

SECTION B: DRIED SAMPLES

1. SOIL SAMPLING, HANDLING, PREPARATION AND STORAGE FOR ANALYSIS OF DRIED SAMPLES

CR Ahern, B Blunden, LA Sullivan and AE McElnea

1.1 SOIL SAMPLING

A sampling program for the analysis of ASS should be designed so that the risks of disturbing these soils can be understood and to provide information that can be used to develop an appropriate management strategy. How detailed the investigation is and how intense the analysis is will depend on the characteristics of the site (particularly site variability), the type of disturbance proposed and the sensitivity of the surrounding environment. The resulting soil and water sampling regime, and the laboratory analysis will also provide baseline data for any monitoring program.

Due to the nature of their formation, acid sulfate soils are likely to have substantial variation within the landscape and with depth (down the profile). As a result, the selection of sample sites to represent the various soil, vegetation, geomorphic and geological unit combinations in the landscape is a highly skilled task. The reliability of the investigation results is very dependent on the quality of the sampling program. The designing of valid sampling programs for sites that have been previously disturbed can be very difficult. The frequency of sampling locations should conform to the latest Sampling Guidelines¹ or other relevant document for the appropriate Australian state.

Field pH testing should be conducted at intervals of no greater than 0.25 m to at least 1 m beyond the maximum depth of proposed development excavation or estimated drop in watertable height, or to at least 2 m depth, whichever is the greater. (Smaller intervals than 0.25 m may be required in highly stratified profiles). *Soil samples for laboratory analysis* should be collected at least every 0.5 m down the profile and for every soil layer/horizon. Upper and lower horizon depths must be recorded for each profile. The depth at which any particular sample is taken within the horizon must also be recorded. Where distinct soil horizons occur in the soil profile (eg. sand to clay), sampling intervals should be adjusted to take account of these horizons (ie. sampling intervals must not be taken across two or more different horizons).

Where the depth of disturbance has not been definitely decided, it is strongly recommended to extend the sampling depth to avoid the need for costly re-drilling. This provides information for the maximum number of management or planning options and to provide for more potential management or planning options (eg. strategic reburial, ie. such as over-excavation and burial of highly sulfidic potential ASS material below the watertable). Full sampling and analysis of at least some sites to 2–3 m beyond the proposed disturbance is strongly advised to facilitate the understanding of site characteristics, the degree of site variability, soil layering, drainage and geomorphic history. Where the deeper sampling has been undertaken and patterns are well established, often an overall sampling intensity less than the guidelines may be approved.

Samples of soil should be a minimum of 0.2 kg each. Large shells and other large fragments such as wood, charcoal, stones and the like should be noted before being removed from the samples in the

¹ For Queensland, this is the *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland* (Ahern et al. 1998), or its latest version.

field. Biological remnants such as small roots may contain sulfides and should not be removed from the soil sample. **The bulking or use of composite samples is not acceptable, except when taking samples for verification purposes.** When taking samples for verification testing (eg. to assess 500 m³ or 1000 m³ of treated soil), it is realised that a single grab sample may not be representative of the entire lot of treated soil, with ameliorant possibly unevenly distributed throughout the entire soil mass (despite the best efforts to thoroughly mix the ameliorant through the soil). In such cases, several grab samples may be bulked to obtain a more accurate average of the ameliorant content in the soil.

Gravels associated with acid sulfate soils from below the watertable have been known to contain sulfides in the weathered rind (Saffigna *et al.* 1996). White and Melville (1993) found that oxidation of sulfidic mud balls or fines coating gravel extracted from a river were the cause of vegetation and fish kills after a rainfall event. It is also possible that sulfides may be a component of the gravel or rock. Yellow jarosite coatings on gravel or rocks can indicate that follow-up laboratory analysis is required. Gravel and sand fractions immersed in a ‘pyritic soup’ have been found to contain pyrite framboids in their fine pores and fractures (Saffigna *et al.* 1996) or as mud coatings (White and Melville 1993). These materials are difficult to sample representatively and require modified sample preparation before laboratory testing.

At the time of sampling, *soil texture*, *field pH* (pH_F; **Method Code 23Af**) and *field pH after oxidation with 30% hydrogen peroxide* (pH_{FOX}; **Method Code 23Bf**) should be determined at regular (minimum 0.25 m) depth intervals down the profile and on all depths sampled for further laboratory analyses. These field tests, together with the strength of the peroxide reaction can indicate those depths where sulfides are most likely to occur.

The field pH can be measured on saturated soil using a spear point pH probe and field pH meter. If the pH_{KCl} (from SPOCAS method, or from other laboratory pH measurements, eg. 1:5 pH_w) is substantially lower than pH_F, then some oxidation of the sample during transport or drying may have occurred. (For more details on field tests see *Section H*).

For estimating both *field moisture* and *bulk density*, a ‘volumetric sample’ can be taken in the field, using a large cut off syringe or suitably designed instrument. This is strongly recommended for peats and other low bulk density samples, as earthworks are often estimated on a cubic metre basis. Care should be exercised in taking volumetric samples, as compression of the sample or inclusion of air pockets can substantially affect the results. (For more details on bulk density and moisture methods, see *Section D*, to be added in a later version).

The onus is on the proponent to justify that sufficient sampling and analysis has been undertaken to understand and manage the site without causing harm to the environment. For large or complex projects it can often be cost efficient to conduct the soil investigations in a number of stages (ie. a ‘staged approach’). When the results of the initial sampling and analysis are known, the sampling program can be refined so the most efficient and cost effective regime can be developed to complete the acid sulfate soil assessment. Consultation with key government authorities at this stage can assist in focusing the investigations.

1.2 SAMPLE HANDLING, TRANSPORT AND STORAGE

Upon collection in the field, soil samples should be immediately placed in leak proof containers that minimise the sample’s contact with air and avoids moisture loss from the sample (eg. soil placed in sealable plastic bags, with air extruded). Ideally the polymer bags should be of a thickness and composition to minimise diffusion of oxygen into the sample. The samples should be kept cold (ideally less than 4 °C) in the field to reduce the possibility of oxidation of sulfidic compounds. A portable 12 V car freezer or cold box containing dry ice are the most efficient coolers but if not

available, ordinary ice should be employed for cooling. It is most important that sample labelling and documentation remain with the samples at all times. Labels should be water-proof and oven-proof.

It is preferable that samples reach the selected laboratory within 24 h of collection. For transport and short-term storage during transit, samples should be chilled and stored in an insulated container so that they reach the laboratory at less than 4 °C.

If samples cannot be received by the laboratory within 24 h of collection, the samples must be managed to minimise the oxidation of sulfides. Methods include:

- ❑ Quick oven drying the sample at 80–85 °C in a large capacity fan-forced convection oven (care must be taken not to overload the oven's moisture removal capacity). The dried samples must then be stored in sealed containers in a low humidity environment.
- ❑ Freezing the sample in sealed, air-tight containers.
- ❑ Vacuum sealing and store cold or frozen.

Note: Samples stored in a refrigerator (ie. not in a frozen state in a freezer) commonly start to oxidise within days to weeks, showing a lowering of pH and sometimes the presence of jarosite.

Samples containing high concentrations of iron monosulfides, usually associated with bottom sediments in drains, lakes or rivers and/or decaying vegetation, oxidise rapidly during oven drying. Special sampling, storage and freeze drying techniques may be used to overcome this problem. Samples containing significant monosulfides are best analysed wet in the field immediately after sampling using the diffusion Acid Volatile Sulfur (S_{DAV}) method (Section C, *to be added*). Moisture content measurements will also be needed (Section D, *to be added*).

It is important to inform the laboratory when samples are about to be delivered for analysis to avoid delays in sample processing which may lead to the potential for oxidisation of sulfides in soil samples. It is also important that the laboratory confirms the receipt of the samples. In the past, the analysis of samples which were delayed or temporarily lost during transport or were not stored appropriately once having reached the laboratory, resulted in incorrect conclusions because of the change in the samples that occurred between collection and laboratory analysis.

These Guidelines recommend that auditable sample records be maintained at all times.

1.3 SOIL SAMPLE PREPARATION

On arrival at the laboratory, samples should be dried (preferably in a quick-drying, fan-forced, air-extracting oven) at 80–85 °C to a constant weight (or if this is not measured, for at least 48 h), to kill bacteria and rapidly remove water to minimise further oxidation of pyrite (Ahern *et al.* 1996). Samples should be spread out in trays to no more than 2–3 cm depth to allow rapid drying. Where possible, cloddy or plastic clay samples should be broken into lumps no more than 1–2 cm in diameter. If an estimate of field moisture is required then retain a representative portion of the soil in a sealed polyethylene bag or 'moisture container'. An 'as received moisture' determination can be made (as per Section D).

Laboratories should examine the drying capacity of their ovens and only load them with appropriate quantities of samples. If the oven is overloaded (eg. particularly with large frozen samples, or even with too many very wet samples), it may not be able to maintain the required temperature or alternatively the oven's drying efficiency may be decreased. As a result, some oxidation of sulfide and substantial drop in pH may occur. Also, samples may not dry sufficiently in the appropriate time period.

Note: Typically, pH decreases of 0.25 to 1 unit have been recorded on oven drying, without any measurable oxidation of sulfides, although Hicks and Bowman (1996) have recorded substantial pH drops on drying large samples and some oxidation averaging 2% of average TPA. Maher et al. (submitted) demonstrated that oxidation of between 3–5% of the reduced inorganic sulfur (as measured by S_{CR}) occurred in a wide variety of ASS materials even when dried quickly in a fan-forced oven, and that this was accompanied by large increases in water soluble sulfate. Oxidation of black iron monosulfides and other unstable sulfides and some reduced iron compounds commence on disturbance and specialised sampling equipment is required to prevent oxidation. Fortunately such compounds seem to occur only rarely in significant amounts in acid sulfate soils (Bush and Sullivan 1998) but may be an appreciable component of drain, lake or stream bottom sediments. For sampling and handling of wet/volumetric samples that contain monosulfides, see Section C1 (to be added). Drying also has the potential to alter the mineralogy of the soil (eg. gypsum may lose its water of crystallisation and be converted to anhydrite when dried above ~40 °C.

After drying, any coarse material not previously removed (especially shell and gravel) should be picked out or removed by preliminary sieving (2 mm). If the amount of the residual coarse material (>2 mm) is considerable (eg. greater than about 5% of the sample by volume) it should be weighed and calculated as a percentage of the total sample weight. Samples that do not easily break up after oven drying (such as some heavy clays), should be rolled/crushed/ground to pass through a 2 mm sieve. It is recognised that grinding equipment is laboratory-specific. As most ASS analyses in these Guidelines only use a small sample weight, it is necessary that samples for acid sulfate soil analyses be finely ground to ensure homogeneity. Additionally, pyrite may be concentrated in organic matter such as root remains. Sullivan *et al.* (2002) stressed the importance of appropriate grinding to ensure optimum recovery of pyrite for the chromium reducible sulfur method (which can use as little as 0.05 g of sample on highly sulfidic materials). One of the reasons advanced was that ring mill grinding abraded away protective coatings around pyrite grains. For these reasons, McElnea *et al.* (2002a) selected ring mill grinding to ensure complete oxidation of sulfides in the SPOCAS method. This has a benefit in that this means a smaller sample weight and lower volumes of reagents during analysis, reducing costs. Given the above information, a ring mill ground sample (or other grinding apparatus capable reducing sample to <75 µm) is necessary for most dry sample methods in these Guidelines. **A representative sub-sample of at least 50 g, sufficient for all analyses (including repeats) should be ground to a powder².**

Warning: As dried acid sulfate soils may contain dusty, strongly acidic substances such as jarosite, workers involved in grinding these soils should use protective clothing including eye protection plus a dust mask, and carry out the operation in an efficient dust extraction cabinet.

Note: It may also be necessary to analyse the gravel component as a separate sample as gravels in acid sulfate soils have been known to contain sulfides in the weathered rind or even as a total component of the rock (Saffigna et al. 1996). Generally, gravelly soil or sediments are extremely variable in particle size and sulfide content. Sampling of gravel material is a challenge requiring large sample volumes, separation via sieves and weighing the various components. Depending on the equipment available, the separation may be done in the field or the laboratory. The gravel components will normally need grinding with specialised equipment and should be analysed separately to that of the finer fractions.

The dried ground sample should be stored in a cool dry location in an airtight plastic or other inert container, or vacuum sealed for subsequent laboratory use. Recent evidence suggests that ASS may

² Where a laboratory does not have equipment to ring mill grind samples, they would need to increase the weight of sample used (keeping extraction ratios the same). Some methods in the Guidelines are not always easily amenable to using larger sample weights (eg. inorganic carbon and total sulfur by combustion furnace, S_{CR}), so the alternative approach would be to conduct analysis of samples in duplicate for methods that do not cater for a large sample.

oxidise appreciably if stored in this manner for more than a couple of months. Ideally, all required sample analyses (eg. for conducting an ABA) should be completed within a short time-frame. If analysis is to be delayed, then dried and ground samples should be vacuum sealed (after being purged with inert gas, eg. N₂) in multi-ply, gas impermeable plastic bags and stored in a moisture-free environment under refrigeration.

1.4 STORING AND RETAINING SAMPLES FOR AUDIT PURPOSES

Representative soil samples collected for acid sulfate soil investigations should be well marked and retained for possible future call or audit purposes. Storage by vacuum sealing in an oven-dried state (as described above) to prevent absorption of moisture and diffusion of atmospheric oxygen into the sample is the safest and preferred approach.

Accredited laboratories (eg. NATA-registered, Certified Laboratory Practice and ISO 9000) will normally have their own registering and management system for keeping track and storing of samples. As most commercial laboratories would discard samples about a month after results are reported, special arrangements may need to be made with the laboratory to retain at least 50 g of sample until approvals have been finalised. Most laboratories will charge a fee for drying and storing samples.

When the retention of representative samples becomes an unreasonable impost, the appropriateness of discarding of samples should be discussed with the regulatory authority. Stored samples may be important in any subsequent legal processes.

References

- Ahern CR, McElnea AE, Baker DE (1996) To dry or not to dry?— That is the question for sulfidic soils. In ‘Proceedings of the Australian and New Zealand National Soils Conference’. pp. 1–2. (Australian Society of Soil Science Inc.: Melbourne, Australia).
- Bush RT, Sullivan LA (1998) Acid volatile sulfur distribution in acid sulfate soil and some implications for management. In ‘Proceedings of the National Soils Conference’. pp.1–6. (Australian Society of Soil Science Inc.: Brisbane, Australia)
- Hicks WS, Bowman GM (1996) Practical aspects of the quantitative assessment of acid sulfate soils. In ‘Proceedings 2nd National Conference of Acid Sulfate Soils’. pp. 100–101 (Robert J Smith and Associates and ASSMAC: Australia).
- Maher, CA, Sullivan LA, Ward NJ (submitted) Sample pre-treatment and the determination of some chemical properties of acid sulfate soil materials. *Australian Journal of Soil Research*.
- McElnea AE, Ahern CR, Menzies NW (2002a) Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soil. *Australian Journal of Soil Research* **40**, 1115–1132.
- Saffigna PG, Holland GL, Joyce AS, Cordwell GB, Cordwell BA, Covey NR (1996) Distribution of pyrite in silt, sand, gravel and wood in a soil profile near Yandina, Queensland. In ‘Proceedings 2nd National Conference of Acid Sulfate Soils’. pp. 59–60 (Robert J Smith and Associates and ASSMAC: Australia).
- Sullivan LA, Maher C, Ward NJ (2002) The effect of grinding pretreatments on the determination of acid sulfate soil chemical properties. In ‘Sustainable Management of Acid Sulfate Soils. Fifth International Acid Sulfate Soil Conference, (Eds. BCT Macdonald, AF Keene, G Carlin, LA Sullivan), Part I, pp. 192–193 (Acid Sulfate Soil Working Group, International Union of Soil Sciences).
- White I, Melville MD (1993) ‘Treatment and containment of potential acid sulphate soils’. CSIRO Centre for Environmental Mechanics, Technical Report No. 53.

ANALYTICAL METHODS FOR DRIED AND GROUND SAMPLES

ACTUAL ACIDITY METHOD

2. KCl EXTRACTABLE pH (pH_{KCl}) AND TITRATABLE ACTUAL ACIDITY (TAA) – METHOD CODES 23A AND 23F

AE McElnea and CR Ahern

Introduction:

This method (McElnea *et al.* 2002a, 2002b) is used to determine soil pH in a 1:40 1 M KCl suspension, and as a means of estimating the actual acidity (ie. soluble and readily exchangeable acidity) component of a soil's existing acidity. In combination with the Titratable Peroxide Acidity (TPA) it is used to calculate Titratable Sulfidic Acidity (TSA).

Reagents:

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity <5 $\mu\text{S}/\text{cm}$.

Warning: Solid NaOH is caustic and deliquescent. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat).

1 M KCl: Prepare (1 L) by dissolving 74.55 g KCl in deionised water then diluting to 1000 mL at 20 °C using deionised water.

Standardised ~0.25 M NaOH (c_1): Prepare (1 L) by dissolving 10.1 g \pm 0.1 g of NaOH pellets in CO₂-free deionised water, then diluting to 1000 mL at 20 °C using deionised water. Standardise against potassium hydrogen phthalate (C₆H₅O₄K) by accurately weighing (to 0.0001 g) 0.25 g \pm 0.05 g of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence/end point volume and calculate the molarity of the NaOH solution. When the concentration of the standardised NaOH solution is not exactly 0.25 M, then the exact concentration of the NaOH should be used in calculations.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO₂. Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO₂ and standardised daily.

Standardised ~0.05 M NaOH (c_2): Prepare (1 L) by dissolving 2.05 g \pm 0.05 g of NaOH pellets in CO₂-free deionised water, then diluting to 1000 mL at 20 °C using deionised water. Standardise against potassium hydrogen phthalate (C₆H₅O₄K) by accurately weighing (to 0.0001 g) 0.10 g \pm 0.02 g of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence/end point volume and calculate the molarity of the NaOH solution. Where the concentration of the standardised NaOH solution is not exactly 0.05 M, then the exact concentration of the NaOH should be used in calculations.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO₂. Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO₂ and standardised daily.

Potassium hydrogen phthalate (C₆H₅O₄K): Dry at 105 °C for 4 h and store in a desiccator prior to use.

Apparatus:

Electronic balances (100 ± 0.01 g and 100 ± 0.0001 g), sample shaker (able to keep soil particles continuously in suspension), plastic extraction container with stopper (not containing sulfur), auto-titrator or other appropriate titration apparatus (eg. pH meter, magnetic stirrer plate, Teflon-coated magnetic stirrer bar and 2 x 10 mL A-grade 0.02 mL graduated burettes, or digital burettes of similar accuracy), titration vessel (of at least 100 mL capacity, made of polyethylene or similar inert material).

Procedure:

- Weigh accurately (to the nearest 0.01 g) between 1.9 g and 2.1 g (**m₁**) of finely ground (eg. in a ring-mill), oven-dried (80–85 °C) soil into a suitable extraction container and make a 1:40 suspension with 80 mL aqueous 1 M KCl solution. (Include a solution blank in each batch and subject it to the same procedure as the soil).

Note: A larger sample weight can be used, providing the soil solution ratio remains at 1:40. Use the exact mass weighed (m₁) in subsequent calculations.

- Stopper the container and extract soil on a reciprocal or end-over-end shaker for 4 h (± 0.25 h), keeping container sealed until just prior to titration. Allow bottle and contents to stand overnight (for at least 12 h but no more than 16 h).
- Resuspend contents after standing by briefly shaking container (~ 5 min) before quantitatively transferring its contents to a separate titration vessel (if not titrating in extraction container) using a minimum volume of deionised water.

Note: The time between resuspension and titration should be minimised to limit possible oxidation.

- While stirring, measure and record the pH of the suspension (pH_{KCl}) using a pH meter calibrated with appropriate buffers (**Method Code 23A**).
- Perform a titration to pH 6.5 with standardised NaOH solution using appropriately calibrated pH meter and burette, or auto-titrator. Use the appropriate option below, depending on the measured pH_{KCl}.
 - i) If pH_{KCl} is <4.0, titrate the suspension with stirring to pH 6.5 using standardised 0.25 M NaOH (**c₁**) and record titre volume (**V₁**).
 - ii) If pH_{KCl} is ≥4.0 but <6.5, titrate the suspension with stirring to pH 6.5 using standardised 0.05 M NaOH (**c₂**) and record titre volume (**V₁**).
 - iii) If pH_{KCl} is ≥6.5, no titration is required and TAA is zero.

Note: In some states, guidelines require that for soils suspected of being ASS, a TAA titration is only required when the pH_{KCl} is less than 5.5.

Note: The titre volume depends somewhat on the rate of titrant addition during titration. When titrating manually, the following procedure may be used as a guide. Add titrant at a slow constant rate (eg. drop-wise every 1 to 2 s), allowing the increase in pH to keep pace with NaOH addition. When within 1 pH unit of endpoint (eg. pH >5.5), cease titrant addition

and allow pH to stabilise. Recommence titration at a slower rate and bring pH to just below endpoint (eg. 6.3), recording pH and corresponding volume of titrant at this point. Titrate to endpoint (pH 6.5) and wait for 20 s. If pH drops by >0.1 pH units in this time (and pH endpoint was not originally overshoot by more than 0.1 pH units) titrate back up to pH 6.5 and wait 20 s. Repeat process until pH remains above 6.5 after 20 s. As a guide, an average time for a manual titration (for a TAA of 100 mol H⁺/t) would be 5 min. If an auto-titrator is being used, the volume of titrant added in each increment should decrease as the endpoint is approached. Follow the instructions in the auto-titrator manufacturer's operator's manual.

- Titrate a blank sample using 0.05 M NaOH (c₂) and record titre volume (V₂), in mL.

Calculations:

- Calculate Titratable Actual Acidity (TAA) (expressed in mol H⁺/t oven-dry soil) (**Method Code 23F**).

If 0.25 M NaOH is used:

$$\text{TAA (mol H}^+/\text{t)} = (V_1 \times c_1 - V_2 \times c_2) \times (1000/m_1) \quad [m_1 \text{ in g, } V_1 \text{ \& } V_2 \text{ in mL, } c_1 \text{ \& } c_2 \text{ in mol/L}]$$

If 0.05 M NaOH is used:

$$\text{TAA (mol H}^+/\text{t)} = [(V_1 - V_2) \times c_1] \times (1000/m_1) \quad [m_1 \text{ in g, } V_1 \text{ \& } V_2 \text{ in mL, } c_1 \text{ in mol/L}]$$

For NaOH molarity $c_1 = 0.05 \text{ M}$, zero blank and suggested weights/volumes as above, this simplifies to:

$$\text{TAA (mol H}^+/\text{t)} = 25 \times (V_1)$$

Notes:

Retain the titrated suspension if KCl-extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) are subsequently to be determined.

References:

- M^cElnea AE, Ahern CR, Menzies NW (2002a) Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soils. *Australian Journal of Soil Research* **40**, 1115–1132.
- M^cElnea AE, Ahern CR, Menzies NW (2002b) The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* **40**, 1133–1157.

POTENTIAL ACIDITY METHODS

3. PEROXIDE pH (pH_{OX}), TITRATABLE PEROXIDE ACIDITY (TPA) AND EXCESS ACID NEUTRALISING CAPACITY (ANC_{E}) – METHOD CODES 23B, 23G AND 23Q

AE McElnea and CR Ahern

Introduction:

This method (McElnea *et al.* 2002a, 2002b; Latham 2002) is used to determine soil pH (pH_{OX}) following oxidation with 30% hydrogen peroxide. It is also used to measure Titratable Peroxide Acidity (TPA), which represents the amount of acid released from the complete oxidation of sulfides (and organic matter) (combined with any pre-existing TAA), balanced against any buffering provided by acid-neutralising components in the soil. In some soil, buffering supplied by acid neutralising components may exceed acid generated by oxidation of sulfides, resulting in an 'excess' acid neutralising capacity (ANC_{E}) result. Measurement of ANC_{E} necessitates a titration with HCl (to pH 4) following initial peroxide digestion as well as a subsequent peroxide digestion step.

Reagents:

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity $<5\mu\text{S}/\text{cm}$.

Warning: 30% hydrogen peroxide is hazardous. The principal routes of exposure are usually by contact of the liquid with the skin or eye. Accordingly analysts should wear appropriate gloves and safety glasses at all times when using this chemical.

Warning: Solid NaOH is caustic and deliquescent. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat).

Warning: Concentrated hydrochloric acid is hazardous. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat). Acid fumes should be avoided by handling the concentrated acid in a fume hood and/or by wearing a suitable gas mask.

~2.66 M KCl: Prepare (1 L) by dissolving 198.81 g KCl in deionised water then diluting to 1000 mL at 20 °C using deionised water.

Standardised ~0.25 M NaOH (c_1): Prepare (1 L) by dissolving 10.1 g \pm 0.1 g of NaOH pellets in CO_2 -free deionised water, then diluting to 1000 mL at 20 °C using deionised water. Standardise against potassium hydrogen phthalate ($\text{C}_6\text{H}_5\text{O}_4\text{K}$) by accurately weighing (to 0.0001 g) 0.25 g \pm 0.05 g of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence/end point volume and calculate the molarity of the NaOH solution. When the concentration of the standardised NaOH solution is not exactly 0.25 M, then the exact concentration of the NaOH should be used in calculations.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO_2 . Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO_2 and standardised daily.

Standardised ~0.05 M NaOH (c_2): Prepare (1 L) by dissolving $2.05 \text{ g} \pm 0.05 \text{ g}$ of NaOH pellets in CO_2 -free deionised water, then diluting to 1000 mL at $20 \text{ }^\circ\text{C}$ using deionised water. Standardise against potassium hydrogen phthalate ($\text{C}_6\text{H}_5\text{O}_4\text{K}$) by accurately weighing (to 0.0001 g) $0.10 \text{ g} \pm 0.02 \text{ g}$ of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence/end point volume and calculate the molarity of the NaOH solution. Where the concentration of the standardised NaOH solution is not exactly 0.05 M, then the exact concentration of the NaOH should be used in calculations.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO_2 . Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO_2 and standardised daily.

Standardised ~0.5 M HCl (c_3): Prepare (1 L) by adding 50 mL of concentrated (31.5–33 %w/V) hydrochloric acid to 700 mL of deionised water with stirring then diluting to 1000 mL at $20 \text{ }^\circ\text{C}$ using deionised water. Standardise against disodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) or recently standardised ~0.25 M NaOH solution. Calculate molarity of HCl solution (c_3). Where the concentration of the standardised HCl solution is not exactly 0.5 M then the exact calculated molarity should be used in calculations.

Note: Solutions of 0.5 M HCl made by diluting commercially available ampoules may also be used.

30%w/w AR grade hydrogen peroxide (H_2O_2): Use only AR grade hydrogen peroxide. Check the pH of the peroxide. Determine a blank TPA and blank sulfur content with each run. Blanks should be low (ie. less than the equivalent of $6 \text{ mol H}^+/\text{t}$). Technical grade peroxides are not recommended as they are usually acid stabilised and vary considerably between bottles in both sulfur content and pH.

30%w/w AR grade hydrogen peroxide (H_2O_2) (pH adjusted): Adjusted to pH 5.5 with dilute (0.05 M) NaOH solution for use in the ‘final oxidation’ step.

$6.30 \times 10^{-3} \text{ M CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (400 mg Cu/L): Prepare (1 L) by dissolving 1.073 g of copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in deionised water and dilute to 1000 mL at $20 \text{ }^\circ\text{C}$ using deionised water.

Potassium hydrogen phthalate ($\text{C}_6\text{H}_5\text{O}_4\text{K}$): Dry at $105 \text{ }^\circ\text{C}$ for 4 h and store in desiccator prior to use.

Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

Apparatus:

Electronic balances ($500 \pm 0.01 \text{ g}$ and $100 \pm 0.0001 \text{ g}$); 250 mL tall-form borosilicate (‘pyrex’) glass beakers (with 50 mL volume accurately marked); wash bottle for deionised water; electric hotplate or steam bath (able to keep beaker and contents at $80\text{--}90 \text{ }^\circ\text{C}$); fume hood; adjustable dispensing pipette (1–10 mL, or separate 1 mL and 10 mL pipettes); manual or automatic volumetric dispenser (capable of dispensing $30 \pm 0.25 \text{ mL}$); auto-titrator or other appropriate titration apparatus (eg. pH meter, magnetic stirrer plate, teflon-coated magnetic stirrer bar and 2 x 10 mL A-grade 0.02 mL graduated burette or digital burettes of similar accuracy); titration vessel (of at least 100 mL capacity made of polyethylene or similar inert material).

Procedure:

Peroxide digest (oxidation)

- Weigh accurately (to the nearest ± 0.01 g) between 1.9 and 2.1 g of finely-ground (eg. in a ring mill) oven-dried (80–85 °C) soil into a suitably labelled, tared flask (eg. 250 mL tall-form borosilicate glass beaker) on which the 50 mL level is accurately marked and record soil mass (m_2). In each analytical run, perform a minimum of two solution blanks and subject them to the same procedure as the soil. (If one or more samples in the run undergo the carbonate modification, then subject one of the blanks to this procedure).
- In a fume hood (and wearing safety-glasses, laboratory coat and gloves), add 10 mL **analytical reagent grade** 30% hydrogen peroxide (H_2O_2)* to each flask and swirl to mix.

**Warning: 30% hydrogen peroxide is hazardous. The principal routes of exposure are usually by contact of the liquid with the skin or eye. Accordingly, analysts should wear appropriate gloves and safety glasses at all times when using this chemical.*

Warning: Soils high in pyrite (or manganese) have the potential to react violently at this stage.

Note: The addition of deionised water (via a narrow aperture wash bottle) at the first sign of a vigorous reaction will help to moderate the subsequent reaction. Great care needs to be taken to avoid samples bubbling/frothing-over when the initial aliquot of peroxide is added.

- If the reaction becomes overly vigorous at this stage and any loss of digest material occurs, the sample must be repeated with greater care and/or with a lesser sample weight (ie. 1 g). When analysing soil of known high sulfide content also use this lesser sample weight. For such repeats, add ~10 mL of deionised water to the soil prior to an incremental addition of the 10 mL of H_2O_2 . The exact mass weighed (m_2) must be used in subsequent calculations.
- After 30 min, add deionised water with swirling to make the total volume of suspension in the beaker between 45 and 50 mL. Swirl digest solution to give a homogeneous suspension, then rinse the inside wall of the beaker with deionised water.

Note: It is important to maintain this volume throughout the remaining digestion by regular addition of deionised water, and also to periodically swirl the sample to prevent soil from settling on and adhering to the bottom of the beaker during the subsequent hotplate heating stages. Rinsing the inside wall of the beaker with small squirts of deionised water also serves to dissolve any salts that may have accumulated there.

- Place the beaker on a hotplate (or steam bath) for a maximum of 30 min and maintain sample at 80–90 °C. Swirl samples periodically (eg. every 10 min) and add deionised water as required to maintain volume between 45 and 50 mL, and to wash soil residue from the inside of the beakers.
 - i) If a digest reacts vigorously after being placed on the hotplate, temporarily remove it from the hotplate and/or moderate the vigour of the reaction by adding small amounts of deionised water. Replace digest solution on hotplate when reaction has moderated. When the digest solution stops reacting while on the hotplate (eg. typically effervescent bubbling has ceased, soil settles and supernatant clears), remove from hotplate. If the digest solution continues to react whilst on the hotplate, remove after 30 min has elapsed.
 - ii) For a digest that reacts only slowly or moderately while on the hotplate, remove only after reaction ceases. If the reaction on the hotplate is continuing after 30 min has elapsed, remove the digest solution from the hotplate.

- iii) For a digest that showed no obvious reaction after peroxide addition prior to being put on the hotplate and that failed to subsequently react while on the hotplate, remove from the hotplate after 30 min has elapsed.
 - iv) For a digest that reacts vigorously after initial peroxide addition (before being put on the hotplate), but does not react further whilst on the hotplate for 10 min (indicating that the added peroxide may have already been consumed), remove at this stage.
- Allow samples to cool to near room temperature.
 - Add a second 10 mL aliquot of H₂O₂, waiting 10 min before returning flask to the hotplate for a maximum of 30 min, adopting the procedure outlined earlier.
 - Allow samples to cool to room temperature and make volume to 50 mL with deionised water.
 - Measure the pH of the suspension (**pH_{OX}**, **Method Code 23B**) while stirring using a suitably calibrated pH meter and electrode. Use the appropriate option below, depending on the measured pH_{OX}.
 - i) If pH_{OX} is ≤2 (indicative of high sulfide levels), repeat digest using 1 g of soil
 - ii) If pH_{OX} is >2 but ≤6.5, continue from peroxide decomposition step
 - iii) If pH_{OX} is >6.5 (meaning that the soil may contain excess carbonates), treat according to carbonate modification before continuing with peroxide decomposition step.

Carbonate modification (HCl titration to pH 4)

- For soil with pH_{OX} >6.5, quantitatively transfer suspensions to titration vessels (if not titrating in digest beaker) with deionised water.
- While stirring perform a slow titration (typically 10–30 min duration, if using an auto-titrator) to pH 4 with standardised 0.5 M HCl (c₃).

Note: Do not titrate solution blank with HCl.

Note: This titration with dilute HCl is designed to dissolve excess carbonate, which interferes with the efficiency of peroxide oxidation. It can be used to estimate a net (excess) acid neutralising capacity of the soil. The reaction between solid carbonate and soil solution as the acid is added is slow. The pH tends to oscillate near the pH 4 end point, so a slow titration is necessary to ensure maximum recovery of carbonate. The conditions of this titration are difficult to standardise and to make consistent (without the use of an auto-titrator). Addition of a set aliquot of HCl at a fixed time interval may be the best approach to standardising the titration if titrating manually. If the endpoint (pH 4.0) is slightly overshoot, do not calculate the volume of titrant added to reach the endpoint, instead use the total volume of HCl solution added in subsequent calculations. However if the pH of the suspension stabilises below 3.5, repeat the analysis.

- Record volume and molarity of titrant added (V₃, in mL). Calculate HCl-titration (mol H⁺/t).
- Quantitatively transfer contents of titration vessel to original digestion beaker (if not titrating in digest beaker).
- Add 25 mL 30% H₂O₂ and place on hotplate. Swirl digest periodically (eg. every 10 min) and then wash the soil residue from the walls of the beaker with a small amount of deionised water for a maximum of 1 h, following the appropriate option below:
 - i) If a digest reacts vigorously after being placed on the hotplate, temporarily remove it from the hotplate and/or moderate the vigour of the reaction by adding small amounts of deionised water. Replace digest solution on hotplate when reaction has moderated. When the digest solution stops reacting while on the hotplate (eg. typically effervescent bubbling has ceased, soil settles and supernatant clears), remove from hotplate. If the digest solution continues to react whilst on the hotplate, remove after 1 h has elapsed. *Con't.....*

- ii) For a digest that reacts only slowly or moderately while on the hotplate, remove only after reaction ceases. If the reaction on the hotplate is continuing after 1 h has elapsed, remove the digest solution from the hotplate.
- iii) For a digest that showed no obvious reaction after peroxide addition prior to being put on the hotplate and that failed to subsequently react while on the hotplate, remove from the hotplate after 30 min has elapsed.

Peroxide decomposition step

- ❑ Add 1 mL of 6.30×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (400 mg Cu/L) to digest solution to decompose any remaining peroxide.
- ❑ Return digests to hotplate and allow samples to reach between 80 and 90 °C (by which time peroxide decomposition should be occurring). Remove digest from hotplate when peroxide decomposition has ceased (eg. effervescent bubbling has stopped and usually supernatant has cleared. If peroxide decomposition has not ceased after 30 min, then remove digest solutions from hotplate. Maintain digest volume at between 45 and 50 mL during this time (adding deionised water as necessary).
- ❑ Where the volume of the digest is >50 mL after peroxide decomposition (eg. in samples that underwent the carbonate modification), decrease volume to between 45 and 50 mL on the hotplate.
- ❑ When samples have cooled to near room temperature, quantitatively transfer beaker contents to a titration vessel using 30 mL of ~2.66 M KCl.
- ❑ Give the digest beaker a final rinse with no more than 5 mL of deionised water (into titration vessel), giving a suspension of approximately 80 mL, 1 M in KCl (ie. for 2 g samples a final soil:solution extraction ratio of 1:40).

Measurement of TPA

All samples with pH <5.5 are first titrated to pH 5.5 with either 0.05 M or 0.25 M NaOH (depending on the initial pH of the suspension – see below). Subsequently all samples are titrated to pH 6.5 using 0.05 M NaOH.

- ❑ Measure and record pH of suspension (TPA pH) using a suitably calibrated pH meter and electrode prior to TPA titration. Use the appropriate option below, depending on the measured TPA pH.

Note: The TPA pH should be similar to the pH_{OX} except where the carbonate modification is carried out. There will be a slight difference due to the addition of KCl solution and the dilution associated with this.

- i) If pH is ≤ 3 , titrate with stirring to pH 5.5 using standardised ~0.25 M NaOH (c_1) and record volume of titre (V_4).
- ii) If pH is >3 but ≤ 5.5 , titrate with stirring to pH 5.5 using standardised ~0.05 M NaOH (c_2) and record volume of titre (V_5).
- iii) If pH is >5.5 but <6.5, go to final oxidation step.
- iv) If pH is ≥ 6.5 then TPA (**Method Code 23G**) is zero. Do not perform final oxidation.

Note: The TPA pH may possibly be ≥ 6.5 , despite the pH_{OX} lying between 5.5 and 6.5. Also the TPA pH may also be ≥ 6.5 , despite an HCl titration being performed (in the carbonate modification) if recovery of carbonates is incomplete.

- ❑ If the blank has a pH <5.5, titrate it to pH 5.5 using 0.05 M NaOH and record titre volume (V_7).

- Perform a ‘final oxidation’ on all samples where pH is now <6.5 by adding 1 mL of 30% H₂O₂ (that has been adjusted to pH 5.5 with dilute NaOH solution). Allow pH to stabilise then measure.

Note: The addition of 1 mL of 30% peroxide converts any Fe²⁺ to Fe³⁺ ensuring complete conversion of iron to Fe(OH)₃ during titration.

- While stirring, titrate those suspensions with pH <6.5 to pH 6.5 using 0.05 M NaOH (c₂). Record molarity (c₂) and titre (V₆ mL) of alkali added to reach pH 6.5. For blanks record corresponding titre (V₈) and molarity (c₂).

Note: The titre volume depends somewhat on the rate of titrant addition during titration. When titrating manually, the following procedure may be used as a guide. Add titrant at a slow constant rate (eg. drop-wise every 1 to 2 s), allowing the increase in pH to keep pace with NaOH addition. When within 1 pH unit of endpoint (eg. pH >5.5), cease titrant addition and allow pH to stabilise. Recommence titration at a slower rate and bring pH to just below endpoint (eg. 6.3), recording pH and corresponding volume of titrant at this point. Titrate to endpoint (pH 6.5) and wait for 20 s. If pH drops by >0.1 pH units in this time (and pH endpoint was not originally overshoot by more than 0.1 pH units) titrate back up to pH 6.5 and wait 20 s. Repeat process until pH remains above 6.5 after 20 s. Titrations may take as long as 5 min, depending on how far the pH dropped in the double oxidation.

Note: If an auto-titrator is being used, titrant addition should be dynamic (ie. with titrant volume increment decreasing as the end point is approached) and the manufacturer’s operator’s manual followed.

Calculation of TPA without carbonate modification

- Calculate TPA result and express as mol H⁺/t of soil (**Method Code 23G**) [where m₂ in g, concentrations (c_x) in mol/L, and titres (V_x) in mL].

If **0.25 M** and **0.05 M NaOH** are used:

$$\text{TPA (mol H}^+/\text{t)} = [(\text{V}_4 \times \text{c}_1) - (\text{V}_7 \times \text{c}_2) + (\text{V}_6 - \text{V}_8) \times \text{c}_2] \times (\mathbf{1000/m_2})$$

For 0.25 M NaOH (c₁) and 0.05 M NaOH (c₂), zero blank, suggested weights, volumes this simplifies to:

$$\text{TPA (mol H}^+/\text{t)} = (125 \times \text{V}_4) + (25 \times \text{V}_6)$$

If only **0.05 M NaOH** is used:

$$\text{TPA (mol H}^+/\text{t)} = [(\text{V}_5 + \text{V}_6 - \text{V}_7 - \text{V}_8) \times \text{c}_2] \times (\mathbf{1000/m_2})$$

For 0.05 M NaOH (c₂), zero blank, suggested weights, volumes this simplifies to:

$$\text{TPA (mol H}^+/\text{t)} = 25 \times (\text{V}_5 + \text{V}_6)$$

Calculation of Excess Acid Neutralising Capacity (ANC_E) or TPA with carbonate modification

- For those samples that underwent the carbonate modification to the method, calculate HCl titration (to pH 4) and express as mol H⁺/t.

$$\text{HCl titration (mol H}^+/\text{t)} = \text{V}_3 \times \text{c}_3 \times (\mathbf{1000/m_2})$$

For 0.5 M HCl (c₃) and suggested weight this simplifies to:

$$\text{HCl titration (mol H}^+/\text{t)} = 250 \times \text{V}_3$$

Note: For some soils that have undergone the HCl-titration and second peroxide digest steps a TPA titration may be required (ie. TPA pH <6.5). Where the HCl-titration result is greater than the NaOH titration (or TPA is zero) this indicates an excess acid neutralising capacity.

- Calculate excess acid neutralising capacity (a-ANC_E) in mol H⁺/t (**Method Code a-23Q**)

$$\mathbf{a-ANC_E = HCl\ titration - TPA\ titration\ (in\ mol\ H^+/t)}$$

If **0.25 M** and **0.05 M NaOH** has been used:

$$\mathbf{a-ANC_E\ (mol\ H^+/t) = [V_3 \times c_3 \times (1000/m_2)] - [(V_4 \times c_1) - (V_7 \times c_2) + (V_6 - V_8) \times c_2] \times (1000/m_2)}$$

If **only 0.05 M NaOH** has been used:

$$\mathbf{a-ANC_E\ (mol\ H^+/t) = [V_3 \times c_3 \times (1000/m_2)] - [(V_5 + V_6 - V_7 - V_8) \times c_2] \times (1000/m_2)}$$

Note: When the net result of this calculation is positive then the sample has intrinsic excess acid neutralising capacity and the TPA is reported as zero.

Note: If the result of either of these calculations is negative, then a-ANC_E is reported as zero and the absolute value is reported as TPA. If the result is zero then both a-ANC_E and TPA are zero.

To report result in conventional ANC units (ie. equivalent %CaCO₃):

$$\mathbf{ANC_E = a-ANC_E/199.8\ (Method\ Code\ 23Q)}$$

Notes:

It is theoretically possible that a net positive TPA can result in soils that have been titrated with HCl. This would occur if the number of moles of NaOH added during titration to pH 6.5 is greater than the number of moles HCl added during the titration to pH 4. In such a situation ANC_E is zero and TPA is calculated by subtracting the HCl-titration result from the TPA titration result (in mol H⁺/t).

Retain the titrated suspension if peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) are to be determined as part of the complete SPOCAS method.

References:

- Latham NP, Grant IJC, Lyons D, McElnea AE, Ahern CR (2002) Peroxide oxidation of self-neutralising soils. In 'Fifth International Acid Sulfate Soil Conference'. 25–30 August 2002 (Eds LA Sullivan, BCT Macdonald, A Keene) Addendum pp. 20–21, (Tweed Shire Council: Murwillumbah, NSW)
- M^cElnea AE, Ahern CR, Menzies NW (2002a) Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soils. *Australian Journal of Soil Research* **40**, 1115–1132.
- M^cElnea AE, Ahern CR, Menzies NW (2002b) The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* **40**, 1133–1157.

4. TITRATABLE SULFIDIC ACIDITY (TSA) – METHOD CODE 23H

Introduction:

Titratable Sulfidic Acidity (TSA) is the acidity attributed to the complete oxidation of all the sulfidic compounds in the soil by hydrogen peroxide. It is calculated from the difference in TPA and TAA results. In ASS with low organic matter and low ANC this value correlates well with a-S_{CR} and with a-S_{POS} from SPOCAS (McElnea *et al.* 2002a, 2002b). (Titratable acidity from organic acids and hydrolysable metal ions released or generated from the breakdown of organic matter during peroxide oxidation is also included in the TSA result. This acidity can be appreciable in highly organic ASS).

Calculation:

TSA is calculated as follows:

$$\text{TSA (mol H}^+\text{/t)} = \text{TPA} - \text{TAA}$$

or

$$\text{Method Code 23H} = \text{Method Code 23G} - \text{Method Code 23F}$$

References:

McElnea AE, Ahern CR, Menzies NW (2002a) Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soils. *Australian Journal of Soil Research* **40**, 1115–1132.

McElnea AE, Ahern CR, Menzies NW (2002b) The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* **40**, 1133–1157.

SULFUR METHODS—FOR ESTIMATING POTENTIAL ACIDITY

5. TOTAL AND PSEUDO TOTAL SULFUR (S_T) – METHOD CODE 20A

CR Ahern and AE McElnea

INTRODUCTION

To determine total sulfur in soil, the various constituent forms of sulfur are converted to a single form (often sulfate) by methods such as: oxidation with mineral acids (eg. $\text{HNO}_3/\text{HClO}_4$) or NaOBr; fusion with Na_2CO_3 + oxidising agent; or oxidation in an induction furnace (eg. Leco™) (Tabatabai 1982). Alternatively, the non-destructive XRF method can be used (Darmody *et al.* 1977; Rayment and Higginson 1992). Most of the wet chemical acid digest methods do not necessarily give a true total sulfur unless a hydrofluoric acid digestion is included, however all acid-producing sulfur forms in the soil will be recovered.

The measurement of total sulfur (S_T) provides a low-cost analytical technique that may be used to estimate the **maximum** potential environmental risk from acid produced by the oxidation of sulfides. The measurement of S_T is a useful screening approach and is widely used in the mining industry when estimating the maximum potential for acid drainage from sulfide sources. For this estimate it is assumed that all sulfur measured is in the form of pyrite or other metal or metalloid disulfides. The use of instruments such as Leco™ furnace or XRF machines, enable rapid low-cost analysis of large numbers of samples. When soluble sulfate salts (eg. gypsum) and organic sulfur from organic matter are appreciable, the S_T may substantially overestimate the risk and indeed may result in unnecessary treatment of material containing no sulfides. This method can be combined with the determination of 4 M HCl extractable sulfur to give what is termed ‘total oxidisable sulfur’ (S_{TOS}) (Section B11.1) to obtain a better estimate of soil sulfide content.

The main disadvantage of this measurement is that in isolation it does not give an estimate of the soil’s ‘actual soil acidity’ from previous or partial oxidation of sulfides since it only follows the sulfur trail. Another drawback is that it does not take into account any acid neutralising capacity present in the soil. Generally, it has higher detection limits than S_{CR} and SPOCAS methods and provides only one result (not necessarily reflecting the sulfide content). In surface soils, S_T may commonly exceed action limits due to sulfur in organic matter. The **instrumental** total sulfur methods (eg. XRF) are generally not suitable for accurate determinations on soil with low sulfur contents (eg. sands).

5.1 TOTAL SULFUR BY X-RAY FLUORESCENCE – METHOD CODE 20A1

The XRF is a suitable technique for routine total S determination in soil. However, Brown and Kanaris-Sotiriou (1969) reported that a correction for matrix effects needs to be applied for organic soil (soil with loss on ignition >30%). Darmody *et al.* (1977) noted that the mineralogical and/or physical-chemical form of the S may markedly affect the element’s X-ray spectrographic response. For this reason, interpretation of the TOS method on highly organic soil or acid peats is difficult without other analysis.

Procedure:

Preparation of pellet for X-ray fluorescence (XRF)

- Oven dry (at 65 °C) approximately 10 g of previously dried and ring mill ground soil.

- ❑ Add 0.5 g H_3BO_3 to serve as a binder, place into a clean 100 g capacity ring and pluck head and grind in a 'shatterbox' for a minimum of 2 min.
- ❑ Pellet approximately 2 g of the above soil mix into a 45 mm diameter disc with a H_3BO_3 backing, using a hydraulic press of around 25 tonne total force.

Note: All grinding equipment should be thoroughly cleaned as contamination between samples can cause a false positive result. Grinding a small quantity of acid-washed silica between each sample can avoid cross-contamination. (Refer Method 9A1, Rayment and Higginson 1992).

Preparation of standard pellets

- ❑ Prepare solid standards of known %S by adding gypsum or volumes of $(NH_4)_2SO_4$ or $CaSO_4 \cdot 2H_2O$ solution to weighed quantities of silica (Refer Method 9A1 and 10A1, Rayment and Higginson 1992).

Calculations:

- ❑ Sulfur contents are measured by comparing the intensity of their X-ray fluorescence with that of the sulfur standards and reported as %S on an oven dry basis.

Note: An alkali fusion approach to produce beads is an alternative approach for determining total sulfur by XRF.

5.2 TOTAL SULFUR BY COMBUSTION FURNACE (EG. LECO™) – METHOD CODE 20A2*

Originally, the Laboratory Equipment Corporation (Leco™) Sulfur Analyser was designed to determine sulfur in steel using low weights <1 g, though recent models are now available for soil which can take up to 3 g of soil. Older model Leco machines were designed on the assumption that the technique quantitatively converted sulfur to SO_2 . The titration procedure did not however, recover sulfur evolved as SO_3 (Tabatabai 1982). In more recent Leco models (eg. Leco CNS-2000 Analyser) the SO_3 complication has been overcome. Lin *et al.* (1996) reported high reproducibility in measurement of total S in sulfidic soil and sediments using such an instrument.

The manufacturer's instructions for the particular model should be consulted to optimise procedures for the range of sulfur values expected. A combustion catalyst (typically vanadium pentoxide) must be used for ASS to ensure complete recovery of sulfate sulfur, particularly from gypsum and jarosite.

5.3 SULFUR BY COMBUSTION WITH CONVERSION TO SULFATE – METHOD CODE 20A4*

Various techniques exist for high temperature combustion including dry ashing/fusion with sodium carbonate (or sodium bicarbonate) combined with an oxidising agent to form sulfate, (see dry ashing with sodium bicarbonate, silver oxide; Steinbergs *et al.* 1962). Once converted to sulfate, the determination can follow one of the many sulfate methods, depending on the laboratory's equipment and preference.

5.4 SULFUR BY OXIDATION WITH SODIUM HYPOBROMITE – METHOD CODE 20A5*

This technique involves the alkaline sodium hypobromite NaOBr oxidation followed by hydrogen iodide reduction (Tabatabai and Bremner 1970).

5.5 SULFUR BY MIXED ACID DIGEST – METHOD CODE 20A6*

This technique involves acid oxidation using nitric, perchloric, phosphoric or hydrochloric acids (Arkley 1961) or variations.

5.6 SULFUR BY BROMINE-NITRIC ACID OXIDATION – METHOD CODE 20A7*

This technique involves bromine/nitric acid oxidation (Vogel 1978).

**Note: For details on reagents, apparatus, procedures and calculations for these methods, consult listed references or appropriate soil chemical method books.*

References:

- Arkley TH (1961) 'Sulfur compounds of soil systems.' PhD thesis, California University, Berkeley.
- Brown G, Kanaris-Sotiriou R (1969) The determination of sulphur in soils by X-ray fluorescence analysis. *The Analyst* **94**, 782–786.
- Darmody RG, Fanning DS, Drummond WJ, Foss JE (1977) Determination of total sulfur in tidal marsh soils by x-ray spectroscopy. *Soil Science Society of America Journal* **41**, 761–756.
- Lin C, Melville MD, White I, Hsu YP (1996) Comparison of three methods for estimation of the reduced-S content in estuarine sediments. *The Science of the Total Environment* **187**, 1–9.
- Rayment GE, Higginson FR (1992) 'Australian Laboratory Handbook of Soil and Water Chemical Methods.' (Inkata Press: Melbourne, Australia)
- Rayment GE, Lyons DJ, Shelley BC (In Press) 'Australian Laboratory Handbook of Soil Chemical Methods.' (CSIRO Publishing: Melbourne)
- Steinbergs A, Iismaa O, Freney JR, Barrow NJ (1962). Determination of total sulphur in soil and plant material. *Analytica Chimica Acta* **27**, 158–164.
- Tabatabai MA (1982) Sulfur. In, 'Methods of Soil Analysis Part 2 Chemical and Microbiological Properties. 2nd Edition (Eds. AL Page, RH Miller and DR Keeney) pp. 501–538 (American Society of Agronomy, Soil Science Society of America Inc.: Madison, Wisconsin, USA)
- Tabatabai MA, Bremner JM (1970) Comparison of some methods for determination of total sulfur in soils. *Soil Science Society of America Journal* **34**, 417–420.
- Vogel AI (1978) 'Vogel's Textbook of Quantitative Inorganic Analysis.' 4th Edn. (Longman, London)

6. CHROMIUM REDUCIBLE SULFUR (S_{CR}) – METHOD CODE 22B

LA Sullivan, RT Bush, D McConchie, G Lancaster, M Clark, C Lin and P Saenger

Introduction:

The Chromium Reducible Sulfur method (Method 22B) is not subject to significant interferences from the sulfur in either organic matter or sulfate minerals (eg. gypsum) as is the Peroxide Oxidisable Sulfur (Method 21D) (Sullivan *et al.* 1999). The ASSMAC Technical Co-ordinating Committee is of the view that ‘greater emphasis will be placed on the Chromium Reducible Sulfur methodparticularly when results are close to the action criteria and for samples containing organic matter or considerable gypsum in conjunction with low sulphide content’ (ASSAY 1999). In addition, the ASSMAC Technical Co-ordinating Committee strongly recommended that when TOS is less than 0.1 %S that additional analysis by the Chromium Reducible Sulfur be undertaken (Assay 1999).

The use of chromium reduction method to measure reduced inorganic sulfur compounds in sediments was proposed by Zhabina and Volkov (1978), was evaluated for its efficacy and selectivity by Canfield *et al.* (1986) and Morse and Cornwell (1987), and has since been widely used in research (eg. Raisewell *et al.* 1988; Luther *et al.* 1992; Rice *et al.* 1993; Holmer *et al.* 1994; Moeslund *et al.* 1994; Wilkin and Barnes 1996; Habicht and Canfield 1997; Rickard 1997). Reduced inorganic sulfur compounds are the constituents of acid sulfate soil that are of environmental concern due to their acid-generating potential. Our examination of the utility of this procedure for acid sulfate soil materials in Australia confirms this method is specific to these compounds and is not measurably affected by sulfur in organic matter or sulfates (see also Canfield *et al.* 1986; Morse and Cornwell 1987).

The chromium reduction method is based on the conversion of reduced inorganic sulfur to H_2S by a hot acidic $CrCl_2$ solution; the evolved H_2S is trapped in a zinc acetate solution as ZnS . The ZnS may be quantified by iodometric titration. The reduced inorganic sulfur compounds measured by this method are: 1) pyrite and other iron disulfides, 2) elemental sulfur, and 3) acid volatile sulfides (eg. greigite and mackinawite). The chromium reduction method can be made specific to the iron disulfide fraction if pretreatments are used to remove the acid volatile sulfides and elemental sulfur fractions.

Our experience with the modified chromium reduction method (Sullivan *et al.* 2000) indicates that it is a quick and low-cost method that reliably measures reduced inorganic sulfur compounds in sediments and soil. The modified method presented here is from Sullivan *et al.* (2000) and the main difference in this method compared to that of Sullivan *et al.* (1998) is in the shorter reaction time of 20 min compared to the original reaction time of 1 h. Although Canfield *et al.* (1986) recommended the use of 10% ammonia in the zinc acetate solution, we have found that a 2.8% concentration of ammonia in this solution produces clearer iodometric titration endpoints without compromising H_2S trapping efficiency.

As discussed in Section A2, for a full determination of the properties that are required for managing ASS, the S_{CR} method will often need to be augmented by other methods such as TAA and ANC to provide information on actual acidity and acid neutralising capacity (eg. Figure A2.2).

a) Amount of soil material to digest

The optimum weight of soil material to digest depends on the reduced inorganic sulfur content and is a compromise between:

- ❑ if too much reduced inorganic sulfur is digested then too much H_2S will be supplied to the trapping solution. This may result in either the capacity of the solution to trap the H_2S as ZnS being exceeded (and a low result) or more likely the need to use large amounts of iodine titrant.
- ❑ if too little reduced inorganic sulfur is digested then only very small quantities (if any) of H_2S will be supplied to the trapping solution. In samples with very low reduced inorganic sulfur

contents, insufficient quantities of sediment being used for the analysis will result in very small quantities of iodine titrant being used and low analytical precision.

Where the maximum likely reduced inorganic sulfur content can be assessed (such as by a screening analysis of total sulfur), we have found the following guidelines useful for determining the optimum sediment weights to use.

- ❑ for samples with likely S_{CR} contents <0.5%, 3 g of dry powdered sample is recommended
- ❑ for samples with likely S_{CR} contents of <1% but >0.5%, 0.5 g of dry powdered sample is recommended
- ❑ for samples with likely S_{CR} contents of >1%, but <3%, 0.1 g of dry powdered sample is recommended
- ❑ for samples with likely S_{CR} contents of >3%, 0.05 g of dry powdered sample is recommended

If the likely S_{CR} content is not known, then at least 0.5 g of dry powdered sample should be used to ensure adequate analytical precision.

Reagents:

Warning: Ammonia solution is highly alkaline. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat).

Warning: Concentrated or 6 M hydrochloric acid is hazardous. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat). Acid fumes should be avoided by handling the concentrated acid in a fume hood and/or by wearing a suitable gas mask.

Warning: Vessels containing iodine solution should be sealed or kept in a fume hood as there can be significant vapour pressure above solutions of aqueous I_3^- .

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity <5 $\mu S/cm$.

Zinc acetate solution: Dissolve 60 g of zinc acetate in 1.5 L of deionised water. Add 200 mL of 28% ammonia solution and make up to 2 L with deionised water.

Standard 0.025 M sodium thiosulfate solution: This solution may be obtained commercially or prepared by dissolving 6.205 g of $Na_2S_2O_3 \cdot 5H_2O$ in deionised water in a 1.0 L volumetric flask. Add 1.5 mL of 6 M NaOH and make to volume with deionised water.

Starch solution: Dissolve 2 g arrowroot starch and 0.2 g salicylic acid in 100 mL of hot deionised water.

Iodine solution: Dissolve 22.50 g of potassium iodide in water and add 3.20 g iodine. After the iodine has dissolved, dilute to 1 L with deionised water and standardise against the standard 0.025 M $Na_2S_2O_3$ solution using the starch solution as an indicator. Record volume (**D**) of standardised $Na_2S_2O_3$ used in titration and the volume (**E**) of iodine solution titrated. Standardisations should be performed daily.

95% Ethanol

Chromium powder (Technical grade)

6 M Hydrochloric acid: Prepare (1 L) by adding ~585 mL of concentrated ($\rho = 1.16 \text{ g/cm}^3$, 31.5–33 %w/V) hydrochloric acid to 400 mL of deionised water slowly with stirring then diluting to 1000 mL at 20 °C using deionised water. Some chemical producers supply concentrated hydrochloric acid of density 1.18 g/cm^3 (~12.3 M or 38 %w/V), in which case ~488 mL of acid should be added to 500 mL of deionised water.

Apparatus:

The apparatus is shown diagrammatically in the following figure.

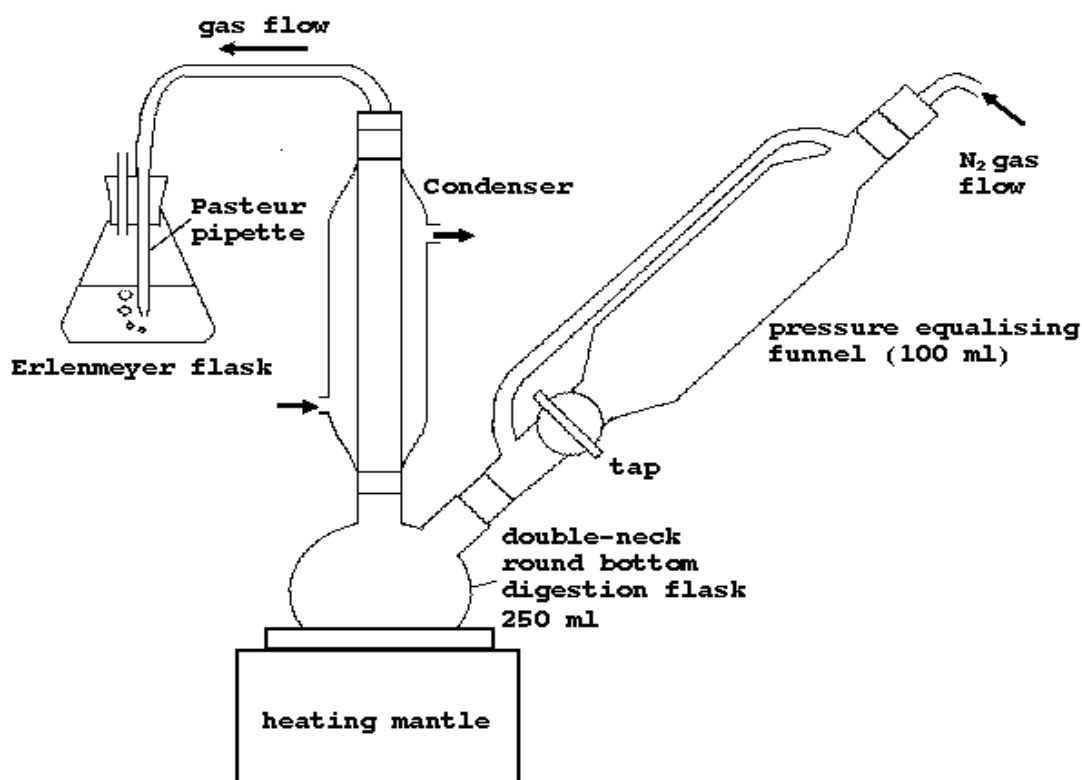


Figure B6.1. Schematic representation of the apparatus used in the chromium reduction method for determination of S_{CR} .

Procedure:

- ❑ Weigh accurately (to the nearest 0.001 g) between 0.475 g and 0.525 g (**m**) of finely ground (eg. ring mill ground) oven dried (80–85 °C) soil (or other appropriate weight as described in the introduction) into a double-neck round-bottom digestion flask. Include a solution blank in each batch and subject it to the same procedure as the soil.
- ❑ Add 2.0 g of chromium powder and then 10 mL ethanol (95% concentration) to the digestion flask and swirl to wet the sample.

Caution: Chromium dust may be toxic if inhaled and may represent a combustion risk. Avoid the use of very fine chromium powder.

- ❑ Place the digestion flask in the heating mantle and connect to the condenser. The digestion apparatus should be set up in a fume hood.
- ❑ Attach the pressure equalising funnel making sure the gas flow arm is facing the condensers and that the solution tap is shut. Attach Pasteur pipette to the outlet tube at the top of the

condenser and insert it into a 100 mL Erlenmeyer flask containing 40 mL zinc acetate solution.

- ❑ Turn on the water flow around the condenser and make sure that all ground glass fittings are tight. Add 60 mL of 6 M HCl to the glass dispenser in the pressure equalising funnel.
- ❑ Connect the N₂ flow to the pressure equalising funnel and adjust the flow to obtain a bubble rate in the zinc acetate solution of about 3 bubbles per second. Allow the N₂ gas to purge the system for about 3 min.
- ❑ Slowly release the 6 M HCl from the dispenser.

Caution: The 6 M HCl should be added to the sediment and chromium powder very slowly in a fume hood.

- ❑ Wait for 2 min before turning on the heating mantle and adjust the heat so that a gentle boil is achieved. Check for efficient reflux in the condenser. Allow to digest for 20 min.

Caution: H₂S gas (a hazardous gas) can be evolved during this digest. Consequently, this part of the procedure should be undertaken in a fume hood.

- ❑ Remove the Erlenmeyer flask and wash any ZnS on the Pasteur pipette into the Erlenmeyer flask with a wash bottle containing deionised water. Add 20 mL of 6 M HCl and 1 mL of the starch indicator solution to the zinc acetate solution and gently mix by swirling or by placing on a magnetic stirrer.

Note: If a large amount of ZnS has formed on the tip of the Pasteur pipette (and is not easily removed by washing with deionised water, the pipette can be left in the Erlenmeyer flask (and trapping solution), washed with a small amount of 6 M HCl and remain there during the titration.

- ❑ Whilst stirring, titrate the zinc acetate trapping solution with the iodine solution to a permanent blue end-point. Record the volume of titrant (**A**) in mL. Perform the same titration on the blank sample and record the volume of titrant (**B**) in mL.

Warning: H₂S gas (a hazardous gas) can be evolved after the acid is added to the zinc acetate trapping solution. Consequently, this part of the procedure should be: 1) carried out with a minimum of delay after the acid has been added, and 2) undertaken in a fume hood or with the aid of a fume extractor. It is recommended that laboratories be equipped suitable gas monitors to guard against accidental exposure to H₂S.

Caution: The acidic chromium digest solution (in the round-bottomed flask) generated by this procedure must not be disposed of down the sink. Consult local or state regulatory authorities for its safe disposal.

Calculation:

The concentration of chromium reducible sulfur (S_{CR}) in %S is calculated as follows:

$$\underline{S_{CR} (\%) = \frac{(A - B) \times C \times 3.2066}{m}}$$

Where:

A = The volume of iodine (in mL) used to titrate the zinc acetate trapping solution following the soil digestion

B = The volume of iodine (in mL) used to titrate the zinc acetate trapping solution following a blank digestion

C = The molarity of the iodine solution (in **M**) as determined by titration of this solution with the standard 0.025 M Na₂S₂O₃ solution (see below)

$$\mathbf{C} = \frac{\mathbf{0.025 \times D}}{\mathbf{2 \times E}}$$

D = Titration volume of standard Na₂S₂O₃ solution (in **mL**)

E = Volume of iodine solution titrated (in **mL**)

m = The mass of the soil weighed (in **g**)

References:

- 'ASSAY—A newsletter about acid sulfate soils' (1999), No. 23, September (ASSMAC: Australia)
- Canfield DE, Raiswell R, Westrich JT, Reaves CM, Berner RA (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology* **54**, 149–155.
- Habicht KS, Canfield DE (1997) Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediment. *Geochimica et Cosmochimica Acta* **61**, 5351–5361.
- Holmer M, Kristensen E, Banta G, Hansen K, Jensen MH, Bussawarit N (1994) Biogeochemical cycling of sulfur and iron in sediments of a south-east Asian mangrove, Phuket Island, Thailand. *Biogeochemistry* **26**, 145–161.
- Luther (III) GW, Kostka JE, Church TM, Sulzberger B, Stumm W (1992) Seasonal iron cycling in the salt-marsh environment: the importance of ligand complexes with Fe(II) and Fe(III) in the dissolution of Fe(III) minerals and pyrite, respectively. *Marine Chemistry* **40**, 81–103.
- Moeslund L, Thamdrup B, Jorgensen BB (1994) Sulfur cycling in a coastal sediment: radiotracer studies and seasonal dynamics. *Biogeochemistry* **27**, 129–152.
- Morse JW, Cornwell JC (1987). Analysis and distribution of iron sulfide minerals in recent anoxic marine sediments. *Marine Chemistry* **22**, 55–69.
- Raiswell R, Buckley F, Berner RA, Anderson TF (1988) Degree of pyritization of iron as a paleoenvironmental indicator of bottom-water oxidation. *Journal of Sedimentary Petrology* **58**, 812–819.
- Rice CA, Tuttle ML and Reynolds RL (1993) The analysis of forms of sulfur in ancient sediments and sedimentary rocks: comments and cautions. *Chemical Geology* **107**, 83–95.
- Rickard DT (1997) Kinetics of pyrite formation by the H₂S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125 °C: The rate equation. *Geochimica et Cosmochimica Acta* **61**, 115–134.
- Sullivan LA, Bush RT, McConchie D, Lancaster G, Clark MW, Norris N, Southon R and Saenger P (1998) Chromium Reducible Sulfur S_{CR} – Method 22B. In: Ahern CR, Blunden B and Stone Y (Eds) *Acid Sulfate Soils Laboratory Methods Guidelines*. Acid Sulfate Soil Management Advisory Committee, Wollongbar, NSW, Australia.
- Sullivan LA, Bush RT, McConchie D, Lancaster G, Haskins PG and Clark MW (1999) Comparison of peroxide oxidisable sulfur and chromium reducible sulfur methods for determination of reduced inorganic sulfur in soil. *Australian Journal of Soil Research* **37**, 255–265.
- Sullivan LA, Bush RT and McConchie DM (2000) A modified chromium reducible sulfur method for reduced inorganic sulfur: optimum reaction time for acid sulfate soil. *Australian Journal of Soil Research* **38**, 729–734.
- Wilkin RT and Barnes HL (1996) Pyrite formation by reactions of iron monosulfide with dissolved inorganic and organic sulfur species. *Geochimica et Cosmochimica Acta* **60**, 4167–4179.
- Zhabina NN and Volkov II (1978) A method of determination of various sulfur compounds in sea sediments and rocks. In: WE Krumbein (Ed.), *'Environmental Biogeochemistry: Methods, Metals, and Assessment'* Vol. 3 Ann Arbor Science Publishers, Ann Arbor, Michigan pp. 735–745.

7. SULFUR–PEROXIDE OXIDATION METHOD – METHOD CODE 23D

AE McElnea and CR Ahern

Peroxide sulfur (S_P) Method Code 23D

Peroxide calcium (Ca_P) Method Code 23W

Peroxide magnesium (Mg_P) Method Code 23T

Introduction:

This method determines peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) after peroxide digestion (and determination of TPA or ANC_E). Peroxide sulfur represents soluble and exchangeable sulfur, sulfate from gypsum, sulfate from oxidation of sulfides and sulfur released by breakdown of organic matter. It is used in conjunction with S_{KCl} to calculate S_{POS} . Sulfate from jarosite and iso-structural minerals is not recovered to any significant degree.

This procedure recovers soluble and exchangeable calcium and magnesium, calcium from gypsum, as well as calcium and magnesium released by acid dissolution of calcium and/or magnesium carbonate, oxide or hydroxide minerals. The Ca_P and Mg_P results are used in conjunction with Ca_{KCl} and Mg_{KCl} to calculate reacted calcium (Ca_A) and magnesium (Mg_A).

Reagents:

Not applicable

Apparatus:

Analytical balance (500 g \pm 0.01 g), thick medium speed high retention filter paper (eg. Whatman #3 paper), beakers or plastic containers (>400 mL capacity).

Procedure:

Proceed from the end of Section B3 [Titratable Peroxide Acidity (TPA) in 1 M KCl Suspension—Method 23G].

- ❑ Quantitatively transfer contents of titration vessels to tared or weighed beakers with deionised water. Subject the solution blanks from Method 23G to the same procedure.
- ❑ Make suspensions to 400 mL (V) and 0.2 M in KCl with deionised water on a balance. The weight of suspensions should be 403.5 g plus the weight of original soil. (This final volume may be varied to suit your technique and/or equipment used for determining sulfur).
- ❑ Stir suspensions to homogenise and filter through thick, medium speed high retention paper.
- ❑ Analyse filtrate for sulfur (S_3) (mg S/L) by a suitable analytical instruments and appropriate range of standards. Determine sulfur on the blank (S_4). Indicate which sulfur finishing step was employed, using the codes from Table F1.3. For sulfur measurement, instrumentation that specifically determines sulfate is preferable to that which measures total sulfur in solution.

Note: An example of an instrument that is specific to sulfate is Ion Chromatography (IC). It is necessary to have an appropriate resin that will handle high levels of chloride introduced by the KCl solution matrix to obtain accurate and reproducible results. Instruments that determine total sulfur in solution (eg. ICP-AES) may measure non-sulfate sulfur species which may give a higher result. This is particularly the case in soil that contains a high concentration of organic sulfur.

- ❑ If analysing filtrate for calcium and magnesium, determine these elements using suitable instrumentation (eg. AAS, ICP-AES) and appropriate range of standards, taking into account

blank determinations. Indicate which technique was used to determine calcium and magnesium (Table F1.3).

Calculations:

- Calculate peroxide sulfur (S_p , **Method Code 23D**) as %S on a dry soil weight basis as shown below:

$$S_p (\%) = (S_3 - S_4) \times (V/m_2) / 10\,000 \quad [V \text{ in mL and } m_2 \text{ in g}]$$

When there is zero blank, $m_2 = 2 \text{ g}$, and $V = 400 \text{ mL}$ this simplifies to:

$$S_p (\%) = S_3 / 50$$

- Calculate peroxide calcium (Ca_p , **Method Code 23W**) and peroxide magnesium (Mg_p , **Method Code 23T**) in a similar fashion.

Notes:

For samples containing shell material, gypsum or those that have been limed it is strongly recommended that calcium and magnesium be determined on the same solution (Ca_p and Mg_p). [See SPOCAS overview (Section B12) and alkali cations (Section B15) for the application of cation measurements].

Retain peroxide digested soil residue if residual acid soluble sulfur (S_{RAS}) (Method 23R, Section B10 or B12) is to be determined (as part of the complete SPOCAS method).

If the presence of jarosite has been recorded or is suspected, it is strongly recommended that residue analysis for sulfur (S_{RAS} , Method 23R) be performed. When performing residue analysis, first take a suitable volume of filtered solution for sulfur (S_p) and cation (Ca_p and Mg_p) analysis, then continue to filter entire soil suspension.

SULFUR—VARIOUS EXTRACTION TECHNIQUES**8. SULFUR 1 M KCl EXTRACTION (S_{KCl}) – METHOD CODE 23C***AE McElnea and CR Ahern**KCl extractable sulfur (S_{KCl}) Method Code 23C**KCl extractable calcium (Ca_{KCl}) Method Code 23V**KCl extractable magnesium (Mg_{KCl}) Method Code 23S****Introduction:***

This method determines KCl-extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}), following determination of pH_{KCl} and TAA on a 1:40 1 M KCl soil suspension. The S_{KCl} result represents soluble plus exchangeable sulfur, sulfate from gypsum, as well as some sulfate from aluminium hydroxy sulfate compounds (eg. basaluminite). The S_{KCl} result can be used in conjunction with hydrochloric acid extractable sulfur (S_{HCl}) to calculate the net acid soluble sulfur (S_{NAS}).

This procedure recovers soluble and exchangeable calcium and magnesium, calcium from gypsum, as well as small quantities of calcium and magnesium from calcium and magnesium carbonates.

Reagents:

Not applicable

Apparatus:

Analytical balance (500 g \pm 0.01 g), thick medium speed high retention filter paper (eg. Whatman #3 paper), beakers or plastic containers (>400 mL capacity).

Procedure:

Proceed from the end of Section B2 [Titratable Actual Acidity (TAA_{KCl}) in 1 M KCl Suspension—Method 23F].

- ❑ Quantitatively transfer contents of titration vessels to tared or weighed beakers with deionised water. Subject the solution blanks from Method 23F to the same procedure.
- ❑ Make suspensions to 400 mL (**V**) and 0.2 M in KCl with deionised water on a balance. The weight of suspensions should be 403.5 g plus the weight of original soil. (This final volume may be varied to suit your technique and/or equipment used for determining sulfur).
- ❑ Stir suspensions to homogenise and filter through thick, medium speed high retention paper.
- ❑ Analyse filtrate for sulfur (S_1) (mg S/L) by a suitable analytical instruments and appropriate range of standards. Determine sulfur on the blank (S_2). Indicate which sulfur finishing step was employed, using the codes from Table F1.3. For sulfur measurement, instrumentation that specifically determines sulfate is preferable to that which measures total sulfur in solution.

Note: An example of an instrument that is specific to sulfate is Ion Chromatography (IC). It is necessary to have an appropriate resin that will handle high levels of chloride introduced by the KCl solution matrix to obtain accurate and reproducible results. Instruments that determine total sulfur in solution (eg. ICP-AES) may measure non-sulfate sulfur species which may give a higher result. This is particularly the case in soil that contains a high concentration of organic sulfur.

- ❑ If analysing filtrate for calcium and magnesium, determine these elements using suitable instrumentation (eg. AAS, ICP-AES) and appropriate range of standards, taking into account

blank determinations. Indicate which technique was used to determine calcium and magnesium (Table F1.3).

Calculations:

- Calculate KCl extractable sulfur (S_{KCl}) as below:

$$S_{KCl} (\%) = [(S_1 - S_2) \times (V/m_1)]/10\ 000 \quad [S_1 \ \& \ S_2 \text{ in mg S/L, } V \text{ in mL and } m_1 \text{ in g}]$$

When there is zero blank, $m_1 = 2 \text{ g}$, and $V = 400 \text{ mL}$ this simplifies to:

$$S_{KCl} (\%) = S_1/50$$

- Calculate KCl extractable calcium (Ca_{KCl} , **Method Code 23V**) and peroxide magnesium (Mg_{KCl} , **Method Code 23S**) can be determined in a similar fashion.

Notes:

For samples containing shell material, gypsum or those that have been limed it is strongly recommended that calcium and magnesium be determined on the same solution (Ca_{KCl} and Mg_{KCl}). These measurements are used in conjunction with calcium and magnesium determinations from the peroxide digest (ie. Ca_P and Mg_P) to calculate Ca_A and Mg_A .

9. SULFUR 4 M HCl EXTRACTION (S_{HCl}) – METHOD CODE 20B

AE McElnea and CR Ahern

HCl extractable sulfur (S_{HCl}) Method Code 20B

HCl extractable calcium (Ca_{HCl}) Method Code 20E

HCl extractable magnesium (Mg_{HCl}) Method Code 20F

Introduction:

This method determines HCl-extractable sulfur (S_{HCl}), calcium (Ca_{HCl}) and magnesium (Mg_{HCl}). This procedure recovers soluble and exchangeable sulfate, sulfate from gypsum and the relatively insoluble iron and aluminium hydroxy sulfate compounds (eg. jarosite, natrojarosite), as well as some sulfur from organic matter. The procedure will dissolve monosulfide minerals (eg. AVS) (that have not been lost in the drying process) but not pyrite sulfur. The S_{HCl} result is used in conjunction with S_{KCl} to calculate net acid soluble sulfur (S_{NAS}), and with S_{T} to calculate S_{TOS} .

The Ca_{HCl} result will comprise soluble and exchangeable calcium, calcium from gypsum, as well as calcium from calcium carbonates, oxides or hydroxides. It is possible that small amounts of calcium may also be extracted from other Ca-containing soil minerals. Similarly, Mg_{HCl} will include soluble and exchangeable magnesium, as well as magnesium from magnesium carbonate, oxide or hydroxide minerals. Also, Ca_{HCl} and Mg_{HCl} can be used in combination with Ca_{KCl} and Mg_{KCl} respectively to determine net acid soluble calcium (Ca_{NAS}) and magnesium (Mg_{NAS}).

Reagents:

Warning: Concentrated or 4 M hydrochloric acid is hazardous. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat). Acid fumes should be avoided by handling the concentrated acid in a fume hood and/or by wearing a suitable gas mask.

Note: All reagents added to samples should be free from sulfur, calcium and magnesium (or these elements accounted for by blank determinations). Reagents should be tested for the presence of these elements whenever a change in source is made (eg. brand or batch).

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity $<5 \mu\text{S/cm}$.

4 M HCl: To prepare (1 L) add ~390 mL of concentrated (31.5–33% w/v) HCl to 400 mL deionised water and dilute to 1000 mL at 20 °C.

Apparatus:

Electronic balance (100 ± 0.01 g), fume hood, plastic extraction bottle with sulfur-free stoppers, sample shaker, thick medium speed high retention filter paper (eg. Whatman #3 paper).

Procedure and calculations:

- ❑ Weigh accurately (to the nearest 0.01 g) between 1.9 g and 2.1 g of finely ground (eg. ring mill) oven dried (80–85 °C) soil into plastic extraction container. Include a solution blank with each analysis batch.
- ❑ In a fume hood, add 80 mL of 4 M HCl to make a 1:40 soil suspension and stopper bottle.

Note: Soils high in carbonates can react vigorously when HCl is added and generate CO_2 gas. Wait until this initial reaction subsides before stoppering sample bottle.

- Stopper bottle and extract overnight ($16 \text{ h} \pm 0.5 \text{ h}$) on reciprocal or end-over-end shaker.
- Centrifuge or filter through thick, medium speed, high retention filter paper to obtain a clear extract.
- Determine S_{HCl} (after appropriate dilution) using an appropriate finishing step and range of standards. Report S_{HCl} in units of %S on an oven-dry soil basis. For sulfur measurement, instrumentation that specifically determines sulfate is preferable to that which measures total sulfur in solution.

Note: An example of an instrument that is specific to sulfate is Ion Chromatography (IC). It is necessary to have an appropriate resin that will handle high levels of chloride introduced by the KCl solution matrix to obtain accurate and reproducible results. Instruments that determine total sulfur in solution (eg. ICP-AES) may measure non-sulfate sulfur species which may give a higher result. This is particularly the case in soil that contains a high concentration of organic sulfur.

- HCl extractable calcium (Ca_{HCl} , **Method Code 20E**) and peroxide magnesium (Mg_{HCl} , **Method Code 20F**) can be determined in a similar fashion, using appropriate instrumentation and range of standards.

10. PEROXIDE RESIDUAL ACID SOLUBLE SULFUR (S_{RAS}) – METHOD CODE 23R

AE McElnea and CR Ahern

Introduction:

After peroxide digest and TPA titration the soil residue may contain insoluble sulfur (eg. in jarosite or similar relatively insoluble iron and aluminium hydroxy sulfate compounds) which was either present initially in the soil or formed during peroxide oxidation. This sulfur represents a store of retained acidity (not measured in the TPA titration) that may be estimated after overnight (16 h) 4 M HCl extraction of the washed soil residue. On soil where the presence of jarosite is suspected (eg. if $pH_{KCl} < 4.5$ or jarosite has been noted in accompanying field sampling notes) it is strongly recommended that residue analysis for sulfur is performed. Alternatively, this fraction of sulfur can be estimated by the net acid soluble sulfur (S_{NAS}) value (Section B11.3).

Reagents:

Warning: Concentrated or 4 M hydrochloric acid is hazardous. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat). Acid fumes should be avoided by handling the concentrated acid in a fume hood and/or by wearing a suitable gas mask.

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity $< 5 \mu S/cm$.

4 M HCl: To prepare (1 L) add ~390 mL of concentrated (ie. 31.5–33% w/V) HCl to 400 mL deionised water and dilute to 1000 mL at 20 °C using deionised water.

1 M KCl: Prepare (1 L) by dissolving 74.55 g KCl in deionised water then diluting to 1000 mL at 20 °C using deionised water.

Apparatus:

Plastic extraction bottle, sample shaker, thick medium speed high retention filter paper (eg. Whatman #3 paper).

Procedure and calculations:

Proceed from the end of Section B7, **Peroxide sulfur (S_P)—Method 23D**

- ❑ When performing residue analysis, first take a suitable volume of filtered solution for sulfur (S_P) and cation (Ca_P and Mg_P) analysis, then continue to filter entire soil suspension (transferring all soil residue to the filter paper).
- ❑ When filtration is complete, wash filter paper with 2 x 10 mL aliquots of 1 M KCl then sufficient deionised water (eg. 4 x 10 mL) to ensure that all soluble and adsorbed sulfate has been washed from the filter paper.
- ❑ When washing is complete, place filter paper (containing washed soil residue) into suitable extraction bottle and add 80 mL of 4 M HCl. Extract overnight (16 ± 0.5 h) on reciprocal or end-over-end shaker.
- ❑ Filter mixture using thick, medium speed, high retention filter paper (or decant and centrifuge) to obtain a clear extract.
- ❑ Determine 'jarositic' or residual acid soluble sulfur (S_{RAS} , **Method Code 23R**) using a suitable technique and range of standards. Report S_{RAS} in units of %S on an oven-dry soil basis.

***SULFUR—PARAMETERS CALCULATED FROM OTHER
SULFUR ANALYSES***

11. CALCULATED SULFUR PARAMETERS

CR Ahern and AE McElnea

11.1 TOTAL OXIDISABLE SULFUR (S_{TOS}) – METHOD CODE 20C

Introduction:

The Total Oxidisable Sulfur (S_{TOS}) is the calculated difference between total sulfur (S_T , **Method Code 20A**) and 4 M HCl extractable sulfur (S_{HCl} , **Method Code 20B**).

The S_{TOS} method is a useful screening approach to determine pyrite levels in soil, providing a low cost measure of pyrite content but giving no estimate of ‘actual soil acidity’ from previous or partial oxidation of sulfides. The TOS method may be unsuitable for accurate determinations on soil with low sulfide levels (for example low analysis organic sands). The XRF and Leco™ instruments usually have higher detection limits than the S_{CR} and SPOCAS methods but detection limits and accuracy are instrument and method dependent. The S_{TOS} measurement may overestimate the potential acid risk on surface soil containing appreciable organic matter resulting in higher treatment than required or even treatment when not required. While this is a conservative approach, use of the S_{CR} technique could result in lower treatment costs or in some cases even clarify that no treatment is required.

Calculations:

The determination of the total oxidisable sulfur (S_{TOS}) can be made by subtracting the 4 M HCl extractable sulfur (S_{HCl}) from the total sulfur (S_T).

$$S_{TOS} = S_T - S_{HCl} (\%)$$

or

$$\text{Method Code 20C} = \text{Method Code 20A} - \text{Method Code 20B}$$

11.2 PEROXIDE OXIDISABLE SULFUR (S_{POS}) – METHOD CODE 23E

Introduction:

Peroxide oxidisable sulfur (S_{POS}) is the calculated difference between the sulfur determined in the peroxide digest (S_P) (**Method Code 23D**) and the sulfur extracted by 1 M KCl (S_{KCl}) (**Method Code 23C**). The S_{POS} result provides a measure of the oxidisable sulfur content of ASS, which is generally in good agreement with the S_{CR} result, except for highly organic soil and surface soil where it may be slightly higher.

Calculation:

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

or

$$\text{Method Code 23E} = \text{Method Code 23D} - \text{Method Code 23C}$$

11.3 NET ACID SOLUBLE SULFUR (S_{NAS}) – METHOD CODE 20J**Net acid soluble or 'jarositic' sulfur (S_{NAS}) Method Code 20J****Net acid soluble calcium (Ca_{NAS}) Method Code 19F1****Net acid soluble magnesium (Mg_{NAS}) Method Code 19G1****Introduction:**

Considerable retained acidity may be stored in ASS in the form of jarosite and similar relatively insoluble iron and aluminium hydroxy sulfate compounds. Their acidity and sulfur is not recovered in the 1 M KCl suspensions of TAA (Method 23F) and S_{KCl} (Method 23C). These compounds are soluble in 4 M HCl as are all other sulfate species. The difference in the sulfur extracted by 4 M HCl (S_{HCl} , **Method Code 20B**) and 1 M KCl (S_{KCl} , **Method Code 20C**) provides an estimate of the insoluble (jarositic) sulfur content of the soil. On highly organic samples, 4 M HCl may extract appreciable organic sulfur and (unless a sulfate specific technique, such as ion chromatography is used) may inflate the S_{NAS} result.

Calculation:

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

or

$$\text{Method Code 20J} = \text{Method Code 20B} - \text{Method Code 23C}$$

Note:

Net acid soluble calcium (Ca_{NAS} , **Method Code 19F1**) and magnesium (Mg_{NAS} , **Method Code 19G1**) can be calculated in a similar fashion.

12. OVERVIEW OF THE COMPLETE SPOCAS METHOD

AE McElnea and CR Ahern

OUTLINE OF SPOCAS FOR LABORATORY USE—METHOD CODE 23

Reagents:

Warning: 30% hydrogen peroxide is hazardous. The principal routes of exposure are usually by contact of the liquid with the skin or eye. Accordingly analysts should wear appropriate gloves and safety glasses at all times when using this chemical.

Warning: Solid NaOH is caustic and deliquescent. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat).

Warning: Concentrated hydrochloric acid is hazardous. Contact with skin and eyes should be avoided by wearing appropriate safety equipment (eg. gloves, safety glasses and laboratory coat). Acid fumes should be avoided by handling the concentrated acid in a fume hood and/or by wearing a suitable gas mask.

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity $<5\mu\text{S}/\text{cm}$.

1 M KCl: Prepare (1 L) by dissolving 74.55 g KCl in deionised water then diluting to 1000 mL at 20 °C using deionised water.

~2.66 M KCl: Prepare (1 L) by dissolving 198.81 g KCl in deionised water then diluting to 1000 mL at 20 °C using deionised water.

Standardised ~0.25 M NaOH (c₁): Prepare (1 L) by dissolving 10.1 g \pm 0.1 g of NaOH pellets in CO₂-free deionised water, then diluting to 1000 mL at 20 °C using deionised water. Standardise against potassium hydrogen phthalate (C₆H₅O₄K) by accurately weighing (to 0.0001 g) 0.25 g \pm 0.05 g of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence/end point volume and calculate the molarity of the NaOH solution. When the concentration of the standardised NaOH solution is not exactly 0.25 M, then the exact concentration of the NaOH should be used in calculations.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO₂. Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO₂ and standardised daily.

Standardised ~0.05 M NaOH (c₂): Prepare (1 L) by dissolving 2.05 g \pm 0.05 g of NaOH pellets in CO₂-free deionised water, then diluting to 1000 mL at 20 °C using deionised water. Standardise against potassium hydrogen phthalate (C₆H₅O₄K) by accurately weighing (to 0.0001 g) 0.10 g \pm 0.02 g of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence/end point volume and calculate the molarity of the NaOH solution. Where the concentration of the standardised NaOH solution is not exactly 0.05 M, then the exact concentration of the NaOH should be used in calculations.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO₂. Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO₂ and standardised daily.

4 M HCl: To prepare (1 L) add ~390 mL of concentrated (ie. 31.5–33% w/V) HCl to 400 mL deionised water and dilute to 1000 mL at 20 °C using deionised water.

Standardised ~0.5 M HCl (c₃): Prepare (1 L) by adding 50 mL of concentrated hydrochloric acid (31.5–33 % w/V) to 700 mL of deionised water with stirring then diluting to 1000 mL at 20 °C using deionised water. Standardise against disodium tetraborate decahydrate (Na₂B₄O₇·10H₂O) or recently standardised 0.25 M NaOH solution. Calculate molarity of HCl solution (c₃). Where the concentration of the standardised HCl solution is not exactly 0.5 M then the exact calculated molarity should be used in calculations.

Note: Solutions of 0.5 M HCl made by diluting commercially available ampoules may also be used.

30%(w/w) AR grade hydrogen peroxide (H₂O₂): Use only AR grade hydrogen peroxide. Check the pH of the peroxide. Determine a blank TPA and blank sulfur content with each run. Blanks should be low (ie. less than the equivalent of 6 mol H⁺/t). Technical grade peroxides are not recommended as they are usually acid stabilised and vary considerably between bottles in both sulfur content and pH.

30%w/w AR grade hydrogen peroxide (H₂O₂) (pH adjusted): Adjusted to pH 5.5 with dilute NaOH solution for use in the ‘final oxidation’ step.

6.30 x 10⁻³ M CuCl₂·2H₂O solution (400 mg Cu/L): Prepare (1 L) by dissolving 1.073 g of copper(II) chloride dihydrate (CuCl₂·2H₂O) in deionised water and dilute to 1000 mL at 20 °C using deionised water.

Potassium hydrogen phthalate (C₆H₅O₄K): Dry at 105 °C for 4 h and store in desiccator prior to use.

Sodium tetraborate (Na₂B₄O₇·10H₂O)

Apparatus:

Electronic balances (100 ± 0.01 g, 500 ± 0.01 g and 100 ± 0.0001 g); sample shaker (able to keep soil particles continuously in suspension); plastic extraction bottle (with stopper not containing sulfur); auto-titrator or other appropriate titration apparatus (eg. pH meter, magnetic stirrer plate, Teflon-coated magnetic stirrer bar and 2 x 10 mL A-grade 0.02 mL graduated burettes or digital burettes); titration vessel (of at least 100 mL capacity made of polyethylene or similar inert material); fume hood; thick medium speed high retention filter paper (eg. Whatman #3 paper); 250 mL tall-form borosilicate (‘pyrex’) glass beakers (with 50 mL volume accurately marked); wash bottle for deionised water; electric hotplate or steam bath (able to keep beaker and contents between 80 and 90 °C); adjustable dispensing pipette (1–10 mL, or separate 1 mL and 10 mL pipettes); manual or automatic volumetric dispenser (capable of dispensing 30 ± 0.25 mL).

Procedure:**Step 1. KCl pH (pH_{KCl}), Titratable Actual Acidity (TAA), and sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) in 1 M KCl****a) KCl extraction**

- Weigh accurately (to the nearest 0.01 g) between 1.9 g and 2.1 g (m_1) of finely ground (eg. in a ring-mill), oven-dried (80–85 °C) soil into a suitable extraction container and make a 1:40 suspension with 80 mL aqueous 1 M KCl solution. (Include a solution blank in each batch and subject it to the same procedure as the soil).

Note: A larger sample weight can be used, providing the soil: solution ratio remains at 1:40. Use the exact mass weighed (m_1) in subsequent calculations.

- Stopper the container and extract soil on a reciprocal or end-over-end shaker for 4 h (± 0.25 h), keeping container sealed until just prior to titration. Allow bottle and contents to stand overnight (for at least 12 h but no more than 16 h).
- Resuspend contents after standing by briefly shaking container (~ 5 min) before quantitatively transferring its contents to a separate titration vessel (if not titrating in extraction container) using a minimum volume of deionised water.

Note: The time between resuspension and titration should be minimised to limit possible oxidation.

b) pH_{KCl} and TAA titration

- While stirring, measure and record the pH of the suspension (pH_{KCl}) using a pH meter calibrated with appropriate buffers (**Method Code 23A**).
- Perform a titration to pH 6.5 with standardised NaOH solution using appropriately calibrated pH meter and burette, or auto-titrator. Use the appropriate option below, depending on the measured pH_{KCl} .
 - i) If pH_{KCl} is <4.0 , titrate the suspension with stirring to pH 6.5 using standardised 0.25 M NaOH (c_1) and record titre volume (V_1).
 - ii) If pH_{KCl} is ≥ 4.0 but <6.5 , titrate the suspension with stirring to pH 6.5 using standardised 0.05 M NaOH (c_2) and record titre volume (V_1).
 - iii) If pH_{KCl} is ≥ 6.5 , no titration is required and TAA is zero.

Note: In some states, guidelines require that for soil suspected of being ASS, a TAA titration is only required when the pH is less than 5.5.

Note: The titre volume depends somewhat on the rate of titrant addition during titration. When titrating manually, the following procedure may be used as a guide. Add titrant at a slow constant rate (eg. drop-wise every 1 to 2 s), allowing the increase in pH to keep pace with NaOH addition. When within 1 pH unit of endpoint (eg. $pH > 5.5$), cease titrant addition and allow pH to stabilise. Recommence titration at a slower rate and bring pH to just below endpoint (eg. 6.3), recording pH and corresponding volume of titrant at this point. Titrate to endpoint (pH 6.5) and wait for 20 s. If pH drops by >0.1 pH units in this time (and pH endpoint was not originally overshoot by more than 0.1 pH units) titrate back up to pH 6.5 and wait 20 s. Repeat process until pH remains above 6.5 after 20 s. As a guide, an average time for a manual titration (for a TAA of 100 mol H^+ /t) would be 5 minutes. If an auto-titrator is being used, the volume of titrant added in each increment should decrease as the endpoint is approached. Follow the instructions in the auto-titrator manufacturer's operator's manual.

- Titrate a blank sample using 0.05 M NaOH (c_2) and record titre volume (V_2 , in mL).

- Calculate titratable actual acidity (TAA) (expressed in mol H⁺/t oven-dry soil) using equations below:

If 0.25 M NaOH is used:

$$\text{TAA (mol H}^+/\text{t)} = (V_1 \times c_1 - V_2 \times c_2) \times (1000/m_1) \quad [m_1 \text{ in g, } V_1 \text{ \& } V_2 \text{ in mL, } c_1 \text{ and } c_2 \text{ in mol/L}]$$

If 0.05 M NaOH is used:

$$\text{TAA (mol H}^+/\text{t)} = [(V_1 - V_2) \times c_1] \times (1000/m_1) \quad [m_1 \text{ in g, } V_1 \text{ \& } V_2 \text{ in mL, } c_1 \text{ in mol/L}]$$

For NaOH molarity $c_1 = 0.05$ M, zero blank and suggested weights/volumes as above, this simplifies to:

$$\text{TAA (mol H}^+/\text{t)} = 25 \times (V_1)$$

c) **KCl extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) determination**

- Quantitatively transfer contents of titration vessels to tared (or weighed) beakers with deionised water.
- Make suspensions to 400 mL (V) and 0.2 M in KCl with deionised water on a balance. The weight of suspensions should be 403.5 g plus the weight of original soil. (This final volume may be varied to suit your technique and/or equipment used for determining sulfur).
- Stir suspensions to homogenise, and filter through thick, medium speed high retention paper.
- Analyse filtrate for sulfur (S_1) (mg S/L) by ICP-AES or using other suitable analytical instruments and appropriate range of standards. Determine sulfur on the blank (S_2). Indicate which sulfur finishing step was employed, using the codes from Table F1.3. Calculate KCl extractable sulfur (S_{KCl} , **Method Code 23C**) as below:

$$S_{KCl} (\%) = [(S_1 - S_2) \times (V/m_1)]/10\,000 \quad [S_1 \text{ \& } S_2 \text{ in mg S/L, } V \text{ in mL and } m_1 \text{ in g}]$$

When there is zero blank, $m_1 = 2$ g, and $V = 400$ mL this simplifies to:

$$S_{KCl} (\%) = S_1/50$$

- Determine KCl-extractable calcium (Ca_{KCl} , **Method Code 23V**) and KCl-extractable magnesium (Mg_{KCl} , **Method Code 23S**) using appropriate instrumentation (eg. AAS, ICP-AES) and range of standards.

Note: For samples containing shell material, gypsum, or which have been limed, it is strongly recommended that calcium and magnesium (ie. Ca_{KCl} and Mg_{KCl}) be determined on the same solution. These measurements are used in conjunction with calcium and magnesium determinations from the peroxide digest (ie. Ca_P and Mg_P) to calculate reacted calcium (Ca_A) and magnesium (Mg_A).

Step 2. Peroxide pH (pH_{OX}), Titratable Peroxide Acidity (TPA), and Peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P)

d) **Peroxide digest (oxidation)**

- Weigh accurately (to the nearest 0.01 g) 2 g of finely-ground (eg. in a ring mill) oven-dried (80–85 °C) soil into a suitably labelled tared flask (eg. 250 mL tall-form borosilicate glass beaker) on which the 50 mL level is accurately marked and record soil mass (m_2). In each analytical run, perform a minimum of two blanks. (If one or more samples in the run undergo the carbonate modification, then subject one of the blanks to this procedure).

- In a fume hood (and wearing safety-glasses, laboratory coat and gloves), add 10 mL **analytical reagent grade** 30% hydrogen peroxide (H₂O₂)* to each flask and swirl to mix.

**Warning: 30% hydrogen peroxide is hazardous. The principal routes of exposure are usually by contact of the liquid with the skin or eye. Accordingly, analysts should wear appropriate gloves and safety glasses at all times when using this chemical.*

Note: Soil high in pyrite (or manganese) has the potential to react violently at this stage. The addition of deionised water (via a narrow aperture wash bottle) at the first sign of a vigorous reaction will help to moderate the subsequent reaction. Great care needs to be taken to avoid samples bubbling/frothing-over when the initial aliquot of peroxide is added. If the reaction becomes overly vigorous at this stage and any loss of digest material occurs, the sample must be repeated with greater care and/or with a lesser sample weight (ie. 1 g). When analysing soil of known high sulfide content also use this lesser sample weight. For such repeats, add ~10 mL of deionised water to the soil prior to an incremental addition of the 10 mL of H₂O₂. The exact mass weighed must be used in subsequent calculations.

- After 30 min, add deionised water with swirling to make the total volume of suspension in the beaker between 45 and 50 mL. Swirl digest solution to give a homogeneous suspension, then rinse the inside wall of the beaker with deionised water.

Note: It is important to maintain this volume throughout the remaining digestion by regular addition of deionised water, and also to periodically swirl the sample to prevent soil from settling on and adhering to the bottom of the beaker during the subsequent hotplate heating stages. Rinsing the inside wall of the beaker with small squirts of deionised water also serves to dissolve any salts that may have accumulated there.

- Place the beaker on a hotplate (or steam bath) for a maximum of 30 min and maintain sample at 80–90 °C. Swirl samples periodically (eg. every 10 min) and add deionised water as required to maintain volume between 45 and 50 mL, and to wash soil residue from the inside of the beakers.
 - i) If a digest reacts vigorously after being placed on the hotplate, temporarily remove it from the hotplate and/or moderate the vigour of the reaction by adding small amounts of deionised water. Replace digest solution on hotplate when reaction has moderated. When the digest solution stops reacting while on the hotplate (eg. typically effervescent bubbling has ceased, soil settles and supernatant clears), remove from hotplate. If the digest solution continues to react whilst on the hotplate, remove after 30 min has elapsed.
 - ii) For a digest that reacts only slowly or moderately while on the hotplate, remove only after reaction ceases. If the reaction on the hotplate is continuing after 30 min has elapsed, remove the digest solution from the hotplate.
 - iii) For a digest that showed no obvious reaction after peroxide addition prior to being put on the hotplate and that failed to subsequently react while on the hotplate, remove from the hotplate after 30 min has elapsed.
 - iv) For a digest that reacts vigorously after initial peroxide addition (before being put on the hotplate), but does not react further whilst on the hotplate for 10 min (indicating that the added peroxide may have already been consumed), remove at this stage.
- Allow samples to cool to near room temperature.
- Add a second 10 mL aliquot of H₂O₂, waiting 10 min before returning flask to the hotplate for a maximum of 30 min, adopting the procedure outlined earlier.
- Allow samples to cool to room temperature and make volume to 50 mL with deionised water.

- Measure the pH of the suspension (**pH_{OX}**, **Method Code 23B**) while stirring using a suitably calibrated pH meter and electrode. Use the appropriate option below, depending on the measured pH_{OX}.
 - i) If pH_{OX} is ≤2 (indicative of high sulfide levels), repeat digest using 1 g of soil
 - ii) If pH_{OX} is >2 but ≤6.5, continue from peroxide decomposition step
 - iii) If pH_{OX} is >6.5 (meaning that the soil may contain excess carbonates), treat according to carbonate modification before continuing with peroxide decomposition step.

Carbonate modification (HCl titration to pH 4)

- For soil with pH_{OX} >6.5, quantitatively transfer suspensions to titration vessels (if not titrating in digest beaker) with deionised water.
- While stirring perform a slow titration (typically 10–30 min duration, if using an auto-titrator) to pH 4 with standardised 0.5 M HCl (c₃).

Note: This titration with dilute HCl is designed to dissolve excess carbonate, which interferes with the efficiency of peroxide oxidation. It can be used to estimate a net (excess) acid neutralising capacity of the soil. The reaction between solid carbonate and soil solution as the acid is added is slow. The pH tends to oscillate near the pH 4 end point, so a slow titration is necessary to ensure maximum recovery of carbonate. The conditions of this titration are difficult to standardise and to make consistent (without the use of an auto-titrator). Addition of a set aliquot of HCl at a fixed time interval may be the best approach to standardising the titration if titrating manually. If the endpoint (pH 4.0) is slightly overshoot, do not calculate the volume of titrant added to reach the endpoint, instead use the total volume of HCl solution added in subsequent calculations. However if the pH of the suspension stabilises below 3.5, repeat the analysis.

- Record volume and molarity of titrant added (V₃, in mL). Calculate HCl titration (mol H⁺/t).
- Quantitatively transfer contents of titration vessel to original digestion beaker (if not titrating in digest beaker).
- Add 25 mL 30% H₂O₂ and place on hotplate. Swirl digest periodically (eg. every 10 min) and the wash soil residue from the walls of the beaker with a small amount of deionised water for a maximum of 1 h, following the appropriate option below.
 - i) If a digest reacts vigorously after being placed on the hotplate, temporarily remove it from the hotplate and/or moderate the vigour of the reaction by adding small amounts of deionised water. Replace digest solution on hotplate when reaction has moderated. When the digest solution stops reacting while on the hotplate (eg. typically effervescent bubbling has ceased, soil settles and supernatant clears), remove from hotplate. If the digest solution continues to react whilst on the hotplate, remove after 1 h has elapsed.
 - ii) For a digest that reacts only slowly or moderately while on the hotplate, remove only after reaction ceases. If the reaction on the hotplate is continuing after 1 h has elapsed, remove the digest solution from the hotplate.
 - iii) For a digest that showed no obvious reaction after peroxide addition prior to being put on the hotplate and that failed to subsequently react while on the hotplate, remove from the hotplate after 30 min has elapsed.

e) Peroxide decomposition step

- Add 1 mL of 6.30 × 10⁻³ M CuCl₂·2H₂O (400 mg Cu/L) to digest solution to decompose any remaining peroxide.
- Return digests to hotplate and allow samples to reach between 80 and 90 °C (by which time peroxide decomposition should be occurring). Remove digest from hotplate when peroxide decomposition has ceased (eg. effervescent bubbling has stopped and usually supernatant has cleared). If peroxide decomposition has not ceased after 30 min, then remove digest solutions

from hotplate. Maintain digest volume at between 45 and 50 mL during this time (adding deionised water as necessary).

- Where the volume of the digest is >50 mL after peroxide decomposition (eg. in samples that underwent the carbonate modification), decrease volume to between 45 and 50 mL on the hotplate.
- When samples have cooled to near room temperature, quantitatively transfer beaker contents to a titration vessel using 30 mL of ~2.66 M KCl.
- Give the digest beaker a final rinse with no more than 5 mL of deionised water (into titration vessel), giving a suspension of approximately 80 mL, 1 M in KCl (ie. for 2 g samples a final soil:solution extraction ratio of 1:40).

f) Measurement of TPA

All samples with pH <5.5 are first titrated to pH 5.5 with either 0.05 M or 0.25 M NaOH (depending on the initial pH of the suspension – see below). Subsequently all samples are titrated to pH 6.5 using 0.05 M NaOH.

- Measure and record pH of suspension (TPA pH) using a suitably calibrated pH meter and electrode prior to TPA titration. Use the appropriate option below, depending on the measured (TPA pH).

Note: The TPA pH should be similar to the pH_{OX} except where the carbonate modification is carried out. There will be a slight difference due to the addition of KCl solution and the dilution associated with this.

- i) If pH is ≤ 3 , titrate with stirring to pH 5.5 using standardised ~0.25 M NaOH (c_1) and record volume of titre (V_4).
- ii) If pH is >3 but ≤ 5.5 , titrate with stirring to pH 5.5 using standardised ~0.05 M NaOH (c_2) and record volume of titre (V_5).
- iii) If pH is >5.5 but <6.5, go to final oxidation step.
- iv) If pH is ≥ 6.5 then TPA (**Method Code 23G**) is zero. Do not perform final oxidation.

Note: The TPA pH may possibly be ≥ 6.5 , despite the pH_{OX} lying between 5.5 and 6.5. Also the TPA pH may also be ≥ 6.5 , despite an HCl titration being performed (in the carbonate modification) if recovery of carbonates is incomplete.

- If the blank has a pH <5.5, titrate it to pH 5.5 using 0.05 M NaOH and record titre volume (V_7).
- Perform a ‘final oxidation’ on all samples where pH is now <6.5 by adding 1 mL of 30% H_2O_2 (that has been adjusted to pH 5.5 with dilute NaOH solution). Allow pH to stabilise then measure.

Note: The addition of 1 mL of 30% peroxide converts any Fe^{2+} to Fe^{3+} ensuring complete conversion of iron to $Fe(OH)_3$ during titration.

- While stirring, titrate those suspensions with pH <6.5 to pH 6.5 using 0.05 M NaOH (c_2). Record molarity (c_2) and titre (V_6 mL) of alkali added to reach pH 6.5. For blanks record corresponding titre (V_8) and molarity (c_2).

Note: The titre volume depends somewhat on the rate of titrant addition during titration. When titrating manually, the following procedure may be used as a guide. Add titrant at a slow constant rate (eg. drop-wise every 1 to 2 s), allowing the increase in pH to keep pace with NaOH addition. When within 1 pH unit of endpoint (eg. pH >5.5), cease titrant addition

and allow pH to stabilise. Recommence titration at a slower rate and bring pH to just below endpoint (eg. 6.3), recording pH and corresponding volume of titrant at this point. Titrate to endpoint (pH 6.5) and wait for 20 s. If pH drops by >0.1 pH units in this time (and pH endpoint was not originally overshoot by more than 0.1 pH units) titrate back up to pH 6.5 and wait 20 s. Repeat process until pH remains above 6.5 after 20 s. Titrations may take as long as 5 min, depending on how far the pH dropped in the double oxidation.

If an auto-titrator is being used, titrant addition should be dynamic (ie. with titrant volume increment decreasing as the end point is approached) and the manufacturer's operator's manual followed.

- Retain the titrated suspension for subsequent determination of peroxide sulfur (S_p), calcium (Ca_p) and magnesium (Mg_p) determination.

g) Calculation of TPA without carbonate modification

- Calculate TPA result (to pH 6.5) and express as mol H^+ /t of soil (**Method Code 23G**) [where m_2 in g, concentrations (c_x) in mol/L, and titres (V_x) in mL].

If **0.25 M** and **0.05 M NaOH** are used:

$$\text{TPA (mol } H^+/t) = [(V_4 \times c_1) - (V_7 \times c_2) + (V_6 - V_8) \times c_2] \times (1000/m_2)$$

For **0.25 M NaOH** (c_1) and **0.05 M NaOH** (c_2), zero blank, suggested weights, volumes this simplifies to:

$$\text{TPA (mol } H^+/t) = (125 \times V_4) + (25 \times V_6)$$

If only **0.05 M NaOH** is used:

$$\text{TPA (mol } H^+/t) = [(V_5 + V_6 - V_7 - V_8) \times c_2] \times (1000/m_2)$$

For **0.05 M NaOH** (c_2), zero blank, suggested weights, volumes this simplifies to:

$$\text{TPA (mol } H^+/t) = 25 \times (V_5 + V_6)$$

h) Calculation of Excess Acid Neutralising Capacity (ANC_E) or TPA with carbonate modification

- For those samples that underwent the carbonate modification to the method, calculate HCl titration (to pH 4) and express as mol H^+ /t.

$$\text{HCl titration (mol } H^+/t) = V_3 \times c_3 \times (1000/m_2)$$

For **0.5 M HCl** (c_3) and suggested weight this simplifies to:

$$\text{HCl titration (mol } H^+/t) = 250 \times V_3$$

Note: For some soils that have undergone the HCl-titration and second peroxide digest steps, a TPA titration may be required (ie. TPA pH <6.5). Where the HCl-titration result is greater than the NaOH titration (or TPA is zero) this indicates an excess acid neutralising capacity.

- Calculate excess acid neutralising capacity (a- ANC_E) in mol H^+ /t (**Method Code a-23Q**)

$$\text{a-}ANC_E = \text{HCl titration} - \text{TPA titration (mol } H^+/t)$$

If **0.25 M** and **0.05 M NaOH** has been used:

$$\mathbf{a-ANC_E (mol H^+/t) = [V_3 \times c_3 \times (1000/m_2)] - [(V_4 \times C_1) - (V_7 \times C_2) + (V_6 - V_8) \times C_2] \times (1000/m_2)}$$

If **only 0.05 M NaOH** has been used:

$$\mathbf{a-ANC_E (mol H^+/t) = [V_3 \times c_3 \times (1000/m_2)] - [(V_5 + V_6 - V_7 - V_8) \times C_2] \times (1000/m_2)}$$

Note: When the net result of this calculation is positive, then the sample has intrinsic excess acid neutralising capacity and the TPA is reported as zero.

Note: If the result of either of these calculations is negative, then a-ANC_E is reported as zero and the absolute value is reported as TPA. If the result is zero then both a-ANC_E and TPA are zero.

To report result in conventional ANC units (ie. equiv. %CaCO₃):

$$\mathbf{ANC_E = a-ANC_E/199.8 (Method Code 23Q)}$$

Note: It is theoretically possible that a net positive TPA can result in soils that have been titrated with HCl. This would occur if the number of moles of NaOH added during titration to pH 6.5 is greater than the number of moles HCl added during titration to pH 4. In such a situation ANC_E is zero and TPA is calculated by subtracting the HCl-titration result from the TPA titration result (in mol H⁺/t).

i) Peroxide digest, sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P) determination

- ❑ Quantitatively transfer contents of titration vessels to tared or weighed beakers with deionised water.
- ❑ Make suspensions to 400 mL (V) and 0.2 M in KCl with deionised water on a balance. The weight of suspensions should be 403.5 g plus the weight of original soil. (This final volume may be varied to suit your technique and/or equipment used for determining sulfur).
- ❑ Stir suspensions to homogenise and filter through thick, medium speed high retention paper.
- ❑ Filter entire suspension and retain filter paper if residue analysis is to be performed.
- ❑ Analyse filtrate for sulfur (S₃) (mg S/L) by ICP-AES or using other suitable analytical instruments and appropriate range of standards. Determine sulfur on the blank (S₄). Indicate which sulfur finishing step was employed, using the codes from Table F1.3.
- ❑ Calculate peroxide sulfur (S_P, **Method Code 23D**) as %S on a dry soil weight basis as shown:

$$\mathbf{S_P (\%) = (S_3 - S_4) \times (V/m_2)/10\ 000 [V \text{ in mL and } m_2 \text{ in g}]}$$

When there is zero blank, m₂ = 2 g, and V = 400 mL this simplifies to:

$$S_P (\%) = S_3/50$$

- ❑ Calculate peroxide calcium (Ca_P, **Method Code 23W**) and peroxide magnesium (Mg_P, **Method Code 23T**) in a similar fashion using appropriate instrumentation (eg. AAS, ICP-AES).

Note: If the pH_{KCl} is <4.5 (or jarosite has been recorded) then a residue analysis for sulfur needs to be performed (part 'j'). When performing residue analysis first take a suitable volume of filtered solution for sulfur (S_P) and cation (Ca_P and Mg_P) analysis, then continue to filter entire soil suspension. When filtering is complete, wash filter paper with 40 mL 1 M KCl and then with sufficient water to ensure all soluble and adsorbed sulfate has been washed from the filter paper. Peroxide residue acid soluble sulfur (S_{RAS}) can be measured if the filter paper is extracted overnight (16 h) with 4 M HCl.

j) Peroxide digest, residual acid soluble sulfur (S_{RAS})

- ❑ After first taking a suitable volume of filtered solution for sulfur (S_P) and cation (Ca_P and Mg_P) analysis, then continue to filter entire soil suspension (transferring all soil residue to the filter paper).
- ❑ When filtration is complete, wash filter paper with 2 x 10 mL aliquots of 1 M KCl then sufficient deionised water (eg. 4 x 10 mL) to ensure that all soluble and adsorbed sulfate has been washed from the filter paper.
- ❑ When washing is complete, place filter paper (containing washed soil residue) into suitable extraction bottle and add 80 mL of 4 M HCl. Extract overnight (16 ± 0.5 h) on reciprocal or end-over-end shaker.
- ❑ Filter mixture using thick, medium speed, high retention filter paper (or decant and centrifuge) to obtain a clear extract.
- ❑ Determine residual acid soluble or 'jarositic' sulfur (S_{RAS} , **Method Code 23R**) using a suitable technique (eg. ICP-AES) and range of standards. Report S_{RAS} in units of %S on an oven-dry soil basis.

Step 3. Calculation of Titratable Sulfidic Acidity (TSA), Peroxide Oxidisable Sulfur (S_{POS}) and Reacted Calcium (Ca_A) and Magnesium (Mg_A)**k) Titratable Sulfidic Acidity (TSA)**

Titratable sulfidic acidity is the acidity attributed to the complete oxidation of all the sulfidic compounds in the soil by hydrogen peroxide. Any existing acidity or TAA from oxidation prior to sampling is not included. TSA is calculated as:

$$TSA = TPA - TAA \text{ (mol H}^+/\text{t)}$$

or

$$\text{Method 23H} = \text{Method 23G} - \text{Method 23F}$$

l) Peroxide Oxidisable Sulfur (S_{POS}) and Reacted Calcium (Ca_A) and Magnesium (Mg_A)

Peroxide oxidisable sulfur (S_{POS} , **Method Code 23E**) is the difference between the sulfur determined in the peroxide digest (S_P , **Method Code 23D**) and the sulfur extracted by 1 M KCl (S_{KCl} , **Method Code 23C**).

$$S_{POS} = S_P - S_{KCl} \text{ (\%)}$$

or

$$\text{Method Code 23E} = \text{Method Code 23D} - \text{Method Code 23C}$$

Reacted calcium (Ca_A , **Method Code 23X**) is the difference between the calcium determined in the peroxide digest (Ca_P , **Method Code 23W**) and the calcium extracted by 1 M KCl (Ca_{KCl} , **Method Code 23V**).

$$Ca_A = Ca_P - Ca_{KCl} \text{ (\%)}$$

or

$$\text{Method Code 23X} = \text{Method Code 23T} - \text{Method Code 23S}$$

Reacted magnesium (Mg_A , **Method Code 23U**) is the difference between the magnesium determined in the peroxide digest (Mg_P , **Method Code 23T**) and the magnesium extracted by 1 M KCl (Mg_{KCl} , **Method Code 23S**).

$$Mg_A = Mg_P - Mg_{KCl} (\%)$$

or

$$\text{Method Code 23U} = \text{Method Code 23W} - \text{Method Code 23V}$$

ACID NEUTRALISING CAPACITY, CARBONATE AND ALKALI CATION METHODS

CR Ahern, AE McElnea and LA Sullivan

Whilst methods for measuring carbonate content in soil are relatively well established, those for measuring acid neutralising capacity (ANC) are in a state of flux, requiring further development, including field validation. The difficulties associated with determining an accurate/realistic value for a soil's **effective** ANC have been discussed earlier in these Guidelines (see Sections A1.2, A2, A3.3). Most of the ANC methods that have been derived from either acid rock drainage or limestone analysis applications are based on soil digestion with added acid followed by back-titration of unreacted acid. The trend with these methods (in their application to soil) has been towards less vigorous digestion with less concentrated acid.

13. ACID NEUTRALISING CAPACITY BACK-TITRATION (ANC_{BT}) METHODS

13.1 CARBONATE RAPID TITRATION OF CaCO₃ EQUIVALENT – METHOD CODE 19A1

Introduction:

The rapid titration Method 19A1 described in Rayment and Higginson (1992) is applicable, though more dilute acid is required for ASS. This is a rapid titration procedure developed from the method of Piper (1944) as compiled by van Reeuwijk (1986). In this titration procedure, soil is treated with dilute HCl and residual acid is titrated. Results are referred to as 'CaCO₃ equivalent' since the reaction is not selective for calcite; other carbonates including dolomite will be included to some extent. It yields approximate values only.

Note: This method is not recommended for ASS as it uses 1 M HCl which has greater potential to react with or break down material including alumino-silicates not normally reacted with at pH above 5.5. This can result in a substantially inflated ANC leading to an underestimate of environmental risk.

13.2 ACID NEUTRALISING CAPACITY (ACID REACTED AND BACK-TITRATION) – METHOD CODE 19A2

Introduction:

This method is the preferred method if back-titration for determination of ANC in ASS materials is selected due to the less concentrated acid used in this method.

Reagents:

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity <5µS/cm.

Note: Solid NaOH is caustic and deliquescent and should be stored away from water. Dilute NaOH solutions absorb CO₂. Avoid unnecessary contact of this solution with the atmosphere. Solutions should be prepared fresh each day, or alternatively stored in apparatus capable of excluding CO₂ and standardised daily.

Standardised 0.10 M HCl (c₁): Prepare (1 L) by adding 10 mL of concentrated hydrochloric acid (31.5–33 % w/V) to 700 mL of deionised water with stirring then diluting to 1000 mL at 20 °C using deionised water. Standardise against disodium tetraborate decahydrate (Na₂B₄O₇·10H₂O) or recently

standardised 0.10 M NaOH solution. Calculate molarity of HCl solution (c_1). Where the concentration of the standardised HCl solution is not exactly 0.10 M then the exact calculated molarity should be used in calculations.

Note: Solutions of 0.1 M HCl made by diluting commercially available ampoules may also be used.

Standardised 0.1 M NaOH (c_2): Prepare (1 L) by dissolving $4.10 \text{ g} \pm 0.10 \text{ g}$ of NaOH pellets in CO₂-free deionised water, then diluting to 1000 mL at 20 °C using deionised water. Standardise against potassium hydrogen phthalate (C₆H₅O₄K) by accurately weighing (to 0.0001 g) $0.20 \text{ g} \pm 0.04 \text{ g}$ of dried potassium hydrogen phthalate into a container and dissolving in deionised water. Titrate phthalate solution with NaOH solution using a pH meter or appropriate pH indicator. Determine the equivalence point volume and calculate the molarity of the NaOH solution. Where the concentration of the standardised NaOH solution is not exactly 0.10 M, then the exact concentration of the NaOH should be used in calculations.

Note: It is acceptable to use standardised 0.25 M NaOH (eg. prepared for the TAA and TPA titrations) instead of 0.1 M, provided calculated are adjusted accordingly.

Potassium hydrogen phthalate (C₆H₅O₄K): Dry at 105 °C for 4 h and store in desiccator prior to use.

Sodium tetraborate (Na₂B₄O₇·10H₂O)

Calcium carbonate (CaCO₃): Dry at 105 °C for 4 h and store in desiccator prior to use.

Apparatus:

Analytical balance ($500 \text{ g} \pm 0.01 \text{ g}$ and $100 \pm 0.0001 \text{ g}$); 250 mL borosilicate ('pyrex') glass beakers or flasks; electric hotplate or steam bath (able to boil contents of beakers or flasks); fume hood; manual or automatic volumetric dispenser pipette (capable of dispensing 50mL); A-grade 25 mL volumetric pipette; auto-titrator or other appropriate titration apparatus (eg. pH meter, magnetic stirrer plate, teflon-coated magnetic stirrer bar and 2 x 10 mL A-grade 0.02 mL graduated burette or digital burettes of similar accuracy); titration vessel (varies depending on whether titrating manually or using an auto-titrator).

Procedure:

This procedure is based on that developed by Lewis and McConchie (1994) and modified by the use of weaker acid.

- ❑ Weigh 1.0 g of finely ground soil into a 250 mL flask and record mass (**m**).
- ❑ Add 50 mL of deionised water and 25 mL (V_{HCl}) of standardised 0.1 M HCl solution (c_1) to each flask.
- ❑ Prepare two blank samples containing only deionised water and acid.
- ❑ Prepare three reference samples containing 0.100 g of AR grade CaCO₃.
- ❑ Place flasks on a hotplate and allow to boil for two minutes, then cool to room temperature.
- ❑ Using a calibrated pH meter, check to see if the sample is acidic (pH <3). If the pH is ≥ 3 , add further 25 mL aliquots of 0.1 M HCl and repeat procedure until pH is <3.
- ❑ Titrate the unreacted acid in the flasks with standardised 0.1 M NaOH solution (c_2) to pH 7 with stirring using a pH meter. If titrating with an auto-titrator, transfer digested solution to titration vessel with a minimum quantity of deionised water and titrate to a pH 7 endpoint with standardised 0.1 M NaOH solution.
- ❑ Record the volume of NaOH (V_{B}) added.

Note: The volume of 0.1 M NaOH solution used for the blank (V_{BL}) should be 25.0 mL (if concentrations of HCl and NaOH are exactly 0.1 M). If exactly 0.1 g of $CaCO_3$ is used as the reference it should require 5.02 mL of 0.1 M NaOH solution.

Calculation:

- Determine the volume of acid consumed (V_A) by the sample as:

$$V_A = 25 - V_B \text{ [} V_B \text{ in mL].}$$

- Calculate the equivalent calcium carbonate content of the sample as:

$$\%CaCO_3 \text{ equivalent} = \frac{0.5004 \times V_A \text{ (mL)}}{m \text{ (g)}}$$

These calculations assume NaOH and HCl solutions of exactly 0.1 M, and a 25 mL volume titration for the blank (V_{BL}). If this is not the case, substitute into the equation below:

$$\%CaCO_3 \text{ equivalent} = \frac{5.0043675 \times [(V_{HCl} \times c_1) - \{V_B + (25 - V_{BL})\} \times c_2]}{m}$$

Note: The $CaCO_3$ reference samples should yield a value of $100 \pm 0.5\%$ $CaCO_3$ equivalent.

Note: The decreased acid strength compared to previous ANC_{BT} methods allows a lower detection limit of 0.05% $CaCO_3$ equivalent, but restricts the upper determination limit to ~10% $CaCO_3$ equivalent for a 1 g sample mass. For samples with higher equivalent % $CaCO_3$ contents (or those that are expected to be high), the quantity of acid used should be increased until an excess of acid is demonstrated by a $pH < 3$, or alternatively (and more easily) the sample weight decreased.

Notes:

The strength of the acid used in the digest of the ANC_{BT} is not sufficient to dissolve jarosite, which is a complication in analysing soil with retained acidity that have been limed (see Section A3.6c).

References:

Lewis DW, McConchie D (1994) 'Analytical Sedimentology'. (Chapman and Hall: New York)
 Piper CS (1944) 'Soil and Plant Analysis'. pp. 135–136. (University of Adelaide: Australia)
 van Reeuwijk LP (Ed.) (1986) 'Procedures for Soil Analysis'. pp. 21–2 (International Soil Reference and Information Centre: Wageningen)
 Rayment GE, Higginson FR (1992) 'Australian Handbook of Soil and Water Chemical Methods.' (Inkata Press: Melbourne)

14. CARBONATE CARBON CONTENT BY DIFFERENCE: LOSS OF CO₂ WITH ACID USING A COMBUSTION FURNACE – METHOD CODE 19C1

BE Monczko

Introduction:

Using a combustion furnace the difference between total carbon (C_T) and total organic carbon (C_{TO}) after mineral acid treatment, is determined, allowing an estimate of the inorganic carbon (C_{IN}) to be made. If this inorganic carbon is assumed to be carbonate, then C_{IN} can be converted to equivalent %CaCO₃ units and the result expressed as Carbonate Acid Neutralising Capacity (ANC_C), or converted to equivalent acid neutralising units (a- C_{IN}). The method has been derived from procedures in Nelson and Sommers (1982), Matejovic (1997), and Yeomans and Bremmer (1991).

Reagents:

Note: Unless otherwise specified, reagents should be of analytical reagent (AR) grade and deionised water of conductivity <5µS/cm.

5–6% Sulfurous acid (H₂SO₃)

Apparatus:

Combustion furnace and associated consumables (eg. sample boats and liners, calibrant standards etc); analytical balance (100 ± 0.0001 g); pasteur pipettes.

Procedure:

a) Total carbon (C_T) by combustion furnace (using an IR CO₂ detection system) – Method 6B4

- Weigh an appropriate mass (m_1) of finely ground sample (ie. ground to <75 µm) into combustion boat. The mass will depend on the carbon content of the soil and the range of the calibration curve used. Typically a mass of 0.5 g is used. For soil with a carbon content of <0.5% a larger sample mass is desirable and for those with a carbon content of >3.5% a lower sample weight is preferable.

Note: Selecting a very wide calibration range can compromise the accuracy of determinations, particularly for samples with very high and very low levels of carbon.

- Determine total carbon (C_T) as per manufacturer's instructions.

Note: Total sulfur (S_T) may be determined on the same sample on a carbon and sulfur analysing machine, provided a combustion catalyst has been added to the sample.

b) Total organic carbon (C_{TO}) – Method 6B5

- Weigh a separate sub-sample (~ 0.5 g) in a combustion boat containing a nickel liner and record the mass (m_2).
- In a fume hood, place the combustion boat on electric hotplate set at between 100 and 120 °C.
- Wearing appropriate safety gear (eg. laboratory coat, safety glasses) treat sample with sulfurous acid (5–6%) by adding slowly to boat using a Pasteur pipette, taking care to avoid excessive effervescence.

Note: Effervescence must not carry sample out of the boat.

- Repeat addition until there is no evidence of CO₂ evolution (eg. effervescence of sample)

- ❑ After acid pre-treatment, leave boat on hotplate until it is dry (eg. hotplate may be turned off after pre-treatment and the boats left there overnight to completely dry the sample).
- ❑ Analyse the treated sample using a combustion furnace, following the manufacturer's instructions.

Note: The acid treatment may not quantitatively remove dolomite.

c) Inorganic carbon (C_{IN})

Calculation:

- ❑ Calculate inorganic carbon (C_{IN})

$$C_{IN} (\%) = C_T - C_{TO}$$

Method Code 19C1 = Method Code 6B4 – Method Code 6B5

References:

- Matejovic I (1997) Determination of carbon and nitrogen in samples of various soils by dry combustion. *Communications in Soil Science and Plant Analysis* **28**, 1499–1511.
- Nelson DW, Sommers LE (1982) Total carbon, organic carbon and organic matter. In, 'Methods of Soil Analysis Part 2 Chemical and Microbiological Properties. 2nd Edition (Eds. AL Page, RH Miller and DR Keeney) pp. 539–579 (American Society of Agronomy, Soil Science Society of America Inc.: Madison, Wisconsin, USA)
- Yeomans JC, Bremner JM (1991) Carbon and nitrogen analysis of soils by automated combustion techniques. *Communications in Soil Science and Plant Analysis* **22**, 834–850.

15. ALKALI CATION (CALCIUM AND MAGNESIUM) METHODS

CR Ahern and AE McElnea

Determination of alkali cations (such as calcium and magnesium) is another means by which the acid neutralising capacity in soil may be estimated. The methods detailed here measure the extra calcium or magnesium that has been dissolved by peroxide digestion compared to that soluble in a 1 M KCl extract (ie. 'reacted' calcium and magnesium), or the difference in calcium and magnesium extracted by 4 M HCl and 1 M KCl (ie. net acid soluble calcium and magnesium). The implication is that this extra calcium and magnesium dissolved by peroxide or acid treatments is derived from carbonate, minerals, with their levels providing a surrogate estimate of the soil's acid neutralising capacity.

15.1 REACTED CALCIUM (Ca_A) AND MAGNESIUM (Mg_A) – METHOD CODES 23X AND 23U

Reacted calcium (Ca_A) is calculated from peroxide calcium (Ca_P) and KCl-extractable calcium (Ca_{KCl}) measurements as shown below:

$$Ca_A = Ca_P - Ca_{KCl}$$

or

$$\text{Method Code 23X} = \text{Method Code 23W} - \text{Method Code 23V}$$

Reacted magnesium (Mg_A) is calculated from peroxide magnesium (Mg_P) and KCl-extractable magnesium (Mg_{KCl}) measurements as shown below:

$$Mg_A = Mg_P - Mg_{KCl}$$

or

$$\text{Method Code 23U} = \text{Method Code 23T} - \text{Method Code 23S}$$

Commonly, Ca_A and Mg_A values reflect the amounts of 'insoluble' calcium and/or magnesium carbonates, oxides and hydroxides dissolved by the acid generated by the oxidation of sulfides in the peroxide digest. In soil with excess carbonates, Ca_A and Mg_A may underestimate actual carbonate contents unless the HCl-titration procedure in SPOCAS has been performed. These calcium and magnesium values can be converted to equivalent acid neutralising capacity (eg. a- Ca_A) assuming two moles of neutralising is provided per mole of calcium and magnesium.

Note: Mg_A results should be treated with some scepticism unless evidence for the presence of $MgCO_3$ or dolomite exists (eg. XRD evidence).

Note: ANC values calculated from reacted calcium and magnesium may give higher results than ANC estimated from C_{IN} measurements since the latter is specific to carbonates and does not measure acid neutralising provided by CaO, MgO or similar alkaline compounds.

Note: On some soil, calcium or magnesium silicates or primary non-neutralising minerals may contribute to the analysis particularly when the stronger acid extracts (4 M HCl) are used, giving an inflated measure of available acid neutralising reactions.

15.2 NET ACID SOLUBLE CALCIUM (Ca_{NAS}) AND MAGNESIUM (Mg_{NAS}) – METHOD CODES 19F1 AND 19G1

Net acid soluble calcium (Ca_{NAS}) is calculated from HCl-extractable calcium (Ca_{HCl}) and KCl-extractable calcium (Ca_{KCl}) measurements as shown below:

$$Ca_{NAS} = Ca_{HCl} - Ca_{KCl}$$

or

Method Code 19F1 = Method Code 20E – Method Code 23V

Net acid soluble magnesium (Mg_{NAS}) is calculated from HCl-extractable magnesium (Mg_{HCl}) and KCl-extractable magnesium (Mg_{KCl}) measurements as shown below:

$$Mg_{NAS} = Mg_{HCl} - Mg_{KCl}$$

or

Method Code 19G1 = Method Code 20F – Method Code 23S

Commonly, Ca_{NAS} and Mg_{NAS} values reflect the maximum amounts of ‘insoluble’ calcium and/or magnesium carbonates, oxides and hydroxides dissolved by HCl extraction. On some soil, calcium or magnesium silicates or primary non-neutralising minerals may contribute to the analysis particularly because of the strong acid (4 M HCl) used in the extraction, giving an inflated measure of available acid neutralising reactions. These result may best be used as part of an ABA with the chromium suite if non-carbonate forms of neutralising are suspected (see Section A2.2). The calcium and magnesium values can be converted to equivalent acid neutralising capacity (eg. a- Ca_{NAS}) if it is assumed that two moles of neutralising is provided per mole of calcium and magnesium.