SLOVENSKI STANDARD
SIST EN 16319:2013

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Nadomešča:

SIST-TS CEN/TS 16319:2012

Gnojila - Določevanje elementov v sledovih - Določevanje kadmija, kroma, svinca in niklja z atomsko emisijsko spektrometrijo z induktivno sklopljeno plazmo (ICP-AES) po raztapljanju v zlatotopki

Fertilizers - Determination of trace elements - Determination of cadmium, chromium, lead and nickel by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after aqua regia dissolution

Düngemittel - Bestimmung von Elementspuren - Bestimmung von Cadmium, Chrom, Blei und Nickel mit Atomemissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP-AES) nach Königswasseraufschluss

Engrais - Dosage des éléments traces - Détermination du cadmium, chromium, plomb et nickel par spectrométrie d'émission atomique avec plasma induit par haute fréquence (ICP-AES) après digestion à l'eau régale

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65.080	Gnojila	Fertilizers

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English Version

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This European Standard was approved by CEN on 15 September 2013.

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (EN 16319:2013) 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of an identical text or by endorsement, at the latest by April 2014, and conflicting national standards shall be withdrawn at the latest by April 2014.

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 16319:2012.

The following changes have been made to the former edition:

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

— an explanation concerning possible interferences when using this method for the determination of Cd, Cr, Ni and Pb in micro-nutrient fertilizers has been added as a NOTE to Clause 1;

— 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 organizations 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 the content of cadmium, chromium, nickel and lead in fertilizers with inductively coupled plasma-atomic emission spectrometry (ICP-AES) after extraction with aqua regia. Limits of quantification are dependent on the sample matrix as well as on the instrument, but can roughly be expected to be 0,3 mg/kg for Cd and 1 mg/kg for Cr, Ni and Pb.

NOTE Due to significant interference from Cu, Fe and Mn, no valid results can be reported using this method for fertilizer matrices containing high concentrations (≥ 10 %) of these micro-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 ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

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

Cadmium, chromium, nickel and lead are extracted from the sample with aqua regia and conventional boiling. The concentrations in the extract are measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES), with axial or radial viewing.

5 Sampling and sample preparation

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

Sample preparation shall be carried out in accordance with EN 1482-2.

6 Reagents

Use only reagents of recognized analytical grade.

Commercially available stock solutions shall be replaced according to the specifications from the supplier or after one year if prepared in the laboratory from available salts. Standard solutions shall be renewed monthly as a general rule.

6.1 Water, conforming to grade 2 according to EN ISO 3696.

6.2 Hydrochloric acid, $c(HCl)$ = 12 mol/l; 37 % volume fraction; $\rho \approx$ 1,18 g/ml.

6.3 Nitric acid, $c(HNO_3)$ = 16 mol/l; not less than 65 % volume fraction; $\rho \approx$ 1,42 g/ml.

6.4 Mixed solution of 0,8 mol/l nitric acid and 1,8 mol/l hydrochloric acid.

Mix 150 ml of hydrochloric acid (6.2) and 50 ml nitric acid (6.3) to 1,0 l of water (6.1).

6.5 Standard stock solutions, cadmium, chromium, nickel and lead standard stock solutions, e.g. ρ = 1 000 mg/l for each element.

Use suitable stock solutions. Both single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available. It is recommended to use commercially available standard stock solutions for cadmium, chromium, nickel and lead.

6.6 Working standard solutions.

Depending on the scope, different working standard solutions may be necessary.

In general, when combining elements in working standard solutions, their chemical compatibility shall be regarded. Spectral interferences from other elements present in working standard solutions also need to be considered. Various combinations of elements at different concentrations may be used, provided that the standard stock solutions (6.5) are diluted with the same acid and in equal concentration as the acid in the test solution.

NOTE In equal concentrations (in mg/l), cadmium, chromium, nickel and lead are compatible in a multi-element standard solution for the determination by ICP-AES for this application.

6.6.1 Working standard solution I, ρ = 100 mg/l for cadmium, chromium, nickel and lead.

Dilute 10,0 ml of each standard stock solution of cadmium, chromium, nickel and lead (6.5) to 100,0 ml with the mixed acid solution (6.4) in the same 100 ml flask. If non-equal concentrations of cadmium, chromium, nickel and lead are needed, dilute the required volumes into 100,0 ml. This solution is used to prepare spiked test solutions and standard and calibration solutions.

6.6.2 Working standard solution II, ρ = 10 mg/l for cadmium, chromium, nickel and lead.

Dilute 10,0 ml of the working standard solution I of cadmium, chromium, nickel and lead (6.6.1) to 100,0 ml with the mixed acid solution (6.4) in a 100 ml flask. If non-equal concentrations of cadmium, chromium, nickel and lead are needed, dilute the require volume from the standard stock solutions (6.5) into 100,0 ml. This solution is used to prepare spiked test solutions and calibration solutions.

7 Apparatus

7.1 Common laboratory glassware.

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

7.3 Inductively coupled plasma-atomic emission spectrometer, with axial or radial viewing of the plasma and with suitable background correction.

The settings of the working conditions (e.g. gas flows, RF or plasma power, sample uptake rate, integration time and number of replicates) shall be optimized according to the manufacturer's instructions. Radial viewing of the plasma may be used if it can be shown that the limits of quantification for cadmium, chromium, nickel and lead are below the required legal limit values.

The use of axial orientation of the viewing optics requires good control of the matrix effects coming from "easily ionisable elements" (i.e. the influence of easily ionisable elements in varying concentrations on the signal intensities of the analytes).

For alkali-elements, this can be achieved by adding caesium-chloride solution (CsCl). In general, matrix matching of calibration solutions or calibration by standard additions with several calibration standards will correct accurately for these matrix effects. Spike recovery of one known standard combined with external calibration can, if used properly, also correct sufficiently for matrix effects (see 8.1). Correction by internal standardization is also a good option, but the accuracy of the measurements after internal standard correction should be validated properly prior to use on unknown fertilizer samples.

7.4 Dilutor.

Instrument used for automated volumetric dilutions or other appropriate equipment (e.g. pipettes and volumetric glassware) to perform dilutions. The precision and accuracy of this type of equipment for volumetric dilutions shall be established, and controlled and documented regularly.

7.5 Ash-free filter paper, i.e. Whatman® 589/2[1)] or equivalent quality.

8 Procedure

8.1 General

Calibrations by standard additions with several standards or by matrix matching are very powerful calibration techniques and can be used to accurately correct for matrix effects from easy-ionisable elements (multiplicative matrix effects). Additive matrix effects (i.e. spectral interferences) are not corrected for with standard additions calibration. For matrix matching, additive matrix effects will be corrected for when the added matrix is the cause of the matrix effect. The main drawback of calibration by standard addition with several standards is the requirement for a calibration function for each sample type, which is a time consuming process. For matrix matching a profound knowledge of the sample matrix is needed, which is not always necessarily available. These two techniques may thus not be practical to use in routine fertilizer laboratories.

Correction by internal standardization is also a good option, but the accuracy of the measurements after internal standard correction should be validated properly prior to use on unknown fertilizer samples.

It is therefore suggested that calibrations are to be performed by means of external calibration and correction of matrix effects by addition of one known spike of a standard solution (spike recovery). The method of external calibration and correction for spike recovery allows for the analysis of fertilizers with unknown matrix composition or with a matrix that cannot be synthetically imitated easily. This calibration technique may not be as precise as calibration by standard additions with several standards but the increased uncertainty is small compared to the total uncertainty of the method, if the total analyte concentration is in the linear working range after the spike and the added spike corresponds to at least a doubling of the analyte concentration. Many matrix errors can be compensated for by this procedure, if they are not additive (e.g. spectral interferences). Aliquots of the sample solution are analyzed by the means of external calibration and then one aliquot is spiked with known concentrations of the analytes without changing the matrix of the sample solution. The calculated spike recovery is then used to correct the concentration calculated from the external calibration function. The concentration of the spikes shall be in the linear working range of the ICP-AES.

8.2 Preparation of the test solution

8.2.1 General

The following extraction procedure leads, in most cases for mineral fertilizers, to trace element results which correspond to the total contents of these elements.

Calibration with several standard additions and external calibration after matrix matching or by correction for matrix effects with internal standardization may also be used.

1) Whatman® 589/2 is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product. Equivalent products can be used if they can be shown to lead to the same results.

8.2.2 Preparation

8.2.2.1 Weigh (3 ± 0,003) g of the prepared sample and transfer it to a suitable reaction vessel (action 1).

8.2.2.2 Moisten the sample with about 0,5 ml to 1,0 ml of water (6.1) and add, whilst mixing, (21 ± 0,1) ml of hydrochloric acid (6.2) followed by (7 ± 0,1) ml of nitric acid (6.3) drop by drop if necessary to reduce foaming. Connect a condenser to the reaction vessel and let the mixture stand at room temperature until any effervescence almost ceases to allow for slow oxidation of any organic mass in the sample (action 2).

8.2.2.3 Transfer to the heating device and raise the temperature of the reaction mixture slowly to reflux conditions. Maintain for 2 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Rinse the condenser a further with 10 ml of water (6.1) (action 3).

If the digested sample contains particulates which can clog nebulizers or interfere with the injection of the sample, the sample should be centrifuged and allowed to settle, or filtered before transferring into a suitable sized volumetric flask. For example, the solution should be allowed to pass through the filter paper and the insoluble residue washed onto the filter paper with a minimum of water (6.1). The method used shall be reported in the test report. Filter paper may cause contaminations (e.g. lead) and it may be necessary therefore to use ash-free filter paper (7.5).

8.2.2.4 Transfer the digested sample into a 150 ml volumetric flask and dilute to the mark with water (6.1). This yields an acid concentration approximately equal to that of the mixed acid solution (6.4). This test solution corresponds to a 50 times dilution of the solid sample (action 4).

8.2.2.5 Test solutions are diluted with the mixed acid solution (6.4) using a dilutor (7.4) to obtain a concentration of chromium, nickel and lead between 0,02 mg/l and 5 mg/l, and a concentration of cadmium between 0,005 mg/l and 5 mg/l (action 5).

NOTE 1 It is important that the total dilution of the test solution is equal to the dilution of the spiked test solution (see 8.3 on how to prepare the spiked test solution).

NOTE 2 The concentrations in the solutions in 8.2.2.5, action 5, are chosen so that they are above the typical limits of quantification, and that the concentrations fall within the linear working range of the analytical technique.

8.3 Preparation of the test solution for the correction of matrix effects by spike recovery

For each test solution analyzed, a spiked test solution with a known addition of a (multi-element) standard solution is required to correct for matrix effects by correcting for the spike recovery measured under close to identical measurement conditions. The addition of a spike of the standard solution shall increase the analyte concentrations by at least 100 % without changing the matrix of the test solution (from 8.2.2.4, action 4) or the diluted test solution (from 8.2.2.5, action 5). See list entries a) and b) below for suggestions on how to spike a diluted and an undiluted test solution respectively when determining cadmium, chromium, nickel and lead.

a) If the test solution (from 8.2.2.4, action 4 or 8.2.2.5, action 5) contains 1,0 mg/l to 5 mg/l of cadmium, chromium, nickel and lead, a spike addition corresponding to 1,0 mg/l of a multi-element standard solution containing cadmium, chromium, nickel and lead may be done while diluting the sample 5 times. Thus, take 2,00 ml of test solution and add 1,00 ml of the 10 mg/l working standard solution II (6.6.2) and 7,00 ml mixed acid solution (6.4). The test solution (from 8.2.2.4, action 4 or 8.2.2.5, action 5) shall also be 5 times diluted with the mixed acid solution (6.4) prior to analysis by ICP-AES.

b) If the test solution (from 8.2.2.4, action 4) contains 0,005 mg/l to 1,0 mg/l cadmium and 0,02 mg/l to 1,0 mg/l chromium, nickel and lead it should be analyzed without further dilution. Add 0,100 ml of a suitable (multi-element) standard solution (e.g. 100 mg/l working standard solution I (6.6.1) corresponding to an addition of 1,0 mg/l of cadmium, chromium, lead and nickel) to 9,90 ml test solution, thus preparing a spiked test solution of 10,0 ml without changing the matrix of the test solution significantly. The test solution (from 8.2.2.4, action 4) is measured using the same dilution (9,90 ml test solution and 0,100 ml mixed acid solution (6.4)) by ICP-AES.