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.