

SLOVENSKI STANDARD

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Nadomešča:

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Gnojila - Določevanje elementov v sledovih - Določevanje kroma (VI) s fotometrijo (metoda A) in z ionsko kromatografijo s spektrofotometrijsko detekcijo (metoda B)

Fertilisers - Determination of trace elements - Determination of chromium(VI) by photometry (method A) and by ion chromatography with spectrophotometric detection (method B)

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Düngemittel - Bestimmung von Elementspuren - Bestimmung von Chrom(VI) mit Photometrie (Verfahren A) und mit Ionenchromatographie mit spektrometrischer Detektion (Verfahren B)

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Engrais - Dosage des éléments traces - Dosage du chrome (VI) par spectrophotométrie (méthode A) et chromatographie ionique avec détection spectrophotométrique (méthode B)

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EUROPEAN STANDARD

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Fertilizers - Determination of trace elements - Determination of chromium(VI) by photometry (method A) and by ion chromatography with spectrophotometric detection (method B)

Engrais - Dosage des éléments traces - Dosage du chrome (VI) par spectrophotométrie (méthode A) et chromatographie ionique avec détection spectrophotométrique (méthode B)

Düngemittel - Bestimmung von Elementspuren - Bestimmung von Chrom(VI) mit Photometrie (Verfahren A) und mit Ionenchromatographie mit spektrometrischer Detektion (Verfahren B)

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

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

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (EN 16318:2013) 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of an identical text or by endorsement, at the latest by April 2014, and conflicting national standards shall be withdrawn at the latest by April 2014.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 16318:2012.

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

The following changes have been made to the former edition:

- the CEN Technical Specification has been adopted as a European Standard;
- a reference to Annex A has been added to Clause 7 concerning the results of inter-laboratory tests on the precision of method A;
- the statistical results of an inter-laboratory test performed by the Technical Group Fertilizers of the German VDLUFA have been added as Annex A (informative);
- the results of a validation study with spiked water samples have been added as Annex B (informative);
- the document has been editorially revised.

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.

EN 16318:2013 (E)**1 Scope**

This European Standard specifies two methods for the determination of the content of soluble chromate in fertilizers.

Method A specifies the determination of chromate after extraction with water by photometry. This method can be used to determine Cr(VI)-mass fractions in solids higher than 1 mg/kg.

Method B specifies the determination of chromate by alkaline digestion and ion chromatography with spectrophotometric detection. This method can be used to determine Cr(VI)-mass fractions in solids higher than 0,1 mg/kg.

NOTE In case of reducing or oxidizing fertilizer matrix, no valid Cr(VI) content can be reported.

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 15192:2006, *Characterisation of waste and soil — Determination of Chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection*

<https://standards.iteh.ai/catalog/standards/sist/385e1a5b-190f-435f-b122-2e99>

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 Sampling and sample preparation

Sampling is not part of the methods specified in this European Standard. A recommended sampling method is given in EN 1482-1 [2].

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

Reasonable precautions have to be taken to prevent oxidation of chromate present in the sample. Samples shall be taken using appropriate devices and placed in containers that do not contain stainless steel (e.g. plastic, glass).

After digestion, the sample shall be analyzed as soon as possible.

5 Method A: Determination by water extraction and spectrophotometric detection

5.1 Principle

Chromate is extracted from the sample with water at room temperature. The chromate concentration in the extract is measured by colorimetry using 1,5-diphenylcarbazide.

When chromate reduces the 1,5-diphenylcarbazide a magenta coloured complex of 1,5-diphenylcarbazone and chromium is formed which can be measured colorimetrically at 540 nm.

5.2 Reagents

Use only reagents of recognized analytical grade and water conforming to 5.2.1.

5.2.1 Water, according to EN ISO 3696, grade 2 (electrical conductivity max. $0,1 \text{ mS} \times \text{m}^{-1}$ equivalent to resistivity greater than $0,01 \text{ M}\Omega\cdot\text{m}$ at $25 \text{ }^\circ\text{C}$).

It is recommended that the water used is obtained from a purification system that delivers ultrapure water having a resistivity greater than $0,18 \text{ M}\Omega\cdot\text{m}$.

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

5.2.3 Hydrochloric acid, diluted, $c(\text{HCl})$ approximately 6 mol/l .

Mix equal volumes of hydrochloric acid (5.2.2) and water (5.2.1).

5.2.4 Diphenylcarbazide solution

Dissolve $1,0 \text{ g}$ Diphenylcarbazide [$\text{CO}(\text{NHNHC}_6\text{H}_5)_2$] in 100 ml acetone and add one drop of acetic acid. If this solution is stored in a glass bottle in the dark at $4 \text{ }^\circ\text{C}$, it may be used for approximately two weeks. This solution shall be clear without colour. If the diphenylcarbazide solution has become coloured, it shall be discarded and freshly prepared before use.

5.2.5 Chromate standard stock solution, $\rho(\text{chromate}) = 1\,000 \text{ mg/l}$.

Dissolve $2\,829 \text{ mg}$ potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in $1\,000 \text{ ml}$ water (5.2.1) using a volumetric flask. This solution may be used for two weeks if stored in the dark at $4 \text{ }^\circ\text{C}$.

5.2.6 Chromate standard stock solution, $\rho(\text{chromate}) = 50 \text{ mg/l}$.

Dilute 5 ml chromate stock solution (5.2.5) to 100 ml with water (5.2.1) using a volumetric flask. This solution shall be freshly prepared on the day of use.

5.2.7 Standard solutions.

Prepare the standard solutions by diluting aliquots of the 50 mg/l chromate standard stock solution (5.2.6) with water (5.2.1) in 100 ml volumetric flasks. The aliquots and final concentrations of chromate are given in Table 1. Other volumes and concentrations may be used for the preparation of standard solutions if appropriate. See 5.4.3 for further instructions on how to prepare the standard solutions.

Table 1 — Aliquots and final concentrations for the preparation of chromate standards from a 50 mg/l chromate standard stock solution in 100 ml volumetric flasks

Aliquot ml	Final concentration of chromate mg/l
0	0 (calibration blank)
0,05	0,025
0,20	0,10
0,50	0,25
1,00	0,50
1,50	0,75

A blank solution shall be prepared in a separate volumetric flask by adding water (5.2.1) only.

The standard solutions shall be prepared freshly on the day of use.

5.3 Apparatus

5.3.1 Common laboratory glassware.

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

5.3.3 Membrane filters and vacuum filtration apparatus.

The filters should be made of cellulose nitrate, pore size 5 μm and fit into the vacuum filtration apparatus.

5.3.4 Mechanical shaker.

5.3.5 Pipettes and/or dilutor, pipettes with fixed or variable volume and volumetric glassware to perform dilutions.

Alternatively, a dilutor may be used, which is an instrument used for automated volumetric dilutions. The precision and accuracy of this equipment for volumetric dilutions shall be proved, controlled, and documented regularly.

5.3.6 Spectrophotometer, capable to measure transmitted light at 540 nm.

5.3.7 100 ml bottles, made from PE or PP, equipped with watertight caps.

5.4 Procedure

5.4.1 Preparation of the test solution

Weigh approximately 10 g, to the nearest 0,01 g, of the prepared sample and transfer to a suitable extraction vessel (5.3.7).

Add 40 ml of water (5.2.1). If the sample material (e.g. organic material) absorbs a high amount of water, add additionally water (5.2.1) to obtain a fluid suspension. Record the amount of additional water added. It may be necessary to use larger extraction vessels in such cases. Close the cap tightly and shake vigorously for 15 min on a mechanical shaker (5.3.4). Filter the suspension immediately through membrane filters with 5 μm pore size using the vacuum filtration apparatus (5.3.3).

Pipette 20 ml of the test solution to a 100 ml volumetric flask and continue immediately with the colorimetric measurement. If the test solution shows a yellow colour, the aliquot should be reduced to minimize interferences by the colour of organic substances.

The test solution may not be stored. The chromate content shall be analyzed on the day of preparation.

5.4.2 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 for the samples.

5.4.3 Spectrophotometric measurement

Add approximately 40 ml of water (5.2.1) to all volumetric flasks containing the standard solutions (5.2.7), the blank test solution (5.4.2) and the sample test solutions (5.4.1). Then add 2 ml diluted hydrochloric acid (5.2.3). The pH-value of the resulting solution should be between pH 1 and pH 2. Add more diluted hydrochloric acid (5.2.3) if the pH-value is higher until a pH-value between pH 1 and pH 2 is reached.

Add 2 ml diphenylcarbazide solution (5.2.4) to each volumetric flask and fill up to the mark with water (5.2.1). Wait 15 min and measure the extinction of the solutions on a spectrophotometer at 540 nm.

5.5 Calculation and expression of the results

5.5.1 Calibration

In the case of a linear calibration curve, the calibration function can be described according to Formula (1).

$$S = c \times b + a \quad (1)$$

where

- S is the net signal for Cr(VI) in a solution;
- c is the concentration of Cr(VI) in this solution, in milligrams per litre or in micrograms per litre;
- b is the slope of the linear calibration function;
- a is the intersection of the linear calibration function.

Calculate the analyte concentration, c_f , in the filtrate of the test portion using the slope b and the intersection a according to Formula (2):

$$c_f = \frac{S_f - a}{b} \quad (2)$$

where

- S_f is the net signal of the test solution.

5.5.2 Calculation of the element content in the sample

Calculate the analyte concentration in the sample or the mass fraction of the analyte, w_E , expressed in milligrams of analyte per kilogram of fertilizer according to Formula (3).

$$w_E = \frac{(c_f - c_{bl})}{m} \times V_t \times 1000 \quad (3)$$

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where

- c_f is the concentration, in milligrams per litre, of the filtrate of the test portion, as determined according to Formula (2);
- c_{bl} is the concentration, in milligrams per litre, of the blank solution;
- m is the mass of the sample, in grams, taken for the extraction, and corrected for water content;
- V_t is the total volume, in litres, of water added to the test portion for extraction.

6 Method B: Determination by alkaline digestion and ion chromatography with spectrophotometric detection

6.1 Principle

6.1.1 Digestion

Cr(VI) is digested from the sample by an alkaline solution.

To quantify the content of Cr(VI) in a solid matrix, the following three criteria shall be satisfied:

- a) the digestion solution shall solubilize all species of Cr(VI);
- b) the conditions of the digestion shall not induce reduction of native Cr(VI) to Cr(III);
- c) the method shall not cause oxidation of native Cr(III) contained in the sample to Cr(VI).

The alkaline digestion described in this document meets these criteria for a wide spectrum of solid matrices. Under the alkaline conditions, neglectable reduction of Cr(VI) or oxidation of native Cr(III) is expected. The addition of Mg^{2+} in a phosphate buffer to the alkaline solution prevents air oxidation of trivalent chromium (see [7], [8] and [9]).

NOTE Background on methods for the determination of Cr(VI) in solid samples is given in EN 15192:2006, Annex D and [10], [11], [8].

6.1.2 Determination

The quantification of Cr(VI) in the alkaline digestion solution should be performed using a suitable technique with appropriate accuracy. For this purpose, ion chromatography is used to separate Cr(VI) from interferences.

Following this ion chromatographic separation, Cr(VI) is measured spectrophotometrically either at 365 nm (direct UV detection) or after post-column derivatization with 1,5-diphenylcarbazide in acid solution at 540 nm. Post-column derivatization involves reaction of 1,5-diphenylcarbazide with Cr(VI) to produce trivalent chromium and diphenylcarbazone. These then combine to form a trivalent chromium-diphenylcarbazone complex containing the characteristic magenta chromagen ($\lambda_{max} = 540$ nm).

NOTE The choice of detection method is based upon the required sensitivity. Direct UV detection is less sensitive than detection after post-column derivatization with 1,5-diphenylcarbazide.

Hyphenated methods with ion chromatographic separation and detection techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectroscopy (ICP-AES), may be used once validation of the chosen analytical method has been performed.

6.1.3 Interferences and sources of error

Use of ion chromatography is necessary for the separation of Cr(VI) from possible interferences in the alkaline digestion solution from solid material [12] (see also EN 15192:2006, D.3).

For waste materials or soils, where the Cr(III)/Cr(VI) ratio is expected to be high, Cr(VI) results may be biased due to method-induced oxidation. This can be particularly expected in soils high in Mn content and amended with soluble Cr(III) salts or freshly precipitated Cr(OH)₃ [10] (see also EN 15192:2006, D.2).

Cr(VI) can be reduced to Cr(III) during digestion from the sample due to reaction with reducing agents such as e.g. divalent iron. This problem is minimized in the described procedure using alkaline digestion solution [8] (see also EN 15192:2006, D.2).

Cr(III) can be oxidized to Cr(VI) in hot alkaline solutions. This problem is minimized in the described procedure by adding magnesium to the alkaline digestion solution [8], [9], [10], [13] (see also EN 15192:2006, D.2).

Overloading the analytical column capacity with high concentrations of anionic species (e.g. chloride) may cause underestimation of Cr(VI) [6].

6.2 Reagents

Use only reagents of recognized analytical grade, and water as specified in 6.2.1.

6.2.1 Water, according to EN ISO 3696, grade 2 (electrical conductivity max. 0,1 mS × m⁻¹ equivalent to resistivity greater than 0,01 MΩ·m at 25 °C).

It is recommended that the water used is obtained from a purification system that delivers ultrapure water having a resistivity greater than 0,18 MΩ·m.

6.2.2 Sulfuric acid, concentrated, $\rho(\text{H}_2\text{SO}_4) \approx 1,84 \text{ g/ml}$, $w(\text{H}_2\text{SO}_4) \approx 98 \%$.

6.2.3 Sodium carbonate, anhydrous, $w(\text{Na}_2\text{CO}_3) > 99,9 \%$.

6.2.4 1,5-Diphenylcarbazine, $w((\text{C}_6\text{H}_5.\text{NH.NH})_2\text{CO}) > 98 \%$.

6.2.5 Acetone.

6.2.6 Methanol.

6.2.7 Potassium dichromate, $w(\text{K}_2\text{Cr}_2\text{O}_7) > 99,9 \%$.

Dry to constant weight at 110 °C, cool and store in a desiccator.

6.2.8 Sodium hydroxide, $w(\text{NaOH}) > 99 \%$.

6.2.9 Magnesium chloride hexahydrate, $w(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) > 99 \%$.

6.2.10 Dipotassium hydrogenphosphate, $w(\text{K}_2\text{HPO}_4) > 99 \%$.

6.2.11 Potassium dihydrogenphosphate, $w(\text{KH}_2\text{PO}_4) > 99 \%$.

6.2.12 Lead chromate, $w(\text{PbCrO}_4) > 99 \%$.

6.2.13 Diphenylcarbazine reagent solution.

Dissolve 0,125 g of 1,5-diphenylcarbazine (6.2.4) in 25 ml of acetone (6.2.5) or methanol (6.2.6) in a 250 ml volumetric flask. Fill 125 ml of water (6.2.1) into a separate container, slowly add 7 ml of concentrated sulfuric acid (6.2.2), swirl to mix and allow to cool. Degas with, e.g. helium or argon, for 5 min to 10 min prior to adding