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Soil quality — Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil-like materials —

Part 4: Influence of pH on leaching with initial acid/base addition

Qualité du sol — Modes opératoires de lixiviation en vue d'essais chimiques et écotoxicologiques ultérieurs des sols et matériaux analogues au sol —

Partie 4: Essai de dépendance au pH avec ajout initial d'acide/de base

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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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 7, *Impact assessment*.

This first edition of ISO 21268-4 cancels and replaces ISO/TS 21268-4:2007, which has been technically revised. The main changes compared to the previous edition are as follows:

— the maximum grain size has been changed to <2 mm as usual for soil;

— references in Clause 2 and the Bibliography have been updated;

— Clause 12 “Performance characteristics” has been technically revised;

— a new informative Annex D “Repeatability and reproducibility data” has been added;

— a new informative Annex E "Calculation of centrifugation duration depending on centrifugation speed and rotor dimensions" has been added.

A list of all parts in the ISO 21268 series can be found on the ISO website.

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

In various countries, tests have been developed to characterize and assess the substances which can be released from materials. The release of soluble substances upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment during the use or disposal of materials. The intent of these tests is to identify the leaching properties of materials. The complexity of the leaching process makes simplifications necessary[1].

Not all of the relevant aspects of leaching behaviour can be addressed in one standard.

Tests to characterize the behaviour of materials can generally be divided into three categories addressed in ISO 18772 and EN 12920. The relationships between these tests are summarized below.

“Basic characterization” tests are used to obtain information on the short- and long-term leaching behaviour and characteristic properties of materials. Liquid/solid ratios (L/S), leachant composition, factors controlling leachability, such as pH, redox potential, complexing capacity, role of dissolved organic carbon (DOC), ageing of material and physical parameters, are addressed in these defined tests.

“Compliance” tests are used to determine whether the material complies with a specific behaviour or with specific reference values. These tests focus on key variables and leaching behaviour previously identified by basic characterization tests.

“On-site verification” tests are used as a rapid check to confirm that the material is the same as that which has been subjected to the compliance test(s). On-site verification tests are not necessarily leaching tests.

The test procedure described in this method belongs to category a) “Basic characterization” tests.

This document was originally elaborated on the basis of CEN/TS 14429:2005. Especially, modifications considering requirements on subsequent ecotoxicological testing and analysis of organic substances have been included. Validation results have been adopted from US-EPA[5].

Soil quality — Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil-like materials —

Part 4: Influence of pH on leaching with initial acid/base addition

1 Scope

This document specifies a test to obtain information on the short- and long-term leaching behaviour and characteristic properties of materials.

The document has been developed to measure the pH-dependent release of inorganic and organic substances from soil and soil-like material as well as to produce eluates for subsequent ecotoxicological testing. For ecotoxicological testing, see ISO 15799 and ISO 17616. The equilibrium condition, as defined in this document, is established by the addition of predetermined amounts of acid or base to reach desired final pH values.

NOTE 1 Volatile organic substances include the low molecular weight substances in mixtures such as mineral oil.

NOTE 2 It is not always possible to optimize test conditions simultaneously for inorganic and organic substances and optimum test conditions can also vary between different groups of organic substances. Test requirements for organic substances are generally more stringent than those for inorganic substances. The test conditions suitable for measuring the release of organic substances will generally also be applicable to inorganic substances.

NOTE 3 Within the category of organic substances, a significant difference in behaviour exists between the more polar, relatively water-soluble compounds and apolar, hydrophobic organic substances (HOCs). In the latter case, mechanisms of release (e.g. particle-bound or dissolved organic carbon-bound) can be more crucial as well as sorption losses of soluble HOCs on different materials with which they come in contact (e.g. bottles, filters). The test and the results should be used for leaching of organic substances only with thorough consideration of the specific properties of the substances in question and the associated potential problems.

NOTE 4 For ecotoxicological testing, eluates representing the release of both inorganic and organic substances are needed. In this document, ecotoxicological testing is meant to include genotoxicological testing.

The test method produces eluates, which can subsequently be characterized by physical, chemical and ecotoxicological methods in accordance with existing standard methods. The test is not suitable for substances that are volatile under ambient conditions.

For the purposes of ecotoxicological tests, the relevant pH range (see 8.2) will usually be pH 5 to pH 9.

This test is mainly aimed at being used for routine and control purposes, and it cannot be used alone to describe all leaching properties of a soil. Additional leaching tests are needed for that extended goal. This document does not address issues related to health and safety. It only determines the leaching properties outlined in Clause 5.

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 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 7027-1, *Water quality — Determination of turbidity— Part 1: Quantitative methods*

ISO 10523, *Water quality — Determination of pH*

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

3 Terms and definitions

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

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/

3.1
leaching test
test during which a material is put into contact with a *leachant* (3.2) under strictly defined conditions and some substances of the material are extracted

3.2
leachant
liquid used in a *leaching test* (3.1)

Note 1 to entry: For the purpose of this document, the leachant is specified in 6.1

3.3
eluate
solution recovered from a *leaching test* (3.1)

Note 1 to entry: Eluate is also referred to as leachate.

3.4
liquid to solid ratio
L/S
ratio between the total volume of liquid (L in litres), which in this extraction is in contact with the soil sample, and the dry mass of the sample (S in kg of dry matter)

Note 1 to entry: L/S is expressed in litres per kilogram (l/kg).

3.5
dry matter content
w_{dm}
ratio, expressed in percent, between the mass of the dry residue, determined in accordance with ISO 11465, and the corresponding raw mass

3.6
water content
w_{H_2O}
ratio, expressed in percent, between the mass of water contained in the material as received and the corresponding dry residue of the material

Note 1 to entry: The basis for the calculation of the water content is the mass of the dry residue in this document, as specified in ISO 11465 (for the determination of the water content of soil).

3.7
laboratory sample
sample or subsample(s) sent to or received by the laboratory

3.8
test sample
sample, prepared from the *laboratory sample* (3.7), from which *test portions* (3.9) are removed for testing or analysis

3.9
test portion
quantity of material of appropriate size for measurement of the concentration or other properties of interest taken from the *test sample* (3.8)

Note 1 to entry: The test portion can be taken from the *laboratory sample* (3.7) directly if no pre-treatment of the sample is required, but usually it is taken from the test sample.

Note 2 to entry: A unit or increment of proper homogeneity, size and fineness, needing no further preparation, can be a test portion.

3.10
soil-like material
excavated soil, dredged materials, manufactured soils, treated soils and fill materials

4 Principle

The test portions, which originally or after suitable pre-treatment have a particle size less than or equal to 2 mm, are brought into contact with water containing a low concentration (0,001 mol/l) of calcium chloride or demineralised water (5.1) under defined conditions. Several separate test portions (up to eight) are leached at a fixed L/S ratio (L/S = 10 l/kg) with leachants containing different preselected amounts of acid or base in order to reach stationary pH values at the end of the extraction period (see 8.4). Each leachant is added in three steps in the beginning of the test. In the full test, eight final pH-values are required, covering the range pH 4 to pH 12 (both included, i.e. the lowest value 4 and the highest value 12). The amount of acid or base needed to cover the pH range can be derived from the results of a preliminary titration, from available experimental data on the material to be tested or from an arbitrary division of the predetermined maximum consumption of acid and base. The tests are carried out at a fixed contact time at the end of which an equilibrium condition can be assumed to be reached for most substances in most soil-like materials to be characterized. The equilibrium condition, as defined in this document, is verified at the end of the extraction period.

The results are expressed in milligrams per litre (mg/l) of substances for each final pH value. For each final pH value, the quantity of acid that is added is also expressed in mol H^+/kg dry matter and the quantity of base that is added is expressed as negative mol H^+/kg dry matter.

NOTE 1 This test may also be performed using continuous pH control. The results are generally consistent (see Annex B).

NOTE 2 Other expressions of results are possible (including mg/kg of dry matter).

From the amount of acid and base used to reach a given end pH, the acid neutralization capacity (ANC) or base neutralization capacity (BNC) of the soil or soil-like material can also be determined.

NOTE 3 The pH range covered by the test can be restricted to a pH range relevant for the specific material and the considered problem (see 8.2).

NOTE 4 The leachant is made with 0,001 mol/l $CaCl_2$ to minimize the mobilization of DOC caused by a too-low ionic strength of the leachant. At the level of 0,001 mol/l $CaCl_2$ the complexation of metals with chloride is considered to be negligible.

The substances in the eluate(s) are measured using methods developed for water analysis adapted to meet criteria for analysis of eluates. The eluate may also be applied for subsequent ecotoxicity or genotoxicity testing.

After the test, the leaching conditions (in terms of pH, electrical conductivity, DOC and, optionally, turbidity and redox potential dictated by the material) are recorded.

NOTE 5 These parameters often control the leaching behaviour of soil-like materials and are therefore important for checking the leaching test.

5 Reagents

Reagents used shall be of analytical grade purity.

5.1 Demineralized water or **deionized water** or **water of equivalent purity** ($5 < pH < 7{,}5$) with a conductivity of < 0,5 mS/m in accordance with grade 3 specified in ISO 3696 made to **0,001 mol/l $CaCl_2$**.

5.2 Calcium chloride ($CaCl_2 \cdot 2\ H_2O$), analytical grade.

5.3 Sodium azide (NaN_3), analytical grade.

5.4 Nitric acid (pro-analysis) (HNO_3), 0,1 mol/l to 5 mol/l, and 0,1 mol/l rinsing solution.

5.5 Sodium hydroxide (NaOH) or **potassium hydroxide** (KOH), 0,1 mol/l to 5 mol/l.

NOTE The use of KOH instead of NaOH may enhance the leaching of certain cations such as NH_4^+ and Cs^+ by cation exchange.

5.6 Organic solvent (acetone, analytical grade) for rinsing and cleaning.

6 Apparatus

6.1 Borosilicate glass, of high purity in accordance with ISO 5667-3, with a nominal volume of 1 l, **glass bottles** having caps of inert material, for example PTFE (polytetrafluoroethylene). Rinsing is compulsory, and it should be assured that previously used bottles have no background level of analyte.

NOTE 1 If only inorganic parameters are analysed, alternative materials such as HDPE/PP bottles are appropriate, except for unpreserved samples for mercury analysis.

NOTE 2 To prevent organic compounds from degradation by light use a dark room, dark colored glassware or place a layer of aluminium-foil around the leaching equipment.

If Boron analyses are necessary, any plastics bottles can be used, e.g. PTFE (polytetrafluoroethylene).

The volume of 1 l is selected in combination with the mass, m_D, of 60 g, in order to minimize headspace in the bottle. For m_D = 15 g and 30 g, bottle sizes of, respectively, 250 ml and 500 ml shall be used. In the case of materials with low density, deviation from this requirement can be necessary while still ensuring minimize headspace. This deviation should be reported.

NOTE 3 Glass of high quality is considered adequate for both metals and organic substances, particularly since the pH range usually covered in soil testing does not reach the conditions (pH > 12 and pH < 3) where the glass itself may be partially dissolved. For ecotoxicity testing, eluates with both inorganic and organic substances are needed, which emphasizes the need to generate integrated eluates.

NOTE 4 Heat treatment of used glassware at 550 °C can be used to remove traces of analytes. However, this treatment has been shown to increase adsorption of organic substances from the air.

6.2 End-over-end tumbler (5 min^{-1} to 10 min^{-1}) **or roller table**, rotating at about 10 min^{-1}. Other shaking devices may be used, provided that they can be shown to provide equivalent results. These agitation devices are specified because excessive abrasion leading to significant particle size reduction should be avoided.

6.3 Filtration apparatus, either a vacuum filtration device (between 2,5 kPa and 4,0 kPa) or a high-pressure filtration apparatus (< 0,5 MPa). Rinsing is compulsory. When semi-volatile substances are to be analysed, vacuum filtration shall not be used.

6.4 0,45 µm membrane filters, prerinsed or similarly cleaned (e.g. rinsed with 0,1 mol/l HNO_3 (5.4) and water (5.1) (only for analysis of inorganic substances).

The filters shall be chosen so as not to adsorb (or release) substances of interest.

NOTE This can be tested in preliminary experiments.

6.5 Glass fibre filters, with a degree of separation of 0,7 µm.

The filters shall be chosen so as not to adsorb (or release) substances of interest.

NOTE This can be tested in preliminary experiments.

6.6 Sieving equipment, with sieves of 2 mm nominal screen size.

NOTE Due to sieving, contamination of the sample can occur to an extent which affects the leaching of some substances of concern, e.g. chromium, nickel and molybdenum from stainless steel equipment or plasticisers from plastic sieves.

6.7 Centrifuge, operating at 20 000 *g* to 30 000 *g* using centrifuge tubes of FEP (fluorinated ethylene propylene) or tubes of an alternative material, which is inert with regard to both inorganic and organic compounds and suitable for high-speed centrifugation.

NOTE Potential sorption of hydrophobic organic substances to the centrifuge tubes can be tested in preliminary experiments.

Alternatively, if a high-speed centrifuge is not available, a centrifuge operating at 2 000 *g* to 2 500 *g* using glass bottles may be used in combination with increased centrifugation time. Cooling shall be applied to maintain the desired temperature.

6.8 Glass bottles, with screw cap and PTFE (polytetrafluoroethylene) inlay for centrifugation.

6.9 Device for measuring electrical conductivity.

6.10 pH meter, in accordance with ISO 10523.

6.11 Redox potential meter (optional).

6.12 Balance, with an accuracy of at least 0,1 g.

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

6.14 Turbidity meter, as specified in ISO 7027-1.

6.15 Crushing equipment, a jaw crusher.

NOTE Due to particle size reduction, contamination of the sample can occur to an extent which affects the leaching of some substances of concern, e.g. chromium, nickel and molybdenum from stainless steel equipment.

7 Sample pretreatment

7.1 Preparation of laboratory sample and specification of particle size

A representative laboratory sample of at least 2 kg (dry matter) is obtained (e.g. as described in ISO 18400 series and ISO 23909) and shall be stored in closed packages and at low temperatures (4 °C), in order to avoid unwanted changes in the material (see e.g. ISO 18400-105).

The test shall be carried out on soil or soil-like material sieved to < 2 mm (e.g. as described in ISO 11464). Oversized material of natural origin in the sample shall be separated and discarded. The type and amount of all discarded material shall be reported. If oversized material of anthropogenic origin is present and assumed to contain substances of interest, this part can be subject to alternative sample preparation or testing.

If the laboratory sample cannot be homogenised or sieved because of its water content, it is allowed in this case only to dry the laboratory sample (e.g. as described in ISO 11464). The drying temperature shall not exceed 30 °C.

NOTE 1 Sieving and drying at more than 30 °C, as well as crushing, can lead to a loss of semi-volatile substances (inorganic and organic) and can alter the leaching characteristics).

NOTE 2 Due to sieving, contamination of the sample can occur to an extent that affects the leaching of some substances of concern, e.g. chromium, nickel and molybdenum from stainless steel equipment or plasticisers from plastic sieves.

7.2 Preparation of test sample

Use a sample splitter (6.13) or apply coning and quartering to split the laboratory sample and obtain a test sample. The size of test sample required depends on the volume of eluate needed for the specific purpose and the subsequent chemical analysis and/or ecotoxicological tests to be carried out on the eluate.

NOTE 1 If needed for chemical analysis or ecotoxicological testing, larger volumes of eluate can be obtained by combining eluates from replicate tests after centrifugation (or filtration). Alternatively, larger volumes of eluate may also be produced in a single test, provided that the ratios in terms of L/S and minimum headspace are maintained.

NOTE 2 The required amount of the test sample is dependent on the particle size distribution of the soil to be analysed (see ISO 23909). The specified sample amount will generally be adequate. In specific cases, a smaller sample amount 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.

7.3 Determination of the dry matter content and of water content

The whole test sample, complying with the size criterion in 7.2, shall not be further dried. The moisture content of the test sample shall be determined on a separate test portion at (105 ± 5) °C. If the soil sample is air-dried prior to testing, the dry matter content w_{dm} of the air-dried sample shall be determined as well. This shall be taken into account when adjusting the L/S. The dry mass of the sample shall be determined at (105 ± 5) °C, in accordance with ISO 11465, and the dry matter content calculated with Formula (1):

$$w_{dm} = 100 \times m_D / m_W \quad (1)$$

where

w_{dm} is the dry matter content, expressed in percent (%);

m_D is the mass of the dried sample, expressed in kilograms (kg);

m_W is the mass of undried sample, expressed in kilograms (kg).

The water content (w_{H_2O} in percent) is calculated with Formula (2):

$$w_{H_2O} = 100 \times (m_W - m_D) / m_D \quad (2)$$

NOTE If volatile or unstable compounds are present in the soil sample, this gravimetric method cannot be used for accurate determination of the water content.

7.4 Preparation of the test portion

Prepare from the test sample at least eight test portions. Based on sample heterogeneity and eluate volume requirement for analysis, the test portion size shall be either m_D = (15 ± 1) g, (30 ± 1) g or (60 ± 1) g [measured with an accuracy of 0,1 g (6.12)] of dry mass (m_D) following Formula (3).

$$m = 100 \times m_D / w_{dm} \quad (3)$$

Use a sample splitter (6.13) or apply coning and quartering to split the sample.

NOTE Sample splitting or coning-and-quartering can lead to loss of semi-volatile substances (inorganic and organic).

In view of the minimum requirements of eluate volume for analytical purposes, it may be necessary to use a larger test portion and a correspondingly larger volume of leachant. This deviation from this document shall be specified in the test report.

If the test is performed on an air-dried sample, use $w_{dm,AD}$ instead of w_{dm} to determine the sample mass of the test portion.

8 Procedure

8.1 Contact time

The leaching procedure consists of three defined stages:

— Period A (acid/base addition) from t_0 to (t_0 + 4 h) for acid/base additions in three steps;

— Period B (equilibration period) from (t_0 + 4 h) to (t_0 + 44 h) equilibration period;

— Period C (verification period) from (t_0 + 44 h) to (t_0 + 48 h) for verification of equilibrium condition.

The total contact period (A + B + C) is 48 h.

8.2 pH-range

The full test shall cover the range pH 4 to pH 12 (both included, i.e. the lowest value ≥ 4 and the highest value ≤ 12) with eight pH values tested, including the natural pH (without acid or base addition). The maximum difference between two consecutive pH values shall not exceed 1,5 pH units.

To ensure that the appropriate pH values can be obtained in one run, additional bottles can be prepared of which only the ones with the desired final pH values are retained for analysis.

The pH range covered by the test may be restricted to a pH range relevant to the specific material and the considered problem. The pH range to be covered may depend on the specific properties of the soil material, the available information on this material and the questions to be answered by performing the test. The number of pH levels considered can be reduced, correspondingly, for example, for the purpose of ecotoxicological tests. The relevant pH range will usually be pH 5 to pH 9.

8.3 Leaching test

8.3.1 General

The following procedure applies to each of the chosen pH values to be tested.

8.3.2 Preparation of leachants

Identify the acid or base consumption for reaching the relevant pH values as A (mol H^+/kg dry matter) or B (mol OH^-/kg dry matter) and the total volume of leachant.

NOTE The acid or base consumption for the considered pH values can be derived from available information, from the preliminary procedures in Annex B, or from information in Annex C.

Calculate the volume V_L of liquid to establish an L/S ratio of 10 ± 0,2 (l/kg) for the actual size of test portion m (see 7.4), including the volume of acid or base, in accordance with Formula (4):

$$V_L = \left[10 - w_{H_2O} / \left(\rho_{H_2O} \times 100 \right) \right] \times m_D \quad (4)$$

where

V_L is the volume of leachant used (l);

m_D is the dry mass of the test portion (kg);

ρ_{H_2O} is the density of water (usually taken as 1 kg/l);

w_{H_2O} is the water content for the test portion (%).

Prepare the leachant from 0,001 mol/l $CaCl_2$ (see 5.1) and acid or base (see 5.4 or 5.5) according to the acid/base consumption for the relevant pH.

Prepare the acid-adjusted leachant in accordance with Formula (5) and Formula (6):

$$V_L = V_d + V_A \quad (5)$$

$$V_A = \frac{n_A \times m_D}{C_A} \quad (6)$$

where

V_L is the volume of prepared leachant, in millilitres (ml);

V_d is the volume of 0,001 mol/l $CaCl_2$ used, in millilitres (ml);

V_A is the volume of acid needed, in millilitres (ml);

n_A is the acid consumption for the particular pH, in mol H^+/kg dry matter;

m_D is the dry mass of the test portion, in grams (g) (see 7.4);

C_A is the concentration of the acid, in moles per litre (mol/l) (see 5.4).

Prepare the base-adjusted leachant in accordance with Formula (7) and Formula (8):

$$V_L = V_d + V_B \quad (7)$$

$$V_B = \frac{n_B \times m_D}{C_B} \quad (8)$$

where

V_L is the volume of prepared leachant, in millilitres (ml);

V_d is the volume of 0,001 mol/l $CaCl_2$ used, in millilitres (ml);

V_B is the volume of base needed, in millilitres (ml);

n_B is the base consumption for the particular pH, in mol OH^-/kg dry matter;

m_D is the dry mass of the test portion, in grams (g) (see 7.4);

C_B is the concentration of the base, in moles per litre (mol/l) (see 5.5).

Split the volume V_L of leachant into three equal parts, $V_L/3$.

8.3.3 Leaching step

Carry out the test at a temperature of (22 ± 3) °C.

Select the appropriate bottle size according to the test portion size. For m_D = 15 g, 30 g and 60 g, this means bottle sizes of, respectively, 250 ml, 500 ml and 1 000 ml.

Place one of the test portions in the rinsed bottle (see 6.1).

Add the leachant volume, $V_L/3$, at three different times:

— first fraction at t_0;

— second fraction at t_0 + 30 min;

— third fraction at t_0 + 2 h.

Close the bottle and agitate the suspension (see 6.2) between each leachant addition. Measure and record the pH (see below for instructions), and, if deviations are observed from the expected pH at that time, prepare additional bottles with modified acid/base additions.

Development of carbon dioxide should be taken into account when using acidic leachants. This may lead to pressure build-up. When this is expected or observed, the pressure can be relieved by opening the bottle a few times during the test. Main gas production will, however, take place in the first period of acid addition.

Continue to agitate after the last leachant addition until $t = t_0$ + 48 h.

Measuring and recording of the pH:

— Measure and record the pH at t_0 + 4 h, t_0 + 44 h, t_0 + 48 h.

— Since the pH is measured directly in the suspension, rinse the pH electrode thoroughly and dry softly before and between uses in order not to contaminate the suspension.

— For the measurement of the pH, stop the agitation and allow the mix to settle for 5 min. Measure the pH by inserting the clean electrode into the supernatant.

— The pH value measured before filtration at t_0 + 48 h will be the one assigned to the analysis of the eluate.

— Report the pH deviation between t_0 + 4 h and t_0 + 44 h.

NOTE 1 For high pH values (pH > 9), CO_2 uptake can affect the leaching process. This can be reduced by minimizing the contact time with the air during handling.

NOTE 2 The pH value at t_0 + 4 h is used for checking that sufficient pH adjustment has been obtained by the acid or base additions, respectively.

NOTE 3 The pH is measured directly in the bottle at t_0 + 48 h before filtration as filtration can change the pH in the eluate.

The deviation between pH at t_0 + 44 h and pH at t_0 + 48 h shall not exceed 0,3 pH units, which is the limit for approaching an equilibrium condition. A special note shall be made in the report if this requirement is not met. If too many experimental points deviate (more than three amongst eight), the conclusion is that this test is not applicable to this material.

NOTE 4 When the equilibrium condition is strictly compulsory for specific use, but is not fulfilled in the test, it is possible to continue the test to a maximum of 7 d for all the eight experimental points (selected pH values) in order to avoid association of results at 48 h with those at a longer leaching time. In this case, the pH deviation can be limited to 0,3 pH units for the last 24 h (maximum between the sixth and seventh day). The experimental point(s), which do not conform to these new conditions, will not be exploited and this fact will be mentioned in the report. This specific procedure is not part of this document.

8.3.4 Liquid/solid separation step

Allow the suspended solids to settle for (15 ± 5) min.

Transfer the supernatant to centrifuge tubes (6.7). The centrifugation containers shall be chosen so as not to adsorb (or release) analytes.

There are two options for solid-liquid separation:

a) Centrifuge the eluate for 30 min at 20 000 *g* to 30 000 *g* using a high-speed centrifuge (6.7).

b) Centrifuge the eluate for 5 h at 2 000 *g* to 3 000 *g* in glass bottles using a lower-speed centrifuge (6.7).

Cooling shall be applied to maintain the temperature at (22 ± 3) °C.

NOTE 1 Based on Stoke's law, the results of both centrifugation methods are expected to be comparable. Other alternative combinations of centrifugation acceleration and time can be applied given comparable conditions are calculated related to the specification of the rotor (see guidance in Annex E).

Gentle breaking of the centrifuge shall be applied in order to avoid resuspension. The deceleration time shall not exceed 20 min.

NOTE 2 In case lightweight substances (e.g. coaly particles) are still floating after centrifugation, a glass fibre filtration (6.5) can be applied to remove such particles or to reduce the turbidity.

After centrifugation, the eluate shall be transferred immediately to an appropriate container for measurement of pH, redox potential and stored for subsequent chemical analysis and/or ecotoxicological testing.

If only inorganic substances are measured, the centrifugation step can be omitted and the decanted eluate can be directly filtered using the appropriate membrane filters (6.4) and a vacuum or pressure filtration device (6.3). When this filtration as specified is not possible in less than 1 h with a liquid flow rate of at least 30 ml/cm^2/h, a liquid-solid separation procedure, specific for the considered case, shall be applied. Report the details in the test report. This specific procedure shall not include the use of additives.

NOTE 3 For inorganic substances, it is often preferable to pre-centrifuge the eluate at 2 000 *g* to 3 000 *g* for 20 min before filtration using glass bottles with a screw cap and polytetrafluoroethylene inlay (or, if possible, using the leaching bottle directly) prior to filtration. Higher speed or longer time can also be applied (see Annex E).

NOTE 4 Such a specific liquid-solid separation procedure can include settling, prefiltration on coarser filter, centrifugation, filtration on large-size membrane filter, filtration at high pressure, filtration at increasing high pressure following a first period without pressure, etc.

NOTE 5 An example of a specific liquid-solid separation procedure is given in Annex A and has been applied to soil samples.

Determine the volume of eluate V_E or record the volume of the aliquot used.

Measure immediately the electrical conductivity (in mS/m), temperature, DOC and pH of the eluate. Measurement of turbidity and redox potential (E_h in mV) is highly recommended.

NOTE 6 Analysis of DOC in the eluate is needed, as the concentration of DOC shows generally a large variation over the applied pH range and is relevant both for release of inorganic substances, as well as for organic substances.

Proceed immediately with the eluate treatment, as specified in 8.5.

8.4 Natural pH

Repeat 8.3 for a test portion without acid or base addition, when determining the volume of 0,001 mol/l $CaCl_2$ to be added. Measure the pH after 4 h, 44 h and 48 h, as in 8.2.

8.5 Further preparation of the eluate for analysis

If necessary, divide the eluate into an appropriate number of sub-samples for different chemical analyses and store them in accordance with the requirements in ISO 5667-3.

Since eluate for bio-assays should not contain NaN_3 (see 5.3), microbial degradation of organic substances may occur during the test and during the period of eluate storage. Therefore, it is highly recommended to perform bio-assays on eluate containing organic substances as soon as possible after completion of the leaching test.

8.6 Blank test

Blank tests shall be carried out at regular intervals in order to check, as far as possible, how well the whole procedure is performed. Obtain three different blank tests by carrying out the procedures specified in 8.3 and 8.5 without the solid material with the addition of:

a) both the maximum amounts of acid and base to the leachant of similar volume as used in the tests;

b) acid to obtain pH 4;

c) base to obtain pH 12.

The eluate of this blank test shall fulfil the following minimum requirements: in the eluate of the blank test, the concentration of each considered element shall be less than 20 % of the concentration determined in the eluate of the tested material or less than 20 % of the concentration in the eluate of a limit value to which the measurement result is to be compared. The elements to be considered are all the elements which are to be determined in the eluate of the tested material.

If the above requirements are not fulfilled, it is necessary to reduce the contamination. The blank test results shall not be deducted from the results of the material leaching test.

The above provision does not take into account the sieving step, crushing step or the splitting step. In order to minimize the possible contamination during these three steps, it is recommended to process a representative portion of the laboratory sample through the sieving device, the crushing device and through the splitting device and to discard such material thereafter. This provision does not cover the situation described in the note under 6.6.

9 Calculation

The concentrations of substances in the extraction solution are measured by appropriate analytical methods. They give concentrations in mg/l. The final result is a mass fraction, calculated on the basis of the extract solution volume and the mass of the test portion used, in mg/kg dry matter.

Calculate the quantity of a substance leached from the material, based on the dry mass of the original material, from Formula (9):

$$A = \rho_{\text{consti}} \times \left\{ \left(V_{\text{L}} / m_{\text{D}} \right) + \left[w_{\text{H}_2\text{O}} / \left(\rho_{\text{H}_2\text{O}} \times 100 \right) \right] \right\} \tag{9}$$

where

A is the release of a substance at a L/S = 10 (mg/kg of dry matter);

ρ_{consti} is the concentration of a particular substance in the eluate (mg/l);

V_{L} is the volume of leachant used (l);

$w_{\text{H}_2\text{O}}$ is the water content as calculated in Formula (2);

m_{D} is the mass of the dried test portion (kg);

$\rho_{\text{H}_2\text{O}}$ is the density of water (usually taken as 1 kg/l).

10 Test report

The test report shall include the following details:

a) a reference to this document (ISO 21268-4);

b) address of laboratory, name of responsible person;

c) any information necessary for the complete identification of the sample;

d) information on sample pretreatment;

e) water content;

f) type of leachant;

g) the acid or base consumption to reach the relevant pH values in mol H^+ /kg dry matter and in mol OH^-/kg dry matter, respectively;

h) centrifugation speed/force, time and type of vessels used, temperature readings;

i) detailed description of the filtration step and results of adsorption tests on the filters applied if hydrophobic organic compounds are reported;

j) the test results including at least pH, electrical conductivity, measured concentrations (mg/l), released quantities (mg/kg dry matter), and limit of detection for each substance;

k) any details that are optional or any deviations from the specifications of this document, and any effects which may have affected the results.

11 Analytical determination

11.1 General

Since the analysis step is not included in the scope of this document, the analytical method applied together with the limit of quantification shall be reported.

11.2 Blank test information

The following shall be included in the test report:

— date of the last blank test performed;

— results of the blank test, including the elements considered for the tested material and the levels above which the results can be considered as valid, when compared with the measured concentrations, in mg/l.

12 Performance characteristics

The performance characteristics of the method as determined in the intercomparison validation of US-EPA method 1313 is given in Annex D. US-EPA method 1313 is very similar in performance to the procedure described in this document both in terms of the sample preparation (the contaminated soil used for validation had a particle sie < 2 mm), the equilibration time (48 h) and the scope of the methods including soil. The main difference in the testing protocol is the way that acid/base is added to the suspensions. US-EPA method 1313 describes addition in one step while this document describes addition of acid/base in three subsequent steps. US-EPA method 1313 uses a larger range in pH values in comparison with ISO 21268-4 and, therefore, the validation results of only pH 4 to pH 12 were used in Annex D. Given the strong similarities between the US-EPA method 1313 and this document, the data on repeatability and reproducibility (see Annex D) are assumed to be applicable to this document.

Annex A
(informative)

Example of a specific liquid-solid separation procedure for soil samples

A.1 General

The original scope of leaching tests covers, in particular, solid substances containing larger amounts of dissolved salts. The general feasibility of these methods has limitations when the solubility of substances has to be determined in soil samples, in particular when, for example, oxidized, adsorbed or organically bound heavy metals are rather insoluble in those materials. Despite their low solubility, heavy metals are important from an environmental point of view. The lower the "pure" solubility of heavy metals in a contaminated soil sample, the higher is the relative influence of colloidal particle portions in eluate on the end result is.

Especially in the case of fine-textured soil samples that are rich in humus but poor in electrolytes, the filter cake produced during filtration exhibits very fine pores and less colloids pass through the membrane filter. Thus, the production of filter cake largely affects the "solubility" of heavy metals, a fact which is identified by this method. To obtain comparable results, it is necessary to stipulate the factors determining the height of the filter cake. In addition to sample-specific properties, the thickness of the filter cake is determined predominantly by the filter diameter and the volume of the eluate to be filtered. Absorption by the filter cake can be reduced when part of the extract solution is filtered.

A.2 Apparatus

A.2.1 Pressure filtration unit, for membrane filter (diameter 142 mm).

A.2.2 Membrane filter, of pore size 0,45 µm.

If another filter size is used, the volume to be filtered is modified according to the filter surface; an essential precondition is that the relationship between the volume to be filtered and the filter surface is complied with [relationship: about 1 l volume to 158 cm^2 filter surface (diameter 142 mm)].

A.2.3 Media-guiding material (in contact with extracts), in polytetrafluoroethylene.

A.3 Procedure

For sedimentation of the larger particles, allow the suspension to stand for 15 min after shaking.

Decant almost completely the supernatant liquid into a centrifuge tube or bottle device.

Apply centrifugation (30 min at 2 000 *g*).

Almost complete decant the supernatant liquid into the membrane pressure filter apparatus.

Apply, after 5 min of filtration without pressure, a pressure of 100 kPa to accelerate filtration. If after 15 min less than two thirds of the eluate have passed through the filter, increase the pressure to 200 kPa. If necessary, increase the pressure to a maximum of 350 kPa after 30 min. Continue the filtration until all the supernatant of centrifugation has passed through the filter. If the filtration is still incomplete after 2 h, stop the filtration, collect the incomplete filtrate and prepare it for analysis.

By using this procedure, a significant reduction in the possible errors resulting from the proportions of colloidal, dissolved heavy metals, in filtrate can be ensured. Consequently, it is not allowed to decant the first part of the filtrate and to put it again on the filter – a method that is quite common in several laboratories.

Annex B
(informative)

Operation and uses of the test — Influence of pH on the leaching behaviour

B.1 Comparison of the mode of operation of the test with the pH continuous control mode — Influence of pH on the leaching behaviour

Two modes of operation can be applied to measure the influence of pH on leaching behaviour; by continuous (automated) pH control, or by addition of preselected amounts of acid or base. Both modes are aimed at determining the influence of pH on the release of inorganic and organic substances from a soil or soil material.

In the test described in this document, an equilibrium condition is established at different pH values, as a result of the reaction between preselected amounts of acid or base and test portions of the soil. Size reduction is performed to accelerate reaching an equilibrium condition.

In addition to the pH influence on leaching, the test addressing the influence of pH on leaching by continuous pH control (see CEN/TS 14997) is suitable for solubility control at a precisely specified pH. The test addressing the influence of pH on leaching by continuous pH control can be particularly suitable when materials are tested which have a very low buffer capacity, or in the case of measurement of pH influence on leaching at a pH where a small pH change leads to strong change in release. Figure B.1 shows typical trends of the pH adjustment to neutralize alkaline materials to the desired setpoint (e.g. pH 5) using the pHstat mode (part a) and the ANC mode (part b).

B.2 Expression of results

Three graphical presentations of the results can be obtained. They provide a visual representation of the test results as a trend (see B.3):

a) pH at t_0 + 48 h (see 8.3.3) versus the amounts of acid/base added (ANC and BNC curve), expressed in mol H^+/OH^- per kg of dry matter;

b) concentration of each analysed substance in eluates in log scale, in milligrams per litre (mg/l), versus pH at t_0 + 48 h;

c) concentration of each analysed substance in eluates in linear scale, in milligrams per litre (mg/l), versus the amounts of acid or base added (mmol H^+/OH^- per kg of dry matter).

NOTE In the third visual representation, the pH at t_0 + 48 h can also be added as a second ordinate.

In the case when the leached amounts (U_x) (mg/kg of dry soil) are needed, they can be directly calculated by multiplying the concentrations in milligrams per litre (mg/l) by the L/S value (usually L/S = 10 l/kg of dry material).

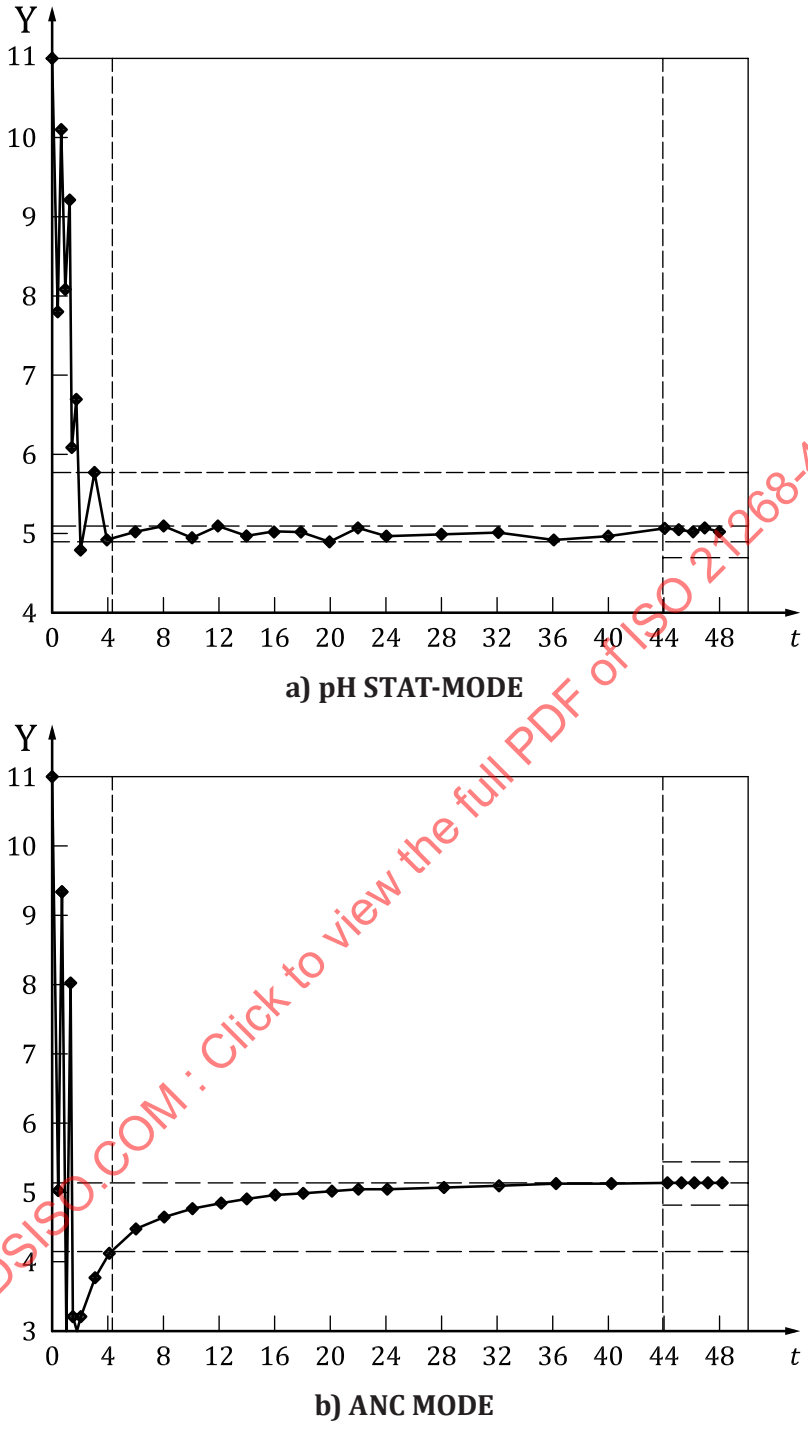


Figure B.1 — Typical pH variations during the two modes of the tests for determining the influence of pH on the leaching behaviour of an alkaline material at a final pH of about 5

B.3 Scope and limits of the application field of the test

This test provides information on the influence of pH on leaching under the experimental conditions specified in this document. It does not directly take the effects of other parameters, such as the influence of acids and bases other than the nitric acid/sodium hydroxide used in the test, dissolved organic carbon, complexation, redox conditions, into account.

This test method is a parameter-specific test, as specified in EN 12920. The application of this test method alone is not sufficient for the determination of the detailed leaching behaviour of a soil under specific conditions.

NOTE This generally requires the application of several test methods, behavioural modelling and model validation, as specified in EN 12920.

Therefore, provided that the nitric acid/sodium hydroxide used in the test, as well as the other experimental conditions, are relevant for the considered scenario, this test is useful to

a) qualify and quantify the material resistance to acid-basic attack through the concentration measured, as a function of the pH and the acid/base amount needed to reach a given final pH;

b) identify the chemical behaviour trends and the availability levels of substances at different pH values under the experimental conditions specified in this test. These values can be used as input to modelling of chemical behaviour using geochemical speciation models (e.g. MINTEQA2, GEOCHEM WORKBENCH, PHREEQC, ECOSAT, ORCHESTRA, CHESS, SPEC, etc.). In many cases, it also provides insight in the relevance of particular solubility controls and release mechanisms (e.g. formulate a hypothesis on the dissolution mechanisms);

c) provide a basis of reference for different leaching tests, as it has been shown that pH is one of the major controlling factors distinguishing tests from one another;

d) compare leaching behaviour, with respect to pH, of the same parameter from different soils or different material classes to be able to demonstrate similarities in solubility controlling conditions irrespective of material matrix;

e) provide data to feed dynamic behavioural models, for instance, under the following relationship: solubilization = f (pH or meq H^+/g) in the physico-chemical context linked with the presence of the other compounds in the material. This is not always possible with available literature data.

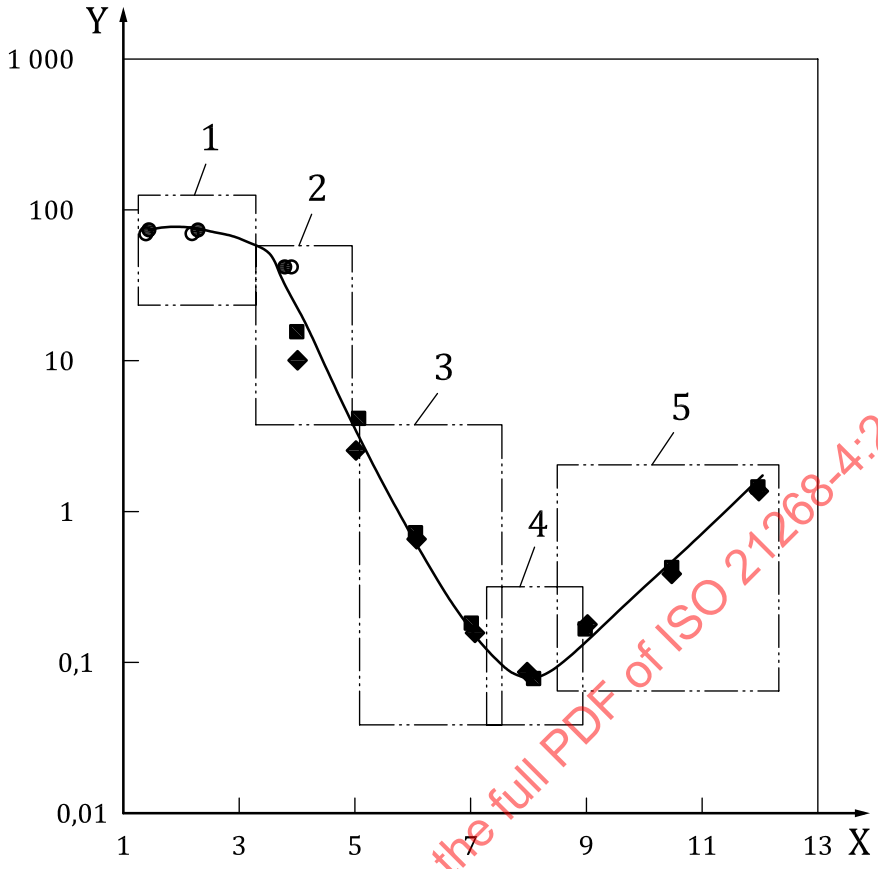
On the contrary, this test is not meant for

— quantifying a maximum removable fraction, as the concentrations obtained correspond to a steady state situation close to chemical equilibrium. For example, the values obtained for the lowest pH and at high pH can only be considered as approaching the maximum removable fraction of, respectively, metals and oxyanions;

— simulating actual situations in specific scenarios, because, in addition, at least information on low L/S will be needed.

B.4 Example: Identification of the sensitivity of leaching to pH over the environmentally relevant pH range

The test provides insight in the sensitivity of leaching of substances from a specific material to pH (see Figure B.2). This factor has been found to be a major release controlling parameter in virtually all materials. Obviously, the relevant pH range for a given application may be limited. However, for characterization purposes, the full pH range from at least 4 to 12 is important, as different uses of the information relate to different pH domains. In Figure B.2, the leaching behaviour under the influence of pH is illustrated for cadmium (Cd) from heavily sewage sludge amended soil[1]. An indication of the repeatability of the method can be obtained from the duplicate test data. The test was performed with an initial acid/base addition. Figure B.2 also indicates pH ranges typical of some “soil” – “conditions of scenarios” combinations.



Key

X	pH
Y	Cd leached at L/S = 10 mg/kg
◆	initial addition mode
■	duplicate
1	ingestion/inhalation
2	acidic environment
3	natural soil
4	soil liming
5	cement stabilization of contaminated soil

Figure B.2 — Illustration of the influence of pH on the leaching behaviour of a heavily sewage-sludge-amended soil, as obtained in a pH range of 4 to 12 (test performed with initial acid/base addition), and its use in relation to different scenarios for the same material

Annex C
(informative)

Preliminary determination of the acid/base consumption

C.1 General

In order to determine the amount and concentration of acid/base, two methods are possible:

a) a titration procedure to estimate the ANC and the BNC (see C.2);

b) an arbitrary division of the maximum acid/base consumption for the extreme pH values (see C.3).

C.2 Titration procedure to estimate the ANC and the BNC

C.2.1 Reagents

C.2.1.1 Nitric acid (per analysis), 0,1 mol/l to 14,4 mol/l.

C.2.1.2 Sodium hydroxide, NaOH (or **potassium hydroxide** (KOH), see NOTE in 5.5), 0,1 mol/l to 5 mol/l.

C.2.1.3 Distilled water, demineralized water or **water of equivalent purity** (5 < pH < 7), with a conductivity of < 0,5 mS/m.

C.2.2 Apparatus

C.2.2.1 Bottles made of polypropylene (PP), PTFE or polyethylene (PE).

C.2.2.2 Stirring or agitation device, i.e. a magnetic stirring device, using a polytetrafluoroethylene (PTFE) coated magnetic stirring rod, or a mechanical stirring device, made of glass or PTFE.

C.2.2.3 Titrator (optional).

C.2.3 Test portion

Test portions are prepared in accordance with the procedure in 7.4. Based on sample heterogeneity, it is recommended that the test portion size is either m_D = 15 g, 30 g or 60 g (dry mass), with a tolerance of ±1 g.

C.2.4 Procedure

C.2.4.1 Preparation

Place the test portions in rinsed bottles one for acid titration and the other for alkaline titration. The test aims at a final L/S ratio of 10 after acid or base addition. If the L/S exceeds 11 because of the high acid or base consumption of the material at the specific pH value, a stronger acid or base should be used for pH adjustment.

Add an amount, *V*, of demineralized water in the bottles establishing a liquid to solid ratio (L/S) about 9. Calculate the volume, *V*, as follows, assuming the density of water to be 1 g/ml:

$$V = 9 \times m_D - (m_W - m_D) \quad \text{(C.1)}$$

where

m_W is the non-dried mass of the test portion, expressed in grams (g);

m_D is the dried mass of the test portion, expressed in grams (g).

Record the amount *V* of water added.

NOTE If information is available on the material concerning a particularly strong ANC or BNC, another initial L/S can be used to allow the final L/S to remain ≤11.

C.2.4.2 Natural pH

Put the two filled bottles on the agitation device. Agitate or stir for 1 h. Determine the pH of the eluate directly in the bottles after settling for 10 min.

C.2.4.3 Acid titration

Add a portion of acid (C.2.1.1), manually or by use of the titrator, into one of the bottles from C.2.4.1 and determine the pH directly in the bottle after 30 min. Record the amount and concentration of acid added, and the pH obtained.

The amount of acid needed to get a decrease in pH varies between materials, and therefore, the initial portions need to be small in order to see the magnitude of the first response by the material.

In the case of a high acid demand, the manual addition of strong acid in the beginning of the determination is practical and a shorter response time than 30 min may be used.

Continue adding portions of acid, and measure the pH after 0,5 h, stirring or agitating after each portion is added. Repeat until the entire pH interval from the natural pH (C.2.4.2) to pH 4 or below is obtained and the distance between the obtained pH values is smaller than the 1,5 pH values. Record the amounts and concentrations of acid added, and the pH values obtained.

C.2.4.4 Base addition

Add a portion of base (C.2.1.2) into the other of the bottles from C.2.4.1, and determine the pH directly in the bottle after 30 min. Record the added amount and concentration of base, and the obtained pH.

The amount of base needed to get an increase in pH varies between materials, and therefore, the initial portions need to be small in order to see the magnitude of the first response by the material.

In the case of a high base demand, the manual addition of strong base in the beginning of the determination is practical and a shorter response time than 30 min may be used.

Continue adding portions of base and measure the pH after 30 min, stirring or agitating after each portion is added. Repeat until the entire pH interval from the initial pH (C.2.4.2) to pH 12 or above is obtained and the distance between the obtained pH values is smaller than the 1,5 pH value.

In order not to underestimate the ANC or the BNC, it is recommended to wait 24 h for pH 4 in the case of very alkaline materials, or pH 12 for materials with a high buffer capacity.

C.2.5 Expression of results

Plot a curve of pH versus amounts of acid and base, expressed in mol H^+/kg and mol OH^-/kg.

C.3 Arbitrary division of the maximum acid/base consumption for the extreme pH values

C.3.1 General

For soils with a very strong acid-base capacity, manual titration may lead to an excessive experimental duration when the maximum acid and base consumption in order to reach, respectively, pH 4 and pH 12 is unknown. In this procedure, the natural pH and acid and base consumption at pH 4 and pH 12, respectively, is estimated.

C.3.2 Reagents

C.3.2.1 Nitric acid (pro-analysis), 0,1 mol/l to 14,4 mol/l.

C.3.2.2 Sodium hydroxide, NaOH, 0,1 mol/l to 5 mol/l.

C.3.2.3 Distilled water, demineralized water or **water of equivalent purity** (5 < pH < 7), with a conductivity of < 0,5 mS/m.

C.3.3 Apparatus

C.3.3.1 Bottles made of polypropylene (PP), PTFE or polyethylene (PE).

C.3.3.2 Stirring or agitation device. This is a magnetic stirring device, using a polytetrafluoroethylene (PTFE) coated magnetic stirring rod, or a mechanical stirring device, made of glass or PTFE.

C.3.3.3 Titrator.

C.3.4 Test portion

Test portions are prepared in accordance with the procedure in 8.4. Based on sample heterogeneity, it is recommended that the test portion size is either m_D = 15 g, 30 g or 60 g (dry mass) (with a tolerance of ±1 g).

C.3.5 Procedure

C.3.5.1 Preparation

Place two of the test portions in rinsed bottles one for acid titration and the other for alkaline titration. The test aims at a final L/S ratio of 10 after acid or base addition. If the L/S exceeds 11 because of the high acid or base consumption of the material at the specific pH value, a stronger acid or base should be used for pH adjustment.

Add an amount, V, of demineralized water in the bottles establishing a liquid to solid ratio (L/S) of about 9. Calculate the volume, V, as follows assuming the density of water to be 1 g/ml:

$$V = 9m_D - (m_W - m_D) \quad \text{(C.2)}$$

where

m_W is the non-dried mass of the test portion, expressed in grams (g);

m_D is the dried mass of the test portion, expressed in grams (g).

Record the amount, *V*, of water added.

NOTE If information is available on the material concerning a particularly strong ANC or BNC, another initial L/S can be used to allow the final L/S to remain ≤ 11.

C.3.5.2 Natural pH

Put the two filled bottles on the agitation device. Agitate or stir for 1 h. Determine the pH of the eluate directly in the bottles after settling for 10 min.

C.3.5.3 Acid titration

Titrate one of the bottles in C.3.3.1 with nitric acid (C.3.2.1) in the titration equipment set at pH 4. Confirm the acid consumption over a titration period of 24 h. Record the added amount and concentration of acid, and the obtained pH.

If the time taken to complete this last point needs to be reduced, samples may be reduced in size to below 0,5 mm (as no analysis is foreseen).

If this equipment is not available, manual titration may be carried out with the objective of achieving pH 4 as soon as possible, including an overnight waiting period to validate the last measurement points.

If the time taken to complete this last point needs to be reduced, samples may be reduced in size to below 0,5 mm (as no analysis is foreseen).

C.3.5.4 Base addition

Titrate the other of the bottles in C.3.3.1 with base (C.3.2.2) in the titration equipment set at pH 12. Confirm the base consumption over a titration period of 24 h. Record the added amount and concentration of base, and the obtained pH.

If this equipment is not available, manual titration may be carried out with the objective of achieving pH 12 as soon as possible, including an overnight waiting period to validate the last measurement points.

If the time taken to complete this last point needs to be reduced, samples may be reduced in size to below 0,5 mm (as no analysis is foreseen).

C.3.6 Expression of results

The acid consumption to reach pH 4 and the base consumption to reach pH 12 is recorded together with the natural pH.

Divide the amount of acid by double the number of pH values intended to be tested within the acid pH range (pH range as a result of acid addition).

Divide the amount of base by double the number of pH values intended to be tested within the alkaline pH range (pH range as a result of base addition).

NOTE 1 If, for example, between the natural pH and pH 4,5, pH values are sought, and if the maximum acid consumption is 5 mol/kg H+, prepare 10 different acid solutions from 50 mmol/l H^+ to 500 mmol/l H^+ at evenly-spaced intervals.

NOTE 2 This method allows limitation of the misevaluation of the ANC and BNC and the selection of the seven solutions to be analysed after reaching the stationary pH. This allows also choosing solutions leading to the same pH, i.e. along a potential pH plateau corresponding to the buffer capacity of the material (e.g. carbonates) of high interest in terms of behaviour.

NOTE 3 Due to buffering of the matrix, equally-spaced portions generally will not lead to proper final pH values. Doubling the number of bottles is no guarantee for obtaining properly spaced final pH values. Through interpolation, it will be possible to estimate the proper amounts needed from the curve of final pH against acid/base consumption.

Annex D
(informative)

Repeatability and reproducibility data

D.1 Soil sample used in the interlaboratory comparison study

The interlaboratory comparison of the pH dependent leaching behaviour of substances from a contaminated soil was carried out with 8 laboratories. The repeatability and reproducibility data for the contaminated soil (from a smelter site) was selected here as this material falls under the scope of this document. The soil was contaminated with heavy metals and collected from a smelter site located in the United States. Approximately 320 kg of contaminated field soil (identified by material code CFS) was collected in 5-US-gallon (19 litre) plastic buckets and shipped to the laboratory for processing. The entire batch of soil was sieved to pass a 2 mm opening in order to remove large rocks and other refuse and transferred to a clean blue plastic tarp for mixing by coning and quartering. After homogenization, the soil was divided into 1-L HDPE jars containing approximately 1 kg each for distribution to the participating laboratories. Each participating laboratory received six randomly selected jars (6 kg) of soil to be used in testing while the reference laboratory retained 12 randomly selected jars (12 kg). Detailed information on the complete interlaboratory comparison study can be found in the final report from US-EPA[5]).

D.2 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2 after log transformation of the test results. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) obtained are shown in Table D.1.