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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

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.

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

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 additon of Mg^{2+} 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 (λ_{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).

6 Apparatus

Use ordinary laboratory apparatus and the following.

6.1 Digestion equipment, hotplate 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 $mS \cdot m^{-1}$ equivalent to a resistivity greater than 0,01 $M\Omega \cdot m$ 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 MΩ·m (usually expressed by manufacturers of water-purification systems as 18 MΩ·cm).

7.2 Sulfuric acid (H_2SO_4), concentrated, $\rho(H_2SO_4) \sim 1{,}84$ g/ml, $w(H_2SO_4) \sim 98$ %.

7.3 Sodium carbonate (Na_2CO_3), anhydrous, $w(Na_2CO_3) > 99{,}9$ %.

7.4 1,5-Diphenylcarbazide $[(C_6H_5NHNH)_2CO]$, $w[(C_6H_5NHNH)_2CO] > 98$ %.

7.5 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 mass at 110 °C, cool and store in a dessiccator.

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

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

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 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 (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 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 ± 2) °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 ± 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 (7.15) 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 ± 2,5) °C while stirring continuously, then maintain the samples at (92,5 ± 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.

10.2.4 In the case of direct detection, adjust the UV/VIS detector to measure within a range of 355 nm to 375 nm, preferably at 365 nm.

In the case of measuring after post-column derivatization 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 (20 µl to 250 µl), e.g. 50 µl, of each calibration solution (7.16.3) into the ion chromatographic system (6.4).

10.3.2 Determine the absorbance for each of the calibration solutions using either the 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 the calibration-solution concentration by a least-squares regression analysis using suitable software.

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 concentrations of Cr(VI) are found to be above the upper calibration solution, dilute the extract with a 1 + 1 diluted alkaline digestion solution (7.15) in order to bring them within the linear range and repeat the analysis. 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 might 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.

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 and/or reagent contamination, 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 negligible and repeat the digestions.

Analyse the blank solutions at least once in each series of measurements.

10.5.3 Verification of method

Prepare a 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 Cr(VI) standard solution, following the same digestion procedure as that applied to the test samples, but omitting the test portion. Process this QC sample within each batch.

Prepare a Cr(III) standard solution from the Cr(III) spiking solution (7.20). In parallel with processing the test samples, prepare a blank solution spiked with this Cr(III) standard solution, following the same digestion

procedure as that applied to the test samples, but omitting the test portion. Process this QC sample within each batch.

10.5.4 Duplicate samples

Process duplicate samples to estimate the method accuracy (at least one per batch).

10.5.5 Cr(VI) spiked samples

Process soluble spikes [e.g. $K_2Cr_2O_7$ (7.7)] 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 predigestion matrix spikes should be analysed (at least one 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.

To evaluate the dissolution of all Cr(VI) species during the digestion process, an insoluble spike [e.g. $PbCrO_4$ (7.12)] may be used.

The recovery of the Cr(VI) spike can be used to assess the following criteria (see 5.1):

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

— conditions of the digestion shall not induce reduction of native Cr(VI) to Cr(III).

10.5.6 Cr(III) spiked samples

Process the Cr(III) spiking solution (7.20) 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 recovery 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).

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 USEPA Method 3060A[26].

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/oxidizing tendency of the sample matrix.

NOTE 2 This can be accomplished by characterization of each sample for additional analytical parameters, such as pH, ferrous iron Fe(II), 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 the following equation:

$$w_{\mathrm{Cr(VI)}} = \frac{\rho_{\mathrm{d}} \cdot F \times 10}{m \cdot w_{\mathrm{dm}}} \quad (1)$$

where

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

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

m is the mass of the test portion, expressed in grams, nominally 2,5 g;

w_{dm} is the dry-matter mass fraction of the test portion, expressed as a percentage (for soil based on ISO 11465, for waste based on EN 14346);

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 and 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 test report which accurately, clearly and unambiguously presents the test results and all other relevant information.

In addition to test results, the test report shall include at least the following information:

a) a reference to this International Standard, ISO 15192:2010;

b) name and address of the testing laboratory, and the location where the test was carried out if it is different from the address of the testing laboratory;

c) unique identification of the test report (such as serial number) and of each page, and total number of pages of the report;

d) identification and description of the laboratory sample(s);

e) quantity and receipt date of the laboratory sample(s) and date(s) the test was performed;

f) relevant information about the alkaline digestion procedure and the sample(s):

— quantity of each test portion;

— sample(s) pretreatment (e.g. milling);

- reference to the actual digestion method (e.g. digestion equipment, reagents);
- technique used for the separation of the solid residue, if any (e.g. centrifugation, filtering);
- description and reasons for any deviation from the standard procedures;
- method and result of dry-matter determination;
- if the recoveries from the spiked samples performed in 10.5.5 and 10.5.6 do not meet the laboratory criteria, report on the reducing/oxidizing tendency of the sample matrix;

g) signature and title, or an equivalent marking, of (a) person(s) accepting technical responsibility for the test report and date of issue;

h) statement that the information contained in the test report relates exclusively to the laboratory sample(s) tested;

i) statement that the test report shall not be reproduced, except in full, without the written approval of the testing laboratory.

The test report may also include the following information:

- information about the sampling;
- results of the analytical determinations carried out with other methods on the same samples, if any;
- some analytical advice or recommendations arising from the test results;
- any factors not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Alternative methods for direct determination of Cr(VI) in the alkaline digestion solution

When it is proven that no species of chromium other than Cr(VI) is present after digestion, then direct determination of Cr(VI) in the alkaline digestion solution with inductively coupled plasma/atomic emission spectroscopy (ICP/AES), atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP/MS) may be possible. In order to prove that Cr(VI) is the only soluble form of chromium present in the alkaline digestion solution, spiking of the sample with Cr(III), followed by the same digestion procedure as applied to the test portion, is required.

After performing the digestion procedure described in 9.2, accurately pipette an appropriate volume (e.g. 5 ml) of the filtrated alkaline digestion solution into individual volumetric flasks (e.g. 50 ml), adjust the pH to the appropriate value of the corresponding technique used and fill up the flask to the mark with water. If a flocculent precipitate should form as a result of pH adjustment, the sample shall be filtered again prior to analysis.

The diluted and acid preserved extracts are analysed for total chromium mass fractions by using appropriate methods, such as AAS, ICP/AES or ICP/MS in accordance with one of the following International Standards:

— ISO 9174:1998;

— ISO 11885:2007;

— ISO 15586:2003;

— ISO 17294-2:2003.

Due to high element concentrations, e.g. sodium, in the alkaline digestion solution, the calibration strategy shall be adapted appropriately. In many cases, matrix matching of the calibration solutions and/or dilution of the sample, together with addition of internal standards or using the standard addition method, is necessary. The analytical method needs to be validated on alkaline digestion solutions prior to routine use.

The results of the validation interlaboratory comparison (see Annex E) show that, for Soil 1, Soil 2 and Waste 1, the recovery of the Cr(III) spike was less than 5 %. In these cases, it can be presumed that Cr(VI) was the only soluble form of chromium present in the alkaline digestion solution. Determination of the total chromium mass fraction, using ICP/AES and AAS, in the digestion solution was in agreement with the Cr(VI) mass fraction determined with the selective methods. For Soil 1, direct spectrophotometric determination of Cr(VI) in the alkaline digestion solution after complexation with diphenylcarbazide was hampered by co-extracted interfering substances and is therefore not recommended. For Waste 2, and thus for samples with oxidizing/reducing tendency, in general, no assessment of validity of the analytical results can be performed with the non-selective direct methods.

Annex B
(informative)

Ion chromatographic system

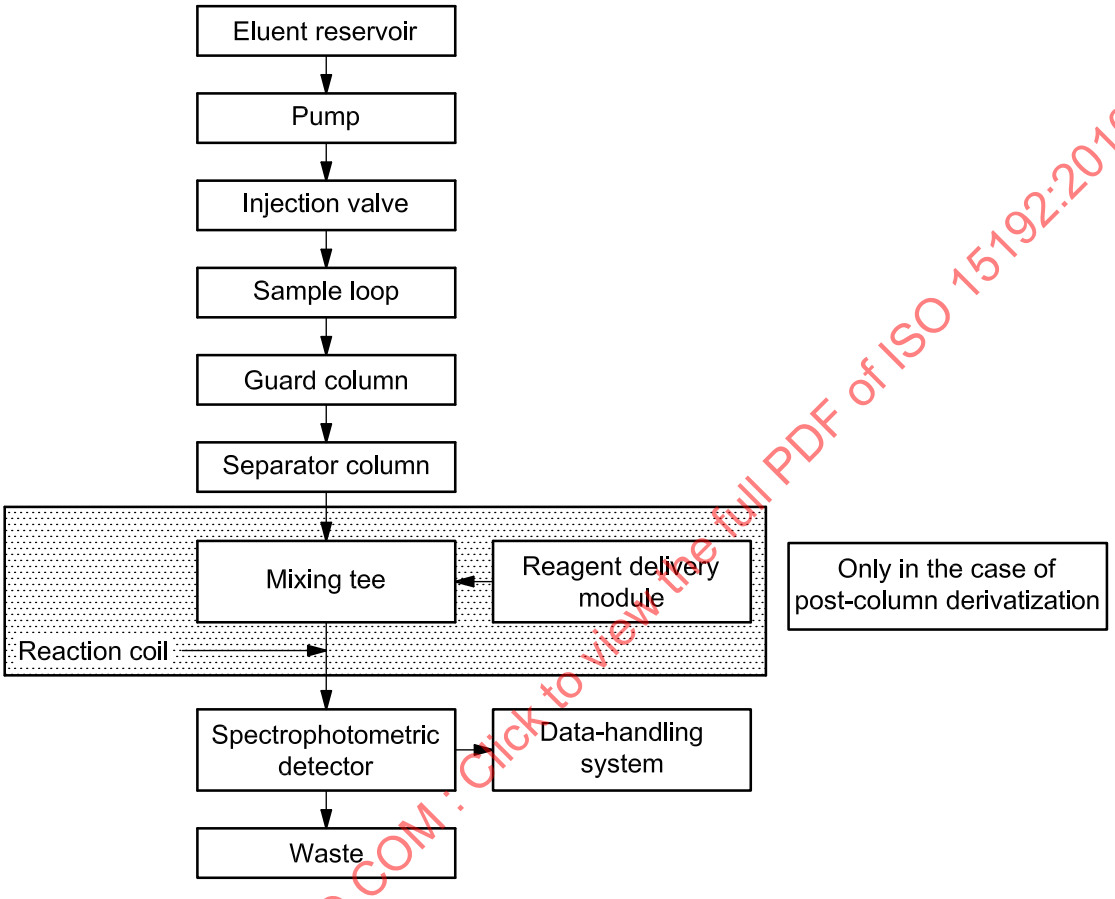

Figure B.1 — Scheme of an ion chromatographic system configured for spectrophotometric detection

For UV determination, the ion chromatography (IC) column is directly coupled to the UV detector. For post-column derivatization, the IC column is coupled to a mixing tee.

A typical eluent used for the separation column is prepared by the following method.

— **Ammonium sulfate/ammonium hydroxide eluent concentrate**, 2,5 mol/l ammonium sulfate $[(NH_4)_2SO_4]$ and 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 $[(NH_4)_2SO_4]$ and 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.

Annex C
(informative)

Requirements for test portion preparation

Table C.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 derivatization; from about 1 mg/kg by direct UV detection
Sampling instruments	Stainless steel is not recommended
Bottle pretreatment	Clean and dry, no special requirements
Bottle material	No stainless steel (e.g. plastics, glass)
Transport conditions	Cooling
Preservation	Cooling at (4 ± 2) °C
Storage conditions	(4 ± 2) °C for a maximum of 1 month
Required amount	Typically 15 g
Test portion	2,5 g
Drying procedure	Soil in accordance with 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 seven days after digestion from soil (Reference [8] in the Bibliography). Sample pretreatment (e.g. oven or hot drying) can influence the redox behaviour (References [10], [52] and [53] in the Bibliography).

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 (Reference [12] in the Bibliography)

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 (References [15] to [31] in the Bibliography). 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 and S. Capri[12].

The digestion procedure described in this International Standard is based on the USEPA Method 3060A[26]. In 1996 USEPA revised Method 3060 for extracting Cr(VI) from soil, sludges, sediments and solid wastes. This new method (3060A) was based on the findings by James et al.[11] 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. Adding Mg^{2+} in a phosphate buffer to the alkaline extraction solution prevented risks of Cr(III) oxidation, which may lead to a Cr(VI) overestimate, particularly in samples with high Cr(III)/Cr(VI) ratios.

D.2 Theoretical kinetic background for Cr(III) to Cr(VI) interconversions (Reference [12] in the Bibliography)

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 (Reference [32] in the Bibliography). Furthermore, the solubility of Fe(III) is markedly increased in strongly alkaline solutions (pH > 10) because of the formation of $Fe(OH)_4^-$ species (Reference [33] in the Bibliography).

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 (References [34] and [35] in the Bibliography).

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 $Fe(OH)_2$ (Reference [37] in the Bibliography), while oxidation rates of Fe(II) with Cr(VI) are not affected by carbonate species (Reference [36] in the Bibliography). 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 $\geqslant$ 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[26] 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) (Reference [24] in the Bibliography). 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) (Reference [38] in the Bibliography). This effect was supposed to be due to the formation of a solid phase of the type $Cr_xMg_{(1-x)1.5}(OH)_3$ that, similarly to the mixed solid phase $Cr_xFe_{(1-x)1.5}(OH)_3$ (Reference [39] in the Bibliography), controls the solubility of Cr(III). This effect of Mg^{2+} is probably observed also in the case of the oxidation of Cr(III) with O_2 and MnO_2 and substantiates the USEPA choice of adding this ion to suppress the oxidation of Cr(III) during the alkaline digestion of solids. A similar influence on Cr(III) aging was also proved in the case of carbonate (Reference [38] in the Bibliography).

Based on these considerations concerning the kinetics of Cr(III) oxidation, a value of pH around 10, high temperature and high concentrations of Mg^{2+} and carbonate ions would minimize risks of Cr(III) conversion to Cr(VI) during the digestion of solid samples.

Although the described procedure gives a maximal dissolution of all forms of Cr(VI) in solid samples while minimizing method-induced oxidation and reduction, species transformation may still occur. To correct for species transformation in the analysis of Cr(VI) in solid samples, speciated isotope dilution mass spectrometry can be used as described by D. Huo and H.M. “Skip” Kingston[51]. USEPA RCRA Method 6800 [Speciated Isotope Dilution Mass Spectrometry (SIDMS)], addresses the correction for such degradations or conversion (Reference [55] in the Bibliography).

D.3 Special needs for Cr(VI) determination in soil extracts (Reference [13] in the Bibliography)

The diphenylcarbazide (DPC) method is the most common method for determining Cr(VI) in aqueous solutions. This method suffers from the presence of interfering compounds, some of which are explicitly reported in published protocols (References [40] and [41] in the Bibliography). In addition to these chemicals (molybdenum, mercury, iron, vanadium), which give a positive interference, the presence of reductants able to compete with DPC under acid conditions leads to Cr(VI) underestimates. Hydrogen peroxide, which reduces Cr(VI) to Cr(III) under acid conditions (References [42] and [43] in the Bibliography), is one of the possible reductants in aqueous solutions. These also include Fe(II), sulfide, sulfite and a number of organic compounds (Reference [44] in the Bibliography). However, the presence of effective concentrations of

reductants of Cr(VI) is not common in the analysis of aqueous samples, while it becomes much more probable in the case of the application of this method to soil extracts.

Strongly alkaline conditions are recommended for digesting solids because of their higher ability to minimize undesired Cr(III) to Cr(VI) interconversions during the digestion (Reference [44] in the Bibliography). These conditions favour the dissolution of Fe(III) species and humic-like matter (HM) that interfere in the determination of Cr(VI) by the DPC method. The dissolution of Fe(III) is driven by the formation of negatively charged Fe(III) hydrolysis products such as $Fe(OH)_4^-$ (Reference [45] in the Bibliography), while the release of humic matter is connected with the formation of humates, which are soluble under strong alkaline conditions (Reference [46] in the Bibliography).

Zhilin et al.[47] stressed that the spectrophotometric DPC method may not be applied in the presence of humic compounds without their complete removal prior to analysis. An ion chromatography (IC) method followed by a post-column derivatization of Cr(VI) with DPC was proposed to separate Cr(VI) from other positive interferences (Reference [48] in the Bibliography). This IC protocol was published as the USEPA Method 7199[49]. The ion chromatographic method obviates most of the problems caused by HM due to dilution of the sample with the eluent stream (ammonium sulfate and ammonium hydroxide at pH 9,0 to 9,5), passage through a guard column that removes organics, and Cr(VI) separation on an anion-exchange column.

Based on these considerations, the use of the ion chromatography method is needed to overcome interferences from reductants when derivatization of Cr(VI) with DPC is used.

Test results for over 1 500 field soil samples demonstrated dissolution of soluble and insoluble Cr(VI) spikes with the alkaline digestion method (Reference [10] in the Bibliography). In soils containing Cr(VI) and in most aerobic soils without native Cr(VI), acceptable Cr(VI) spike recoveries were obtained. Auxiliary parameters, including oxidation-reduction potential, pH, sulfide and total organic carbon, demonstrated that strongly reducing samples cannot maintain Cr(VI) laboratory matrix samples. Correct interpretation of poor Cr(VI) spike recovery should avoid labelling these data as unacceptable results without auxiliary parameter characterization of such samples.

D.4 Determination of Cr(VI) in glass

For the determination of Cr(VI) in glass, a reference method has been developed by the International Commission on Glass, Technical Committee 2 (Reference [50] in the Bibliography). In this recommended procedure, the glass sample is digested with a mixture of sulfuric acid and ammonium hydrogen fluoride at room temperature, then diphenylcarbazide is added to form a violet complex which is measured with a spectrophotometer. The method is sensible down to 2 mg Cr(VI)/kg of glass.

D.5 Determination of Cr(VI) in air particulate matter

For the determination of Cr(VI) in air particulate matter, a reference method has been developed by the International Organization for Standardization (ISO/TC 146, SC 2). ISO 16740:2005 specifies a method for the determination of the time-weighted average mass concentration of hexavalent chromium in workplace air. Separate sample preparation methods are specified for the extraction of soluble and insoluble hexavalent chromium.

Annex E
(informative)

Validation interlaboratory comparison

E.1 Robustness study

Prior to the organization of the interlaboratory comparison, a robustness study was performed. The objectives of the robustness study were the evaluation of different digestion equipments (hotplate, 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 soils [with low and high Cr(VI) contamination] and three waste materials (fly ash, filter cake and paint sludge) were analysed. The following conclusions could be formulated, based on these analyses.

Hotplate and heating-block digestions gave comparable results on all samples when continuous stirring was performed and the temperature was controlled. Ultrasonic bath extraction (at 25 °C and 60 °C) gave significant lower recoveries of Cr(VI) mass fraction on all samples.

The addition of magnesium in a phosphate buffer has been shown to suppress Cr(III) oxidation in the soil samples. Based on the results of the Cr(III) spiking, the filter cake showed an oxidizing tendency. Drying of this sample at different temperatures (40 °C, 60 °C, 80 °C and 105 °C) showed an increase of the Cr(VI) mass fraction, indicating an increase of oxidation potential with drying (Reference [52] in the Bibliography).

Ion chromatography with direct spectrophotometric detection and ion chromatography with detection after post column derivatization with 1,5-diphenylcarbazide gave comparable results. Direct determination of the total chromium mass fraction 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.

E.2 Interlaboratory comparison

An interlaboratory comparison was organized within CEN/TC 292 WG 3 in December 2005/January 2006 with participants from seven member countries. For the interlaboratory comparison, two polluted topsoils and two waste materials were selected from the robustness study with low and high mass fractions of Cr(VI) and distributed to the participants. Table E.1 shows the performance characteristics. Repeatability and reproducibility were calculated according to the principles of ISO 5725 (all parts).

Table E.1 — Performance characteristics of an international interlaboratory comparison on Cr(VI) determination [calculations according to ISO 5725 (all parts)]

Sample	N	N_{res}	$\bar{w}_{Cr(VI)}$ mg/kg	s_R mg/kg	$C_{V,R}$ %	s_r mg/kg	$C_{V,r}$ %	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 is the number of accepted laboratories;
N_{res} is the number of accepted results;
$\bar{w}_{Cr(VI)}$ is the mean mass fraction of Cr(VI) calculated from N quality-control sets, in milligrams per kilogram of dry matter;
s_R is the reproducibility standard deviation;
s_r is the repeatability standard deviation;
$C_{V,R}$ is the relative reproducibility standard deviation;
$C_{V,r}$ is the relative repeatability standard deviation;
R is the reproducibility limit;
r is the repeatability limit.

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

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

Method B: Hotplate digestion and ion chromatography with spectrophotometric detection after post-column derivatization 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 derivatization with 1,5-diphenylcarbazide.

Table E.2 — Data for Cr(VI) determination and spike recoveries on Soil 1 (topsoil with low contamination)

Method	N	N_{res}	$\bar{w}_{Cr(VI)}$ mg/kg	$s_{\bar{w}}$ mg/kg	$C_{V,\bar{w}}$ %	rec. Cr(VI) %	$s_{rec\ Cr(VI)}$ %	rec. Cr(III) %	$s_{rec\ Cr(III)}$ %
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