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

Déchets et sols — 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.

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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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*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 444, *Environmental Characterization,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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.

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. Chromium 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 document.

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

1 Scope

This document specifies 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 8466-1, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function*

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

No terms and definitions are listed in this document.

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

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

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

4 Safety remarks

Anyone dealing with waste and soil analysis shall 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, 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. It is presupposed that national regulations are 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:

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

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

c) 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 soils and wastes. Under the alkaline conditions of the digestion, negligible 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 minimises air oxidation of trivalent chromium[1][5][8].

NOTE Background on methods for the determination of Cr(VI) in solid samples is given in Annex C.

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 (see Annex C).

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.

6.1.1 Hotplate with a magnetic stirrer, thermostatically controlled with a digestion vessel of 250 ml covered with a watch glass, or

6.1.2 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.

6.6.1 UV-VIS spectrophotometer, at 365 nm, or

6.6.2 VIS spectrophotometer, at 540 nm after post column derivatisation.

7 Reagents

7.1 General.

During the analysis, only use reagents of recognised analytical grade, and water as specified in 7.2.

7.2 Water.

Water with an 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).

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

7.4 Sodium carbonate (Na_2CO_3), anhydrous, $w(Na_2CO_3)$ >9,9 %.

7.5 1,5-Diphenylcarbazide ($C_{13}H_{14}N_4O$), $w(C_{13}H_{14}N_4O)$ >98 %; CAS RN 140-22-7.

7.6 Propanone (acetone) (C_3H_6O).

7.7 Methanol (CH_4O).

7.8 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.

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

7.10 Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), $w(MgCl_2 \cdot 6H_2O)$ >99 %.

7.11 Dipotassium hydrogenphosphate (K_2HPO_4), $w(K_2HPO_4)$ >99 %.

7.12 Potassium dihydrogenphosphate (KH_2PO_4), $w(KH_2PO_4)$ >99 %.

7.13 Lead chromate ($PbCrO_4$), $w(PbCrO_4)$ >99 %.

7.14 Diphenylcarbazide reagent solution.

Dissolve 0,125 g of 1,5-diphenylcarbazide (7.5) in 25 ml of propanone (7.6) or methanol (7.7) in a 250 ml volumetric flask. Fill 125 ml of water into a separate container, slowly add 7 ml of concentrated sulphuric acid (7.3), 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.

7.15 Eluent solution.

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

NOTE Eluents can be prepared manually by in-line dilution or electrochemically in situ.

7.16 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 (7.9) in approximately 500 ml of water (7.2). Add 30,0 g of sodium carbonate (7.4) 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 to 12. Store in a polyethylene bottle at room temperature. This reagent is stable for one month.

7.17 Calibration solutions of Cr(VI).

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

Dissolve 0,282 9 g of potassium dichromate (7.8) in 75 ml of water (7.2) in a 100 ml volumetric flask. Dilute to the mark with water (7.2), close and mix thoroughly. Store the solution in a polypropylene bottle. This reagent is stable for one year.

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

Pipette 10,0 ml of the Cr(VI) standard stock solution (7.17.1) into a 1 l volumetric flask, dilute to the mark with water (7.2), close and mix thoroughly. This reagent is stable for one month.

7.17.3 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 (7.16). Add 25 ml of the alkaline digestion solution (7.16) into a 50 ml volumetric flask, pipette the appropriate volume of Cr(VI) working standard solution (7.17.2) into the volumetric flask and dilute to the mark with water (7.2), close and mix thoroughly. Prepare fresh solutions on the day of use.

7.17.4 Cr(VI) spiking solutions.

The Cr(VI) working standard solution (7.17.2) can be used to spike samples.

7.18 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 (7.11) and 68,04 g of KH_2PO_4 (7.12) 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.

7.19 Magnesium chloride solution.

Dissolve 85,4 g $MgCl_2 \cdot 6H_2O$ (7.10) in a 100 ml volumetric flask, dilute to the mark with water (7.2), close and mix thoroughly.

7.20 Chromium chloride hexahydrate ($CrCl_3.6H_2O$).

$w(CrCl_3 \cdot 6H_2O)$ >96 %.

7.21 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 (7.20) in water (7.2) in a 100 ml volumetric flask, dilute to the mark with water (7.2), close and mix thoroughly. Store the solution in a polypropylene bottle. This reagent is stable for one year. Before using, determine the Cr concentration of the spiking solution.

8 Sample pretreatment

Samples shall be collected using appropriate devices and placed in plastic or glass containers.

NOTE Requirements for test portion preparation are summarised in Annex B.

Samples shall be stored field moist at (4 ± 2) °C until analysis. Pre-treat the sample according to EN 16179, ISO 11464 or EN 15002 if not otherwise specified.

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 shall be avoided.

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

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 digestion solution 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 ± 2,5) °C. Do not allow the solution to boil or evaporate to dryness.

9.2.2 Transfer (2,5 ± 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 (7.16) to each sample using a graduated cylinder, and also add 1 ml of magnesium chloride solution (7.19) containing approximately 400 mg of $MgCl_2$ and 0,5 ml of phosphate buffer solution (7.18). Cover all digestion vessels. If using a heating block, reflux condensers can be used.

9.2.4 Heat the samples to (92,5 ± 2,5) °C with continuous stirring, then maintain the samples at (92,5 ± 2,5) °C for at least (60 ± 5) 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 (7.2). Filter through a 0,45 µm membrane filter (6.3). Rinse the filtration equipment (6.2) with water (7.2) and transfer the filtrate to a 100 ml volumetric flask and fill up to the mark with water (7.2).

NOTE Alternatively the sample can be centrifuged or allowed to settle and fill up the mark with water.

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 is possible (see Annex A).

10.2 Instrumental set-up

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

10.2.2 For post column derivatisation, optimise the ratio of eluent solution and reagent flow rates or adjust the sulphuric acid concentration of the diphenylcarbazide reagent solution (7.14) to obtain the best signal to background ratio. It is important that the ratio between the eluent solution and reagent flow rates is kept constant, that the total flow rate does not exceed the maximum flow rate for the detector and the diphenylcarbazide reagent is 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.

10.2.3 For direct detection, adjust the UV-VIS detector to measure within a range of 355 nm to 375 nm, preferably at 365 nm.

For measuring after post-column derivatisation with 1,5-diphenylcarbazide, adjust the VIS detector to measure within a range of 530 nm to 550 nm, preferably at 540 nm.

10.3 Calibration

10.3.1 Inject a suitable volume (typically 20 µl to 250 µl), of each calibration solution (7.17.3) into the ion chromatographic system (6.4).

10.3.2 Determine the absorbance for each of the calibration solutions using either peak height or peak area mode.

10.3.3 Prepare a calibration graph using a linear plot of the peak height or peak area as a function of calibration solution concentration by least squares regression analysis using suitable software, according to ISO 8466-1.

10.4 Test solution measurement

10.4.1 Inject a suitable volume, e.g. 50 µl, of filtered sample solutions (9.2) into the ion chromatographic system.

10.4.2 Determine the concentrations of Cr(VI) in the test solutions (9.2) by comparison with the calibration graph (10.3.3).

10.4.3 If the Cr(VI) concentration of the sample exceeds the calibration range, dilute the sample with a 1 + 1 diluted alkaline digestion solution (7.16) and re-analyse. Take note of the dilution when calculating the mass concentration of Cr(VI) in the material under investigation.

NOTE For samples expected to have very high concentrations of Cr(VI), it can be necessary to dilute the test solutions before they are first analysed. Otherwise, swamping of the diphenylcarbazide reagent can occur and no colour will develop.

If the chromium (VI) concentration of the sample falls lower than the calibration range, establish a separate calibration function for the lower working range, if necessary.

10.5 Quality control

10.5.1 General

Process quality control (QC) samples with each batch of test samples, as detailed below.

10.5.2 Blank test solution

To assess glassware contamination and/or reagents, process in parallel at least one blank solution following the same digestion procedure as applied to the test samples but omitting the test portion. If contamination is detected control the procedure until the level of Cr(VI) is less than 0,5 times the lowest concentration to be reported and repeat the digestions.

Analyse the blank solutions according to a frequency of 1 blank per 20 test portions or at least once in each series of measurement.

10.5.3 Verification of method

Prepare a soluble Cr(VI) standard solution from a stock standard solution from a different source than that used for preparing the calibration solutions. In parallel with processing the test samples, prepare a blank solution spiked with this soluble Cr(VI) standard solution following the same digestion procedure as applied to the test samples but omitting the test portion. Recovery of Cr(VI) must be within range of 80 % to 120 %. Process this QC sample within each batch.

Alternatively, to evaluate the dissolution of all Cr(VI) species during the digestion process, an insoluble spike, e.g. $PbCrO_4$ (7.13), may be used. In parallel with processing the test samples, prepare a blank solution spiked with , e.g., 20 mg of $PbCrO_4$ following the same digestion procedure as applied to the test samples but omitting the test portion. Recovery of Cr(VI) must be within range of 75 % to 120 %.

Prepare a Cr(III) standard solution from the Cr(III) spiking solution (7.21). In parallel with processing the test samples prepare a blank solution spiked with this Cr(III) standard solution following the same digestion procedure as applied to the test samples but omitting the test portion. Conversion of Cr(III) to Cr(VI) shall be less than 5 %. Process this QC sample within each batch.

10.5.4 Duplicate samples

Process method duplicated samples to estimate the method accuracy according to a frequency of at least 1 duplicate sample per 20 test portions or minimum of 1 per batch.

Duplicate samples must have a relative percent difference of <20%, if both the original and the duplicate are greater than four times the laboratory reporting limit. A control limit of ± the laboratory reporting limit is used when either the original or the duplicate sample is less than four times the laboratory reporting limit.

10.5.5 Soluble Cr(VI) spiked samples

Process soluble spikes, e.g. $K_2Cr_2O_7$ (7.17.4), on a routine basis to estimate the method accuracy in relation to possible reduction processes. Spiked samples consist of solid material to which known amounts of Cr(VI) have been added.

Soluble pre-digestion matrix spikes should be analyzed at a frequency of at least 1 spike sample per 20 test portions or 1 per batch. The matrix spike is then carried through the digestion process. More frequent matrix spikes should be analysed if the sample characteristics within the analytical batch appear to have significant variability based on visual observation. An acceptance range for matrix spike recoveries is 75 % to 125 %.

10.5.6 Cr(III) spiked samples

Process the Cr(III) spiking solution (7.21) on a routine basis to estimate the method accuracy in relation to the possible oxidation processes, expressed as a percent Cr(VI) recovery relative to the spiked amount of Cr(III). Spiked samples consist of solid material to which known amounts of Cr(III) have been added.

The conversion of the Cr(III) spike can be used to assess the risk of method induced oxidation of native Cr(III) contained in the sample to Cr(VI) and shall be less than 5 %.

10.5.7 Interpretation of quality control data

If the verification procedure performed in 10.5.3 and the recoveries from the spiked samples performed in 10.5.5 and 10.5.6 meet laboratory criteria, the analytical result can be judged to be valid.

NOTE 1 An acceptable range for Cr(VI) spike recoveries is 75 % to 125 % in soil, sludge, sediments and similar waste materials according to EPA-method 3060 A[7].

If the verification procedure performed in 10.5.3 meets the laboratory criteria, but the recoveries from the spiked samples performed in 10.5.5 and 10.5.6 do not meet the laboratory criteria, it is appropriate to determine the reducing/oxidising tendency of the sample matrix.

NOTE 2 This can be accomplished by characterisation of each sample for additional analytical parameters, such as pH, ferrous iron (FeII), sulfides, organic carbon content and the oxidation potential. Analysis of these additional parameters establishes the tendency of Cr(VI) to exist or not exist in the unspiked samples and assists in interpreting QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

11 Calculation

Calculate the mass fraction of Cr(VI) in the solid waste material or soil, using Formula (1):

$$w_{\mathrm{Cr(VI)}} = \frac{\rho_d \cdot F \cdot 10}{m \cdot w_{\mathrm{dm}}} \tag{1}$$

where

$w_{\mathrm{Cr(VI)}}$ is the mass fraction of Cr(VI) in the solid material, expressed in milligram per kilogram (mg/kg) dry matter;

ρ_{d} is the concentration of Cr(VI) in the alkaline digested test solution, expressed in microgram per litre (µg/l);

m is the weight of the test portion, expressed in grams (g), nominally 2,5 g;

w_{dm} is the dry matter content of the test portion, expressed as a percentage, determined as specified by ISO 11465 for soil and EN 15934 for waste;

F is the dilution factor (F = 1 if the alkaline digestion solution of nominally 100 ml has not been diluted prior to analysis).

12 Expression of results

Values should be rounded to 0,01 mg/kg, only three significant figures should be expressed.

EXAMPLE:

$w_{\mathrm{Cr(VI)}}$ = 0,15 mg/kg

$w_{\mathrm{Cr(VI)}}$ = 15,3 mg/kg

13 Test report

Work carried out by the testing laboratory shall be covered by a report which accurately, clearly and unambiguously presents the test results and all other relevant information as specified in ISO/IEC 17025.

The test report shall include at least the following information:

a) a reference to this document (ISO 15192:2021);

b) identity of the sample;

c) expression of results according to Clause 12;

d) any deviation from this method;

e) any details not specified in this document or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Ion chromatographic system

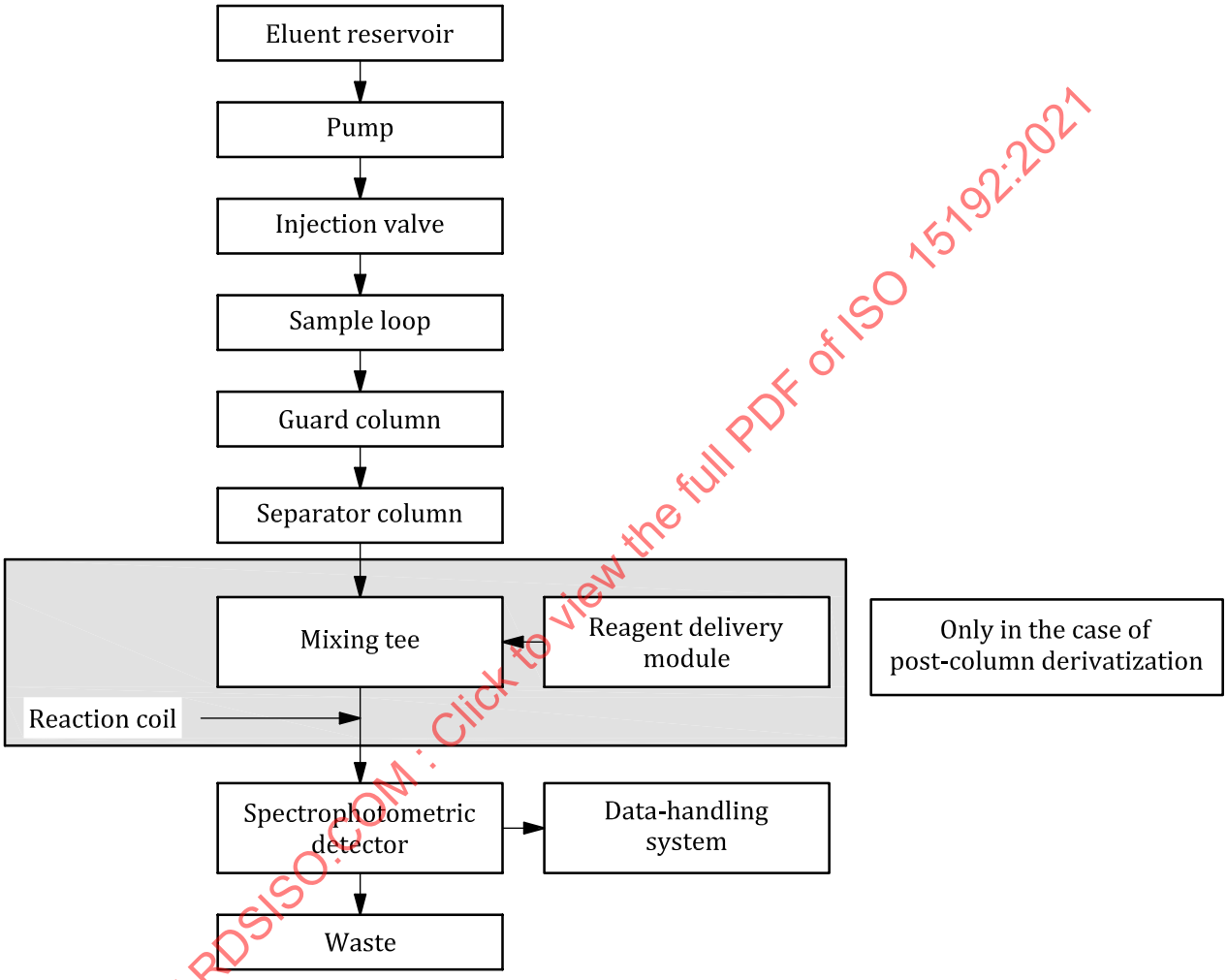

Figure A.1 — Scheme of an ion chromatographic system configured for spectrophotometric detection

An ion chromatography system (Figure A.1), in general, consists of the following components: - Eluent reservoir;

The preparation of a typical eluent used for the seperation column is described by the following:

Ammonium sulfate/ammonium hydroxide eluent concentrate, 2,5 mol/l ammonium sulfate $(NH_4)_2SO_4$/0,5 mol/l ammonium hydroxide (NH_4OH). Dissolve 331 g of ammonium sulfate in approximately 500 ml of water. Quantitatively transfer the solution into a 1 l one-mark volumetric flask, add 75 ml of concentrated ammonium hydroxide and swirl to mix. Dilute to the mark with water, stopper and mix thoroughly.

Eluent solution, 0,25 mol/l ammonium sulfate $(NH_4)_2SO_4$/0,05 mol/l ammonium hydroxide (NH_4OH), pH 8. Add 100 ml of eluent concentrate to a 1 l one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

— Metal- free HPLC pump, 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;

— Sample injection system, incorporating a sample loop of appropriate volume or autosampler device;

— Guard and separator column, suitable for chromate separation with a sufficient ion exchange capacity;

— Spectrophotometric detection system;

In case of direct determination, the IC column is directly coupled to the detector. In case of post column derivatisation, the IC column is coupled to a mixing tee (reaction coil) and then connected to the detector.

— UV-VIS spectrophotometer at 365 nm; or

— VIS spectrophotometer at 540 nm after post column derivatisation.

Data handling system, e.g. a computer with software for data acquisition and evaluation.

Annex B
(informative)

Requirements for test portion preparation

Table B.1 — Requirements for test portion preparation

	Requirement
Parameter	Cr(VI)
Matrix	Solid waste, soil
Typical working range	From about 0,1 mg/kg by post column derivatisation; from about 1 mg/kg by direct UV detection
Sampling instruments	Stainless steel not recommended
Bottle pretreatment	Clean and dry, no special requirements
Bottle material	No stainless steel (e. g. plastic, glass)
Transport conditions	Cooling
Preservation	Cooling at (4 ± 2) °C
Storage conditions	(4 ± 2) °C for at maximum 1 month
Required amount	Typically 15 g
Test portion	2,5 g
Drying procedure	Soil according to ISO 11464 (air-dried); Air-drying is recommended for solid waste in case particle size reduction is needed
Sieving (particle size)	—
Grinding	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.
Compatibility	—

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]. Sample pretreatment (e.g. oven or hot drying) can influence the redox behaviour[3][10][11].

Annex C
(informative)

Validation

C.1 General

Prior to the organisation of the interlaboratory comparison a robustness study was performed. The objectives of the robustness study were the evaluation of different digestion equipments (hot plate, heating block and ultrasonic bath) and evaluation of different measurement methods (ion chromatography with spectrophotometric detection, IC-ICP-MS, ICP-AES, AAS and direct spectrophotometry).

For this purpose three (low and high Cr(VI) contaminated) soils and three waste materials (fly ash, filter cake and paint sludge) were analysed. The following conclusions could be formulated based on these analyses:

Hot plate and heating block digestions gave comparable results on all samples when continuously stirring was performed and temperature was controlled. Ultrasonic bath extraction (at 25 °C and 60 °C) gave significant lower recovery's of Cr(VI) content on all samples.

The addition of magnesium in a phosphate buffer has shown to suppress Cr(III) oxidation in the soil samples. Based on the results of the Cr(III) spiking, the filter cake showed an oxidising tendency. Drying of this sample at different temperatures (40 °C, 60 °C, 80 °C and 105 °C) showed an increase of the Cr(VI) content, indicating an increase of oxidation potential with drying[10].

Ion chromatography with direct spectrophotometric detection and ion chromatography with detection after post column derivatisation with 1,5-diphenylcarbazide gave comparable results. Direct determination of the total chromium content in the alkaline digestion solution of the different materials with AAS and ICP-AES gave comparable results when dilution and/or matrix matching was performed. As could be shown for some of the materials under investigation, direct analysis of the alkaline digestion solution with spectrophotometry may be hampered by co-extracted interfering substances and is therefore not recommended.

An interlaboratory comparison was organized within CEN/TC 292 in December 2005/January 2006 with participants from seven countries. For the interlaboratory comparison, two polluted topsoils and two waste materials were selected from the robustness study with low and high contents of Cr(VI) and distributed to the participants. Table C.1 shows the performance characteristics. Repeatability and reproducibility were calculated according to the principles of ISO 5725-2.

Table C.1 — Performance characteristics of an international interlaboratory comparison on Cr(VI) determination (calculations according to ISO 5725-2)

Sample	N	N_{res}	$w_{Cr(VI)}$ mg/kg	S_R mg/kg	V_R %	S_r mg/kg	V_r %	R mg/kg	r mg/kg
Soil 1	15	45	1,69	0,43	25,19	0,22	13,08	1,18	0,61
Soil 2	19	57	2 007	205	10,22	88	4,36	568	242
Waste 1	19	57	11 360	1 308	11,51	788	6,94	3 622	2 183
Waste 2	13	39	12,90	8,97	69,55	1,59	12,31	24,85	4,40

N number of accepted laboratories.

N_{res} number of accepted results.

$w_{Cr(VI)}$ mean content of Cr(VI) calculated from N data sets, in mg/kg dry matter.

S_R reproducibility standard deviation.

S_r repeatability standard deviation.

V_R relative reproducibility standard deviation.

V_r relative repeatability standard deviation.

R reproducibility limit.

In Tables C.2 to C.5, an overview of the Cr(VI) determination is given per sample and per combination of digestion and detection method:

Method A: Hot plate digestion and ion chromatography with direct spectrophotometric detection.

Method B: Hot plate digestion and ion chromatography with spectrophotometric detection after post-column derivatisation with 1,5-diphenylcarbazide.

Method C: Heating block digestion and ion chromatography with direct spectrophotometric detection.

Method D: Heating block digestion and ion chromatography with spectrophotometric detection after post-column derivatisation with 1,5-diphenylcarbazide.

Table C.2 — Data for Cr(VI) determination and spike recoveries on soil 1 (low contaminated topsoil)

Method	N	N_{res}	$w_{Cr(VI)}$ mg/kg	SD_w mg/kg	$C_{V,w}$ %	$rec_{Cr(VI)}$ %	$SD_{recCr(VI)}$%	$rec_{Cr(III)}$ %	$SD_{recCr(III)}$%
A	3	9	1,75	0,46	26,32	98,0	7,9	3,5	5,1
B	7	21	1,83	0,23	12,61	94,8	11,7	−1,7	12,4
C	2	6	1,58	0,56	35,13	95,5	10,6	3,6	0,8
D	3	9	1,36	0,51	37,25	96,5	2,7	1,1	3,7

N number of accepted laboratories.

N_{res} number of accepted results.

$w_{Cr(VI)}$ mean content of Cr(VI) calculated from N data sets, in mg/kg dry matter.

SD_w is the standard deviation calculated from N laboratory means.

$C_{V,w}$ is the coefficient of variation of laboratory means.

$rec_{Cr(VI)}$ is the mean recovery of Cr(VI) spike.

$SD_{recCr(VI)}$ is the standard deviation of recoveries of Cr(VI) spike.

$rec_{Cr(III)}$ is the mean recovery of Cr(III) spike detected as Cr(VI).

$SD_{recCr(III)}$ is the standard deviation of recoveries of Cr(III) spike detected as Cr(VI).

Table C.3 — Data for Cr(VI) determination and spike recoveries on soil 2 (high contaminated topsoil)

Method	N	N_{res}	$w_{Cr(VI)}$ mg/kg	SD_w mg/kg	$C_{V,w}$ %	$rec_{Cr(VI)}$ %	$SD_{recCr(VI)}$%	$rec_{Cr(III)}$ %	$SD_{recCr(III)}$%
A	4	12	2 010	209	10,41	98,5	5,1	3,0	3,6
B	8	24	2 073	102	4,92	99,1	16,9	1,4	10,7
C	4	12	1 843	269	14,57	101,2	12,2	4,9	2,8
D	3	9	2 044	221	10,82	101,1	10,8	1,3	5,0

N number of accepted laboratories.

N_{res} number of accepted results.

$w_{Cr(VI)}$ mean content of Cr(VI) calculated from N data sets, in mg/kg dry matter.

SD_w *is* the standard deviation calculated from N laboratory means.

$C_{V,w}$ is the coefficient of variation of laboratory means.

$rec_{Cr(VI)}$ is the mean recovery of Cr(VI) spike.

$SD_{recCr(VI)}$ is the standard deviation of recoveries of Cr(VI) spike.

$rec_{Cr(III)}$ is the mean recovery of Cr(III) spike detected as Cr(VI).

$SD_{recCr(III)}$ is the standard deviation of recoveries of Cr(III) spike detected as Cr(VI).

Table C.4 — Data for Cr(VI) determination and spike recoveries on waste 1 (paint sludge)

Method	N	N_{res}	$w_{Cr(VI)}$ mg/kg	SD_w mg/kg	$C_{V,w}$ %	$rec_{Cr(VI)}$ %	$SD_{recCr(VI)}$%	$rec_{Cr(III)}$ %	$SD_{recCr(III)}$%
A	4	12	10 695	838	7,84	96,9	5,5	2,4	2,8
B	8	24	11 299	867	7,67	95,5	5,6	-1,7	8,5
C	4	12	11 478	1 327	11,56	97,9	13,0	1,7	6,0
D	3	9	12 249	1 796	14,66	96,7	7,6	4,2	3,4

N number of accepted laboratories.

N_{res} number of accepted results.

$w_{Cr(VI)}$ mean content of Cr(VI) calculated from N data sets, in mg/kg dry matter.

SD_w *is* the standard deviation calculated from N laboratory means.

$C_{V,w}$ is the coefficient of variation of laboratory means.

$rec_{Cr(VI)}$ is the mean recovery of Cr(VI) spike.

$SD_{recCr(VI)}$ is the standard deviation of recoveries of Cr(VI) spike.

$rec_{Cr(III)}$ is the mean recovery of Cr(III) spike detected as Cr(VI).

$SD_{recCr(III)}$ is the standard deviation of recoveries of Cr(III) spike detected as Cr(VI).

Table C.5 — Data for Cr(VI) determination and spike recoveries on waste 2 (fly ash)

Method	N	N_{res}	$w_{Cr(VI)}$ mg/kg	SD_w mg/kg	$C_{V,w}$ %	$rec_{Cr(VI)}$ %	$SD_{recCr(VI)}$%	$rec_{Cr(III)}$ %	$SD_{recCr(III)}$%
A	2	6	11,91	6,16	51,70	67,9	53,9	25,5	26,2
B	5	15	14,09	8,88	63,03	90,3	46,1	13,8	20,3
C	3	9	14,64	10,09	68,93	74,0	38,0	6,6	7,7
D	3	9	9,83	13,08	133,04	49,1	55,8	3,1	7,1

N number of accepted laboratories.

N_{res} number of accepted results.

$w_{Cr(VI)}$ mean content of Cr(VI) calculated from N data sets, in mg/kg dry matter.

SD_w *is* the standard deviation calculated from N laboratory means.

$C_{V,w}$ is the coefficient of variation of laboratory means.

$rec_{Cr(VI)}$ is the mean recovery of Cr(VI) spike.

$SD_{recCr(VI)}$ is the standard deviation of recoveries of Cr(VI) spike.

$rec_{Cr(III)}$ is the mean recovery of Cr(III) spike detected as Cr(VI).

$SD_{recCr(III)}$ is the standard deviation of recoveries of Cr(III) spike detected as Cr(VI).

C.2 Evaluation

The performance characteristics for Cr(VI) determination in the case of both soils and waste 1 are acceptable. However, for waste 2 the large relative reproducibility standard deviation suggests strong matrix effects. This indicates that for unknown matrices, supplementary quality control data are needed in order to assess the validity of the analytical result.

C.3 Soil samples

The spike recoveries obtained with the four methods are good in the case of the two soil samples [recovery Cr(VI) spike >95 %, recovery Cr(III) spike <5 %]. Method B (hot plate digestion and ion chromatography with spectrophotometric detection after post-column derivatisation with 1,5-diphenylcarbazide) gives for both soils the most reproducible results. Especially for soil 1 (low contaminated) this will be related to the superior sensitivity of the detection method.

C.4 Waste samples

The spike recoveries obtained with the four methods are good in the case of the paint sludge (recovery Cr(VI) spike >95 %, recovery Cr(III) spike <5 %). However, for the fly ash sample the recovery data are bad. The ranges of recoveries for Cr(VI) and Cr(III) are very large and can be attributed to the poor reproducibility of the determination due to the reducing tendency of the sample matrix. The latter was deduced based on additional tests applying spiking with isotopically enriched chromium species in the digestion procedure [according to method described in Reference [12]]. Based on these results sample heterogeneity as major cause of poor recoveries could be excluded as well. In this case no valid Cr(VI) content can be reported on the fly ash sample and the test report should include a remark on the recoveries of the spiked samples. Further investigation on the reducing/oxidising tendency of the sample matrix is appropriate.

Annex D
(informative)

Background on methods for the determination of Cr(VI) in solid samples

D.1 Summary of literature methods for Cr(VI) determinations in solids[5]

The first efforts to set up an analytical protocol for determining Cr(VI) in solid material dates back to the end of the seventies. Since then, many studies and new analytical protocols for Cr(VI) analysis and, more generally, Cr speciation in solid matrices have been proposed[7]to[16]. An overwiew of Cr(VI) speciation in solid materials is given in the state-of-the-art document CEN/TR 14589. Literature methods for Cr(VI) determinations in solids have been reviewed by M. Pettine et al.[5], Unceta et al.[47] , and Seby et al.[48]

The digestion procedure described in this International Standard is based on the USEPA Method 3060A. In 1996, USEPA[7] revised Method 3060[20] for extracting Cr(VI) from soil, sludges, sediments and solid wastes. This new method (3060A) was based on the findings by James et al.[4] and consisted of alkaline digestion at 90 °C to 95 °C for 60 min. According to this method, 2,5 g of a field-moist and homogenized sample were placed into a 250 ml digestion vessel; 50 ml of digestion solution (0,28 mol/l Na_2CO_3/0,5 mol/l NaOH) followed by 400 mg of $MgCl_2$ and 0,5 ml of 1,0 mol/l phosphate buffer (0,5 mol/l K_2HPO_4/0,5 mol/l KH_2PO_4) were added to the solid sample. The addition of Mg^{2+} in a phosphate buffer to the alkaline extraction solution prevented risks of Cr(III) oxidation, which may lead to Cr(VI) overestimate, particularly in samples with high Cr(III)/Cr(VI) ratios.

In 2018, a critical assessment of hexavalent chromium species from different solid environmental, industrial and food matrices was published[48]. With regards to the extraction procedures, it was concluded that the use of 0,5 M NaOH/0,28 M Na_2CO_3 solutions and heating at 90 °C to 95 °C is still the more widespread procedure. Such alkaline extraction allows both the extraction of all the Cr(VI) compounds and its stabilization in the extracts while Cr(III) precipitates. Nevertheless, and although method-induced oxidation and reduction are minimized, species transformation can still occur with this procedure. As a result, the importance of spiking tests for the identification of possible matrix effects have been stressed by different authors while studying the influence of sample matrix on the alkaline extraction of Cr(VI) in soils and industrial materials[49].

Because of its better selectivity and sensitivity, on-line hyphenated techniques between liquid chromatography and ICP-MS are preferred[48]. Another advantage of using HPLC-ICP-MS is the possibility to quantify Cr(VI) with speciated isotope dilution allowing correction of Cr(VI) reduction and/or Cr(III) oxidation during extraction. Moreover, methods enabling the speciation of both Cr(VI) and Cr(III) are receiving more and more interest. EDTA extraction at alkaline pH to stabilize both Cr redox species (Cr(VI) via the alkaline pH and Cr(III) via the complexation with EDTA) is usually applied. The Cr(VI) and Cr(III)-EDTA complex, both negative species at alkaline pH, can then be separated on an anion-exchange column and detected by ICP-MS. However, this procedure is still not sufficient to totally extract Cr(III). To overcome this issue, Wolle et al. developed a strategy to quantify hexavalent (Cr(VI)), soluble trivalent (Cr(III)) and insoluble chromium (Cr) species in soil by integrating existing methods of Cr(VI) and total Cr determination with speciated isotope dilution mass spectrometry (SIDMS)[50]. Two different extraction methods that utilize a NaOH–Na_2CO_3 solution (EPA Method 3060A) and alkaline solution of ethylenediaminetetraacetic acid (EDTA) were used to extract Cr(VI) (along with soluble Cr(III) in the latter case). The extracted Cr was speciated by ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS), and the separated species were quantified using the mathematical relationships in SIDMS with simultaneous correction for their method-induced transformations. The Cr species that fell out as insoluble solid during extraction were determined by

isotope dilution mass spectrometry (IDMS) after decomposing the extraction residues by microwave digestion in a mixture of HNO_3 and HF.

D.2 Theoretical kinetic background for Cr(III) to Cr(VI) interconversions[5]

The experimental conditions adopted for the extraction of Cr(VI) from solid matrices significantly influence the reliability of the final results owing to possible undesired Cr(VI) to Cr(III) interconversions.

Cr(VI) may react with many inorganic reductants, such as Fe(II) and sulfide; a number of organic compounds, including carboxylic and hydroxo-carboxylic acids, aldehydes, phenols, humic acid (HU), etc., are also able to reduce Cr(VI). Humic material and Fe are common components in soil and sediments and can be easily released from these solids under strong alkaline solutions. The attack of solid material with 0,5 mol/l NaOH solution is in fact suggested to solubilize humic substances[31]. Furthermore, the solubility of Fe(III) is markedly increased in strongly alkaline solutions (pH > 10) because of the formation of $Fe(OH)_4^-$ species[32].

Thermodynamic calculations also suggest that a number of chemicals including molecular oxygen and Mn(IV) oxides are potential oxidants for Cr(III) under acid and alkaline conditions, while hydrogen peroxide and Mn(III) oxides may be oxidants or reductants depending on pH[33][34]

Cr(III) to Cr(VI) interconversions may take place when reactants, which are able to reduce Cr(VI) or oxidize Cr(III), are present, and the operational conditions are suitable for these redox reactions to occur. Therefore, the kinetic characteristics of the redox reactions, which on a thermodynamic basis may be responsible for Cr(VI) to Cr(III) interconversions during the digestion, need to be carefully evaluated and are briefly described hereunder.

Fe(II) is a common reducing compound in solid matrices and its reaction with Cr(VI) during the extraction treatment leads to Cr(VI) concentrations, which are lower than the real ones. Under strong alkaline conditions, the rates of the oxidation of Fe(II) with dissolved oxygen becomes faster than those for the oxidation of Fe(II) with Cr(VI). The increase of temperature has a higher influence on the rates of the oxidation of Fe(II) with O_2 with respect to those for the oxidation of Fe(II) with Cr(VI). In high alkaline, carbonate-rich solutions, rates for the oxidation of Fe(II) with O_2 are strongly increased by the species $Fe(CO_3)_2^{2-}$ that reacts faster than $Fe(OH)_2$[36] while oxidation rates of Fe(II) with Cr(VI) are not affected by carbonate species[35]. The positive effect of carbonates on the rates of oxidation of Fe(II) with O_2 should widely balance the diminished concentration of O_2 with increasing temperature up to 80 °C to 90 °C. On the contrary, under acid conditions, the oxidation of Fe(II) with Cr(VI) becomes dominant with respect to the parallel oxidation of Fe(II) with molecular oxygen. The above considerations suggest that a value of pH ≥ 10, along with high carbonate concentration and high temperatures, would be able to prevent interference by Fe(II) since they favour its oxidation by dissolved oxygen.

The alkaline digestion also minimizes other possible reactions leading to the reduction of Cr(VI) by sulfide, sulfite, humic material and other organic compounds. Kinetic and thermodynamic characteristics of the reactions for Cr(VI) reduction and increased competition by molecular oxygen reacting faster than Cr(VI) with possible reductants contribute to lower the risk of reduction of Cr(VI) at a pH > 10.

Contrary to the diminished risk of reduction of Cr(VI) with increasing pH, the risk of oxidative processes converting Cr(III) to Cr(VI) tends to increase with increasing pH. Cr(III) aging is also strongly and positively affected by an increase in pH and temperatures, thus reducing, as a matter of fact, the potential oxidation of Cr(III).

Molecular oxygen and manganese oxides are possible oxidants during the digestion of solids. The USEPA

Method 3060A[7][20] took into account the possibility that native Cr(III) in solid matrices could be oxidized under alkaline conditions and suggested that, in the case where oxidation was suspected, Mg^{2+} was added to the alkaline extracting solution to suppress oxidation. It was hypothesized that the suppression was due to Cr(III) coprecipitation with Mg^{2+} or to sorption of Mg^{2+} on Mn oxides rendering them less prone to oxidize Cr(III)[25]. Mg^{2+} was also proved to play a strong negative effect on the rates of oxidation of Cr(III) with H_2O_2 because of its influence on the aging of Cr(III)[8]. This effect was