BRITISH STANDARD

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Fertilizers and liming materials — Determination of carbon dioxide

Part 1: Method for solid fertilizers

ICS 65.080

British Standards

National foreword

This British Standard is the UK implementation of EN 14397-1:2010.

The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Engrais et amendements minéraux basiques - Détermination de la teneur en dioxyde de carbone - Partie 1: Méthode applicable aux engrais solides

Düngemittel und Calcium-/Magnesium-Bodenverbesserungsmittel - Bestimmung von Kohlenstoffdioxid - Teil 1: Verfahren für feste Düngemittel

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Foreword

This document (EN 14397-1:2010) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2010, and conflicting national standards shall be withdrawn at the latest by September 2010.

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This document supersedes CEN/TS 14397-1:2004.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

The following text has been added to the former edition of the European Standard:

a) Clause 9 "Precision";

b) Annex A "Results of the inter-laboratory tests".

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This document specifies a method for the determination of carbon dioxide in solid fertilizers.

The method applies to all fertilizers that contain carbonates and/or bicarbonates.

NOTE If the fertilizer contains any other substances that release carbon dioxide on treatment with phosphoric acid, this will also be determined and expressed as carbon dioxide.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Principle

The carbon dioxide is liberated by treatment with phosphoric acid and absorbed in a solution of barium hydroxide. Barium carbonate precipitates and the excess barium hydroxide is back-titrated with hydrochloric acid.

4 Reagents

Use only reagents of recognized analytical grade.

4.1 Water, conforming to EN ISO 3696:1995, grade 3.

Boil the water immediately before use, to drive off any dissolved carbon dioxide.

4.2 Nitrogen, with a low content of carbon dioxide and organic impurities.

4.3 Hydrochloric acid, standard volumetric solution, $c(HCl) = 0{,}1$ mol/l.

4.4 Barium hydroxide, standard volumetric solution, $c(Ba(OH)_2) = 0{,}05$ mol/l approximately.

Standardize the barium hydroxide solution by titrating against the hydrochloric acid solution (4.3), using the phenolphthalein solution (4.6) as indicator.

NOTE The barium hydroxide solution should be stored so that absorption of carbon dioxide from the atmosphere is not possible (see Figure 1).

4.5 Phosphoric acid, with a volume concentration of $\varphi = 500$ ml/l.

4.6 Phenolphthalein solution.

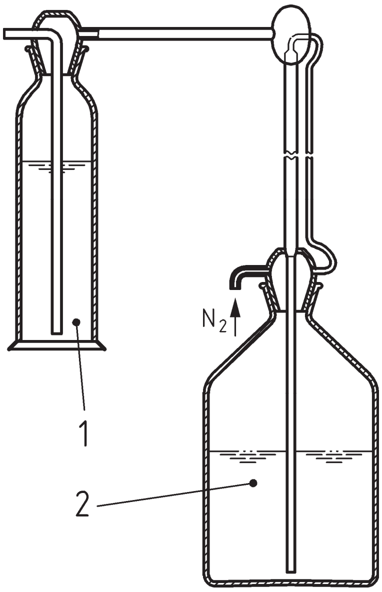
5 Apparatus

Usual laboratory apparatus and the following are required.

5.1 **Analytical balance,** capable of weighing to an accuracy of 0,1 mg.

5.2 **Laboratory grinder or mortar and pestle**.

5.3 **Burette,** for barium hydroxide solution (see Figure 1).



Key

1 reservoir and burette
2 washing flask, 250 ml, filled with soda lime pellets and indicator

Figure 1 — Burette for barium hydroxide solution

5.4 **Glassware assembly,** as shown in Figure 2, comprising the following:

a) flow meter for nitrogen (1);

b) pressure relief tube with 850 mm water column (2);

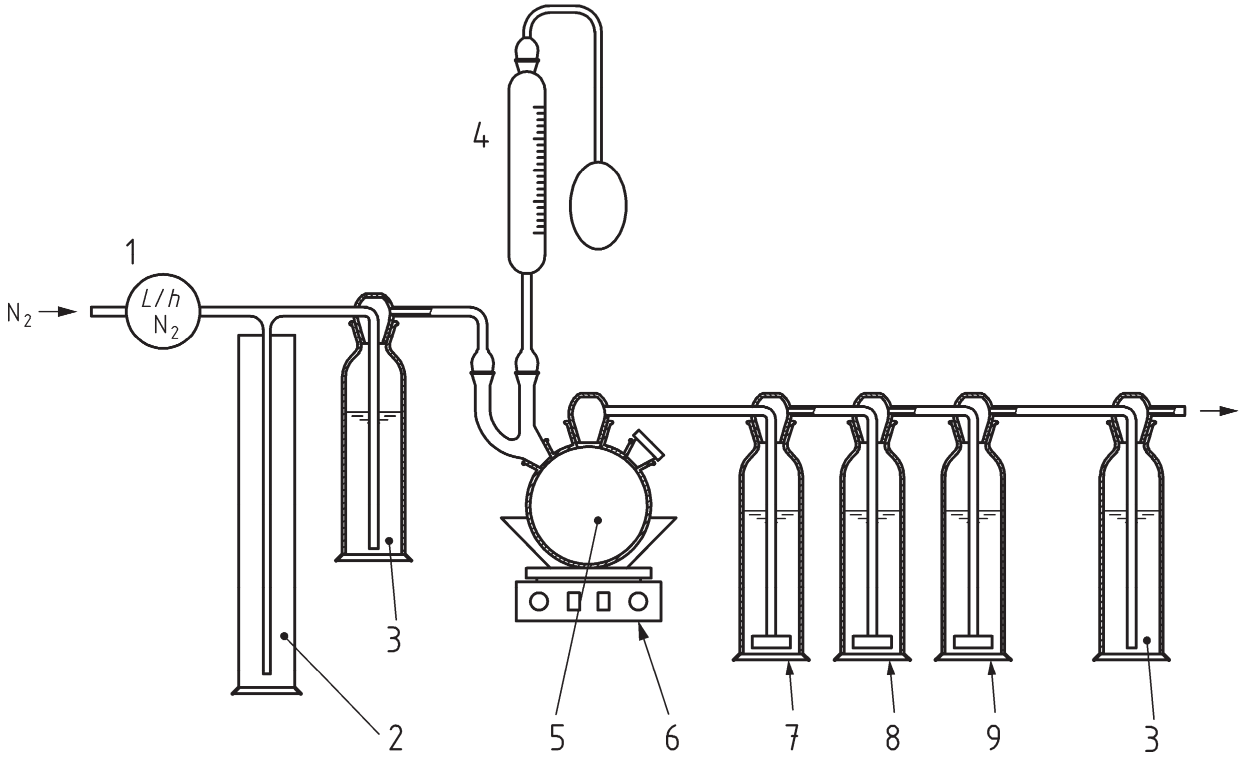
c) washing flasks with 250 ml capacity, filled with soda lime pellets and indicator (3);

d) 500 ml reservoir for phosphoric acid with rubber ball used as acid dosing unit (4);

e) round-bottom, three-necked reaction flask fitted with a splash head (5);

f) three absorption vessels, each of 250 ml capacity, with fritted glass tubes to ensure full absorption of the liberated carbon dioxide (7), (8), (9).

The frit in the first vessel (7) should be coarse enough to avoid blockage during the absorption. Alternatively, the frit may be replaced by a mushroom bubbler with small holes.



Key

1	flow meter for nitrogen
2	pressure relief tube
3	washing flasks
4	500 ml reservoir for phosphoric acid with rubber ball
5	three-necked reaction flask fitted with a splash head
6	hot plate (with magnetic stirrer and oil bath)
7,8,9	absorption vessels with fritted glass tubes

Figure 2 — Apparatus for carbon dioxide absorption

5.5 Weighing boat.

5.6 Hot plate, see (6) in Figure 2.

6 Sampling and sample preparation

Sampling is not part of the method specified in this document. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2. Prepare the sample to obtain a laboratory sample of at least 100 g. Grind the laboratory sample to give a test sample with a particle size of less than 200 µm and mix thoroughly.

7 Procedure

SAFETY PRECAUTIONS — Appropriate precautions should be taken to avoid harmful compounds, which can be given off during the phosphoric acid treatment, from getting into the laboratory atmosphere.

7.1 Test portion

Weigh in the weighing boat (5.5), to the nearest 0,1 mg, an amount of the test sample containing not more than 40 mg of carbon dioxide. As a guide, the test portion should be no more than 200 mg for calcium ammonium nitrate (CAN) and 90 mg for dolomite.

7.2 Determination

Carefully assemble the apparatus shown in Figure 2 ensuring there are no leaks. Purge the entire apparatus with nitrogen (4.2) for 30 min. Disconnect the three absorption vessels in the order (9), (8) and (7) whilst maintaining the nitrogen stream. Pipette into each vessel 50 ml of the barium hydroxide solution (4.4). Reconnect the vessels to the apparatus and purge for a further 5 min. Disconnect the bulb and flexible tube and add 20 ml of phosphoric acid solution (4.5) to the acid-dosing unit (4).

Introduce the test portion (7.1) to the round bottom three-necked reaction flask (5) through the stopper. Rinse the weighing boat and the neck of the stopper into the flask using 20 ml to 25 ml of water.

Reduce the nitrogen flow to five litre per hour. Create an overpressure in the reservoir with the rubber ball so that by opening the valve of the acid-dosing unit (4) the phosphoric acid passes to the round bottom reaction flask (5).

Start the magnetic stirrer and heat the contents of the round bottom reaction flask (5) by means of the hot plate (5.6) to boiling and boil gently for 2 h. Ensure that the temperature in the flask does not exceed 100 °C. Discontinue heating and disconnect the absorption vessels in the order (9), (8) and (7). Rinse the absorption vessels from above with water.

Slowly back-titrate the excess barium hydroxide in each absorption vessel with the hydrochloric acid (4.3) using the phenolphthalein solution (4.6) as indicator. Carry out the titration under nitrogen, to prevent absorption of carbon dioxide from the atmosphere.

NOTE Local excesses of hydrochloric acid should be avoided as these can dissolve some of the precipitated barium carbonate. Magnetic stirring during the titration helps to minimize the local excess of acid.

If the equivalent of more than 1 ml of barium hydroxide solution in absorption vessel (9) has been consumed by reaction with carbon dioxide, repeat the determination with a reduced flow of nitrogen.

7.3 Blank test

Carry out a blank test by the procedure described in 7.2 but omitting the test portion (7.1).

8 Expression of results

Calculate the mass fraction of carbon dioxide, w_{CO2}, expressed in grams of carbon dioxide per kilogram of fertilizer, using the following equation:

$$w_{\mathrm{CO_2}} = \frac{\left\{\left\{V_1 c_1 - \left(\frac{V_2 c_2}{2}\right)\right\} - \left\{V_{1,\mathrm{b}} c_1 - \left(\frac{V_{2,\mathrm{b}} c_2}{2}\right)\right\}\right\} \times 44 \times 1\,000}{m} \qquad (1)$$

where

V_1 is the volume, in millilitres, of barium hydroxide solution added to the three absorption vessels (150 ml);

V_2	is the total volume, in millilitres, of hydrochloric acid used in the back-titration;
c_1	is the amount-of-substance concentration, in moles per litre, of the barium hydroxide solution;
c_2	is the amount-of-substance concentration, in moles per litre, of the hydrochloric acid solution;
$V_{1,b}$	is the volume, in millilitres, barium hydroxide added to the three absorption vessels during the blank test;
$V_{2,b}$	is the total volume, in millilitres, of hydrochloric acid solution used in the back-titration during the blank test;
m	is the mass, in milligrams, of the test portion.

9 Precision

9.1 Inter-laboratory test

An inter-laboratory test was carried out in 2002 with 8 participating laboratories and five different samples of fertilizers and phosphate types. This test yielded the data given in Annex A. Repeatability and reproducibility were calculated according to ISO 5725-2.

The values derived from this inter-laboratory test might not be applicable to concentration ranges and matrices other than those given in Annex A.

9.2 Repeatability

The absolute difference between two independent single test results, obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will exceed, in not more than 5 % of the cases, the values of r given in Table 1.

9.3 Reproducibility

The absolute difference between two single test results, obtained with the same method on identical test material in different laboratories by different operators using different equipment, will exceed, in not more than 5 % of the cases, the values of R given in Table 1.

Table 1 — Mean values, repeatability and reproducibility limits

Sample	$\bar{x}$ %	r %	R %
CAN	8,0	0,8	1,4
Dolomite	40,4	1,7	9,3
Nitromag	15,6	0,8	2,3
NK	10,4	0,9	1,8
NPK	4,01	0,44	0,61

10 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this European Standard;

c) test results obtained expressed in grams of carbon dioxide per kilogram of fertilizer;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this European Standard, or regarded as optional, together with details of any incidents occurred when performing the method which might have influenced the test result(s).

Annex A
(informative)

Results of the inter-laboratory tests

The precision of the method was established in 2002 by Task Force 1 “Carbon dioxide” of CEN/TC 260 “Fertilizers and liming materials” in an inter-laboratory test evaluated in accordance with ISO 5725-2. The statistical results are given in Table A.1.

Table A.1 — Statistical results of the inter-laboratory test

Parameter	**Sample**				
	CAN	Dolomite	Nitromag	NK	NPK
Number of participating laboratories	8	8	8	8	8
Number of laboratories after elimination of outliers (accepted test results)	7	6	6	6	6
Mean value $\bar{x}$ (%)	8,0	40,4	15,6	10,4	4,01
Repeatability standard deviation s_r (%)	0,3	0,6	0,3	0,3	0,16
RSD_r (%)	3,0	1,5	1,8	3,0	4,0
Repeatability limit r (%)	0,8	1,7	0,8	0,9	0,44
Reproducibility standard deviation s_R (%)	0,5	3,3	0,8	0,6	0,22
RSD_R (%)	6,0	8,2	5,3	6,0	5,0
Reproducibility limit R (%)	1,4	9,3	2,3	1,8	0,61

Bibliography

[1] Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers, Official Journal L 304, 21/11/2003 P. 1-194

[2] EN 1482-1, *Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling*

[3] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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