
**Soil quality — Determination of
chromium(VI) in solid material by alkaline
digestion and ion chromatography with
spectrophotometric detection**

*Qualité du sol — Dosage du chrome(VI) dans les matériaux solides par
digestion alcaline et chromatographie ionique avec détection
spectrophotométrique*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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ISO 15192 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

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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 minimized, to the extent possible, by the sample preparation methods specified in this International Standard.

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Soil quality — Determination of chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection

1 Scope

This International Standard specifies a method for 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 greater than 0,1 mg/kg.

NOTE In the case of reducing or oxidizing waste matrix, no valid Cr(VI) mass fraction can be reported.

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.

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

ISO 9174:1998, *Water quality — Determination of chromium — Atomic absorption spectrometric methods*

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

ISO 11885:2007, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 15586:2003, *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace*

ISO 17294-2:2003, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements*

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

3 Terms and definitions

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

3.1

alkaline digestion

process for obtaining a solution containing the analyte of interest from a sample under alkaline conditions

NOTE Alkaline digestion may or may not involve complete dissolution of the sample.

3.2
speciation analysis

activities for measuring the quantity of one or more individual chemical species in a sample

EXAMPLE Cr(VI) in a particular sample or matrix.

4 Safety

SAFETY PRECAUTIONS — 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 be handled with special care. The gases which may be produced by microbiological or chemical activity are potentially flammable and can pressurize 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

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This International 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 mass fraction of Cr(VI) in a solid matrix, 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 International 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 Mg²⁺ in a phosphate buffer to the alkaline solution prevents air oxidation of trivalent chromium (References [7], [12] and [38] in the Bibliography).

NOTE Background information on methods for the determination of Cr(VI) in solid samples is given in Annex D and References [10], [11] and [12] in the Bibliography.

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 ultraviolet (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 1 The choice of the detection method is based upon the required sensitivity. Direct UV detection is less sensitive than detection after post-column derivatization 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), can 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 (Reference [13] in the Bibliography) (see also 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 manganese (Mn) content and amended with soluble Cr(III) salts or freshly precipitated Cr(OH)₃ (Reference [10] in the Bibliography) (see also D.2).

Cr(VI) can be reduced to Cr(III) during digestion of the sample, due to reaction with reducing agents such as, for example, divalent iron. This problem is minimized in the described procedure using alkaline digestion solution (Reference [12] in the Bibliography) (see also 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 (References [9], [10], [12] and [38] in the Bibliography) (see also D.2).

Overloading the analytical column capacity with high concentrations of anionic species (e.g. chloride) may cause underestimation of Cr(VI) (Reference [49] in the Bibliography).

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6 Apparatus

Use ordinary laboratory apparatus and the following.

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6.1 Digestion equipment, ~~hot plate with a magnetic stirrer, thermostatically controlled, with a digestion vessel of 250 ml covered with a watch-glass; or a 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, of pore size 0,45 µm, 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, ultraviolet/visible light (UV/VIS) spectrophotometer at 365 nm; or VIS spectrophotometer at 540 nm after post-column derivatization.

7 Reagents

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

7.1 Water.

Water complying with the requirements of ISO 3696 for grade 2 water (electrical conductivity less than 0,1 mS·m⁻¹ equivalent to a resistivity greater than 0,01 MΩ·m at 25 °C). It is recommended that the water

used be obtained from a purification system that delivers ultrapure water having a resistivity greater than 0,18 M Ω -m (usually expressed by manufacturers of water-purification systems as 18 M Ω -cm).

7.2 Sulfuric acid (H₂SO₄), concentrated, ρ (H₂SO₄) ~ 1,84 g/ml, w (H₂SO₄) ~ 98 %.

7.3 Sodium carbonate (Na₂CO₃), anhydrous, w (Na₂CO₃) > 99,9 %.

7.4 1,5-Diphenylcarbazide [(C₆H₅NHNH)₂CO], w [(C₆H₅NHNH)₂CO] > 98 %.

7.5 Acetone (C₃H₆O).

7.6 Methanol (CH₄O).

7.7 Potassium dichromate (K₂Cr₂O₇), w (K₂Cr₂O₇) > 99,9 %.

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

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

7.9 Magnesium chloride hexahydrate (MgCl₂·6H₂O), w (MgCl₂·6H₂O) > 99 %.

7.10 Dipotassium hydrogenphosphate (K₂HPO₄), w (K₂HPO₄) > 99 %.

7.11 Potassium dihydrogenphosphate (KH₂PO₄), w (KH₂PO₄) > 99 %.

7.12 Lead chromate (PbCrO₄), w (PbCrO₄) > 99 %.

7.13 Diphenylcarbazide reagent solution.

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Dissolve 0,125 g of 1,5-diphenylcarbazide (7.4) in 25 ml of acetone (7.5) or methanol (7.6) in a 250 ml volumetric flask. Pour 125 ml of water (7.1) into a separate container, then slowly add 7 ml of concentrated sulfuric acid (7.2), swirl to mix and allow to cool. Degas with, for example, 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 degas again for 5 min to 10 min. The reagent solution is stable for 5 days when stored at 2 °C to 8 °C in the dark.

7.14 Eluent solution.

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

7.15 Alkaline digestion solution, 0,5 mol/l sodium hydroxide (NaOH) and 0,28 mol/l sodium carbonate (Na₂CO₃).

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 shall 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 five 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 to a 50 ml volumetric flask, accurately pipette 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) and 0,5 mol/l potassiumdihydrogenphosphate (KH_2PO_4), pH 7.

Dissolve 87,09 g of K_2HPO_4 (7.10) and 68,04 g of KH_2PO_4 (7.11) in approximately 700 ml of water (7.1) 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 of $MgCl_2 \cdot 6H_2O$ (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, 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

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

Samples shall be stored in a field-moist state at $(4 \pm 2) ^\circ C$ until analysis. Waste samples shall be homogenized in accordance with EN 15002; soil samples shall be homogenized in accordance with 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 (Reference [8] in the Bibliography).

9 Alkaline digestion procedure

9.1 General

Use either the hotplate or heating-block method specified in 9.2 to prepare test solutions for the 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 of 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 while stirring continuously, then maintain the samples at $(92,5 \pm 2,5)$ °C for at least 60 min while 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 can be centrifuged or allowed to settle.

10 Analytical procedure

10.1 General information

The standard method for the determination of Cr(VI) in the alkaline digestion solution is the ion chromatographic method with spectrophotometric detection as described in this clause.

NOTE In certain cases, direct determination of Cr(VI) in the alkaline digestion solution might be possible (see Annex A).

10.2 Instrumental set-up

10.2.1 Set up the ion chromatograph in accordance with the manufacturer's instructions.

10.2.2 Adjust the flow rate of the eluent solution (7.14) to a value that is compatible with the columns used (typically 0,3 ml/min to 1 ml/min).

10.2.3 If post-column derivatization occurs, optimize the ratio of eluent solution and reagent flow rates or adjust the sulfuric acid concentration of the diphenylcarbazide reagent solution (7.13) to obtain the best signal-to-background ratio. It is important that the ratio between the eluent solution and reagent flow rates be kept constant, that the total flow rate does not exceed the maximum flow rate for the detector and that the diphenylcarbazide reagent be present in excess. A typical value for the ratio between the eluent solution and reagent flow rates is 3:1. After the flow rates are adjusted, allow the system to equilibrate for 15 min.