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ISO 14388-2

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

Part 2: Chromium reducible sulfur (CRS) methodology

Qualité de l'eau — Méthode de comptage acide-base pour les sols sulfatés acides —

Partie 2: Méthode de sulfato réduction au chrome

Reference number
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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

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Contents

Page

Foreword

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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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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*

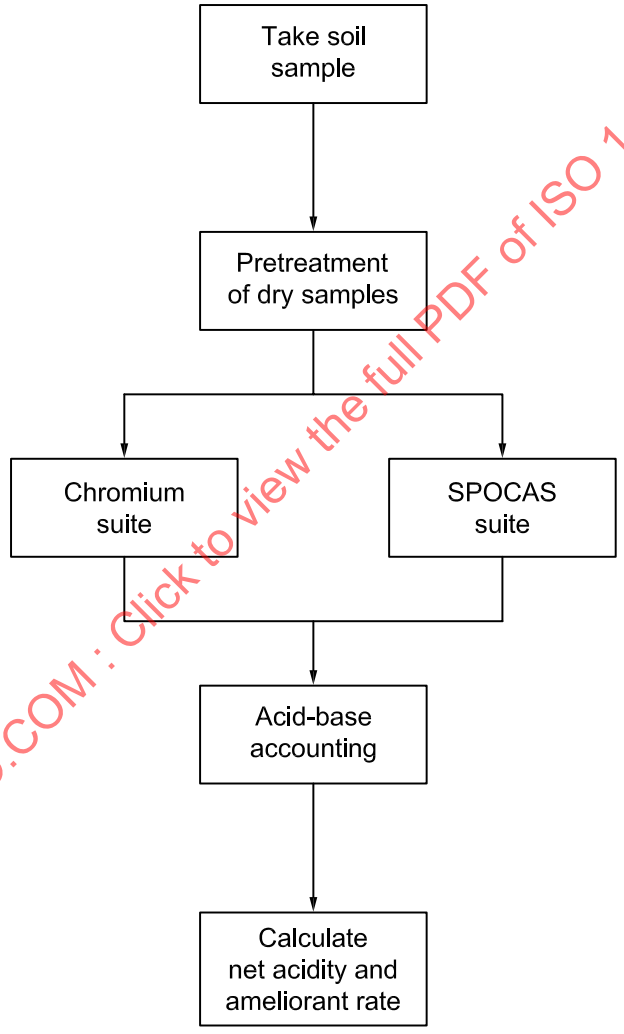
— *Part 2: Chromium reducible sulfur (CRS) methodology*

— *Part 3: Suspension peroxide oxidation combined acidity and sulfur (SPOCAS) suite analysis*

Introduction

The objective of this part of ISO 14388 is to determine the net acidity (or alkalinity) of acid sulfate soils by providing a streamlined approach for determination of the various components of soil acidity and/or alkalinity, depending on pH. The chromium suite combines the measurement of chromium reducible sulfur (S_{CR}) with various measures of existing acidity and acid neutralizing capacity (ANC) using a decision-tree based on the value of pH_{KCl} (Figure 1) as the basis for determining an acid-base account for acid sulfate soils.

The results required to determine net acidity vary with the soil's actual acidity, as represented by pH_{KCl}. Table A.1 of ISO 14388-1 shows the analyses required for the Chromium suite. This table uses results reported in acidity units. Alternatively, results in sulfur units can be utilized.



Key

a acidity titration
b sulfur determination
c acid neutralising determination
d calculated parameter

Figure 1 — Chromium suite flow diagram

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

Part 2:
Chromium reducible sulfur (CRS) methodology

WARNING — Persons using this part of ISO 14388 should be familiar with usual laboratory practice. This part of ISO 14388 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 the net acidity in acid sulfate soils. This part of ISO 14388 specifies a method for measuring chromium reducible sulfur (S_{CR}) by iodimetric titration of distilled hydrogen sulfide trapped as zinc sulfide, following acidic chromous chloride digestion. This method determines inorganic sulfides (e.g. pyrite, marcasite, greigite, mackinawite) and elemental sulfur in acid sulfate soil without interferences from organic sulfur and oxidized forms of sulfur such as sulfate.

On a separate test portion of soil, the pH in a 1 mol/l KCl soil suspension (pH_{KCl}) is determined. When pH_{KCl} is < 6,5, titratable actual acidity (TAA) is then determined. Subsequently, potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}), and magnesium (Mg_{KCl}) can also be determined. Where jarosite is identified in the soil (or where pH_{KCl} is < 4,5), net acid-soluble sulfur (S_{NAS}) is determined by the difference between hydrochloric acid extractable sulfur (S_{HCl}) and potassium chloride extractable sulfur. On samples where pH_{KCl} is < 6,5, acid neutralizing capacity is determined by measuring either inorganic carbon (C_{IN}) by combustion furnace, or ANC_{BT} (ANC measured by back-titration of acid remaining following an acid digest).

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 835-1, *Laboratory glassware — Graduated pipettes — Part 1: General requirements*

ISO 835-2, *Laboratory glassware — Graduated pipettes — Part 2: Pipettes for which no waiting time is specified*

ISO 835-3, *Laboratory glassware — Graduated pipettes — Part 3: Pipettes for which a waiting time of 15 s is specified*

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 10694, *Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis)*

ISO 14388, *Soil quality — Acid sulfate soil — Part 1: Introduction, terminology, soil preparation and acid-base accounting*

3 Terms and definitions

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

4 Principle

4.1 Potential sulfidic acidity

The **potential sulfidic acidity** is determined as chromium reducible sulfur (S_{CR}). In this method, sulfur is distilled as H_2S from acid sulfate soil digested in an acidic chromous chloride solution produced by the reaction of powdered chromium metal and hydrochloric acid. The evolved H_2S gas is precipitated as ZnS in a zinc acetate/ammonia trapping solution with the trapped sulfur, then quantified by iodimetric titration.

4.2 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** is determined as net acid-soluble sulfur (S_{NAS}). Net acid-soluble sulfur is the difference between 4 mol/l hydrochloric acid extractable sulfur (S_{HCl}) and potassium chloride extractable sulfur (S_{KCl}). In highly organic soils, S_{NAS} might overestimate retained acidity due to the inclusion of organic S in the result.

4.3 Acid neutralizing capacity

In soils where pH_{KCl} > 6,5, and hence where there is a chance of acid neutralizing capacity (ANC) being present, ANC can be estimated by various methods such as inorganic carbon analysis (e. g. C_{IN} by combustion furnace according to ISO 10694), and ANC by back titration (ANC_{BT}). In this manner, a full acid-base account can be made of the soil.

5 Reagents for analysis of chromium reducible sulfur

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).

Commercially available ampoules of standardized solutions can also be used where available.

5.1 Chromium powder.

NOTE Different sources or batches of chromium powder can yield different blank values.

CAUTION — CHROMIUM DUST CAN BE TOXIC IF INHALED AND CAN REPRESENT A COMBUSTION RISK. AVOID THE USE OF VERY FINE CHROMIUM POWDER.

5.2 Ethanol (C_2H_5OH), 95 % solution.

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

5.4 Hydrochloric acid solution, 6 mol/l.

Dilute concentrated hydrochloric acid (5.3) with water.

5.5 Iodine solution, 0,012 5 mol/l.

Dissolve 22,5 g ± 0,1 g of potassium iodide in water and add 3,2 g ± 0,01 g of iodine. After the iodine has dissolved, dilute to 1 l with water. Standardize iodine solution against the standardised 0,025 mol/l sodium thiosulfate solution (5.8) using the starch solution (5.9) as an indicator. Calculate the molarity (C) of the iodine solution, in moles per litre, according to Formula (1):

$$C_1 = \frac{F \times D}{2 \times E} \quad (1)$$

where

D is the titration volume of standard sodium thiosulfate solution, in millilitres (ml);

E is the volume of iodine solution titrated, in millilitres (ml);

F is the molarity of sodium thiosulfate solution used, in mole per litre (mol/l);

The iodine solution should be standardised on a daily basis, or immediately prior to use.

5.6 Nitrogen gas, high purity grade.

5.7 Sodium hydroxide solution (NaOH), 6 mol/l.

CAUTION — Solid sodium hydroxide is caustic and hygroscopic, and should be stored away from water.

Dissolve 240 g ± 1 g of solid sodium hydroxide in water, then transfer quantitatively to a 1-l volumetric flask. Cool to room temperature and fill to the mark with water.

5.8 Sodium thiosulfate solution, 0,025 0 mol/l (standardized).

Accurately weigh 6,205 g ± 0,001 g of $Na_2S_2O_3 \cdot 5\ H_2O$ and dissolve in water. Transfer quantitatively to a 1-l volumetric flask. Add 1,5 ml ± 0,01 ml of 6 mol/l sodium hydroxide solution (5.7) and fill to the mark with water. Standardize against potassium iodate or potassium dichromate solutions.

NOTE Commercially available ampoules of standardized sodium thiosulfate solution can also be used.

5.9 Starch indicator solution.

Dissolve 2,0 g ± 0,1 g of arrowroot starch and 0,20 g ± 0,01 g of salicylic acid in 100 ml of hot water. Allow to cool to room temperature before use.

5.10 Zinc acetate/2,8 % ammonia solution (trapping solution).

Dissolve 30 g ± 0,5 g of zinc acetate dihydrate in 750 ml water. Add 100 ml of 28 % ammonia solution. Transfer to 1-l volumetric flask and fill to the mark with water.

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 835-1, ISO 835-2 and ISO 835-3. The use of volumetric glassware shall conform to ISO 8655-1, ISO 8655-2, and ISO 8655-3.

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, with 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, complying with Class A according to ISO 385-1, or a similarly accurate digital burette or a suitably calibrated burette from an automatic titration instrument can be used.

6.4 Centrifuge, capable of centrifuging 80 ml and 400 ml of suspension.

6.5 Dispenser 1 (manual or automatic), capable of accurately dispensing 50 ml and 80 ml ± 0,5 ml.

6.6 Double-necked digestion flask, of 250 ml capacity made of borosilicate glass, with ground-glass or quick-fit joints capable of forming a gas-tight seal. Use round-bottomed flask if employing a heating mantle, or flat-bottomed for hotplates.

6.7 Balance 1, capable of weighing to an accuracy of ± 0,01 g.

6.8 Balance 2, capable of weighing to an accuracy of ± 0,001 g.

6.9 Balance 3, capable of weighing to an accuracy of ± 0,000 1 g.

6.10 Erlenmeyer flask, of 100 ml capacity made of borosilicate glass.

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

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

6.13 Glass beaker borosilicate (digestion beaker), a tall form and 250 ml capacity recommended.

6.14 Heating mantle or electric hotplate, with adjustable temperature control, capable of maintaining gentle boiling of the digestion solution.

6.15 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.

6.16 Pasteur pipette, glass.

6.17 Pipettes, 25 ml pipettes or piston operated volumetric apparatus (POVA) can be used.

6.18 Pressure equalizing funnel, of 100 ml capacity made of borosilicate glass with ground-glass or quick-fit joints capable of forming a gas-tight seal.

6.19 Reflux condenser, straight-through type with conical ground-glass joints.

6.20 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.

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

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

NOTE For example, end-over-end shaker.

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

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

6.24 Thermometer, 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.

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

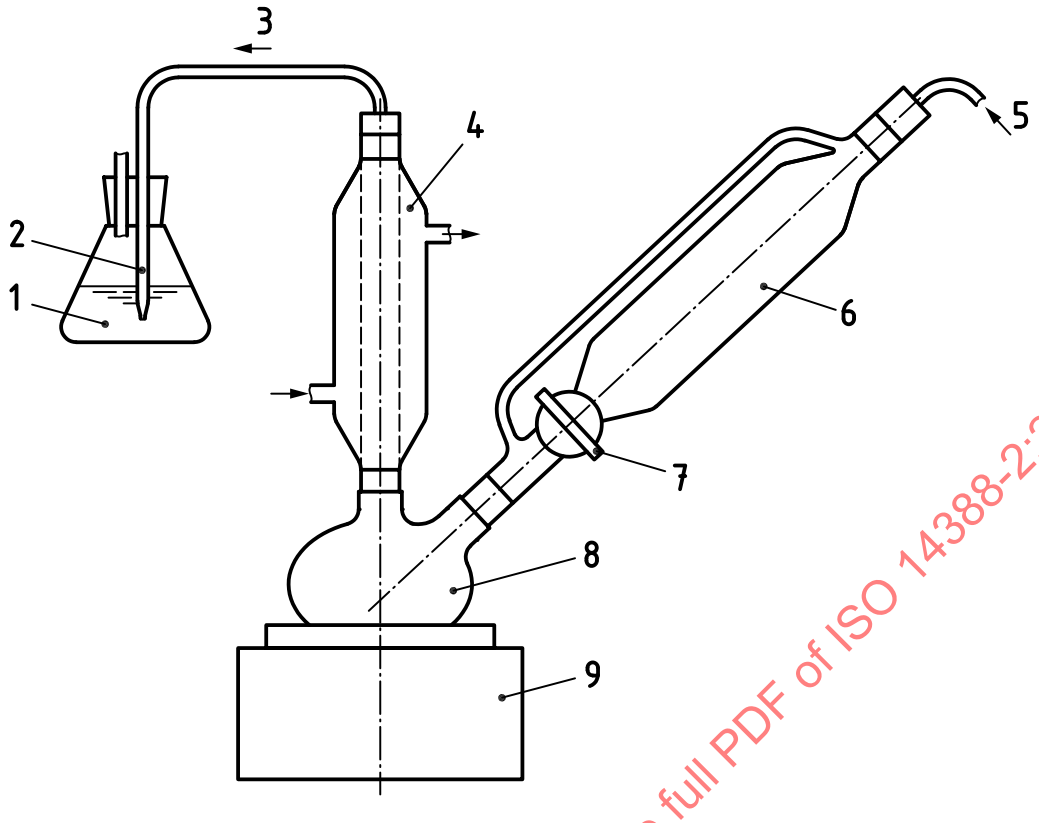
6.26 Wash bottle with narrow aperture, containing water.

7 Procedure for determining chromium reducible sulfur

Accurately weigh a test portion of 0,50 g ± 0,05 g (6.8) of the test sample prepared in accordance with ISO 14388-1, into a tared digestion flask (6.6) (see Figure 2) and record the mass (m_1). Subject at least one blank to the same extraction procedure as the test portion in each analytical run.

The optimum weight of soil material to digest depends on the reduced inorganic sulfur content. If analysing soil materials of known high sulfide content, use a smaller test portion. Where the reduced inorganic sulfur contents can be assessed, the following guidelines are useful for determining the optimum test portion to use.

1) For a test sample with an S_{CR} content of ≤ 0,5 %, a 3 g test portion is recommended.
2) For a test sample with an S_{CR} content of > 0,5 % but < 1 %, a 0,5 g test portion is recommended.
3) For a test sample with an S_{CR} content of ≥ 1 %, a 0,1 g test portion is recommended.
4) If the S_{CR} content is not known, then a test portion of at least 0,5 g should be used.
5) If a large quantity of reduced inorganic sulfur is digested, then this can exceed the capacity of the zinc acetate solution to trap the H_2S as ZnS or result in the use of excessive volumes of iodine titrant.
6) If too small a quantity of reduced inorganic sulfur is digested, then only very small quantities of H_2S is generated, which results in very small volumes of iodine titrant being used and therefore low analytical precision.



Key

1 Erlenmeyer flask (6.10)
2 Pasteur pipette (6.16)
3 Gas flow
4 Reflux condenser (6.19)
5 N_2 gas flow
6 Pressure equalizing funnel (100 ml) (6.18)
7 Tap
8 Double-necked digestion flask (250 ml) (6.6)
9 Heating mantle or electric hotplate (6.14)

Figure 2 — Schematic diagram of the apparatus used to determine chromium reducible sulfur

Add 2,0 g ± 0,1 g of chromium powder (5.1) to the digestion flask (6.6).

Add 10 ml ± 0,5 ml ethanol (5.2) to the digestion flask (6.6) and swirl.

NOTE 1 Ethanol acts as a soil wetting agent.

Place the digestion flask (6.6) and contents in the heating mantle or on an electric hotplate (6.14) and connect to the reflux condenser (6.19).

The apparatus should be assembled as shown in Figure 2 and set up in a fume cupboard.

WARNING — Soil materials high in sulfides have the potential to react vigorously at this stage. H_2S is a poisonous gas generated from digest solution.

Attach the pressure equalizing funnel (6.18), making sure that the gas flow arm is facing the condenser and that the solution tap is shut.

Ensure that ground-glass connections and fittings are gas-tight.

Attach Pasteur pipette (6.16) to the outlet tube at the top of the reflux condenser (6.19) and insert it into a 100-ml Erlenmeyer flask (6.10) containing 40 ml zinc acetate solution (5.10).

Turn on the water flow around the condenser.

Add 60 ml of 6 mol/l HCl (5.4) to the glass dispenser in the pressure equalizing funnel.

Connect the N_2 flow to the pressure equalizing funnel and adjust the flow to obtain a bubble rate in the zinc acetate solution of about 3 bubbles per second. Allow the N_2 gas to purge the system for about 3 min.

Gradually release the 6 mol/l hydrochloric acid from the dispenser (e.g. over 1 min or more slowly if the presence of carbonates in the test portion causes vigorous effervescence).

Wait for 2 min before turning on the heating mantle (6.14) or turning up the hotplate and adjust the heat so that a gentle boil is achieved. Check for efficient reflux in the condenser. Allow to digest for at least 20 min to ensure complete reaction of all sulfide.

NOTE 2 Vigorous boiling results in high vapour production and the risk of low H_2S trapping efficiency, which can result in an underestimation of chromium reducible sulfur content.

Remove the Erlenmeyer flask (6.10). Place the Pasteur pipette (6.16) in the Erlenmeyer flask (6.10) as it might contain traces of ZnS. Break the tip of the Pasteur pipette (6.16) and leave it in the flask prior to the removal of the body of the pipette (which should be discarded), to ensure that any sulfide adhering to the tip is completely dissolved. If not titrating immediately, seal flask and store in a fume cupboard.

CAUTION — Hydrogen sulfide can be evolved after the acid is added to the zinc acetate trapping solution. Therefore, the following steps of the procedure should be carried out with a minimum of delay after the acid has been added and undertaken in a fume cupboard or with the aid of a fume extractor.

Add 20 ml of 6 mol/l hydrochloric acid and 1 ml of the starch indicator solution (5.9) to the zinc acetate solution (5.10) in the Erlenmeyer flask and gently mix.

Titrate the zinc acetate trapping solution (5.10) with the iodine solution (5.5) to a permanent blue end-point. Record the volume of titrant (A). Perform the same titration on the blank sample and record the volume of titrant (B).

8 Calculation of S_{CR}

The concentration of chromium reducible sulfur (S_{CR}) in % S is calculated according to Formula (2):

$$S_{CR} = \frac{(A-B)\times C_1 \times 3{,}2066}{m_1} \qquad (2)$$

where

A is the volume of iodine used to titrate the zinc acetate trapping solution following the soil digestion, in millilitres (ml);

B is the volume of iodine used to titrate the zinc trapping solution following a blank digestion, in millilitres (ml);

C_1 is the molarity of the iodine solution as determined by titration of this solution with the standardized 0,025 mol/l sodium thiosulfate solution, in moles per litre (mol/l);

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

The S_{CR} value can be expressed in equivalent acidity units using the following conversion, assuming all sulfur is present as iron disulfide [See Formula (3)]:

$$a\text{-}S_{CR}\ (\text{mmol } H^+/\text{kg}) = S_{CR} \times 623{,}7 \quad (3)$$

NOTE The conversion assumes 1 mole of sulfur produces 2 moles of acidity.

9 Reagents for determination of pH_{KCl} and TAA

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

9.1 Calibration solutions for the pH meter

9.1.1 General

For pH determinations, buffer solutions as specified in 9.1.2 and 9.1.3 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 can be used.

9.1.2 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.

9.1.3 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.

9.1.4 Buffer solution, pH 9,22 at 20 °C.

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 9.1.2, 9.1.3 and 9.1.4 are stable for one month when stored in polyethylene bottles.

9.2 Potassium chloride solution, 1 mol/l.

Dissolve 74,55 g of potassium chloride (KCl) in water, transfer to a 1-l volumetric flask and fill to the mark with water.

9.3 Standardized sodium hydroxide (NaOH) solutions.

CAUTION — Solid sodium hydroxide is caustic and hygroscopic and should be stored away from water. Dilute sodium hydroxide solutions absorb carbon dioxide. Avoid unnecessary contact of the solutions with the atmosphere.

9.3.1 0,25 mol/l sodium hydroxide solution (NaOH).

Dissolve 10,1 g ± 0,1 g of sodium hydroxide in water, then 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 sodium hydroxide solution (C_2).

9.3.2 0,05 mol/l sodium hydroxide solution (NaOH).

Dissolve 2,05 g ± 0,05 g of sodium hydroxide in water, then 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 sodium hydroxide solution (C_3).

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

The actual molarities of the standardized sodium hydroxide solutions (C_2, C_3) shall be used in the calculation, not their nominal molarities.

Solutions shall be prepared fresh each day, or alternatively can 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.

10 Procedure for determination of pH_{KCl} and TAA

10.1 Preparation of the suspension

Weigh a test portion of 2,0 g ± 0,1 g (6.7) from the test sample prepared in accordance with ISO 14388-1 into a tared sample bottle (6.20) and record the mass to 0,01 g (m_2). 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 (9.2) 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 (6.21). 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 can be used, provided the ratio of soil weight to potassium chloride solution volume remains at 1:40.

Using the shaking or mixing machine (6.21), shake the suspension for a further 5 min. If using an automatic titration instrument, quantitatively transfer the contents of the sample bottle (6.20) to the titration vessel (6.25) through a wash bottle (6.26) using minimum amount of water.

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

10.2 Measurement of pH_{KCl}

10.2.1 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 9.1.

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

10.2.2 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.

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}.

The reading can be considered stable when the pH measured over a period of 10 s varies by not more than 0,02 pH units.

NOTE The time required for stabilization is usually 1 min or less, but can depend on a number of factors including:

1) the value of pH_{KCl} (at high pH values, it is more difficult to reach stabilization);
2) the quality of the glass electrode (differences of manufacture between electrodes) and its age;
3) the differences in pH_{KCl} between samples in a series;
4) whether mechanical mixing is performed before the measurement, which helps to achieve stable readings in a shorter time.

10.3 Measurement of TAA

10.3.1 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:

1) 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.
2) 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:
   i) Sodium hydroxide solution should be added at a slow constant rate (e. g. drop-wise every 1 s to 2 s), allowing pH increase to keep pace with sodium hydroxide addition.
   ii) When within 1 pH unit of end-point (i. e. pH > 5,5), stop titration and let pH stabilize.
   iii) Resume titration at a decreased rate and bring pH to between 6,3 and 6,5.
   iv) Titrate to the end-point and wait for 20 s.
   v) 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).
3) As a guide, 5 min would be an average time for manual titrations (for TAA > 100 mmol H^+/kg).

10.3.2 Procedure based on pH_{KCl} result

Depending on the resulting pH_{KCl} value obtained in 10.2.2 (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 (9.3.1) and record volume (V_1).

b) If 4,0 ≤ pH_{KCl} < 6,5, titrate with stirring to pH 6,5 using standardized 0,05 mol/l sodium hydroxide solution (9.3.2) and record volume (V_1).

c) If pH_{KCl} ≥ 6,5, no titration is required and TAA is zero. If pH_{KCl} of the blank is less than 6,5, titrate with stirring using 0,05 mol/l sodium hydroxide solution (9.3.2) and record the volume (V_2).

If pH_{KCl} ≥ 6,5, determine acid neutralizing capacity on a separate sub-sample of soil according to Clauses 17 to 19.

If pH_{KCl} < 4,5, determine retained acidity on a separate sub-sample of soil according to Clauses 13 to 18.

11 Calculation of TAA

Calculate the TAA in mmol H^+/kg according to the following formulae:

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

$$\mathrm{TAA} = \left[\left(V_1 \times C_2\right) - \left(V_2 \times C_3\right)\right] \times \left[1\,000 / m_2\right] \quad (4)$$

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

$$\mathrm{TAA} = \left[\left(V_1 - V_2\right) \times C_3\right] \times \left[1\,000 / m_2\right] \quad (5)$$

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_2 is the standardised concentration of 0,25 mol/l sodium hydroxide solution, in mole per litre (mol/l);

C_3 is the standardised concentration of 0,05 mol/l sodium hydroxide solution, in mole per litre (mol/l);

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

12 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 11, quantitatively transfer the contents from titration vessel (6.25) to a tared or weighed beaker (6.2) with water. Subject the solution blanks from Clause 11 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 (6.7), 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 11.

Homogenize the suspension with a mechanical stirrer or stirring rod (6.23).

Centrifuge (6.4) or filter (6.11) 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) can 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.

13 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 11 and express as percentages on an oven-dry weight basis.

14 Reagents for determination of sulfur (S_{HCl}), calcium (Ca_{HCl}), and magnesium (Mg_{HCl}) extractable with hydrochloric acid

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

14.2 Hydrochloric acid solution 4 mol/l.

Add 400 ml of hydrochloric acid (14.1) 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.

15 Procedure for determination of sulfur (S_{HCl}), calcium (Ca_{HCl}), and magnesium (Mg_{HCl}) extractable with hydrochloric acid

This procedure provides a method for the determination of sulfur (S_{HCl}), calcium (Ca_{HCl}), and magnesium (Mg_{HCl}) in acid sulfate soil following extraction with 4 mol/l hydrochloric acid.

NOTE 1 This extraction procedure recovers soluble and exchangeable sulfate, sulfate from gypsum, the relatively insoluble iron and aluminium hydroxy-sulfate compounds (e. g. jarosite, natrojarosite, basaluminite), as well as some sulfur from organic matter. It also recovers soluble and exchangeable calcium and magnesium, calcium from gypsum, as well as calcium and magnesium from oxides, hydroxides and carbonates of these two elements.

NOTE 2 The S_{HCl}, Ca_{HCl}, and Mg_{HCl} measurements can be used in combination with potassium chloride extractable sulfur, calcium, and magnesium to determine the net acid-soluble sulfur, calcium and magnesium.

The procedure shall be as follows:

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 sample bottle (6.20) and record the mass to 0,01 g. At least one solution blank should be subjected to the same procedure as the test portion in each analytical run.

In a fume cabinet using the dispenser (6.5), add 80 ml ± 0,5 ml of 4 mol/l hydrochloric acid (14.2) to the sample bottle, to make a 1:40 soil solution ratio. Swirl and place stopper in sample bottle.

Soils high in carbonate have the potential to react vigorously at this stage and generate carbon dioxide gas. Wait until this initial reaction subsides before placing stopper on sample bottle.

Shake or mix the suspension for 16 h ± 0,5 h, using the mechanical shaker or mixing machine (6.21).

Filter soil suspension through filter paper (6.11) or centrifuge (6.4) to obtain a clear extract.

After appropriate dilution, determine hydrochloric acid extractable sulfur (S_{HCl}), calcium (Ca_{HCl}), and magnesium (Mg_{HCl}) using a suitable analytical technique. For sulfur measurement, instrumentation that specifically determines sulfate is preferable to that which measures total sulfur in solution.

NOTE 3 The high acidity and chloride concentration can preclude the use of certain analytical techniques for determining sulfur.

NOTE 4 Instruments that determine all sulfur species in solution (e. g. ICP-AES) can give higher results than instruments that specifically measure sulfate. This is particularly the case in soils with high organic matter that contain appreciable hydrochloric acid extractable organic sulfur.

Calculate hydrochloric acid extractable sulfur (S_{HCl}), calcium (Ca_{HCl}), and magnesium (Mg_{HCl}) taking into account their respective solution blank concentrations and express as percentages on an oven-dry weight basis.

16 Calculation of net acid-soluble sulfur (S_{NAS}), calcium (Ca_{NAS}), and magnesium (Mg_{NAS})

Calculate the net acid-soluble sulfur (S_{NAS}) as % S on an oven-dry soil basis according to Formula (6):

$$S_{NAS}\ (\%) = S_{HCl} - S_{KCl} \quad (6)$$

Calculate the net acid-soluble calcium (Ca_{NAS}) and magnesium (Mg_{NAS}) as % Ca and % Mg on an oven-dry soil basis according to Formulae (7) or (8), respectively:

$$Ca_{NAS}\ (\%) = Ca_{HCl} - Ca_{KCl} \quad (7)$$

$$Mg_{NAS}\ (\%) = Mg_{HCl} - Mg_{KCl} \quad (8)$$

17 Reagents for determining acid neutralizing capacity by back-titration (ANC_{BT})

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).

17.1 Calibration solutions for the pH meter.

Refer to 9.1.

17.2 Calcium carbonate, dried at 105 °C for 4 h and stored in a desiccator prior to use.

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

17.4 Hydrochloric acid solution 0,1 mol/l.

Add 10 ml of concentrated hydrochloric acid (17.3) 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 (C_4).

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

17.5 0,10 mol/l Sodium hydroxide solution (NaOH).

Dissolve 4,10 g ± 0,10 g of sodium hydroxide in water, then transfer quantitatively to a 1-l 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 sodium hydroxide solution (C_5).

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

The actual molarity of the standardized NaOH solution (C_5) shall be used in the calculation, not the nominal molarity.

Solutions shall be prepared fresh each day or alternatively can 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.

18 Procedure for determining acid neutralizing capacity by back-titration (ANC_{BT})

18.1 Hotplate digestion with hydrochloric acid solution

Weigh (6.8) a test portion of 1,0 g ± 0,1 g from the test sample prepared in accordance with ISO 14388-1 into a beaker (6.13) and record the mass to 0,001 g (m_3). Two solution blanks should be subjected to the same procedure as the test portion in each analytical run.

Weigh (6.8) in triplicate 0,100 ± 0,01 g of calcium carbonate (17.2) to an accuracy of ± 0,001 g into separate beakers (6.13) to be used as a reference sample.

Add 50 ml of water using a dispenser (6.5) and 25 ml (V_{HCl}) of 0,1 mol/l hydrochloric acid solution (17.4) using a pipette or POVA (6.17) to all beakers and gently swirl to mix.

Place beakers on steambath or hotplate (6.22) and allow boiling for 2 min, removing immediately from the hotplate and cooling to room temperature.

Boiling for longer periods results in high ANC_{BT} values that do not represent natural reactions, especially for feldspar and clay rich soils.

Using a calibrated pH meter (6.1) and pH electrode (6.15), check that pH of the sample suspension is < 3. If pH ≥ 3, add a further 25 ml aliquot of 0,1 mol/l hydrochloric acid and repeat procedure until pH < 3. Record the total volume of 0,1 mol/l hydrochloric acid added (as V_{HCl}) if it differs from 25 ml.

The upper determination limit is about 10 % for a 1 g test portion. For samples with a higher % $CaCO_3$ equivalent content (or those expected to be higher), the quantity of the acid used should be increased until an excess is demonstrated by pH < 3, or alternatively (and more easily) the sample weight decreased (to not less than 0,1 g). If a larger quantity of acid is used on a sample, then a blank should also be run to which that same quantity of acid has been added.

18.2 Titration of unreacted acid in digested soil suspension

If not titrating in a glass beaker (6.13), transfer digested soil suspension to titration vessel (6.25) using a minimum quantity of water.