COMMISSION DIRECTIVE 95/8/EC

of 10 April 1995

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

(Methods of analysis for trace elements at a concentration greater than 10 %)

THE COMMISSION OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European 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 89/530/EEC [2], and in particular Article 9 (2) thereof,

Whereas Article 8a of the Treaty establishes an area without internal frontiers in which the free movement of goods, persons, services and capital in ensured;

Whereas Directive 89/530/EEC supplement and amends Directive 76/116/EEC in respect of the trace elements boron, cobalt, copper, iron, manganese, molybdendum and zinc in fertilizers;

Whereas Commission Directive 77/535/EEC [3], as last amended by Directive 93/1/EEC [4], provides for official controls for Community fertilizers for the purpose of checking compliance with the requirements imposed by the Community provisions concerning the quality and composition of fertilizers; whereas Directive 77/535/EEC should be supplemented so that fertilizers to which Council Directive 89/530/EEC should be supplemented so that fertilizers to which Council Directive 89/530/EEC relates, can also be checked;

Whereas, in view of the scope and effects of the proposed action, the Community measures provided for by this Directive are not only necessary but also indispensable for the attainment of the stated objectives, whereas these objectives cannot be achieved by Member States individually and whereas their attainment at Community level is, in fact, already provided for by Directive 76/116/EEC;

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

The text set out in the Annex of this Directive is hereby added to Annex II of Directive 77/535/EEC.

The methods are applicable to Community fertilizers for the determination of each trace element, the declared contant of which is more than 10 %.

Article 2

1. Member States shall bring into force the provisions necessary to comply with this Directive by 31 December 1995. They shall immediately inform the Commission thereof.

When Member States adopt these provisions, they shall contain a reference to this Directive or shall be accompanied by such reference at the time of their official publication. The procedure for such reference shall be adopted by Member States.

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

Article 3

This Directive shall enter into force on the third day following its publication in the *Official Journal of the European Communities.*

Done at Brussels, 10 April 1995.

For the Commission

Martin BANGEMANN

Member of the Commission

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[1] OJ No L 24, 30. 1. 1976, p. 21.
[2] OJ No L 281, 30. 9. 1989, p. 116.
[3] OJ No L 213, 22. 8. 1977, p. 1.
[4] OJ No L 113, 7. 5. 1993, p. 17.

ANNEX

'Methods 10:

TRACE ELEMENTS AT A CONCENTRATION GREATER THAN 10 %

Method 10.1

EXTRACTION OF TOTAL TRACE ELEMENTS

1. SCOPE

This method defines the procedure for extracting the following trace elements: total boron, total cobalt, total copper, total iron, total manganese, total molybdenum and total zinc. The aim is to carry out the minimum number of extractions, making use wherever possible of the same extact to determine the total level of each of the trace elements list above.

2. FIELD OF APPLICATION

This procedure concerns Community fertilizers covered by Directive 89/530/EEC containing one or more of the following trace elements: boron, cobalt, copper, iron, manganese, molybdenum and zinc. It is applicable to each trace element, the declared content of which is more than 10 %.

3. PRINCIPLE

Dissolution in boiling diluted hydrochloric acid.

Note: The extraction is empirical and may not be quantitative depending on the product or the other constituents of the fertilizer. In particular, in the case of certain manganese oxides, the quantity extracted may be substantially smaller than the total quantity of manganese which the product contains. It is the responsibility of the fertilizer manufacturers to ensure that the declared content actually corresponds to the quantity extracted under the conditions pertaining to the method.

4. REAGENTS

4.1. Diluted hydrochloric acid (HCl) solution, about 6 M

Mix 1 volume of hydrochloric acid (ρ = 1,18 g/ml) with 1 volume of water.

4.2. Concentrated ammonia solution (NH_4OH, ρ = 0,9 g/ml)

5. APPARATUS

5.1. Electric hotplate with variable temperature control.

5.2. pH meter

Note: Where the boron content of an extract is to be determined, do not use borosilicate glassware. As the method involves boiling, teflon or silica is preferable. Rinse the glassware thoroughly if it has been washed in detergents containing borates.

6. PREPARATION OF THE SAMPLE

See Method 1 (Directive 77/535/EEC).

7. PROCEDURE

7.1. Test sample

Take a quantity of fertilizer weighing 1 or 2 g depending on the declared content of element in the product. The following table shall be used to obtain a final solution which, after appropriate dilution, will be within the measuring rane for each method. Samples should be weighed to within 1 mg.

Declared content of trace element in the fertilizer (%)	> 10 < 25	≥ 25
Mass of test sample (g)	2	1
Masss of element in the sample (mg)	> 200 < 500	≥ 250
Volume of extract V (ml)	500	500
Concentration of element in extract (mg/l)	> 400 < 1 000	≥ 500

Place the sample in a 250 ml beaker.

7.2. Preparation of the solution

If necessary moisten the sample with a little water, add 10 ml of dilute hydrochloric acid (4.1) per gram of fertilizer carefully, in small amounts, then add about 50 ml of water. Cover the beaker with a watchglass and mix. Bring to the boil on the hotplate and boil for 30 minutes. Allow to cool, stirring occasionally. Transfer quantitatively to a 500 ml volumetric flask. Make up to volume with water and mix thoroughly. Filter through a dry filter into a dry container. Discard the first portion. The extract must be perfectly clear.

It is recommended that the determinations be carried out without delay on aliquot portions of the clear filtrate, if not the containers should be stoppered.

Note: Extracts in which the boron content has to be determined.

Adjust the pH to between 4 and 6 with concentrated ammonia solution (4.2).

8. DETERMINATION

The determination of each trace element is to be carried out on the aliquot portions indicated in the method for each individual trace element.

Methods 10.5, 10.6, 10.7, 10.9 and 10.10 cannot be used to determine elements present in a chelated or complexed form. In such cases Method 10.3 must be used prior to the determination.

In the case of determinations by AAS (Methods 10.8 and 10.11) such treatment may not be necessary.

Method 10.2

EXTRACTION OF WATER-SOLUBLE TRACE ELEMENTS

1. SCOPE

This method defines the procedure for extracting water-soluble forms of the following trace elements : boron, cobalt, copper, iron, manganese, molybdenum and zinc. The aim is to carry out the minimum number of extractions, making use wherever possible of the same extract to determine the level of each of the elements listed above.

2. FIELD OF APPLICATION

This procedure concerns Community fertilizers covered by Directive 89/530/EEC containing one or more of the following trace elements : boron, cobalt, copper, iron, manganese, molybdenum and zinc. It is applicable to each trace element, the declared content of which is more than 10 %.

3. PRINCIPLE

The trace elements are extracted by shaking the fertilizer in water at 20 ± 2 °C.

Note: The extraction is empirical and may or may not be quantitative.

4. REAGENTS

4.1. Diluted hydrochloric acid (HCl) solution, about 6 M

Mix 1 volume of hydrochloric acid (ρ = 1,18 g/ml) with 1 volume of water.

5. APPARATUS

5.1. Rotary shaker set at about 35 to 40 rpm.

Note: Where the boron content of the extract is to be determined, do not use borosilicate glassware. Teflon or silica is preferable for this extraction. Rinse the glassware thoroughly if it has been washed in detergents containing borates.

6. PREPARATION OF THE SAMPLE

See Method 1 (Directive 77/535/EEC).

7. PROCEDURE

7.1. Test sample

Take a quantity of fertilizer weighing 1 or 2 g depending on the declared content of the product. The following table shall be used to obtain final solution which, after appropriate dilution, will be within the measuring range for each method. The samples should be weighed to within 1 mg.

Declared content of trace element in the fertilizer (%)	> 10 < 25	≥ 25
Mass of test sample (g)	2	1
Mass of element in the test sample (mg)	> 200 < 500	≥ 250
Volume of extract V (ml)	500	500
Concentration of element in extract (mg/l)	> 400 < 1 000	≥ 500

Place the sample in a 500 ml flask.

7.2 Preparation of the solution

Add about 400 ml of water.

Stopper the flask well. Shake vigorously by hand to disperse the sample, then place the flask on the shaker and shake for 30 minutes.

Make up to volume with water and mix thoroughly.

7.3 Preparation of the test solution

Filter immediately into a clean, dry flask. Stopper the flask. Carry out the determination immediately after filtering.

Note: If the filtrate gradually becomes cloudy, make another extraction following 7.1 and 7.2 in a flask of volume Ve. Filter into a calibrated flask of volume W wich has previously been dried and has received 5 ml of dilute hydrochloric acid (4.1). Stop the filtration at the exact moment when the calibration mark is reached. Mix thoroughly.

Under these conditions the value of V in the expression of results is:

$$V = V_e \times W/(W-5)$$

The dilutions in the expression of results depend on this value of V.

8. DETERMINATION

The determination of each trace element is carried out on the aliquot portions indicated in the method for each individual trace element.

Methods 10.5, 10.6, 10.7, 10.9 and 10.10 cannot be used to determine elements present in a chelated or complexed form. In such cases Method 10.3 must be used prior to the determination.

In the case of determinations by AAS (Methods 10.8 and 10.11) such treatment may not be necessary.

Method 10.3

REMOVAL OF ORGANIC COMPOUNDS FROM FERTILIZER EXTRACTS

1. SCOPE

This method defines a procedure for removing organic compounds from fertilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to analysing samples of fertilizers extracted by Methods 10.1 and 10.2 for which a declaration of total and/or water-soluble element is required by Directive 89/530/EEC.

Note: The presence of small quantities of organic matter usually does not affect determinations by means of atomic absorption spectrometry.

3. PRINCIPLE

The organic compounds in an aliquot portion of the extract are oxidized with hydrogen peroxide.

4. REAGENTS

4.1 Diluted hydrochloric acid (HCl) solution, about 0,5 M

Mix 1 volume of hydrochloric acid ($\rho = 1{,}18$ g/ml) with 20 volumes of water.

4.2 Hydrogen peroxide solution (30 % H_2O_2, $\rho = 1{,}11$ g/ml), free from trace elements.

5. APPARATUS

Electric hotplate with variable temperature control.

6. PROCEDURE

Take 25 ml of the extract solution obtained by Method 10.1 or Method 10.2 and place in 100 ml beaker. In the case of Method 10.2, add 5 ml of the dilute hydrochloric acid solution (4.1). Then add 5 ml of the hydrogen peroxide solution (4.2). Cover with a watchglass. Allow oxidation to occur at room temperature for about one hour, then bring gradually to boiling and boil for half an hour. If necessary, add a further 5 ml of the hydrogen peroxide to the solution once it has cooled. Then boil to remove the excess hydrogen peroxide. Allow to cool and transfer quantitatively to a 50 ml volumetric flask and make up to volume. Filter where necessary.

Account should be taken of this dilution when taking aliquot portions and calculating the percentage of trace element in the product.

Method 10.4

DETERMINATION OF TRACE ELEMENTS IN FERTILIZER EXTRACTS BY ATOMIC ABSORPTION SPECTROMETRY

(GENERAL PROCEDURE)

1. SCOPE

This document defines a general procedure for determining the levels of iron and zinc in fertilizer extracts by atomic absorption spectrometry.

2. FIELD OF APPLICATION

This procedure is applicable to analysing samples of fertilizers extracted by Methods 10.1 and 10.2 for which a declaration of total and/or water-soluble iron or zinc is required by Directive 89/530/EEC. Adaptations of this procedure for the various trace elements are detailed in the methods defined specifically for each element.

Note: In most cases the presence of small quantities of organic matter will not affect determinations by means of atomic absorption spectrometry.

3. PRINCIPLE

After the extract has been treated where necessary to reduce or eliminate interfering chemical species, the extract is diluted so that its concentration is in the optimum range of the spectrometer at a wavelength suitable for the trace element to be determined.

4. REAGENTS

4.1 Diluted hydrochloric acid solution (HCl), about 6 M

Mix one volume of hydrochloric acid ($\rho = 1{,}18$ g/ml) with 1 volume of water.

4.2 Diluted hydrochloric acid solution (HCl), about 0,5 M

Mix one volume of hydrochloric acid ($\rho = 1{,}18$ g/ml) with 20 volumes of water.

4.3 Lanthanum salt solutions (10g of La per litre)

This reagent is used for determinations of iron and zinc. It can be prepared either:

(a) with lanthanum oxide dissolved in hydrochloric acid (4.1). Place 11,73 g of lanthanum oxide (La_2O_3) in 150 ml of water in a 1 litre volumetric flask and add 120 ml of 6 M hydrochloric acid (4.1). Allow to dissolve and then make up to 1 litre with water and mix thoroughly. This solution is approximately 0,5 M in hydrochloric acid; or

(b) with solutions of lanthanum chloride, sulfate or nitrate.

Dissolve 26,7 g of lanthanum chloride heptahydrate ($LaCl_3 7H_2O$) or 31,2 g of lanthanum nitrate hexahydrate ($La(NO_3)_3 6H_2O$) or 26,2 g of lanthanum sulfate nonahydrate ($La_2(SO_4)_3 9H_2O$) in 150 ml of water, then add 85 ml of 6 M hydrochloric acid (4.1). Allow to dissolve and then make up to 1 litre with water. Mix thoroughly. This solution is approximately 0,5 M in hydrochloric acid.

4.4 Calibration solutions

For the preparation of these, see the individual determination method for each trace element.

5. APPARATUS

Atomic absorption spectrometer fitted with sources emitting radiation characteristic of the trace elements to be determined.

The analyst must follow the manufacturer's instructions and be familiar with the apparatus. The apparatus must allow background correction so that it can be used whenever necessary (e.g. Zn). The gases to be used are air and acetylene.

6. PREPARATION OF THE SOLUTION TO BE ANALYSED

6.1. Preparation of extract solutions containing the elements to be determined

See Method 10.1 and/or 10.2 and, if appropriate, 10.3.

6.2. Treatment of the test solution

Dilute an aliquot portion of the extract obtained by Method 10.1, 10.2 or 10.3 with water and/or hydrochloric acid (4.1) or (41.2) so as to obtain, in the final solution for measurement, a concentration of the element to be determined that is appropriate to the calibration range used (7.2) and a hydrochloric acid concentration of at least 0,5 M and not more than 2,5 M. This operation may require one or more successive dilutions.

The final solution has to be obtained by placing an aliquot portion of the diluted extract in a 100 ml volumetric flask. Let the volume of this aliquot portion be (a) ml. Add 10 ml of the lanthanum salt solution (4.3). Make up to volume with 0,5 M hydrochloric acid solution (4.2) and mix thoroughly. Let D be the dilution factor.

7. PROCEDURE

7.1. Preparation of a blank solution

Prepare a blank solution by repeating the whole procedure from the extraction stage, omitting only the test sample of fertilizer.

7.2. Preparation of calibration solutions

From the working calibration solution prepared using the method given for each individual trace element, prepare in 100 ml volumetric flasks a series of at least five calibration solutions of increasing concentration within the optimum measuring range of the spectrometer. If necessary, adjust the concentration of hydrochloric acid to bring it as close as possible to that of the diluted test solution (6.2). When determining iron or zinc add 10 ml of the same lanthanum salt solution (4.3) as used in (6.2). Make up to volume with the 0,5 hydrochloric acid solution (4.2) and mix thoroughly.

7.3. Determination

Prepare the spectrometer (5) for the determination and adjust to the wavelength given in the method for the individual trace element concerned.

Spray three times in succession the calibration solutions (7.2), the test solution (6.2) and the blank solution (7.1), noting each result and flushing the instrument with distilled water between individual sprayings.

Construct the calibration curve by plotting the average spectrometer reading for each calibration solution (7.2) along the ordinate and the corresponding concentration of the element, expressed in µg/ml, along the abscissa.

From this curve, determine the concentrations of the relevant trace element in the test solution X_s (6.2) and in the blank solution X_b (7.1), expressing these concentrations in µg per ml.

8. EXPRESSION OF RESULTS

The percentage of trace element (E) in the fertilzer is given by:

$$E\ (\%) = [(X_s - X_b) \times V \times D] / (M \times 10^4)$$

If Method 10.3 has been used:

$$E\ (\%) = [(X_s - X_b) \times V \times 2D] / (M \times 10^4)$$

where:

E is the amount of the trace element determined, expressed as a percentage of the fertilizer;

X_s is the concentration in the test solution (6.2), in µg/ml;

X_b is the concentration in the blank solution (7.1) in µg/ml;

V is the volume of the extract obtained by Method 10.1 or 10.2, in ml;

D is the factor corresponding to the dilution carried out in (6.2);

M is the mass of the test sample taken in accordance with Method 10.1 or 10.2, in grams.

Calculation of dilution factor D:

If (a_1), (a_2), (a_3), ..., (a_i) and (a) are the aliquot portions and (v_i), (v_2), (v_3), ..., (v_i) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D will be equal to:

$$D = (v_1/a_1) \times (v_2/a_2) \times (v_3/a_3) \times \ldots \times (v_i/a_i) \times (100/a)$$

Method 10.5

DETERMINATION OF BORON IN FERTILIZER EXTRACTS BY MEANS OF ACIDIMETRIC TITRATION

1. SCOPE

This document defines a procedure for determining the boron content of fertilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertilizers obtained by Method 10.1 or Method 10.2 and for which a declaration for the total boron content and/or of the water-soluble boron content is required by Directive 89/530/EEC.

3. PRINCIPLE

A mannitoboric complex is formed by the following reaction of the borate in with mannitol :

$$C_6H_8(OH)_6 + H_3BO_3 \rightarrow C_6H_{15}O_8B + H_2O$$

The complex is titrated with sodium hydroxide solution to a pH of 6,3.

4. REAGENTS

4.1. Methyl red indicator solution

Dissolve 0,1 g of methyl red ($C_{15}H_{15}N_3O_2$) in 50 ml of ethanol (95 % in a 100 ml volumetric flask. Make up the volume to 100 ml with water. Mix thoroughly.

4.2. Diluted hydrochloric acid solution, about 0,5 M

Mix 1 volume of hydrochloric acid HCI, p : 1,18 g/ml) with 20 volumes of water.

4.3. Sodium hydroxide solution, about 0,5 M

Must be free of carbon dioxide. Dissolve 20 g of sodium hydroxide (NaOH) in pellet form in a 1 litre volumetric flask containing about 800 ml of boiled water. When the solution has cooled, make up to 1 000 ml with boiled water and mix thoroughly.

4.4. Standard sodium hydroxide solution, about 0,025 M

Must be free of carbon dioxide. Dilute the 0,5 M sodium hydroxide solution (4.3) 20 times with boiled water and mix thoroughly. The value of the solution expressed as boron (B) is to be determined (see paragraph 9).

4.5. Boron calibration solution (100 µg/ml B)

Dissolve 0,5719 g of boric acid (H_3BO_3), weighed to the nearest 0,1 mg, in water in a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly. Transfer to a plastic bottle for storage in a refrigerator.

4.6. D-mannitol ($C_6H_{14}O_6$) powder

4.7. Sodium chloride (NaCl)

5. APPARATUS

5.1. pH meter with glass electrode

5.2. Magnetic stirrer

5.3. 400 ml beaker with teflon rod

6. PREPARATION OF THE SOLUTION TO BE ANALYSED

6.1. Preparation of the boron solution

See Methods 10.1, 10.2 and, where appropriate, 10.3.

7. PROCEDURE

7.1. Test

Place in a 400 ml beaker (5.3) an aliquot (a) of the extract (6.1) containing 2 to 4 mg B. Add 150 ml of water.

Add several drops of the methyl red indicator solution (4.1).

In the case of extraction with Method 10.2, acidify by adding 0,5 M hydrochloric acid (4.2) up to the point of change of the indicator solution, then add a further 0,5 ml of 0,5 M hydrochloric acid (4.2).

After adding 3 g of sodium chloride (4.7), bring to boiling to drive off the carbon dixoide. Allow to cool. Place the beaker on the magnetic stirrer (5.2) and insert the precalibrated pH meter electrodes (5.1).

Adjust the pH to exactly 6,3, first with the 0,5 M sodium hydroxide solution (4.3), then with the 0,025 M solution (4.4).

Add 20 g of D-mannitol (4.6), dissolve completely and mix thoroughly. Titrate with the 0,025 M sodium hydroxide solution (4.4) to pH 6,3 (at least 1 minute stability). Let x_1, be the volume required.

8. BLANK SOLUTION

Preparage a blank solution by repeating the whole procedure from the preparation of solution stage, omitting only the fertilizer. Let x_0 be the volume required.

9. BORON (B) VALUE OF THE SODIUM HYDROXIDE SOLUTION (4.4)

Pipette 20 ml (2,0 mg B) of the calibration solution (4.5), into a 400 ml beaker and add several drops of methyl red indicator solution (4.1). Add 3 of sodium chloride (4.7) and the hydrochloric acid solution (4.2) up to the point of change of the indicator solution (4.1).

Make up the volume to about 150 ml and bring gradually to the boil so as to eliminate carbon dioxide. Allow to cool. Place the beaker on the magnetic stirrer (5.2), and insert the precalibrated pH meter electrodes (5.1). Adjust the pH to exactly 6,3, first with the 0,5 m sodium hydroxide solution (4.3), then with the 0,025 M solution (4.4).

Add 20 g of D-mannitol (4.6), dissolve completely and mix thoroughly. Titrate with the 0,025 M sodium hydroxide solution (4.4) to pH 6,3 (at least 1 minute stability). Let V_1 be the volume required.

Prepare a blank solution in the same way, substituting 20 ml of water for the calibration solution. Let V_0 be the volume required.

The boron value (F) in mg/ml of the standard NaOH solution (4.4) is as follows:

$$F \text{ (in mg/ml)} = 2/(V_1 - V_0)$$

1 ml of exactly 0,025 M sodium hydroxide solution corresponds to 0,27025 mg B.

10. EXPRESSION OF RESULTS

The percentage of boron in the fertilizer is given by:

$$B(\%) = \frac{(X_1 - X_0) \times F \times V}{10 \times a \times M}$$

where:

B (%) is the percentage of boron in the ferlizer;

X_1 is the volume, in ml, of the 0,025 M sodium hydroxide solution (4.4);

X_0 is the volume, in ml, of the 0,025 M sodium hydroxide solution M (4.4);

F is the boron (B) value, in mg/ml, of the 0,025 M sodium hydroxide solution M (4.4);

V is the volume, in ml, of the extract solution obtained in accordance with Method 10.1 or 10,2;

a is the volume, in ml, of the aliquot (7.1) taken from the extract solution (6.1);

M is the mass, in grams, of the test sample taken in accordance with Method 10.1 or 10.2.

Method 10.6

DETERMINATION OF COBALT IN FERTILIZER EXTRACTS BY THE GRAVIMETRIC METHOD WITH 1-NITROSO-2-NAPHTHOL

1. SCOPE

This document defines a procedure for determing cobalt in fertilzer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertilizers obtained by Method 10.1 or Method 10.2 for which a declaration of cobalt content is required by Directive 89/530/EEC.

3. PRINCIPLE

Cobalt III combines with 1-nitroso-2-naphthol to give a red precipitate Co $(C_{10}H_6ONO)_3$, $2H_2O$. After the cobalt present in the extract has been brought to the cobalt III state, the cobalt is precipitated in an acetic acid medium by a solution of 1-nitroso-2-naphthol. After filtration, the precipitate is washed and dried to constant weight and then weighed as Co $(C_{10}H_6ONO)_3$, $2H_2O$.

4. REAGENTS

4.1. Hydrogen peroxide solution (H_2O_2 p = 1,11 g/ml) 30 %

4.2. Sodium hydroxide solution, about 2 M

Dissolve 8 g of sodium hydroxide in pellet form in 100 ml of water.

4.3. Diluted hydrochloric acid solution, about 6 M

Mix one volume of hydrochloric acid (p = 1,18 g/ml) with 1 volume of water.

4.4. Acetic acid (99,7 % CH_3CO_2H) (p = 1,05 g/ml)

4.5. Acetic acid solution (1 : 2), about 6 M

Mix one volume of acetic acid (4.4) with 2 volumes of water.

4.6. Solution of 1-nitroso-2-naphthol in 100 ml of acetic acid (4.4). Add 100 ml of lukewarm water. Mix thoroughly. Filter at once. The solution obtained must be used immediately.

5. APPARATUS

5.1. Filter crucible P 16/ISO 4793, porosity 4, capacity 30 or 50 ml

5.2. Drying oven at 130 ± 2 °C

6. PREPARATION OF THE SOLUTION TO BE ANALYSED

6.1. Preparation of the cobalt solution

See Methods 10.1 or 10.2.

6.2. Preparation of the solution to be analysed

Place an aliquot of the extract containing not more than 20 m Co in a 400 ml beaker. If the extract is obtained according to Method 10.2, acidify with five drops of hydrochloric acid (4.3). Add about 10 ml of the hydrogen peroxide solution (4.1). Allow the oxidant to act in the cold state for 15 minutes, then make up to about 100 ml with water. Cover the beaker with a watchglass. Bring the solution to boiling point and allow to boil for about 10 minutes. Cool. Make alkaline with the sodium hydroxide solution (4.21) drop by drop until black cobalt hydroxide begins to precipitate.

7. PROCEDURE

Add 10 ml of acetic acid (4.4) and make up the solution with water to about 200 ml. Heat until boiling. Using a burette, add 20 ml of the 1-nitroso-2-naphthol solution (4.6) drop by drop, stirring constantly. Complete by vigorous stirring to make the precipitate coagulate.

Filter through a previously weighed filter curcible (5.1), taking care not to clog up the crucbile. With this in mind, ensure that liquid is left above the precipitate throughout the filtration process.

Wash the beaker with dilute acetic acid (4.5) to remove all the precipitate, wash the precipitate on the filter with dilute acetic acid (4.5) and then three times with hot water.

Dry in a drying oven (5.2) at 130 ± 2 °C until constant weight is achieved.

8. EXPRESSION OF THE RESULTS

1 mg of Co $(C_{10}H_6ONO)_3$, $2H_2O$ precipitate corresponds to 0,096381 mg Co.

The percentage of Cobalt (Co) in the fertilizer is given by :

$$Co\ (\%) = X \times 0{,}0096381 \times \frac{V \times D}{a \times M}$$

where :

X is the mass in mg of the precipitate ;

V is the volume in ml of the extract solution obtained in accordance with Method 10.1 or Method 10.2 ;

a is the volume in ml of the aliquot taken from the last dilution ;

D is the dilution factor of this aliquot ;

M is the mass in g of the test sample.

Method 10.7

DETERMINATION OF COPPER IN FERTILIZER EXTRACTS BY THE TITRIMETRIC METHOD

1. SCOPE

This document defines a procedure for determining copper in fertilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertlizers obtained by Method 10.1 or Method 10.2 for which a declaration of copper content is required by Directive 89/530/EEC.

3. PRINCIPLE

The cupric ions are reduced in an acidic medium with potassium iodide :

$$2\ Cu^{++} + 4\ I^{-} \rightarrow 2\ CuI + I_2$$

The iodine released in this way is titrated with a standard sodium thiosulphate solution in the presence of starch as an indicator in accordance with :

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$$

4. REAGENTS

4.1, Nitric acid (HNO_3, p = 1,40 g/ml)

4.2. Urea $[(NH_2)_2\ C=0]$

4.3. Ammonium bifluoride (NH_4HF_2) solution 10 % w/v

Keep the solution in a plastic container.

4.4. Ammonium hydroxyde solution (1 + 1)

Mix 1 volume of ammonia (NH_4OH, p : 0,9 g/ml) with 1 volume of water.

4.5. Sodium thiosulphate standard solution

Dissolve 7,812 g of sodium thiosulphate pentahydrate ($NA_2S_2O_35H_2O$) with water in a 1 litre volumetric flask. This solution must be prepared so that 1 ml = 2 mg Cu. For stabilization, add several drops of chloroform. The solution must be kept in a glass container and protected from direct light.

4.6. Potassium iodide (KI)

4.7. Potassium thiocyanate (KSCN) solution (25 % w/v)

Keep this solution in a plastic flask.

4.8. Starch solution (about 0,5 %)

Place 2,5 g of starch in a 600 ml beaker. Add about 500 ml of water. Boil while stirring. Cool to ambient temperature. The solution has a short preservation period. Its preservation can be extended by adding about 10 mg of mercury iodide.

5. PREPARATION OF THE SOLUTION TO BE ANALYSED

Preparation of the copper solution

See Methods 10.1 and 10.2.

6. PROCEDURE

6.1. Preparation of the solution for titration

Place an aliquot portion of the solution containing not less than 20-40 mg Cu in a 500 ml Erlenmeyer flask.

Drive off any excess oxygen present by boiling briefly. Make up to a volume af about 100 ml water. Add 5 ml of nitric acid (4.1), bring to boiling and allow to boil for about half a minute.

Remove the Erlenmeyer flask from the heating apparatus, add about 3 g of urea (4.2) and resume boiling for about half a minute.

Remove from the heating apparatus and add 200 ml of cold water. Where necessary, cool the contents of the Erlenmeyer flask to ambient temperature.

Gradually add ammonia hydroxide solution (4.4) until the solution becomes blue, then add 1 ml in excess.

Add 50 ml of ammonium bifluoride solution (4.3) and mix.

Add 10 g of potassium iodide (4.6) and dissolve.

6.2. Titration of the solution

Place the Erlenmeyer flask on a magnetic stirrer. Insert the rod into the Erlenmeyer flask and adjust the stirrer to the desired speed.

Using a burette, add standard sodium thiosulphate solution (4.5) until the brown colour of the iodine released from the solution becomes less intense.

Add 10 ml of the starch solution (4.8).

Continue to titrate with the sodium thiosulphate solution (4.5) until the purple colour has almost disappeared.

Add 20 ml of the potassium thiocyanate solution (4.7) and continue titration until the violet blue colour has completely disappeared.

Note the volume for thiosulphate solution employed.

7. EXPRESSION OF RESULTS

1 ml of standard sodium thiosulphate solution (4.5) corresponds to 2 mg Cu.

The percentage of copper in the fertilizer is given by:

$$\text{Cu (\%)} = X \quad \frac{V}{a \times M \times 5}$$

where:

X is the volume in ml of the sodium thiosulphate solution used;

V is the volume in ml of the extract solution in accordance with Methods 10.1 and 10.2;

a is the volume in ml of the aliquot portion;

M is the mass in g of the test sample treated in accordance with Methods 10.1 and 10.2.

Method 10.8

DETERMINATION OF IRON IN FERTILIZER EXTRACTS BY ATOMIC ABSORPTION SPECTROMETRY

1. SCOPE

This method describes a procedure for determining iron in fertilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of total and/or water-soluble iron is required by Directive 89/530/EEC.

3. PRINCIPLE

After suitable treatment and dilution of the extract, the iron content is determined by atomic absorption spectrometry.

4. REAGENTS

4.1. Hydrochloric acid solution, about 6 M

See Method 10.4, (4.1).

4.2. Hydrochloric acid solution, about 0,5 M

See Method 10.4, (4.2).

4.3 Hydrogen peroxide solution (30 % H_2O_2, d = 1,11 g/ml) free from trace elements

4.4. Lanthanum salt solutions (10 g of La per litre)

See Method 10.4, (4.3).

4.5. Iron calibration solution

4.5.1. Iron stock solution (1 000 µg/ml)

In a 500 ml beaker, weigh to the nearest 0,1 mg, 1 g of pure iron wire, add 200 ml of 6 M hydrochloric acid (4.1) and 15 ml of hydrogen peroxide solution (4.3). Heat on a hotplate until the iron is completely dissolved. When cool, transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.

4.5.2. Iron working solution (100 µg/ml)

Place 20 ml of the stock solution (4.5.1) in a 200 ml volumetric flask. Make up to volume with the 0,5 M hydrochloric acid solution (4.2) and mix thoroughly.

5. APPARATUS

Atomic absorption spectrometer : see Method 10.4, (5). The instrument must be fitted with a source of rays characteristic of iron (248,3 nm).

6. PREPARATION OF THE SOLUTION TO BE ANALYSED

6.1. Iron extract solution

See Methods 10.1 and/or 10.2 and, if appropriate, 10.3.

6.2. reparation of the test solution

See Method 10.4, (6.2). The test solution must contain 10 % (v/v) of a lanthanum salt solution.

7. PROCEDURE

7.1. Preparation of blank solution

See Method 10.4 (7.1). The blank solution must contain 10 % (v/v) of the lanthanum salt solution used in 6.2.

7.2. Preparation of calibration solutions

See Method 10.4, (7.2).

For an optimum determination range of 0 to 10 µg/ml of iron, place 0, 2, 4, 6, 8 and 10 ml respectively of working solution (4.5.2) in a series of 100 ml volumetric flasks. If necessary adjust the hydrochloric acid concentration as closely as possible to that of the test solution. Add 10 ml of the lanthanum salt solution used in 6.2. Make up to volume with 0,5 M hydrochloric acid solution (4.2) and mix thoroughly. These solutions contain 0, 2, 4, 6, 8 and 10 µg/ml respectively of iron.

7.3. Determination

See Method 10.4, (7.3). Prepare the spectrometer (5) for measurement at a wavelength of 248,3 nm.

8. EXPRESSION OF RESULTS

See Method 10.4, (8).

The percentage of iron in the fertilizer is given by :

$$Fe\ (\%) = [(X_s - X_b) \times V \times D] / (M \times 10^4)$$

If Method 10.3 is used :

$$FE\ (\%) = [(X_s - X_b) \times V \times 2D] / (M \times 10^4)$$

where :

Fe is the quantity of iron expressed as a percentage of the fertilizer ;

X_s is the concentration in µg/ml of the test solution (6.2) ;

X_b is the concentration in µg-ml of the blank solution (7.1) ;

V is the volume in ml of extract obtained in accordance with Method 10.1 or 10.2 ;

D is the factor of the dilution carried oujt in 6.2 ;

M is the mass in grams of the test sample taken in accordance with Method 10.1 or 10.2.

Calculation of the dilution factor D : if (a_1), (a_2), (a_3), . . ., (ai) and (a) are aliquot portions and (v_1) (v_2) (v_3), . . ., (v_i) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D is given by :

$$D = (v_1/a_1) \times (v_2/a_2) \times (v_3/a_3) \times \ldots \times (v_i/a_i) \times (100/a)$$

Method 10.9

DETERMINATION OF MANGANESE IN FERTILIZER EXTRACTS BY TITRATION

1. SCOPE

This method describes a procedure for determining manganese in fertilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of manganese is required by Directive 89/530/EEC.

3. PRINCIPLE

If chloride ions are present in the extract, they are driven off by boiling the extract 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

4.1. Concentrated sulfuric acid (H_2SO_4, ρ = 1.84 g/ml)

4.2. Sulfuric acid, about 9 M

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

4.3. Nitric acid, 6 M

Mix 3 volumes of nitric acid (HNO_3, ρ = 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 ($NaBiO_3$) (85 %)

4.6. Kieselguhr

4.7. Orthophosphoric acid, 15 M (H_3PO_4, ρ = 1,71 g/ml)

4.8. Ferrous sulphate solution, 0,15 M

Dissolve 41,6 g of ferrous sulphate heptahydrate ($FeSO_4$, $7H_2O$) in a 1-litre volumetric flask.

Add 25 ml of concentrated sulphuric acid (4.1) and 25 ml phosphoric acid (4.7). Make up to 1 000 ml. Mix.

4.9. Potassium permanganate solution, 0,020 M

Weigh out 3,160 g of potassium permanganate ($KMnO_4$) to within 0,1 mg. Dissolve and make up to 1 000 ml with water.

4.10. Silver nitrate solution, 0,1 M

Dissolve 1,7 g of silver nitrate ($AgNO_3$) in water and make up to 100 ml.

5. APPARATUS

5.1. Filter crucible P16/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

6.1. Manganese extract solution

See Methods 10.1 and 10.2. 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 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 sulphuric acid (4.1).

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

Place an aliquot of the extract containing 10 to 20 mg of manganese in a tall form 400 ml beaker. Add 5 ml of 9 M sulphuric acid (4.2.). Under a fume hood, bring to boiling on a hot-plate 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 sulphuric acid (4.2).

7. PROCEDURE

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 serveral 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 sulphate solution (4.8). If the filtrate turns yellow after the addition of ferrous sulphate, add 3 ml of 15 M orthophosphoric acid (4.7).

Using a burette, titrate the excess ferrous sulphate 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.

8. EXPRESSION OF RESULTS

1 ml of 0,02 M potassium permanganate solution corresponds to 1,099 mg of manganese (Mn)

The percentage of manganese in the fertilizer is given by:

$$M_n\ (\%) \text{ where } = (X_b - X_s) \times 0{,}1099 \times \frac{V}{a \times M}$$

where:

X_b is the volume in ml of the permanganate used for the blank;

X_s 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 10.1 and 10.2;

a is the volume in ml of the aliquot portion taken from the extract;

M is the mass in g of the test sample.

Method 10.10

DETERMINATION OF MOLYBDENUM IN FERTILIZER EXTRACTS BY THE GRAVIMETRIC METHOD WITH 8-HYDROXYQUINOLINE

1. SCOPE

This document describes a procedure for determining molybdenum in ferilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertilizers obtained by Method 10.1 and 10.2 for which a declaration of molybdenum is required by Directive 89/530/EEC.

3. PRINCIPLE

The molybdenum level is determined by precipitation as molybdenyl oxinate under specific conditions.

4. REAGENTS

4.1. Sulphuric acid solution, approximately 1 M

Carefully pour 55 ml of sulphuric acid (H_2SO_4, ρ = 1,84 g/ml) into a 1-litre volumetric flask containing 800 ml of water. Mix. After cooling, make up to one litre. Mix.

4.2. Diluted ammonia solution (1 : 3)

Mix 1 volume of concentrated ammonia solution (NH_4OH, ρ = 0,9 g/ml) with 3 volumes of water.

4.3. Diluted acetic acid solution (1 : 3)

Mix 1 volume of concentrated acetic acid (99,7 % CH_3COOH, ρ = 1,049 g/ml) with 3 volumes of water.

4.4. Solution of disodium salt of ethylene diamine tetraacetic acid (EDTA)

Dissolve 5 g of Na_2EDTA in water in a 100 ml volumetric flask. Make up to the calibration mark and mix.

4.5. Buffer solution

In a 100-ml volumetric flask dissolve 15 ml of concentrated acetic acid and 30 g of ammonium acetate in water. Make up to 100 ml.

4.6. 7-Hydroxyquinoline (oxine) solution

In a 100-ml volumetric flask dissolve 3 g of 8-hydroxyquinoline in 5 ml of concentrated acetic acid. Add 80 ml of water. Add the ammonia solution (4.2) drop by drop until the solution becomes cloudy and then add the acetic acid (4.3) until the solution becomes clear again.

Make up to 100 ml with water.

5. APPARATUS

5.1. Filter crucible P16/ISO4793, porosity 4, capacity 30 ml.

5.2. pH meter with glass electrode.

5.3. Drying oven at 130 to 135 °C.

6. PREPARATION OF THE SOLUTION TO BE ANALYSED

6.1. Preparation of the molybdenum solution. See Method 10.1 and Method 10.2.

7. PROCEDURE

7.1. Preparation of the test solution

Place an aliquot portion containing 25 to 100 mg Mo in a 250-ml beaker. Make up the volume to 50 ml with water.

Adjust this solution to pH of 5 by adding the sulfuric acid solution (4.1) drop by drop. Add 15 ml of EDTA solution (4.4) and then 5 ml of buffer solution (4.5). Make up to about 80 ml with water.

7.2. Obtaining and washing the precipitate

Obtaining the precipitate

Heat the solution slightly. Stirring constantly, add the oxine solution (4.6). Continue the precipitation until formation of a deposit is no longer observed. Add further reagent until the supernatant solution turns slightly yellow. A quantity of 20 ml should normally be sufficient. Continue to heat the precipitate slightly for two to three minutes.

Filtration and washing

Filter through a filter crucible (5.1). Rinse several times with 20 ml of hot water. The rinse water should gradually become colourless indicating that oxine is not longer present.

7.3. Weighing the precipitate

Dry the precipitate at 130 to 135 °C to constant weight (at last one hour)

Allow to cool in a desiccator and then weigh.

8. EXPRESSION OF THE RESULTS

1 mg of molybdenyl oxinate, $MoO_2(C_9H_6ON)_2$, corresponds to 0,2305 mg Mo.

The percentage of molybdenum in the fertilizer is given by:

$$Mo\ (\%) = X \times 0{,}02305 \times \frac{V \times D}{a \times M}$$

where:

X is the mass in mg of the molybdenyl oxinate precipitate;

V is the volume in ml of the extract solution in accordance with Methods 10.1 or 10.2;

a is the volume in ml of the aliquot taken from the last dilution;

D is the dilution factor of the aliquot;

M is the mass in g of the test sample.

Method 10.11

DETERMINATION OF ZINC IN FERTILIZER EXTRACTS BY ATOMIC ABSORPTION SPECTROMETRY

1. SCOPE

This method describes a procedure for determining zinc in fertilizer extracts.

2. FIELD OF APPLICATION

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of zinc is required by Directive 89/530/EEC.

3. PRINCIPLE

After suitable treatment and dilution of the extracts, the zinc level is determined by atomic absorption spectrometry.

4. REAGENTS

4.1. Hydrochloric acid solution, about 6 M

See Method 10.4, (4.1).

4.2. Hydrochloric acid solution, about 0.5 M

See Method 10.4, (4.2).

4.3. Lanthanum salt solutions (10 g of La per litre)

See Method 10.4, (4.3).

4.4. Zinc calibration solutions

4.4.1. Zinc stock solution (1 000 µg/ml)

In a 1 000 ml volumetric flask dissolve 1 g of zinc powder or flakes weighed to within 0,1 mg in 25 ml of 6 M hydrochloric acid (4.1). When completely dissolved, make up to volume with water and mix thoroughly.

4.4.2. Zinc working solution (100 µg/ml)

In a 200 ml volumetric flask, dilute 20 ml of the stock solution (4.4.1) in 0,5 M hydrochloric acid solution (4.2). Make up to a volume with the 0,5 M hydrochloric acid solution and mix thoroughly.

5. APPARATUS

Atomic absorption spectrometer

See Method 10.4, (5). The apparatus must be fitted with a source of lines characteristic of zinc (213,8 nm). The spectrometer must allow background correction to be made.

6. PREPARATION OF THE SOLUTION TO BE ANALYSED

6.1. Zinc extract solution

See Methods 10.1 and/or 10.2.

6.2. Preparation of the test solution

See Method 10.4, (6.2). The test solution must contain 10 % by volume of lanthanum salt solution (4.3).

PROCEDURE

7.1. Preparation of the blank solution.

See Method 10.4, (7.1). The blank solution must contain 10 % by volume of the lanthanum salt solution used in 6.2.

7.2. Preparation of the calibration solutions

See Method 10.4 (7.2). For an optimum interval of 0 to 5 µg/ml of zinc, place 0, 0,5, 1, 2, 3, 4 and 5 ml, respectively, of the working solution (4.4.2) in a series of 100 ml volumetric flasks. Where necessary, adjust the concentration of hydrochloric acid to bring it as close as possible to that of the test solution. Add 10 ml of the lanthanum salt solution used in (6.2) to each volumetric flask. Make up to 100 ml with the 0,5 M hydrochloric acid solution (4.2) and mix thoroughly.

These solutions contain, respectively: 0, 0,5, 1, 2, 3, 4 and 5 µg/ml of zinc.

7.3. Determination

See Method 10.4, (7.3). Prepare the spectrometer (5) for measurements at a wavelength of 213,8 nm.

8. EXPRESSION OF RESULTS

See Method 10.4 (8)

The percentage of zinc in the fertilizer is given by:

$$Zn\ (\%) = [(X_s - X_b) \times V \times D] / (M \times 10^4)$$

If method 10.3 has been used :

$$Zn\ (\%) = [(X_s - X_b) \times V \times 2D] / (M \times 10^4)$$

where :

Zn is the quantity of zinc expressed as a percentage of the fertilizer ;

X_s is the concentration in µg/ml of the test solution ;

X_b is the concentration in µg/ml of the blank solution ;

V is the volume in ml of the extract solution obtained in accordance with Method 10.1 or 10.2 ;

D is the factor corresponding to the dilution performed in (6.2) ;

M is the mass in g of the test sample taken in accordance with Method 10.1 or 10.2.

Calculation of the dilution factor D : where (a_1), (a_2), (a_3), . . .,. (a_i) and (a) are successive aliquot portions and (v_1), (v_2), (v_3), . . ., (v_i) and (100) are the volumes corresponding to their respective dillutions, the dilution factor D will be :

$$D = (v_1/a_1) \times (v_2/a_2) \times (v_3/a_3) \times \ldots \times (v_i/a_i) \times (100/a).'$$