INTERNATIONAL STANDARD

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

Part 2:
Extraction of crystalline iron oxides and hydroxides with dithionite

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

Partie 2: Extraction des oxydes et hydroxydes de fer cristallin avec le dithionite

Reference number
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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 12782-2 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*

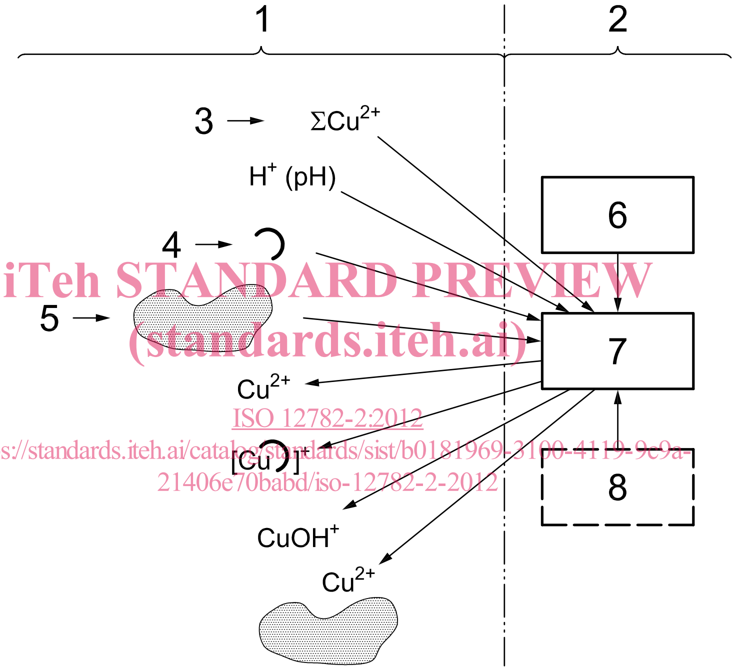
— *Part 4: Extraction of humic substances from solid samples*

— *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 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 permits 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[5], amended soils[6][7], municipal incinerator bottom ash[8], steel slag[9][10], bauxite residues[11], and recycled concrete aggregate[12]. Hence, the scope of the ISO12782 series extends from soils to materials including soil amendments and waste materials.

This part of ISO 12782 aims to determine crystalline iron (hydr)oxides in soil and materials. The procedure is based on References [13] and [14] and described in Reference [15]. Although generic thermodynamic adsorption parameters for crystalline iron (hydr)oxides are currently available for a limited number of constituents, such parameters for a wider variety of constituents are available for amorphous iron (hydr)oxides with similar structure and properties[16]. These parameters have been successfully applied to crystalline iron (hydr)oxides, as justified and demonstrated in Reference [17].

Thermodynamic parameters for adsorption models other than those used in Reference [16] are also available in the literature and may also be used to model the binding of constituents to crystalline iron (hydr)oxides.

Iron can be present in several forms in soils, of which the most important for the binding of trace constituents are well-crystallized and insoluble oxides and hydroxides (e.g. goethite, haematite, magnetite) and the poorly ordered, more soluble oxides and hydroxides (e.g. ferrihydrite, hydrous ferric oxide). Amorphous and crystalline forms have a different reactivity towards binding of trace constituents as a result of differences in specific surface areas and characteristics of the binding “sites” on the surface.

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

Part 2:
Extraction of crystalline iron oxides and hydroxides with dithionite

1 Scope

This part of ISO 12782 specifies the determination of the content of “reactive” iron in the form of crystralline iron oxides and hydroxides in soil and other materials by extraction with dithionite. Other materials also include waste. The content of “reactive” iron can be used as input in geochemical models to represent the content of crystalline iron (hydr)oxides.

NOTE Although the ammonium oxalate/oxalic acid extraction (ISO 12782-3) is commonly used to estimate “reactive” iron in the form of iron oxides and hydroxides, this part of ISO 12782, in conjunction with ISO 12782-1, has been shown to be more specific for the extraction of crystalline and amorphous iron (hydr)oxides, respectively[7].

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 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
water content
mass fraction
w_w
mass of water evaporating from one soil sample when dried to constant mass at 105 °C, divided by the dry mass of the soil sample

[ISO 11074:2005]

3.2
laboratory sample
sample intended for laboratory inspection or testing

NOTE 1 When the laboratory sample is further prepared (reduced) by subdividing, mixing, grinding, or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or for analysis.

NOTE 2 The laboratory sample is the final sample from the point of view of sample collection but it is the initial sample from the point of view of the laboratory.

NOTE 3 Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes.

[ISO 11074:2005]

3.3
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 pre-treatment, and having the size (volume/mass) necessary for the desired testing or analysis

NOTE Adapted from ISO 11074:2005.

3.4
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]

3.5
material
excavated soil, dredged material, manufactured soil, treated soil and fill material, and other relevant materials, including soil amendments and waste materials

4 Principle

The extraction principle is based mainly on the reduction of Fe(III) phases to the more soluble Fe(II) phases, as well as on the complexing affinity of the chemicals to extract iron from crystalline materials[5]. The amount of *crystalline* iron (hydr)oxides is determined by the present dithionite extraction *minus* the amount of *amorphous* iron (hydr)oxides as obtained from ascorbate extraction, in accordance with ISO 12782-1, and possible other reactive iron phases extracted with the dithionite extraction that may be important in specific materials such as acid volatile sulfides (AVS) and silicates.

The extraction is operationally defined as that which obtains *total* reactive iron (all crystalline and amorphous Fe(III) oxide phases, AVS, and iron-containing silicates which are possibly amorphous)[5]. The extraction dissolves only a small amount of iron-containing silicates[5], and AVS generally comprises only a minor fraction, even in salt marsh sediments[5]. The contribution of iron phases other than amorphous and crystalline oxides and hydroxides may therefore be assumed to be low in most natural, oxidized and transition-zone systems such as soils.

5 Apparatus

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

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

5.2 Centrifuge, preferably at 3 000g. For other appropriate conditions, see Annex A.

5.3 Water bath rotary shaker, adjustable to 60 °C.

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

5.4 Filter holders for syringes, 0,2 µm, cellulose acetate, diameter 30 mm, cleaned with at least 10 ml of distilled water before use.

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

5.6 Plastic syringe, 50 ml, rinsed in accordance with ISO 5667-3.

5.7 Balance, with an accuracy of at least 1 mg.

5.8 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.

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

5.10 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.

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

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 Water: use distilled and demineralized water with a specific conductivity of at most 0,2 mS/cm at 25 °C and a pH $>$ 5,6.