

Australian Standard[®]

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

Method 3: Determination of peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralizing capacity (ANC_E)

PREFACE

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

The objective of this Standard is to provide a laboratory method for the determination of peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralizing capacity (ANC_E) in acid sulfate soil.

METHOD

1 SCOPE

This Standard specifies a method for the determination of peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralizing capacity (ANC_E) in acid sulfate soil following digestion with 30% hydrogen peroxide.

NOTES:

- 1 The TPA measurement does not quantitatively recover retained acidity held in iron and aluminium hydroxy-sulfate minerals such as jarosite $[KFe_3(SO_4)_2(OH)_6]$ and similar minerals. Methods to determine the retained acidity are given in AS 4969.6 and AS 4969.11.
- 2 The suspension obtained from this method can be analysed subsequently to determine peroxide sulfur, calcium and magnesium (AS 4969.5) followed by the determination of S_{RAS} on the digested soil residue (AS 4969.6).

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS

- | | |
|--------|---|
| 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) |

AS

- 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
- 4969.2 Method 2: Determination of pH_{KCl} and titratable actual acidity (TAA)
- 4969.5 Method 5: Determination of peroxide sulfur (S_p), calcium (Ca_p) and magnesium (Mg_p)
- 4969.6 Method 6: Determination of acid extractable sulfur in soil residue after peroxide oxidation (S_{RAS})
- 4969.11 Method 11: Calculation of net acid-soluble sulfur (S_{NAS}), calcium (Ca_{NAS}) and magnesium (Mg_{NAS})

AS/NZS

- 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

- 3696 Water for analytical laboratory use—Specification and test methods

3 DEFINITIONS

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

4 PRINCIPLE

Soil is digested with hydrogen peroxide and acidity is generated from the oxidation of sulfides and organic matter; pH_{OX} is measured on the digest solution. Resulting acidity (TPA) is determined by titration to pH 6.5. For samples with $pH_{OX} > 6.5$ additional steps are necessary to determine ANC_E .

5 REAGENTS

5.1 General

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

If the suspension is to be used in methods that determine sulfur, calcium and magnesium (AS 4969.5 and AS 4969.6), the purity of all reagents (for these elements) 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 solutions (5.9) 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 8).

5.6 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 SHALL COMPLY WITH AS/NZS 2243, PARTS 1 AND 2.

5.6.1 *Checking acidity of hydrogen peroxide*

Hydrogen peroxide solutions (5.6) can contain appreciable acidity, especially if the pH is <3.5. If the pH is <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 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 (5.9.2). In the latter 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 0.0005%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.

5.7 **Hydrogen peroxide H₂O₂ 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 5.6).

Where pH of bulk peroxide (Clause 5.6) is less than 5.5, adjust pH to 5.5 ±0.1 by adding 0.05 M NaOH (5.9.2) dropwise with stirring, ensuring that this pH value remains stable thereafter.

NOTE: Refer to Warning in Clause 5.6.

5.8 **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.

5.9 **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.

5.9.1 *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 (6.5) of potassium hydrogen phthalate and dissolve in water.
- Titrate (6.3) potassium hydrogen phthalate solution with NaOH solution (5.9.1) and record equivalence point volume.
- Calculate molarity of the NaOH solution (*C*₁).

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

5.9.2 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:

- (a) Accurately weigh 0.10 ± 0.02 g (6.5) of potassium hydrogen phthalate and dissolve in water.
- (b) Titrate (6.3) potassium hydrogen phthalate solution with NaOH solution (5.9.2) and record equivalence point volume.
- (c) Calculate molarity of the NaOH solution (C_2).

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

NOTES:

- 1 The molarity of the standardized NaOH solutions (C_1 , C_2) should be used in the calculations (Clause 8).
- 2 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.
- 3 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 to 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 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.

6.4 Dispenser (manual or automatic)

Capable of accurately dispensing 30 ± 0.25 mL.

6.5 Electronic balance 1

Capable of weighing to an accuracy of ± 0.0001 g.

6.6 Electronic balance 2

Capable of weighing to an accuracy of ± 0.01 g.

6.7 Glass beaker borosilicate (Digestion beaker)

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

6.8 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.

6.9 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.

6.10 Steambath, or electric hotplate

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

6.11 Stirrer

Overhead propeller, or magnetic type with PTFE coated stirrer bar.

6.12 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.

6.13 Titration vessel

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

6.14 Wash bottle with narrow aperture

Containing water.

7 PROCEDURE

7.1 Peroxide digestion of sample

The procedure shall be as follows:

- (a) Weigh a test portion of 2.0 ± 0.1 g (6.6) from the test sample prepared in accordance with AS 4969.1 into a tared beaker (6.7) 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 undergoes the carbonate modification (Clause 7.3), one of the blanks should also undergo this procedure.

NOTE: If analyzing soil of known high sulfide content (i.e. >2 %S), use a smaller test portion mass (e.g. 1.0 ± 0.05 g). Alternatively see Clause 7.2.3(a).

- (b) In a fume cupboard, digest the test portion by adding 10 mL of H_2O_2 (5.6) using a pipette (6.9) then gently swirl to mix. At the first sign of a vigorous reaction, add water via wash bottle (6.14) 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 (6.14) 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.

WARNING: SAFETY PRECAUTIONS IN ACCORDANCE WITH AS/NZS 2243 PART 2 SHOULD BE TAKEN. THE DIGESTION SHOULD BE CARRIED OUT IN A WELL VENTILATED FUME CUPBOARD IN ACCORDANCE WITH AS 2243.8.