INTERNATIONAL STANDARD

ISO 14388-3

First edition
2014-08-01

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
ISO 14388-3:2014(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

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 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*

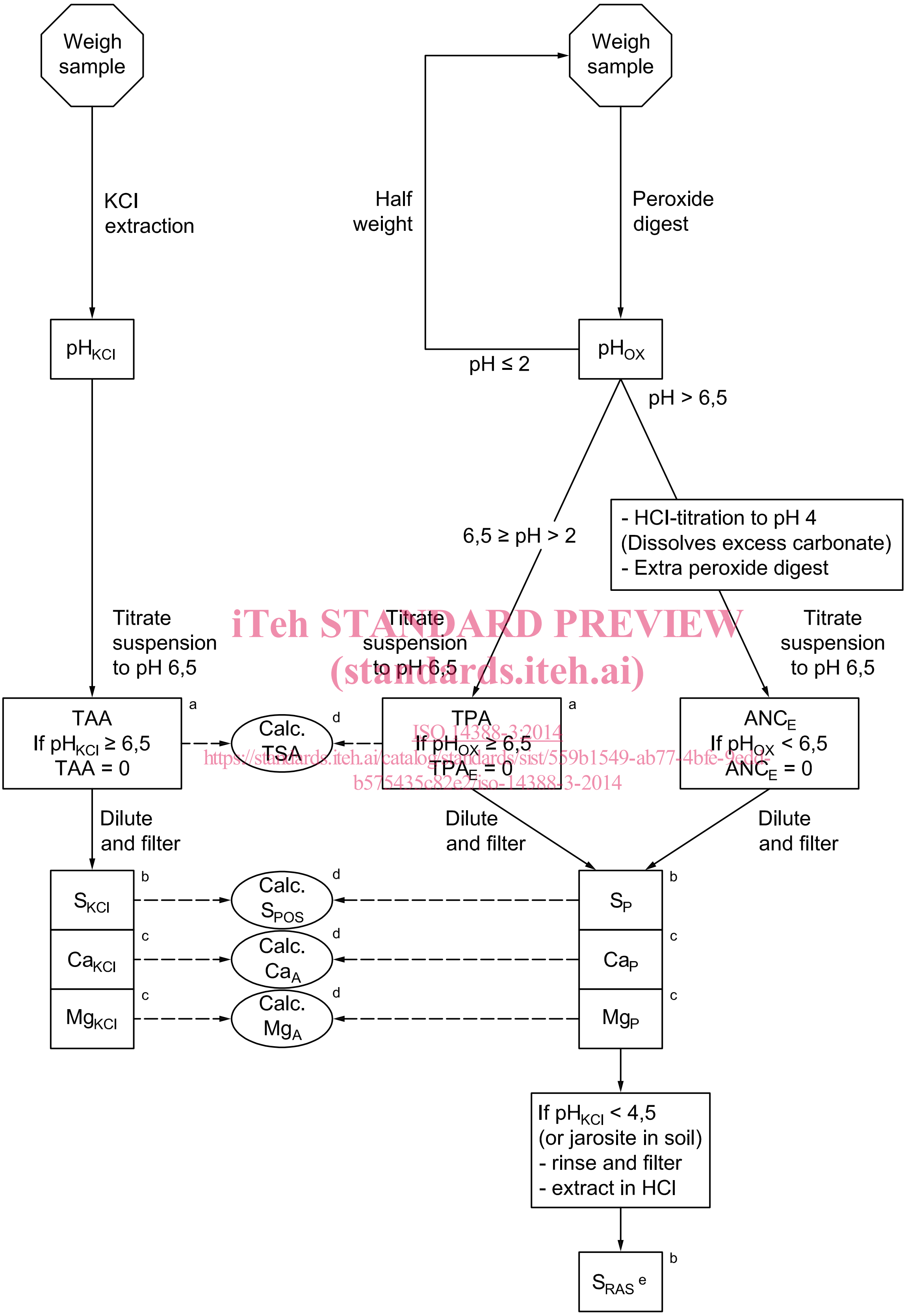
Introduction

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.

---

[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

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).

---

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.