Acid Sulfate Soils

Laboratory Methods Guidelines

Version 2.1—June 2004

Joint Project of
Queensland Acid Sulfate Soils Investigation Team (QASSIT), Queensland Department of Natural Resources, Mines and Energy (Qld NRM&E)
Southern Cross University (SCU)
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This document supersedes the chapter *Acid Sulfate Soils Laboratory Methods Guidelines* (Ahern *et al*. 1998) in the *Acid Sulfate Soil Manual 1998* (Stone *et al.* 1998).

DISCLAIMER

STATUS OF THESE GUIDELINES AND UPCOMING AUSTRALIAN STANDARDS

The SPOCAS method and its components, along with chromium reducible sulfur, acid volatile sulfur and acid neutralising capacity methods are currently being compiled in association with Standards

Australia with the intention of producing a united set of laboratory methods (in the form of Australian Standards) that will be applicable nationwide. Separate Standards are expected to be completed for analysis of wet samples and for dried samples.

At this stage, what is being proposed to Standards Australia is essentially that which is being proposed here. It is the intention that when the Australian Standards are issued that they will supersede and replace the methods herein. It is believed that there will be no substantial differences between these Guidelines and the Standards Australia methods.

These Guidelines will be updated periodically. Readers should either contact QASSIT directly, or visit the QASSIT web-site (http://www.nrme.qld.gov.au/land/ass) to ensure that they have the most recent version of the Guidelines.

REVIEWING AND UPDATING THE GUIDELINES

It is expected that these Guidelines will be updated from time to time to strengthen and refine the acid sulfate soil analytical methods as a result of experience and research. Any updates of the methods will aim to make them more effective tools for understanding the risks associated with ASS and improve the economics of providing dependable information for environmental management. Technical questions may be discussed with Col Ahern (e-mail Col.Ahern@nrm.qld.gov.au) or Angus McElnea (e-mail Angus.McElnea@nrm.qld.gov.au) or the authors of the individual methods (with an information copy for Col Ahern).

Any suggestions or recommendations should be directed in writing (with supporting data) to QASSIT. ASSMAC, QASSMAC and NatCASS will be responsible for organising, refereeing, reviewing and approving changes to the Guidelines, in consultation with other relevant professional organisations, industry and government departments. To receive future updates to the Acid Sulfate Soils Laboratory Methods Guidelines and information on new methods, please contact Kristie Watling (e-mail Kristie.Watling@nrm.qld.gov.au) or Angus McElnea (e-mail Angus.McElnea@nrm.qld.gov.au), QASSIT, Department of Natural Resources, Mines and Energy, Gate 2, Block C, 80 Meiers Road, Indooroopilly Qld 4068.

RISKS ASSOCIATED WITH CHEMICAL METHODS

There are risks inherent in performing any chemical method. It is the responsibility of any laboratory that performs chemical methods to minimise these risks (to persons, property and the environment) by putting in place appropriate safeguards and following good laboratory practice.

Relevant Materials Safety Data Sheets (MSDS) should be at hand for all chemicals and reagents used. Analysts must wear protective equipment appropriate to the method being performed (eg. as safety glasses/goggles/face shield/face mask, gloves, covered shoes, laboratory coat). Where indicated in particular methods, fume hoods that comply with appropriate Australian Standards need to be used due to the generation of toxic, carcinogenic and potentially flammable gases. Laboratories should provide adequate training of analysts in performing analytical methods including an explanation of the risks involved.

In these Guidelines, the attention of operators is drawn to the most acute risks associated with particular methods. However, the stated risks and warnings are not comprehensive and operators should be cognisant of other more general risks associated with particular methods (eg. from concentrated acids or alkalis). Finally, it is the duty of laboratories that any wastes generated from these methods are disposed of in an environmentally responsible manner.

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These Guidelines were circulated to over 180 people in Australia and overseas.

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SECTION A: OVERVIEW

1. BACKGROUND TO ACID SULFATE SOIL ANALYSIS

CR Ahern, AE McElnea and LA Sullivan

1.1 THE PURPOSE OF THE GUIDELINES

The *Acid Sulfate Soils Laboratory Methods Guidelines* set out the standard methods for routine laboratory analysis of existing acidity (ie. actual and retained acidity) and of the potential acid production from oxidation of iron sulfides in estuarine and coastal sediments that should be used to provide information for the assessment and management of acid sulfate soil (ASS). The Guidelines also recommend best practice methods in the sampling, handling and transport of soil samples.

These guideline methods are not the only tools available for assessing ASS. It is acknowledged that there are many more variations of these methods, plus more complex or costlier 'research methods' available for analysing ASS. Some of these other methods may be equally suitable or more appropriate in some circumstances. However, in order to develop assessment standards and formulate regulations, some standardisation of methodology is necessary. Therefore, unless otherwise negotiated initially with the approving authorities, the laboratory analysis results submitted as part of any site assessment or investigation should use at least one, and in many cases a combination, of the standard methods listed in these Guidelines.

Other methods may supplement the standard ones, but fuller explanations of any 'non-standard method', together with their interpretation and correlations with standard approaches will normally be necessary. Provided the submissions made are logical and based on rational soil science, sedimentological and geomorphological principles, assessors/regulators should be prepared to judge each submission on its merit.

a) Significant changes and developments since Laboratory Methods Guidelines, 1998 ASS Manual

These Guidelines have been expanded (in size) from the Chapter in the 1998 ASS Manual (Stone *et al*. 1998). To facilitate easier use, the Guidelines have been divided into a number of sections (detailed below):

- Section A: Overview
- Section B: Dried Samples
- Section C: Wet Samples
- Section D: Soil Physical Methods
- Section E: ASS Water Methods
- Section F: Codes
- Section G: Miscellaneous Research Methods
- Section H: Field Methods
- Section I: Appendix

As ASS research continues, there will be further revisions and/or additions to the methods described in these Guidelines. (Note: See also previous section on 'Reviewing and Updating the Guidelines'). A

greater emphasis is now placed on measuring existing acidity (including forms of iron and aluminium that contribute to acidity), particularly that derived from prior oxidation of reduced inorganic sulfur, since it is this acidity that may be exported in the next rainfall event. In contrast, reduced inorganic sulfur compounds such as pyrite represent a threat only if they are allowed to oxidise. (This statement is not intended to downplay the risk posed by oxidation of sulfides, which can be rapid when ASS are exposed).

Revised procedure/s are included for measuring actual acidity. Additionally, a method for estimating retained acidity (the 'less available' existing acidity) that may be released by hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, and other iron and aluminium hydroxy sulfates) is included. Such compounds do not necessarily require oxygen to hydrolyse and produce acidity, however for jarosite and natrojarosite, the rate at which acid is released is likely to be limited by their extremely low solubility.

The digestion procedure for peroxide-based methods has also been improved as a result of recent research (McElnea *et al*. 2002a, 2002b). This has improved recoveries, lessened the potential for jarosite formation and overcome potential sulfur and acid loss problems identified by Ward *et al*. (2002a, 2002b). **The improved *Suspension POCAS method (SPOCAS)* must now be used in place of the outdated POCAS and POCASm versions** (see Section B12). New result and method codes (eg. Method Code 23, see Section F, Table F1.2) have been added to distinguish SPOCAS results in databases from those results obtained using the previous POCAS or POCASm methods (Method Code 21).

In the 1998 Methods Guidelines, the chromium reducible sulfur (S_{CR}) method was a late addition as a 'Miscellaneous Research Method'. Due to considerable research (Sullivan *et al*. 1998, 1999, 2000) and experience with the method in a number of Australian laboratories, it is now firmly established as a relatively straight-forward routine method, albeit a method that does involve the use and production of very toxic chemicals. At present, it provides the most reliable and direct measure of reduced inorganic sulfur over the wide range of values encountered in ASS (provided that the optimum sample weight is used, McElnea *et al*. 2002a). The S_{CR} method is particularly recommended for measuring sulfide contents close to the action limits, and on soil with appreciable organic sulfur (see Section B6).

Some methods have been added for measuring carbonate content (Section B14) and acid neutralising capacity (Section B13), while less appropriate ones have been removed. A *fineness factor* (FF) has been introduced to account for variation in reactivity associated with the particle size of shell and other acid neutralising material. Miscellaneous 'Research methods' and soil physical methods (eg. soil moisture, bulk density) are detailed in separate sections to be included in a later version. A method for the quantification of 'total acidity' in acid sulfate waters (Section E1) will also be added in a later version.

With the development of new and/or improved methods, the Total Sulfur (S_T) and Total Oxidisable Sulfur (S_{TOS}) approaches have become less relevant and are appropriate only as screening methods. However they may still be used where laboratories can demonstrate that their equipment can provide sufficient accuracy both at low sulfur values (eg. below the action criteria[1]) and throughout the entire (large) range of sulfur values encountered in ASS analysis. (Note: Detections limits and reproducibilities for these techniques can be very instrument-dependent).

Standard analysis suites

To simplify assessment, particularly for development proposals, a number of general rules have been applied to selecting soil analyses to allow routine laboratories to provide a more effective service and to give regulators sufficient information to properly assess the proposed management plan based on complete laboratory data. These general rules have been translated into two standard analytical suites

[1] See the *Soil Management Guidelines* (Dear *et al*. 2002) for information about the acid sulfate soil texture-based action criteria.

for ASS. **At least one of two main suites of analyses will normally be required** for most acid sulfate soil situations:

- the ***chromium suite*** (Figure A2.2), or
- the ***SPOCAS suite*** (Figure A2.3).

—these are discussed in later sections.

Acid Base Accounting
A new section (Section A3) on acid base accounting for calculating **net acidity** has been included. It requires input of results from the Chromium suite or the SPOCAS suite. Other methods listed in these Guidelines (but which are not part of the Chromium or SPOCAS suites) may be used, but it will usually be necessary to justify departures from the main approaches (with additional explanations and interpretation of data provided, eg. to regulatory bodies). With the adoption of these Guidelines, **calculations for quantity of neutralising materials will need to be based on the net acidity from acid base accounting** (section A3).

Wet sample techniques
A separate section for the analysis of **wet samples** (Section C) will be included in a later version. Recent research (Sullivan and Bush 2000; Bush *et al*. 2002) has shown that substantial quantities of 'monosulfides' or acid volatile sulfides (AVS) can accumulate in drains, which if disturbed (eg. in drain maintenance, or in storm/flood events) can produce acidity and deoxygenate water, with disastrous environmental consequences. Proper sampling and storage of monosulfide-containing samples prior to their analysis is critical and they must be analysed wet. Methods for measuring AVS and elemental sulfur in wet sediments are therefore contained in a discrete section (Section C) of these Guidelines.

b) Summary

Identification, and assessment of the distribution and severity of acid sulfate soils is the first step in land use assessment. Because acid sulfate soils are highly variable and have extremely dynamic characteristics, identification in the field and quantification of potential hazards can be extremely difficult. Therefore, the identification and assessment of acid sulfate soils is highly dependent on appropriate appraisal of these soils by field survey, field and laboratory analysis, and sound interpretation of the results.

The number of laboratory analyses undertaken for any proposal will depend on the level of risk that it represents, which will be a function of the size and type of the proposed disturbance, the presence of any existing and/or potential acidity, as well as other soil characteristics. The sampling and analysis program should provide sufficient information to ensure the proposal can be managed in an ecologically sustainable manner. Other guidelines exist detailing the amount of sampling required for ASS disturbances, eg. *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998* (Ahern *et al*. 1998).

1.2 CHEMICAL PROPERTIES OF ACID SULFATE SOIL

To interpret the results from analysis of ASS, it is necessary to have at least a rudimentary knowledge of the chemical processes involved. Some fundamental processes and properties of acid sulfate soil, particularly with regard to iron sulfides and pyrite (FeS_2) oxidation are summarised below.

a) Oxidation of pyrite

Potential acid sulfate soils (PASS) are typically waterlogged soils, rich in pyrite, which have not been oxidised. Any disturbance which exposes PASS to the air (oxygen) can lead to the development of

extremely acidic soil layers or horizons with field pH values of ≤4. These highly acidic soil horizons (with pH ≤4) are termed actual acid sulfate soils (AASS). Actual and potential acid sulfate soils can occur together in the same profile, with actual ASS typically overlying potential ASS. Commonly, in the zone of oxidation, AASS (ie. soil with pH ≤4) may still have reserves of unoxidised sulfides (ie. potential sulfidic acidity).

The mechanism by which the oxidation of pyrite is initiated is not comprehensively understood. One mechanism suggests that the initial step in pyrite oxidation is the production of elemental sulfur and ferrous ion, 'Fe^{2+}' (White and Melville 1993):

$$FeS_2 + {}^1/_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2S^0 + H_2O \quad (1)$$

The elemental sulfur is then oxidised to sulfate and acid (ie. sulfuric acid):

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \quad (2)$$

Other mechanisms for the oxidation of pyrite exist (eg. McKay and Halpern 1958, Singer and Stumm 1970, Moses *et al*. 1987, Luther III 1987) and are reviewed in Evangelou (1995) and Evangelou and Zhang (1995).

The conversion of pyrite to ferrous ion and sulfate can be written as:

$$FeS_2 + {}^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1) + (2) = (3)$$

The soluble ferrous ion may then be oxidised to ferric ion, Fe^{3+}:

$$Fe^{2+} + {}^1/_4O_2 + H^+ \rightarrow Fe^{3+} + {}^1/_2H_2O \quad (4)$$

If the pH is greater than 4, then various pH-dependent precipitation reactions may occur, one of which is the precipitation of ferric hydroxide and the liberation of more acid in a reaction termed hydrolysis:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+ \quad (5)$$

If equations 4 and 5 are added together, the net result of the oxidation of ferrous iron is the production of 2 moles of acidity per mole of ferrous iron.

$$Fe^{2+} + {}^1/_4O_2 + {}^5/_2H_2O \rightarrow Fe(OH)_3\downarrow + 2H^+ \quad (4)+(5) = (6)$$

If the pH is less than 4, Fe^{3+} can remain in solution. The dissolved Fe^{3+} greatly accelerates the oxidation process of pyrite (by a rapid electron-transfer mechanism) and does not require oxygen to oxidise pyrite:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

The reaction can result in considerable acid production when existing ASS containing Fe^{3+} are re-flooded or buried under water without neutralising the existing acidity. This is because oxidation reactions (such as the oxidation of pyrite by ferric ion, see Eqn 7) do not necessarily need oxygen to occur. The notion that oxygen must be present for pyrite to oxidise is a popular misconception. Some initial oxidation is required to produce ferric ion, but once it is present, exclusion of oxygen alone may not prevent further acid generation until all ferric ion is consumed.

However, if the buried material is completely denied oxygen, the oxidation process eventually ceases when all Fe^{3+} is consumed. Generally, oxygen is required to produce more Fe^{3+} by Eqn 4. So,

although some further oxidation can occur on burial (and produce additional acid), this management approach is still a better option than leaving material untreated and exposed to oxygen, where ultimately all acid potential may be realised.

> *Note: Another possible source of acidity in ASS that have been buried can be from hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, schwertmannite and other iron and aluminium hydroxy sulfates).*

The soluble ferrous ion, Fe^{2+} (produced in Eqns 1, 3 or 7) can easily be transported downstream where the following reaction (Eqn 8) removes dissolved oxygen from the water during the oxidation process to produce more acid:

$$Fe^{2+} + {}^{1}/_{4}O_2 + {}^{3}/_{2}H_2O \rightarrow \underset{\text{(goethite)}}{FeO.OH\downarrow} + 2H^{+} \quad (8)$$

(*Various forms of iron oxy-hydroxides can precipitate, depending on pH*).

The **overall equation for the complete oxidation of pyrite** can be written as:

$$FeS_2 + {}^{15}/_{4}O_2 + {}^{7}/_{2}H_2O \rightarrow Fe(OH)_3\downarrow + 2SO_4^{2-} + 4H^{+} \quad (9)$$

The prediction of the maximum theoretical acid production from reduced inorganic sulfur, peroxide oxidisable sulfur, or total oxidisable sulfur analysis is based on the stoichiometry of Eqn (9) (ie. one mole of pyrite ultimately produces 4 moles of (H^+) acidity). However, there are many pathways for acid production and removal of products where the ultimate result is not that of Eqn (9).

b) Iron oxidation products

There are characteristic iron oxidation reactions that are frequently associated with the development of actual acid sulfate soils and the transport of acidic leachate (White and Melville 1993). In streams for example, the secondary oxidation of Fe^{2+} can produce characteristic iron oxy-hydroxides flocs, usually reddish or yellowish brown in colour (eg. goethite, FeO.OH) (Eqn 8). The oxidation of Fe^{2+} and hydrolysis of Fe^{3+} can liberate large amounts of acid, often a significant distance away from the oxidation of pyrite in the acid sulfate soil (Eqns 4 and 5). Many other products of iron sulfide oxidation are also observed in the soil, such as the characteristic yellow mottles of jarosite, $KFe_3(SO_4)_2(OH)_6$, or natrojarosite $NaFe_3(SO_4)_2(OH)_6$, minerals that typically form at or below pH 3.7 under strongly oxidising conditions (White and Melville 1993). Another iron hydroxy sulfate mineral that is increasingly being found in ASS areas is schwertmannite [$Fe_8O_8(OH)_6(SO_4)$]. Such minerals can act as a store of acidity which can be slowly released on hydrolysis, without the need for oxygen.

c) Jarosite, and iron and aluminium hydroxy sulfate compounds

Jarosite, $KFe_3(SO_4)_2(OH)_6$, is an acidic by-product of ASS oxidation commonly found in disturbed or drained ASS. Its formation (Eqn 10) represents incomplete hydrolysis of Fe^{3+} during the oxidation of pyrite (Dent 1986):

$$FeS_2 + {}^{15}/_{4}O_2 + {}^{5}/_{2}H_2O + {}^{1}/_{3}K^{+} \rightarrow {}^{1}/_{3}KFe_3(SO_4)_2(OH)_6 + {}^{4}/_{3}SO_4^{2-} + 3H^{+} \quad (10)$$

Jarosite is relatively insoluble and most stable at a pH between 3 and 4, though it can persist at higher pH under dry conditions. In moist environments, jarosite slowly decomposes (usually by hydrolysis) releasing iron and acid into waterways, and is often a major source of acidity in waterways draining areas of ASS have been disturbed sometime in the past. One mole of jarosite releases 3 moles of acidity (as per Eqn 11):

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3\downarrow + 2SO_4^{2-} + 3H^+ + K^+ \quad (11)$$

Natrojarosite, $NaFe_3(SO_4)_2(OH)_6$, an insoluble hydroxy sulfate mineral similar to jarosite (but with Na^+ replacing K^+ in the mineral structure), also provides 3 moles of acidity on hydrolysis:

$$NaFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3\downarrow + 2SO_4^{2-} + 3H^+ + Na^+ \quad (12)$$

Many sparingly soluble sulfate salts of iron and aluminium which can release acid on hydrolysis may be present in AASS.

By way of example, basaluminite, $Al_4(OH)_{10}SO_4$, is an aluminium hydroxy sulfate mineral that can release acidity by hydrolysis as pH rises (as shown by Eqn 13):

$$Al_4(OH)_{10}SO_4 + 2H_2O \rightarrow 4Al(OH)_3 + SO_4^{2-} + 2H^+ \quad (13)$$

The S_{POS} and S_{CR} methods do not measure acidity retained in these iron or aluminium hydroxy-sulfate compounds. However, the SPOCAS method can provide an estimate of these sulfates if the digested soil residue is extracted with 4 M HCl to calculate S_{RAS} (or residual acid soluble sulfur) (**Method Code 23R**). Alternatively, the difference between 4 M HCl extractable sulfur (S_{HCl}) and 1 M KCl extractable sulfur (S_{KCl}) (ie. the net acid soluble sulfur or S_{NAS}, **Method Code 20J**) can also be used to estimate the amount of iron or aluminium hydroxy-sulfate compounds present.

Note: Titratable Actual Acidity (TAA) and Titratable Peroxide Acidity (TPA) methods do not quantitatively recover retained acidity from jarosite (McElnea et al. *2002b), despite a widely held view to the contrary.*

d) Existing acidity

Existing acidity in ASS includes '**actual**' acidity and '**retained**' acidity. Actual acidity is largely readily soluble and exchangeable acidity measured in the laboratory by titration of a 1 M KCl suspension and is termed Titratable Actual Acidity (TAA) (**Method Code 23F**). Retained acidity is the acidity stored in largely insoluble compounds such as jarosite and other iron and aluminium sulfate minerals, which tends not to be measured by the TAA titration. These 'insoluble' sulfur compounds can be extracted by 4 M HCl and then the sulfur determined. The difference between the sulfur in the HCl extraction (S_{HCl}) and sulfur in the KCl extraction (S_{KCl}) is attributed to these acid-producing sulfur compounds and is referred to as retained or 'net acid soluble' sulfur (S_{NAS}) in these Guidelines. The retained or net acid-soluble sulfur **acidity** (a-S_{NAS}) can be estimated from S_{NAS} by assuming 1 mole of net acid-soluble sulfur produces 3 moles of acidity (as is the case for jarosite or natrojarosite) (See Sections A3.4 and F1–6 for explanation and calculation). Alternatively, a 4 M HCl extraction performed on the washed soil residue after peroxide digestion gives the residual acid soluble sulfur (S_{RAS}) which can also be used to estimate retained acidity. These retained forms of existing acidity are held transiently in the soil and may be subject to slow re-mobilisation by wetting and drying, or if geochemical conditions change (eg. as a consequence of liming, or re-flooding with brackish water, etc.).

While on a 'per weight' basis, jarosite is not as acid-producing a mineral as pyrite (eg. in PASS, or AASS with reserves of pyrite), in disturbed sites substantial crusts of jarosite and similar minerals may form on soil surfaces, making acidity from jarosite an important issue in such cases.

e) Monosulfides

Modern sediments may contain reactive reduced sulfur phases (such as iron 'monosulfides') that oxidise readily on contact with air. Iron monosulfides (≈ 'FeS') are often associated with organic-rich

new sediments, drains and lake bottoms, and oxidise rapidly when exposed to oxygen. These monosulfides include 'amorphous FeS', mackinawite (≅ FeS) and greigite (≅ Fe_3S_4) (Bush and Sullivan 1997). These compounds are often referred to as acid volatile sulfides (or AVS). Due to their high reaction rates in air, if their contents in sediments are to be accurately measured then these samples require specialised sampling and treatment[2], and should not be dried prior to analysis. The Acid Volatile Sulfur (S_{AV}) method (**Method Code 22A**) should be used to analyse for these compounds and sequentially chromium reducible sulfur to measure the remaining reduced inorganic sulfur compounds. As acid volatile sulfur measurements are made on wet samples, a moisture determination on another sub-sample is necessary to convert the result to a dry weight basis. Normally analyses performed using small weights of wet sample need to be conducted at least in duplicate.

> *Note: Most of the routine laboratory methods in these Guidelines are designed primarily to determine pyrite sulfur. Most calculations are based on the assumption that 'non-sulfate' sulfur is present as iron disulfide (FeS_2). The presence of monosulfides with variable iron to sulfur ratios complicates predictions using the common stoichiometric calculations. However, monosulfides are usually present in only minor amounts in most acid sulfate soils (Bush and Sullivan 1998). Nevertheless, amounts can be appreciable in bottom sediments of rivers, lakes and drains (Sullivan and Bush 2000).*

f) Acid neutralising capacity of soil material

The acid neutralising capacity (or ANC) is a measure of a soil's inherent ability to buffer acidity and resist the lowering of the soil pH. A variety of definitions for ANC and methods for its determination exist in the literature. Acid buffering in the soil may be provided by dissolution of calcium and/or magnesium carbonates (eg. shell), cation exchange reactions, and by reaction with the organic and clay fractions. Additionally, other soil minerals can provide some neutralisation of acid, the amount dependent on particle size and degree of weathering. The effectiveness of these buffering components in maintaining soil pH at acceptable levels (eg. pH 6.5–9.0) will depend on the types and quantities of clay minerals in the soil, and on the type, amount and particle size of the carbonates or other minerals present.

> *Note: Exo-skeletons of fossilised marine micro fauna (eg. foraminifera) can also be a source of carbonate or neutralising compounds in certain soils, which may not be visible to the naked eye.*

The presence of carbonates, in excess of the potential acidity held by sulfides, does not necessarily prevent soil acidification if the carbonates' acid buffering is not readily or rapidly available (eg. if it is locked up in shells, or as unreactive coarse fragments). Formation of insoluble or sparingly soluble surface coatings (eg. of iron oxides, gypsum, etc.) can also limit the neutralising ability and reactivity of calcium carbonate. It is extremely important to know the *in situ* form and distribution of the carbonates in the sediment to enable a correct interpretation of analytical results and the choice of appropriate management techniques. It should be noted that normal laboratory soil preparation (especially the grinding process) affects the fineness and reactivity of shell, yielding an analytical acid neutralising capacity in excess of that which would normally be available from the soil *in situ*.

Finely divided $CaCO_3$ (eg. agricultural lime) is commonly used as a source of neutralising capacity. The reaction of calcium carbonate with the acid produced from pyrite oxidation can result in precipitation of calcium sulfate (usually gypsum) and the generation of carbon dioxide, though the

[2] If specialised sampling and treatment is not used then it is highly likely that partial or complete oxidation of monosulfides has taken place, producing some acidity and elemental sulfur. Therefore in addition to S_{AV} and S_{CR}, a measure of pH (pH_{KCl}) and, if necessary, of actual acidity (TAA) is needed on AVS-containing sediments that have not been treated appropriately.

neutralisation product (gypsum) is sparingly soluble in water (ie. 2.6 g/L). The complete reaction is as follows:

$$CaCO_3 + 2H^+ + SO_4^{2-} + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \quad (14)$$

1 mole $CaCO_3$ will theoretically neutralise 2 moles H^+ (1 mole $CaCO_3$ = 100.0873 g)

1 mole H_2SO_4 contains 2 moles H^+ (1 mole H_2SO_4 = 98.0795 g)

Thus, on a weight basis, 1 g H_2SO_4 requires (100.0873/98.0795) or 1.0205 g of pure $CaCO_3$ to totally neutralise it.

> *Note: An **excess** of calcium carbonate is always required, as this reaction does not go to completion at near-neutral or alkaline pH values (eg. pH >6.5) (Rose and Daub 1994; Nicholson* et al. *1988) due to the equilibrium with bicarbonate ions (HCO_3^-). Ultimately, this bicarbonate provides buffering against formation of very low pH (<4), but in order to keep pH values around neutral, excess calcium carbonate is required. Ward* et al. *(2002c) documented that for certain acid sulfate soils, oxidation of pyrite may be quicker in soil limed at less than the calculated stoichiometric rate compared to unlimed ASS. This reinforces the need for safety factors of at least 1.5 to 2. Coarse-textured neutralising material may require much larger safety factors.*

In many of the acid sulfate soils in Australia the amounts of shell deposits, carbonates or natural clay buffering capacity are **insufficient** to neutralise the acid produced by pyrite oxidation (White and Melville 1993). However, 'self-neutralising' ASS are not uncommon in northern and central coastal Queensland (eg. East Trinity Cairns; Latham *et al*. 2002) particularly where fine shell and coral associated with the Great Barrier Reef detritus/debris can occur. Recent studies in southern Australia (eg. Merry *et al*. 2003) have found areas of ASS associated with deposits of powdered shell or carbonate, particularly in areas influenced by erosion of naturally occurring limestone (eg. the erosion of limestone cliffs common on coastlines adjacent to the Southern Ocean).

g) Soil texture

Soil texture is an important factor that influences the acid buffering capacity of the soil. For example, in pyritic sandy deposits, in the absence of significant quantities of shell material there is little acid-buffering capacity due to a lack of cation exchange sites on the soil minerals (which are typically highly weathered). Conversely, clay size minerals commonly have a greater acid buffering capacity than sands. 'Action criteria' which trigger the need for management of acid sulfate soils are linked to three broad texture groups, as acid-buffering capacity generally increases, from little or none in sands to higher levels in heavy clays. Recent data from Southern Cross University suggests that the action criteria for peat ASS materials should be the same as those for sandy textured materials (Sullivan *pers. comm.*).

> *Note: Soils in the same broad texture categories can have substantially different acid-buffering capacities, depending on the mineralogy of the soil. A proponent may be able to provide the necessary evidence to show that their particular soil(s) has a greater buffering or neutralising ability than acid producing potential.*

1.3 COMPLEXITY OF ASS AND ASSOCIATED ANALYSES

The main aim of 'static' laboratory tests is to provide realistic, cost-effective estimates of *existing acidity* and predict future acid generation from oxidation of sulfides (ie. *potential sulfidic acidity).* Affordability is a key consideration, given the variable nature of acid sulfate soils, both spatially and

with time. Thus a balance needs to be struck between conducting highly detailed and exact analyses on a limited number of samples and the need for the analysis of a sufficient number of samples to adequately characterise a site.

Laboratory testing also aims to predict the amount of neutralising agent required (including safety factors) to prevent any future soil acidification under any conceivable conditions and hence avoid the export of acid, iron, aluminium and heavy metals into the receiving environment.

'Static' laboratory tests cannot be expected to *accurately* predict how soils will perform in any particular environment or climate, but do provide an indication of their probable behaviour. The use of more time-consuming 'kinetic' or 'temporal' testing (eg. over a period of a few months to several years, using incubation or leaching column approaches) is likely to give a better estimate of the ultimate behaviour of ASS over time. However, such tests are extremely costly and not likely to be used extensively, other than for large-scale projects or research (eg. McElnea and Ahern 2000a). Ultimately, it is difficult to predict how a large volume of ASS will behave over time in a particular environment. Temperature, rainfall, porosity, oxygen supply, wetting and drying regimes, pH, hydraulic conductivity, soil texture, sulfide content, sulfide crystal size, bacteria, coatings, soil minerals, neutralising material, shell size and other factors combine to control the ultimate rate of oxidation of sulfides, the by-products formed and the extent of acidification (if any) in the soil. The static tests are designed to ensure that under any feasible management regime soils will not produce net acidity if they have been ameliorated at dosing rates calculated from these tests and using appropriate safety or fineness factors.

The range of oxidation states of sulfur (–2 to +6) in sulfur minerals and the variety of oxidation products present makes the analysis of sulfur components in ASS complicated. Superimposed on the complex sulfur chemistry of ASS is the chemistry of acid generation and the by-products generated by this acid (eg. iron, manganese and aluminium species). In addition, these species' subsequent interaction with and neutralisation within the soil matrix further increases the complexity of ASS analysis (McElnea and Ahern 2000b). Hydrolysis of iron and aluminium species can be a major source of acidity (eg. Eqns 5, 11, 12 and 13). Only some of the reactions of acid sulfate soils are summarised in Section A1.2; there are many more reactions and compounds that occur in ASS.

It is clear that sulfur in soil can exist in many forms:

- organic compounds
- readily soluble sulfates (eg. of sodium, potassium and magnesium)
- sparingly soluble sulfates (eg. gypsum, $CaSO_4.2H_2O$)
- 'almost insoluble' sulfate minerals (eg. jarosite, $KFe_3(SO_4)_2(OH)_6$; and natrojarosite $NaFe_3(SO_4)_2(OH)_6$ and other iron or aluminium sulfates)
- disulfide minerals (eg. pyrite or marcasite, FeS_2)
- monosulfide minerals (eg. greigite, Fe_3S_4; mackinawite, $\cong FeS$; and various other iron monosulfides
- elemental sulfur

Not all these forms of sulfur produce acid (eg. gypsum does not produce acid) and those that do produce acid can produce differing amounts per mole of sulfur present (eg. pyrite compared with jarosite). Hence, some fractionation of the various sulfur compounds is necessary in order to use stoichiometric relationships to more accurately predict future acid generation. Even when the various sulfur components are accurately quantified, the use of sulfur analysis to predict acid generation is still an indirect approach based on various theoretical assumptions and may not reflect the situation that occurs in the natural environment.

Note: Sulfur analysis alone provides no measure of actual acidity in ASS. Neither does it take into account the effect of any acid neutralising reactions in the soil (that may decrease or negate the potential acidity).

A direct approach for measuring acidity is to titrate it (to a defined pH end point) using a base (such as NaOH). In order to measure potential sulfidic acidity it is necessary first to chemically oxidise any sulfides present (eg. using 30% hydrogen peroxide) and then titrate the acidity generated. Some of the issues associated with the titration approach are:

- the pH end point
- the use of suspensions or filtered extracts
- the chemical oxidation conditions used
- organic matter and organic acidity effects
- recovery of acidity from insoluble compounds (eg. jarosite)
- that titrations usually reflects the net acidity (as some acid may be neutralised by various soil components, eg. carbonates)

Note: Further discussion of these and other issues associated with the measurement of acidity in ASS can be found in McElnea et al. *(2002a, 2002b).*

Hence, for some ASS, there are fundamental reasons why acidity measured by titration methods does not correspond with acidity predicted from sulfur analyses.

Given the complexity associated with ASS analysis, it is unrealistic to expect that there will be a universal, low cost, single analytical procedure that provides all the required information to effectively manage ASS. These Guidelines detail a variety of methods that can be used to predict net acid production in ASS to provide a basis for the sound management of ASS materials.

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2. OVERVIEW OF ANALYTICAL METHODS FOR DRIED AND GROUND ASS SAMPLES

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To facilitate interpretation by regulatory authorities, the chemical methods detailed in these Guidelines have been adopted as the standards to be used for site assessments, Environmental Impact Assessments (EIA) or Environmental Management Plans (EM Plans).

The principal analytical methods for ASS and their standard symbols are listed in Tables F1.1–F1.7. The results of some methods can be used directly (eg. S_{CR}), while in other cases the calculated difference between a pair of determinations is used (eg. S_{POS}, calculated by $S_P - S_{KCl}$).

2.1 METHODOLOGY

ACIDITY METHODS

The 'acid trail' involves direct determination of acidity by titration, as opposed to the 'sulfur trail' which employs indirect means of predicting acidity using a combination of sulfur determinations and stoichiometric relationships.

(a) Potassium chloride pH (pH_{KCl}) and Titratable Actual Acidity (TAA)
Determination of actual acidity is necessary on soil with a laboratory pH_{KCl} of <5.5[1]. The pH_{KCl} is measured in the laboratory after 4 h extraction with 1 M KCl (followed by overnight standing). Titratable Actual Acidity[2] is then determined by suspension titration to pH 6.5. For full description of the method, see Section B2.

(b) Peroxide oxidised pH (pH_{OX}) and Titratable Peroxide Acidity (TPA)
This method involves the use of 30% hydrogen peroxide to oxidise sulfides (usually pyrite) and produce sulfuric acid, as shown below.

$$FeS_2 + {}^{15}/_{2}H_2O_2 \rightarrow Fe(OH)_3 + 4H_2O + 2SO_4^{2-} + 4H^+ \quad (15)$$

Following oxidation pH_{OX} is measured. After peroxide decomposition and addition of KCl, Titratable Peroxide Acidity (TPA) is measured by suspension titration to pH 6.5.

> *Note: Where the pH after initial peroxide oxidation (pH_{OX}) is >6.5, then a titration with HCl (to pH 4), followed by additional peroxide digestion must be performed. (This so-called 'carbonate modification' is particularly important when carbonate has been identified in the soil, for instance by testing for effervescence by adding 1 M HCl, sometimes referred to as the 'fizz' test, see Section H2). Where there is appreciable carbonate present in the soil, oxidation of pyrite by peroxide can be severely retarded, and unless the carbonate modification has been performed, complete oxidation of pyrite is not assured (with the risk that potential acidity is substantially underestimated). This applies equally to soils that have been limed. This procedure (of the HCl-titration and the additional peroxide digestion) enables the calculation*

[1] Soils with a pH_{KCl} between 5.5 and 6.5 and no sulfides, are deemed to pose a lower risk and need not have TAA measured unless being analysed according to the SPOCAS suite. Soils with a pH_{KCl} in this range that do contain sulfides should have TAA measured.

[2] A method for measuring actual acidity involving the use of 0.5 M $BaCl_2$ as the extractant and suspension titration to pH 5.5 has been documented by Lin *et al*. (2000). They used a correction factor to convert 'quick titration' results to 'long-term titration' values, which they considered to be a complete measure of existing acidity in ASS. However work of McElnea *et al*. (2002b) indicated that these correction factors may be inappropriate for some soils, since long-term titration values can include a component of potential acidity. Therefore, the $BaCl_2$ method (Section G1, to be added) has not been included as a standard method. If the $BaCl_2$ extraction method is used, extractions should be restricted to 25 h and no correction factor applied. (A safety factor of at least 1.5 is still required for lime application). It is advisable to contact the relevant regulatory authority and provide justification before conducting substantial numbers of analyses.

of an 'excess acid neutralising capacity' (ANC_E) for materials/soil where ANC exceeds acidity generated by oxidation of sulfides (and which would otherwise only yield a TPA result of zero). For a full description of the method, see Section B3.

The TPA method is a measure of net acidity, since the acid produced by oxidation of sulfides has the opportunity to react with any acid buffering components in the sample (eg. carbonates). When the TPA is zero, it indicates that under laboratory conditions (using a finely-ground sample) the acid-neutralising components in the soil material exceed the acid-producing components. Often neutralising material (eg. coarse shell) present in the field may have low reactivity because of particle size and/or insoluble coatings. Thus, the TPA measured on finely ground samples in the laboratory could underestimate the net acid risk likely to be experienced in the field. To allow for the above, all measurements of the neutralising material (ANC) are divided by a fineness factor (FF) during acid base accounting (see Sections A2.2 and A3.3).

As mentioned in the previous section, for some ASS there is a scientific basis why acidity measured by titration methods may not correspond with acidity predicted from sulfur analyses. For example, using the earlier peroxide methods (POCAS, POCASm), Ward *et al*. (2002b) found that the low pH during the digestion with peroxide led to dissolution of clay minerals, and with titration of the filtered solution led to underestimation of acidity (eg. a lower TPA compared to that predicted using the S_{CR} method). However, modifications to the digestion and titration procedure employed in the new SPOCAS method has been shown by McElnea *et al*. (2002b) to have largely overcome such problems. This reinforces the instruction in these Guidelines that the **previous peroxide methods (eg. POSA, POCAS, POCASm) should not be used and should be replaced by SPOCAS when a peroxide based method is to be employed**.

The use of the TPA **alone** as a basis for the management of ASS materials (eg. to predict liming requirements) is not recommended. Acid base accounting (see Section A3) is the recommended approach for the assessment of ASS as a basis for their management, especially for the purpose of predicting lime requirements. The reasons for this are set out below. At least three situations may exist for a soil that has a TPA of zero: (i) the soil has no pyrite, (ii) the soil has a small amount of pyrite and a stoichiometric amount of carbonate, and (iii) the soil has a large amount of pyrite and carbonate. The TPA by itself cannot distinguish between these three possibilities. The third possibility is of most concern, as there could be considerable acid export in the field if the particle size of the carbonate source (eg. shell fragments) is large and the reactivity of the carbonate is low. A TPA of zero gives no indication of whether the appropriate excess of carbonate is present (eg. a minimum safety factor of 1.5). Hence the need for determining the excess acid neutralising capacity and some measure of pyrite content (eg. S_{CR} or S_{POS}).

Calculated acidity parameters

(c) Titratable Sulfidic Acidity (TSA)

Titratable Sulfidic Acidity is defined as the difference between TPA and TAA.

$$TSA = TPA - TAA$$

For unoxidised soil material in many situations (with negligible acid-buffering/acid-neutralising components) the TSA is comparable to the potential sulfidic acidity predicted from sulfur measurements (eg. S_{POS}, S_{CR}). In the absence of any appreciable ANC, where there is a difference between S_{POS} and TSA (when expressed in equivalent units), the general approach in acid base accounting (ABA) is to use sulfur measurements to estimate sulfidic acidity. However, should the TSA substantially exceed the sulfidic acidity predicted from the sulfur trail (eg. S_{POS}, S_{CR}) a cautionary approach is advisable. Such differences can indicate release of complexed iron and aluminium from organic sources and/or formation of simple organic acids during peroxide oxidation. While this acidity is commonly not rapidly released in the environment in the short term, it should not be

immediately dismissed as being of no consequence. The proponent should be aware that there may be some risk if soils are only managed according to the acidity from the sulfides. As a precaution in such circumstances, the proponent may want to increase the application rate of neutralising materials to nearer that indicated when TSA is substituted into the ABA equation.

SULFUR (AND ASSOCIATED CATION) METHODS

The 'sulfur trail' employs an indirect approach for predicting *potential acidity*, using a combination of sulfur determinations and stoichiometric relationships. This approach also needs to take into account the fact that some sulfur compounds are non-acid-producing (eg. gypsum), while other compounds can produce differing amounts of acid per mole of sulfur (eg. jarosite compared to pyrite). Unlike the acidity approach, sulfur methods alone cannot provide an estimate of net acid production. This is because no account is made of any inherent buffering/acid-neutralising components in the soil which may lessen or negate the acid risk. In soil material that is already strongly acidic (ie. a pH_{KCl} <5.5) a measure of actual acidity (eg. using the TAA method) is also necessary.

(a) Total Sulfur (S_T)

Total sulfur (S_T) can be measured using a variety of chemical and instrumental techniques (see Section B5). The measurement of total sulfur provides a low-cost alternative for estimating the maximum potential environmental risk from acid produced by the oxidation of sulfides. It is widely used in the mining industry when estimating the maximum potential for acid drainage from sulfide sources, with predicted acid generation based on the stoichiometry of Eqn (9) (assuming all sulfur is present as sulfide).

When the content of sulfate salts (eg. gypsum) is appreciable, total sulfur may substantially overestimate the potential acid risk and can result in unnecessary or excessive application of lime to soil containing little or no sulfides. Additionally, no account is made of any acid-neutralising components in the soil. Furthermore, S_T measurements alone (like all sulfur-based methods) give no estimate of 'actual acidity' in soil that is already acidic due to previous oxidation of sulfides.

Instrumental total sulfur determination is a useful screening approach, but is generally not suitable for accurate determinations on soil with low sulfur contents (eg. sands) unless instruments have been specifically set up for low levels analysis. (Detection limits and reproducibilities can be very instrument-dependent). Moreover, total sulfur is not recommended for surface and/or highly organic soil, because S_T may exceed action limits (on non-sulfidic soil) purely due to sulfur in organic matter.

(b) Chromium Reducible Sulfur (S_{CR})

The Chromium Reducible Sulfur (S_{CR}) method (**Method Code 22B**) provides accurate, low-cost determinations of (non-sulfate) inorganic sulfur and is not subject to significant interferences from the sulfur, either in organic matter or sulfate minerals (eg. gypsum; Sullivan *et al.* 1999). The inorganic sulfur compounds measured by this method are: i) pyrite and other iron disulfides; ii) S_E, elemental sulfur; iii) thiosulfate, tetrathionate, polythionites; and iv) S_{AV}, acid volatile sulfides (eg. greigite, mackinawite, amorphous FeS), provided these have not been lost during sample transport and preparation. On wet samples, the chromium reduction method can be made specific to the iron disulfide fraction if pre-treatments are used to remove the acid volatile sulfide and elemental sulfur fractions. However, laboratories routinely oven-dry and grind samples, causing some or all of the acid volatile sulfides to oxidise (Bush and Sullivan 1997). Thus the S_{CR} results reported for oven-dry samples may only contain a small proportion of the acid volatile sulfur that was present in the original wet sample. With the exception of specific depositional environments (eg. drains and lake bottom sediments), this is not considered a significant issue as the sulfide content of most Australian ASS is generally dominated by pyrite.

The chromium reducible sulfur method is the preferred technique for estimating acid-producing inorganic sulfur in ASS, particularly near the action limits and on organic-rich samples.

If differences occur between results from various sulfur methods used to predict sulfidic acidity (eg. S_{CR}, S_{POS}) then the S_{CR} result should take precedence for use in the acid base account).

> *Note: If there is no obvious reason (eg. a highly organic/peaty sample) for a substantial difference (between S_{CR} and S_{POS}), then the first step is to conduct a repeat analysis to ensure the veracity of the analytical results.*

(c) Peroxide Sulfur (S_P)

Peroxide sulfur is measured on a filtered solution, following soil digestion with peroxide and TPA titration. The S_P measurement by itself has limited application since it includes sulfate salts with no acid-generating potential (such as gypsum), sulfur from the oxidation of organic matter, as well as that derived from sulfides. The principal reason for measuring peroxide sulfur is to allow calculation of peroxide oxidisable sulfur (S_{POS}). In ASS without appreciable jarositic sulfur or other relatively insoluble acid-producing sulfates, the peroxide sulfur should approximately equal the total sulfur.

> *Note: In soil with pH_{OX} >6.5 after initial peroxide digestion (but prior to TPA titration) particularly those containing carbonates, titration with HCl to pH 4 and further peroxide digestion must be performed to ensure complete oxidation of sulfides.*

'**Peroxide' calcium (Ca_P)** and **'peroxide' magnesium (Mg_P)** can also be measured on the same filtered solution as S_P following the peroxide digestion and TPA titration.

(d) 1 M KCl extractable Sulfur (S_{KCl})

KCl-extractable sulfur is measured on a filtered solution following the TAA titration. This method provides a measure of adsorbed and soluble sulfate (including gypsum). It is used in combination with the S_P measurement to calculate peroxide oxidisable sulfur (S_{POS}). Additionally, it can be used in combination with HCl-extractable sulfur (S_{HCl}) to estimate net acid soluble sulfur (S_{NAS}).

KCl-extractable calcium (Ca_{KCl}) and **KCl-extractable magnesium (Mg_{KCl})** can also be measured on the filtered solution following the TAA titration. These determinations largely measure soluble (plus exchangeable) calcium and magnesium.

(e) 4 M HCl extractable Sulfur (S_{HCl})

HCl-extractable sulfur recovers soluble and adsorbed sulfate, sulfate from gypsum, as well as sulfur from relatively insoluble iron and aluminium hydroxy sulfate compounds (eg. jarosite, natrojarosite). It may include a contribution of sulfur from organic sources, particularly when sulfur is measured on an ICP-AES instrument (or another instrument that does not specifically measure sulfate). HCl-extractable sulfur (S_{HCl}) can be used in combination with KCl-extractable sulfur (S_{KCl}) to estimate retained acidity as net acid-soluble sulfur (S_{NAS}). Another common use of S_{KCl} is in the calculation of total oxidisable sulfur (S_{TOS}) when total sulfur (S_T) has also been determined.

HCl-extractable calcium (Ca_{HCl}) and **HCl-extractable magnesium (Mg_{HCl})** can be determined along with S_{HCl}. The 1:40 4 M HCl extraction employed should dissolve all calcium and magnesium carbonates, oxides and hydroxides in the soil, as well as extracting soluble and exchangeable calcium and magnesium.

(f) SPOCAS residual acid soluble sulfur (S_{RAS})

This 4 M HCl acid extraction procedure is performed on the soil residue remaining after the peroxide digestion in the SPOCAS method. As a result of the peroxide digestion procedure and subsequent washing of the soil residue, there should be no soluble, adsorbed or oxidisable sulfur remaining.

However, minerals such as jarosite and other 'almost insoluble' sulfate-containing compounds originally present in the soil material are largely unaffected by the peroxide digest. These compounds are soluble in HCl and are determined by this procedure. This sulfur measurement is used to estimate retained acidity, particularly from jarosite (see Eqn 11) and/or natrojarosite (Eqn 12).

Calculated sulfur (and cation) parameters

(g) Total Oxidisable Sulfur (S_{TOS})

Total oxidisable sulfur (S_{TOS}) is calculated from two sulfur measurements, total sulfur (S_T) and HCl-extractable sulfur (S_{HCl}), as shown below:

$$S_{TOS} = S_T - S_{HCl}$$

The limitations associated with this parameter generally include those associated with the determination of S_T and S_{HCl}. Typically, S_{TOS} is not suitable for accurate determinations on soil with low sulfur content (eg. sands). Moreover, it is not recommended for surface and/or highly organic soil, because S_{TOS} may exceed action limits (on non-sulfidic soil) due to sulfur in organic matter. Where the soil contains actual acidity, TAA needs to be measured. On soil material with jarositic salts present, or with pH <4.5 on a KCl extract, then measurement of S_{KCl} is also needed to estimate the contribution from such minerals. Despite these limitations, S_{TOS} provides a measure of oxidisable sulfur that is useful in screening soil for potential acidity.

(h) Peroxide Oxidisable Sulfur (S_{POS})

Peroxide oxidisable sulfur (S_{POS}) is calculated from peroxide sulfur (S_P) and KCl-extractable sulfur (S_{KCl}) measurements as shown below:

$$S_{POS} = S_P - S_{KCl}$$

As this method employs a strong chemical oxidant (30% w/w H_2O_2), it provides a measure of the maximum amount of potentially oxidisable sulfur in the soil sample and hence can be used to estimate the potential sulfidic acidity (Eqn 15). This method can overestimate the potential sulfidic acidity in soil where appreciable organic sulfur is present and is oxidised by the peroxide (eg. soil layers rich in organic matter). For soil with oxidisable sulfur results close to the action criteria, particularly sands (current action limit = 0.03 %S or 18 mol H^+/t), the S_{CR} method generally gives a better estimate of the soil's sulfide content. Whenever there is a discrepancy between the sulfur measurements used to calculate the potential sulfidic acidity, then those from the S_{CR} method will take precedence.

The S_{POS} can only estimate maximum sulfidic acidity as sulfur measurements give no indication of any acid-neutralising components in the soil. However, where calcium and magnesium have been determined on the same solutions used to measure S_P and S_{KCl}, an estimate of the acid neutralising ability of the soil can be made if 'reacted' calcium (Ca_A) and 'reacted' magnesium (Mg_A) are calculated.

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

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

Commonly, Ca_A and Mg_A 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. These values may include some calcium and magnesium from other soil minerals that may not have acid neutralising properties, and hence if used in acid base accounting the measurements may overestimate the effective ANC in soil with minimal carbonate. These measures of calcium and magnesium can be used in the ABA (see Tables A3.3 and 3.4) , however their principal utility is as a confirmation of the presence of calcium and/or magnesium carbonates and hydroxides (and their

amounts) in the ABA when ANC has been calculated by other means. (See Section B15.1 for further details). Where Ca_A and Mg_A values do not exceed 0.1% they should be ignored in the ABA.

(i) Net acid-soluble Sulfur (S_{NAS})

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

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

This sulfur measurement is used to estimate retained acidity, particularly from jarosite (see Eqn 11) and/or natrojarosite (Eqn 12). In most soil materials S_{NAS} should approximately equal S_{RAS}, however usually only one of these determinations is performed on any sample.

Net acid-soluble calcium (Ca_{NAS}) and **magnesium (Mg_{NAS})** can be calculated in a similar fashion.

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

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

Commonly, Ca_{NAS} and Mg_{NAS} reflect the **maximum** amounts of 'insoluble' calcium and/or magnesium carbonates, oxides and hydroxides dissolved by 4 M HCl. (These values may include some calcium and magnesium from other soil minerals that may not have acid neutralising properties, and hence if used in acid base accounting the measurements may overestimate the effective ANC). (See Section B15.2 for further details).

COMBINED (SPOCAS) METHOD

In the 1998 Laboratory Guidelines, the Peroxide Oxidation Combined Acidity & Sulfate (POCAS) method (Ahern *et al.* 1998) was included as the accepted peroxide-based laboratory procedures for determining the potential acidification of acid sulfate soils (ASS). It combined the principles of two commonly used peroxide oxidation methods: POSA (or peroxide oxidisable sulfuric acidity) (Lin and Melville 1993) which follows the 'sulfur trail' and the method of Dent and Bowman (1996) which follows the 'acid trail' (measuring TAA, TPA and by difference TSA). POCAS enabled the sulfur and acid trails of ASS to be directly compared using the one method. Where agreement between the acid and sulfur trails was poor, data provided by analysis of calcium and magnesium (indicating the presence of shell or naturally occurring carbonate) often accounted for the apparent discrepancy.

The **Suspension** Peroxide Oxidation Combined Acidity & Sulfur **(SPOCAS) method** (McElnea *et al.* 2002a; Latham *et al.* 2002) described in these Guidelines (Section B12) includes changes to the peroxide oxidation procedure that ensures quantitative recovery of pyritic sulfur and overcomes anomalies of sulfur loss and jarosite precipitation reported by Ward *et al.* (2002a, 2002b) using the earlier peroxide methods. Other changes include an increase in the titration pH end point (to 6.5) and the use of suspension titration. The complete SPOCAS method provides 12 individual analytes (plus 5 calculated parameters), enabling the quantification of some key fractions in the soil sample, leading to better prediction of its likely acid-generating potential (Table F1.2, Section F1). Put most simply, the SPOCAS method involves the measurement of pH, titratable acidity, sulfur and cations on two soil sub-samples. One soil sub-sample is oxidised with hydrogen peroxide and the other is not. The differences between the two values of the analytes from the two sub-samples are then calculated.

The Titratable Actual Acidity or **TAA** (the first component of the **'acidity trail'**) is a measure of the soluble and exchangeable acidity already present in the soil, often as a consequence of previous oxidation of sulfides. It is this acidity that will be mobilised and discharged following a rainfall event.

The Titratable Peroxide Acidity or **TPA** measurement (the second part of the acid trail) is the net result of the reactions between the acidifying and neutralising components in the soil (following peroxide digestion). A TPA of zero indicates that for a finely ground sample (under laboratory oxidation conditions), the soil's buffering/acid neutralising capacity exceeds (or equals) the potential acidity from oxidation of sulfides. A valuable feature of the TPA peroxide digestion component of the SPOCAS method is that for soil with pH_{OX} >6.5, any excess acid neutralising capacity (ANC_E) can be quantified by means of an HCl titration. This feature is particularly useful when trying to confirm whether a soil has been treated with sufficient neutralising agent (including whether an appropriate liming safety factor has been applied, ie. verification testing). The TPA, being a measure of net acidity, includes a contribution from the material's ANC[3].

The sulfidic acidity component is determined by the difference between TPA and TAA. This is termed Titratable Sulfidic Acidity (**TSA**).

The '**sulfur trail**' of SPOCAS (ie. S_{POS}) gives a measure of the **maximum** 'oxidisable' sulfur (usually predominantly sulfides) present in the soil sample. Since the chemical oxidising conditions employed in the laboratory are more rigorous than those experienced in the field, the S_{POS} result may, as a consequence, include some of the sulfur from the organic fraction in soil layers with appreciable organic matter. In such soil samples, S_{POS} is often slightly greater than S_{CR} (which specifically excludes organic forms of sulfur). Generally, S_{CR} and S_{POS} results are well correlated for reduced or PASS samples, but may differ on partially oxidised and surface samples. In some ASS, S_{CR} or S_{POS} may be below the action limit but the soil may still have an appreciable TPA. Sometimes this may reflect organic acidity, but it may also reflect acidity from oxidation and/or titration of iron- or manganese-containing compounds. This is particularly the case for peat soil and coffee rock. Various aluminium-containing compounds or complexes may also contribute to this acidity. This acidity may be present whether or not there is any appreciable potential sulfidic acidity (ie. any significant S_{CR} or S_{POS} result). While this acidity is commonly not rapidly released in the environment in the short term, it should not be immediately dismissed as being of no consequence. The proponent should be aware that there may be some risk if soils are only managed according to the acidity from the sulfides. As a precaution in such circumstances, the proponent may want to increase the application rate of neutralising materials to nearer that indicated when TSA is substituted into the ABA equation.

In the SPOCAS method, the S_{POS} (sulfur trail) result can be compared to the TSA (acid trail) result, provided the two quantities are expressed in equivalent units (eg. mol H^+/t). To do this, the stoichiometry of the pyrite oxidation reaction (Eqn 9) is assumed (ie. 2 moles of pyrite S produce 4 moles of H^+ acid). For example, the S_{POS} result (in units of %S) can be multiplied by 623.7 to convert it to 'equivalent' mol H^+/t. To signify that this result is in 'equivalent' **acidity** units, the S_{POS} symbol is prefixed by an **'a-'** (ie. a-S_{POS}). The TSA (in mol H^+/t) can similarly be converted to 'equivalent' sulfide **sulfur** units (in which case the result is prefixed by an **'s-'**, ie. s-TSA).

> *Note: The convention of prefixing result symbols with an 'a-' or 's-' to signify that they have been converted to equivalent acidity and 'pyrite S' units has been adopted throughout these Guidelines. This is further described in Section F1.1.*

In soil where the acid trail is lower than the sulfur trail (but the TPA is >0), calculation of the **reacted calcium (Ca_A)** and **magnesium (Mg_A)** can provide strong evidence for the presence of acid neutralising components in the soil. If it is assumed that this calcium and magnesium is derived from alkaline oxides, hydroxides or carbonates (and each mole of these elements provides 2 moles of acid neutralising), then these values can be converted to equivalent sulfur or acidity units and used in acid base accounting.

[3] The usual limitations associated with sample preparation (eg. fine grinding of nominally 'unreactive' carbonates) apply (as discussed in sections A2.1b, B15.3 and elsewhere).

For example:

$$\mathbf{Ca_A}\ (\%Ca)\ \mathbf{x\ 0.8 = s\text{-}Ca_A}\ (\text{equiv. \%S})$$

$$\mathbf{Ca_A\ (\%Ca)\ x\ 499 = a\text{-}Ca_A}\ (\text{equiv. mol } H^+/t)$$

Similarly for Mg_A:

$$\mathbf{Mg_A}\ (\%Mg)\ \mathbf{x\ 1.319 \cong s\text{-}Mg_A}\ (\text{equiv. \%S})$$

$$\mathbf{Mg_A}\ (\%Mg)\ \mathbf{x\ 822.9 = a\text{-}Mg_A}\ (\text{equiv. mol } H^+/t)$$

The sum of reacted calcium and magnesium (in equivalent acidity or sulfur units) can be compared to the difference between a-S_{POS} and TSA (or alternatively S_{POS} and s-TSA). It is common in soils with appreciable neutralising components for this sum to largely account for the difference between the acid and sulfur trails.

Reacted calcium and magnesium can be used in the ABA instead of the TSA, (particularly in soils with appreciable organic matter where the TSA may be elevated) yielding a lower net acidity and hence lower required liming rate.

Another useful parameter that can also be determined in the SPOCAS method (especially for soil with existing acidity and jarosite) is the **residual acid soluble sulfur (S_{RAS})**. This 4 M HCl acid extraction procedure is performed on the soil residue remaining after peroxide digestion and it measures sulfur from jarosite and other 'insoluble' sulfate-containing compounds originally present in the soil. (The acidity retained in these compounds is not recovered in the peroxide digest and subsequent titration). In some AASS (eg. particularly oxidised surface samples such as spoils), the acidity held in these compounds can be much greater than either the sulfidic or actual acidity. (See Section A3 for a discussion of sulfidic, actual and retained acidity).

In such soils, the retained acidity needs to be taken into account when calculating treatment or liming rates. The S_{RAS} value can be converted to an acid equivalent 'a-S_{RAS}' with a factor of 467.8 (see following conversion) in order to estimate 'retained' acidity, if it is assumed this sulfur has a similar 'per mole' acid-producing capacity as jarosite and/or natrojarosite sulfur (see Eqns 11 & 12). In such soil samples, TAA and a-S_{RAS} needs to be added to a-S_{POS} before calculating liming rates. (See Acid Base Accounting, Section A3 for details).

$$\mathbf{S_{RAS}}\ (\%)\ \mathbf{x\ 467.8 = a\text{-}S_{RAS}}\ (\text{equiv. mol } H^+/t)$$

Note: When using the SPOCAS method, S_{RAS} (or alternatively S_{NAS}) needs to be determined for all soil samples/horizons with $pH_{KCl} \leq 4.5$. An exception to the need for S_{RAS} to be determined on all samples with $pH_{KCl} \leq 4.5$ may be where a detailed soil profile description has been submitted by a 'skilled operator' [4] *verifying the absence of jarosite type minerals. In these instances, S_{NAS} must be determined on at least 20% of such samples (using those with the lowest pH_{KCl} values) to corroborate the conclusion that jarosite is absent. Organic samples are particularly difficult to interpret, though they present less of an interference to the S_{RAS} determination compared to S_{NAS}. Another exception may be where a sample from underneath the permanent (and undisturbed) watertable has a pH_{KCl} of ≤4.5.*

[4] An example of a skilled operator would be a qualified ASS consultant (such as a Certified Professional Soil Scientist, CPSS), experienced in ASS morphological descriptions.

Table A2.1. Acid yields for various iron and aluminium sulfates and hydroxy-sulfate minerals.

Iron and aluminium sulfates and hydroxy-sulfates minerals	H^+:Sulfur Ratio*
$KFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3\downarrow + \mathbf{2}SO_4^{2-} + \mathbf{3}H^+ + K^+$ ***Jarosite: pK_{SP} = 93***	**1.5**
$NaFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3\downarrow + \mathbf{2}SO_4^{2-} + \mathbf{3}H^+ + Na^+$ ***Natrojarosite***	**1.5**
$KAl_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Al(OH)_3\downarrow + \mathbf{2}SO_4^{2-} + \mathbf{3}H^+ + K^+$ ***Alunite: pK_{SP} = 85***	**1.5**
$NaAl(SO_4)_2.6H_2O \rightarrow Al(OH)_3 + 3H_2O + \mathbf{2}SO_4^{2-} + \mathbf{3}H^+ + Na^+$ ***Tamarugite***	**1.5**
$Al(OH)SO_4 + 2H_2O \rightarrow Al(OH)_3 + SO_4^{2-} + \mathbf{2}H^+$ ***Jurbanite: pK_{SP} = 17.8***	**1.5**
$Al_4(OH)_{10}SO_4.5H_2O \rightarrow 4Al(OH)_3 + 3H_2O + SO_4^{2-} + \mathbf{2}H^+$ ***Basaluminite: pK_{SP} = 117***	**2.0**
$Al_2(SO_4)_3.17H_2O \rightarrow 2Al(OH)_3 + 11H_2O + \mathbf{3}SO_4^{2-} + \mathbf{6}H^+$ ***Alunogen: pK_{SP} = 7***	**2.0**

*Note: For comparison, the H^+:Sulfur ratio for complete oxidation of pyrite is 2.0.

ACID NEUTRALISING CAPACITY (ANC), CARBON, CALCIUM AND MAGNESIUM METHODS

At this stage there is a clear need for further method development for the measurement of effective acid neutralising capacity (ANC) in ASS. The methods for estimating ANC that have been developed for acid rock drainage and/or limestone analysis are not necessarily directly transferable to acid sulfate soils. Typically, the ANC methods involve heating samples in an excess of a strong mineral acid, followed by a back-titration with alkali of the remaining 'unreacted' acid. When using such an approach on soils, some of the acid that is added is consumed through the breakdown of clay minerals and the release of aluminium, or other soil components by 'undesirable' reactions occurring at the very low pH of the acid digest. On some soils, an appreciable amount of the measured ANC may be due to these reactions that will only occur at low pH. It is desirable that the ANC measurements reflect the amount of the acid-neutralising material present in the soil that is capable of buffering (or maintaining) the soil at pH 6.5 or above. Finely-divided carbonate minerals are generally considered to be capable of providing this form of acid neutralising capacity.

The net acidity leached to the environment depends not only on the amount and rate of acid generation, but also on the amount and reactivity of the neutralising components in the soil. Coarse shell fragments in the soil may have little **effective** acid neutralising capacity due to their small surface area to volume ratio, and/or the presence of surface coatings. If coarse shell is not removed before soil grinding, the ANC measurement on the finely ground sample may poorly reflect the effective ANC in the field.

Note: A separate, large, unground sample is necessary for credible ANC analysis on soil where naturally occurring coarse shell or carbonates are present. To ensure representativeness of samples, 0.5 kg of sample will need to be picked clean of shell fragments.

Methods that add acid very slowly (eg. maintaining pH ≥4), producing a titration curve, are more likely to correlate to field reactivity than those that add excess strong acid and back-titrate with base. As the 'slow titration curve' approach has rarely been conducted by commercial laboratories, the ANC data commonly supplied in the past was usually an overestimate of the soil's effective ANC and may be of limited value.

Other chemical techniques detailed here (such as estimation of inorganic carbon, or reacted calcium and magnesium from SPOCAS) may more closely reflect the reactive calcium and/or magnesium carbonate content of soils and hence better reflect the effective acid neutralising capacity of the soil. However, again these measurements are made on finely ground soil samples and as such, these measurements may also poorly reflect the effective ANC in the field.

Note: If the pH in KCl (pH_{KCl}) of the soil is less than or equal to 6.5, then this indicates that any acidity produced in the soil (eg. by sulfide oxidation) will not be able to be neutralised quickly enough in the soil to maintain a pH of 6.5 or above. Consequently, the ANC of samples in which pH_{KCl} is less than or equal to 6.5, ***must be ignored*** *and considered to be zero. (There is no need to carry out any specific ANC analysis in this case where pH_{KCl} is <6.5).*

In the acid rock drainage literature the acid neutralising capacity of the soil material has frequently been expressed in units of equivalent %$CaCO_3$. The ANC can also be expressed in 'equivalent acid-neutralising units' (mol H^+/t) (see following conversion):

ANC (% $CaCO_3$) **x 199.8 = a-ANC** (mol H^+/t)

Similarly, to express ANC in 'equivalent' sulfur units for acid-base accounting purposes:

ANC (% $CaCO_3$) **/3.121 = s-ANC** (equiv. %S)

Note: ANC is also expressed in kg $CaCO_3$/tonne soil (which can be converted to kg $CaCO_3/m^3$ if the bulk density is known). (See Table F1.10 for conversions).

(a) ANC: Back-titration (ANC_{BT})

This approach involves the addition of a defined volume of standardised acid, followed by a hotplate digestion step. The excess acid remaining (ie. the added acid that has not been consumed by soil neutralising and buffering reactions—at very low pH) is 'back-titrated' to neutral pH using dilute NaOH solution. The 1 M HCl 'rapid titration' method (Method Code 19A1, Rayment and Higginson 1992, or Section B13.1) detailed in the 1998 *Laboratory Methods Guidelines* (Ahern *et al*. 1998) is not recommended for ASS for the reasons discussed earlier. Consequently, this method has been superseded and is replaced by another method (Method Code 19A2), which uses a more dilute (0.1 M) acid (see Section B13.2). Despite a lower concentration of acid being used, there are still reservations concerning the possibility that this method may still result in an overestimate of the effective ANC for ASS where the desired final pH of the soil material is ≥6.5. With further research, this method may be modified in the future.

Note: If the pH_{KCl} is ≤6.5, then ANC is treated as zero in the ABA equation, irrespective of the measured result.

(b) ANC: Excess—SPOCAS (ANC_E)

This measurement is carried out as part of the peroxide digestion component of the SPOCAS method. When the pH of the soil suspension is >6.5 after the initial peroxide oxidation stage, this may indicate the presence of carbonate or other alkaline minerals in the soil (eg. oxides/hydroxides of calcium and magnesium) in excess of that needed to neutralise the soil's sulfidic acidity. Soil suspensions should be titrated with HCl to pH 4, then digested again with peroxide. After this further peroxide digest, soil suspensions are titrated to pH 6.5 with NaOH (if pH <6.5). This NaOH titration result is subtracted from the HCl-titration result to give the **excess acid neutralising capacity** (ANC_E). As well as producing an estimate of excess ANC, this HCl-titration and re-digestion procedure is necessary to ensure complete peroxide oxidation of sulfides, which is slower and less efficient in the presence of excess carbonates.

Carbon methods for estimating carbonate content

(c) Carbon: Total (C_T)

Total carbon (C_T) is determined by dry combustion in an oxygen charged furnace (eg. Leco™ furnace) or similar device. It is used in the calculation of total inorganic carbon (see Section B14).

(d) Carbon: Total Organic (C_{TO})

Total organic carbon is determined by a combustion furnace or similar device following acid pre-treatment to dissolve inorganic carbon (carbonate) and evolve CO_2 (see Section B14).

Calculated ANC parameters from carbon and alkali cation measurements

(e) Carbon: Inorganic (C_{IN})

Total Inorganic carbon (C_{IN}) is calculated from total carbon (C_T) and total organic carbon (C_{TO}) measurements as shown below:

$$C_{IN} = C_T - C_{TO}$$

This carbon measurement is used to estimate carbonate content in the soil. Whilst calcium carbonates (or magnesium substituted $CaCO_3$, eg. dolomite) are likely to predominate in ASS, this approach is also likely to measure any iron or manganese carbonates in the soil[5]. Assuming the measured carbon is derived from calcium or magnesium carbonates then C_{IN} can be converted to its acid-neutralising equivalent 'a-C_{IN}' (see below):

$$\mathbf{C_{IN}}\ (\%)\ \mathbf{x\ 1665 = a\text{-}C_{IN}}\ (\text{mol } H^+/t)$$

(f) Reacted calcium (Ca_A) and magnesium (Mg_A)

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

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

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

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

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

[5] Iron-bearing carbonate minerals are also theoretically possible, but have not been identified in Qld ASS. Iron carbonate (siderite) is important in acid rock drainage. It is not an effective source of ANC since the ferrolysis reaction of the iron negates the acid neutralising reaction of the carbonate, and this can be a complication when measuring ANC by back-titration [Weber *et al*. (2004)]. When there is a substantial disagreement between the ANC calculated from ANC_{BT} and C_{IN}, this may be resolved by the measurement of Ca_{NAS} and Mg_{NAS}.

peroxide digest. In soil with excess carbonates, Ca_A and Mg_A will usually underestimate actual carbonate contents unless the HCl-titration procedure in SPOCAS has been performed. The reacted 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:

$$\mathbf{Ca_A}\ (\%)\ \mathbf{x\ 499 = a\text{-}Ca_A}\ (\text{mol } H^+/t)$$

$$\mathbf{Mg_A}\ (\%)\ \mathbf{x\ 822.6 = a\text{-}Mg_A}\ (\text{mol } H^+/t)$$

Note: ANC values calculated from reacted calcium and magnesium may give higher results than ANC estimated from inorganic carbon (C_{IN}) measurements, since the latter is specific to carbonates and does not measure acid neutralising provided by CaO, $Ca(OH)_2$, MgO, $Mg(OH)_2$ or similar alkaline compounds.

The recommended methods for ANC determination for the purpose of ABA are: ANC_{BT} (using 0.1 M HCl, Section B13.2), C_{IN} (Section B14), **(S_{POS} + s-ANC_E), (S_{POS} – s-TSA)** and reacted alkali cations (Ca_A and Mg_A) (from SPOCAS). The appropriateness of each of these values for use in determining ANC is given in Tables A3.1 to A3.4. The values derived from each of these methods need to be divided by the relevant fineness factor to yield an ANC value that can be used in an ABA. Whilst this does not preclude the use of other methods to estimate ANC, those other methods would need to be justified as appropriate to the relevant regulatory authorities.

Note: The use of C_{IN} without determining net acid soluble sulfur may be inappropriate for validation/verification testing where appreciable jarosite/retained acidity was present in the unameliorated soil. Jarosite is not recovered by the ANC_{BT} procedure.

SUMMARY OF MAIN METHODS

A number of decisions are necessary if submitting ASS (or suspected ASS) to laboratories for analysis. The first decision to make is whether samples should be submitted for conventional drying and grinding (and therefore 'Dry Analysis').

If samples are likely to contain significant monosulfides (eg. sludges or oozes from drains or lake bottoms), it is important that they are sampled (and stored) appropriately and analysed as wet samples. A flow diagram illustrating this fundamental decision-making process is shown in Figure A2.1.

Figure A2.1 shows that for dry samples it is easiest to select one of either the chromium or the SPOCAS suites of analysis, which will allow straight-forward calculation of net acidity using acid base accounting that should be readily acceptable to regulatory authorities. For those operators highly experienced in ASS, or for sites with previous analysis available, it is possible to select various combinations of methods in the Guidelines to conduct an acid base account. However, the onus will be on the consultant/proponent to clearly demonstrate the appropriateness of their selection/combination of methods for their particular site.

The advantage of the approach to use one of the main suites of analysis is that the laboratory follows a set of pre-determined rules to decide what analyses need to be conducted. The person submitting the samples need only decide between the two main options (eg. the Chromium or SPOCAS suites). Further explanation of the Chromium and SPOCAS suites is given in Section A2.2.

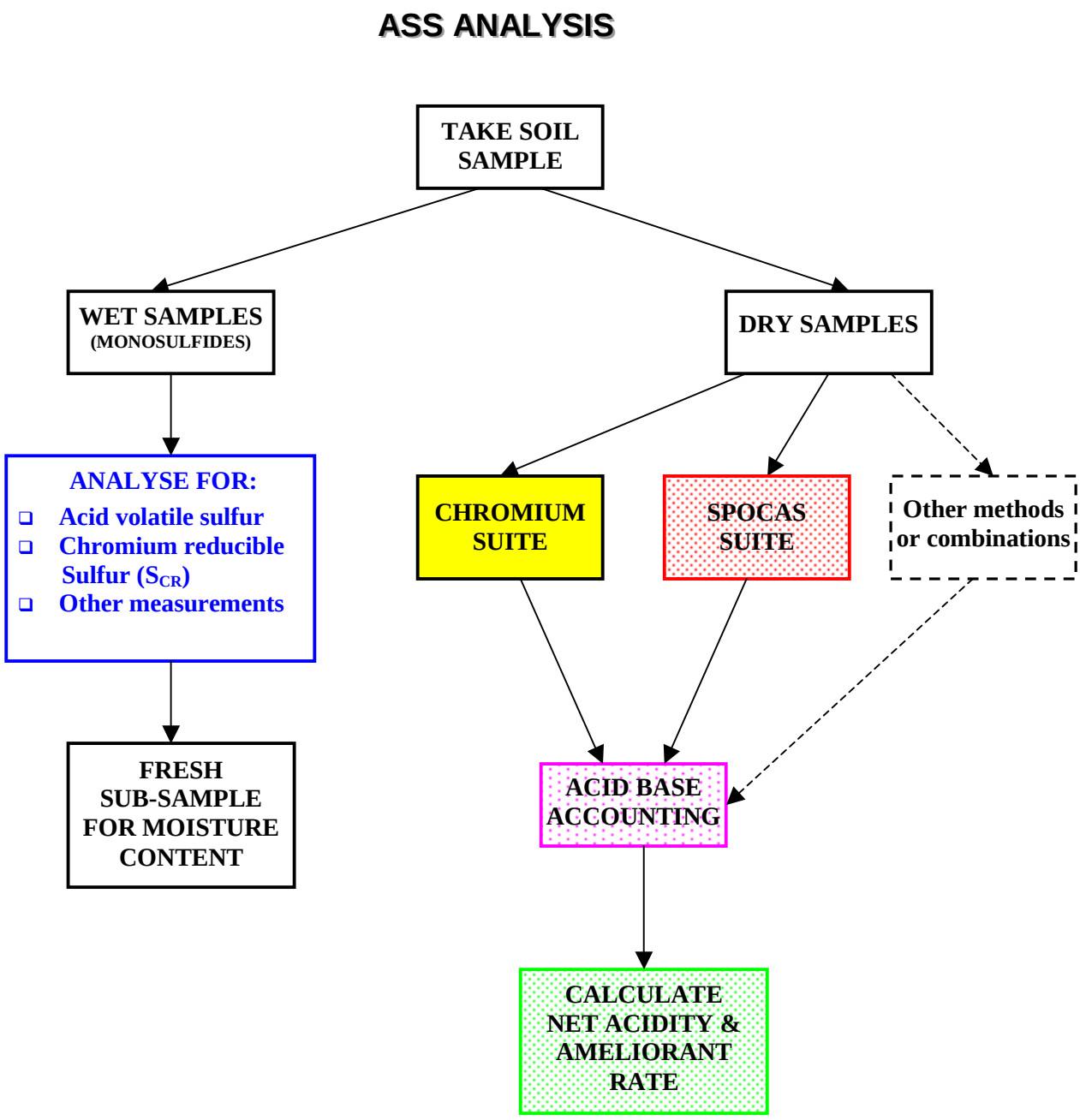

Figure A2.1. Flow diagram for analysis of ASS.

2.2 USING LABORATORY METHODS TO DETERMINE ACID RISK

Chemical analysis of ASS is undertaken to determine whether these soils are likely to generate any net acidity, and if so to quantify this acidity. From the analytical results, the amount of ameliorant needed to be added to these soils to prevent the possibility of net acid export is calculated. Fundamentally, what we are trying to measure is the net effect of acid generating processes in the soil balanced against any acid-neutralising (or basic) components that may be present. In other words, we are trying to construct an acid base account.

The acid base accounting (ABA) approach has long been used in the mining industry (both in Australia and overseas) in an effort to predict net acidity from oxidation of sulfidic material—with varying degrees of success. Whilst there are many similarities between the acid rock drainage and ASS situations, there are also fundamental differences. The principal difference is to do with the relative particle size of the sulfides in the two settings (ie. ores *vs* soils) (Caruccio 1975).

Generally, in ASS, sulfide crystals/particles are microscopic in size, typically with a diameter in the order of 0.5 µm for individual crystals (Bush and Sullivan 1999) or 20–50 µm for framboids (Hámor 1994) and are dispersed in a clay and silt particle size matrix with varying amounts of relatively inert sand present. This results in a substantially greater surface area and hence reactivity of sulfides in ASS compared to even finely ground rock in the acid rock drainage environment. Organic matter is usually present in ASS, ranging from minor amounts in some sands to extremely high levels in some peats. The presence of organic sulfur in many ASS represents a potential interference to some analytical methods that needs to be considered. Such components have a complicating effect both on analysis of ASS and on how they react in the environment. Organic sulfur compounds are generally not considered a significant environmental risk as they do not produce considerable net acidity on oxidation, in contrast to reduced inorganic sulfur compounds such as pyrite. Organic materials (particularly peats) however may contain significant organic acidity in the form of organic acids. Additionally, organic ligands can complex considerable quantities of iron and/or aluminium that may be released when the organic matter oxidises. These iron and aluminium ions may then produce acidity on hydrolysis. When attempting to raise the pH of an ASS by the addition of neutralising agents (such as agricultural lime), the effect of organic acidity needs to be factored in when formulating management plans, since this acidity needs to be neutralised along with acidity from pyrite oxidation when attempting to raise the pH of an acidic soil.

An ABA approach is widely used for predicting net acidity from sulfide oxidation of ASS. While several ABA models have been used for ASS, they all share a common underlying principle/approach, encapsulated in the following equation:

Net Acidity = Potential Sulfidic acidity + *Existing Acidity – ANC

For our purposes, existing acidity is defined as follows:

***Existing Acidity = Actual Acidity + Retained Acidity**[6]

and ANC as follows:

ANC = measured ANC/fineness factor

The components in the right hand side of the **Net Acidity** expression (or various combinations of these components) are determined using appropriate analytical methods. It is not usually necessary to determine every component in the expression. For example, the occurrence of existing acidity and acid neutralising capacity can be considered mutually exclusive for the purposes of ASS management to maintain the pH to >6.5 (ie. if a soil has existing acidity it has no effective acid neutralising capacity).

[6]* Refer to Acid Base Accounting (Section A3) for further explanation of terms.

In the mining industry, it has commonly been assumed that if the calculated ***net acidity*** is zero or negative (ie. there is supposedly '***net neutralising***'), then there is no risk. However, this assumption has proved invalid for many situations, and there have been cases where substantial environmental harm has occurred when this assumption has been made. Considerations such as the particle size or fineness of acid neutralising material and slowed reaction rates due to coating (or 'armouring') of particles with gypsum or iron precipitate, may prevent effective neutralisation and result in the net export of acid. The calculated net acidity in an ABA is critically dependent on which ANC method is used. As discussed earlier, ANC methods based on acid rock drainage procedures (in which excess acid is added and the soil digested at a very low pH, followed by back-titration with alkali) may overestimate the ***effective*** ANC in ASS[7].

For all these reasons, the ***measured*** ANC in the previous equation is moderated by the use of a fineness factor (**FF**) when estimating the soil's ANC. The minimum fineness factor is 1.5 (in the case of fine agricultural lime), increasing to larger values (in the case of coarse shell or similar material).

There is no single 'right' way to determine each of the components of the ABA, and a number of alternatives are possible. However in this section, discussion will be limited to the two main approaches recommended for the calculation of net acidity.

USE OF LABORATORY METHODS TO DETERMINE AN ACID BASE ACCOUNT

It is strongly recommended that the ABA be conducted on dried samples. While the drying process may convert small amounts of sulfide to actual acidity, this acid is still accounted for in the ABA procedure. A dried sample has many advantages over wet samples. The drying and grinding process permits larger and more representative samples to be homogenised. Wet/moist and unground samples on the other hand are often heterogeneous. When making an ABA, it is important that the sub-samples taken to measure each of the components of the ABA expression are representative of the entire sample. This is difficult to achieve using a wet sample, and as a consequence each analysis must necessarily be replicated. Sub-sampling issues have not been adequately addressed for wet samples. It is strongly recommended that the ABA not be conducted on wet samples unless acid volatile sulfides (AVS) are suspected to be present.

Chromium suite

The Chromium suite is a set of independent analytical methods each of which determines a component of the acid base account. Only the required components of the acid base account are measured using this approach. To decide which components are needed, refer to the flow diagram (Figure A2.2). The initial step in the chromium suite is to measure the reduced inorganic sulfur content (by the chromium reducible sulfur method) to estimate the potential sulfidic acidity (the first component of the ABA equation), which must be determined in all cases.

Next, the pH_{KCl} of the soil must be assessed to determine whether it has existing acidity, or if it contains any ANC. The presence of **existing acidity** precludes the existence of any effective ANC and *vice versa*. If the pH_{KCl} is <5.5, then **TAA** must be determined (ie. the **actual acidity** measured). If the pH_{KCl} is ≥5.5 and <6.5, then TAA should also be determined if the S_{CR} result indicates the presence of sulfides (ie. the sulfidic acidity it is above the action limit for its texture). Where the pH_{KCl} is <4.5 (or when yellow mottles of jarosite/natrojarosite/schwertmannite etc. have been noted in the sample) an estimate of the **retained acidity** should be made, (from the measurement S_{KCl}, S_{HCl} and hence of **net acid soluble sulfur, S_{NAS}**).

[7] For this reason, the use of 0.1 M HCl is recommended in ANC_{BT} methods (see Section B13.2).

If pH_{KCl} is >6.5, the presence of carbonates[8] (or other minerals/compounds capable of providing acid neutralising) is possible. The greater the pH is above 6.5, the more likely that the ANC will be effective ANC and therefore the more important it is to determine this. The measurement of **ANC** is desirable, since this will decrease the net acidity, and may even reveal that there is no net acidity present (ie. that there is net neutralising), meaning that the soil may not even require liming. An estimate of ANC can be made from: the **inorganic carbon C_{IN},** (eg. by Leco™ furnace), the **net acid soluble calcium**, **Ca_{NAS}** (and Mg_{NAS} if dolomite/magnesite is present) if non-carbonate forms of neutralising are suspected, or from **acid neutralising capacity** by **back-titration** (**ANC_{BT}**). If the pH is between 5.5 and 6.5, no measure of ANC or existing acidity is necessary, as TAA is usually low. Obviously, if the S_{CR} result is below the action limits, then no measurement of ANC is necessary. The Chromium suite can also be used for verification testing to validate whether the required neutralising agent has been added to the ASS material (see Section A3.6).

[8] An acid effervescence test (with 1 M HCl, see *Section H2*) indicates the presence of $CaCO_3$, and making the determination of ANC worthwhile. However, this test should not be the only criterion, since non-carbonate forms of alkalinity (eg. calcium and magnesium oxides or hydroxides) do not give a positive result to the test, but are effective contributors to the ANC.

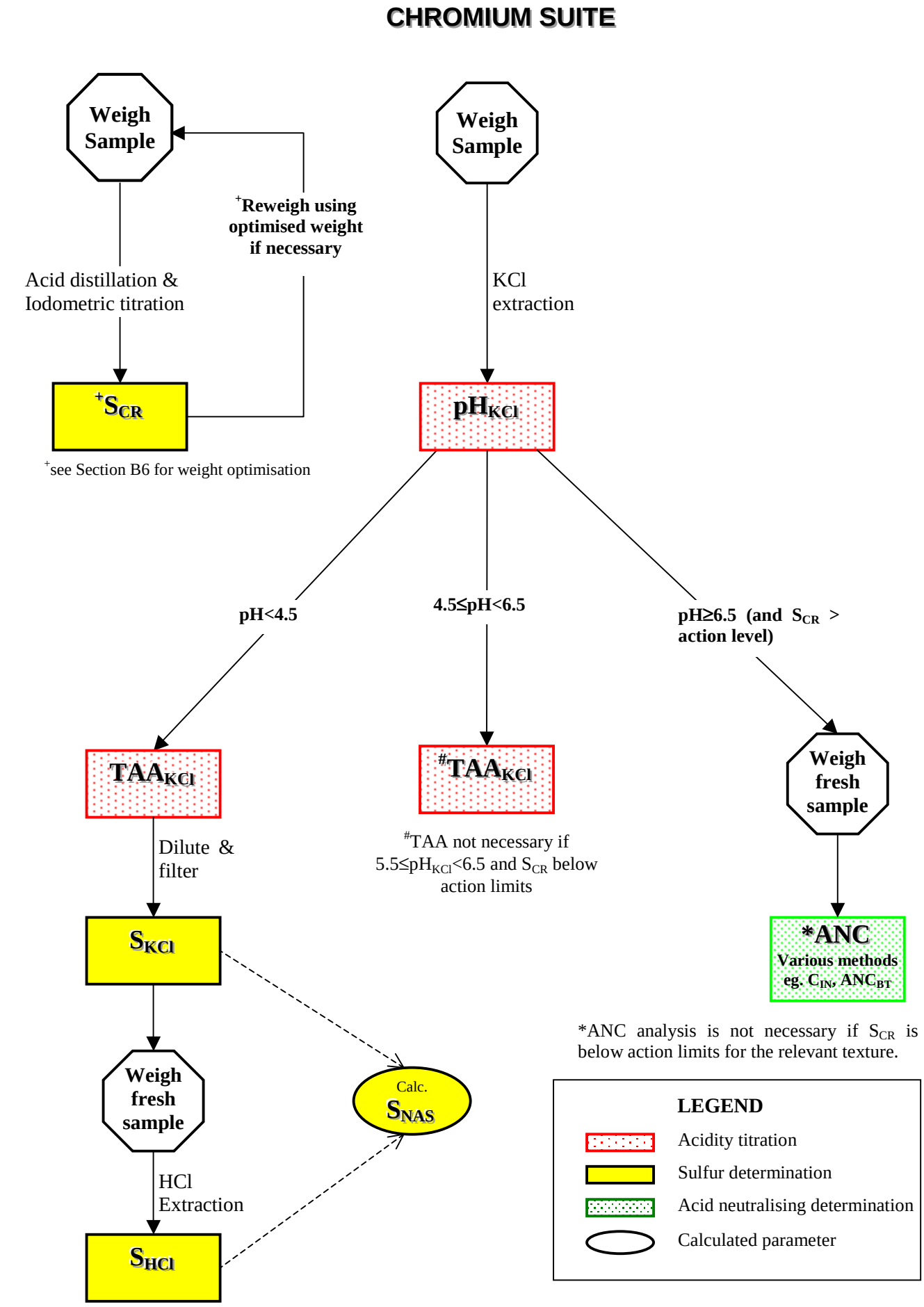

Figure A2.2. Flow diagram for Chromium suite.

SPOCAS Suite

A second approach is to perform the complete SPOCAS method (see Figure A2.3). The SPOCAS method is in essence a self-contained ABA. The TPA result of SPOCAS represents a measure of the net acidity, effectively equivalent to the sum of the soil's **potential sulfidic acidity** and **actual acidity**.

The initial step in the SPOCAS suite is to determine pH_{KCl}. If pH_{KCl} is ≥6.5 then the TAA is zero. Whether or not a TAA titration has been performed, KCl extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) are then measured. Where the pH_{KCl} is <4.5 (or when jarosite has been noted in the sample), then the **residual acid soluble sulfur (S_{RAS})**[9] must be performed on the peroxide digested soil residue, since the TAA and TPA results do not measure the **retained acidity**.

The next stage in the SPOCAS suite is to perform the peroxide digestion procedure. After the addition of two aliquots of peroxide (and two hotplate heating steps) the pH_{OX} is measured. If pH_{OX} is ≤2 then the digest should be repeated using half the weight of soil. If the pH_{OX} is >2 and ≤6.5, then TPA is measured by titration with NaOH. If the pH_{OX} of the soil is >6.5 (and the soil may be 'self-neutralising', ie. the TPA = 0), then the HCl-titration step in SPOCAS (ie. the carbonate modification) must be performed to ensure complete oxidation of sulfides. This allows calculation of the **excess acid neutralising capacity (ANC_E)**, or in effect the **net alkalinity**.

Again, irrespective of which path has been followed (ie. determination of TPA or ANC_E) then the titrated suspension must be analysed for peroxide sulfur (S_P), calcium (Ca_P) and magnesium (Mg_P). In the final stage of the SPOCAS suite, for soil where pH_{KCl} is <4.5, then an extraction with 4 M HCl on the peroxide digested soil residue is performed to determine residual acid sulfur (S_{RAS}).

The SPOCAS suite can also be used for verification testing (see Section A3.6). The ANC_E (together with the S_{POS} and an appropriate fineness factor) is used in the ABA to determine whether or not additional treatment of the soil material is needed.

To perform the complete SPOCAS method, the S_{RAS} (or S_{NAS}) **must** be performed on soil with a pH_{KCl} of <4.5, and the HCl-titration **must** be performed where the pH_{OX} is >6.5. Anything less than this is unacceptable and does not constitute the complete SPOCAS method.

[9] S_{NAS} can be used as an alternative measure of retained acidity.

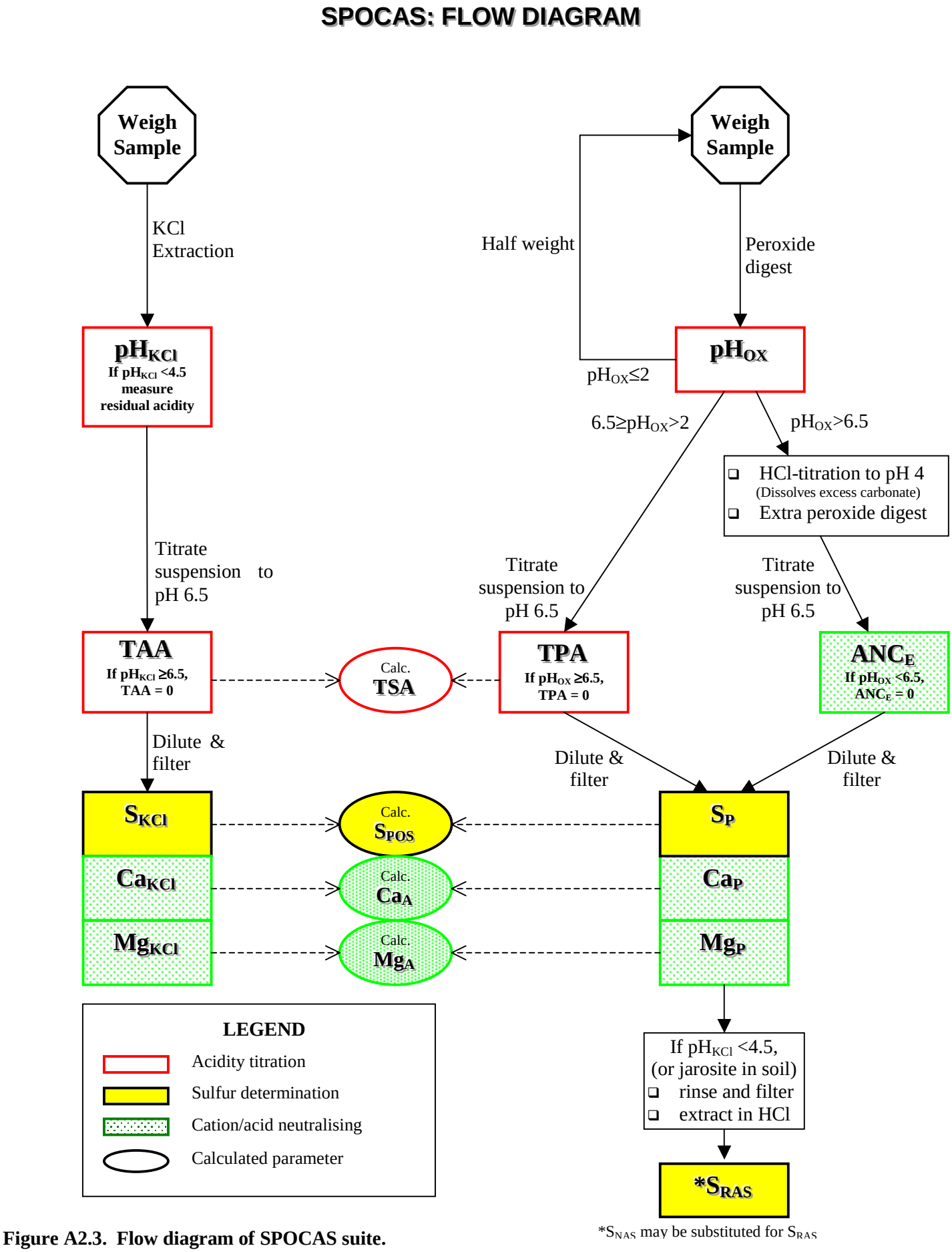

Figure A2.3. Flow diagram of SPOCAS suite.

*S_{NAS} may be substituted for S_{RAS}

2.3 CHOOSING A LABORATORY, SELECTING CONSULTANTS AND MEETING REGULATOR EXPECTATIONS

a) Choosing a laboratory

The selection of a laboratory to conduct ASS analysis is a commercial as well as a personal decision, commonly based on a combination of factors such as the laboratory's data quality and reliability, prices, location, sample turn-around time, equipment, and ability to interpret results.

It is expected that for any ASS analytical method used in the selected laboratory that there are strict quality assurance procedures in place. In most Australian states, NATA (National Association of Testing Authorities) accreditation of laboratories for each analytical method used is highly desirable. Where a laboratory is not NATA-accredited for a particular method then some further evidence of quality assurance will be necessary. Such evidence may take the form of a comparison between the selected laboratory and a NATA-accredited laboratory on a range of paired samples for that method. In the case of non-NATA-accredited methods, a request should also be made to the analysing laboratory to supply precision and validation data.

Further, it would be expected that laboratories conducting ASS analysis would take part in the Laboratory Sample Exchange Program for ASS, due to be conducted following final adoption of these Guidelines. (It would be reasonable to request information on the performance of the selected laboratory in the sample exchange program).

b) Selection of consultants

It is strongly recommended that consultants with qualifications in agricultural, environmental soil or geological science (specialising in soil chemistry, hydrology, pedology or geochemistry), experienced in acid sulfate soils management and accredited with a professional organisation (such as the Australian Society of Soil Science Inc.) be engaged to undertake soil investigations. Consultants familiar with the special sampling requirements for ASS are necessary.

c) Meeting regulator expectations

Approval authorities will principally be concerned with the selection of **appropriate methods** and on the **quality of the data**, since major developmental decisions are based on laboratory data. Generally, a regulator would expect a full Acid Base Account (ABA) to be conducted using the Chromium or SPOCAS suites on samples, in accordance with the latest sampling and assessment guidelines for the relevant state. Other combinations of methods from the Guidelines may be accepted on a case-by-case basis. After the data has been collated and assessed, further analysis may still be needed. (For instance, an S_{CR} determination may be added to the SPOCAS suite for samples where organic components may be contributing to an elevated S_{POS} result).

If other analytical methods (or variants of approved methods) are employed, a detailed justification will usually be required (eg. a regression analysis comparing the chosen method with an approved method). If variant or other methods are to be employed, their use should be negotiated with the approval authority prior to beginning analysis.

The *regulator or assessment manager* reviewing the final report/EIS/EM Plan will need to be convinced that the quantity and quality of sampling, analysis and relevant methods of analysis have been performed to adequately assess the site. Important information such as soil pH, actual acidity, potential acidity, jarosite or other acid producing compounds, and potential reactivity of inherent soil neutralising material will be needed (using appropriate laboratory analysis) to develop a cost-efficient, environmentally safe management plan. Field descriptions (eg. texture, inclusions and horizons) need to be integrated with the laboratory data to present an understanding of the layers/horizons likely to be encountered on disturbance. If any of these or other issues are deficient, then more drilling, sampling,

laboratory analysis or other types of analysis may be required to obtain development approval—often causing costly delays and frustration to all parties concerned.

In general, calculations from laboratory results of acid risk should take into account the need to neutralise **with a safety factor**, *the sum of actual, retained and potential acidity* from the eventual complete oxidation of all iron sulfides and complete hydrolysis of the oxidised products.

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3. PROCEDURE FOR PREDICTING ACID RISK *VIA* THE ACID BASE ACCOUNT (ABA)

CR Ahern, AE McElnea and LA Sullivan

3.1 BACKGROUND TO ACID BASE ACCOUNTING

As stated in Section A2.2, the ABA approach is not new; it has had a long history in one form or another in acid rock drainage, where the oxidation of various sulfide or disulfide minerals is problematic. Miller (1986) defined the term **Net Acid Generating Potential (NAGP)** for use in the mining industry as:

NAGP = 3.13 x S (%) **– ANC** (%$CaCO_3$)

This is the essentially the same form as the ABA equation given in Section A2.2—except that it does not contain a term for the existing acidity which is common in acid sulfate soils. The sulfur result substituted into the NAGP expression was commonly total sulfur (S_T).

Mulvey (1993) adapted the NAGP concept to ASS, using more precise measures of pyritic sulfur.

> *Note: The similarities and differences between the acid rock drainage and ASS situations are discussed in Section A2.2.*

Mulvey and Willett (1996) defined NAGP in terms of kg H_2SO_4/t:

NAGP = 30.6 x S (% sulfide S) **– ANC** (kg H_2SO_4/t)

Equally, this equation/relation can be expressed in units of %S:

NAGP = S (%S) **– ANC** (%$CaCO_3$) **/3.125** (%S)

Obviously, these expressions are only applicable to PASS. Written more generally:

Net Acidity = Potential Sulfidic Acidity – Acid Neutralising Capacity*

A refinement of the above ABA concepts to allow for the use of these methods for AASS as well as PASS, was made by Sullivan *et al.* (2001) who defined Net Acidity as below:

Net Acidity = Potential Sulfidic Acidity + Actual Acidity – Acid Neutralising Capacity

This ABA has been used widely in NSW for prediction of Net Acidity in ASS materials.

As has been discussed previously, there are various ways by which each of the components of the ABA expression can be measured. However, the net result can depend critically on which results are substituted into the ABA expression, and more particularly the methods used to determine them. We shall discuss each of the ABA expression's components in turn.

3.2 MEASUREMENT OF POTENTIAL SULFIDIC ACIDITY

The first component of the ABA is the **potential sulfidic acidity** (which must be measured in all cases of acid base accounting for ASS, irrespective of soil pH). Potential sulfidic acidity can be measured with varying degrees of sophistication. The simplest approach is to measure **total sulfur** and take this as the sulfide content. This is a cheap, easy approach analytically and has often been used in the mining industry (eg. NAGP; Miller 1986), however it is likely to be an overestimate of the potential sulfidic acidity/sulfide content in ASS, leading to excessive (sometimes even unnecessary) liming, (particularly when appreciable sulfur is present as soluble sulfate salts or organic sulfur in surface soil where sulfide content may be negligible). Substituting $\mathbf{S_{TOS}}$ into the equation provides a better estimate of potential sulfidic acidity, with sulfur species soluble in 4 M HCl salts removed from the total sulfur result. Whether the S_T or the S_{TOS} approach is used, it is vital that the S_T value be accurate—especially where S_T is low, or where S_{TOS} is low.

A preferable approach is to use $\mathbf{S_{CR}}$, or the $\mathbf{S_{POS}}$ result from the SPOCAS method as estimates of potential sulfidic acidity. The most accurate approach and the preferred one for organic samples and those with low levels of sulfide (close to the action limit) is the use of the $\mathbf{S_{CR}}$ result. The methods for estimating potential sulfidic acidity have become more sophisticated and accurate in recent times. This has culminated in the two main approaches of S_{CR} and S_{POS} for acid base accounting purposes.

Having determined or estimated the potential sulfidic acidity it is necessary to measure either the **existing acidity**, or the **acid neutralising capacity**. To establish which one of these two quantities has to be measured it is necessary to measure the pH_{KCl} of the soil. If the pH_{KCl} is <5.5, then the existing acidity must be determined. If the pH is ≥6.5 then the ANC should be determined, unless the sulfur result (S_{CR} or S_{POS}) is less than the action limit for the relevant texture class.

3.3 MEASUREMENT OF ACID NEUTRALISING CAPACITY

While techniques for measuring acid neutralising capacity are relatively easy to perform in the laboratory, the results obtained do not necessarily reflect the material's effective acid neutralising capacity in the environment. There has been relatively little research conducted on the measurement of acid neutralising capacity in ASS. With refinement in estimates of potential sulfidic acidity, the focus is now shifting to improving the accuracy of the measurement of ANC. Some of the methods used for ASS, which have been derived from the acid rock drainage or lime analysis disciplines are unsuitable, as they can be an overestimate of the soil's effective ANC. When S_T was the index used for sulfidic acidity, accuracy of the ANC measurement was less critical, but with the use of S_{CR} or S_{POS}, then if the ANC result used is an overestimate, there is the risk of net acidity production in the environment, despite calculations indicating there should be **no net acidity**. Kinetic factors, such as the rate of acid production compared to the rates at which the neutralising materials dissolve becomes more important. Coatings on the neutralising materials (eg. iron oxides, gypsum) may further decrease their effectiveness.

While relatively small amounts of ANC can be provided by cation exchange or from organic matter, this acid buffering is often inconsequential in comparison to that required to neutralise the acidity produced by the oxidation of sulfides. It is desirable that any acid neutralising components in the soil maintain pH at or above 5.5 (and preferably at or above 6.5). Such ANC is commonly provided by calcium and magnesium carbonates[1]. Some of the methods available for estimating ANC (especially those that involve acid digestion and back-titration of unreacted acid) have the potential to include buffering as a result of the breakdown of clay minerals at the low pH of the acid digest solution. Clearly this is undesirable. The current ANC back-titration method ($\mathbf{ANC_{BT}}$) is incapable of distinguishing between the contributions of exchangeable bases and organic matter from the buffering

[1] In treated materials, oxides and hydroxides of calcium and magnesium may be present, depending on the ameliorant used.

provided by the breakdown of clay minerals. It has the potential to overestimate the soil's effective ANC (particularly if titration of suspension is not performed).

> *Note: Any ASS material with a pH_{KCl} of <6.5 must be assumed to have an effective ANC of zero (even if shell is present in the sample). Clearly, if the pH has dropped below 6.5 then acid neutralising components in the soil are not reactive/available enough to keep pace with acid generation from sulfide oxidation and to maintain pH of the material above 6.5 (the desired level). Measurement of ANC on soil with pH_{KCl} <6.5 (especially using the acid digest/back-titration approaches) can sometimes give a substantial result, but this ANC is not effective in maintaining the ASS material at or above pH 6.5.*

To minimise the chance that ANC is overestimated, it is desirable to use methods that are more specific to the measurement of the soil's calcium and magnesium carbonate.

An approach that is less likely to overestimate effective ANC is to use the reacted calcium (Ca_A) and magnesium (Mg_A) results from the SPOCAS method. The technique that is least likely to overestimate the soil's effective ANC is the measurement of inorganic carbon (C_{IN}, eg. by combustion furnace), which is specific to carbonates. However, this technique does not quantify neutralising from oxide and hydroxide minerals, so has the potential to underestimate ANC in some cases. Where the neutralising agent used is 'red mud' or similar 'non-carbonate' or 'non-oxide' material, measurements of carbonate or alkali cation content (eg. C_{IN}, Ca_A and Mg_A) are clearly inappropriate. The use of the ANC_{BT} method or ANC_E from SPOCAS would appear the best alternatives in such cases, but the research has yet to be conducted.

Analytical precision of the ANC measurements is not the only consideration. An important issue is the effectiveness of the acid neutralising materials. The presence of almost unaltered coarse shell material (except for surface iron staining) commonly observed in very acidic oxidised ASS is testament to the lack of neutralising effectiveness of such coarse shell material. The effectiveness of carbonates (and other neutralising components in the soil) is dependent on their form (eg. finely divided *vs* coarse). The typical laboratory sample preparation (which includes fine grinding) may greatly alter the size (and hence reactivity) of $CaCO_3$ in shell fragments and may artificially increase the reactivity of the neutralising components. In the field, even when $CaCO_3$ is added as finely divided, high quality agricultural lime, problems such as coating, slow reaction kinetics or poor mixing through the soil decreases its effectiveness. These considerations are part of the rationale of the 1.5 safety factor required when neutralising the soil. Despite the presence of coarse shell material (or other neutralising soil constituents), if they are unreactive to such an extent that the acid produced by sulfide oxidation cannot be neutralised effectively enough to maintain pH_{KCl} ≥6.5, then the ANC must be considered to be **zero**. There is clearly a need to account for particle size and reactivity of neutralising materials and this is done by the application of a fineness factor.

a) Application of a fineness factor (FF) to the ANC measured in ASS

These Guidelines deal with the limitations of methods for determining ANC on ASS materials by dividing the **measured ANC** by a **fineness factor** (FF). When ameliorating PASS by mixing it well with finely-divided, pure agricultural lime, a safety factor of 1.5 must be applied. Equally, this reasoning (of a minimum 1.5 safety factor) should be applied to any naturally occurring ANC that is present in the soil. The minimum fineness factor that should be applied to any ANC is 1.5, however larger factors (eg. 2, 2.5 or 3) may be applicable for shell or other forms of neutralising inclusions in the soil. For application of fineness factors in the ABA, see Tables A3.1–A3.4.

3.4 MEASUREMENT OF EXISTING ACIDITY

If soils are already acidic (eg. pH_{KCl} <6.5), the ABA equation needs to include the **existing acidity** component (unless pH_{KCl} is >5.5, and the S_{CR} or S_{POS} is below action limits for that soil's texture).

Existing acidity is comprised of both actual acidity and retained acidity, ie.

Existing Acidity = Actual Acidity + Retained Acidity

Note: Existing acidity may be determined where the pH_{KCl} is between 5.5 and 6.5, but it is not mandatory (many coastal non-ASS can fall in this pH range) unless the SPOCAS method is being performed.

Whilst the research into the measurement of existing acidity in ASS has been neglected in the past (in favour of the measurement of sulfidic acidity), this is changing. Methods for measuring actual acidity are becoming more refined, though a considerable research effort needs to be expended into the measurement of retained acidity.

To measure actual acidity (ie. the soluble and exchangeable acidity) it is necessary to measure the titratable actual acidity (TAA, Section B2). The retained acidity is usually only appreciable when the pH is <4.5 (and particularly when pH_{KCl} is <4), where jarosite and other hydroxy sulfate minerals are stable and sometimes present in substantial amounts. Knowledge of the form and abundance of the various iron and aluminium hydroxy sulfate minerals in ASS is relatively poor, as is the understanding of the rate of release of acidity from the hydrolysis/decomposition of these compounds.

a) Retained acidity via *the Chromium suite*

If the **Chromium suite** (Section A2) has been followed, an estimate of retained acidity can be obtained by the difference between sulfur determined on the titrated TAA suspension (ie. S_{KCl}), and the sulfur extracted by 4 M HCl on a separate soil sub-sample (S_{HCl}). This will yield the **net acid soluble sulfur** result ($\mathbf{S_{NAS}}$ = S_{HCl} − S_{KCl}), from which retained acidity can be calculated (see theoretical conversion below), if it is assumed that this sulfur will produce 1.5 moles of acidity per mole of sulfur, as is the case for jarosite and natrojarosite (see Eqns 11 and 12, Section A1.2c).

$$\mathbf{a\text{-}S_{NAS}}\ (\text{mol } H^+/t) = \mathbf{S_{NAS}}\ (\%)\ \mathbf{x\ 0.75\ x\ 623.7}$$

b) Retained acidity using the SPOCAS suite

If the **SPOCAS suite** (Section A2) has been used, then the measurement of **residual acid soluble sulfur** ($\mathbf{S_{RAS}}$) can be used to calculate retained acidity:

$$\mathbf{a\text{-}S_{RAS}}\ (\text{mol } H^+/t) = \mathbf{S_{RAS}}\ (\%)\ \mathbf{x\ 0.75\ x\ 623.7}$$

Alternatively, if a 4 M HCl extraction on another sub-sample has been conducted, $\mathbf{S_{NAS}}$ can be calculated from S_{HCl} − S_{KCl} (as described above *via* the Chromium suite) rather than measuring residual acid soluble sulfur (S_{RAS}).

The amount of acidity released per mole of sulfur is variable [eg. basaluminite and $AlOHSO_4$ produces 2 moles of acidity per mole sulfur, while jarosite produces 1.5 moles (Table A2.1)]. Further research is needed into the release of acidity from the various hydroxy sulfate minerals.

The **SPOCAS method** represents an all-in-one acid base account. The TPA result of SPOCAS represents a measure of the net acidity, effectively equivalent to the sum of potential sulfidic acidity and actual acidity. Where the pH_{KCl} is <4.5, then the S_{RAS} component of SPOCAS should be performed, since the TPA result does not measure the retained acidity.

In soil horizons, jarosite is frequently concentrated along root channels, soil cracks and on ped faces, while the remainder of the soil can remain largely unoxidised and at near neutral pH. Therefore a dried and ground soil sample may have a pH higher than 4.5, but still contain appreciable jarosite. This is one of the reasons why a pH higher than the pH of <3.7 needed for jarosite formation, (ie. a pH of 4.5), has been chosen as the cut-off point for measurement of retained acidity. It is important if jarosite has been noted that retained acidity be analysed for, irrespective of soil pH.

3.5 GENERAL ABA EQUATION

In summary, the general form of the ABA applicable to ASS is shown below:

Net Acidity = Potential Sulfidic Acidity + Existing Acidity – measured ANC/FF

This further expands to:

Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF

The following tables illustrate which results are needed to complete the ABA equation for various pH_{KCl} ranges using the Chromium suite and SPOCAS suite approaches. (Tables are given both in acidity units and sulfur units, see Tables A3.1–A3.4). Once the **Net Acidity** has been calculated from these tables, it is a simple matter of looking up the conversion table (**Table F1.10**) and applying the appropriate safety factor to calculate the required liming rate (taking into account the neutralising value of the ameliorant being applied).

Table A3.1. Chromium suite acid base accounting—sulfur units. Analyses required.

Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF

Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
$pH_{KCl} \geq 6.5$ if S_{CR} < action limit, do not need ANC	S_{CR}			– $[s\text{-}C_{IN}/FF]$* or
	S_{CR}			– $[s\text{-}ANC_{BT}/FF]$*
$5.5 \leq pH_{KCl} < 6.5$	S_{CR}	+ Optional**		
$4.5 \leq pH_{KCl} < 5.5$	S_{CR}	+ s-TAA		
$pH_{KCl} < 4.5$	S_{CR}	+ s-TAA	+ $s\text{-}S_{NAS}$	

An empty field indicates that the determination of that property is not required
*FF = Fineness factor (at least 1.5)
**s-TAA not required if S_{CR} is below action limits for relevant soil texture

Table A3.2. Chromium suite acid base accounting—acidity units. Analyses required.

Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
$pH_{KCl} \geq 6.5$ if S_{CR} < action limit, do not need ANC	$a\text{-}S_{CR}$			– $[a\text{-}C_{IN}/FF]$* or
	$a\text{-}S_{CR}$			– $[a\text{-}ANC_{BT}/FF]$*
$5.5 \leq pH_{KCl} < 6.5$	$a\text{-}S_{CR}$	+ Optional**		
$4.5 \leq pH_{KCl} < 5.5$	$a\text{-}S_{CR}$	+ TAA		
$pH_{KCl} < 4.5$	$a\text{-}S_{CR}$	+ TAA	+ $a\text{-}S_{NAS}$	

An empty field indicates that the determination of that property is not required
*FF = Fineness factor (at least 1.5)
**TAA not required if S_{CR} is below action limits for relevant soil texture

Table A3.3. SPOCAS suite acid base accounting—sulfur units. Analyses required.

Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF

Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
TPA = 0 **$pH_{KCl} \geq 6.5$**	**S_{POS}**			**– [(S_{POS}+s-ANC_E)/FF]***
				or
	S_{POS}			**– [(s-Ca_A+s-Mg_A)/FF]***
TPA >0 **$pH_{KCl} \geq 6.5$**	**S_{POS}**			**– [(S_{POS} – s-TSA)/FF]***
				or
	S_{POS}			**– [(s-Ca_A+s-Mg_A)/FF]***
TPA >0 **$4.5 \leq pH_{KCl} < 6.5$**	**S_{POS}**	**+ s-TAA**		
TPA >0 **$pH_{KCl} < 4.5$**	**S_{POS}**	**+ s-TAA**	**+ **s-S_{RAS}**	

An empty field indicates that the determination of that property is not required
*FF = Fineness factor (at least 1.5)
**S_{RAS} may alternatively be substituted by S_{NAS} if available.

Table A3.4. SPOCAS suite acid base accounting—acidity units. Analyses required.

Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
TPA = 0 **$pH_{KCl} \geq 6.5$**	**a-S_{POS}**			**– [(a-S_{POS}+a-ANC_E)/FF]***
				or
	a-S_{POS}			**– [(a-Ca_A+a-Mg_A)/FF]***
TPA >0 **$pH_{KCl} \geq 6.5$**	**a-S_{POS}**			**– [(a-S_{POS} – TSA)/FF]***
				or
	a-S_{POS}			**– [(a-Ca_A+a-Mg_A)/FF]***
TPA >0 **$4.5 \leq pH_{KCl} < 6.5$**	**a-S_{POS}**	**+ TAA**		
TPA >0 **$pH_{KCl} < 4.5$**	**a-S_{POS}**	**+ TAA**	**+ **a-S_{RAS}**	

An empty field indicates that the determination of that property is not required
*FF = Fineness factor (at least 1.5)
**S_{RAS} may alternatively be substituted by S_{NAS} if available.

3.6 VERIFICATION TESTING

The objective when ameliorating ASS with alkaline material is to ensure that there will be no chance that net acidity will be generated from the complete oxidation of any sulfides in these soils. Verification testing is a tool that is used to confirm whether sufficient ameliorant (neutralising agent) has been incorporated into the ASS to prevent any future acidification. During the verification phase of the sampling, soil that has been treated with a neutralising agent such as agricultural lime is analysed. If the results of the verification testing indicate a failure (to comply with the performance criteria for the site), then the soil should be re-treated. The acid base account (and specifically the ABA equation) is used in verification testing to assess whether ASS have the potential to produce net acidity. In the ABA equation, any measured ANC is moderated by the use of a fineness factor (using a minimum of 1.5) to take into account the fineness of the acid neutralising material, reactivity, incomplete mixing, coatings etc.

Verification testing helps ensure that appropriate treatment of ASS has occurred, and provides some security against later accusations of insufficient treatment of these soils/litigation. The more comprehensive the initial soil sampling and site characterisation, and the better the mixing of the neutralising agent, the more likely soils are to pass verification.

When submitting ameliorated samples for analysis it should be made clear to the laboratory that the soil requires verification testing and also whether the soil contained jarosite prior to being ameliorated. The neutralising agent used in amelioration (especially if it is not $CaCO_3$/agricultural lime) is also valuable information to provide to the laboratory and regulatory authorities. The methods in these Guidelines have not been tested for uncommon neutralising agents.

Previously, the TPA result from the POCAS or POCASm methods has been used to assess whether sufficient ameliorant has been added (in the absence at the time of specific methodology for the purpose). A TPA value of zero was typically the benchmark used for verification testing. There are a number of reasons why a TPA result by itself is no longer acceptable. The first reason relates to the need to ameliorate the soil with at least 1.5 times the acid neutralising material theoretically required to neutralise the potential acidity. The TPA by itself cannot assess whether there is sufficient excess acid neutralising present to meet the minimum 1.5 'safety' factor. To do this, a measure of oxidisable sulfur must also be made. Moreover, recent work has shown that TPA in isolation is inadequate because the peroxide digest of POCAS and POCASm does not ensure complete oxidation of sulfides in the presence of large amounts of carbonates. (Hydrogen peroxide oxidation of pyrite is less efficient at alkaline pH in the presence of carbonates) (See Section A2.1b).

a) Using the SPOCAS suite

The use of the SPOCAS suite and the associated ABA is one option for verification testing. The SPOCAS method overcomes problems with the peroxide digest procedures of POCAS and POCASm by use of a titration with HCl that ensures that complete oxidation of sulfides occurs, as well as quantifying the soil's excess acid neutralising capacity (ANC_E). The S_{POS} result can be compared to the ANC_E result to determine whether the appropriate safety factor has been achieved.

Obviously, in a properly ameliorated soil, the pH_{KCl} should be ≥6.5 and TAA equal to zero. Similarly, the pH_{OX} should be >6.5 and the TPA equal to zero. Additionally, the **net acidity** result from the ABA should be zero or negative (having applied the appropriate fineness factor to the ANC). To see what conditions should be met and what data should be substituted into the ABA, refer to Tables A3.5–A3.6. See Section F1.10 for an example of calculating net acidity from verification testing results using the SPOCAS suite.

Table A3.5. SPOCAS suite acid base accounting—acidity and sulfur units. Verification.

UNITS	Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
SULFUR	**TPA = 0** **pH_{KCl} ≥ 6.5^^**	**S_{POS}**		–	**[(S_{POS}+s-ANC_E)/FF]*** **or**
		S_{POS}		–	**[(s-Ca_A+s-Mg_A)/FF]***
ACIDITY	**TPA = 0** **pH_{KCl} ≥ 6.5^^**	**a-S_{POS}**		–	**[(S_{POS}+a-ANC_E)/FF]*** **or**
		a-S_{POS}		–	**[(a-Ca_A+a-Mg_A)/FF]***

An empty field indicates that the determination of that property is not required.
*FF = Fineness factor (at least 1.5).
^^If an ameliorated soil fails the pH_{KCl} criterion (ie. pH_{KCl} is <6.5), then the decision tree/flow diagram (Fig. A2.3) should be followed and the net acidity calculated using the relevant equations in Tables A3.3 and A3.4.

b) Using the Chromium suite

Another approach for verification is to use the Chromium suite of analyses. Again, in a properly ameliorated soil, pH_{KCl} should be ≥6.5 and TAA should be zero. The S_{CR} result is compared to a measure of soil ANC (either the back-titration approach, ANC_{BT}, or measurement of inorganic carbon, eg. C_{IN} by induction furnace) and it then can be assessed whether the appropriate safety factor has been met. In any case, if the **net acidity** from the ABA equation is zero or negative (with the appropriate fineness factor applied to the ANC) then the soil has passed verification. There is however an exception to this for soil that contained retained acidity (eg. jarosite) prior to amelioration (see Section A3.5c below). See Section F1.10 for an example of calculating net acidity from verification testing results using the Chromium suite.

Table A3.6. Chromium suite acid base accounting—acidity and sulfur units. Verification.

UNITS	Analysis Results	Potential Acidity	Actual Acidity		Retained Acidity		ANC
SULFUR	**pH_{KCl} ≥ 6.5^^ retained acidity NOT present**	**S_{CR}**				–	**[s-C_{IN}/FF]*#** **or**
		S_{CR}				–	**[s-ANC_{BT}/FF]***
	pH_{KCl} ≥ 6.5^^ retained acidity present before liming	**S_{CR}**		+	**s-S_{NAS}**	–	**[s-C_{IN}/FF]*** **or**
		S_{CR}		+	**s-S_{NAS}**	–	**[s-ANC_{BT}/FF]***
ACIDITY	**pH_{KCl} ≥ 6.5^^ retained acidity NOT present**	**a-S_{CR}**				–	**[a-C_{IN}/FF]*#** **or**
		a-S_{CR}				–	**[a-ANC_{BT}/FF]***
	pH_{KCl} ≥ 6.5^^ retained acidity present before liming	**a-S_{CR}**		+	**a-S_{NAS}**	–	**[a-C_{IN}/FF]*** **or**
		a-S_{CR}		+	**a-S_{NAS}**	–	**[a-ANC_{BT}/FF]***

An empty field indicates that the determination of that property is not required.
*FF = Fineness factor (at least 1.5).
#The use of C_{IN} is not appropriate where a non-carbonate or oxide neutralising agent has been used (see Section 3.3).
^^If an ameliorated soil fails the pH_{KCl} criterion (ie. pH_{KCl} is <6.5), then the decision tree/flow diagram (Fig. A2.2) should be followed and the net acidity calculated using the relevant equations in Tables A3.1 and A3.2. If pH_{KCl} is <4.5, retained acidity obviously also needs to be measured.

Note: This approach can be slightly modified, for example by the substitution of another estimate of sulfide content in place of the S_{CR} value (eg. S_{TOS}).

c) Jarosite complications

A complication arises when soil material that contains jarosite (and similar minerals) is treated with low solubility alkaline products such as agricultural lime ($CaCO_3$). Jarosite and $CaCO_3$ should not naturally co-exist in a soil at equilibrium. In a lime-treated soil material that contained jarosite, there may have been insufficient time and/or moisture for all the jarosite to hydrolyse/decompose and reach equilibrium. Hence, in a lime-treated soil, field and lab pH are likely to be poor indicators of the presence or absence of jarosite. This means that even if the pH_{KCl} is ≥6.5 in the TAA analysis (because of the presence of carbonate), one cannot be sure that the long-term equilibrium pH will not be strongly acidic. Kinetic factors mean that jarosite may not have had sufficient time to react.

In the peroxide digest of the SPOCAS suite, most or all of the jarosite dissolves/reacts in the presence of excess $CaCO_3$). Under these conditions the retained acidity is neutralised by the ameliorant present. Thus an ANC_E result will have accounted for retained acidity (unlike other measures of ANC, eg. ANC_{BT} and C_{IN}).

If using the chromium suite on treated soil that contained jarosite, the situation is slightly different. It is necessary to measure pH_{KCl} (and TAA if the pH_{KCl} is <6.5), as well as S_{KCl} and S_{HCl} (in order to calculate S_{NAS}). The measurement of S_{NAS} is necessary as the estimation of ANC by either the inorganic carbon method (C_{IN}) or the back-titration method (ANC_{BT}) are essentially unaffected by the presence of absence of jarosite. Therefore retained acidity also needs to be measured by S_{NAS} in this situation.

In summary, if the SPOCAS suite is used for verification of treated soil material, it is not necessary to know whether jarosite is present as the results will account for the presence of jarosite. In contrast, if the chromium suite is used it is essential that the laboratory be notified that jarosite may be present and that S_{KCl} and S_{HCl} are measured. Failure to take S_{NAS} into account could result in an erroneous acid base account. If you are unsure of the jarosite status of the soil either use the SPOCAS suite for verification, or alternatively include measurement of S_{NAS} if using the chromium suite.

3.7 PRESENTATION OF RESULTS

With the multitude of results generated by ASS methods and the need to perform various calculations and conversions so that results are in the appropriate units to allow the construction of an acid base account, the way in which these results are presented is an important consideration. A standard format (or standard formats) for the presentation of laboratory data, or at least a consistent order in which analytes are listed in spreadsheets has advantages for laboratories, their clients, consultants and regulators. Suggested formats for SPOCAS and chromium suites and combined data (as well as field data) are provided in the Appendix (Section I, Tables I1.1–I1.3). Excel template files for calculation of an acid base account will be available by contacting Kristie Watling (e-mail Kristie.Watling@nrm.qld.gov.au) or Angus McElnea (e-mail Angus.McElnea@nrm.qld.gov.au), QASSIT Qld Department of Natural Resources and Mines, Gate 2, Block C, 80 Meiers Road, Indooroopilly Qld 4068.

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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 Guidelines[1] 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 it's 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 m^3 or 1000 m^3 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 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 powder**[2].

<u>Warning</u>: 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. N_2) 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.

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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 µS/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 ± 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.25 g ± 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 g ± 0.05 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.10 g ± 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 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.

Potassium hydrogen phthalate ($C_6H_5O_4K$): 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 ($\mathbf{m_1}$) 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.

- 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 ($\mathbf{c_1}$) and record titre volume ($\mathbf{V_1}$).
  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 ($\mathbf{c_2}$) and record titre volume ($\mathbf{V_1}$).
  iii) If pH_{KCl} is ≥6.5, no titration is required and TAA is zero.

  Note: In some states, guidelines require that for 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 overshot 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 ($\mathbf{c_2}$) and record titre volume ($\mathbf{V_2}$), 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:

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

If 0.05 M NaOH is used:

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

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

TAA (mol H^+/t) = 25 x (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^{c}Elnea 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^{c}Elnea 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 <5µS/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 ± 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.25 g ± 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 g ± 0.05 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.10 g ± 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 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 °C using deionised water. Standardise against disodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) 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 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 (H_2O_2) (pH adjusted): Adjusted to pH 5.5 with dilute (0.05 M) NaOH solution for use in the 'final oxidation' step.

6.30×10^{-3} M $CuCl_2.2H_2O$ solution (400 mg Cu/L): Prepare (1 L) by dissolving 1.073 g of copper(II) chloride dihydrate ($CuCl_2.2H_2O$) in deionised water and dilute to 1000 mL at 20 °C using deionised water.

Potassium hydrogen phthalate ($C_6H_5O_4K$): Dry at 105 °C for 4 h and store in desiccator prior to use.

Sodium tetraborate ($Na_2B_4O_7.10H_2O$)

Apparatus:

Electronic balances (500 ± 0.01 g and 100 ± 0.0001 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 80–90 °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 ± 0.25 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 H_2O_2, 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 (**c_3**).

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 overshot, 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 (**V_3**, 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% H_2O_2 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 x 10^{-3} M $CuCl_2.2H_2O$ (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% 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 overshot 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 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:

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

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

TPA (mol H^+/t) = (125 x V_4) + (25 x V_6)

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

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

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

TPA (mol H^+/t) = 25 x (V_5 + 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.

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

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

HCl titration (mol H^+/t) = 250 x 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***)

$$\textbf{a-ANC}_\textbf{E} \textbf{ = HCl titration – TPA titration} \text{ (in mol } H^+/t)$$

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

$$\textbf{a-ANC}_\textbf{E} \textbf{ (mol } H^+/t) = [V_3 \text{ x } c_3 \text{ x } (1000/m_2)] - [(V_5 + V_6 - V_7 - V_8) \times c_2] \times (1000/m_2)$$

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

$$\textbf{a-ANC}_\textbf{E} \textbf{ (mol } H^+/t) = [V_3 \text{ x } c_3 \text{ x } (1000/m_2)] - [(V_4 \times c_1) - (V_7 \times c_2) + (V_6 - V_8) \times c_2] \times (1000/m_2)$$

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 %$CaCO_3$):

$$\textbf{ANC}_\textbf{E} \textbf{ = a-ANC}_\textbf{E}\textbf{/199.8 (}\textit{\textbf{Method Code 23Q}}\textbf{)}$$

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:

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M^{c}Elnea 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:

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

or

Method Code 23H = Method Code 23G – Method Code 23F

References:

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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. $HNO_3/HClO_4$) 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 ^oC) 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 $CaSO_4.2H_2O$ 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.*

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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 method ……..particularly 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 μS/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 $Na_2S_2O_3.5H_2O$ 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 (ρ = 1.16 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.

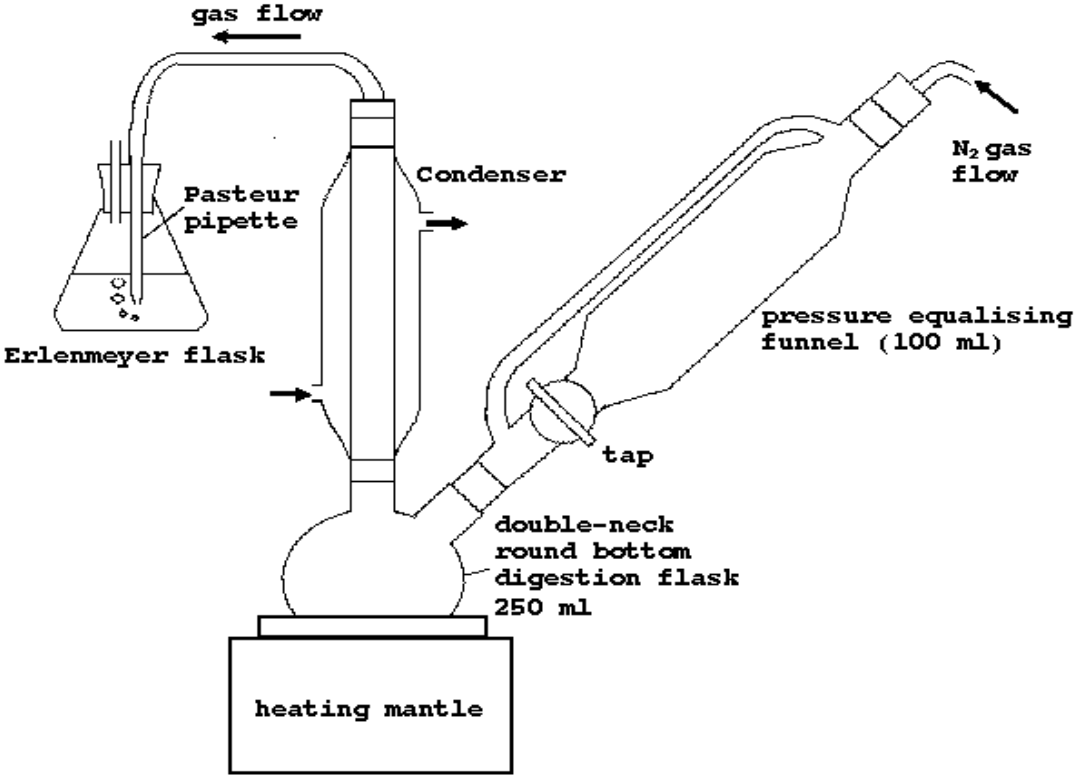

Figure B6.1. Schematic representation of the apparatus used in the chromium reduction method for determination of S_{CR}.

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 N_2 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 N_2 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: H_2S 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: H_2S 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 H_2S.

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:

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

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 $Na_2S_2O_3$ solution (see below)

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

D = Titration volume of standard $Na_2S_2O_3$ solution (in **mL**)
E = Volume of iodine solution titrated (in **mL**)
m = The mass of the soil weighed (in **g**)

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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 ± 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:

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

When there is zero blank, m_2 = 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.

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 ± 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:

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

  When there is zero blank, m_1 = 2 g, and V = 400 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 µS/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 h ± 0.5 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 µS/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).

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

or

Method Code 20C = Method Code 20A – 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:

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

or

Method Code 23E = Method Code 23D – 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:

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

or

Method Code 20J = Method Code 20B – 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 <5µS/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 (c_1): Prepare (1 L) by dissolving 10.1 g ± 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.25 g ± 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 g ± 0.05 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.10 g ± 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 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.

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 (c_3): 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 ($Na_2B_4O_7.10H_2O$) or recently standardised 0.25 M NaOH solution. Calculate molarity of HCl solution ($\mathbf{c_3}$). 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 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 (H_2O_2) (pH adjusted): Adjusted to pH 5.5 with dilute NaOH solution for use in the 'final oxidation' step.

6.30×10^{-3} M $CuCl_2.2H_2O$ solution (400 mg Cu/L): Prepare (1 L) by dissolving 1.073 g of copper(II) chloride dihydrate ($CuCl_2.2H_2O$) in deionised water and dilute to 1000 mL at 20 °C using deionised water.

Potassium hydrogen phthalate ($C_6H_5O_4K$): Dry at 105 °C for 4 h and store in desiccator prior to use.

Sodium tetraborate ($Na_2B_4O_7.10H_2O$)

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 ($\mathbf{m_1}$) 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 ($\mathbf{c_1}$) and record titre volume ($\mathbf{V_1}$).
  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 ($\mathbf{c_2}$) and record titre volume ($\mathbf{V_1}$).
  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 overshot 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 ($\mathbf{c_2}$) and record titre volume ($\mathbf{V_2}$, 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:

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

If 0.05 M NaOH is used:

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

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

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

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 ($\mathbf{S_1}$) (mg S/L) by ICP-AES or using other suitable analytical instruments and appropriate range of standards. Determine sulfur on the blank ($\mathbf{S_2}$). 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:

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

When there is zero blank, m1 = 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 ($\mathbf{m_2}$). 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 (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.*

  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 H_2O_2. 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 H_2O_2, 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 (**c_3**).

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 overshot, 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 (**V_3**, 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% H_2O_2 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 x 10^{-3} M $CuCl_2.2H_2O$ (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 ($\mathbf{c_1}$) and record volume of titre ($\mathbf{V_4}$).
  ii) If pH is >3 but ≤5.5, titrate with stirring to pH 5.5 using standardised ~0.05 M NaOH ($\mathbf{c_2}$) and record volume of titre ($\mathbf{V_5}$).
  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 ($\mathbf{V_7}$).
- 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 ($\mathbf{c_2}$). Record molarity ($\mathbf{c_2}$) and titre ($\mathbf{V_6}$ mL) of alkali added to reach pH 6.5. For blanks record corresponding titre ($\mathbf{V_8}$) and molarity ($\mathbf{c_2}$).

  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 overshot 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:

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

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

TPA (mol H^+/t) = (125 x V_4) + (25 x V_6)

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

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

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

TPA (mol H^+/t) = 25 x (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.

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

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

HCl titration (mol H^+/t) = 250 x 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***)

$$\textbf{a-ANC}_\textbf{E} \textbf{ = HCl titration – TPA titration} \text{ (mol } H^+/t)$$

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

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

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

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

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. $\%CaCO_3$):

$$\textbf{ANC}_E = \textbf{a-ANC}_E\textbf{/199.8} \quad (\textbf{\textit{Method Code 23Q}})$$

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 ($\mathbf{S_3}$) (mg S/L) by ICP-AES or using other suitable analytical instruments and appropriate range of standards. Determine sulfur on the blank ($\mathbf{S_4}$). 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:

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

When there is zero blank, m_2 = 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:

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

or

Method 23H = Method 23G – 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**).

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

or

Method Code 23E = Method Code 23D – 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**).

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

or

Method Code 23X = Method Code 23T – 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**).

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

or

Method Code 23U = Method Code 23W – 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 $CaCO_3$ 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 '$CaCO_3$ 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 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 0.10 M HCl (c_1): 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 ($Na_2B_4O_7.10H_2O$) or recently

standardised 0.10 M NaOH solution. Calculate molarity of HCl solution ($\mathbf{c_1}$). 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 ($\mathbf{c_2}$): Prepare (1 L) by dissolving 4.10 g ± 0.10 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 ($C_6H_5O_4K$) by accurately weighing (to 0.0001 g) 0.20 g ± 0.04 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 ($\mathbf{C_6H_5O_4K}$): Dry at 105 °C for 4 h and store in desiccator prior to use.

Sodium tetraborate ($\mathbf{Na_2B_4O_7.10H_2O}$)

Calcium carbonate ($\mathbf{CaCO_3}$): Dry at 105 °C for 4 h and store in desiccator prior to use.

Apparatus:

Analytical balance (500 g ± 0.01 g and 100 ± 0.0001 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 ($\mathbf{V_{HCl}}$) of standardised 0.1 M HCl solution ($\mathbf{c_1}$) to each flask.
- Prepare two blank samples containing only deionised water and acid.
- Prepare three reference samples containing 0.100 g of AR grade $CaCO_3$.
- 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 ($\mathbf{c_2}$) 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 ($\mathbf{V_B}$) 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 ($\mathbf{V_A}$) by the sample as:

  $V_A = 25 - V_B$ [V_B in mL].

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

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

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:

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

Note: The $CaCO_3$ reference samples should yield a value of 100 ± 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 CO_2 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 $\%CaCO_3$ 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 (H_2SO_3)

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 CO_2 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 CO_2 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})*

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

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, Bremmer 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:

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

or

Method Code 23X = Method Code 23W – Method Code 23V

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

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

or

Method Code 23U = Method Code 23T – 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:

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

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:

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

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.

SECTION C: WET SAMPLES

Note: Section C to be included at a later date.

SECTION D: SOIL PHYSICAL METHODS

Note: Section D to be included at a later date.

SECTION E: ASS WATER METHODS

Note: Section E to be included at a later date.

SECTION F: CODES

1. CODES FOR ACID SULFATE SOIL ANALYTICAL METHODS

CR Ahern, AE McElnea and GE Rayment

1.1 INTRODUCTION

The principal analytical methods for the analysis of ASS are listed below. The results of some methods can be used directly (eg. S_{CR}), while in other cases the calculated difference between a pair of determinations is used (eg. $S_{POS} = S_P - S_{KCl}$). When sulfidic acidity (in mol H^+/t) is estimated from sulfur measurements using the stoichiometry of various chemical equations, the symbol for the calculated result is prefixed by an '**a-**', eg. S_{CR} (in units of %S) becomes **a-S_{CR}** (mol H^+/t) and S_{POS} becomes **a-S_{POS}** (mol H^+/t). Similarly, the various acid neutralising capacity method results (including reacted Ca and Mg) may be expressed in mol H^+/t and their symbols are also prefixed by '**a-**', eg. Ca_A becomes **a-Ca_A** (mol H^+/t) and ANC_{BT} becomes **a-ANC_{BT}** (mol H^+/t). When all measurements are converted to the same (eg. acidity) units, it allows acid-base accounting to be performed. Acid base accounting (ABA) is one of the tools used to predict whether a soil will theoretically produce net acidity upon complete oxidation.

An alternative approach that has been used is to convert acidity measurements to equivalent (sulfide) sulfur units using the stoichiometry of appropriate equations. In such cases the symbol for the calculated result is prefixed by an '**s-**', eg. TSA (mol H^+/t) becomes **s-TSA** (%S).

A special case exists for S_{NAS} and S_{RAS} results when they are used in ABA. The conversion to equivalent acidity units (of mol H^+/t) is relatively straight-forward (see Tables F1.6 & F1.2), however when these results are used in ABA, and calculations are expressed in units of equivalent % pyrite S, then a 0.75 factor needs to be employed. These converted results are then signified by the symbols '**s-S_{NAS}**' and '**s-S_{RAS}**'.

In the following Tables are listed the method analysis codes, the symbols and units of the various analytes, as well as a brief description of each analyte.

It was originally intentioned that the codes detailed here would be compatible with the successor volume to the *Australian Laboratory Handbook of Soil and Water Chemical Methods* (Rayment and Higginson 1992), tentatively titled the *Australian Laboratory Handbook of Soil Chemical Methods*, however due to the complexity of ASS methods (and their codes) and because only a single chapter will be devoted to their analysis in the new Handbook, it means that the two sets of codes will necessarily have to be inconsistent. It is envisaged that the codes appearing in these Guidelines will appear in their entirety as an appendix in the new Handbook for purposes of cross-referencing.

ACIDITY METHODS

- KCl pH (pH_{KCl}) & Titratable Actual Acidity (TAA)
- Peroxide pH (pH_{OX}), Titratable Peroxide Acidity (TPA) and Excess acid neutralising capacity (ANC_E) after peroxide oxidation

Calculated parameter—from acidity measurements

- Titratable Sulfidic Acidity (TSA)

SULFUR METHODS

- Total Sulfur (S_T)
- Chromium Reducible Sulfur (S_{CR})
- Acid Volatile Sulfur (S_{AV})
- Acid Volatile Sulfur, diffusible (S_{DAV})
- Disulfide Sulfur (S_D)
- Elemental Sulfur (S_E)
- Peroxide Sulfur (S_P)
- 1 M KCl Extractable Sulfur (S_{KCl})
- 4 M HCl Extractable Sulfur (S_{HCl})
- Peroxide Residual Acid-Soluble Sulfur (S_{RAS})

Calculated parameters—from sulfur measurements

- Total Oxidisable Sulfur (S_{TOS} = $\mathbf{S_T - S_{HCl}}$)
- Peroxide Oxidisable Sulfur (S_{POS} = $\mathbf{S_P - S_{KCl}}$)
- Net Acid-Soluble Sulfur (S_{NAS} = $\mathbf{S_{HCl} - S_{KCl}}$)

COMBINED METHOD

- Suspension Peroxide Oxidation Combined Acidity & Sulfur method (SPOCAS)

ACID NEUTRALISING CAPACITY (ANC), CARBON AND ALKALI CATION METHODS

- ANC: Back Titration (ANC_{BT})
- Carbon: Inorganic (C_{IN} = $\mathbf{C_T - C_{TO}}$)

Calculated parameters—from alkali cation measurements

- Ca – Additional released by SPOCAS method (Ca_A)
- Mg – Additional released by SPOCAS method (Mg_A)
- Ca – Net Acid Soluble by HCl (Ca_{NAS} = $\mathbf{Ca_{HCl} - Ca_{KCl}}$)
- Mg – Net Acid Soluble by HCl (Mg_{NAS} = $\mathbf{Mg_{HCl} - Mg_{KCl}}$)

1.2 CHROMIUM REDUCIBLE (S_{CR}), DISULFIDE (S_D), ACID VOLATILE (S_{AV} AND S_{DAV}) AND ELEMENTAL (S_E) SULFUR METHODS

Table F1.1. Analytical method codes for Method 22.

Method Code	*Symbol & Units*	*Analysis and description*
22B	S_{CR} (%S)	Chromium Reducible Sulfur
22A	S_{AV} (%S)	Acid Volatile Sulfur
22C	S_{DAV} (%S)	Diffusible Acid Volatile Sulfur
22D	S_D (%S)	Disulfide Sulfur
22E	S_E (%S)	Elemental Sulfur
Sulfur results expressed in acid equivalent units		
a-22B	a-S_{CR} (mol H^+/t)	(22B x 623.7) (*calculated as equivalent acidity units*)
a-22A	a-S_{AV} (mol H^+/t)	(22A x 623.7) (*calculated as equivalent acidity units*)
a-22C	a-S_{DAV} (mol H^+/t)	(22C x 623.7) (*calculated as equivalent acidity units*)
a-22D	a-S_D (mol H^+/t)	(22D x 623.7) (*calculated as equivalent acidity units*)
a-22E	a-S_E (mol H^+/t)	(22E x 623.7) (*calculated as equivalent acidity units*)

1.3 SUSPENSION PEROXIDE OXIDATION COMBINED ACIDITY & SULFUR (SPOCAS) – METHOD CODE 23

The codes for the various components of SPOCAS are in Table F1.2 (Analytical method codes) and Table F1.3 (Supplementary finishing codes). See also McElnea *et al*. (2002a, 2002b).

Table F1.2. Analytical method codes for Method 23.

Method Code	*Symbol & Units*	*Analysis and description*
pH measurements		
23A	pH_{KCl}	**pH** of suspension 1:40 1 M KCl extract, overnight shake (TAA)
23Af	pH_F	**pH** measured in the field on saturated soil sample using pH electrode
23B	pH_{OX}	**pH** of suspension 1:25 after initial peroxide digestion
23Bf	pH_{FOX}	**pH** measured in the field – 30% peroxide reaction, pH electrode
Acidity methods		
23F	TAA (mol H^+/t)	**Titratable Actual Acidity** in 1 M KCl titrated to pH 6.5 (suspension)
23G	TPA (mol H^+/t)	**Titratable Peroxide Acidity** in 1 M KCl peroxide digest titrated to pH 6.5 (suspension)
23H	TSA (mol H^+/t)	**Titratable Sulfidic Acidity** [*calculated* as 23G minus 23F]
s-23F	s-TAA (equiv. %S)	(23F/623.7) (*TAA calculated as equivalent % pyrite S for comparison purposes*)
s-23G	s-TPA (equiv. %S)	(23G/623.7) (*TPA calculated as equivalent % pyrite S for comparison purposes*)
s-23H	s-TSA (equiv. %S)	(23H/623.7) (*TSA calculated as equivalent % pyrite S for comparison purposes*)
Sulfur methods (additional codes added for S determination, see Table F1.3)		
23C	S_{KCl} (%)	**KCl extractable sulfur** (after TAA titration)
23D	S_P (%)	**Peroxide sulfur** (after TPA digestion & titration)
23E	S_{POS} (%)	**Peroxide oxidisable sulfur** [23D minus 23C]
a-23E	a-S_{POS} (mol H^+/t)	(23E x 623.7) *(S_{POS} calculated as equivalent acidity units)*
23R	S_{RAS} (%)	Residual acid soluble S after peroxide oxidation (for estimating 'jarositic' sulfur)
a-23R	a-S_{RAS} (mol H^+/t)	(23R x 0.75 x 623.7) *(S_{RAS} expressed in equivalent acidity units)*
s-23R	s-S_{RAS} (% pyrite S)	(23R x 0.75) *(S_{RAS} converted to equiv. % pyrite S for ABA purposes*)
Calcium *values from SPOCAS to estimate additional Ca from carbonate/shell reaction with acid*		
23V	Ca_{KCl} (%)	**Ca extracted in 1 M KCl** (after TAA titration)
23W	Ca_P (%)	**Ca in peroxide** digest (after TPA digestion & titration)
23X	Ca_A (%)	**Ca reacted** with acid generated by peroxide digest [23W minus 23V]
a-23X	a-Ca_A (mol H^+/t)	(23X x 499.0) *(Ca_A calculated as equivalent acid neutralising units)*
s-23X	s-Ca_A (equiv. %S)	(23X x 0.800) *(Ca_A in equiv. % pyrite S it will neutralise)*
Magnesium *values from SPOCAS to estimate additional Mg from acid-shell/dolomite/carbonate reaction*		
23S	Mg_{KCl} (%)	**Mg extracted in 1 M KCl** (after TAA titration)
23T	Mg_P (%)	**Mg in peroxide** digest (after TPA digestion & titration)
23U	Mg_A (%)	**Mg reacted** with acid generated by peroxide digest [23T minus 23S]
a-23U	a-Mg_A (mol H^+/t)	(23U x 822.6) *(Mg_A calculated as equivalent acid neutralising units)*
s-23U	s-Mg_A (equiv. %S)	(23U x 1.319) *(Mg_A in equiv. % pyrite S it will neutralise)*
Excess Acid Neutralising Capacity *from SPOCAS*		
23Q	ANC_E (%$CaCO_3$)	**Excess Acid Neutralising Capacity** (back titration with acid to pH 4 minus TPA titration to pH 6.5) *(expressed in equivalent %$CaCO_3$)*
a-23Q	a-ANC_E (mol H^+/t)	(23Q x 199.8) (*calculated in equivalent acid neutralising units)*
s-23Q	s-ANC_E (equiv. %S)	(23Q / 3.121) (*ANC_E in equiv. % pyrite S it will neutralise*)

SUPPLEMENTARY FINISHING STEP CODES

Supplementary finishing step codes for sulfur (23C, 23D, 23E, 23R), calcium (23V, 23W, 23X) and magnesium (23S, 23T, 23U) are given in Table F1.3.

Table F1.3. Supplementary finishing codes for SPOCAS (Method 23) and S_{HCl} (Method 20B).

Supplement code	*Analyte and finishing step*	*Similar to Rayment and Higginson (1992) method*
Sulfur		
a	Sulfate, turbidimetric	J1a
b	Sulfate, gravimetric	J1b
c	Sulfate, automated colour	J1c
d	Sulfate, ion chromatography	J1d
e	Sulfur, ICP-AES	J2a
f	Sulfate, automated turbidimetric	J1a
g	Sulfate, indirect, barium remaining by AAS	
Calcium		
h	Calcium, ICP-AES	L1c
j	Calcium, atomic absorption (AAS)	L1b
k	Calcium, titration EDTA	L1a
Magnesium		
m	Magnesium, ICP-AES	L2c
n	Magnesium, atomic absorption (AAS)	L2b
p	Magnesium, titration EDTA	L2a

*For example, Method Code **23Ce** is KCl extractable sulfur with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) finishing step to determine sulfur.*

1.4 TOTAL SULFUR (S_T) – METHOD CODE 20A

Table F1.4. Analytical method codes for total sulfur.

Method Code	*Symbol & Units*	*Analysis and description*
20A	S_T (%)	Total Sulfur
a-20A	a-S_T (mol H^+/t)	Total Sulfur *(expressed in acidity units)* (assumes all S is sulfide)

Table F1.5. Finishing codes for Method 20A—Total sulfur (S_T).

Method Code	*Analysis and Description*
1	X-ray fluorescence (similar to method 10A1) (Rayment and Higginson 1992)
2	Leco™ (use of combustion catalyst is recommended)
3	Combustion, titration end-point
4	Combustion, dry ashing sodium bicarbonate, silver oxide (Steinbergs *et al.* 1962)
5	Alkaline sodium hypobromite oxidation + reduction hydriodic acid reduction (Tabatabai and Bremner 1970)
6	Mixed acid digest using nitric, perchloric, hydrofluoric, hydrochloric acids
7	Bromine – nitric acid oxidation (Vogel 1978)

*For example, Method Code **20A1** represents total sulfur by X-ray fluorescence or Method Code **20A2** represents total sulfur by Leco ™ furnace.*

1.5 4 M HCl EXTRACTABLE SULFUR (S_{HCl}) – METHOD 20B

Table F1.6. Analytical method codes for 4 M HCl extractions and associated calculations.

Method Code	*Symbol & Units*	*Analysis and description*
20B	S_{HCl} (%)	Sulfur in 4 M HCl extract
20E	Ca_{HCl} (%)	Calcium in 4 M HCl extract
20F	Mg_{HCl} (%)	Magnesium in 4 M HCl extract
Calculations		
20C	S_{TOS} (%)	Total Oxidisable Sulfur [20A minus 20B]
a-20C	a-S_{TOS} (mol H^+/t)	(20C x 623.7) *(calculated in equivalent acidity units)*
20J	S_{NAS} (%)	Net acid soluble Sulfur or 'jarositic' sulfur [Method 20B minus 23C]
a-20J	a-S_{NAS} (mol H^+/t)	(Method 20J x 467.8) *(calculated in equivalent acidity units)*
s-20J	s-S_{NAS} (%)	(Method 20J x 0.75) *(S_{NAS} converted to equivalent % pyrite S for ABA purposes)*

SUPPLEMENTARY FINISHING STEP CODES FOR 4 M HCl EXTRACT

Table F1.3 lists Supplementary finishing step codes for Method 20B for HCl extractable sulfur (as well as the finishing steps for calcium and magnesium extracted by 4 M HCl).

> *For example, Method Code **20Be** is hydrochloric acid (4 M) extractable sulfur (S_{HCl}), using an ICP-AES finishing step to determine sulfur.*

Total oxidisable sulfur (S_{TOS}) is calculated as the difference between total sulfur (S_T) and 4 M HCl extractable sulfur (S_{HCl}).

The 'full code' for S_{TOS} (Method 20C) involves addition of the appropriate numeral from Table F1.5 to define the total sulfur method and addition of the appropriate lower case alphabetic character from Table F1.3 to define the method used to determine S_{HCl}.

> *For example Method Code **20C1e** is Total sulfur by X-ray fluorescence minus 4 M HCl extractable sulfur by ICP-AES finish.*

1.6 ACID NEUTRALISING CAPACITY – METHOD CODE 19

Table F1.7. Acid neutralising capacity, carbon and net acid soluble alkali cation codes.

Method Code	*Symbol & units*	*Analysis and description*
Acid Neutralising Capacity (ANC)–Acid reacted & back titration methods		
19A1[#]	ANC_{BT} (%$CaCO_3$)	**Acid Neutralising Capacity** (Back Titration after 1 M HCl treatment – **not recommended for ASS**)
19A2	ANC_{BT} (%$CaCO_3$)	**Acid Neutralising Capacity** (Back Titration after 0.1 M HCl treatment – Lewis and McConchie 1994) (*expressed in equivalent %$CaCO_3$ units*)
a-19A2	a-ANC_{BT} (mol H^+/t)	(19A2 x 199.8) (ANC_{BT} *in equivalent acid neutralising units)*
s-19A2	s-ANC_{BT} (%S)	(19A2 / 3.121) (ANC_{BT} *in equiv. % pyrite S it will neutralise)*
Leco™ Carbon Methods		
6B4	C_T (%)	**Carbon: Total** (Leco™) (Method 6B4 from Revised Rayment *et al.* (In Press)
6B5	C_{TO} (%)	**Carbon: Total Organic** (Leco™) (Method 6B5 from Revised Rayment *et al.* (In Press)
19C1	*C_{IN} (%)	**Carbon: Inorganic** [Method 6B4 minus 6B5]
a-19C1	a-C_{IN} (mol H^+/t)	(19C1 x 1665) (C_{IN} *calculated in equivalent acid neutralising units)*
s-19C1	s-C_{IN} (%)	(19C1 x 2.67) (C_{IN} *in equiv. % pyrite S it will neutralise*)
Net acid soluble Ca and Mg		
19F1	Ca_{NAS} (%)	**Calcium: Net acid soluble** (Net Ca released by 4 M HCl) [Method 20E minus 23V]
a-19F1	a-Ca_{NAS} (mol H^+/t)	(19F1 x 499.0) *(Ca_{NAS} calculated in equivalent acid neutralising units*)
19G1	Mg_{NAS} (%)	**Magnesium: Net acid soluble**–(Net Mg released by 4 M HCl) [Method 20F minus 23S]
a-19G1	a-Mg_{NAS} (mol H^+/t)	(19G1 x 822.6) *(Mg_{NAS} calculated in equivalent acid neutralising units*)

Table notes:

[#]similar to Rayment and Higginson (1992)

**C_{IN} can also be expressed in ANC units of equivalent %$CaCO_3$ (ie. ANC_C)*

1.7 ANALYTICAL METHOD CODES FOR 'OUTDATED' PEROXIDE OXIDATION COMBINED ACIDITY & SULFATE (POCAS) – METHOD CODE 21

The codes for the outdated POCAS are in Table F1.8 (Analytical method codes) and the finishing steps are the same as Table F1.3 (Supplementary finishing codes).

Table F1.8. Analytical method codes for outdated Method 21.

Method Code	*Symbol & Units*	*Analysis and description*
pH measurements		
21A	pH_{KCl}	pH of filtered 1:20 1 M KCl extract, overnight shake (TAA)
21Af	pH_F	pH done in the field on saturated soil sample using pH probe
21B	pH_{OX}	pH of filtered 1:20 1 M KCl after peroxide digestion
21Bf	pH_{FOX}	pH measured in the field – 30% peroxide reaction, pH probe
Sulfur methods		
21C	S_{KCl} (%)	KCl extractable S (additional codes added for S determination)
21D	S_P (%)	Peroxide sulfur after peroxide digestion
21E	S_{POS} (%)	Peroxide oxidisable S [21D minus 21C]
Acidity methods		
21F	TAA (mol H^+/t)	Total Actual Acidity in 1 M KCl titrated to pH 5.5
21G	TPA (mol H^+/t)	Total Potential Acidity in 1 M KCl peroxide digest titrated to pH 5.5
21H	TSA (mol H^+/t)	Total Sulfidic Acidity [21G minus 21F]
21J	S_{TAA} (%)	TAA *calculated as equivalent* pyrite S % for comparison and arithmetic purposes
21K	S_{TPA} (%)	TPA *calculated as equivalent* pyrite S % for comparison purposes
21L	S_{TSA} (%)	TSA *calculated as equivalent* pyrite S % for comparison with 21E using the same units
Calcium *values from POCASm to estimate additional Ca from acid-shell/carbonate reaction*		
21V	Ca_{KCl} (%)	Ca extracted in 1 M KCl (TAA)
21W	Ca_P (%)	Ca in peroxide digest (TPA)
21X	Ca_A (%)	Ca reacted with acid generated by peroxide digest [21W minus 21V]
Magnesium *values from POCASm to estimate additional Mg from acid-shell/dolomite/carbonate reaction*		
21S	Mg_{KCl} (%)	Mg extracted in 1 M KCl (TAA)
21T	Mg_P (%)	Mg in peroxide digest (TPA)
21U	Mg_A (%)	Mg reacted with acid generated by peroxide digest [21T minus 21S]
Sodium *values from POCASm*		
21M	Na_{KCl} (%)	Na extracted in 1 M KCl (TAA)
21N	Na_P (%)	Na in peroxide digest (TPA)
21P	Na_A (%)	Na difference (21N minus 21M)
Neutralising *methods*		
21Q	NQ (%$CaCO_3$)	Quick residual neutralising capacity
21R	NQ_S (S_R %)	Quick residual neutralising capacity 21Q, calculated as equivalent pyrite %S

The codes for the ***outdated*** POCAS are similar to the SPOCAS codes in Table F1.2 (Analytical method codes) but with some changes. The finishing steps are identical to Table F1.3 (Supplementary finishing steps) except 21 is used instead of 23. The codes appear in the earlier guidelines.

It is important that where the *outdated* POCAS or POCASm method has been used that results be clearly coded as Method 21 to distinguish them from result obtained using the improved Suspension Peroxide method (SPOCAS).

1.8 MOISTURE CODES

Table F1.9. Acid sulfate soil moisture codes.

Method Code	*Symbol & units*	*Analysis and description*
Moisture content methods from Rayment and Higginson (1992)		
2B1	W_{105} (%)	As received moisture content 105 °C
Methods to be added to Rayment et al. *(In Press)*		
2B2	W_{85} (%)	As received moisture content 85 °C

1.9 ACID SULFATE SOIL LIMING CONVERSIONS

Conversions between some of the common units used to express analytical result from acid sulfate soils are given in Table F1.10. The conversions are based on 1 mole pyrite producing 2 moles of sulfuric acid or 4 moles of H^+ with the equivalent liming rates using a safety factor of 1.5.

Table F1.10. Conversions for some units of reporting acid sulfate soils analysis.

Net Acidity *Sulfur units* ***(% pyrite S)*** [A]	***Net Acidity*** ***mol H^+/kg*** [A] ***(%S x 0.6237)***	***Net Acidity*** ***mol H^+/t*** ***or*** ***(mol H^+/m^3 [B]*)*** ***(%S x 623.7)***	***kg $CaCO_3$/t soil*** ***or*** ***(kg $CaCO_3/m^3$ *)*** ***(mol H^+/t) /19.98)*** ***No safety factor***	***kg $CaCO_3$/t soil*** ***or*** ***(kg $CaCO_3/m^3$ *)*** ***(mol H^+/t) /13.32)*** ***Safety factor = 1.5 *****
0.01	0.0062	6.237	0.312	0.45
0.03	0.0187	18.71	0.936	1.40
0.06	0.0374	37.42	1.87	2.81
0.1	0.0624	62.37	3.12	4.68
0.2	0.1247	124.7	6.24	9.36
0.3	0.1871	187.1	9.36	14.0
0.5	0.3119	311.9	15.6	23.4
1.0	0.6237	623.7	31.2	46.8
2.0	1.2474	1247	62.4	93.6
5.0	3.1185	3119	156	234

Notes on Table F1.10

[A] *The value for net acidity in units of mol H^+/t or % pyrite sulfur can generally be obtained using the ABA equation or tables (eg. Section A3, Tables A3.1–A3.4) after performing the Chromium or SPOCAS suites of analysis.*

[B] *Commonly, laboratories report acid trail results (ie. TAA, TPA, TSA) as moles H^+/t of soil. To convert from moles H^+/t to %S, divide the acid trail results by 623.7. Similarly to convert oxidisable sulfur results (%S) to acidity units (mol H^+/t) multiply by 623.7.*

***Assumes a bulk density of 1.0 g/cm^3 or 1 t/m^3 (the bulk density range can be 0.7–2.0 and as low as 0.2 for peats). Where bulk density is >1 g/cm^3 then the factor will increase for lime rates/m^3 soil (eg. if BD = 1.6, then 1 m^3 of soil with 1.0% will require 75 kg lime/m^3 instead of 47 kg lime/m^3).*

****Minimum safety factor of 1.5 to allow for non-homogeneous mixing and poor reactivity of lime. The factor only applies for the addition of good quality fine agricultural lime ($CaCO_3$) with a neutralising value of 100. Where the neutralising value is less than 100, the factor*

must be increased. If the neutralising value is greater than 100 (eg. MgO), the factor may be reduced accordingly. Coarse grade limestone will require a higher safety factor, as will the application of neutralising agents in environmentally sensitive sites. Excess lime must always be used to keep the soil pH >5.5 and generally >6.5.

1.10 EXPLANATION OF CALCULATIONS AND EXAMPLES

As discussed in earlier sections, the calculation of acidity from the oxidation of ASS is based on the stoichiometry of the pyrite oxidation reaction.

$$FeS_2 + {}^{15}/_4O_2 + {}^{7}/_2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

1 mole pyrite (FeS_2) $\rightarrow$ 4 moles acid (H^+)
1 mole sulfur (S) $\rightarrow$ 2 moles acid (H^+)

Examples:

A) Converting %S to mol H^+/t

A soil has a S_{CR} value of 1.23 %S, which in other words is 1.23 g sulfur (as pyrite) per 100 g of oven dry soil.
The first step is to convert grams of sulfur to moles of sulfur. The molar mass of sulfur (ie. the weight of 1 mole of sulfur) is 32.066 g/mol.

1.23 %S (or g S/100 g soil) ÷ 32.066 = 3.836×10^{-2} mol S/100 g soil

Now, we want to convert from moles S to moles H^+. From the above equation, for every mole of pyrite S oxidised, 2 moles of H^+ is produced.

3.836×10^{-2} mol S/100 g soil x 2 = 7.672×10^{-2} mol H^+/100 g soil

All that remains is to convert from per 100 g to per tonne. There are 1000 kg, or 1 000 000 g in a tonne, so we need to multiply the previous result by 1 000 000/100 (ie. multiply by 10 000).

7.672×10^{-2} mol H^+/100 g soil x 10 000 = 767 mol H^+/t.

Hence, to convert **from %S to mol H^+/t**: %S ÷ 32.066 x 2 x 10 000, or **multiply %S by x 623.7**

Conversely, to convert **from mol H^+/t to %S**, **divide by 623.7**

B) Calculating net acidity from laboratory results

Calculate the Net Acidity (in units of equivalent % pyrite S) for a soil (analysed by the SPOCAS suite) which has a pH_{KCl} of 3.3, a TAA of 73 mol H^+/t, an S_{POS} of 0.13 %S and an S_{RAS} of 0.45 %S.

Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF

We have an estimate of the potential acidity already in the correct units: S_{POS} = 0.13 %S

We have an actual acidity result: s-TAA = TAA/623.7 = 73/623.7 = 0.12 %S

Finally we have an estimate of retained acidity: s-S_{RAS} = S_{RAS} x 0.75 = 0.45 x 0.75 = 0.34 %S

∴ Net Acidity = 0.13 + 0.12 + 0.34 = 0.59 %S

C) Calculating net acidity and lime requirement from laboratory results

We have an ASS that needs to be treated with alkaline material to prevent any future net acid generation. The S_{CR} method gave a result of 2.2 %S. The pH_{KCl} was 4.9 and the TAA was 26 mol H^+/t. We want to calculate the amount of super-fine agricultural lime (with a neutralising value of 96) that needs to be added to 5 cubic metres of the wet soil to fully ameliorate it. The wet soil has a bulk density of 1.3 g/cm^3.

Step 1: We need to conduct an acid base account for the dry soil using the ABA equation.

Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF

First, we have to determine the individual components of the ABA equation. At this stage it is necessary to work out what components are applicable for this particular soil. The pH_{KCl} is <6.5, so the soil does not have any effective ANC, so ANC does not need to be measured. The pH_{KCl} is >4.5, so there is no retained acidity to consider. There is however some actual acidity, which has been measured by TAA. There is also potential sulfidic acidity and this has been measured using the Chromium method.

Now we must decide which units we want to use for the ABA. In this case, we will use units of mol H^+/t. The chromium reducible sulfur result (S_{CR}) is in units of %S, which needs to be converted to a-S_{CR} (in units of mol H^+/t). The TAA is already in the required units.

Potential Sulfidic Acidity: a-S_{CR} = S_{CR} x 623.7 = 2.2 x 623.7 = 1372 mol H^+/t
Actual Acidity : TAA = 26 mol H^+/t
Net Acidity: Potential Sulfidic Acidity + Actual Acidity = 1372 + 26 = 1398 mol H^+/t

Step 2: We now want to work out the weight of pure $CaCO_3$ needed to neutralise this Net Acidity. We use the stoichiometry of the reaction showing the acid dissolution of $CaCO_3$ which shows that each mole of $CaCO_3$ neutralises 2 moles of H^+.

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$$

Hence 1398 mol H^+/t is neutralised by 1398 ÷ 2 = 699 mol $CaCO_3$/t

To convert to g $CaCO_3$/t, multiply by molar mass of $CaCO_3$ (100.087 g/mol), then divide by 1000 to get to kg $CaCO_3$/t.

699 mol $CaCO_3$/t x 100.087 ÷ 1000 = 69.97 kg $CaCO_3$/t.

Hence, to convert **from mol H^+/t** to **kg $CaCO_3$/t**: mol H^+/t ÷ 2 x 100.087 ÷ 1000, or **divide by 19.98**

Step 3: We now need to consider the neutralising value of the Ag Lime and the application of a suitable safety factor. The neutralising value of pure $CaCO_3$ is 100 and that of the Ag Lime is 96, hence to convert from kg $CaCO_3$/t to kg Ag Lime/t we need to multiply by (100/96).

69.97 kg $CaCO_3$/t x (100/96) = 72.88 kg Ag Lime/t

The Ag Lime is super-fine grade, so the minimum safety factor of 1.5 is applicable.

Ag Lime rate x safety factor = 72.88 kg Ag Lime/t x 1.5 = 109.3 kg Ag Lime/t.

Step 4: We have worked out the required rate for the dry soil. All that remains is to calculate the rate for the wet soil (knowing the bulk density). The bulk density is 1.3 g/cm^3 which is equivalent to 1.3 t/m^3.

109.3 kg Ag Lime/t x 1.3 t/m^3 = 142.1 kg Ag Lime/m^3

So for 5 m^3 we need a total of 710.6 kg of Ag Lime.

D) Calculating net acidity from verification testing results

(i) Some acid sulfate soil has been treated with agricultural lime (using the 1.5 safety factor). Samples have been collected for verification testing (ie. to ensure the appropriate amount of lime has been used and that there will be no net acidity) using the SPOCAS suite of analysis and the following results were obtained:
pH_{KCl} = 8.6 pH_{OX} = 7.5
S_{POS} = 0.67 %S
ANC_E = 5.51 %$CaCO_3$
(TAA and S_{RAS} did not need to be determined as pH_{KCl} >6.5 and there was no jarosite found in the initial investigation).

In order to calculate net acidity, we firstly need to convert all results to equivalent units (either %S or mol H^+/t). For this example, we will use %S. The S_{POS} result is already in the required units.

Potential Sulfidic Acidity: S_{POS} = 0.67 %S
Acid Neutralising Capacity: s-ANC_E = ANC_E/3.121 = 5.51/3.121 = 1.77 %S

We can now calculate net acidity using the following equation (as outlined in Table A3.5):
Net Acidity = Potential Sulfidic Acidity – measured ANC/FF
= S_{POS} – ([S_{POS} + s-ANC_E[1]] / 1.5)
= 0.67 – ([0.67 + 1.77] / 1.5)
= 0.67 – 1.63
= –0.96 %S

This net acidity result shows that sufficient lime has been added to this soil and verification testing has passed.

(ii) Some acid sulfate soil has been treated with agricultural lime (using the 1.5 safety factor). The soils had not oxidised before treatment (ie. no jarosite was present in the soil). Samples have been collected for verification testing (ie. to ensure the appropriate amount of lime has been used and that there will be no net acidity) using the Chromium suite of analysis and the following results were obtained:
pH_{KCl} = 8.5
S_{CR} = 0.41 %S
ANC_{BT} = 4.19 %$CaCO_3$
(TAA and S_{RAS} did not need to be determined as pH_{KCl} >6.5 and there was no jarosite found in the initial investigation).

[1] In the SPOCAS suite, the acid neutralising capacity result to be substituted into the ABA equation is comprised of both the excess acid neutralising capacity, plus the ANC that was already spent in neutralising the acid released by the peroxide oxidation of sulfides (which is equivalent to S_{POS}; hence ANC = (S_{POS} + ANC_E)/1.5).

In order to calculate net acidity, we firstly need to convert all results to equivalent units (either %S or mol H^+/t). For this example, we will use %S. The S_{CR} result is already in the required units.

Potential Sulfidic Acidity: S_{CR} = 0.41 %S
Acid Neutralising Capacity: s-ANC_{BT} = ANC_{BT}/3.121 = 4.19/3.121 = 1.34 %S

We can now calculate net acidity using the following equation (as outlined in Table A3.6):
Net Acidity = Potential Sulfidic Acidity – measured ANC/FF
= S_{CR} – (s-ANC_{BT} /1.5)
= 0.41 – (1.34 /1.5)
= 0.67 – 0.89
= –0.22 %S

This net acidity result shows that sufficient lime has been added to this soil and verification testing has passed.

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SECTION G: MISCELLANEOUS RESEARCH METHODS

Note: Section G to be included at a later date.

SECTION H: FIELD TESTS

1. ACID SULFATE SOIL FIELD pH TESTS

KM Watling, CR Ahern and KM Hey

1.1 INTRODUCTION

The field pH (pH_F) and field pH peroxide (pH_{FOX}) tests have been developed for a rapid assessment in the field of the likelihood of acid sulfate soils. These tests are easy to conduct, quick, and have a minimum set-up cost. The field tests have been developed to give reasonable prediction for many soils (provided the tests are performed properly) whilst at the same time being relatively easy to perform with a minimal amount of equipment. Soil field pH tests provide a useful indication of the existing and potential acidity levels in the soil. Although these field tests may provide an indication of ASS presence, they are purely qualitative and do not give any quantitative measure of the amount of acid that has been or could be produced through the oxidation process.

Field pH tests should be part of any ASS investigation. The field pH tests (both pH_F and pH_{FOX}) should be conducted at 0.25 m intervals on the soil profile, ensuring at least one test per horizon. It is recommended that field tests be conducted on-site, in the field. If the tests can't be performed in the field on-site, tests should be conducted within 24 hours of soil sample collection, ensuring appropriate sample handling procedures (see Section B). Samples suspected of containing monosulfides should undergo field pH testing immediately in the field.

1.2 FIELD pH TEST (pH_F)

The procedure for the field pH test (pH_F) is outlined below:

- **Calibrate battery powered field pH meter** according to manufacturer's instructions.
- **Prepare the test tubes in the test tube rack**. Make sure the rack is marked with the depths so there is no confusion about the top and bottom of the profile. Use of separate racks for the pH_F and pH_{FOX} tests is recommended as contamination may occur when the pH_{FOX} reactions are violent. As the soil:water paste is inclined to stick to the walls of tubes, it is best to use shallow, broad test tubes as this makes cleaning easier.
- **Conduct tests at intervals on the soil profile of 0.25 m or at least one test per horizon** whichever is lesser.
- **Remove approximately 1 teaspoon of soil from the profile. Place approximately ½ teaspoon of that soil into the pH_F test tube and place ½ teaspoon of the soil into the pH_{FOX} test tube** for the corresponding depth test. It is important that these two sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
- **Place enough deionised water** (or demineralised water if deionised water is not available; never use tap water) **in the pH_F test tube** to make a paste similar to 'grout mix' or 'white sauce', **stirring the soil:water paste** with a skewer, strong tooth pick or similar to ensure all soil 'lumps' are removed. Do not leave the soil samples in the test tubes without water for more than 10 minutes. This will reduce the risk of sulfide oxidation—the pH_F is designed to indicate the existing pH of a soil in the field; any oxidation subsequent to the soil's removal

from the ground will not reflect the true field pH. In some instances, in less than 5 minutes, monosulfidic material may start to oxidise and substantially affect the pH_F results.

- **Immediately place the spear point electrode (preferred method) into the test tube**, ensuring that the spear point is totally submerged in the soil:water paste. Never stir the paste with the electrode. This will damage the semi-permeable glass membrane.
- **Measure the pH_F** using a pH meter with spear point electrode.
- **Wait for the reading to stabilise and record the pH measurement.**
- **All measurements should be recorded on a data sheet**.

1.3 FIELD pH PEROXIDE TEST (pH_{FOX})

It is recommended that 30% hydrogen peroxide (H_2O_2) be used in the pH_{FOX} test. 30% H_2O_2 is highly corrosive and care should be taken when handling and using the peroxide. Safety glasses and gloves should be worn when handling and using peroxide. All chemical bottles should be clearly labelled and Material Safety Data Sheets (MSDS) should be kept with the chemicals at all times. Appropriate health and safety precautions should be adhered to. Peroxide should be kept in the fridge when not in use.

The procedure for the field pH peroxide test (pH_{FOX}) is outlined below:

- **Adjust the pH of the hydrogen peroxide to pH 4.5–5.5 before going into the field**. This can be done by adding a few drops of dilute NaOH stirring and checking the pH with the electrode regularly until the correct range is reached. NaOH is highly caustic so safety precautions must be exercised. NaOH can raise the pH quickly or slowly, so the pH needs to be monitored. Recheck the pH after allowing the peroxide to stand for 15 minutes. Do NOT buffer a large quantity of hydrogen peroxide at one time. Only buffer the amount to be used in the field for about a month. This must be kept in a fridge, well labelled with only small quantities to be taken into the field at one time. This will ensure the longevity of the peroxide. Further, over time, the pH of the peroxide that has already been buffered may change. It is important to check the pH of the peroxide in the morning before departing to the field. Having a small quantity of NaOH in the field kit is recommended so the peroxide can be buffered if required.
- **Calibrate battery powered field pH meter** according to manufacturer's instructions.
- **Prepare the test tubes in the test tube rack as for pH_F test**. Make sure the rack is marked with the depths so there is not confusion about the top and bottom of the profile. Use of separate racks for the pH_F and pH_{FOX} tests is recommended as contamination may occur when the pH_{FOX} reactions are violent. It is important to use **heat-resistant test tubes** for the pH_{FOX} test as the reaction can generate considerable heat (up to 90°C). It is recommended that a tall, wide tube be used for this test as considerable bubbling may occur, particularly on highly sulfidic or organic samples.
- **Conduct pH_{FOX} tests at intervals on the soil profile of 0.25 m or at least one per horizon** whichever is lesser.
- **From the teaspoon of soil previously collected for the pH_F test, place approximately ½ teaspoon of the soil into the pH_{FOX} test tube** for the corresponding depth test. It is important that these two sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
- **Add a few millilitres of 30% H_2O_2** (adjusted to pH 4.5–5.5) **to the soil** (sufficient to cover the soil with peroxide) **and stir the mixture**. Do NOT add the peroxide to the test tube in which the pH_F test was conducted, that is, the pH_{FOX} test tube should not have any deionised water in it. Beakers can be used, however glass is usually easily broken when conducting field work, and when multiple tests are being conducted it is difficult to handle large beaker

sizes efficiently. Do NOT add more than a few millilitres at a time. This will prevent overflow and wastage of peroxide. A day's supply of peroxide should be allowed to reach room temperature prior to use (cold peroxide from the fridge may be too slow to react).

- **Rate the reaction of soil and peroxide using a XXXX scale** (see below and Table H1.1).
- **Ideally, allow approximately 15 minutes for any reactions to occur**. If substantial sulfides occur, the reaction will be vigorous and may occur almost instantly. In this case, it may not be necessary to stir the mixture. Careful watch will be needed in the early stages to ensure that there is no cross contamination of samples in the test tube rack. If the reaction is violent and the soil:peroxide mix is escaping from the test tube, a small amount of deionised water (or demineralised water; not tap water) can be added (using a wash bottle) to cool and calm the reaction. Usually this controls overflow. Do NOT add too much deionised water as this may dilute the mixture and affect the pH value. It is important to only use a small amount of soil otherwise violent reactions will overflow and the sample will be lost.
- **Steps 6 to 8 may be repeated** until the soil:peroxide mixture reaction has slowed. This will ensure that most of the sulfides have reacted. In the lab this procedure would be repeated until no further reaction occurs, however in the field, best judgement is recommended. Usually one or two extra additions of a few millilitres of peroxide are sufficient.
- If there is no initial reaction, individual test tubes containing the soil:peroxide mixture can be placed into a container of hot water (especially in cooler weather) or in direct sunlight. This will encourage the initial reaction to occur. When the sample starts to 'bubble', remove the test tube immediately from the hot water and replace into test tube rack.
- **Wait for the soil:peroxide mixture to cool** (may take up to 10 minutes). The reactions often exceed 90°C. Placing an electrode into these high temperature situations may result in physical damage and inaccurate readings. Check the temperature range of the pH meter and probe to see what temperature is suitable. Note that a more exact pH is achieved if a temperature probe is also used, however this may be impractical in some field situations.
- U**se an electronic pH meter (preferred method) to measure the pH_{FOX}**. Place a spear point electrode into the test tube, ensuring that the spear point is totally submerged in the soil:peroxide mixture. Never stir the mixture with the electrode. This will damage the semi-permeable glass membrane.
- **Wait for the reading to stabilise and record the pH_{FOX} measurement**.
- **All measurements should be recorded on a data sheet**.

a) Rating soil reactions of the pH_{FOX} test using the XXXX scale

The rate of the reaction generally indicates the level of sulfides present, but depends also on texture and other soil constituents. A soil containing very little sulfides may only rate an 'X' however a soil containing high levels of sulfides (remember the exact level of sulfides cannot be determined using the pH_{FOX} test) is more likely to rate a 'XXXX' although there are exceptions. This rating scale alone should not be used to identify ASS. It is not a very reliable feature in isolation as there are other factors including manganese and organic acids which may trigger reactions. Reactions with organic matter tend to be more 'frothing' and don't tend to generate as much heat as sulfidic reactions. Manganese reactions will be quite extreme, but don't tend to lower the pH_{FOX}. Table H1.1 indicates the reaction scale for pH_{FOX} tests.

Table H1.1. Soil reaction rating scale for the pH_{FOX} test.

Reaction scale	Rate of reaction
X	Slight reaction
XX	Moderate reaction
XXX	High reaction
XXXX	Very vigorous reaction, gas evolution and heat generation commonly >80°C

1.4 INTERPRETATION OF FIELD pH TESTS

For information on interpreting field pH test results, please consult the following documents and publications:

Ahern CR, Ahern MR, Powell B (1998). 'Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998'. pp. 28–30 (Queensland Department of Natural Resources: Brisbane)

Ahern CR, Stone Y, Blunden B (1998). Acid Sulfate Soils Assessment Guidelines. In 'Acid Sulfate Soils Manual 1998'. pp. 56–58 (Acid Sulfate Soil Management Advisory Committee: Wollongbar, NSW)

Hey KM, Ahern CR, Watling KM (2000) Using Chemical Field Tests to Identify Acid Sulfate Soils Likelihood. In 'Acid Sulfate Soils: Environmental Issues, Assessment and Management, Technical Papers.' (Eds CR Ahern, KM Hey, KM Watling, VJ Eldershaw) pp. 16/9–16/12 (Queensland Department of Natural Resources: Brisbane)

Hey KM (Ed) (2002). 'Field Testing, Sampling and Safety for Acid Sulfate Soils'. pp. 12–16 (Queensland Department of Natural Resources and Mines: Brisbane)

2. EFFERVESCENCE TEST ('FIZZ TEST') FOR CARBONATES

This test is used to determine the presence of carbonates in soil. It is a quick, easy, cheap test to conduct in the field. The test should be conducted on samples suspected of containing carbonates (eg. fine shell, crushed coral etc).

The procedure for the fizz test is outlined below:

- **Place a small sample of soil (approximately one teaspoon) into a clear test tube**. Clear test tubes are preferred as this makes it easier to see any reactions. It is important that test tubes used in the fizz test are not used for the field pH tests as cross-contamination may occur, affecting pH readings.
- **Place two or three drops of 1 M hydrochloric acid (HCl) onto the soil sample**. HCl is highly corrosive so safety precautions must be exercised.
- **Rate the reaction** (see Table H2.1).
- **All measurements should be recorded on a data sheet**.

Table H2.1. Soil reaction rating scale for the fizz test (as described in McDonald *et al*. 1990, pp. 147–148).

Reaction scale	Rate of reaction
N – non-calcareous	No audible or visible effervescence
S – slightly calcareous	Slightly audible but no visible effervescence
M – moderately calcareous	Audible and slightly visible effervescence
H – highly calcareous	Moderate visible effervescence
V – very highly calcareous	Strong visible effervescence

References

McDonald RC, Isbell RF, Speight JG, Walker J, Hopkins MS (1990) 'Australian Soil and Land Survey Field Handbook, 2nd Edn.' (CSIRO Publishing: Canberra)

SECTION I: APPENDIX

1. SUGGESTED REPORT FORMAT FOR SPOCAS AND CHROMIUM SUITE AND COMBINED DATA RESULTS

Table I1.1. Suggested Chromium suite report format.

Field morphology summary								Laboratory Results									
Borehole No/ID	Soil Texture	Field pH				Sample depth	Lab No/ID	pH_{KCl}	S_{CR}	TAA	S_{HCl}	S_{KCl}	S_{NAS}	ANC_{BT}	C_T	C_{TO}	C_{IN}
		Depth	pH_F	pH_{FOX}	Reaction												
		(m)				(m)			%S	mol H^+/t	%S			$\%CaCO_3$	%C		
								23A	22B	23F	20B	23C	20J	19A2	6B4	6B5	19C1

Table I1.2. Suggested SPOCAS suite report format.

Field Morphology Summary								Laboratory Results																					
Borehole No/ID	Soil texture	Field pH				Sample depth	Lab No/ID	pH_{KCl}	pH_{OX}	TAA	TPA	S_{KCl}	S_P	S_{RAS}	S_{HCl}	Ca_{KCl}	Ca_P	Mg_{KCl}	Mg_P	TSA	ANC_E	S_{POS}	S_{NAS}	Ca_A	Mg_A
		Depth	pH_F	pH_{FOX}	Reaction																								
		(m)				(m)				mol H^+/t		%S				%Ca		%Mg		mol H^+/t	$\%CaCO_3$	%S	%S	%Ca	%Mg
								23A	23B	23F	23G	23C	23D	23R	20B	23V	23W	23S	23T	23H	23Q	23E	20J	23X	23U

Table I1.3. Suggested combined data report format.

Field Morphology Summary								Laboratory Results																												
Borehole No/ID	Soil texture	Field pH				Sample depth	Lab No/ID	pH_{KCl}	pH_{OX}	TAA	TPA	TSA	S_{KCl}	S_P	S_{POS}	S_{CR}	S_{RAS}	S_T	S_{HCl}	S_{TOS}	S_{NAS}	Ca_{KCl}	Ca_P	Ca_A	Mg_{KCl}	Mg_P	Mg_A	ANC_E	ANC_{BT}	C_T	C_{TO}	C_{IN}
		Depth	pH_F	pH_{FOX}	Reaction																													
		(m)				(m)				mol H+/t			%S									%Ca			%Mg			$\%CaCO_3$		%C		
								23A	23B	23F	23G	23H	23C	23D	23E	22B	23R	20A	20B	20C	20J	23V	23W	23X	23S	23T	23U	23Q	19A2	6B4	6B5	19C1

2. GLOSSARY

(Acid) Fizz test: The field test used for soils to test for the presence of carbonate minerals, whereby dilute hydrochloric acid is added to the soil. An effervescent fizzing reaction indicates the presence of carbonate minerals.

Acid Base Accounting (ABA): The process by which the various acid-producing components of the soil are compared with the acid neutralising components so that the soil's net acidity can be calculated.

Action criteria: The critical net acidity values (expressed in units of equivalent % pyrite sulfur, or equivalent mol H^+/t) for different soil texture groups and sizes of soil disturbance that trigger the need for ASS management.

Actual Acidity: A component of existing acidity. The soluble and exchangeable acidity already present in the soil, often as a consequence of previous oxidation of sulfides. It is this acidity that will be mobilised and discharged following a rainfall event. It is measured in the laboratory using the TAA method. It does not include the less soluble acidity (ie. retained acidity) held in hydroxy-sulfate minerals such as jarosite.

ANC: Acid neutralising capacity. A measure of a soil's inherent ability to buffer acidity and resist the lowering of the soil pH.

ANC_{BT}: Acid neutralising capacity by back titration. Acid neutralising capacity measured by acid digest followed by back titration of the acid that has not been consumed.

ANC_E: Excess acid neutralising capacity. Found in soils with acid neutralising capacity in excess of that needed to neutralise the acidity generated by oxidation of sulfides. The soil is oxidised with peroxide, then a titration is performed with dilute hydrochloric acid to a pH of 4, followed by a second peroxide digestion. If a soil has a positive ANC_E result then the TPA result is zero and vice versa.

Ca_A: Reacted calcium. The calcium soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. ($Ca_P - Ca_{KCl}$). It can be used (in combination with Mg_A) to provide an estimate of the soil carbonate content, but may be an underestimate if the HCl-titration to pH 4 has not been performed as part of the TPA/ANC_E procedure.

Ca_{HCl}: Calcium soluble in 4 M HCl, which includes soluble and exchangeable calcium as well as calcium found in certain carbonate minerals (eg. dolomite, calcite, aragonite).

Ca_{KCl}: Potassium chloride extractable calcium measured following the TAA analysis, which includes soluble and exchangeable calcium as well as calcium from gypsum.

Ca_{NAS}: Net acid soluble calcium. The calcium soluble in 4 M HCl that is not soluble in 1 M KCl. ($Ca_{HCl} - Ca_{KCl}$). It can be used (in combination with Mg_{NAS}) to provide an estimate of the soil carbonate content, but may be an overestimate if calcium is dissolved from non-carbonate or non-acid-neutralising minerals.

Ca_P: Peroxide calcium. Calcium measured following the TPA analysis, which includes soluble and exchangeable calcium, calcium from gypsum, as well as calcium (eg. from carbonates) dissolved as a result of acid produced due to oxidation of sulfides by peroxide.

Chromium Suite: The acid base accounting approach used to calculate net acidity which uses the chromium reducible sulfur method to determine potential sulfidic acidity. A decision tree approach based on the pH_{KCl} result is then used to determine the other components of the acid base account.

C_{IN}: Inorganic carbon. ($C_T - C_{TO}$). It is used to estimate the carbonate content of the soil.

CRS: The acronym often given to the Chromium Reducible Sulfur method.

C_T: Total carbon. A measure of the total carbon content of the soil, encompassing both organic and inorganic forms.

C_{TO}: Total organic carbon. The carbon in sample measured following a sulfurous acid digestion procedure used to remove carbonate carbon.

Existing Acidity: The acidity already present in acid sulfate soils, usually as a result of oxidation of sulfides, but which can also be from organic material or acidic cations. It can be further sub-divided into actual and retained acidity, ie. Existing Acidity = Actual Acidity + Retained Acidity.

Fineness factor: A factor applied to the acid neutralising capacity result in the acid base account to allow for the poor reactivity of coarser carbonate or other acid neutralising material. The minimum factor is 1.5 for finely divided pure agricultural lime, but may be as high as 3.0 for coarser shell material.

Mg_A: Reacted magnesium. The magnesium soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. ($Mg_P - Mg_{KCl}$). It can be used (in combination with Ca_A) to provide an estimate of the soil carbonate content, but may be an underestimate if the HCl-titration to pH 4 has not been performed as part of the TPA/ANC_E procedure.

Mg_{HCl}: Magnesium soluble in 4 M HCl, which includes soluble and exchangeable magnesium as well as magnesium found in certain carbonate minerals (eg. dolomite, magnesite).

Mg_{KCl}: Potassium chloride extractable magnesium measured following the TAA analysis, which includes soluble and exchangeable magnesium.

Mg_{NAS}: Net acid soluble magnesium. The calcium soluble in 4 M HCl that is not soluble in 1 M KCl. ($Mg_{HCl} - Mg_{KCl}$). It can be used (in combination with Ca_{NAS}) to provide an estimate of the soil carbonate content, but may be an overestimate if magnesium is dissolved from non-carbonate or non-acid-neutralising minerals.

Mg_P: Peroxide magnesium. Magnesium measured following the TPA analysis, which includes soluble and exchangeable magnesium, as well as magnesium (eg. from carbonates) dissolved as a result of acid produced due to oxidation of sulfides by peroxide.

Monosulfides: The term given to the highly reactive iron sulfide minerals found in ASS that have the approximate formula 'FeS' and which are soluble in hydrochloric acid (as opposed to iron disulfides such as pyrite that aren't appreciably soluble in hydrochloric acid).

Net Acidity: The result obtained when the values for various components of soil acidity and acid neutralising capacity are substituted into the Acid Base Accounting equation. Calculated as: Net Acidity = Potential sulfidic Acidity + Existing Acidity – (Acid Neutralising Capacity/Fineness Factor)

pH_F: Field pH. Field determination of pH in a soil:water paste.

pH_{FOX}: Field peroxide pH. Field determination of pH in a soil:water mixture following reaction with hydrogen peroxide.

pH_{KCl}: Potassium chloride pH. pH in a 1:40 (W/V) suspension of soil in a solution of 1 M potassium chloride measured prior to TAA titration.

pH_{OX}: Peroxide oxidised pH. pH in a suspension of soil in a solution after hydrogen peroxide digestion in the SPOCAS method.

POCAS: An acronym standing for Peroxide Oxidation Combined Acidity and Sulfate method (Method Code 21). This method has been superseded by the SPOCAS method.

POCASm: An acronym standing for the modified Peroxide Oxidation Combined Acidity and Sulfate method. This method has been superseded by the SPOCAS method.

Potential (sulfidic) acidity: The latent acidity in ASS that will be released if the sulfide minerals they contain (eg. pyrite) are fully oxidised. It can be estimated by titration (ie. TSA) if no acid neutralising material is present, or calculated from S_{POS} or S_{CR} results.

Retained Acidity: The 'less available' fraction of the existing acidity (not measured by the TAA) that may be released slowly into the environment by hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, and other iron and aluminium hydroxy-sulfate minerals).

S_{CR}: The symbol given to the result from the Chromium Reducible Sulfur method (Method 22B). The S_{CR} method provides a measure of reduced inorganic sulfide content using iodometric titration after an acidic chromous chloride reduction. This method is not subject to interferences from organic sulfur.

S_{HCl}: Sulfur soluble in 4 M HCl which includes soluble and adsorbed sulfate, sulfate from gypsum, as well as sulfate from hydroxy-sulfate minerals such as jarosite and natrojarosite.

S_{KCl}: Potassium chloride extractable sulfur measured following the TAA analysis, which includes soluble and adsorbed sulfate as well as sulfate from gypsum.

S_{NAS}: Net acid soluble sulfur. ($S_{HCl} - S_{KCl}$). The sulfur soluble in 4 M HCl that is not soluble in 1 M KCl. It provides an estimate of the sulfate contained in jarosite and similar low solubility hydroxy-sulfate minerals (and can be used to estimate retained acidity).

S_P: Peroxide sulfur. Sulfur measured following the TPA analysis, which includes soluble and exchangeable sulfate, sulfate from gypsum, as well as sulfide converted to sulfate and that released from organic matter as a result of peroxide oxidation.

S_{POS}: Peroxide oxidisable sulfur from the SPOCAS method. The sulfur soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. ($S_P - S_{KCl}$). It provides an estimate of the soil sulfide content, but is affected by the presence of organic sulfur.

S_{RAS}: Residual acid soluble sulfur. The sulfur measured by 4 M HCl extraction on the soil residue remaining after peroxide digestion and TPA titration of the SPOCAS method. It provides an estimate of the sulfate contained in jarosite and similar low solubility hydroxy-sulfate minerals (and can be used to estimate retained acidity).

S_T: Total sulfur. A measure of the total sulfur content of the soil, encompassing both organic and inorganic forms.

S_{TOS}: Total oxidisable sulfur. An estimate of soil oxidisable sulfur made from determining the sulfur not soluble in 4 M HCl. ($S_T - S_{HCl}$). It tends to provide an overestimate of soil sulfide content.

Self-neutralising soils: This term is given to ASS where there is sufficient acid neutralising capacity (with the relevant safety factor applied) to neutralise the potential sulfidic acidity held in the soil (ie. the net acidity from the Acid Base Account is zero or negative). Soils may be 'self-neutralising' due to an abundance of naturally occurring calcium or magnesium carbonates (eg. crushed shells, marine animal exoskeletons, coral) or other acid-neutralising material.

SPOCAS: An acronym standing for Suspension Peroxide Oxidation Combined Acidity and Sulfur method (Method Code 23), the peroxide-based method that supersedes the previous POCAS and POCASm methods.

SPOCAS Suite: The acid base accounting approached used to calculate net acidity based on the Suspension Peroxide Oxidation Combined Acidity and Sulfur method. A decision tree approach based on the values of pH_{KCl} and pH_{OX} is used to decide what analytical path is followed in order to allow calculation of net acidity.

TAA: Titratable actual acidity. The acidity measured by titration with dilute NaOH following extraction with KCl-solution in the SPOCAS method. Previously referred to as Total Actual Acidity in the POCAS and POCASm methods.

TPA: Titratable peroxide acidity. The acidity measured by titration with dilute NaOH following peroxide digestion in the SPOCAS method. Previously referred to as Total Potential Acidity in the POCAS and POCASm methods.

TSA: Titratable sulfidic acidity. The difference in acidity measured by titration with dilute NaOH following extraction with KCl-solution and the acidity titrated following peroxide digestion in the SPOCAS method. (TPA – TAA). Previously referred to as Total Sulfidic Acidity in the POCAS and POCASm methods.