

Characterisation of waste and soil - Determination of Chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection

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Charakterisierung von Abfällen und Boden - Bestimmung von sechswertigem Chrom in Feststoffen durch alkalischen Aufschluss und Ionenchromatographie mit photometrischer Detektion

Caractérisation des déchets et des sols - Dosage du chrome (VI) dans les matériaux solides par digestion alcaline et chromatographie ionique avec détection spectrophotométrique

Ta slovenski standard je istoveten z: EN 15192:2006

ICS:

13.030.10	Trdni odpadki	Solid wastes
13.080.10	Sestavine kemijskega značilnosti tal	Chemical characteristics of soils

SIST EN 15192:2007

en

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ICS 13.030.10; 13.080.10

English Version

Characterisation of waste and soil - Determination of
Chromium(VI) in solid material by alkaline digestion and ion
chromatography with spectrophotometric detection

Caractérisation des déchets et des sols - Dosage du
chrome VI dans les matériaux solides par digestion alcaline
et chromatographie ionique avec détection
spectrophotométrique

Charakterisierung von Abfällen und Boden - Bestimmung
von sechswertigem Chrom in Feststoffen durch alkalischen
Aufschluss und Ionenchromatographie mit photometrischer
Detektion

This European Standard was approved by CEN on 6 October 2006.

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Foreword

This document (EN 15192:2006) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by May 2007, and conflicting national standards shall be withdrawn at the latest by May 2007.

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, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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Introduction

Under environmental conditions chromium in compounds exists in the trivalent, Cr(III), or the hexavalent, Cr(VI) state. Cr(III) is an essential trace element for mammals, including man, whereas it is presumed that Cr(VI) compounds are genotoxic and potentially carcinogenic in humans. Interconversion of trivalent and hexavalent chromium species can occur during sample preparation and analysis, but these processes are minimised, to the extent possible, by the sample preparation methods prescribed by this standard.

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1 Scope

This standard describes the determination of Cr(VI) in solid waste material and soil 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 oxidising waste matrix no valid Cr(VI) content can be reported.

2 Normative references

The following referenced documents are indispensable for the application of this European Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

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

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 1705:2005)*

ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

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3 Terms and Definitions (standards.iteh.ai)

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

3.1

alkaline digestion

process of obtaining a solution containing the analyte of interest from a sample under alkaline conditions. Alkaline digestion may or may not involve complete dissolution of the sample

3.2

speciation analysis

activities of measuring the quantity of one or more individual chemical species in a sample, e.g. Cr(VI) in a particular sample or matrix

4 Safety remarks

Anyone dealing with waste and soil analysis has to be aware of the typical risks of the material irrespective of the parameters determined. Waste and soil samples may contain hazardous (e.g. toxic, reactive, flammable, infectious) substances, which can be liable to biological and/or chemical reaction. Consequently, it is recommended that these samples should be handled with special care. The gases which may be produced by microbiological or chemical activity are potentially flammable and can pressurise sealed bottles. Bursting bottles are likely to result in hazardous shrapnel, dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

Avoid any contact with the skin, ingestion or inhalation of Cr(VI) compounds. Cr(VI) compounds are genotoxic and potentially carcinogenic to humans.

5 Principle

5.1 Digestion

This standard describes an alkaline digestion procedure for extracting Cr(VI) from soluble, adsorbed and precipitated forms of chromium compounds in solid waste materials and soil. To quantify the content of Cr(VI) in a solid matrix, three criteria must be satisfied:

- 1) digestion solution must solubilize all species of Cr(VI);
- 2) conditions of the digestion must not induce reduction of native Cr(VI) to Cr(III);
- 3) method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI).

The alkaline digestion described in this standard meets these criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the digestion, 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 [1], [6], [32].

NOTE Background on methods for the determination of Cr(VI) in solid samples is given in Annex D and [4], [5], [6].

5.2 Determination

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 derivatisation with 1,5-diphenylcarbazide in acid solution at 540 nm. Post-column derivatisation 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 ($\lambda_{max} = 540 \text{ nm}$).

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

NOTE 2 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.

5.3 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 [7] (see also Annex 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 $Cr(OH)_3$ [4] (see also Annex 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 minimised in the described procedure using alkaline digestion solution [6] (see also Annex D.2).
- Cr(III) can be oxidised to Cr(VI) in hot alkaline solutions. This problem is minimised in the described procedure by adding magnesium to the alkaline digestion solution [3], [4], [6], [32] (see also Annex D.2).
- Overloading the analytical column capacity with high concentrations of anionic species (e.g. chloride) may cause underestimation of Cr(VI) [43].

6 Apparatus

6.1 Digestion equipment

- hotplate with a magnetic stirrer, thermostatically controlled with a digestion vessel of 250 ml covered with a watch glass; or
- heating block with a magnetic stirrer, thermostatically controlled with a digestion vessel of 250 ml covered with a watch glass

NOTE Other thermostatically controlled digestion equipment with a magnetic stirrer can be used once validation has been performed.

6.2 Filtration equipment,

suitable for using 0,45- μm membrane filters.

6.3 Membrane filters,

0,45 μm pore size, chemically inert.

6.4 Ion chromatographic system,

all components which come into contact with the sample or eluent stream shall be comprised of inert materials, e.g. polyetherether ketone (PEEK), as shall all connecting tubing (see Annex B).

6.5 Ion chromatographic column,

suitable for chromate separation with a sufficient ion exchange capacity.

6.6 Detection system

- UV-VIS spectrophotometer at 365 nm; or
- VIS spectrophotometer at 540 nm after post column derivatisation.

7 Reagents

During the analysis, only use reagents of recognised analytical grade, and water as specified in clause 7.1.

7.1 Water

Water complying with the requirements for EN ISO 3696 grade 2 water (electrical conductivity less than $0,1 \text{ mS m}^{-1}$ equivalent to resistivity greater than $0,01 \text{ M}\Omega \text{ m}$ 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 $0,18 \text{ M}\Omega \text{ m}$ (usually expressed by manufacturers of water purification systems as $18 \text{ M}\Omega \text{ cm}$).

7.2 Sulphuric acid (H_2SO_4), concentrated, $\rho(\text{H}_2\text{SO}_4) \sim 1,84 \text{ g/ml}$, $w(\text{H}_2\text{SO}_4) \sim 98 \%$

7.3 Sodium carbonate (Na_2CO_3), anhydrous, $w(\text{Na}_2\text{CO}_3) > 99,9 \%$

7.4 1,5-Diphenylcarbazide ($(\text{C}_6\text{H}_5\text{.NH.NH})_2\text{CO}$), $w((\text{C}_6\text{H}_5\text{.NH.NH})_2\text{CO}) > 98\%$

7.5 Acetone ($\text{C}_3\text{H}_6\text{O}$)

7.6 Methanol (CH_4O)

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

Dry to constant weight at $110 \text{ }^\circ\text{C}$, cool and store in a desiccator

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

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

7.10 Dipotassium hydrogenphosphate (K_2HPO_4), $w(\text{K}_2\text{HPO}_4) > 99 \%$

7.11 Potassium dihydrogenphosphate (KH_2PO_4), $w(\text{KH}_2\text{PO}_4) > 99 \%$

7.12 Lead chromate (PbCrO_4), $w(\text{PbCrO}_4) > 99 \%$

7.13 Diphenylcarbazide reagent solution

Dissolve $0,125 \text{ g}$ of 1,5-diphenylcarbazide (7.4) in 25 ml of acetone (7.5) or methanol (7.6) in a 250 ml volumetric flask. Fill 125 ml of water into a separate container, slowly add 7 ml of concentrated sulphuric acid (7.2), swirl to mix and allow to cool. Degass with e.g. helium or argon for 5 min to 10 min prior to adding to the 1,5-diphenylcarbazide solution. After combining the solutions, fill up to the mark with water and degass additionally for 5 min to 10 min . The reagent solution is stable for 5 days.

7.14 Eluent solution

Use an eluent solution appropriate to separate chromate over the ion chromatographic column (6.5).

7.15 Alkaline digestion solution, $0,5 \text{ mol/l}$ sodium hydroxide (NaOH) / $0,28 \text{ mol/l}$ sodium carbonate (Na_2CO_3)

Dissolve $20,0 \text{ g}$ of sodium hydroxide (7.8) in approximately 500 ml of water (7.1). Add $30,0 \text{ g}$ of sodium carbonate (7.3) and swirl to mix. Quantitatively transfer the solution into a 1 l volumetric flask. Dilute to the

mark with water. The pH of the digestion solution must be checked before use. The pH must be 11,5 or higher. Store in a polyethylene bottle at room temperature and prepare fresh monthly.

7.16 Calibration solutions of Cr(VI)

7.16.1 Cr(VI) standard stock solution, 1 000 mg/l Cr(VI)

Dissolve 0,282 9 g of potassium dichromate (7.7) in 75 ml of water (7.1) in a 100 ml volumetric flask. Dilute to the mark with water (7.1), close and mix thoroughly. Store the solution in a polypropylene bottle for a maximum period of 1 year.

Alternatively a commercial standard solution with a certified Cr(VI) concentration traceable to national standards can be used. Observe the manufacturer's expiration date or recommended shelf life.

7.16.2 Cr(VI) working standard solution, 10 mg/l Cr(VI)

Accurately pipette 10,0 ml of the Cr(VI) standard stock solution (7.16.1) into a 1 l volumetric flask, dilute to the mark with water (7.1), close and mix thoroughly. Prepare this solution fresh monthly.

7.16.3 Cr(VI) calibration solutions

Prepare a set of at least 5 calibration solutions by diluting the Cr(VI) working standard solution with a 1 + 1 diluted alkaline digestion solution (7.15). Add 25 ml of the alkaline digestion solution (7.15) into a 50 ml volumetric flask, pipette accurately the appropriate volume of Cr(VI) working standard solution (7.16.2) into the volumetric flask and dilute to the mark with water (7.1), close and mix thoroughly. Prepare these calibration solutions fresh daily.

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7.16.4 Cr(VI) spiking solutions

The Cr(VI) working standard solution (7.16.2) can be used to spike samples.

7.17 Phosphate buffer solution,

0,5 mol/l dipotassiumhydrogenphosphate (K_2HPO_4)/0,5 mol/l potassiumdihydrogenphosphate (KH_2PO_4), pH 7.

Dissolve 87,09 g K_2HPO_4 (7.10) and 68,04 g of KH_2PO_4 (7.11) in approximately 700 ml of water and swirl to mix. Transfer the solution into a 1 l volumetric flask. Dilute to the mark with water.

7.18 Magnesium chloride solution

Dissolve 85,4 g $MgCl_2 \cdot 6H_2O$ (7.9) in a 100 ml volumetric flask, dilute to the mark with water (7.1), close and mix thoroughly.

7.19 Chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$), $w(CrCl_3 \cdot 6H_2O) > 96\%$

7.20 Cr(III) spiking solution

Use a commercial standard solution with a certified Cr(III) concentration, e.g 1 000 mg/l Cr (III) traceable to national standards. Observe the manufacturer's expiration date or recommended shelf life.

Alternatively dissolve an appropriate known amount of chromium chloride hexahydrate (7.19) in water (7.1) in a 100 ml volumetric flask, dilute to the mark with water (7.1), close and mix thoroughly. Store the solution in a polypropylene bottle for a maximum period of 1 year. Before using, determine the Cr concentration of the spiking solution.

8 Sample pretreatment

Samples shall be collected using appropriate devices and placed in containers that do not contain stainless steel (e.g. plastic, glass).

Samples shall be stored field moist at (4 ± 2) °C until analysis. Waste samples shall be homogenised according to EN 15002, soil samples according to ISO 11464. Soil samples shall preferably be air-dried before digestion.

Particle size reduction below 250 µm is necessary for solid waste and soil especially when Cr(VI) is suspected to be included in the matrix, whereby heating and contact with stainless steel have to be avoided.

After digestion the sample shall be analysed as soon as possible.

NOTE Cr(VI) has been shown to be quantitatively stable in field moist soil samples for 30 days from the time of sample collection. In addition, Cr(VI) has also been shown to be stable in the alkaline digest for up to 7 days after digestion from soil [2].

9 Alkaline digestion procedure

9.1 General

Use either the hotplate or heating block method prescribed in 9.2 to prepare test solutions for determination of Cr(VI) in solid waste materials and soil.

9.2 Preparation of test solutions using a hotplate or heating block

9.2.1 Adjust the temperature setting by preparing and monitoring a temperature blank (a 250 ml vessel filled with 50 ml digestion solution). Maintain a digestion solution temperature of $(92,5 \pm 2,5)$ °C. Do not allow the solution to boil or evaporate to dryness.

9.2.2 Transfer $(2,5 \pm 0,1)$ g of the test portion weighed to the nearest 0,1 mg into a clean 250 ml digestion vessel.

NOTE For very high expected concentrations of Cr(VI) a smaller representative test portion can be used.

9.2.3 Add (50 ± 1) ml of the alkaline digestion solution (7.15) to each sample using a graduated cylinder, and also add 1 ml of magnesium chloride solution (7.18) containing approximately 400 mg of $MgCl_2$ and 0,5 ml of phosphate buffer solution (7.17). Cover all digestion vessels. If using a heating block, reflux condensers can be used.

9.2.4 Heat the samples to $(92,5 \pm 2,5)$ °C with continuous stirring, then maintain the samples at $(92,5 \pm 2,5)$ °C for at least 60 min with stirring continuously.

9.2.5 Cool each solution to room temperature. Transfer the contents quantitatively to the filtration equipment (6.2), rinsing the digestion vessel three times with small portions of water (7.1). Filter through a 0,45 µm membrane filter (6.3). Rinse the filtration equipment (6.2) with water (7.1) and transfer the filtrate to a 100 ml volumetric flask and fill up to the mark with water (7.1).

NOTE Alternatively the sample may be centrifuged or allowed to settle.