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Fertilizers — Manganimetric determination of extracted calcium following precipitation in the form of oxalate

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National foreword

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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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Fertilizers - Manganimetric determination of extracted calcium following precipitation in the form of oxalate

Engrais - Dosage manganimétrique du calcium extrait après précipitation sous forme d'oxalate

Düngemittel - Manganometrische Bestimmung von Calcium nach Oxalatfällung

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Management Centre: Avenue Marnix 17, B-1000 Brussels

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Contents

Page

Foreword

This document (EN 16196:2012) 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of an identical text or by endorsement, at the latest by May 2013, and conflicting national standards shall be withdrawn at the latest by May 2013.

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The following changes have been made to the former edition:

a) the CEN Technical Specification has been adopted as a European Standard;

b) the document has been editorially revised.

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1 Scope

This European Standard specifies a manganimetric method for the determination of the calcium content in fertilizer extracts.

This method is applicable to EC fertilizers for which a declaration of the total and/or water-soluble calcium content is provided for in Regulation (EC) No 2003/2003, Annex I [3].

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 12944-1:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 1: General terms*

EN 12944-2:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 2: Terms relating to fertilizers*

EN 15960, *Fertilizers — Extraction of total calcium, total magnesium, total sodium and total sulfur in the forms of sulfates*

EN 15961, *Fertilizers — Extraction of water soluble calcium, magnesium, sodium and sulfur in the form of sulfates*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1:1999 and EN 12944-2:1999 apply.

4 Sampling

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. Grinding of the laboratory sample is recommended for homogeneity reasons.

5 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.

6 Reagents

6.1 Diluted hydrochloric acid, one volume of hydrochloric acid, ρ = 1,18g/ml, and one volume of water.

6.2 Sulfuric acid, 1:10 diluted, one volume of sulfuric acid, ρ = 1,84 g/ml, in ten volumes of water.

6.3 Ammonia solution, 1:1 diluted, one volume of ammonia, ρ = 0,88 g/ml, and one volume of water.

6.4 Ammonia oxalate, [$(NH_4)_2\ C_2O_4\ H_2O$], saturated solution at ambient temperature, approximately ρ = 40 g/l.

6.5 Citric acid solution, 30 % (mass concentration).

6.6 Ammonium chloride solution, 5 % (mass concentration).

6.7 Solution of bromothymol blue in ethanol, at 95 %, 0,1 % (mass concentration).

6.8 Solution of bromocresol green in ethanol, at 95 %, 0,04 % (mass concentration).

6.9 Standard solution of potassium permanganate, c = 0,02 mol/l.

7 Apparatus

7.1 Filter crucible, with 5 µm to 20 µm porosity sintered glass.

7.2 Hot water bath.

7.3 400 ml beaker.

8 Preparation of the test portion

Using a pipette, take an aliquot portion of the extraction solution obtained according to EN 15960 or EN 15961, containing between 15 mg and 50 mg of Ca (= 21 mg to 70 mg of CaO). The volume of this aliquot is v_2. Pour into a beaker (7.3). If necessary, neutralise, turning of indicator (6.7) from green to blue, with a few drops of the ammonia solution (6.3).

Add 1 ml of the citric acid solution (6.5) and 5 ml of ammonium chloride solution (6.6).

9 Procedure

9.1 Preparation of the calcium oxalate

Add approximately 100 ml of water. Bring to the boil, add eight to ten drops of indicator solution (6.8) and, slowly, 50 ml of a hot ammonium oxalate solution (6.4). If a precipitate forms, dissolve by adding a few drops of hydrochloric acid (6.1). Neutralise very slowly with ammonia solution (6.3) while stirring continuously to a pH of 4,4 to 4,6, turning of indicator (6.8) from green to blue. Place the beaker in a boiling hot water bath (7.2) for approximately 30 min.

Remove the beaker from the bath, leave standing for 1 h and filter through the crucible (7.1).

9.2 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 beaker (7.3) and dissolve the precipitate with 50 ml of hot sulfuric acid (6.2). Add water to the beaker in order to obtain a volume of approximately 100 ml. Bring to a temperature of 70 °C to 80 °C and titrate drop by drop with a permanganate solution (6.9) until the pink colour lasts for a minute. This volume is v.

10 Calculation and expression of the result

Calculate the calcium (Ca) content, w_{Ca}, in percent of the fertilizer analysed according to Formula (1).

$$w_{Ca} = v \times 0{,}200\,4 \times \frac{t}{0{,}02} \times \frac{v_1}{v_2 \times m} \quad (1)$$

where

v is the volume of permanganate used, in millilitres;

m is the mass of the test portion, in grams;

v_2 is the aliquot volume, in millilitres;

v_1 is the volume of the extraction solution, in millilitres;

t is the substance concentration of the permanganate solution in moles per litre.

CaO (%) = Ca (%) × 1,400

11 Precision

11.1 Inter-laboratory test

Repeated inter-laboratory tests have been carried out in 2007 and 2009 with different numbers of participating laboratories and several different samples (see Table A.1 to Table A.4). Repeatability and reproducibility were calculated according to ISO 5725-2.

The values derived from these inter-laboratory tests may not be applicable to concentration ranges and matrices other than those given in Annex A.

11.2 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 in not more than 5 % of the cases exceed the values of r given in Table 1 and Table 2.

11.3 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 in not more than 5 % of the cases exceed values of R given in Table 1 and Table 2.

Table 1 — Results ring test 2007

Sample	Extraction method	$\bar{x}$ %	r %	R %
CAN	EN 15960	6,39	0,19	1,13
	EN 15961	2,49	0,38	1,85
NPK1:23-4-13+7SO3	EN 15960	0,51	0,08	0,43
	EN 15961	0,36	0,07	0,31
NPK2:12-11-18+2+8	EN 15960	3,49	0,15	1,20
	EN 15961	0,53	0,10	0,49

Table 2 — Results ring test 2009

Sample	Extraction method	$\bar{x}$ %	r %	R %
CAN	EN 15960	6,20	0,25	1,2
	EN 15961	2,61	0,19	4,05
NPK:12-12-17S+2	EN 15960	5,80	0,13	0,74
	EN 15961	3,52	0,27	3,93

12 Test report

The test report shall contain at least the following information:

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

b) the test method used with reference to this document;

c) the method of preparation of the extraction solution (EN 15960 or EN 15961);

d) the test results obtained;

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

f) date when the analysis was finished;

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

h) all operating details not specified in this document, 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)

Statistical results of the inter-laboratory tests

The precision of the method was established in 2007 and in 2009 by Working Group 7 “Chemical analysis” of CEN/TC 260 “Fertilizers and liming materials” in several inter-laboratory tests evaluated in accordance with ISO 5725-2. The statistical results are given in Table A.1 to Table A.4.

Table A.1 — Statistical results of the inter-laboratory test in 2007 – Extraction method EN 15960

Parameter	Sample		
	CAN	NPK1:23-4-13+7SO3	NPK2:12-11-18+2+8
Number of participating laboratories	14	11	13
Number of laboratories after elimination of outliers (accepted test results)	12	11	13
Mean value $\bar{x}$ (%)	6,39	0,51	3,49
Repeatability standard deviation s_r (%)	0,07	0,03	0,06
RSD_r (%)	1,1	6,0	1,6
Repeatability limit r (%)	0,19	0,08	0,15
Reproducibility standard deviation s_R (%)	0,40	0,15	0,43
RSD_R (%)	6,3	30,0	12,3
Reproducibility limit R (%)	1,13	0,43	1,20

Table A.2 — Statistical results of the inter-laboratory test in 2007 – Extraction method EN 15961

Parameter	Sample		
	CAN	NPK1:23-4-13+7SO3	NPK2:12-11-18+2+8
Number of participating laboratories	14	10	12
Number of laboratories after elimination of outliers (accepted test results)	14	10	12
Mean value $\bar{x}$ (%)	2,49	0,36	0,53
Repeatability standard deviation s_r (%)	0,14	0,02	0,03
RSD_r (%)	5,0	6,0	7,0
Repeatability limit r (%)	0,38	0,07	0,10
Reproducibility standard deviation s_R (%)	0,66	0,11	0,18
RSD_R (%)	27,0	31,0	33,0
Reproducibility limit R (%)	1,85	0,31	0,49

Table A.3 — Statistical results of the inter-laboratory test in 2009 – Extraction method EN 15960

Parameter	Sample	
	CAN	NPK:12-12-17S+2
Number of participating laboratories	12	12
Number of laboratories after elimination of outliers (accepted test results)	12	10
Mean value $\bar{x}$ (%)	6,20	5,80
Repeatability standard deviation s_r (%)	0,09	0,05
RSD_r (%)	1,4	0,8
Repeatability limit r (%)	0,25	0,13
Reproducibility standard deviation s_R (%)	0,43	0,26
RSD_R (%)	6,9	4,5
Reproducibility limit R (%)	1,2	0,74

Table A.4 — Statistical results of the inter-laboratory test in 2009 – Extraction method EN 15961

Parameter	Sample	
	CAN	NPK:12-12-17S+2
Number of participating laboratories	12	12
Number of laboratories after elimination of outliers (accepted test results)	10	12
Mean value $\bar{x}$ (%)	2,61	3,52
Repeatability standard deviation s_r (%)	0,07	0,10
RSD_r (%)	3,0	3,0
Repeatability limit r (%)	0,19	0,27
Reproducibility standard deviation s_R (%)	1,45	1,40
RSD_R (%)	55,0	40,0
Reproducibility limit R (%)	4,05	3,93

Bibliography

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

[2] 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*

[3] *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. 0001-0194, Annex I and Annex IV, method 8.6

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