BS EN 16198:2012

BSI Standards Publication

Fertilizers — Determination of magnesium by complexometry

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 16198:2012. It supersedes DD CEN/TS 16198:2011, which is withdrawn.

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.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Published by BSI Standards Limited 2012.

ISBN 978 0 580 78186 5

ICS 65.080

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 December 2012.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16198

November 2012

ICS 65.080

Supersedes CEN/TS 16198:2011

English Version

Fertilizers - Determination of magnesium by complexometry

Engrais - Dosage du magnésium par complexométrie

Düngemittel - Komplexometrische Bestimmung von Magnesium

This European Standard was approved by CEN on 6 October 2012.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 16198:2012: E

Contents

Page

Foreword

This document (EN 16198:2012) 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TS 16198:2011.

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.

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

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

1 Scope

This European Standard specifies a method for the determination of magnesium in fertilizer extracts by complexometry.

The method is applicable to the following EC fertilizer extracts for which the determination of total magnesium and/or water-soluble magnesium is provided for according to the Regulation (EC) No 2003/2003, Annex I [3]:

— fertilizers listed in [3], Annex I: straight nitrogenous fertilizers, type 1b + 1c (calcium magnesium nitrate), type 7 (magnesium sulfonitrate), type 8 (nitrogenous fertilizers with magnesium) and straight potassic fertilizers, type 2 (enriched kainite), type 4 (potassium chloride containing magnesium), type 6 (potassium sulfate containing magnesium salt);

— fertilizers listed in [3], Annex I D relating to secondary nutrients.

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 Principle

The magnesium is solubilised according to EN 15960 or EN 15961. First titration: with EDTA of Ca and Mg in the presence of Eriochrome black-T. Second titration: with EDTA of Ca in the presence of calcein or of calcone carbonic acid. Determination of magnesium by difference.

5 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.

6 Reagents

6.1 Magnesium standard solution, c = 0,05 mol/l.

6.1.1 Dissolve 1,232 g of magnesium sulfate ($MgSO_4$ $7H_2O$) in the hydrochloric acid solution (6.11) and make up to 100 ml with the same acid,

or

6.1.2 Weigh 2,016 g of magnesium oxide, previously calcined to remove all traces of carbonation. Place it in a beaker with 100 ml of water.

Stir in approximately 120 ml of hydrochloric acid (6.12).

After dissolution, transfer quantitatively into a graduated 1 000 ml flask. Make up to volume and mix.

1 ml of these solutions should contain 1,216 mg of Mg (= 2,016 mg of MgO).

The laboratory is responsible for testing the strength of this standard solution.

6.2 EDTA solution, c = 0,05 mol/l.

Weigh 18,61 g of the dihydrated disodium salt of ethylenediaminetetraacetic (EDTA) ($C_{10}H_{14}N_2Na_2O_8,2H_2O$), place it in a beaker (7.4) and dissolve in 600 ml to 800 ml of water. Transfer the solution quantitatively into a graduated flask (7.3). Make up the volume and mix. Check this solution with the standard solution (6.1) by taking a sample of 20 ml of the latter and by titration according to the analytical procedure described in 9.2.

1 ml of the EDTA solution should correspond to 1,216 mg of Mg (= 2,016 mg of MgO) and to 2,004 mg of Ca (= 2,804 mg CaO) (see remarks 11.1 and 11.6).

6.3 Calcium standard solution, c = 0,05 mol/l.

Weigh 5,004 g of dry calcium carbonate. Place it in a beaker with 100 ml of water. Progressively stir in 120 ml of hydrochloric acid (6.12).

Bring to the boil in order to drive off the carbon dioxide, cool, transfer quantitatively into a graduated 1 l flask, make up the volume with water and mix. Check this solution against the EDTA solution (6.2) following analytical procedure (9.3). 1 ml of this solution should contain 2,004 mg of Ca (= 2,804 mg of CaO) and should correspond to 1 ml of the EDTA solution (6.2).

6.4 Calcein indicator.

Carefully mix in a mortar 1 g of calcein with 100 g of sodium chloride. Use 10 mg of this mixture. The indicator changes from green to orange. Titration shall be carried out until an orange is obtained which is free from green tinges.

6.5 Calcon carbonic acid indicator.

Dissolve 400 mg of calcon carbonic in 100 ml of methanol. This solution may only be kept for approximately four weeks. Use three drops of this solution. The indicator changes from red to blue. Titration shall be carried out until a blue is obtained which is free from red tinges.

6.6 Eriochrome black-T indicator.

Dissolve 300 mg of Eriochrome black-T in a mixture of 25 ml of propanol-1 and 15 ml of triethanolamine. This solution may only be kept for approximately four weeks. Use three drops of this solution. This indicator turns from red to blue and titration shall be carried out until a blue is obtained which is free from red tinges. It

changes colour only when magnesium is present. If necessary add 1 ml of the magnesium standard solution (6.1).

When both calcium and magnesium are present the EDTA first forms a complex with the calcium and then with the magnesium. In that case two elements are determined concurrently.

6.7 Potassium cyanide solution, aqueous solution of w(KCN) = 2 %.

SAFETY PRECAUTIONS — Do not pipette by mouth and see 11.7.

6.8 Solution of potassium hydroxide and potassium cyanide.

Dissolve 280 g of KOH and 66 g of KCN in water, make up the volume to 1 l and mix.

6.9 Buffer solution, pH = 10,5.

In a graduated flask (7.5), dissolve 33 g of ammonium chloride in 200 ml of water, add 250 ml of ammonia (ρ_{20} = 0,91 g/ml) make up the volume with water and mix. Check the pH of the solution regularly.

6.10 Diluted hydrochloric acid, one volume of hydrochloric acid (ρ_{20} = 1,18 g/ml) plus one volume of water.

6.11 Hydrochloric acid solution, approximately c = 0,5 mol/l.

6.12 Hydrochloric acid solution, approximately c = 1 mol/l.

6.13 Sodium hydroxide solution, c = 5 mol/l.

7 Apparatus

7.1 Magnetic or mechanical stirrer.

7.2 pH meter.

7.3 1 000 ml graduated flask.

7.4 1 000 ml beaker.

7.5 500 ml graduated flask.

7.6 400 ml beaker.

8 Preparation of the extraction solution

Prepare the extraction solution according to EN 15960 or EN 15961.

9 Procedure

9.1 Control test

Carry out a determination on aliquot parts of solutions (6.1 and 6.3) such that the Ca/Mg ratio is approximately equal to that of the solution to be analysed. To this end take v_1 ml of Ca standard solution (6.3) and (v_2-v_1) ml of standard solution (6.1), where v_1 and v_2 are the volumes, in millilitres, of the EDTA solution used in the two titrations performed on the solution to be analysed. This procedure is correct only if the solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make corrections.

9.2 Aliquot samples to be taken

The aliquot part will as far as possible contain between 9 mg and 18 mg of magnesium (= 15 mg to 30 mg of MgO).

9.3 Titration in the presence of Eriochrome black-T

Pipette an aliquot part (9.2) of the solution to be analysed into a beaker (7.6). Neutralise the surplus acid with the sodium hydroxide solution (6.13) using the pH meter. Dilute with water to approximately 100 ml. Add 5 ml of the buffer solution (6.9). The pH measured shall be 10,5 ± 0,1. Add 2 ml of the potassium cyanide solution (6.7) and three drops of the Eriochrome black-T indicator (6.6). Titrate with the EDTA solution (6.2). Stir gently with the stirrer (7.1) (see 11.2, 11.3 and 11.4). Take v_2 as the volume, in millilitres, of the EDTA solution (6.2).

9.4 Titration in the presence of calcein or of calcon carbonic acid

Pipette an aliquot part of the solution to be analysed equal to that taken from the above titration (9.3) and place it in a beaker (7.6). Neutralise the surplus acid with the sodium hydroxide solution (6.13) using the pH meter. Dilute with water to about 100 ml. Add 10 ml of the KOH/KCN solution (6.8) and the indicator (6.4 or 6.5). Stir gently with the stirrer (7.1) titrate with the EDTA solution (6.2) (see 11.2, 11.3 and 11.4). Take v_1 as the volume, in millilitres, of the EDTA solution (6.2).

10 Calculation and expression of the result

For the EEC fertilizers to which the method is applicable (5 g of fertilizer in 500 ml of extract), calculate the MgO content as a mass fraction, w_{MgO}, in percent of the fertilizer according to Formula (1).

$$w_{MgO} = \frac{(v_2 - v_1) \times T}{M} \quad (1)$$

For the EEC fertilizers to which the method is applicable (5 g of fertilizer in 500 ml of extract), calculate the Mg content as a mass fraction, w_{Mg}, in percent of the fertilizer according to Formula (2).

$$w_{Mg} = \frac{(v_2 - v_1) \times T'}{M} \quad (2)$$

where

v_1 is the volume of the EDTA solution (6.2), in millilitres, used for the titration in the presence of calcein or calcon carbonic acid;

v_2 is the volume of the EDTA solution (6.2), in millilitres, used for the titration in the presence of Eriochrome black-T;

M is the mass of the sample present in the aliquot part taken, in grams;

T is 0,201 6 × mol/l of the EDTA solution (6.2) 0,05;

T' is 0,121 6 × mol/l of the EDTA solution (6.2) 0,05.

11 Remarks

11.1 The stoichiometric EDTA-metal ratio in the complexometric analyses is always 1:1 whatever the valency of the metal and in spite of the fact that EDTA is quadrivalent. The EDTA titration solution and the standard solutions will therefore be molar and not normal.

11.2 Complexometric indicators are often sensitive to air. The solution may lose colour during titration. In this case, one or two drops of indicator shall be added. This is true particularly in the case of eriochrome black and calcon carbonic acid.

11.3 The metal-indicator complexes are often relatively stable and it may take some time for the colour to change. The last drops of EDTA shall therefore be added slowly and a drop of magnesium solution (6.1) or calcium solution (6.3) added to ensure that the colour change has not already taken place. This is particularly true in the case of the eriochrome-magnesium complex.

11.4 The turning of the indicator shall be observed not vertically, but horizontally across the solution and the beaker shall be placed against a white background in a well-lit position. The turning of the indicator may also be observed easily by placing the beaker on frosted glass lit moderately from below (25 W lamp).

11.5 This analysis requires a certain amount of experience. The task will involve, *inter alia*, observing the colour changes of standard solutions 6.1 and 6.3. It is recommended that the determinations be carried out by the same laboratory chemist.

11.6 If an EDTA solution of guaranteed strength is used (Titrisol, Normex, for example) this may simplify the control of the equivalence of standard solutions 6.1, 6.2 and 6.3.

11.7 The solutions containing potassium cyanide shall not be poured down the sink until the cyanide has been converted into a harmless compound, for example, by oxidisation with sodium hydrochloride following alkalisation.

12 Precision

12.1 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.

12.2 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.

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

Table 1 — Results ring test 2007

Sample	Extraction method	$\bar{x}$ %	r %	R %
CAN	EN 15960	4,80	0,13	0,51
	EN 15961	2,29	0,21	1,43
KALI ROH	EN 15960	6,28	0,25	0,58
	EN 15961	6,22	0,09	0,52
NPK2:12-11-18+2+8	EN 15960	3,46	0,26	0,51
	EN 15961	2,10	0,37	3,22

Table 2 — Results ring test 2009

Sample	Extraction method	$\bar{x}$ %	r %	R %
CAN-dol	EN 15960	4,61	0,18	0,55
	EN 15961	1,83	0,14	1,19
NPK:12-12-17S+2	EN 15960	1,90	0,15	0,57
	EN 15961	1,55	0,08	0,75

13 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 test

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	KALI ROH	NPK2:12-11-18+2+8
Number of participating laboratories	12	12	7
Number of laboratories after elimination of outliers (accepted test results)	10	11	6
Mean value $\bar{x}$ (%)	4,80	6,28	3,46
Repeatability standard deviation s_r (%)	0,05	0,09	0,09
RSD_r (%)	1,0	1,4	3,0
Repeatability limit r (%)	0,13	0,25	0,26
Reproducibility standard deviation s_R (%)	0,18	0,21	0,18
RSD_R (%)	3,8	3,3	5,0
Reproducibility limit R (%)	0,51	0,58	0,51

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

Parameter	Sample		
	CAN	KALI ROH	NPK2:12-11-18+2+8
Number of participating laboratories	9	12	7
Number of laboratories after elimination of outliers (accepted test results)	9	10	7
Mean value $\bar{x}$ (%)	2,29	6,22	2,10
Repeatability standard deviation s_r (%)	0,08	0,03	0,13
RSD_r (%)	3,0	0,5	6,0
Repeatability limit r (%)	0,21	0,09	0,37
Reproducibility standard deviation s_R (%)	0,51	0,19	1,15
RSD_R (%)	22,0	3,0	55,0
Reproducibility limit R (%)	1,43	0,52	3,22

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

Parameter	Sample	
	CAN-dol	NPK:12-12-17S+2
Number of participating laboratories	10	9
Number of laboratories after elimination of outliers (accepted test results)	9	9
Mean value $\bar{x}$ (%)	4,61	1,90
Repeatability standard deviation s_r (%)	0,06	0,05
RSD_r (%)	1,4	3,0
Repeatability limit r (%)	0,18	0,15
Reproducibility standard deviation s_R (%)	0,20	0,20
RSD_R (%)	4,3	11,0
Reproducibility limit R (%)	0,55	0,57

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

Parameter	Sample	
	CAN-dol	NPK:12-12-17S+2
Number of participating laboratories	10	9
Number of laboratories after elimination of outliers (accepted test results)	9	8
Mean value $\bar{x}$ (%)	1,83	1,55
Repeatability standard deviation s_r (%)	0,05	0,03
RSD_r (%)	3,0	1,8
Repeatability limit r (%)	0,14	0,08
Reproducibility standard deviation s_R (%)	0,42	0,27
RSD_R (%)	23,0	17,3
Reproducibility limit R (%)	1,19	0,75

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 8.8

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.

...making excellence a habit.™