II

*(Acts whose publication is not obligatory)*

# COMMISSION

## COMMISSION DIRECTIVE 93/1/EEC

**of 21 January 1993**

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

**(Analysis methods for trace elements)**

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 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 is ensured;

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

Whereas Commission Directive 77/535/EEC (3), as last amended by Directive 89/519/EEC (4), provides for official controls for Community fertilizers for the purpose of checking compliance with the requirements imposed by Community provisions concerning the quality and composition of fertilizers; whereas Directive 77/535/EEC should be supplemented so that fertilizers to which Directive 89/530/EEC applies 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 to this Directive is hereby added to Annex II to Directive 77/535/EEC.

The methods are applicable to Community fertilizers for the determination of each trace element the declared content of which is less than or equal to 10 %.

*Article 2*

1. Member States shall bring into force the provisions necessary to comply with this Directive by 31 December 1993. They shall immediately inform the Commission thereof.

When Member States adopt these provisions, these 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.

(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 265, 12. 9. 1989, p. 30.

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, 21 January 1993.

*For the Commission*
Martin BANGEMANN
*Member of the Commission*

*ANNEX*

*'Methods 9*

## TRACE ELEMENTS

*Method 9.1*

### 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 extract to determine the total level of each of the trace elements listed above.

2. FIELD OF APPLICATION

This procedure concerns EEC fertilizers covered by Council Directive 89/530/EEC (1) 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 less than or equal to 10 %.

3. PRINCIPLE

Dissolution in boiling dilute 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. Dilute hydrochloric acid (HCl) solution, about 6 M:

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

4.2. Concentrated ammonia solution ($NH_4OH$, $\rho$ = 0,9 g/ml)

5. APPARATUS

Electric hotplate with variable temperature control.

*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, OJ No L 213, 22. 8. 1977, p. 1).

7. PROCEDURE

7.1. Test sample

Take a quantity of fertilizer weighing between 2 and 10 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 range for each method. Samples should be weighed to within 1 mg.

| Declared content of trace element in the fertilizer (%) | < 0,01 | 0,01- < 5 | ≥ 5-10 |
|---|---|---|---|
| Mass of test sample (g) | 10 | 5 | 2 |
| Mass of element in the sample (mg) | 1 | 0,5-250 | 100-200 |
| Volume of extract V (ml) | 250 | 500 | 500 |
| Concentration of element in extract (mg/l) | 4 | 1-500 | 200-400 |

Place the sample in a 250 ml beaker.

(1) OJ No L 281, 30. 9. 1989, p. 116.

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 250 or 500 ml volumetric flask (see Table). 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.

*Remark:* Extracts in which the boron content has to be determined: Adjust the pH to between 4 and 6 with concentrated ammonia (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.

If necessary, remove organic chelating or complexing substances from an aliquot portion of the extract by using Method 9.3. In the case of determination by atomic absorption spectrometry, such removal may not be necessary.

*Method 9.2*

## 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 trace elements listed above.

2. FIELD OF APPLICATION

This procedure concerns EEC 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 less than or equal to 10 %.

3. PRINCIPLE

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

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

4. REAGENTS

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

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

5. APPARATUS

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

5.2. pH-meter.

*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, (OJ No L 213, 22. 8. 1977, P. 1)).

7. PROCEDURE

7.1. Test sample

Take a quantity of fertilizer weighing between 2 and 10 g depending on the declared content of the element in the product. The following table shall be used to obtain a 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 (%) | < 0,01 | 0,01 - < 5 | ≥ 5-10 |
|---|---|---|---|
| Mass of test sample (g) | 10 | 5 | 2 |
| Mass of element in the test sample (mg) | 1 | 0,5-250 | 100-200 |
| Volume of extract V (ml) | 250 | 500 | 500 |
| Concentration of element in extract (mg/l) | 4 | 1-500 | 200-400 |

Place the sample in a 250 or 500 ml flask (according to the Table).

7.2. Preparation of the solution

Add about 200 ml of water to the 250 ml flask or 400 ml of water to the 500 ml flask.

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.

*NB:* 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 which has previously been dried and has received 5,00 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:

$$V = Ve \times W / (W - 5).$$

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.

If necessary, remove organic chelating or complexing substances from an aliquot portion by using Method 9.3. In the case of determination by atomic absorption spectrometry, such removal may not be necessary.

*Method 9.3*

## 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 9.1 and 9.2 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.