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Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials —

Part 4:
Extraction of humic substances from solid samples

Qualité du sol — Paramètres pour la modélisation géochimique de la lixiviation et de la spéciation des constituants des sols et des matériaux —

Partie 4: Extraction des substances humiques des échantillons solides

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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 12782-4 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 7, *Soil and site assessment*.

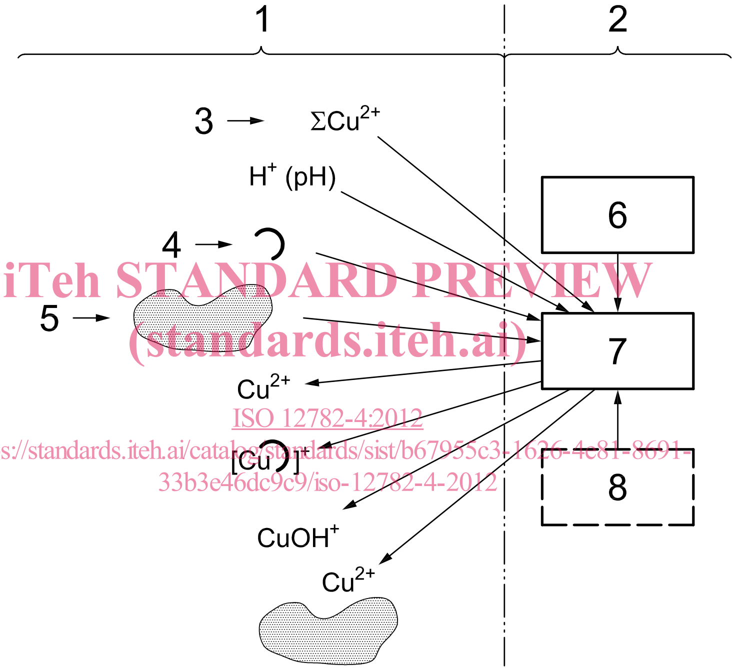
ISO 12782 consists of the following parts, under the general title *Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials*:

- *Part 1: Extraction of amorphous iron oxides and hydroxides with ascorbic acid*
- *Part 2: Extraction of crystalline iron oxides and hydroxides with dithionite*
- *Part 3: Extraction of aluminium oxides and hydroxides with ammonium oxalate/oxalic acid*
- *Part 4: Extraction of humic substances from solid samples*
- *Part 5: Extraction of humic substances from aqueous samples*

Introduction

In addition to leaching procedures for subsequent chemical and ecotoxicological testing of soil and other materials including waste, predictive models are becoming indispensable tools in the environmental risk assessment of these materials. Models are particularly required when the results of laboratory leaching tests are to be translated to specific scenarios in the field, with regard to assessing the risks of both contaminant migration and bioavailability.

In the past few years, geochemical models have been shown to be valuable tools to be combined with the data obtained from characterization leaching standards, such as pH-dependence and percolation tests. These models have the advantage of being based on fundamental thermodynamic parameters that have a general validity. In order to enable extrapolation of laboratory leaching data to the mobility and/or bioavailability of a constituent in a specific field scenario, these models require additional input parameters for specific soil properties (see Figure 1).



Key

1 experiment
2 geochemical speciation modelling
3 available metal concentration
4 dissolved humic substances
5 reactive (solid) surfaces
6 database with stability constants
7 computer program
8 assumptions

Figure 1 — Relationships between experimental data, as obtained from laboratory leaching/extraction tests, and geochemical modelling of the speciation of a heavy metal in the environment (modified after M. Gfeller & R. Schulin, ETH, Zürich)

Characterization leaching standards provide information on the concentrations of the contaminant of interest as a function of, in particular, pH and liquid/solid (L/S) ratio. In addition, a more complete analysis of the leachates also provides information on the major ion composition and dissolved organic carbon (DOC), parameters that are particularly important for the chemical speciation of constituents through processes such as precipitation, complexation and competition for adsorption on reactive mineral and organic surfaces in the soil. As illustrated in Figure 1 for the example of copper, geochemical modelling enables calculation of the metal distribution among these different chemical species in the system of interest. This provides necessary information for risk-assessment purposes, as these different chemical forms play distinct roles in the mobility and bioavailability of the metal in the soil. In addition to information obtained from the leaching standards (in their current state of development/definition), two additional types of information are required.

a) The “available” (sometimes also referred to as “active” or “exchangeable”) concentration of the constituent in the solid phase, as opposed to the total concentration determined by acid destruction of the solid matrix. This “available” concentration can be obtained by leaching at low pH, a condition that can be obtained by extending the pH range in the pH-dependent leaching test (ISO/TS 21268-4) down to pH ≈ 0,5 to pH ≈ 1.

b) The concentration of reactive organic and mineral surfaces in the soil, which constitute the major binding (adsorption) sites for most constituents in the soil matrix.

The major reactive surfaces that control the binding of constituents by sorption processes to the soil matrix are particulate organic matter and iron and aluminium (hydr)oxides. It is generally accepted that the reactivity of these mineral and organic surfaces can strongly vary as a function of their specific surface area/crystallinity [iron and aluminium (hydr)oxides] and composition (organic matter). When the results are intended to be used for the above-described purposes of geochemical modelling in conjunction with leaching tests, it is important that the methods be selective for reactive surfaces for which generic thermodynamic adsorption parameters are also available for the most important major and trace elements.

These reactive surfaces have been identified in soils, as well as in a variety of other materials for which the leaching of constituents is of relevance. It has been shown that the binding properties of these surfaces play a generic role in the speciation and leaching of constituents among these different materials. As an example, a similar geochemical modelling approach, using model input from the partial or complete ISO 12782 series, has been successfully applied to different soils[3], amended soils[4][5], municipal incinerator bottom ash[6], steel slag[7][8], bauxite residues[9], and recycled concrete aggregate[10]. Hence, the scope of the ISO 12782 series extends from soils to materials including soil amendments and waste materials.

This part of ISO 12782 aims to determine important reactive organic surfaces in soil and materials, for which generic thermodynamic adsorption parameters exist, i.e. humic and fulvic acids. The procedure is based on Reference [11], while generic thermodynamic adsorption parameters for humic and fulvic acids are available in References [12] and [13].

Thermodynamic parameters for adsorption models other than those used in References [12] and [13] are also available in the literature and may also be used to model the binding of constituents to humic and fulvic acids.

The method[14] is based on a conventional isolation and purification method[11] that is also used by the International Humic Substances Society (IHSS).

Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials —

Part 4:
Extraction of humic substances from solid samples

1 Scope

This part of ISO 12782 specifies a procedure to determine the concentration of humic substances in soil or other materials. Other materials also include waste. The content of humic substances can be used as input in geochemical models.

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 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8245, *Water quality — Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

ISO 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 10381-2, *Soil quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 10381-3, *Soil quality — Sampling — Part 3: Guidance on safety*

ISO 10381-4, *Soil quality — Sampling — Part 4: Guidance on the procedure for investigation of natural, near-natural and cultivated sites*

ISO 10381-5, *Soil quality — Sampling — Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination*

ISO 10381-6, *Soil quality — Sampling — Part 6: Guidance on the collection, handling and storage of soil under aerobic conditions for the assessment of microbiological processes, biomass and diversity in the laboratory*

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*

EN 14899, *Characterization of waste — Sampling of waste materials — Framework for the preparation and application of a sampling plan*

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

CEN/TR 15310-3, *Characterization of waste — Sampling of waste materials — Part 3: Guidance on procedures for sub-sampling in the field*

3 Terms and definitions

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

3.1
dissolved organic carbon
DOC
sum of organically bound carbon present in water originating from compounds (including cyanate and thiocyanate) which will pass a membrane filter of pore size 0,45 µm

3.2
humic substance
HS
(partial) decomposition product from plant and animal tissue

NOTE 1 Humic substances form a series of relatively high-molecular-weight, brown-to-black-coloured substances formed by secondary synthesis reactions.

NOTE 2 The term is used as a generic name to describe coloured material or its fractions (e.g. humic and fulvic acids) obtained on the basis of solubility characteristics.

3.3
humic acid
HA
fraction of a humic substance that is not soluble in water under acidic conditions (pH <1 to 2) but is soluble at higher pH values

NOTE Humic acids are dark brown to black in colour.

3.4
fulvic acid
FA
fraction of a humic substance that is soluble in water under all pH conditions

NOTE 1 Fulvic acids remain in solution after removal of humic acid by acidification.

NOTE 2 Fulvic acids are light yellow to yellow-brown in colour.

3.5
hydrophilic organic carbon
Hy
organic carbon compound consisting of non-humic and humic-like substances

NOTE In this part of ISO 12782, Hy is essentially regarded as the extractable organic carbon fraction that is not identified as humic acid, fulvic acid or hydrophobic neutral organic carbon in accordance with the procedure specified in Clause 8. Hydrophilic organic carbon generally consists of molecules with a lower molecular weight and higher COOH/C ratios than humic acids and fulvic acids. Examples of compounds are: oxidized carbohydrates with carboxylic acid groups, low-molecular-weight carboxylic acids, and sugar phosphates.

3.6
hydrophobic neutral organic carbon
HON
difference between the amount of adsorbed fulvic acid and hydrophilic organic carbon and the amount of desorbed fulvic acid

NOTE Hydrophobic neutral organic carbon can include non-humic and humic-like compounds.

3.7
laboratory sample
sample intended for laboratory inspection or testing

[ISO 11074:2005]

3.8
test sample
sample, prepared from the laboratory sample, from which the test portions are removed for testing or for analysis; this portion of material, resulting from the laboratory sample by means of an appropriate method of sample pretreatment, and having the size (volume/mass) necessary for the desired testing or analysis

NOTE Adapted from ISO 11074:2005.

3.9
test portion
analytical portion
quantity of material, of proper size, for measurement of the concentration or other property of interest, removed from the test sample

NOTE 1 The test portion may be taken from the primary sample or from the laboratory sample directly if no preparation of sample is required (e.g. with liquids), but usually it is taken from the prepared test sample.

NOTE 2 A unit or increment of proper homogeneity, size, and fineness, needing no further preparation, may be a test portion.

[ISO 11074:2005]

3.10
soil material
excavated soil, dredged material, manufactured soil, treated soil and fill material and other relevant materials, including soil amendments and waste materials

4 Principle

Specific dissolved organic carbon species are isolated based on defined operational conditions. Humic acids are precipitated at pH 1 and fulvic acids (and the hydrophobic organic neutral fraction) are adsorbed onto DAX-8 resin. The organics remaining in solution after resin addition are classified as hydrophilic organic substances. The DOC concentrations are measured after every step, from which the total individual concentrations of humic and fulvic acids, hydrophobic organic neutrals, and hydrophilic organic substances, are calculated.

5 Apparatus

The following apparatus shall be used. All materials that come into contact with the sample (material or reagents) should not contaminate the compounds to be determined or adsorb the compounds of interest.

5.1 Balance, with an accuracy of 0,1 g.

5.2 Usual laboratory glass or plastic ware, rinsed in accordance with ISO 5667-3.

5.3 pH-meter with a measurement accuracy of at least ±0,05 pH units.

5.4 End-over-end shaking machine (5 min^{-1} to 10 min^{-1}).

NOTE Other shaking methods can be used provided they can be shown to provide equivalent results.

5.5 Filtration apparatus, either a vacuum filtration device (between 2,5 kPa and 4,0 kPa) or a high-pressure filtration apparatus (<0,5 MPa). Cleaning is compulsory.

5.6 Filters, pore size 20 µm, for use in the Büchner-funnel filtration device (5.7).

5.7 Büchner-funnel filtration device.

5.8 Membrane filters, for the filtration device, fabricated from inert material with a pore size of 0,45 µm. Filters shall be pre-washed with demineralized water in order to remove DOC.

5.9 Soxhlet extraction device.

5.10 Soxhlet extraction thimbles, glass-fibre extraction thimbles for the Soxhlet extraction device (5.9).

5.11 Centrifuge, preferably at 3 000g. For other appropriate conditions, see Annex C.

5.12 Centrifuge bottles, e.g. polycarbonate, of appropriate size, rinsed in accordance with ISO 5667-3.

5.13 Crushing equipment: jaw crusher or cutting device.

NOTE Due to crushing, contamination of the sample may occur to an extent which affects the leaching of some constituents of concern, e.g. cobalt and tungsten from tungsten carbide equipment, or chromium, nickel and molybdenum from stainless-steel equipment.

5.14 Sieving equipment, with a nominal screen size of 2 mm or 4 mm.

NOTE Due to sieving, contamination of the sample may occur to an extent which affects the leaching of some constituents of concern e.g. cobalt and tungsten from tungsten carbide equipment, or chromium, nickel and molybdenum from stainless-steel equipment.

5.15 Sample splitter, for sub-sampling of laboratory samples (optional).

6 Reagents

The reagents used shall be of analytical grade and the water used shall comply with grade 3 in accordance with ISO 3696.

6.1 Demineralized water, deionized water or water of equivalent purity ($5 < pH < 7,5$) with a conductivity $< 0,5$ mS/m according to grade 3 specified in ISO 3696.

6.2 Potassium hydroxide, c(KOH) = 0,1 mol/l and 1 mol/l.

6.3 Hydrochloric acid, c(HCl) = 0,1 mol/l to 6 mol/l.

6.4 Sodium hydroxide, c(NaOH) = 0,1 mol/l to 5 mol/l.

6.5 Acetonitrile, (CH_3CN), suitable for liquid chromatography.

6.6 Methanol, (CH_3OH), suitable for liquid chromatography.

6.7 DAX-8 resin, e.g. Sigma-Aldrich1).

NOTE Various documented methods for HS isolation and purification make use of XAD-8 resin to adsorb HA and/or FA. This resin is no longer commercially available; therefore, the comparability of the substitute resin DAX-8 was tested. See Annex B for information.

6.8 Nitric acid, c(HNO_3) = 0,1 mol/l.

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1) DAX-8 resin from Sigma-Aldrich is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

7 Sample pretreatment

7.1 Sample size

The laboratory sample shall consist of a mass equivalent to at least 1 kg of dry mass. Perform sampling in accordance with ISO 10381-1 in order to obtain a representative laboratory sample.

Sampling shall be performed in accordance with the guidelines for preparing a sampling plan for soil materials, as specified in ISO 10381-1 to ISO 10381-6 and for waste in accordance with EN 14899, in order to obtain representative laboratory samples. Obtain a representative laboratory sample of at least 200 g (dry matter) for soil and soil materials and 2 kg (dry matter) for waste material. Follow instructions for sample pretreatment:

- for soil and soil materials according to ISO 11464;
- for waste according to CEN/TR 15310-3 and EN 15002.

Use a sample splitter (5.15) or apply coning and quartering to split the sample.

NOTE The required size of the laboratory sample is dependent on the particle size distribution of the soil or the material to be analysed (see ISO 11277). The specified sample size is generally adequate. In specific cases, a smaller sample size can be accepted — for instance if, for specific reasons, less material is available — provided that the test can be carried out as specified in 7.2 to 7.4.

Any deviation(s) to accommodate sample size or volume requirements shall be recorded in the test report.

7.2 Particle size reduction

7.2.1 General

The tests shall be carried out preferably on material as received.

7.2.2 Particle size reduction of soil

For soil and soil material, the test portion to be prepared shall have a grain size < 1 mm. If oversized material is not of natural origin and exceeds 5 % (mass fraction), the entire oversized fraction shall be separated by sieving (see 5.14) and crushed using suitable crushing equipment (5.13). On no account shall the material be finely ground. Oversized material of natural origin (e.g. stones, pebbles, twigs) in the sample shall be separated and discarded. Irrespective of any necessary size reduction, the separate fractions, with the exception of non-crushable and discarded material, shall be mixed to constitute the test sample. If the laboratory sample cannot be crushed or sieved because of its water content, it is permitted, in this case only, to reduce the water content until the laboratory sample can be sieved. The drying temperature shall not exceed 25 °C.

7.2.3 Particle size reduction of waste

For waste, the test shall be carried out on material with a grain size of at least 95 % (mass fraction) < 4 mm. Therefore, the laboratory sample shall be sieved (5.14). If oversized material exceeds 5 % (mass fraction) the entire oversized fraction shall be crushed using crushing equipment (5.13). On no account shall the material be finely ground. Non-crushable material (e.g. metallic parts such as nuts, bolts, scrap) in the sample shall be separated and the mass and nature of the material shall be recorded. The method of size reduction applied shall be documented and recorded in the test report. Irrespective of any necessary size reduction, the separate fractions, with the exception of the non-crushable material and the material that may be used according to the second paragraph after Note 1, shall be mixed to constitute the test sample. If the laboratory sample cannot be crushed or sieved because of its moisture content, it is permitted, in this case only, to reduce the water content until the laboratory sample can be sieved. The drying temperature shall not exceed 25 °C. Any necessary deviation in the drying procedure shall be given in the test report.

NOTE 1 Fibrous materials and plastics can often be reduced in size after cryogenic treatment.

Any drying step can change other properties of the waste. Care should be taken to minimize such changes.

In order to minimize a possible contamination during sieving, fragmentation and splitting, it is recommended, before preparing the test sample, that a portion of the laboratory sample be processed through the devices for sieving, fragmentation and splitting, discarding the material thereafter. This recommendation does not cover the possible contamination described in the Notes in 5.13 and 5.14.

NOTE 2 Important differences may occur in the leaching test results for a given material, depending on the crushing procedure and the waste material being crushed. Particle-size-related differences may be made evident by determining the particle size distribution. It is to be noted that, in the case of a very narrow size distribution, such differences in the leaching result may be enhanced, especially in the upper part of the size range.

7.3 Determination of dry residue

The whole test sample, complying with the size criteria in 7.2, shall not be dried further. The dry residue (w_{dr}) of the test sample shall be determined on a separate test portion.

Determine the dry residue at (105 ± 5) °C in accordance with ISO 11465. Calculate the dry residue using Equation (1):

$$w_{dr} = 100 \cdot \frac{m_d}{m_r} \qquad (1)$$

where

w_{dr} is the dry residue of the sample, expressed as a percentage (%);

m_d is the mass after drying, expressed in grams (g);

m_r is the mass before drying, expressed in grams (g).

7.4 Test portion

The test portion size shall be 20 g (with a tolerance of ±10 %) in compliance with the size criteria in 7.2.

Calculate the undried mass of the test portion (M_w) to be used for the test using Equation (2):

$$M_w = \frac{M_d}{w_{dr}} \times 100 \qquad (2)$$

where

M_d is the dry mass of the test portion, expressed in grams (g);

M_w is the total mass of the test portion, expressed in grams (g)

w_{dr} is the dry residue of the sample, expressed as a percentage (%).

8 Procedure

8.1 Preparation of DAX-8 resin

Clean every new batch of DAX-8 resin (6.7) to remove organic impurities with five 0,1 mol/l hydrochloric acid (6.3) extractions (for 24 h). Renew the solution after each extraction. Repeat this cycle with 0,1 mol/l sodium hydroxide (6.4). Then, clean the resin thoroughly by Soxhlet extractions (5.9) with acetonitrile (6.5) and methanol (6.6), each for 24 h. The cleaned resin is stored in methanol (6.6) until use.