SLOVENSKI STANDARD
SIST EN 14888:2005

01-december-2005

Gnojila in sredstva za apnjenje - Določ evanje kadmija

Fertilizers and liming materials - Determination of cadmium content

Düngemittel und Calcium-/Magnesium-Bodenverbesserungsmittel - Bestimmung des Cadmiumgehaltes

Engrais et amendements minéraux basiques - Dosage de la teneur en cadmium

Ta slovenski standard je istoveten z: **EN 14888:2005**

ICS:

65.080	Gnojila	Fertilizers

SIST EN 14888:2005	**en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 14888

August 2005

ICS 65.080

English version

Fertilizers and liming materials - Determination of cadmium content

Engrais et amendements minéraux basiques - Dosage du cadmium

Düngemittel und Calcium-/Magnesium-Bodenverbesserungsmittel - Bestimmung des Cadmiumgehaltes

This European Standard was approved by CEN on 27 June 2005.

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 Central Secretariat 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 Central Secretariat has the same status as the official versions.

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

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 14888:2005: E

Contents

Page

Foreword

This document (EN 14888:2005) 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of an identical text or by endorsement, at the latest by February 2006, and conflicting national standards shall be withdrawn at the latest by February 2006.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association to provide a means of conforming to Essential Requirements of the Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers.

Once this standard is cited in the Official Journal of the European Communities under that Regulation and has been implemented as a national standard in at least one Member State, compliance with the normative clauses of this standard confers, within the limits of the scope of this standard, a presumption of conformity with the relevant Essential Requirements of that Regulation and associated EFTA regulations.

WARNING — Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

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

Introduction

Because flame atomic absorption spectrometry (flame AAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) are widely used techniques for the determination of cadmium, both are described in this European Standard (as method A and method B respectively). Much of the procedure and many of the reagents are common to both methods.

1 Scope

This European Standard specifies two methods for the determination of the cadmium content, after extraction with nitric acid, of solid mineral fertilizers and rock phosphates. It is not applicable to organic and organo-mineral fertilizers. It is applicable to the determination of cadmium contents greater than 1 mg/kg.

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, *Sampling of solid fertilizers and liming materials*

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
limit of detection
smallest measured content from which it is possible to deduce the presence of the analyte with reasonable statistical certainty

NOTE The limit of detection is numerically equal to three times the standard deviation of the mean of blank determinations (n > 10, where n is the number of measurements).

3.2
limit of quantification
lowest content of the analyte which can be measured with reasonable statistical certainty

NOTE If both accuracy and precision are constant over a concentration range around the limit of detection, then the limit of quantification is numerically equal to ten times the standard deviation of the mean of blank determinations (n > 10, where n is the number of measurements).

4 Principle

The cadmium is extracted from the fertilizer by means of a nitric acid digestion. Its concentration is measured either by flame atomic absorption spectrometry (Flame-AAS) (Method A) or by inductively coupled plasma–optical emission spectrometry (ICP-OES) (Method B). Both methods are relative techniques. Cadmium concentrations are determined by the standard addition method.

5 Reagents

5.1 General

Use only reagents of recognized analytical grade, and water conforming to grade 2 of EN ISO 3696:1995.

Stock solutions shall be replaced after a maximum of one year, but the standard solution shall be renewed monthly as a minimum. If a stock solution is prepared directly from a metal, care needs to be taken to ensure that the metal used is free of surface oxide layers.

WARNING — Cadmium is highly toxic. It is essential that all necessary measures are taken to avoid ingestion.

5.2 Nitric acid, 65 %, ρ approximately 1,42 g/ml

5.3 Diluted nitric acid, diluted to a concentration of about 7 mol/l (1 + 1 volume fraction).

Mix 1 volume of nitric acid (5.2) with 1 volume of water.

5.4 Diluted nitric acid, diluted to a concentration of about 4,3 mol/l (1 + 3 volume fraction).

Mix 1 volume of nitric acid (5.2) with 3 volumes of water.

5.5 Diluted nitric acid, diluted to a concentration of 2 % (volume fraction).

Pipette 20,00 ml nitric acid (5.2) in a 1 000 ml volumetric flask and fill to the mark with water.

5.6 Cadmium stock solution, corresponding to 1 000 mg/l.

Weigh to the nearest 0,1 mg, approximately 1,000 g of metallic cadmium (minimum purity 99,5 %) and dilute in a covered 250 ml glass beaker with 40 ml of nitric acid (5.4). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1 000 ml volumetric flask and fill to the mark with water.

NOTE Cadmium stock solution of 1 000 mg/l is also readily available commercially, and may be used instead.

5.7 Cadmium standard solution, corresponding to 50 mg/l.

Pipette 50,00 ml of the cadmium stock solution (5.6) into a 1 000 ml volumetric flask and fill to the mark with the diluted 2 % nitric acid (5.5).

5.8 Cadmium standard solution, corresponding to 1 mg/l.

Pipette 20,00 ml of the cadmium standard solution (5.7) into a 1 000 ml volumetric flask and fill to the mark with the diluted 2 % nitric acid (5.5).

6 Apparatus

6.1 General

Ordinary laboratory glassware.

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

6.3 Laboratory grinder, capable of grinding to a particle size of less than or equal to 0,5 mm.

6.4 Electric hot plate, with temperature control.

6.5 Flame atomic absorption spectrometer

The instrument shall be equipped with a cadmium source, a background correction system and a burner suitable for an air/acetylene flame. It shall be operated according to the manufacturer's instructions.

6.6 Inductively coupled plasma – Optical emission spectrometer

The instrument shall be equipped with radial plasma as a minimum requirement; axial plasma is equally acceptable, as long as it can be shown that the results are statistically equal to the results obtained with radial plasma. Background correction shall also be performed. Settings of the working conditions (e.g. viewing height, gas flows, RF or plasma power, sample uptake rate, integration time, number of replicates) shall be optimized according the manufacturer's instructions.

7 Sampling and sample preparation

7.1 Sampling

Sampling shall be carried out in accordance with EN 1482.

7.2 Sample preparation

Grind the laboratory sample, using a grinder or mortar, until a particle size of 0,5 mm or less has been reached, and mix thoroughly for reasons of homogeneity.

The grinding shall be done in conditions such that the substance is not appreciably heated.

The operation is to be repeated as many times as is necessary and it shall be effected as quickly as possible in order to prevent any gain or loss of constituents (water, ammonia).

Place the whole ground sample in a flask which can be stoppered.

Before any weighing is carried out for the analysis, mix the whole sample thoroughly.

7.3 Special cases of grinding

Blended fertilizers: in this case, separation frequently occurs. It is therefore essential to grind to a particle size of 0,2 mm or less.

Products, that decompose on heating: grinding shall be carried out in such a way as to avoid any heating. It is preferable in this case to use a mortar for grinding.

8 Procedure

8.1 Preparation of the test solution

8.1.1 Digestion

Weigh to the nearest 0,1 mg an amount of test sample between 1 g and 12,5 g depending on the expected cadmium content (as specified in Table 1), into a beaker or reaction vessel.

Moisten the sample with a small amount of water. Add the appropriate amount of nitric acid (5.3), according to Table 1. Cover the beaker with a watch glass and boil gently for 30 min on a hot plate. In order to maintain the initial volume, add some more water during boiling if necessary. Cool, transfer to an appropriate volumetric flask and fill to the mark with water.

After homogenizing, filter through a dry filter into a dry container. Use the first portion of the filtrate to rinse the glassware and discard that part. If the determination is not carried out immediately, the container with the filtrate shall be stoppered.

The filtrate will be used for the preparation of the final test solution as well as for the preparation of the calibration solutions (8.3).

Table 1 — Preparation of the test portion

Expected (declared) content of cadmium in the fertilizer mg/kg	1 to 5	5 to 15	15 to 30	30 to 100
Mass of sample g	12,5	5	2,5	1
Volume of HNO_3 ml (5.3)	125	50	25	10
Total volume of extract ml	250	250	250	250
Concentration of cadmium in extract mg/l	0,05 to 0,25	0,10 to 0,30	0,15 to 0,30	0,12 to 0,40
NOTE Masses and volumes of the extracts are chosen such that the concentrations in the solutions to be measured are above the typical limits of quantification of flame AAS and ICP-OES, that the concentrations fall within their (linear) working area, and that salt concentrations are not too high.				

8.1.2 Test solution

Pipette 50,00 ml of the filtrate of the test portion (8.1.1) into a 100 ml volumetric flask and fill to the mark with the diluted 2 % nitric acid (5.5).

8.2 Preparation of the blank test solution

Carry out a blank test at the same time as the extraction, with only the reagents and follow the same procedure as before.

8.3 Preparation of the calibration solutions

Calibration shall be performed by means of the standard addition technique.

NOTE An (external) calibration curve method can also be used instead of the standard addition method where the analytical results are demonstrated to be statistically equal.

Appropriate matrix matching of the calibration solutions shall be performed if an (external) calibration method is used (see Annex B).

8.3.1 Addition 1

Pipette 50,00 ml of the filtrate of the test portion (8.1.1) into a 100 ml volumetric flask, add 2,00 ml of the cadmium standard solution of 1 mg/l (5.8), and fill to the mark with the diluted 2 % nitric acid (5.5).

8.3.2 Addition 2

Pipette 50,00 ml of the filtrate of the test portion (8.1.1) into a 100 ml volumetric flask, add 5,00 ml of the cadmium standard solution of 1 mg/l (5.8), and fill to the mark with the diluted 2 % nitric acid (5.5).

8.3.3 Addition 3

Pipette 50,00 ml of the filtrate of the test portion (8.1.1) into a 100 ml volumetric flask, add 10,00 ml of the cadmium standard solution of 1 mg/l (5.8), and fill to the mark with the diluted 2 % nitric acid (5.5).

8.4 Determination

8.4.1 General

Set up the instruments, used in method A and method B, according to the manufacturer's instructions using appropriate conditions, and with the suitable background correction system in operation.

For each instrument used, selectivity, limits of detection and quantification, precision, linear working area, and interference shall be established separately.

8.4.2 Method A – Determination by Flame-AAS

Aspirate the blank test solution (8.2), the test solution (8.1.2), and the various additions (8.3.1, 8.3.2, 8.3.3) in ascending order separately into the flame, and measure the absorbance of cadmium. Read the solutions at least twice. Average the values if the values fall within an accepted range. After each measurement, aspirate the blank and re-adjust the zero if necessary.