydrochloric acid ($d = 1,18$) and one volume of water.

4.2 1:10 dilute sulphuric acid:

one volume of sulphuric acid ($d = 1,84$) in ten volumes of water.

4.3 1:1 dilute ammonia solution:

one volume of ammonia ($d = 0,88$) and one volume of water.

4.4 Saturated solution of ammonia oxalate ($(\text{NH}_4)_2 \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) at ambient temperature (approximately 40 grams 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 ethanol, at 95 %, 0,1 % (m/v).

4.8 Solution of bromocresol green in ethanol, at 95 % 0,04 % (m/v).

4.9 Standard solution of potassium permanganate, 0,02 M.

5. APPARATUS

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

5.2 Hot water bath.

6. PREPARATION OF THE ALIQUOT TO BE ANALYSED

Using a pipette, take an aliquot portion of the extraction solution obtained by method 8.1 or 8.3, containing between 15 and 50 milligrams of Ca (= 21 to 70 milligrams of CaO). Let the volume of this aliquot be v_2 . Pour into a 400 millilitre beaker. If necessary, neutralize (turning of indicator (4.7) from green to blue) with a few drops of the ammonia solution (4.3).

Add one millilitre of the citric acid solution (4.5) and five millilitres of ammonium chloride solution (4.6).

7. PRECIPITATION OF THE CALCIUM OXALATE

Add approximately 100 millilitres of water. Bring to the boil, add eight to 10 drops of indicator solution (4.8) and, slowly, 50 millilitres of a hot ammonium oxalate solution (4.4). If a precipitate forms, dissolve by adding a few drops of hydrochloric acid (4.1). Neutralize very slowly with

ammonia solution (4.3) while stirring continuously to a pH of 4.4 to 4.6 (turning 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 into the crucible (5.1).

8. TITRATION OF THE OXALATE PRECIPITATE

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 millilitre beaker and dissolve the precipitate with 50 millilitres of hot sulphuric acid (4.2). Add water to the beaker in order to obtain a volume of approximately 100 millilitres. Bring to a temperature of 70 to 80 °C and titrate drop by drop with a permanganate solution (4.9) until the pink colour lasts for a minute. Let this volume be n .

9. EXPRESSION OF RESULTS

The calcium (Ca) content of the fertilizer is as follows:

$$\text{Ca} (\%) = n \times 0,2004 \times \frac{t}{0,02} \times \frac{v_1}{v_2 \times m}$$

Where:

n = the number of millilitres of permanganate used,

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.

$$\text{CaO} (\%) = \text{Ca} (\%) \times 1,400.$$

Method 8.7

DETERMINATION OF MAGNESIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

1. SCOPE

This document defines the procedure for determining the magnesium in fertilizer extracts.

2. FIELD OF APPLICATION

This method applies to EEC fertilizer extracts obtained by methods 8.1 and 8.3, for which a declaration of the total magnesium and/or water soluble magnesium is required, with the following exceptions:

fertilizers listed in the Annex to the Directive on secondary nutrients (89/284/EEC):

type 4 (kieserite),

type 5 (magnesium sulphate) and

type 7 (kieserite with potassium sulphate)

to which method 8.8 applies.

The method set out below applies to all fertilizer extracts containing elements in quantities that might interfere with the complexometric determination of magnesium.

3. PRINCIPLE

Determination of magnesium by atomic absorption spectrophotometry after appropriate dilution of the extract.

4. REAGENTS

4.1 Hydrochloric acid, 1 M solution

4.2 Hydrochloric acid, 0,5 M solution

4.3 Standard solution of magnesium, 1,00 milligrams per millilitre.

4.3.1 Dissolve 1,013 grams of magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in the 0,5 M hydrochloric acid solution (4.2).

- 4.3.2. Weigh out 1,658 grams of magnesium oxide (MgO), previously calcined to remove all traces of carbonation. Place in a beaker with 100 millilitres of water and 120 millilitres of 1 M hydrochloric acid (4.1). When it has dissolved, decant quantitatively into a 1 000 millilitre graduated flask. Make up the volume by adding and mix.

or:

- 4.3.3 Commercial standard solution.

The laboratory is responsible for testing such solutions.

- 4.4 Strontium chloride solution.

Dissolve 75 grams of strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) in a hydrochloric acid solution (4.2) and make up to 500 millilitres with the same acid solution.

5. APPARATUS

Spectrophotometer fitted for atomic absorption, with a magnesium lamp, set at 285,2 nm.

Air-acetylene flame.

6. PREPARATION OF THE SAMPLE

See methods 8.1 and 8.3.

7. PROCEDURE

- 7.1 If the fertilizer has a declared magnesium (Mg) content of more than 6% (i. e. 10% as MgO), take 25 millilitres (V_1) of the extraction solution (6). Transfer into a 100 millilitre graduated flask, and make up to volume with water and mix. The dilution factor is $D_1 = 100/V_1$.

- 7.2 Using a pipette, take 10 millilitres of the extraction solution (6) or the solution (7.1). Transfer into a 200 millilitre graduated flask. Make up to volume with the 0,5 M hydrochloric acid solution (4.2) and mix. The dilution factor is 200/10.

- 7.3 Dilute this solution (7.2) with the 0,5 M hydrochloric acid solution (4.2) so as to obtain a concentration in the optimum working field of the spectrophotometer (5.1). V_2 is the volume of the sample in 100 millilitres. The dilution factor is $D_2 = 100/V_2$.

The final solution should contain 10% v/v of the strontium chloride solution (4.4).

- 7.4 Preparation of blank solution

Prepare a blank solution by repeating the whole procedure from the extraction (method 8.1 or 8.3), omitting only the test sample of fertilizer.

- 7.5 Preparation of calibration solutions

By diluting the standard solution (4.3) with the 0,5 M hydrochloric acid, prepare at least five calibration solutions of increasing concentration within the optimum measuring range of the apparatus (5.1).

These solutions should contain 10% v/v of the strontium chloride solution (4.4).

- 7.6 Measurement

Set up the spectrophotometer (5.1) at a wavelength of 285,2 nm.

Spray, successively, the calibration solutions (7.5), the sample solution (7.3) and the blank solution (7.4), washing the instrument through with the solution to be measured next. Repeat this operation three times. Plot the calibration curve using the mean absorbances of each of the calibrations (7.5) as the ordinates and the corresponding concentration of magnesium in $\mu\text{g/ml}$ as the abscissae. Determine the concentration of magnesium in the sample (7.3), X_s , and blank (7.4), X_b , by reference to the calibration curve.

8. EXPRESSION OF RESULTS

Calculate the amount of magnesium (Mg) or magnesium oxide (MgO) in the sample by reference to the calibration solutions and taking into consideration the blank.

The percentage of magnesium (Mg) in the fertilizer is equal to:

$$\text{Mg (\%)} = \frac{(X_s - X_b) D_1 (200/10) D_2 500.100}{1\ 000.1\ 000\ M}$$

X_s = the concentration of the solution to be analysed recorded on the calibration curve, in $\mu\text{g/ml}$.

X_b = the concentration of the blank solution as recorded on the calibration curve, in $\mu\text{g/ml}$.

D_1 = the dilution factor when the solution is diluted (7.1).

It is equal to four if 25 millilitres are taken.

It is equal to one when the solution is not diluted.

D_2 = the dilution factor in 7.3.

M = the mass of the test sample at the time of extraction.

$$\text{MgO (\%)} = \text{Mg (\%)} / 0,6$$

Method 8.8

DETERMINATION OF MAGNESIUM BY COMPLEXOMETRY

1. SCOPE

This document defines the procedure for the determination of magnesium in fertilizer extracts.

2. FIELD OF APPLICATION

This method applies to the following EEC fertilizer extracts for which the determination of total magnesium and/or water-soluble magnesium is provided for:

- fertilizers listed in Directive 76/116/EEC: straight nitrogenous fertilizers, type 1 b (calcium magnesium nitrate), type 7 (magnesium sulphonitrate), type 8 (nitrogenous fertilizers with magnesium) and straight potassic fertilizers, type 2 (enriched kainite), type 4 (potassium chloride containing magnesium), type 6 (potassium sulphate containing magnesium salt),
- fertilizers listed in the Annex to the Directive on secondary nutrients (89/284/EEC).

3. PRINCIPLE

The magnesium is solubilized by methods 8.1 and/or 8.3. 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 calcone carbonic acid. Determination of magnesium by difference.

4. REAGENTS

4.1 Standard 0,05 molar solution of magnesium:

4.1.1 Dissolve 1,232 grams of magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in the 0,5 M hydrochloric acid solution (4.11) and make up to 100 millilitres with the same acid.

or:

4.1.2 Weigh out 2,016 grams of magnesium oxide, previously calcined to remove all traces of carbonation. Place it in a beaker with 100 millilitres of water.

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

After dissolution, transfer quantitatively into a graduated 1 000 millilitre flask. Make up to volume and mix.

One millilitre of these solutions should contain 1,216 milligrams of Mg (= 2,016 milligrams of MgO).

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

4.2 0,05 molar solution of EDTA

Weigh out 18,61 grams of the dihydrated disodium salt of ethylenediaminetetraacetic ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$), place it in a 1 000 millilitre beaker and dissolve in 600 to 800 millilitres

of water. Transfer the solution quantitatively into a graduated 1 000 millilitre flask. Make up the volume and mix. Check this solution with the standard solution (4.1) by taking a sample of 20 millilitres of the latter and by titration according to the analytical procedure described at (7.2).

One millilitre of the EDTA solution should correspond to 1,216 milligrams of Mg (= 2,016 milligrams of MgO) and to 2,004 milligrams of Ca (= 2,804 milligrams CaO) (see remarks 10.1 and 10.6).

4.3 0,05 molar standard solution of calcium

Weigh out 5,004 grams of dry calcium carbonate. Place it in a beaker with 100 millilitres of water. Progressively stir in 120 millilitres 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 (7.3). One millilitre of this solution should contain 2,004 milligrams of Ca (= 2,804 milligrams of CaO) and should correspond to one millilitre of the 0,05 molar EDTA solution (4.2).

4.4 Calcein indicator

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

4.5 Calcon carbonic acid indicator.

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

4.6 Eriochrome black-T indicator

Dissolve 300 milligrams of Eriochrome black-T in a mixture of 25 millilitres of propanol-1 and 15 millilitres of triethanolamine. This solution may only be kept for approximately four weeks. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue is obtained which is free from red tinges. 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 with the magnesium. In that case two elements are determined concurrently.

4.7 Potassium cyanide solution

Aqueous solution of KCN at 2%. (Do not pipette by mouth and see 10.7).

4.8 Solution of potassium hydroxide and potassium cyanide

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

4.9 pH 10,5 buffer solution

In a 500 millilitre graduated flask, dissolve 33 grams of ammonium chloride in 200 millilitres of water, add 250 millilitres of ammonia ($d = 0,91$) make up the volume with water and mix. Test the pH of the solution regularly.

4.10 Diluted hydrochloric acid: one volume of hydrochloric acid ($d = 1,18$) 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

5.1 Magnetic or mechanical stirrer.

5.2 pH meter.

6. CONTROL TEST

Carry out a determination on aliquot parts of solutions (4.1 and 4.3) such that the Ca/Mg ratio is approximately equal to that of the solution 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 numbers of millilitre EDTA solution 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

See methods 8.1 and 8.3.

8. DETERMINATION

8.1. Aliquot samples to be taken.

The aliquot part will as far as possible contain between nine and 18 milligrams of magnesium (= 15 to 30 milligrams of MgO).

8.2. Titration in the presence of Eriochrome black-T

Pipette an aliquot part (8.1) of the solution to be analysed into a 400 millilitre beaker. Neutralize the surplus acid with the 5 M sodium hydroxide solution (4.12) using the pH meter. Dilute with water to approximately 100 millilitres. Add 5 millilitres of the buffer solution (4.9). The pH measured by the meter must be $10,5 \pm 0,1$. Add 2 millilitres 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 number of millilitres of 0,05 molar EDTA solution.

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

Pipette an aliquot part of the solution to be analysed equal to that taken from the above titration and place it in a 400 millilitres beaker. Neutralize the surplus acid with the 5 M sodium hydroxide solution (4.13) using the pH meter. Dilute with water to about 100 millilitres. Add 10 millilitres of the KOH/KCN solution (4.8) and 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 number of millilitres of 0,05 molar EDTA solution.

9. EXPRESSION OF THE RESULTS

For the EEC fertilizers to which the method is applicable (5 grams of fertilizer in 500 millilitres of extract), the percentage content of the fertilizer is:

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

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

Where:

a = the number of millilitres of 0,05 molar EDTA solution used for the titration in the presence of calcein or calcon carbonic acid,

b = the number of millilitres of 0,05 molar EDTA solution used for the titration in the presence of Eriochrome black-T,

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

T = $0,2016 \times$ molarity of the EDTA solution/0,05 (see 4.2),

T' = $0,1216 \times$ molarity of the EDTA solution/0,05 (see 4.2).

10. REMARKS

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 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 turning of the indicator must be observed not vertically, but horizontally across the solution and the beaker must be placed against a white background in a well-lit position. The turning 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, *inter alia*, 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 oxidization with sodium hypochlorite following alkalization.

Method 8.9

DETERMINATION OF SULPHATES

1. SCOPE

This document defines the procedure for determining the sulphur present in fertilizer extracts in the form of sulphates.

2. FIELD OF APPLICATION

This method applies to the determination of sulphates present in the extractions performed in methods 8.1, 8.2, 8.3 and 8.4.

3. PRINCIPLE

Gravimetric determination as barium sulphate.

4. REAGENTS

4.1. Diluted hydrochloric acid:

One volume of hydrochloric acid ($d = 1,18$) and one volume of water.

4.2. Barium chloride solution $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$: 122 grams per litre.

4.3. Silver nitrate solution: 5 grams per litre.

5. APPARATUS

5.1. Porcelain crucibles.

5.2. Hot water bath.

5.3. Drying oven set at $105\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$.

5.4. Electric oven set at $800\text{ }^\circ\text{C} \pm 50\text{ }^\circ\text{C}$.

6. PROCEDURE

6.1. Sampling of the solution

Pipette an aliquot part of one of the extraction solutions indicated at 2 containing between 20 and 100 milligrams of S or 50 and 250 milligrams of SO₃.

Place this aliquot in a beaker of suitable capacity. Add 20 millilitres of dilute hydrochloric acid (4.1). Make up to about 300 millilitres with water.

6.2. Preparation of the precipitate

Bring the solution to the boil. Add, drop by drop, about 20 millilitres of the barium chloride solution (4.2) while stirring the solution vigorously. Boil for a few minutes.

Place the beaker, covered with a watch glass, in a boiling hot water bath (5.2) for an hour. Then leave standing hot (± 60 °C) until the supernatant liquor is clear. Decant the clear solution through a slow filtration ash-free filter. Wash the precipitate several times with hot water. Continue to wash the precipitate on the filter until the filtrate is chloride free. This can be checked by using silver nitrate solution (4.3).

6.3. Incineration and weighing of the precipitate

Place the filter paper and precipitate in a porcelain crucible (5.1) previously weighed to the nearest 0,1 milligrams. Dry in the oven (5.3) and ash at approximately 800 °C for half an hour (5.4). Allow to cool in a desiccator and weigh to within 0,1 milligrams.

7. EXPRESSION OF THE RESULTS

One milligram of barium sulphate corresponds to 0,137 milligrams of S or to 0,343 milligrams of SO₃.

The percentage S content of the fertilizer is as follows:

$$S (\%) = w \times 0,0137 \times \frac{v_1}{v_2 \times m}$$

$$SO_3 (\%) = S (\%) \times 2,5$$

Where:

w = the mass of the barium sulphate precipitate in milligrams,

v₁ = the volume of the extraction solution in millilitres,

v₂ = the aliquot volume in millilitres,

m = the mass of the test sample in grams.

Method 8.10

DETERMINATION OF THE SODIUM EXTRACTED

1. SCOPE

This document defines the procedure for determining the sodium in fertilizer extracts.

2. FIELD OF APPLICATION

This method applies to EEC fertilizers for which a declaration of the sodium is provided for in Council Directive 89/284/EEC.

3. PRINCIPLE

Following suitable dilution of the extract obtained via method 8.1 and/or 8.3, the sodium content of the solution is determined by flame-emission spectrophotometry.

4. REAGENTS

4.1. Diluted hydrochloric acid:

One volume of hydrochloric acid for analysis ($d = 1,18$) plus one volume of water.

4.2. Aluminium nitrate $\text{Al}(\text{NO}_3)_3, 9\text{H}_2\text{O}$.4.3. Caesium chloride, CsCl .4.4. Anhydrous sodium chloride, NaCl .

4.5. Caesium chloride and aluminium nitrate solution

Dissolve in water 50 grams of caesium chloride (4.3) and 250 grams of aluminium nitrate (4.2) in a 1 000 millilitres graduated flask. Make up to volume with water and mix.

4.6. Standard sodium solution of one milligram/millilitre of Na.

Dissolve in water 2,542 grams of sodium chloride (4.4) in a 1 000 millilitre graduated flask. Add 10 millilitres of hydrochloric acid (4.1). Make up to volume with water and mix.

5. APPARATUS

Spectrophotometer equipped for flame emission, set at 589,3 nm.

6. CALIBRATION SOLUTIONS

6.1. Place 10 millilitres of standard solution (4.6) in a 250 millilitre graduated flask. Make up to volume and mix. Concentration of solution: 40 $\mu\text{g}/\text{ml}$ of Na.6.2. Place 0, 5, 10, 15, 20, 25 millilitres of the intermediate solution (6.1) in 100 millilitres graduated flasks. Add 10 millilitres of the solution (4.5). Make up to volume and mix. Concentration of solutions: 0, 2, 4, 6, 8, 10 $\mu\text{g}/\text{ml}$ of Na.

7. PREPARATION OF SOLUTIONS TO BE MEASURED

Depending upon the foreseeable sodium content of the extraction solution as in method 8.1 or 8.3 (five grams of fertilizer in 500 millilitres), carry out the dilutions in accordance with the following table:

| Na_2O (%) | Na (%) | Intermediate dilution | | Final dilution | | Degree of dilution |
|---------------------------|---------|-----------------------|--------------------------|-----------------------|----------------|--------------------|
| | | Sample (ml) (v_2) | Dilution to ml (v_3) | Sample (ml) (v_4) | Dilution to ml | |
| 3—5 | 2,2—3,7 | 10 | 50 | 10 | 100 | 50 |
| 5—10 | 3,7—7,4 | 10 | 100 | 10 | 100 | 100 |
| 10—20 | 7,4—15 | 10 | 100 | 5 | 100 | 200 |
| 20—38 | 15—28 | 5 | 100 | 5 | 100 | 400 |

Make up the intermediate dilution with water. For the final dilution add ten millilitres of the solution (4.5) to the 100 millilitre graduated flask.

For a test sample of one gram multiply the volume of the final dilution (v_4) by five.

8. DETERMINATION

Prepare the spectrophotometer (5.1) for the measurements at 589,3 nm. Calibrate the instrument by measuring the response of the calibration solutions (6.2). Then adjust the sensitivity of the instrument to use its entire scale when the most concentrated calibration solution is used. Then measure the response of the sample solution to be analysed (7). Repeat this operation three times.

9. CALCULATION OF RESULTS

Draw a calibration curve by plotting the average response for each calibration solution along the ordinate and the corresponding concentrations, expressed in μg per millilitre on the abscissa. Determine from this the sodium concentration of the test solution. Calculate the quantity of sodium from the standard solutions taking account of the levels of dilution. Express the results as a percentage of the sample.

The percentage sodium (Na) content of the fertilizer is as follows:

$$\text{Na (\%)} = x \cdot \frac{v_3}{v_4} \frac{v_1}{v_2} \frac{10^{-2}}{m}$$
$$\text{Na}_2\text{O (\%)} = \text{Na (\%)} \times 1,348$$

Where:

- x = the concentration of the solution introduced into the spectrophotometer in $\mu\text{g/ml}$,
 - v_1 = the volume of the extraction solution in millilitres,
 - v_2 = the aliquot volume in the intermediate dilution in millilitres,
 - v_3 = the volume of intermediate dilution in millilitres,
 - v_4 = the aliquot volume in ml of the final dilution (in 100 millilitres),
 - m = The mass of the test sample in grams.'
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