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

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical and physical characterization.*

This second edition cancels and replaces the first edition (ISO 15192:2010), which has been technically revised.

The main changes compared to the previous edition are as follows:

— The text has been editorially revised, including updating of references;

— Annex D has been deleted.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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.

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

1 Scope

This document 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

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

EN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

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 document 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 shall be satisfied:

1) digestion solution shall solubilize all species of Cr(VI);

2) conditions of the digestion shall not induce reduction of native Cr(VI) to Cr(III);

3) 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 of the digestion, neglectable reduction of Cr(VI) or oxidation of native Cr(III) is expected. The additon of Mg^{2+} in a phosphate buffer to the alkaline solution prevents air oxidation of trivalent chromium [1], [5], [8].

NOTE Background on methods for the determination of Cr(VI) in solid samples is given in [3], [4], [5].

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 (λ_{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 derivatisation 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.

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 [6].

— 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 $Cr(OH)_3$ [3].

— 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 [5].

— 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 [2], [3], [5], [8].

— Overloading the analytical column capacity with high concentrations of anionic species (e. g. chloride) may cause underestimation of Cr(VI) [9].

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 7.1.

7.1 Water

Water complying with the requirements for ISO 3696 grade 2 water (electrical conductivity less than 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 (usually expressed by manufacturers of water purification systems as 18 MΩ cm).

7.2 Sulphuric acid (H_2SO_4),

concentrated, $\rho(H_2SO_4)$ ~ 1,84 g/ml, $w(H_2SO_4)$ ~ 98 %

7.3 Sodium carbonate (Na_2CO_3),

anhydrous, $w(Na_2CO_3)$ > 99,9 %

7.4 1,5-Diphenylcarbazide ($(C_6H_5.NH.NH)_2CO$),

$w((C_6H_5.NH.NH)_2CO)$ > 98 %

7.5 Propanone (acetone) (C_3H_6O)

7.6 Methanol (CH_4O)

7.7 Potassium dichromate ($K_2Cr_2O_7$), $w(K_2Cr_2O_7)$ > 99,9 %

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

7.8 Sodium hydroxide (NaOH), w(NaOH) > 99 %

7.9 Magnesium chloride hexahydrate ($MgCl_2.6H_2O$), $w(MgCl_2.6H_2O)$ > 99 %

7.10 Dipotassium hydrogenphosphate (K_2HPO_4), $w(K_2HPO_4)$ > 99 %

7.11 Potassium dihydrogenphosphate (KH_2PO_4), $w(KH_2PO_4)$ > 99 %

7.12 Lead chromate ($PbCrO_4$), $w(PbCrO_4)$ > 99 %

7.13 Diphenylcarbazide reagent solution

Dissolve 0,125 g of 1,5-diphenylcarbazide (7.4) in 25 ml of propanone (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 mol/l sodium hydroxide (NaOH) / 0,28 mol/l sodium carbonate (Na_2CO_3)

Dissolve 20,0 g of sodium hydroxide (7.8) in approximately 500 ml of water (7.1). Add 30,0 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 shall 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.

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 $MgCl_2.6H_2O$ (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 ($CrCl_3.6H_2O$), $w(CrCl_3.6H_2O) > 96$ %

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).