

Australian Standard®

Analysis of acid sulfate soil—Dried samples— Methods of test

Method 12: Complete suspension peroxide oxidation combined acidity and sulfur (SPOCAS) method

PREFACE

This Standard was prepared by the Australian members of the Joint Standards Australia/Standards New Zealand Committee EV-009, Sampling and Analysis of Soil and Biota and Working Group EV-009-02-01, Analysis of Acid Sulfate Soil.

The objective of this Standard is to encompass the determination of the various components of soil acidity and/or alkalinity, depending on pH, into a combined method to streamline the process of acid base accounting. It specifies methods for the determination of pH_{KCl} , titratable actual acidity (TAA), potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) in acid sulfate soil (ASS), as well as for the determination of pH_{OX} , titratable peroxide acidity (TPA), excess acid neutralizing capacity (ANC_E), peroxide sulfur (S_P), calcium (Ca_P), magnesium (Mg_P) and residual acid soluble sulfur (S_{RAS}). These results can be used to calculate titratable sulfidic acidity (TSA), reacted calcium (Ca_A), reacted magnesium (Mg_A) and peroxide oxidizable sulfur (S_{POS}).

The term ‘informative’ has been used in this Standard to define the application of the appendix to which it applies. An ‘informative’ appendix is only for information and guidance.

METHOD

1 SCOPE

This Standard specifies a method for the determination of pH in a 1 M KCl soil suspension, and, where required, titratable actual acidity (TAA) in acid sulfate soil. Following this, potassium chloride extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) are determined. On a separate test portion, peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralizing capacity (ANC_E) are determined following digestion with 30% hydrogen peroxide. Following this, peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) are determined. On samples where jarosite is present, or $pH_{KCl} < 4.5$, residual acid soluble sulfur (S_{RAS}) is determined on the soil residue remaining after peroxide digestion.

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS

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| 1006 | Solid-stem general purpose thermometers |
| 2162 | Verification and use of volumetric apparatus |
| 2162.1 | Part 1: General—Volumetric glassware |
| 2162.2 | Part 2: Guide to the use of piston-operated volumetric apparatus (POVA) |
| 2164 | Laboratory glassware—One-mark volumetric flasks |
| 2165 | Laboratory glassware—Burettes |
| 2166 | Laboratory glassware—One-mark pipettes |
| 2167 | Graduated straight pipettes |
| 4969 | Analysis of acid sulfate soil—Dried samples—Methods of Test |
| 4969.0 | Part 0: Introduction and definitions, symbols and acronyms |
| 4969.1 | Method 1: Pre-treatment of samples |
| 4969.8 | Method 8: Determination of hydrochloric acid extractable sulfur (S_{HCl}), calcium (Ca_{HCl}) and magnesium (Mg_{HCl}) |
| 4969.11 | Method 11: Calculation of net acid-soluble sulfur (S_{NAS}), calcium (Ca_{NAS}) and magnesium (Mg_{NAS}) |

AS/NZS

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| 2243 | Safety in laboratories |
| 2243.1 | Part 1: Planning and operational aspects |
| 2243.2 | Part 2: Chemical aspects |
| 2243.8 | Part 8: Fume cupboards |

ISO

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| 3696 | Water for analytical laboratory use—Specification and test methods |
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3 DEFINITIONS

For the purpose of this Standard the terms and definitions set out in AS 4969.0 apply.

4 PRINCIPLE

A suspension of soil in 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).

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 peroxide digestion is greater than 6.5, a HCl titration is performed, followed by an additional peroxide digest step. This allows the calculation of excess acid neutralizing capacity (ANC_E). Titratable peroxide acidity (TPA) is then determined by titration to pH 6.5 in a KCl suspension. After appropriate dilution of the soil suspension, peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) are measured by suitable analytical techniques. After appropriate washing of the soil residue, the sulfur is extracted with hydrochloric acid and the residual acid soluble sulfur (S_{RAS}) is measured by a suitable analytical technique on samples where $pH_{\text{KCl}} < 4.5$, or where the presence of jarosite has been noted in the submitted sample.

5 REAGENTS

5.1 General

All reagents shall be of analytical grade (AR grade). Deionized 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).

5.2 Calibration solutions for the pH meter

5.2.1 General

For pH determinations, buffer solutions as specified in Clauses 5.2.2 and 5.2.3 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.

5.2.2 Buffer solution, pH 4.00 at 20°C

Dissolve 10.21 g of potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{O}_4\text{K}$) in water and dilute to 1000 mL at 20°C.

The potassium hydrogen phthalate shall be dried before use for 4 h at 105°C.

5.2.3 Buffer solution, pH 6.88 at 20°C

Dissolve 3.40 g of potassium dihydrogen phosphate (KH_2PO_4) and 3.55 g of disodium hydrogen phosphate (Na_2HPO_4) in water and dilute to 1000 mL at 20°C.

Both salts shall be dried before use for 4 h at 105°C.

5.2.4 Buffer solution, pH 9.22 at 20°C

Dissolve 3.81 g of disodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water and dilute to 1000 mL at 20°C.

NOTES:

- 1 Disodium tetraborate decahydrate may lose water of crystallization when stored for a long time.
- 2 The buffer solutions as specified in Clauses 5.2.2, 5.2.3 and 5.2.4 are stable for one month when stored in polyethylene bottles.
- 3 The pH 9.22 buffer solution (5.2.4) is used when calibrating the pH meter prior to standardizing the sodium hydroxide solution (5.11) and/or when alkaline or lime-treated samples are analysed.

5.3 Copper chloride solution, 400 mg Cu/L as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

Dissolve 1.073 g of copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1000 mL at 20°C.

5.4 Hydrochloric acid, ρ_{20} 1.16 g/mL (HCl)

WARNING: CONCENTRATED HYDROCHLORIC ACID IS A CORROSIVE AGENT. AVOID CONTACT WITH SKIN AND EYES. SAFETY GLASSES AND GLOVES AND OTHER SUITABLE PROTECTIVE CLOTHING AND FOOTWEAR SHALL BE WORN AND SHALL COMPLY WITH AS/NZS 2243, PARTS 1 AND 2.

5.5 Hydrochloric acid solution, 0.5 M (Standardized)

Add 50 mL of concentrated HCl (5.4) 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 ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and calculate molarity of HCl solution (C_3).

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

NOTE: The molarity (C_3) of the standardized HCl solution should be used in the calculations (see Clause 12.3).

5.6 Hydrochloric acid solution 4 M

Add 400 mL of hydrochloric acid (5.4) 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.

WARNING: HYDROCHLORIC ACID IS A CORROSIVE AGENT. AVOID CONTACT WITH SKIN AND EYES. SAFETY GLASSES, GLOVES AND OTHER SUITABLE PROTECTIVE CLOTHING AND FOOTWEAR SHALL BE WORN AND SHALL COMPLY WITH AS/NZS 2243, PARTS 1 AND 2.

5.7 Hydrogen peroxide, 30% (w/w) H_2O_2 (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. SAFETY GLASSES AND GLOVES AND OTHER SUITABLE PROTECTIVE CLOTHING AND FOOTWEAR SHALL BE WORN AND COMPLY WITH AS/NZS 2243, PARTS 1 AND 2.

5.7.1 Checking acidity of hydrogen peroxide

Hydrogen peroxide solutions (5.7) 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 (5.7) 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 KCl. 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 mol H^+ /tonne, 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 with NaOH solution (5.11.2). In the latter case, repeat the blank determination to ensure acceptably low acidity.

5.7.2 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 0.0005%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.

5.8 Hydrogen peroxide H_2O_2 30% (w/w) (pH adjusted)

NOTE: This reagent is used to oxidize ferrous ions in the final titration. This reagent is not for the digestion of samples (for which see Clause 5.7).

Where pH of bulk peroxide (5.7) is less than 5.5, adjust pH to 5.5 ± 0.1 by adding 0.05 M NaOH (5.11.2) dropwise with stirring, ensuring that this pH value remains stable thereafter.

NOTE: Refer to Warning in Clause 5.7.

5.9 Potassium chloride solution, 1 M

Dissolve 74.55 g of KCl in water, transfer to a 1 L volumetric flask and fill to the mark with water.

5.10 Potassium chloride solution, 2.66 M

Dissolve 198.80 g of KCl in water, transfer to a 1 L volumetric flask and fill to the mark with water.

5.11 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.

5.11.1 0.25 M NaOH

Dissolve 10.1 ± 0.1 g of NaOH in water, 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.

The procedure shall be as follows:

- Accurately weigh 0.25 ± 0.05 g (6.8) of potassium hydrogen phthalate and dissolve in water.
- Titrate (6.4) potassium hydrogen phthalate solution with NaOH solution (5.11.1) and record equivalence point volume.
- Calculate the molarity of NaOH solution (C_1).

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

5.11.2 0.05 M NaOH

Dissolve 2.05 ± 0.05 g of NaOH in water, 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.

The procedure shall be as follows:

- Accurately weigh 0.10 ± 0.02 g (6.8) of potassium hydrogen phthalate and dissolve in water.
- Titrate (6.4) potassium hydrogen phthalate solution with NaOH solution (5.11.2) and record equivalence point volume.
- Calculate the molarity of NaOH solution (C_2).

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

NOTES:

- The molarity of the standardized NaOH solutions (C_1 , C_2) should be used in the calculations (see Clause 12).
- Solutions should be prepared fresh each day or alternatively may be stored in apparatus capable of excluding CO₂. Solutions should be stored in high density polyethylene or borosilicate glass containers.
- Absorption of CO₂ changes the concentration of NaOH solutions and decreases the extent of the reaction near the endpoint in titration of weak acids. Solutions should be standardized weekly and discarded one month after being prepared.

6 APPARATUS

6.1 General

Grade A volumetric glassware shall be used throughout. Volumetric flasks shall comply with AS 2164 and pipettes shall comply with AS 2166 and AS 2167. The use of volumetric glassware shall conform with AS 2162, Parts 1 and 2.

6.2 Automatic titration instrument or pH meter

With slope adjustment and temperature control capable of measuring to an accuracy of 0.01 pH units.

6.3 Beaker or other container

Of at least 450 mL capacity, made of polyethylene, glass or similar inert material.

6.4 Burette

A-grade, 10 mL capacity, graduated at 0.02 mL intervals, complying with Class A according to AS 2165. Alternatively, a similarly accurate digital burette, or a suitably calibrated burette from an automatic titration instrument may be used.

6.5 Centrifuge

Capable of centrifuging 400 mL of suspension.

6.6 Dispenser (manual or automatic)

Capable of accurately dispensing 80 ± 0.5 mL.

6.7 Dispenser (manual or automatic)

Capable of accurately dispensing 30 ± 0.25 mL.

6.8 Electronic balance 1

Capable of weighing to an accuracy of ± 0.0001 g.

6.9 Electronic balance 2

Capable of weighing to an accuracy of ± 0.01 g.

6.10 Filter paper

Thick, medium speed, high retention filter paper.

NOTE: Whatman No. 3 paper has been found to be suitable.

6.11 Funnel

Made of glass or plastic for placing filter paper.

6.12 Glass beaker borosilicate (Digestion beaker)

A tall form, 250 mL capacity beaker is recommended with 50 mL volume level clearly marked.

6.13 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.

6.14 Pipettes

1–10 mL range or 1 mL and 10 mL pipettes, or piston operated volumetric apparatus (POVA) may be used in accordance with AS 2162.2 as an alternative.

6.15 Sample bottle

Of 100 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.

6.16 Shaking or mixing machine

Capable of keeping soil particles continuously in suspension.

NOTE: For example end-over-end shaker.

6.17 Steambath, or electric hotplate

With adjustable temperature control, capable of maintaining the digestion solution between 80 and 90°C.

6.18 Stirrer

Overhead propeller, or magnetic type with PTFE coated stirrer bar or stirring rod capable of stirring 400 mL of suspension.

6.19 Temperature sensor

A thermometer capable of measuring to the nearest 1°C and complying with Type C according to AS 1006 is required, connected to an automatic titrator or pH meter.

6.20 Titration vessel

Of at least 100 mL capacity, made of polyethylene or other inert material.

6.21 Wash bottle with narrow aperture

Containing water.

7 PROCEDURE FOR DETERMINATION OF pH_{KCl} AND TAA

7.1 Preparation of the suspension

The procedure shall be as follows:

- (a) Weigh a test portion of 2.0 ± 0.1 g (6.9) from the test sample prepared in accordance with AS 4969.1 into a tared sample bottle (6.15) 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.
- (b) Using the dispenser (6.6), add 80 ± 0.5 mL of 1 M KCl solution (5.9) 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 ± 0.25 h, using the shaking or mixing machine (6.16). Allow the suspension to stand for at least 12 h, but no more than 16 h ensuring that the sample remains sealed.

NOTE: The test portion should be a minimum of 2 g, but a larger test portion may be used, provided the ratio of soil weight to KCl solution volume remains at 1:40.
- (c) Using the shaking or mixing machine (6.16) shake the suspension for a further 5 min. If using an automatic titration instrument, quantitatively transfer the contents of the sample bottle (6.15) to the titration vessel (6.20) using a minimum amount of water (6.21).

NOTE: The time between re-suspension and titration should be minimized 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 (6.2) according to the manufacturer's recommendations, using the buffer solutions specified in Clause 5.2.

NOTE: There should be a regular check of the calibration of the pH electrode.

7.2.2 Measurement of pH

The procedure shall be as follows:

- (a) Measure the temperature of the suspension to ensure that it is within 1°C of the temperature at which the pH electrode was calibrated.
- (b) Measure the pH in the suspension whilst it is being stirred.

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

- (c) Record the pH value to 0.1 pH units after stabilization is reached and report as pH_{KCl} .

NOTE: 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 (6.4) of the stirred soil suspension and should be either of the following:

- (a) If an automatic titrator is being used, the volume of NaOH added in each increment should decrease as the endpoint pH is approached. Follow automatic titrator operation manual.
- (b) When titrating manually, the following should be observed:
 - (i) 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 endpoint is approached. This allows an accurate interpolation of endpoint volume, if the endpoint pH is slightly exceeded in the titration.
 - (ii) The titration volume is dependent on the rate at which the NaOH solution is added. As a guide when titrating manually, the following points should be observed:
 - (A) NaOH solution should be added at a slow constant rate (e.g. dropwise every 1 to 2 s), allowing pH increase to keep pace with NaOH addition.
 - (B) When within 1 pH unit of endpoint (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 endpoint 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 endpoint has not been overshoot by more than 0.1 units).
 - (iii) As a guide, 5 min would be an average time for manual titrations (for TAA > 100 mol H^+ /tonne).

7.3.2 Procedure based on pH_{KCl} result

Depending on the resulting pH_{KCl} value obtained in Clause 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 M NaOH solution (5.11.1) 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 M NaOH solution (5.11.2) 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 M NaOH solution (5.11.2) and record the volume (V_2).