BS ISO 14388-3:2014

BSI Standards Publication

Soil quality — Acid-base accounting procedure for acid sulfate soils

Part 3: Suspension peroxide oxidation combined acidity and sulfur (SPOCAS) methodology

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National foreword

This British Standard is the UK implementation of ISO 14388-3:2014.

The UK participation in its preparation was entrusted to Technical Committee EH/4, Soil quality.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Soil quality — Acid-base accounting procedure for acid sulfate soils —

Part 3:
Suspension peroxide oxidation combined acidity and sulfur (SPOCAS) methodology

Qualité du sol — Méthode de comptage acide-base pour les sols sulfatés acides —

Partie 3: Méthode par oxydation au peroxyde en suspension combinée à l'acidité et aux sulfures (SPOCAS)

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

ISO 14388 consists of the following parts, under the general title *Soil quality — Acid-base accounting procedure for acid sulfate soils*:

- *Part 1: Introduction and definitions, symbols and acronyms, sampling and sample preparation*
- *Part 2: Chromium reducible sulfur (CRS) methodology*
- *Part 3: Suspension peroxide oxidation combined acidity and sulfur (SPOCAS) methodology*

Introduction

The ‘SPOCAS’ suite uses the suspension peroxide oxidation combined acidity and sulfur (SPOCAS) method as the basis for determining an acid-base account for acid sulfate soils. Like the chromium suite, a decision-tree type process is followed (Figure 1). Various components of soil acidity and/or alkalinity are determined, depending on pH. Once the decision-tree process is completed, the various components can be used to calculate an acid-base account.

The results required to complete the acid-base accounting vary with the soil’s existing acidity, as represented by pH_{KCl}. Table A.2 in ISO 14388-1:—1) shows the analyses required for the SPOCAS suite. This table uses results reported in acidity units. Alternatively, results in equivalent sulfur units may be utilized.

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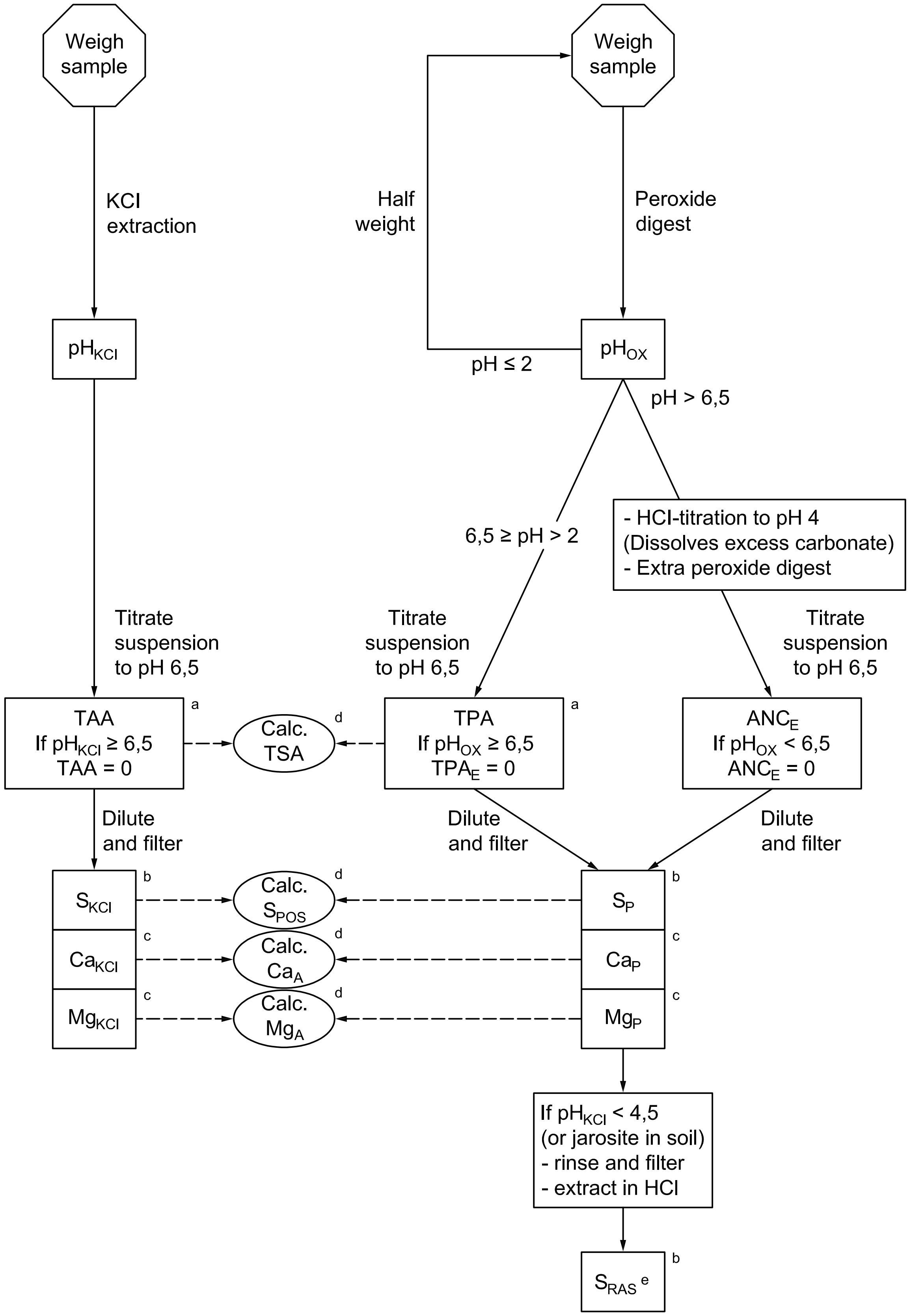
1) To be published.



Key

a Acidity titration

b Sulfur determination

c Cation/acid neutralising

d Calculated parameter

e Alternatively, S_{NAS} may be substituted for S_{RAS}

Figure 1 — Flow diagram of SPOCAS suite

INTERNATIONAL STANDARD **ISO 14388-3:2014(E)**

Soil quality — Acid-base accounting procedure for acid sulfate soils —

Part 3:
Suspension peroxide oxidation combined acidity and sulfur (SPOCAS) methodology

WARNING — Persons using this International Standard should be familiar with usual laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This part of ISO 14388 specifies a suite of methods used to determine net acidity in acid sulfate soils. This part of ISO 14388 specifies a method for the determination of pH in a 1 mol/l potassium chloride soil suspension (pH_{KCl}) and where required, titratable actual acidity (TAA). Following this, potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) are determined. On a separate test portion, following digestion with 30 % hydrogen peroxide, peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralizing capacity (ANC_E) are determined. Following this, peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) are determined. On samples where jarosite is present, or where pH_{KCl} is < 4,5, residual acid soluble sulfur (S_{RAS}) is determined on the soil residue remaining after peroxide digestion. Titratable sulfidic acidity (TSA), reacted calcium (Ca_A), reacted magnesium (Mg_A) and peroxide oxidizable sulfur (S_{POS}) are then determined by difference. For peat samples containing substantial levels of organic sulfur, the SPOCAS suite is generally unsuitable for estimating sulfide content, and the chromium reducible suite of procedures should be used instead.

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 648, *Laboratory glassware — Single-volume pipettes*

ISO 835, *Laboratory glassware — Graduated pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 1770, *Solid-stem general purpose thermometers*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 8655-1, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Piston pipettes*

ISO 8655-3, *Piston-operated volumetric apparatus — Part 3: Piston burettes*

ISO 8655-5, *Piston-operated volumetric apparatus — Part 5: Dispensers*

ISO 14388-1:—2), *Piston-operated volumetric apparatus — Part 5: Dispensers*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14388-1 apply.

4 Principle

4.1 Actual acidity and retained acidity

To determine **actual acidity**, a 1:40 suspension of soil in 1 mol/l KCl solution is shaken for 4 h and allowed to stand overnight. The suspension is then briefly shaken prior to determining pH (pH_{KCl}). If pH_{KCl} is less than 6,5, titratable actual acidity (TAA) is determined by titrating the soil suspension to pH 6,5. After appropriate dilution of the soil suspension, potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) are measured by suitable analytical technique(s). Where pH_{KCl} is < 4,5 (or where the presence of jarosite has been noted in the submitted sample), **retained acidity** can be determined as residual acid-soluble sulfur (S_{RAS}). This is measured by 4 mol/l hydrochloric acid extraction of the soil residue remaining after the peroxide digestion of the soil following determination of titratable peroxide acidity (after appropriate washing of the residue to remove soluble sulfate). Alternatively, retained acidity is measured as the difference between S_{HCl} (the sulfur measured following overnight extraction of a separate sub-sample with 4 mol/l hydrochloric acid) and S_{KCl} (known as net acid-soluble sulfur, S_{NAS}). The **former** approach is preferable in highly organic soils where S_{NAS} may overestimate retained acidity due to the inclusion of organic S in the result.

4.2 Titratable peroxide acidity, excess acid neutralizing capacity and potential sulfidic acidity

A separate test portion of soil is digested with 30 % hydrogen peroxide and acidity is generated from the oxidation of sulfides (and organic matter where present). Following digestion, pH_{OX} is measured on the digest solution. If the pH after initial peroxide digestion is ≤ 6,5 then KCl solution is added to the sample which is then titrated to pH 6,5 to determine titratable peroxide acidity (TPA). If after peroxide digestion the pH is > 6,5 a HCl titration to pH 4 is performed, followed by an additional peroxide digest step. This allows the calculation of excess acid neutralizing capacity (ANC_E), i. e. the available ANC in excess of that needed to neutralize the potential acidity from the presence of sulfides or other acid generating species in the soil.

After appropriate dilution of the soil suspension, peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) are measured by suitable analytical technique(s). These analytes allow the calculation of various other soil parameters. Acid neutralizing capacity can also be calculated from reacted calcium (Ca_A) and magnesium (Mg_A) results (i. e. the difference in soluble calcium and magnesium before and after peroxide oxidation).

Potential sulfidic acidity, (the acidity latent in reduced inorganic iron sulfide compounds), can be determined as peroxide oxidizable sulfur (S_{POS}) (the calculated difference between peroxide sulfur (S_P) peroxide and KCl-extractable sulfur (S_{KCl})).

5 Reagents

All reagents shall be of analytical grade. Deionised or glass distilled water of grade 2 as defined in ISO 3696 shall be used throughout.

The purity of all reagents should be verified by performing a blank test for the presence of sulfur, calcium and magnesium. Reagents should also be tested for the presence of these elements whenever a change in source is made (e. g. brand or batch).

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[2] To be published.

5.1 Calibration solutions for the pH meter

5.1.1 General

For pH determinations, buffer solutions as specified in 5.1.2 and 5.1.3 are sufficient for calibrating the pH meter. It is the responsibility of the analytical laboratory to verify the accuracy of the buffer solutions.

NOTE Commercially available buffer solutions covering a comparable pH range may be used.

5.1.2 Buffer solution, pH 4,00 at 20 °C

Dissolve 10,21 g ± 0,01 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in water and dilute to 1 000 ml.

5.1.3 Buffer solution, pH 6,88 at 20 °C

Dissolve 3,40 g ± 0,005 g of potassium dihydrogen phosphate (KH_2PO_4) and 3,55 g ± 0,005 g of disodium hydrogen phosphate (Na_2HPO_4) in water and dilute to 1 000 ml.

5.1.4 Buffer solution, pH 9,22 at 20 °C (see Clause 4 in ISO 14254:2001)

Dissolve 3,81 g ± 0,005 g of disodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10\ H_2O$) in water and dilute to 1 000 ml.

NOTE The buffer solutions as specified in 5.1.2, 5.1.3 and 5.1.4 are stable for one month when stored in polyethylene bottles.

5.2 Copper chloride solution, 400 mg Cu/l as $CuCl_2 \cdot 2\ H_2O$

Dissolve 1,073 g of copper (II) chloride dihydrate ($CuCl_2 \cdot 2\ H_2O$) in water and dilute to 1 000 ml at 20 °C.

5.3 Hydrochloric acid (HCl), ρ 1,16 g/ml

5.4 Hydrochloric acid solution, 0,5 mol/l

Add 50 ml of concentrated hydrochloric acid (5.3) with stirring to approximately 700 ml of water. Cool to room temperature, transfer to a 1 l volumetric flask and fill to the mark with water. Standardize against disodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10\ H_2O$) and calculate molarity of hydrochloric acid solution (C_3).

Solutions made by diluting commercially available ampoules may also be used.

5.5 Hydrochloric acid solution, 4 mol/l

Add 400 ml of hydrochloric acid (5.3) with stirring to approximately 400 ml of water. Cool to room temperature, transfer to a 1 l volumetric flask and fill to the mark with water.

5.6 Hydrogen peroxide (H_2O_2), 30 % (w/w) (bulk peroxide for digestion)

WARNING — HYDROGEN PEROXIDE IS A CORROSIVE OXIDIZING AGENT. CONTACT WITH COMBUSTIBLE MATERIAL MAY CAUSE FIRE. AVOID CONTACT WITH SKIN AND EYES.

5.6.1 Checking acidity of hydrogen peroxide

Hydrogen peroxide solutions (5.6) can contain appreciable acidity, especially if the pH is less than 3,5. If the pH is less than 3,5 then the acidity of the peroxide should be quantified to ascertain whether the blank is unacceptably high. Add 20 ml of 30 % hydrogen peroxide (5.6) to 30 ml of water and note the pH. Follow the same procedure as for a sample digest, including the decomposition of peroxide with copper chloride solution and addition of potassium chloride. Measure the pH and titrate to pH 6,5 (if required) and calculate the acidity of the blank. If the titration for the blanks yields a result in excess of the equivalent of 6 mmol H^+/kg, then either switch to another batch of hydrogen peroxide with lower acidity, or alternatively partially neutralize the 30 % peroxide to a pH of approximately 5,0 with sodium hydroxide solution (5.10.2). In either case, repeat the blank determination to ensure acceptably low acidity.

5.6.2 Checking sulfur content of hydrogen peroxide

As sulfur is commonly measured in solutions following TPA determination, the sulfur content of the peroxide should be determined. Acceptable sulfur values are below 0,000 5 % S.

NOTE Technical grade peroxides are not recommended as they are usually acid stabilized and vary considerably between bottles in both sulfur content and pH.

5.7 Hydrogen peroxide H_2O_2, 30 % (w/w) (pH adjusted)

NOTE 1 This reagent is used to oxidize ferrous ions in the final titration. This reagent is not for the digestion of samples (for which see 5.6).

Where pH of bulk peroxide (5.6) is less than 5,5, adjust pH to 5,5 ± 0,1 by adding 0,05 mol/l sodium hydroxide (5.10.2) drop-wise with stirring, ensuring that this pH value remains stable thereafter.

NOTE 2 Refer to Warning in 5.6.

5.8 Potassium chloride solution, 1 mol/l

Dissolve 74,55 g of potassium chloride in water, transfer to a 1 000 ml volumetric flask and fill to the mark with water.

5.9 Potassium chloride solution, 2,66 mol/l

Dissolve 198,80 g of potassium chloride in water, transfer to a 1 000 ml volumetric flask and fill to the mark with water.

5.10 Sodium hydroxide (NaOH) solutions

5.10.1 0,25 mol/l sodium hydroxide solution

Dissolve 10,1 g ± 0,1 g of sodium hydroxide in water, transfer quantitatively to a 1 000 ml volumetric flask and fill to the mark with water. Standardize against potassium hydrogen phthalate previously dried for 4 h at 105 °C and stored in a desiccator. Calculate the molarity of the sodium hydroxide solution (C_1).

Solutions made by diluting commercially available ampoules may also be used.

5.10.2 0,05 mol/l sodium hydroxide solution

Dissolve 2,05 g ± 0,05 g of sodium hydroxide in water, transfer quantitatively to a 1 000 ml volumetric flask and fill to the mark with water. Standardize against potassium hydrogen phthalate previously dried for 4 h at 105 °C and stored in a desiccator. Calculate the molarity of the sodium hydroxide solution (C_2).

Solutions made by diluting commercially available ampoules may also be used.

The actual molarities of the standardized sodium hydroxide solutions (C_1, C_2) shall be used in the calculation, not their nominal molarities.

Solutions shall be prepared fresh each day or alternatively may be stored in apparatus capable of excluding CO_2. Solutions should be stored in high density polyethylene or borosilicate glass containers.

Absorption of CO_2 changes the concentration of sodium hydroxide solutions and decreases the extent of the reaction near the end point in titration of weak acids. Solutions shall be standardized at least weekly, or immediately prior to use and discarded one month after being prepared.

6 Apparatus

Grade A volumetric glassware shall be used throughout. Volumetric flasks shall comply with ISO 1042 and pipettes shall comply with ISO 648 and ISO 835. The use of volumetric glassware shall conform to ISO 8655-1, ISO 8655-2, ISO 8655-3 and ISO 8655-5.

6.1 Automatic titration instrument or pH meter, with slope adjustment and temperature control capable of measuring to an accuracy of 0,01 pH units.

6.2 Beaker or other container, capacity of at least 450 ml, made of polyethylene, glass or similar inert material.

6.3 Burette, A-grade, 10 ml capacity, graduated at 0,02 ml intervals, or a similarly accurate digital burette, or a suitably calibrated burette from an automatic titration instrument may be used.

6.4 Centrifuge, capable of centrifuging 400 ml of suspension.

6.5 Dispenser 1 (manual or automatic), capable of dispensing 80 ml ± 0,5 ml.

6.6 Dispenser 2 (manual or automatic), capable of dispensing 30 ml ± 0,25 ml.

6.7 Balance 1, capable of weighing to an accuracy of ± 0,000 1 g.

6.8 Balance 2, capable of weighing to an accuracy of ± 0,01 g.

6.9 Filter paper, thick, medium speed, high retention.

NOTE Paper of 185 mm diameter has been found suitable.

6.10 Funnel, made of glass or plastic for supporting filter paper.

6.11 Glass beaker borosilicate (digestion beaker), tall form, 250 ml capacity recommended with 50 ml volume level clearly and accurately marked.

6.12 pH electrodes, glass electrode and a reference electrode, or a combination pH electrode of equivalent performance.

NOTE In soil suspensions, the danger of deterioration of performance caused by breakage or contamination of the electrodes is increased.

6.13 Pipettes, 1 ml to 10 ml range or 1 ml and 10 ml pipettes, or piston-operated volumetric apparatus (POVA) may be used in accordance with ISO 8655-1, ISO 8655-2 and ISO 8655-3.

6.14 Sample bottle, of 100 ml to 250 ml capacity to allow efficient mixing and also to minimize the head space, made of polyethylene or other inert material, with a tightly fitting cap or stopper to prevent leakage.

NOTE Sample bottle and stopper should be made of material not containing sulfur.

6.15 Shaking or mixing machine, capable of keeping soil particles continuously in suspension.

NOTE For example, end-over-end shaker.

6.16 Steambath, or electric hotplate, with adjustable temperature control, capable of maintaining the digestion solution between 80 °C and 90 °C.

6.17 Stirrer, overhead propeller, or magnetic type with polytetrafluoroethylene (PTFE) coated stirrer bar or stirring rod capable of stirring 400 ml of suspension.

6.18 Thermometer or temperature sensor, capable of measuring to the nearest 1 °C and complying with Type C according to ISO 1770 is required, connected to an automatic titrator or pH meter.

6.19 Titration vessel, capacity of at least 100 ml, made of polyethylene or other inert material.

6.20 Wash bottle with narrow aperture, containing water.

7 Procedure for determination of pH_{KCl} and TAA

7.1 Preparation of the suspension

Weigh a test portion of 2,0 g ± 0,1 g (6.8) from the test sample prepared in accordance with ISO 14388-1 into a tared sample bottle (6.14) and record the mass to 0,01 g (m_1). At least one solution blank should be subjected to the same procedure as the test portion in each analytical run.

Using the dispenser (6.5), add 80 ml ± 0,5 ml of 1 mol/l potassium chloride solution (5.8) to the sample bottle to make a 1:40 soil solution ratio. Place stopper in sample bottle and shake or mix the suspension for 4 h ± 0,25 h, using the shaking or mixing machine (6.15). Allow the suspension to stand for at least 12 h, but no more than 16 h ensuring that the sample remains sealed.

The test portion shall be a minimum of 2 g, but a larger test portion may be used, provided the ratio of soil weight to potassium chloride solution volume remains at 1:40.

Using the shaking or mixing machine (6.15), shake the suspension for a further 5 min. If using an automatic titration instrument, quantitatively transfer the contents of the sample bottle (6.14) to the titration vessel (6.19) via a wash bottle (6.20) using a minimum amount of water.

NOTE The time between re-suspension and titration should be minimised to limit oxidation.

7.2 Measurement of pH_{KCl}

7.2.1 Calibration of automatic titrator, or pH meter

Calibrate the automatic titrator or pH meter (6.1) according to the manufacturer's recommendations, using the buffer solutions specified in 5.1.

There shall be a regular check of the calibration of the pH electrode.

7.2.2 Measurement of pH

Measure the temperature of the suspension to ensure that it is within 1 °C of the temperature at which the pH electrode was calibrated.

Measure the pH in the suspension while it is being stirred.

NOTE 1 The stirring should be at a rate to achieve a homogeneous suspension of the soil particles, however, entrainment of air should be avoided.

Record the pH value to 0,1 pH units after stabilization is reached and report as pH_{KCl}.

NOTE 2 The reading may be considered stable when the pH measured over a period of 10 s varies by not more than 0,02 pH units. The time required for stabilization is usually 1 min or less, but may depend on a number of factors including:

a) the value of pH_{KCl} (at high pH values, it is more difficult to reach stabilization):

b) the quality of the glass electrode (differences of manufacture between electrodes) and its age;

c) the differences in pH_{KCl} between samples in a series; and

d) whether mechanical mixing is performed before the measurement, which helps to achieve stable readings in a shorter time.

7.3 Measurement of TAA

7.3.1 General

Measurement of TAA involves titration (6.3) of the stirred soil suspension and should be either of the following:

If an automatic titrator is being used, the volume of sodium hydroxide added in each increment should decrease as the end point pH is approached. Follow automatic titrator operation manual.

When titrating manually, the following should be observed:

a) Care should be taken not to overshoot the end point pH. Keep a record of titration volumes and associated pH values as the pH 6,5 end point is approached. This allows an accurate interpolation of end point volume, if the end point pH is slightly exceeded in the titration.

b) The titration volume is dependent on the rate at which the sodium hydroxide solution is added. As a guide when titrating manually, the following points should be observed:

    a) Sodium hydroxide solution should be added at a slow constant rate (e. g. drop-wise every 1 to 2 s), allowing pH increase to keep pace with sodium hydroxide addition.

    b) When within 1 pH unit of end point (i. e. pH > 5,5) stop titration and let pH stabilize.

    c) Resume titration at a decreased rate and bring pH to between 6,3 and 6,5.

    d) Titrate to the end point and wait for 20 s.

    e) Continue titrating in the same manner until pH drops by < 0,1 pH units in 20 s (assuming that the end point has not been overshot by more than 0,1 units).

c) As a guide, 5 min would be an average time for manual titrations (for TAA > 100 mmol H^+/kg).

7.3.2 Procedure based on pH_{KCl} result

Depending on the resulting pH_{KCl} value obtained in 7.2.2 (c), select one of the following options:

a) If $pH_{KCl} < 4,0$, titrate with stirring to pH 6,5 using standardized 0,25 mol/l sodium hydroxide solution (5.10.1) and record volume (V_1).

b) If $4,0 \leq pH_{KCl} < 6,5$, titrate with stirring to pH 6,5 using standardized 0,05 mol/l sodium hydroxide solution (5.10.2) and record volume (V_1).

c) If $pH_{KCl} \geq 6,5$, no titration is required and TAA is zero.

d) If pH_{KCl} of the blank is less than 6,5, titrate with stirring using 0,05 mol/l sodium hydroxide solution (5.10.2) and record the volume (V_2).

8 Calculation of TAA

Calculate the TAA in mmol H^+/kg according to Formulae (1) and (2):

a) When 0,25 mol/l NaOH is used:

$$\text{TAA} = \left[(V_1 \times C_1) - (V_2 \times C_2) \right] \times \left[1\,000 / m_1 \right] \quad (1)$$

b) When 0,05 mol/l NaOH is used:

$$\text{TAA} = \left[(V_1 - V_2) \times C_2 \right] \times \left[1\,000 / m_1 \right] \quad (2)$$

where:

V_1 is the volume of sodium hydroxide required to reach the pH end point, in millilitres (ml);

V_2 is the volume of sodium hydroxide required for the blank, in millilitres (ml);

C_1 is the standardised concentration of 0,25 mol/l sodium hydroxide solution, in mole per litre (mol/l);

C_2 is the standardised concentration of 0,05 mol/l sodium hydroxide solution, in mole per litre (mol/l);

m_1 is the mass of the oven-dried test portion, in grams.

9 Procedure for determination of sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) extractable with 1 mol/l potassium chloride

The procedure for dilution and filtration of soil suspension following TAA titration shall be as follows:

After completion of the procedures in Clause 7, quantitatively transfer the contents from titration vessel (6.19) to a tared or weighed beaker (6.2) with water. Subject the solution blanks from Clause 7 to the same procedure.

Dilute the suspension with water to a final volume appropriate to the analytical instrumental technique.

NOTE 1 This can be achieved by using the balance (6.8), taking into account the mass of the beaker or other container (6.2), the density of the potassium chloride matrix (which is dependent on the final volume chosen) and the mass of the test portion in Clause 7.

Homogenize the suspension with a mechanical stirrer or stirring rod (6.17).

Centrifuge (6.4) or filter (6.9) an appropriate volume of the homogenized soil suspension to obtain a clear solution.

Take volumes of centrifuged or filtered solution (sufficient for the instrumental finish to be employed) and determine potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) using appropriate analytical techniques. For sulfur measurement, instrumentation that specifically determines sulfate is preferable to that which measures total sulfur in solution. An example of a technique that is specific to sulfate is ion chromatography (IC). To obtain accurate and reproducible results it is necessary to have an appropriate column that will handle high levels of chloride introduced by the potassium chloride solution matrix.

NOTE 2 Instruments that determine all sulfur species in solution (e. g. ICP-AES) may give higher results than instruments that specifically measure sulfate. This is particularly the case in soils high in organic matter that contain appreciable potassium chloride extractable organic sulfur.

10 Calculation of S_{KCl}, Ca_{KCl} and Mg_{KCl}

Calculate potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) taking into account their respective solution blank concentrations and the mass of the test portion used in Clause 7 and express as percentages on an oven-dry weight basis.

11 Procedure for determination of peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralizing capacity (ANC_E)

11.1 Peroxide digestion of sample

11.1.1 Weigh a test portion of 2,0 g ± 0,1 g (6.8) from the test sample prepared in accordance with ISO 14388-1 into a tared beaker (6.11) and record the mass to 0,01 g (m_2). At least two solution blanks should be subjected to the same procedure as the test portion in each analytical run. When one or more of the test portions undergo the carbonate modification (see 11.3), one of the blanks should also undergo this procedure. If analysing soil of known high sulfide content (i. e. > 2 % S), use a smaller test portion mass (e. g. 1,0 g ± 0,05 g). Alternatively, see 11.2.3.1.

11.1.2 In a fume cupboard, digest the test portion by adding 10 ml of H_2O_2 (5.6) using a pipette (6.13) then gently swirl to mix. At the first sign of a vigorous reaction, add water via wash bottle (6.20) to suppress the subsequent reaction.

CAUTION — Soils high in sulfide or organic matter have the potential to react violently. The addition of water via wash bottle (6.20) at the first sign of a vigorous reaction should moderate the subsequent reaction. Great care needs to be taken to avoid samples bubbling/frothing over when the initial aliquot of peroxide is added.

If the reaction becomes overly vigorous and any loss of the digest solution occurs, the procedure shall be repeated with a 1 g test portion. In this case, first add 10 ml of water to the test portion, followed by 10 ml of H_2O_2 (5.6) incrementally.

11.1.3 30 min after the peroxide addition, swirl digest solution to achieve a homogeneous suspension, rinse the inside wall of the beaker with water using a wash bottle (6.20). Add water with swirling to make the total volume of suspension in the beaker from 45 ml to 50 ml to minimize the potential for precipitation of sulfates.

It is important to maintain this volume throughout the remaining digestion by regular addition of water, and also to periodically swirl the digested solution (at least every 10 min) to prevent soil from settling on and adhering to the bottom of the beaker during the subsequent hotplate/steambath heating stages. Rinsing the inside wall of the beaker with small amounts of water also serves to dissolve any salts that may have accumulated there.

11.1.4 Place the beaker on a hotplate or steambath (6.16) to maintain digest solution between 80 °C and 90 °C for a maximum of 30 min. Swirl digest solution periodically (at least every 10 min). Add water to wash soil residue from the inside of the beaker and also to maintain volume from 45 ml to 50 ml. Follow the appropriate scenarios from those described below:

a) A digest solution that reacts vigorously at this stage (e. g. vigorous effervescence) needs to be temporarily removed from the hotplate and/or the reaction moderated with the addition of water. When the reaction has moderated, replace the digest solution on the hotplate. When the digest solution has ceased reacting while on the hotplate, as evidenced by cessation of effervescence, remove it from the hotplate. In a digest solution where a reaction is still taking place, it is removed from the hotplate when 30 min has elapsed.

b) A digest solution that reacts slowly or moderately on the hotplate is left there until the reaction ceases and then removed from the hotplate. Where a reaction is still taking place after 30 min has elapsed, remove the digest solution from the hotplate.

c) For a digest solution that did not obviously react following hydrogen peroxide addition prior to being initially placed on the hotplate, and subsequently failed to do so while on the hotplate, remove from the hotplate when 30 min has elapsed.

d) A digest solution that reacts vigorously after initial addition of hydrogen peroxide and fails to react further while being on the hotplate for 10 min shall be removed. Such a digest solution typically has a yellow green colour (indicative of soluble iron from the oxidation of pyrite), with all the peroxide generally having been consumed prior to being placed on the hotplate.

11.1.5 Allow digest solution to cool to room temperature.

11.1.6 Add a second 10 ml aliquot of H_2O_2 (5.6), waiting 10 min before returning the beaker to the hotplate. Follow the appropriate scenario outlined in 11.1.4, maintaining volume above 45 ml in all cases.

11.1.7 Allow digest solution to cool to room temperature and if volume is below 50 ml make up to this volume with water.

11.2 Measurement of pH_{OX}

11.2.1 Calibration of automatic titrator, or pH meter (see 7.2.1).

11.2.2 Measurement of pH

11.2.2.1 Measure the temperature of the suspension to ensure that it is within 1 °C of the temperature at which the electrode was calibrated.

11.2.2.2 Measure the pH in the suspension while it is being stirred.

NOTE 1 The stirring should be at a rate to achieve a homogeneous suspension of the soil particles, however, entrainment of air should be avoided.

11.2.2.3 Record the pH value to 0,1 pH units after stabilization is reached, and report as pH_{OX}.

NOTE 2 The reading may be considered stable when the pH measured over a period of 10 s varies by not more than 0,02 pH units. The time required for stabilization is usually 1 min or less, but may depend on a number of factors including:

i) the value of pH_{OX} (at high pH values, it is more difficult to reach stabilization);

ii) the quality of the glass electrode (differences of manufacture between electrodes) and its age;

iii) the differences in pH_{OX} between samples in a series; and

iv) whether mechanical mixing is performed before the measurement, which helps to achieve stable readings in a shorter time.

11.2.3 Procedures based on pH_{OX} result

Depending on the resulting pH_{OX} value obtained in 11.2.2.3, select one of the following procedures:

11.2.3.1 If $pH_{OX} \leq 2{,}0$ (indicating high sulfide levels), repeat from 11.1.1 using half of the original test portion.

11.2.3.2 If $2{,}0 < pH_{OX} \leq 6{,}5$, continue with peroxide decomposition step (11.4).

11.2.3.3 A suspension with $pH_{OX} > 6{,}5$, treat according to the carbonate modification (11.3), before continuing with peroxide decomposition (11.4).

11.3 Carbonate modification (HCl titration to pH 4)

11.3.1 If pH_{OX} is greater than or > 6,5, quantitatively transfer suspension to a titration vessel (6.19) (if not titrating in digest beaker) using a minimum quantity of water.

11.3.2 While stirring perform a slow titration (typically 10 min to 30 min, if using an auto-titrator) to pH 4 with standardized 0,5 mol/l hydrochloric acid (5.4). Record the total volume (V_3) of hydrochloric acid added and its molarity (C_3). If the target pH 4 end point is slightly overshot during titration, use the full volume of hydrochloric acid added in the titration for calculating the hydrochloric acid titration result. However, if the pH of the suspension stabilizes below 3,5, the analysis shall be repeated with another test portion. Do not perform hydrochloric acid titration on the blank sample.

NOTE This hydrochloric acid titration is designed to dissolve carbonate not consumed during peroxide digest. The presence of carbonates and/or high pH can interfere with the efficiency of peroxide oxidation of sulfides. This determination is used to calculate the excess acid neutralizing capacity (ANC_E) of the test sample. The reaction between solid carbonate in soil suspension and the added acid is slow at pH > 4. The pH tends to oscillate near the pH 4 end point, so a slow titration is essential to ensure maximum recovery of carbonate. Without the use of an auto-titrator, the conditions of this titration are difficult to standardize and make consistent. Addition of a set volume of hydrochloric acid (5.4) at a fixed time interval may be the best approach to standardizing the titration if titrating manually.

11.3.3 Quantitatively transfer contents from the titration vessel to the original digestion beaker (6.11) using minimum quantity of water (if the suspension was not titrated in the digest beaker).

11.3.4 Add 25 ml of H_2O_2 (5.6), to the digest solution and place the beaker on the hotplate. Swirl the digest solution periodically (at least every 10 min). Add water to wash the soil residue from the inside of the beaker. Follow the appropriate scenario from those described below:

a) A digest solution that reacts vigorously at this stage should be temporarily removed from the hotplate and/or the reaction moderated with the addition of water. When the reaction has moderated replace the digest solution on the hotplate. When the digest solution has ceased reacting while on the hotplate, as evidenced by cessation of effervescence, remove it from the hotplate. In a digest solution where reaction is still taking place, it is removed from the hotplate when 1 h has elapsed.

b) A digest solution that reacts slowly or moderately on the hotplate is removed when the reaction ceases or else left for a maximum of 1 h.

c) A digest solution that shows no apparent signs of reaction while on the hotplate for 30 min, is removed and the procedure continued from 11.4.

11.4 Decomposition of excess peroxide

11.4.1 Add 1 ml of copper chloride solution (5.2) to the digest solution to decompose any remaining peroxide.

11.4.2 Return the digest solution to the hotplate and bring the temperature to between 80 °C to 90 °C; this is to ensure complete peroxide decomposition. Do not allow digest volume to fall below 45 ml; maintain volume from 45 ml to 50 ml with water. Once decomposition has ceased as evidenced by lack of effervescence, or after 30 min has elapsed, the solution shall be removed unless further heating is required to reduce the volume to 45 ml to 50 ml.

11.4.3 Once decomposition and/or volume reduction is complete, remove beaker from hotplate and allow digest solution to cool to room temperature.

11.4.4 Quantitatively transfer contents from the beaker to a titration vessel (6.19) with the aid of 30 ml of 2,66 mol/l potassium chloride (5.9) using the dispenser (6.6).

11.4.5 Wash any residue remaining in the digest beaker (6.11) into the titration vessel with no more than 5 ml of water using a fine jet from a wash bottle (6.20) giving a total volume of approximately 80 ml. (For a 2 g test portion, this represents a final soil solution ratio of 1:40).

11.5 Measurement of titratable peroxide acidity (TPA)

11.5.1 General

Measurement of TPA involves titration (6.3) of the stirred soil suspension to a pH of around 5,5 and addition of 1 ml of H_2O_2 (5.7) to oxidize any remaining ferrous ion to ferric ion followed by titration to a final pH of 6,5. Titration should be either of the following:

11.5.1.1 If an automatic titrator is being used, the volume of sodium hydroxide solution added in each increment should decrease as the end point pH is approached. Follow automatic titrator operation manual.

11.5.1.2 When titrating manually, the following points should be observed:

a) Care should be taken not to overshoot the end point pH. Keep a record of titration volumes and associated pH values as the pH 6,5 end point is approached. This allows an accurate interpolation of end point volume, if the end point pH is slightly exceeded in the titration.

b) The titration volume is dependent on the rate at which the sodium hydroxide solution is added. As a guide when titrating manually, the sodium hydroxide solution should be added at a slow constant rate (e. g. drop-wise every 1 to 2 s), allowing pH increase to keep pace with sodium hydroxide solution addition. When within 1 pH unit of end point (i. e. pH > 5,5) stop titration and let pH stabilize. Resume titration at a decreased rate and bring pH to between 6,3 and 6,5. Titrate to the end point and wait for 20 s. Continue titrating in the same manner until pH drops by less than 0,1 pH units in 20 s (assuming that the end point has not been overshot by more than 0,1 units).

c) An average time for manual titrations might be 5 min, though titrations as long as 10 min may be possible for samples with very high TPA (e. g. > 2 000 mmol H^+/kg).

11.5.2 Procedure

11.5.2.1 Measure the pH of the suspension using a calibrated pH meter (see 11.2.1) and follow the procedure detailed in 11.2.2.1 to 11.2.2.3.

11.5.2.2 Depending on the pH of the suspension, select one of the following options:

a) If pH ≤ 3,0, titrate with stirring to pH 5,5 with standardised 0,25 mol/l sodium hydroxide solution (5.10.1) and record volume (V_4).

b) If 3,0 < pH < 5,5, titrate with stirring to pH 5,5 with standardized 0,05 mol/l sodium hydroxide solution (5.10.2) and record volume (V_5).

c) If 5,5 ≤ pH < 6,5, proceed to 11.5.2.4.

d) If pH ≥ 6,5, TPA is defined as zero (see Note 2) and proceed to Clause 12.

NOTE 1 The pH of the suspension should be similar to the pH_{OX}, except where the carbonate modification has been carried out. However, some difference is expected due to the absence of potassium chloride and the smaller soil:solution extraction ratio in the pH_{OX} measurement.

NOTE 2 It is sometimes possible that the pH may slowly rise above 6,5 for samples that have undergone the carbonate modification.

11.5.2.3 If the blank digest has a pH of less than 5,5, titrate with 0,05 mol/l sodium hydroxide solution (C_2) to pH 5,5 and record volume (V_7).

11.5.2.4 Perform a final oxidation on the suspension by adding 1 ml of pH adjusted 30 % H_2O_2 (5.7) with stirring. Allow pH to stabilize prior to measurement.

NOTE The addition of 1 ml of H_2O_2 at this stage converts ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}), ensuring complete conversion of iron to $Fe(OH)_3$ during titration.

11.5.2.5 If the suspension has a pH of less than 6,5 after final oxidation, titrate to pH 6,5 with stirring using 0,05 mol/l sodium hydroxide solution (C_2). Record the volume (V_6) of sodium hydroxide solution required to reach pH 6,5. For blanks, record corresponding volume (V_8) and molarity (C_2).

12 Calculation of TPA and ANC_E

12.1 Notation

The following quantity symbols are used in Clause 12:

C_1 is the standardised concentration of 0,25 mol/l sodium hydroxide solution, in mole per litre (mol/l);

C_2 is the standardised concentration of 0,05 mol/l sodium hydroxide solution, in mole per litre (mol/l);

C_3 is the standardised concentration of 0,5 mol/l hydrochloric acid used in 11.3, in mole per litre (mol/l);

V_3 is the volume of 0,5 mol/l hydrochloric acid used in the hydrochloric acid titration, in millilitres (ml);

V_4 is the volume of 0,25 mol/l sodium hydroxide required to reach the pH 5,5 end point in the titratable acidity procedure (11.5.2(b)(i)) prior to the final oxidation step (where pH ≤ 3,0), in millilitres (ml);

V_5 is the volume of 0,05 mol/l sodium hydroxide required to reach the pH 5,5 end point in the titratable acidity procedure (11.5.2)(b)(ii)) prior to the final oxidation step (where 3,0 < pH < 5,5), in millilitres (ml);

V_6 is the volume of 0,05 mol/l sodium hydroxide required to reach the pH 6,5 end point in the final oxidation step (where pH < 6,5), in millilitres (ml);

V_7 is the or the blank, volume of 0,05 mol/l sodium hydroxide required to reach the pH 5,5 end point in the TPA titration prior to the final oxidation step (where pH < 5,5), in millilitres (ml);

V_8 is the for the blank, volume of 0,05 mol/l sodium hydroxide required to reach the pH 6,5 end point in the TPA titration following the final oxidation step (where pH after final oxidation is less than 6,5), in millilitres (ml);

m_2 is the mass of the oven-dried test portion, in grams (g).

12.2 TPA without carbonate modification

If the carbonate modification procedure has not been followed, calculate the titratable peroxide acidity (TPA) in mmol H^+/kg according to the following equations:

a) If both 0,25 mol/l and 0,05 mol/l sodium hydroxide solution have been used (Formula 3):

$$\text{TPA} = \left[(V_4 \times C_1) - (V_7 \times C_2) + \left\{ (V_6 - V_8) \times C_2 \right\} \right] \times \left[1\,000 / m_2 \right] \tag{3}$$

b) If only 0,05 mol/l sodium hydroxide solution has been used (Formula 4):

$$\mathrm{TPA} = \left[\left(V_5 + V_6 - V_7 - V_8 \right) \times C_2 \right] \times \left[1\,000 / m_2 \right] \tag{4}$$

When pH measured in 11.5.2.1 is ≥ 6,5, TPA is reported as zero.

12.3 ANC$_E$ (or TPA) with carbonate modification

12.3.1 Calculation of acidity from HCl titration

For a test portion with $\mathrm{pH_{OX}} > 6{,}5$ that has been analysed using the ‘carbonate modification’ part of the procedure (11.3), calculate the acidity added during the hydrochloric acid titration in mmol H$^+$/kg according to Formula (5):

$$\mathrm{HCl}_{\mathrm{titr}} = V_3 \times C_3 \times \left[1\,000 / m_2 \right] \tag{5}$$

12.3.2 Calculation of excess acid neutralizing capacity in acidity units

Calculate the excess neutralizing capacity in mmol H$^+$/kg following the sodium hydroxide titration (11.5.2) according to the appropriate equation as follows:

a) If both 0,25 mol/l and 0,05 mol/l sodium hydroxide solution have been used (Formula (6)):

$$\text{a-ANC}_{\mathrm{E}} = \mathrm{HCl}_{\mathrm{titr}} - \left[\left[\left(V_4 \times C_1 \right) - \left(V_7 \times C_2 \right) + \left\{ \left(V_6 - V_8 \right) \times C_2 \right\} \right] \times \left[1\,000 / m_2 \right] \right] \tag{6}$$

b) If only 0,05 mol/l sodium hydroxide solution has been used (Formula (7)):

$$\text{a-ANC}_{\mathrm{E}} = \mathrm{HCl}_{\mathrm{titr}} - \left[\left(V_5 + V_6 - V_7 - V_8 \right) \times C_2 \right] \times \left[1\,000 / m_2 \right] \tag{7}$$

If the result of the calculations in 12.3.2 a) or 12.3.2 b) is:

— Negative, then a-ANC$_E$ is reported as zero and the absolute value is reported as TPA (i. e. despite the pH$_{OX}$ being greater than 6,5, the sample’s potential to produce acidity is greater than its neutralizing capacity).

— Positive, then the sample has intrinsic excess acid neutralizing capacity and TPA is reported as zero.

— Zero, then both a-ANC$_E$ and TPA are zero.

NOTE The use of units of a-ANC$_E$ in mmol H$^+$/kg permit direct subtraction in acid-base accounting since acid production is also measured in units of mmol H$^+$/kg. The convention is that acid production is positive in the acid-base account.

Acid neutralizing capacity can be expressed in units of ‘equivalent % CaCO$_3$’. The a-ANC$_E$ result can be expressed in these units using the following conversion:

$$\mathrm{ANC_E}\ (\text{equivalent \% } \mathrm{CaCO_3}) = \mathrm{ANC_E}/199{,}8 \tag{8}$$

13 Procedure for determining peroxide sulfur (S$_P$), calcium (Ca$_P$) and magnesium (Mg$_P$)

13.1 After completion of the procedures set out in Clause 11, quantitatively transfer contents from the titration vessel (6.19) to a tared beaker (6.2) with water. Subject the solution blanks from 11.5 to the same procedure.

13.2 Dilute the suspension with water to a final volume appropriate to the analytical instrumental technique.

NOTE This can be achieved by using the balance (6.8), taking into account the mass of the container (6.2), the density of the potassium chloride matrix (which is dependent on the final volume chosen) and the mass of the test portion (m_2) used in Clause 11.

13.3 Homogenize the suspension with a mechanical stirrer or stirring rod (6.17).

13.4 Centrifuge (6.4) or filter (6.9) an appropriate volume of the homogenized soil suspension to obtain a clear solution. If measuring S_{RAS} (Clause 15) on the digested residue, the entire suspension shall be filtered and residue retained.

13.5 Take volumes of centrifuged or filtered solution (sufficient to the instrumental technique used) and determine 'peroxide' sulfur (S_{P}), calcium (Ca_{P}) and magnesium (Mg_{P}) using appropriate analytical techniques. For sulfur measurement, instrumentation that specifically determines sulfate is preferable to that which measures total sulfur in solution. An example of a technique that is specific to sulfate is ion chromatography (IC). To obtain accurate and reproducible results it is necessary to have an appropriate resin that will handle high levels of chloride introduced by the potassium chloride solution matrix.

NOTE 1 Instruments that determine all sulfur species in solution (e. g. ICP-AES) may give higher results than instruments that specifically measure sulfate. This is particularly the case in soils high in organic matter that may contain appreciable organic sulfur in solution following the peroxide digestion.

NOTE 2 This method recovers soluble and exchangeable sulfate, sulfate from gypsum, sulfate formed by oxidation of sulfide, sulfur released by the breakdown of organic matter, as well as variable amounts of sulfate from iron and aluminium sulfate minerals or compounds. Sulfate from jarosite and natrojarosite is not appreciably recovered. The residual acid soluble sulfur (S_{RAS}, see Clause 15) can be measured to obtain an estimate of jarosite/natrojarosite sulfur.

NOTE 3 The peroxide digestion procedure also recovers soluble and exchangeable calcium and magnesium and calcium from gypsum. Calcium and/or magnesium released by the acid dissolution of carbonate, oxide or hydroxide minerals are also recovered.

NOTE 4 The peroxide sulfur (S_{P}) measurement can be used in combination with potassium chloride extractable sulfur (S_{KCl}, see Clause 9) to calculate the peroxide oxidizable sulfur (S_{POS}, see Clause 18).

NOTE 5 The peroxide calcium (Ca_{P}) and magnesium (Mg_{P}) measurements can be used in combination with potassium chloride extractable calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) to determine 'reacted' calcium (Ca_{A}) and magnesium (Mg_{A}) (see Clause 18).

14 Calculation of peroxide sulfur (S_{P}), calcium (Ca_{P}) and magnesium (Mg_{P})

Calculate peroxide sulfur (S_{P}), calcium (Ca_{P}) and magnesium (Mg_{P}) taking into account their respective solution blank concentrations and the mass of the test portion used in Clause 11, and express as percentages on an oven-dry weight basis.

15 Procedure for determining acid extractable sulfur in soil residue after peroxide oxidation (S_{RAS})

15.1 General

This procedure should be followed where pH_{KCl} (7.2.2) is less than 4,5, or the presence of jarosite has been noted in the field sample.

NOTE For acid-base accounting purposes, the S_{RAS} result can be substituted with S_{NAS} (ISO 14388-2), obtained by difference from the S_{HCl} result (ISO 14388-2) and the S_{KCl} result (Clause 10).

15.2 Rinsing of peroxide digested soil residue, extraction with 4 mol/l hydrochloric acid and determination of extractable sulfur

15.2.1 Ensure that the entire suspension from Clause 13 has been filtered, so that complete recovery of the soil residue is achieved.

IMPORTANT — TAKE CARE TO ENSURE THAT NO SOIL RESIDUE IS LOST IN THE FOLLOWING RINSING STEPS.

15.2.2 Rinse filter paper containing the soil residue with 2 × 10 ml ± 1 ml aliquots of 1 mol/l potassium chloride solution (5.8). Subject the filter papers from the blank solution to the same procedure.

NOTE A pipette or piston-operated volumetric apparatus (POVA) or other suitable apparatus may be used for rinsing.

15.2.3 Rinse filter paper containing the soil residue with 4 × 10 ml ± 1 ml aliquots of water.

NOTE A pipette or piston-operated volumetric apparatus (POVA) or other suitable apparatus may be used for rinsing.

15.2.4 Place filter paper containing the soil residue into the sample bottle (6.14).

15.2.5 In a fume cupboard using the dispenser (6.5), add 80 ml ± 0,5 ml of 4 mol/l hydrochloric acid (5.5) to the sample bottle, to make a 1:40 soil solution ratio. Swirl and place stopper in sample bottle.

SAFETY PRECAUTIONS — FOR SAFETY REASONS, STEP 15.2.5 SHOULD BE CARRIED OUT IN A WELL VENTILATED FUME CUPBOARD.

15.2.6 Shake or mix the suspension for 16 h ± 0,5 h, using the mechanical shaker or mixer (6.15).

15.2.7 Filter soil suspension through filter paper (6.9) placed in a funnel (6.10), or centrifuge (6.4) to obtain a clear extract.

15.2.8 After appropriate dilution, determine residual acid-soluble sulfur (S_{RAS}) using a suitable analytical technique.

NOTE 1 The high acidity and chloride concentration may preclude the use of certain analytical techniques for determining sulfur.

NOTE 2 Instruments that determine all sulfur species in solution (e. g. ICP-AES) may give higher results than instruments that specifically measure sulfate.

16 Calculation of S_{RAS}

Calculate residual acid soluble sulfur (S_{RAS}) and express as a percentage on an oven-dry weight basis, using the mass of the test portion in Clause 11.

16.1 Calculation of acidity attributed to S_{RAS} (acid-base accounting)

If it is assumed that this sulfur is from jarosite, natrojarosite or similar iron hydroxy-sulfate minerals, then the amount of acidity (a-S_{RAS}) that may be slowly released by hydrolysis may be estimated using the conversion below:

$$\text{a-}S_{RAS}\ (\text{mmol H}^+/\text{kg}) = S_{RAS} \times 0{,}75 \times 623{,}7 = S_{RAS} \times 467{,}8$$

NOTE The factor 0,75 is used because 1 mol of residual acid soluble sulfur is assumed to produce 1,5 mol of acidity, whereas 1 mol of pyritic sulfur is assumed to produce 2 mol of acidity.

17 Calculation of TSA

Calculate the titratable sulfidic acidity (TSA) in units of mmol H^+/kg on an oven-dry weight basis according to Formula (9):

$$\mathrm{TSA} = \mathrm{TPA} - \mathrm{TAA} \qquad (9)$$

Where TPA is zero and TAA is positive, TSA is reported as zero.

18 Calculation of S_{POS}, Ca_A and Mg_A

Calculate the peroxide oxidizable sulfur (S_{POS}) as % S on an oven-dry weight basis according to Formula (10):

$$S_{POS} = S_P - S_{KCl} \qquad (10)$$

Calculate the reacted calcium (Ca_A) and magnesium (Mg_A) as % Ca and % Mg on an oven-dry weight basis according to Formulae (11.a) and (11.b)

$$Ca_A = Ca_P - Ca_{KCl} \qquad (11.a)$$

$$Mg_A = Mg_P - Mg_{KCl} \qquad (11.b)$$

19 Precision

To test the inter-laboratory and within-laboratory precision of the test procedures described in this part of ISO 14388, six homogenized acid sulfate soils were analysed in triplicate by a number of laboratories. Samples were assessed prior to dispatch to confirm homogeneity.

As dictated by the procedures, certain samples did not require all the analytical steps defined for the SPOCAS method and were omitted, e. g. samples for which pH_{KCl} was greater than 6,5 do not require determination of TAA. Additionally, not all laboratories submitted results for all components of this test method. As a consequence the statistical sample size (*n*) varies for different components in Table 1. Where concentrations of a particular analyte in a sample were at, or close to minimum detectable, such data were excluded in precision estimates.

The data were then examined for the presence of statistical outliers using the Cochran test, (to test homogeneity of variance), and the Grubbs test for mean outliers; data that failed were excluded from further statistical analysis. The remaining data were used to determine the precision of each test component using pooled data of test results from laboratories across all relevant samples. These are presented in Table 1.

Table 1 — Interlaboratory precision data

	S	L	**Range** %	**Pooled** σr	**Pooled** σR	r	R
$\mathrm{pH_{KCl}}$	6	16	3,3 to 9,0	0,04	0,12	0,12	0,35
TAA	4	16	15 to 400	0,047	0,098	0,13	0,28
$\mathrm{pH_{OX}}$	6	14	1,8 to 4,0	0,05	0,18	0,13	0,51
TPA	5	14	50 to 1720	0,023	0,16	0,07	0,45
$\mathrm{S_{KCl}}$	6	14	0,03 to 0,32	0,056	0,195	0,16	0,55
$\mathrm{Ca_{KCl}}$	6	11	0,03 to 0,55	0,049	0,20	0,14	0,57
$\mathrm{Mg_{KCl}}$	6	9	0,01 to 0,20	0,042	0,147	0,12	0,42
$\mathrm{S_P}$	6	11	0,15 to 2,5	0,036	0,14	0,10	0,40
$\mathrm{Ca_P}$	6	10	0,0 to 6,5	0,048	0,17	0,14	0,47
$\mathrm{Mg_P}$	6	8	0,01 to 0,37	0,041	0,175	0,12	0,49
$\mathrm{S_{RAS}}$	2	8	0,05 to 1,2	0,032	0,11	0,09	0,32

S is the number of soil samples from which data was pooled for the statistical calculation
L is the number of laboratories that submitted acceptable results
Range is the range of values reported by L laboratories used for calculation
Pooled σr is the pooled repeatability standard deviation
Pooled σR is the pooled reproducibility standard deviation
r is the repeatability limit
R is the reproducibility limit

20 Test report

The test report shall contain at least the following information:

a) Reference to this ISO Standard.

b) Sample identification as submitted to the laboratory.

c) The results of the determination of $\mathrm{pH_{KCl}}$, $\mathrm{pH_{OX}}$ to the nearest 0,1 pH-unit.

d) Where $\mathrm{pH_{KCl}} < 6{,}5$, report the result of the TAA determination to the nearest 1 mmol $\mathrm{H^+}$/kg on an oven-dry weight basis.

e) Where $\mathrm{pH_{KCl}} \geq 6{,}5$, by definition, TAA is reported as zero.

f) The result of the determination of TPA to the nearest 1 mmol $\mathrm{H^+}$/kg on an oven-dry weight basis. TPA is reported as zero when either the pH measured in 11.5.2 is greater than 6,5 or when the $a\text{-}ANC_E$ is greater than zero.

g) The result of the excess acid neutralizing capacity ($\mathrm{a\text{-}ANC_E}$) determination to the nearest 1 mmol $\mathrm{H^+}$/kg on an oven-dry weight basis (when a hydrochloric acid titration has been performed).

h) The result of the determination of TSA to the nearest 1 mmol $\mathrm{H^+}$/kg on an oven-dry weight basis.

i) Where TPA is less than TAA, TSA shall be reported as zero (e. g. TPA = 0 and TAA > 0, TSA is reported as zero.

j) The results of the determination of $\mathrm{S_{KCl}}$, $\mathrm{S_P}$, $\mathrm{S_{POS}}$, $\mathrm{Ca_{KCl}}$, $\mathrm{Ca_P}$, $\mathrm{Ca_A}$, $\mathrm{Mg_{KCl}}$, $\mathrm{Mg_P}$ and $\mathrm{Mg_A}$ expressed as % S, % Ca and % Mg on an oven-dry weight basis.

k) A reference to the analytical technique(s) used to measure $\mathrm{S_{KCl}}$, $\mathrm{S_P}$, $\mathrm{Ca_{KCl}}$, $\mathrm{Ca_P}$, $\mathrm{Mg_{KCl}}$ and $\mathrm{Mg_P}$.

l) A reference to the analytical technique used to measure S_{RAS}.

m) The results of the determination of S_{RAS} expressed as % S on an oven-dry weight basis.

The test report may also include estimates of measurement uncertainty.

Bibliography

[1] ISO 14254:2001, *Soil quality — Determination of exchangeable acidity in barium chloride extracts*

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