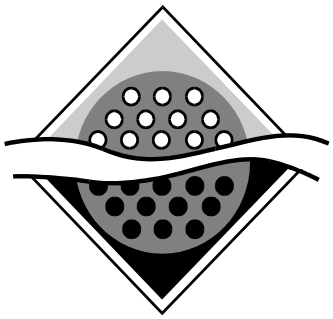

Acid Sulfate Soils

Laboratory Methods

New South Wales
Acid Sulfate Soils Management Advisory Committee
August 1998

ACID SOIL ACTION
An Initiative of the NSW Government

The Acid Sulfate Soils Laboratory Methods Guidelines as a component of the ASS Manual, forms part of an 'all of government' approach to the management of acid sulfate soils in New South Wales.

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ABOUT THE GUIDELINE

The methods in the Laboratory Methods Guidelines provide a standardised approach to routine laboratory determination of actual and potential acid production from oxidation of iron sulfides, mainly pyrite (FeS_2) in estuarine and coastal sediments. The methods are not exhaustive in dealing with this complex subject but represent a consultative compromise reached with the industry, acid sulfate soil regulators and acid sulfate soil researchers. This publication on analytical methods for acid sulfate soils is endorsed by the Acid Sulfate Soil Management Advisory Committee Technical Committee (ASSMACTC), July 1998.

This guideline replaces the methodology in the *Environmental Guidelines: Assessing and Managing Acid Sulfate Soils* (NSW EPA 1995), the *Interim Acid Sulfate Soils Analytical Method* (ASSMACTC 1996) and the Analytical Methods in the *ASS Workshop Resource Manual* (1997). The Laboratory Methods Guidelines should be used in conjunction with the *Assessment Guidelines* and the *Management Guidelines* in the ASS Manual.

Because of the diversity, nature and oxidation states of the sulfur minerals and organic sulfur materials present in acid sulfate soils, it is unlikely there will be a universal low cost analytical procedure that provides all required information. However to assist standardisation and interpretation by authorities, the Peroxide Oxidation Combined Acidity & Sulfate (POCAS) method has been adopted as the standardised method for determining acid sulfate soil potential risk for general environmental impact assessment (EIA). The POCAS method follows both the 'acid and sulfur trail' on the same solution and allows a measure of both existing acidity and potential acidity. The calcium determinations (Ca_P, Ca_{KCl}, and Ca_A) on the POCAS extracts are strongly recommended; (optional Mg and Na determinations can also be useful in some situations).

The multiple results from the POCAS method assist in greater understanding of the complex nature of many acid sulfate soils. By comparing results from the acid and sulfur trail under the same extractant and 'digestion' conditions, this method allows for easier detection of 'false positives' from the presence of organic material and 'false negatives' from coarse neutralising materials.

An alternative method - Total Oxidisable Sulfur (TOS), based on the sulfur trail only, has been approved as a low cost method for calculating *potential acidity* from pyrite oxidation. The TOS method does not measure existing acidity, and on *actual* acid sulfate soils will usually need to be supplemented with Total Actual Acidity (TAA) measurements from the POCAS method. Both methods can have difficulty on low analysis samples and highly organic material such as peat.

Actual acidity (indicated by low field or laboratory pH <5.5 or measured TAA) needs to be taken into account in liming calculations or other treatments methods. Other methods, such as acid volatile sulfur and chromium reducible sulfur, may be undertaken in addition to the standard methods where appropriate and may be necessary in some cases to fully understand the soil components.

In general, calculations from laboratory results of acid risk should take into account the need to neutralise with a safety factor, both existing acidity and *potential acidity* from the eventual complete oxidation of all iron sulfides or their partially oxidised products. Initially, the calculation of potential acidity risk should be presented based on the sulfur trail (usually S_{POS} or S_{TOS}) rather than acid trail determinations (TPA or TSA). Stoichiometric calculations based on oxidisable sulfur normally assume pyrite (FeS_2) as the main potential acid source with one mole of pyrite producing two mole of H_2SO_4 or four mole of H^+. It is appropriate to further identify acid risk based on other analytical results such as the POCAS 'acid trail', further sulfur species fractionation/identification (eg acid volatile monosulfides), compensating neutralising sources and site characteristics.

In developing the overall site management plan the following factors provide a basis for negotiating a reduction in the assessment and management requirement calculated from the sulfur analysis only:

- Data on differences between the sulfur and acid trail (if shown by POCAS analysis)
- Substantially lower or no risk indicated by the acid trail (TPA or TSA = 0)
- Significant ANC results (with data on the neutralising material's effectiveness, reactivity, shell size, quantity, etc.). The calcium result from POCAS will help confirm this.
- Net acid generation potential (NAGP) calculations or other acid base accounting techniques suggesting no risk.
- Significant organic sulfur content.

The methods for acid neutralising capacity (ANC) are less developed and somewhat left to the discretion of the laboratory. The acid neutralising methods based on back titration of unreacted acid after strong acid application to the soil give an artificially higher ANC than can be expected under field conditions, and can not be consistently relied upon.

Until further research is completed on the reactivity of shells, soil carbonates and the effect of strong mineral acids on soil, ASSMACTC have not approved the automatic calculation of Net Acid Generation Potential (NAGP) for use as the risk indicator. Whether ANC can be subtracted from the oxidisable sulfur result need to be considered on a site by site basis, taking into account fineness and distribution of shell or carbonate in the soil profile. Further research is underway. Where disturbances could benefit substantially by allowing for the ANC in calculations, pilot projects or further kinetic studies may be necessary.

REVIEWING AND UPDATING THE GUIDELINE

It is expected that this guideline 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 will aim to make the methods more effective in understanding the risks and improve the economics of providing information for management options. Technical questions may be discussed with Col Ahern (*email* ahernc@dnr.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 the Chairman, ASSMACTC c/$_o$ ASS Information Officer ***email*: woodwoj@agric.nsw.gov.au**. ASSMACTC will be responsible for organising refereeing, reviewing and approving changes to the guideline, in consultation with other relevant professional organisations, industry and government departments.

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It is recommended that users of the guideline register with the ASS Information Officer on the registration form provided so they can be notified when changes to the methods have occurred.

CONSULTATION AND ACKNOWLEDGMENTS

The scientists listed below met in Sydney 17 October 1996 and agreed on the main components of a total sulfur based approach (**TOS,** Method 20) and the peroxide oxidation based approach- (**POCAS,** Method 21) for acid sulfate soil routine methods for environmental assessment purposes. Their contribution of ideas and their participation in the review of drafts are gratefully acknowledged.

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NSW ASSMAC Technical Committee
and
Queensland Acid Sulfate Soils
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NATURAL RESOURCES

Register of Users of the Laboratory Methods

To receive future updates to the Acid Sulfate Soils Laboratory Methods and information on new methods, please complete the form and mail or fax to:

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Organisation .....

Testing Laboratory? **Yes** □ **No** □

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.....

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1. INTRODUCTION

C R Ahern and B Blunden

1.1 The purpose of the guideline

This guideline sets out the standard methods for routine laboratory analysis of soil samples to provide information for the assessment and management of acid sulfate soils. This guideline also recommends best practice methods in the sampling, handling and transport of soil samples.

The extent of analysis undertaken for any proposal will depend on the level of risk associated with the soil characteristics and the type of disturbance proposed. The sampling and analysis program should be developed to provide sufficient information to ensure the proposal can be managed in a sustainable manner.

1.2 Chemical properties of acid sulfate soils

To interpret results from the analysis of acid sulfate soils, it is necessary to have a sound knowledge of the chemical processes involved. Some fundamental processes and properties of acid sulfate soils, particularly with regard to iron disulfide (FeS_2) or pyrite oxidation are listed below.

a. Oxidation of pyrite

Acid sulfate soils are acidic soil horizons or layers resulting from the aeration of materials that are rich in iron sulfides, primarily pyrite (FeS_2). Potential acid sulfate soils are typically waterlogged soils rich in pyrite that have not been oxidised. Any disturbance which exposes potential acid sulfate soil to the air (oxygen) will lead to the development of extremely acidic, actual acid sulfate soil layers with pH < 4.

The identification and assessment of the distribution and severity of acid sulfate soil conditions is the first step for land use assessment. However, acid sulfate soils are highly variable and have extremely dynamic characteristics. Also, the source of the acid (sulfides) has a very heterogeneous distribution. These characteristics can make identification in the field and quantification of the problem extremely difficult. Therefore the identification and assessment of acid sulfate soil conditions is highly dependent on appropriate assessment of these soils by survey, field and laboratory analysis and sound interpretation of the results.

Oxidation of pyrite, the main source of the acidity, can be described by the following equations. The initial step in pyrite oxidation is the production of elemental sulfur and ferrous iron II (White and Melville 1993):

$$FeS_2 + {}^1/_2O_2 + 2\,H^+ \rightarrow Fe^{2+} + S^0{}_2 + H_2O \qquad (1)$$

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

$$S^o{}_2 + 3O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad (2)$$

The complete reaction of pyrite to ferrous iron II and sulfate can be written as:

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

The soluble ferrous ion may then be oxidised further from iron II (ferrous) to iron III (ferric):

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

If the pH is greater than 4, the final step is the precipitation of ferric hydroxide and the liberation of more acid in a reaction known as hydrolysis:

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

If the pH is less than 4, iron III can remain in solution. The dissolved iron III greatly accelerates the oxidation process of pyrite (by electron transfer) and does not require oxygen to oxidise pyrite.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + SO_4^{2-} \quad (6)$$

The reaction can result in considerable acid production when existing acid sulfate soils containing iron III are re-flooded or buried under water without lime treatment. This is because oxidation-reduction processes involve electron transfer and do not necessarily need oxygen for oxidation of pyrite to occur as popularly believed. The soluble ferrous iron (Fe^{2+}) can easily be transported downstream where the reaction removes dissolved oxygen from the water during the oxidation process to produce more acid.

$$Fe^{2+} + {}^1/_4O_2 + {}^3/_2 H_2O \rightarrow FeOOH + 2H^+ \quad (7)$$

The overall reaction for the complete oxidisation of pyrite can be given as Dent (1986):

$$FeS_2 + {}^{15}/_4O_2 + {}^7/_2 H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (8)$$

b. Iron oxidation products

Frequently, there are characteristic iron oxidation reactions associated with the development of actual acid sulfate soils and the transport of acidic leachate (White and Melville 1993). For example, in streams the secondary oxidation of Fe^{2+} can produce characteristic goethite (FeOOH) flocs. The oxidation of Fe^{2+} can liberate large amounts of acid, often at a significant distance away from the oxidation of pyrite in the acid sulfate soil. Partial oxidation products are also observed in the soil such as the characteristic yellow mottles of jarosite, $KFe_3(SO_4)_2(OH)_6$, a mineral that forms at pH below 3.7 under strongly oxidising conditions (White and Melville 1993). Such salts can act as a store of acidity.

c) Monosulfides

Modern sediments may contain reactive sulfur phases (such as Fe-monosulfides) which oxidise readily on air contact. These include 'amorphous FeS', mackinawite ($\cong$ FeS) and greigite ($\cong Fe_3S_4$) (Bush and Sullivan 1997). These compounds are often referred to as acid volatile sulfides. Due to their high reaction rates in air, special drying procedures such as freeze-drying are required when preparing these samples for analysis.

The routine laboratory methods of this manual are designed primarily to determine pyrite sulfide. Most calculations are based on the assumption that non-sulfate sulfur is present as iron disulfide, so monosulfides interfere with stoichiometric calculations. Generally, monosulfides are usually absent or present in only minor amounts in most acid sulfate soils. However, they are significant in bottom sediments of lakes and drains. Organic sulfur compounds may also interfere with laboratory analysis and making analyse and the interpretation of results difficult. Elemental sulfur may occur as intermediate products of the oxidation of sulfides.

c. Soil texture

The soil's texture and characteristics are extremely important factors governing the buffering capacity of the soil. Sandy pyritic deposits, for example, in the absence of significant quantities of shell material, have little self-buffering capacity due to a lack of cation exchange sites on the soil minerals.

d. Acid neutralising capacity of soil material

The *in situ* buffering capacity of soil material is the soil's ability to counteract acidity and lowering of the soil pH. The buffering capacity of a soil may include calcium carbonate deposits (eg shell), reaction with the organic fraction (eg peat layer) or cation exchange and reaction with the soil clay fraction (White and Melville 1993). The effectiveness of the buffering capacity however, and the actual pH which is produced in the soil, depends on the types and quantities of clay minerals, the form of the carbonates (fine or coarse) and the rate of oxidation and acid production.

The presence of carbonate deposits in excess of potential acidity does not necessarily prevent soil acidification if the carbonates are locked up in shells or as unreactive coarse fragments. It is extremely important to know the *in situ* form of the carbonates for a correct interpretation of analytical results and the identification of appropriate management techniques. It should be noted that normal laboratory preparation methods of grinding the soil affects the fineness and reactivity of shell and may artificially increase the apparent acid neutralising capacity of a soil.

Finely divided $CaCO_3$ is a source of neutralising capacity (Dent and Bowman 1993). One mole of $CaCO_3$ will neutralise two moles of acidity (H^+).

1 mole $CaCO_3$ will neutralise 2 moles H^+ (1 mole $CaCO_3$ = 100.0872 g)

1 mole H_2SO_4 is equivalent to 2 moles H^+ (1 mole H2SO4 = 98.0795 g)

So, 1 part $CaCO_3 \approx$ 1 part H_2SO_4 (by weight)

The reaction of acid produced from pyrite with calcium carbonate results in precipitates of calcium sulfate, usually gypsum, and carbon dioxide.

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

In most of the acid sulfate soils in Australia, there are insufficient shell deposits, carbonates or natural clay buffering capacity to neutralise the acid produced by pyrite oxidation (White and Melville 1993). Details on neutralising materials are provided in the Management Guidelines in the *ASS Manual*.

1.3

Acid sulfate soil conversions

Conversions between some of the common units used to express soil analysis of acid sulfate soils are given in Table 1.1. The conversions are based on 1 mole pyrite producing 2 mol sulfuric acid or 4 mole of H^+ and the equivalent liming rates using a safety factor of 1.5.

Table 1.1 Conversions for some units of reporting Acid Sulfate Soils Analysis

S_{OX} (%)	***moles H^+ / kg*** ***(S_{OX} % x 0.6237)***	***moles H^+ / tonne*** ***or*** ***moles H^+ / m^3 **** ***(S_{OX} % x 623.7)***	***kg H_2SO_4/tonne*** ***or*** ***kg H_2SO_4 /m^3 **** ***(S_{OX} % x 30.59)***	***kg lime/tonne soil*** ***or*** ***kg lime/ m^3 **** ***Safety factor =1.5*****
0.01	0.0062	6.237	0.306	0.45
0.03	0.0187	18.71	0.918	1.4
0.06	0.0374	37.42	1.84	2.8
0.1	0.0624	62.37	3.06	4.7
0.2	0.1247	124.7	6.12	9.4
0.3	0.1871	187.1	9.18	14.0
1.0	0.6237	623.7	30.5	46.8
5.0	3.1190	3119	153.0	234.0

Notes on Table 1.1

- *The value for oxidisable sulfur (S_{OX} %) can generally be obtained from one of the following analysis: peroxide oxidisable sulfur (S_{POS} %) or total oxidisable sulfur (S_{TOS} %) or if they are not available total sulfur (S_T %). Total sulfur could overestimate liming rates but is environmentally conservative. Calculations based on the acid trail (TPA, TSA) may underestimate risk particularly where shell is present.*
- ***Assumes a bulk density of 1.0 g/cm^3 or 1 tonne/m^3 (range can be 0.7-2.0 and as low as 0.2 for peats). Where bulk density is > 1 g/cm^3 then factor will increase for lime rates/m^3 soil (eg. if BD=1.6, then 1 m^3 of soil with 1.0 % S 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 neutralising value of 100. Where 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.*

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Bush,RT and Sullivan,LA (1997) *Morphology and behaviour of greigite from a Holocene sediment in Eastern Australia* Australian Journal of Soil Research 35, 853-61

Dent,D (1986) *Acid sulphate soils: a baseline for research and development* International Institute for Land Reclamation and Improvement Wageningen, The Netherlands

White,I and Melville,MD (1993) *Treatment and containment of potential acid sulphate soils* Technical Report No53, CSIRO, Centre for Environmental Mechanics

2. DESIGNING A SOIL SAMPLING AND ANALYSIS PROGRAM

C R Ahern and B Blunden

2.1 Introduction

A sampling and analysis program should be designed to understand the risks of disturbing acid sulfate soils and to provide information to develop a management strategy. The level of investigation and analysis 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 and 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 by depth (down the profile). As a result, the selection of sample sites to represent the various soils, vegetation, geomorphic and geological unit combinations in the landscape is a highly skilled task. The reliability of the investigation results is greatly dependent on the quality of the sampling program. The designing of valid sampling programs for sites that have been previous disturbed can be very difficult.

The onus is on the proponent to justify that sufficient sampling and analysis has been undertaken to understand and manage the site without causing environmental harm. It can often be cost efficient to stage the soil investigations for large or complex projects. 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.

2.2 Responsibility of those undertaking the field survey

a. Number of soil sampling sites

The frequency of sampling locations should conform to Assessment Guidelines in the *ASS Manual*. This requires, for general disturbance, a minimum of 4 holes for a site up to 1 ha, 6 for 2 ha, 7 for 3 ha and then 2 holes per ha for areas >4 ha. Greater intensity of sampling, such as sampling every 50 metres will be required for significant trench or canal excavations. Professional judgement will be necessary to ensure the sampling program identifies any actual or potential acid sulfate soil "hot spots" on the site. The location of each borehole or sampling site must be clearly marked on a map or overlaid on an aerial photograph. Grid references for each sample site and height (m AHD) must be documented.

b. Samples

Professional judgement will be necessary to ensure that the sampling program provides representative and adequate samples to understand the risks and to develop a management strategy. The advice in the Assessment Guideline in the *ASS Manual* on the recommended soil sampling methods should be noted.

Soil samples should be collected for every soil layer or at least every half (0.5) metre. The depth of the sample within the layer must be recorded, along with the upper and lower horizon depths. Where distinct soil layers or horizons occur in the soil profile, sampling intervals should be adjusted to take account of these horizons. Sampling intervals must not be taken across two (2) or more different horizons. The depth of investigation should be at least one (1) metre beyond the depth of the proposed

excavation or estimated drop in watertable height, or to a minimum two (2) metres below the land surface, whichever is the greatest.

Where 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 and to provide for more potential management or planning options - such as over-excavation and burial of highly sulfidic material below the water table. Full sampling and analysis of at least 3 sites or 25% of the profiles to 2-3 metres beyond the proposed disturbance is strongly advocated to understand the site characteristics, soil layering, drainage and geomorphic history. Where the deeper sampling has been undertaken and patterns are established, often an overall sampling intensity less than the guidelines may be approved.

Ideally, samples of soil should be at least 0.5 kg each. Large shells and other large fragments such as wood, charcoal, stones and the like, should be noted and removed from the samples in the 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.

Gravels associated with acid sulfate soils or from below the water table, have been known to contain sulfides in the weathered rind (Saffigna *et al.* 1996). White and Melville (1993) found 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 *et al.*, 1993). These materials are difficult to sample representatively and require modified sample preparation before laboratory testing.

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. However, in taking volumetric samples, compression of the sample or inclusion of air pocket can substantially affect the results. Chapter 7 provides greater detail on bulk density and moisture methods.

c. Field pH testing

At the time of sampling, soil texture, field pH (pH_F; **Method 21Af**) and field pH after oxidation with 30% hydrogen peroxide (pH_{FOX} ; **Method 21Bf**) should be determined within regular depth intervals (eg. 0.25 m, maximum 0.5 m) or horizons in the profile and at least 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. This may assist in allocating similar samples to particular batches in the laboratory, which can assist in optimising procedures and improve the accuracy and detection limits.

The field pH can be measured on saturated soil using a spear point pH probe and field pH meter. If pH_{KCl} is substantially lower than pH_F then some oxidation of the sample during transport or drying may have occurred. (For more details see *Assessment Guidelines*)

d.

Soil 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. The samples should be kept cold (ideally less than 4^{o}C) in the field to reduce the possibility of oxidation of sulfidic compounds. A portable freezer and cold box (esky) containing dry ice are the most efficient coolers but if not available, at least 'frozen bricks' or 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 and ovenproof.

It is preferable that samples be sent to the selected laboratory within 24 hours 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 that 4^{o}C.

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

- quick oven drying the sample at 80-85^{o}C in a forced convection large capacity oven (care must be taken not to overload the oven's moisture removal capacity). The dried samples must then be stored in a low humidity environment
- freezing the sample in sealed, plastic microwaveable container.

Samples containing high concentrations of iron monosulfides, usually associated with bottom sediments and/or decaying vegetation, may generate acidity on oven drying. Special sampling, storage and freeze drying techniques may be used to overcome this problem. Bush and Sullivan (1997) showed that greigite readily oxidises within hours at room temperature and oxidises in minutes on drying at 88 °C. Special precautions to prevent oxidation at sampling and drying are costly and laborious and generally used for research rather than routine analysis. Provided the monosulfide content is low then any oxidation on drying should be detectable by a significant lowering (>1 unit) of laboratory pH compared to field pH. The change would not be easily detectable using the sulfur trail but the acid trail would show a high TAA result. Dioxane replacement of moisture (Crockford and Willet 1995) may be useful where no freeze-drying facilities are available. Greigite is relatively stable once dried (Bush and Sullivan 1997).

2.3 Responsibility of those undertaking the laboratory analysis

a. Notification of sample dispatch and receipt

To avoid delays in sample processing and the potential for the oxidisation of sulfides in soil samples, it is important that the laboratory is contacted so that the laboratory manager knows that samples will soon be delivered for analysis. It is important that the laboratory confirm 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 state which occurred between collection and laboratory analysis.

There is no legal requirement to submit a Chain of Custody declaration to the relevant State or Local Government authorities. However, auditable sample records should be maintained at all times.

b. Oven drying - routine approach

On arrival at the laboratory, samples should dried preferably in a quick drying, fan forced, air extracting oven at 80-85 °C for at least 48 hours, to prevent further oxidation of pyrite (Ahern *et. al,* 1996). 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 Chapter 7.

Laboratories should examine the drying capacity of their ovens and only apply appropriate loading. If the oven is overloaded particularly with large frozen samples, it may not be able to maintain the required temperature or its drying efficiency may be reduced. As a result, some oxidation of sulfide and substantial reduction in pH may occur (Hicks and Bowman, 1996).

> *Note: Typically, pH decrease 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. Oxidation of black iron monosulfides and other unstable sulfide and some reduced iron compounds commence on disturbance and specialised sampling equipment is required to prevent oxidation. Fortunately such compounds rarely occur in significant amounts in most acid sulfate soils but may be an appreciable component of drain, lake or stream bottom sediments. Wet/volumetric sampling methods may be more suitable when highly unstable compounds are expected. Immediate freezing with dry ice pellets followed by freeze drying in the laboratory is required for samples containing unstable sulfide compounds.*

c. Sample preparation

After drying, any coarse material not previously removed (especially shell and gravel) should be picked out or removed by preliminary sieving (2 mm). The weight of the residual coarse material (>2 mm) may need to be measured and calculated as a percentage of the total sample weight. Samples which 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 but it is recommended that samples for acid sulfate soil analyses be fine-ground (<0.5 mm) to ensure greater homogeneity. This means a smaller sample weight and less volume of reagents can be used during analysis, reducing costs. The sample should be stored in a cool dry place in an airtight plastic or other inert container for subsequent laboratory use.

It may be necessary to also 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. Generally gravely soils 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 the finer fractions.

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

d.

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 in an oven-dried state is the safest and preferred approach. A less desirable method of storage particularly when conducting a staged approach is freezing.

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 arrangement 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 could be important in defence of legal action.

2.4 Selection of consultants and laboratories

NATA accredited, Certified Laboratory Practice, or ISO 9000 laboratories that use the methods in this guideline and who successfully participate in the acid sulfate soil quality assurance program under the supervision of the ASSMAC Technical Committee, are recommended. Non-accredited laboratories may be acceptable, provided that they have successfully participated in the acid sulfate soil quality assurance program.

It is strongly recommended that consultants with qualifications in agricultural or environmental soil science (specialising in soil chemistry, hydrology or pedology), experienced in acid sulfate soils management and accredited with a professional organisation such as the Australian Society of Soil Science be engaged to undertake soil investigations.

When calling tenders for acid sulfate soil investigations, proponents should request a sampling and analysis program with a break down based on a sample-based approach including the proposed number of sites/cores to be drilled, samples taken down the profile and proposed laboratory analyses. Without a sample-based approach, the cheapest quote often involves insufficient sites, samples and analysis, resulting in costly delays and the need for further supplementary investigations and costly variations.

For large complex projects or where the level of acid sulfate risks are not known, consultants should be encouraged to submit a staged approach. A staged investigation enables the sampling design to be adjusted and refined as a result of earlier site information. As a result, savings can be considerable, particularly where stage 1 shows acid sulfate soils are minor or insignificant.

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3. CODES FOR ACID SULFATE SOILS ANALYTICAL METHODS

C R Ahern and G E Rayment

3.1 Introduction

Method codes have been established for the principal analytical methods for the analysis of acid sulfate soils. These methods are:

- Peroxide Oxidation Combined Acidity & Sulfate POCAS - Method 21
- Total Oxidisable Sulfur (TOS) - Method 20
- Acid Neutralising Capacity - Method 19

The method codes have been negotiated for addition to existing codes in the *Australian Laboratory Handbook of Soil and Water Chemical Methods* (Rayment and Higginson 1992). These codes are compatible with the system established in the handbook.

3.2 Codes for Peroxide Oxidation Combined Acidity & Sulfate (POCAS) - Method 21

The codes for POCAS are in Table 3.1 (Analytical Methods) and Table 3.2 (Supplementary Finishing Steps).

Table 3.1 Analytical Method Codes for Method 21

Analysis Code	*Symbol & Units*	*Analysis and description*
pH measurements		
21A	pH_{KCl}	pH of filtered 1:20, 1M 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 1M 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^+/tonne)	Total Actual Acidity in 1M KCl titrated to pH 5.5
21G	TPA (mol H^+/tonne)	Total Potential Acidity in 1M KCl peroxide digest titrated to pH 5.5
21H	TSA (mol H^+/tonne)	Total Sulfidic Acidity [21G-21F]
21J	S_{TAA} %	TAA *calculated as equivalent* pyrite S % for comparison 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 POCAS to estimate additional Ca from acid-shell/carbonate reaction*		
21V	Ca_{KCl} (Ca %)	Ca extracted in 1M KCl (TAA)
21W	Ca_{P} (Ca %)	Ca in peroxide digest (TPA)
21X	Ca_{A} (Ca %)	Ca reacted with acid generated by peroxide digest (21W-21V)
Magnesium *values from POCAS to estimate additional Mg from acid-shell /dolomite/carbonate reaction*		
21S	Mg_{KCl} (Mg %)	Mg extracted in 1M KCl (TAA)
21T	Mg_{P} (Mg %)	Mg in peroxide digest (TPA)
21U	Mg_{A} (Mg %)	Mg reacted with acid generated by peroxide digest (21T-21S)

Sodium *values from POCAS*		
21M	Na_{KCl} (Na %)	Na extracted in 1M KCl (TAA)
21N	Na_{P} (Na %)	Na in peroxide digest (TPA)
21P	Na_{A} (Mg %)	Na difference (21N-21M)
Neutralising *methods*		
21Q	NQ ($CaCO_3$ %)	Quick residual neutralising capacity
21R	NQ_{S} (S_{R} %)	Quick residual neutralising capacity 21Q, calculated as equivalent S %

Supplementary Finishing Step Codes

Supplementary Finishing Step Codes for sulfur (21C, 21D, 21E), calcium (21V, 21W, 21X) magnesium (21S, 21T, 21U) and sodium (21M, 21N, 21P) are in Table 3.2.

*For example, Method Code **21Ce** is KCl extractable sulfur with Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) Finishing Step to determine S.*

Table 3.2: Codes for the Supplementary Finishing Steps for the POCAS Methods

Supplement code	Analyte and finishing step	Similar to Rayment & Higginson (1992) method
Sulfur		
a	sulfate, turbidimetric	J1a
b	sulfate, gravimetric	J1b
c	sulfate, automated colour	J1c
d	sulfate, ion chromatography	J1d
e	sulfur, ICPAES	J2a
f	sulfate, automated turbidimetric	J1a
g	sulfate, indirect, barium remaining by AAS	
Calcium		
h	calcium, ICPAES	L1c
j	calcium, atomic absorption (AAS)	L1b
k	calcium, titration EDTA	L1a
Magnesium		
m	magnesium, ICPAES	L2c
n	magnesium, atomic absorption (AAS)	L2b
p	magnesium, titration EDTA	L2a
Sodium		
s	sodium, ICPAES	L4c
t	sodium, atomic absorption	L4b
u	sodium, flame emission	L4a

3.3

Total Oxidisable Sulfur (TOS) - Method 20

Two approaches for deriving total oxidisable sulfur is provided in Method 20

- Method 20 C = Method 20 A (Total Sulfur) - Method 20B (Hydrochloric Acid Extractable Sulfur)
- Method 20 D (Pre-washed Hydrochloric Acid Extractable Sulfur)

The codes for Method 20A for **Total Sulfur (S_T %)** are given in Table 3.3. For example, Method Code **20A1** represents total sulfur by X-ray fluorescence.

Table 3.3 Codes for Method 20A - Total Sulfur (S T %)

Code	*Analysis and Description*
1	X-ray fluorescence (similar to method 10A1 Rayment and Higginson 1992)
2	Leco (the older model Leco furnace is unsuitable)
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	Acid oxidation using nitric, perchloric, phosphoric, hydrochloric acids (Arkley, 1961)
7	Bromine - nitric acid oxidation (Vogel 1978)
9	Total Sulfur by Summation (S_{TOS} + S_{HCl})

Supplementary Finishing Step Codes

Table 3.4 lists Supplementary Finishing Step Codes for Method 20B for hydrochloric acid (4M) extractable sulfur (calcium, magnesium, sodium and potassium).

*For example, Method Code **20Be** is Hydrochloric Acid (4m) Extractable Sulfur (S_{HCl} %), using an ICPAES Finishing Step to determine S.*

Table 3.4 Codes for Method 20B; Hydrochloric Acid Extractable Sulfur (S HCl %),

Supplement code	*Analyte and finishing step*	*Similar to Rayment & Higginson (1992) method*
Sulfur		
a	sulfate, turbidimetric	J1a
b	sulfate, gravimetric	J1b
c	sulfate, automated colour	J1c
d	sulfate, ion chromatography	J1d
e	sulfur, ICPAES	J2a
f	sulfate, automated turbidimetric	J1a
g	sulfate, indirect, barium remaining by AAS	
Calcium		
h	calcium, ICPAES	L1c
j	calcium, atomic absorption (AAS)	L1b
k	calcium, titration EDTA	L1a
Magnesium		
m	magnesium, ICPAES	L2c
n	magnesium, atomic absorption (AAS)	L2b
p	magnesium, titration EDTA	L2a
Sodium		
s	sodium, ICPAES	L4c
t	sodium, atomic absorption	L4b
u	sodium, flame emission	L4a
Potassium		
v	potassium, ICPAES	L3c
w	potassium, atomic absorption (AAS)	L3b
x	potassium, flame emission	L3a

The 'full code' for Method 20C involves addition of the appropriate numeral from table 3.3 to define the total S method and addition of the appropriate lower case alphabetic character from Table 3.4 to define the method used to determine S_{HCl}%. Some examples are shown in Table 3.5.

Table 3.5 Examples of 'Full Codes' for Method 20C; Total Oxidisable Sulfur (S TOS%)

Code	*Analysis methods [20A - 20B]*
20C1e	Total S by X-ray (1) - HCl extractable S by ICP (e)
20C2e	Total S by LECO (2) - HCl extractable S by ICP (e)
20C2a	Total S by LECO (2) - HCl extractable S by Turbidimetric (a)

The codes for Method 20D; Total Oxidisable Sulfur (S_{TOS}%) after pre-washed 4M HCl and water are provided in Table 3.6.

*For example, Method Code **20D2** is Total Oxidisable Sulfur after HCl pre-wash determined by Leco (2).*

Table 3.6 Codes for method 20D; Total oxidisable sulfur after HCl pre-wash (S TOS%)

Code	*Analysis and Description*
1	X-ray fluorescence (similar to method 10A1 Rayment and Higginson 1992)
2	Leco (the older model Leco furnace is unsuitable)
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	Acid oxidation using nitric, perchloric, phosphoric, hydrochloric acids (Arkley, 1961)
7	Bromine - nitric acid oxidation (Vogel 1978)

3.3 Acid Neutralising Capacity – Method 19

Table 3.7 Acid neutralising capacity codes

Code	*Symbol & units*	*Analysis and description*
***Acid Neutralising methods** (non-POCAS) from Rayment and Higginson (1992)*		
19A1	NT ($CaCO_3$ %)	Neutralising –Titration Carbonates - back titration expressed as $CaCO_3$ %
19B1	NV ($CaCO_3$ %)	Neutralising –Volumetric Carbonates - manometric expressed as $CaCO_3$ %
Methods to be added to Rayment and Higginson (1992)		
19A2	NTL ($CaCO_3$ %)	Neutralising –Titration Carbonates (Lewis & McConchie) $CaCO_3$ %
19C1	NG ($CaCO_3$ %)	Neutralising – Gravimetric loss of CO_2 expressed as $CaCO_3$ %
19D1	NC ($CaCO_3$ %)	Neutralising – Curve (titration) expressed as $CaCO_3$ %

3.4 Moisture codes

Table 3.8 Acid Sulfate Soil Moisture codes

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

3.5 Acid Sulfate Soils 'Miscellaneous' Acid Sulfate Soils Methods- Code 22

Method 22A: Acid Volatile Sulfur (S_{AV} %)
Method 22B: Chromium Reducible Sulfur (S_{CR} %)
Method 22C: Scanning Electron Microscopic methods

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4. PEROXIDE OXIDATION COMBINED ACIDITY & SULFATE

POCAS – METHOD 21

CR Ahern, A. McElnea and DE Baker

Introduction

The POCAS method aims to standardise laboratory procedures for determining the potential acidification of acid sulfate soils by combining two commonly used peroxide oxidation methods. Peroxide Oxidisable Sulfuric Acidity (POSA) (Lin and Melville, 1993) follows the 'sulfur trail' and the method of Dent and Bowman (1996) follows the 'acidity trail' measuring total actual acidity [TAA], total potential acidity [TPA] and by difference, total sulfidic acidity [TSA]**.** The combined method[1] is essentially similar to the Ahern *et al*. (1996) 'combined peroxide method' slightly modified by further research and in response to the ASSMACTC Methods Workshop, October 1996. After trials by Government, University and private laboratories, POCAS was approved at a further specially convened ASSMACTC meeting on 29 August 1997.

In some cases, neither the 'sulfur trail' nor the 'acidity trail' method supply enough information. For more complete interpretation of acid sulfate soils, results from both trails are an advantage. The POSA method takes no account of carbonate content or the buffering capacity of the soil. An earlier version of the TPA method has been shown to record 'false positives' in some laboratories (Clarke *et al*. 1996), although the updated double oxidation TPA method is claimed to have no such difficulties provided digestion conditions are closely adhered to (Dent and Bowman, 1996). On some soils, TPA may underestimate the potential risk of acid leakage to the environment because not all the shell in the soil is immediately available for neutralisation of acid, due to low surface area and insoluble coatings forming on the shells. The combination method also includes pH measurements in 1M KCl (pH_{KCl}) before and after oxidation (pH_{OX}), providing additional information to assist in better defining the potential environmental risk.

The combined method is not meant to be a research scientist's tool. It is intended to be a standardised set of procedures to help assess the potential environmental impact of soils suspected of containing pyrite and other iron sulfides. The combined method is designed to suit most routine private, governmental and institutional laboratory facilities by supplying sufficient information for quality acid sulfate soils environmental assessment and management decisions at the lowest possible cost. Cheaper screening methods are available but often lead to incorrect conclusions.

Laboratories not equipped for sulfate analyses should still follow the procedure to determine TAA and TPA. (They have the option of sending the extraction/digested solutions to other laboratories for sulfate analyses). Similarly, where only the sulfur trail or POSA has been requested, the analyst should follow the combined procedure, only omitting the TAA and TPA titration components.

Codes compatible with the 'Green Book' *Australian Laboratory Handbook of Soil and Water Chemical Methods* (Rayment and Higginson 1992) have been allocated for the various individual components of the combined method (Chapter 3). These codes define the procedures followed, and

[1] The comparative work of Lin *et al.* (1996), laboratory analyses and method comparisons data on a range of soils prepared by A. McElnea, D. Baker and laboratory staff of the Resource Sciences Centre, Analytical Centre, Indooroopilly Queensland along with the comments or advice of various individuals, laboratories and ASS consultants is acknowledged in the development of this method, particularly Graham Lancaster, Warren Hicks, Greg Bowman, Mike Melville, Steve Dobos, David Dent, Peter Edmiston, Sharon Denny, Errol Best and Dave Mazlen.

allow concise reference and use in databases or reporting formats. They should be strictly followed and new codes should not be invented. Recommended changes or additions should be made to ASSMAC for consideration of the ASSMACTC.

The Total Oxidisable Sulfur (TOS) Method 20 should be regarded as predominantly a 'screening method'. The TOS method follows the sulfur trail only. It provides a measure of pyrite content at a cheaper price, but gives no estimate of 'actual acidity' from previous or partial oxidation of sulfides. It usually has higher detection limits, does not provide as much data on the sample and often needs supplementing with the POCAS method, particularly in partially oxidised soil layers. However, if used in combination with the POCAS method in a soil analysis program, it can be used to minimise the cost of analysis.

4.1 Overview of the POCAS method

The procedure is comprised of three distinct parts:

Step 1. **extraction** with 1M KCl to determine soluble and adsorbed sulfur (S_{KCl}%) and the total actual acidity (TAA) of the soil.

Step 2. **oxidation** of the soil with hydrogen peroxide to produce maximum acidity from any reduced sulfidic material, determining the sulfur (sulfate) content (S_{P}%) of the digested solution, and titration of the total potential acidity (TPA) of the solution.

Step 3. **calculating** the differences between steps 2 and 1, the **sulfur trail** is used to predict the potential acid risk from unoxidised (peroxide oxidisable) sulfur compounds (S_{POS}%) **or** the **acid trail** is used to predict total sulfidic acidity (TSA) .

Section 4.2 details the complete steps in the POCAS method while Section 4.3 provides a discussion of the method. Section 4.5 provides an outline of the method for ease of laboratory use. The complete method in addition to the discussion in Section 4.3 should be read and understood before proceeding to analyse or interpret the data.

4.2 The POCAS method

Step 1. KCl Extractable Sulfur (S_{KCl}) and Acidity (TAA)

The step involves the extraction of the sample with 1M KCl to determine soluble and adsorbed sulfur (S_{KCl}%) and the total actual acidity (TAA) of the soil.

a. KCl Extraction

(i) Weigh accurately a minimum of 2.5 g of fine-ground, oven-dry sample

(ii) Make a 1:20 suspension with 50 mL of 1M KCl. (for a <2 mm, coarsely ground sample, a minimum of 5 g is required and correspondingly larger volumes of reagents to achieve the same 1:20 soil:solution ratio). Prepare a blank.

Note: Larger volumes and weights should be used for samples with low concentration of pyrite (such as sands) with the 1:20 ratio being maintained.

(iii) Extract the solution on reciprocal or end-over-end shaker for 1hr and let stand overnight (16 hr).

Note: A 1:20 suspension was selected as a compromise between keeping the soil:solution ratio as low as possible and having a solution ratio which will dissolve the gypsum crystals that can occur naturally in acid sulfate soils. The overnight stand is intended to suit routine laboratory procedures and achieve equilibrium closer to the 24 hr standing after titration used by Dent and Bowman (1996). There are suggestions that some pyrite oxidation of low analysis dredged sands may occur on prolonged shaking or standing and hence standing time may have to be reduced

on such samples. This is under further investigation and is only expected to be significant on low analysis sands.

Gypsum has a solubility of only 0.2% in water but a greatly enhanced solubility in 1M KCl. However, samples with very high gypsum contents may require a 1:50 ratio of soil:extractant ratio to dissolve all the gypsum, particularly if the analysed sulfur content approaches 3.15%.(McElnea and Baker 1998); (see general comments section 4.3).

(iv) Re-shake briefly after overnight standing then filter the suspension or centrifuge at an appropriate speed to obtain a clear solution. Take a 25 mL aliquot for titration of acidity and an aliquot for sulfate determination (the aliquot size depends on the sulfate method employed).

Note: Measuring TAA on a filtered or centrifuged extract generally produces a lower value than from titrating the entire suspension. However, use of the clear extract makes the titration end-point more abrupt, (Figure 1, Ahern *et al*. 1996) *with less pH drift and avoids the need for a correction factor usually applied when a suspension is used.*

b. KCl Extractable Sulfur (S_{KCl}%)

(i) Determine KCl extractable sulfur (generally sulfate) by making up the aliquot to suitable volume for sulfate determination. This final volume will depend on the particular laboratory's technique and/or equipment for measuring sulfate.

(ii) Report KCl extractable S result on a dry soil basis as S KCl % **(Method 21C).**

Note: Extractable sulfur may be determined by ICPAES spectrometer commonly called ICP, or as sulfate using automated or manual turbidimetry or gravimetry. If an HPLC is to be used then a chloride reduction pre treatment is needed. The ICP has the advantage of reading solution sulfur, including any extracted organic S compounds, in addition to the sulfate. This effectively reduces some of the contribution to S_{POS}% of organic sulfur.

*Additionally, if ICP is used, then calcium (**Method 21Vh**) and magnesium (**Method 21Sm**) can usually be determined on the aliquot at little extra cost. See 'general comments on the method' section 4.3 for their use. A lower case alphabetic character (as shown in Table 3.2) is added to the **Method 21C** code to indicate the laboratory's sulfur/sulfate method. The finishing codes generally follow that of Rayment and Higginson (1992) for sulfate water analyses with some additions eg. **21Ce** is KCl extractable sulfur using an ICP finish.*

c.

KCl extractable acidity - TAA Titration:

(i) Measure and record pH_{KCl} **(Method 21A)** of aliquot prior to 'TAA' titration.

(ii) If pH_{KCl} is ≥ 5.5 then TAA is zero.

(iii) if pH_{KCl} is less than 5.5, titrate a 25 mL aliquot with standardised 0.05M NaOH (or NaOH prepared from an ampoule according to manufacturer's instructions) to pH 5.5 while stirring the solution.

Note: NaOH solutions should be prepared fresh each day or stored in an apparatus capable of excluding CO_2. Titrations should be carried out using an autotitrator, or manually using an A-grade 10 mL burette graduated to 0.02 mL. If titrating manually, record a pH and alkali volume at a pH close to but just below 5.5 for accurate endpoint volume interpolation if the endpoint pH is slightly exceeded. Other molarity NaOH solutions may be prepared to suit the range of samples encountered. If an accurate result is required on a low analysis sample (or those suspected of being low because pH_{KCl} is close to 5.5) a lower molarity NaOH solution may be used, but the increased accuracy thus achieved must be balanced against the risk of CO_2 contamination. It may be preferable to initially use 5 g of fine ground sample (remembering to keep the extraction ratio constant at 1:20) and hence be able to titrate double the aliquot of extractant.

(iv) Record the volume of alkali required to reach pH 5.5, calculate result and express as mol H^+/tonne of dry soil **(Method 21F).**

Step 2. Peroxide oxidation Sulfur (S_P%) and Acidity (TPA)

This step involves the oxidation of the soil with hydrogen peroxide to produce maximum acidity from any reduced sulfidic material, determining the sulfur (sulfate) content (S_P%) of the digested solution, and titration of the total potential acidity (TPA) of the solution.

d. Peroxide digest (oxidation)

(i) Weigh accurately 2.5 g of fine-ground oven-dry sample (for a coarsely ground (<2 mm) sample a minimum of 5 g is required and correspondingly larger volumes of reagents are required to achieve the same soil:extractant ratio).

Note: for sandy materials (samples with ≤5 % clay) a minimum of 5 g fine-ground or 10 g coarse sample will be required to provide greater volume of sample for titration, thereby enhancing accuracy on low analyses samples. Please see 'Method Variation for Sandy Material' section 4.2 g) and the slight alteration in the method).

(ii) Record the total weight of flask plus sample for later use in making up accurate final volumes of extractant.

(iii) Make a homogenous 1:5 suspension with 12.5 mL 2M KCl. A 1:5 ratio is initially selected to enhance peroxide oxidation but the final ratio is 1:20 as in the TAA / S_{KCl} procedure

(iv) Completely oxidise samples with 5 mL aliquots of analytical grade (or equivalent) 30 % hydrogen peroxide (H_2O_2). Care needs to be taken to avoid samples bubbling/frothing-over when the initial aliquot of peroxide is added. If the reaction is too vigorous, add more deionised water to the sample. It is recommended that after addition of the initial aliquot of peroxide, samples should be left standing at room temperature for at least 2 hours before they

are gently heated. Some laboratories prefer to add most of the peroxide in one addition, but careful management including cooling with ice for reactive samples is required.

(v) Swirl, and if necessary, gently heat (max. 55-60 ^{o}C) samples between additions of peroxide aliquots until oxidation is complete. Record the number (or total volume) of H_2O_2 aliquots used for calculating blank corrections where necessary. Blanks should always be included with every batch of samples.

Note: Complete oxidation of the sample is vital to avoid erroneous TPA results. Complete oxidation has occurred when addition of peroxide produces no further reaction on prolonged standing, the mineral soil has become grey to light brown, and the supernatant is clear and transparent (though not necessarily colourless). Generally, around two days of room temperature oxidation is required. Some samples do not easily fit this description, so extra time and care is needed to ensure complete oxidation. Peaty soils and those with high organic matter may froth initially and require considerably more peroxide (and time) than mineral soils for complete oxidation. Samples containing jarosite, goethite or gypsum and very little or no pyrite may continue to react very slowly for a number of days without appreciable acid generation.

Caution must be exercised when digesting these samples to avoid adding excessive volumes of peroxide which will prolong the following boiling stage. Use of heat to speed up the oxidation procedure may lead to excessive peroxide usage and incomplete oxidation of the sample as peroxide is easily decomposed on heating. Substantial loss of sample volume and subsequent crystallisation of gypsum or other sparingly soluble salts must be avoided. Experienced operators may develop their own laboratory oxidation procedures to match the types of samples being analysed (with a minimum of 24 hours required even under accelerated oxidation conditions) but reagents and ratios must be consistent with the approved method. Appropriate internal laboratory quality control samples should be run with each batch to ensure complete oxidation. The oxidation step is the most difficult to standardise and describe at this stage. As details from the exchange sample system and further research data come to hand, some modifications of the above description may be required. There is much conflicting information from laboratories but probably the biggest problems are created from the use of technical grade peroxide and attempts to adjust pH or correct for blanks. Possibly, some AR grade peroxide supplies are also problematic.

For low sulfur analysis of sands, sulfur blanks may have to be run on batches of peroxide and AR grade KCl before use.

(vi) When oxidation is complete add 12.5 mL 2M KCl and if total volume is < 50 mL add sufficient deionised water to make volume approximately 50 mL.

Note: Water addition is necessary to dissolve any gypsum originally present in the sample and/or formed as a result of the digestion process. It is also very important to keep the volume close to 50 mL *during the following heating stage by addition of deionised water when necessary.*

(vii) Decompose excess peroxide by heating between 85ºC and 95°C until bubbling has stopped and solutions have cleared. If total volume exceeds 50 mL (1:20 ratio) reduce volume of sample, by further heating.

Note: Do not allow solution to boil at this stage. Boiling will remove excess volume quickly but precautions must be taken to prevent excessive loss of solution.

(viii) Allow to cool to room temperature. Weigh flask plus contents and add de-ionised H_2O until weight coincides with original weight + a constant weight (equivalent to the weight of 50 mL 1M KCl).

Note: The weighing approach provides better accuracy than making up the solution to 50 mL in a flask. Samples with very high gypsum contents may require a 1:50 ratio of soil:extractant to dissolve all gypsum this includes the original gypsum in the sample or gypsum produced by reaction of the sulfuric acid with any fine shell material, calcium carbonate or other calcium source in the sample. If the result of the acidity trail exceeds the result of the sulfur trail on samples showing high sulfide content, the solubility of gypsum may be implicated in giving a lower sulfur trail result. In these circumstances a repeat analysis using 1:50 ratio may be required. (See 'general comments in Section 4.3).

(ix) Filter the suspension or centrifuge at a sufficient speed to obtain a clear solution. Take a 25 mL aliquot for titration of acidity (TPA) and an appropriate aliquot for sulfur determination, depending on the method employed (see (b)(i) below).

e. Peroxide digest, Sulfur determination (S_P)

(i) Determine total solution sulfur (which should all be sulfate if the sample has been completely oxidised by the peroxide) by taking an aliquot of suitable volume for sulfate determination. This volume will depend on the laboratory's technique and/or equipment for measuring sulfate.

(ii) Determine sulfate on the blank and adjust results if necessary, according to the volume of peroxide used for each sample.

(iii) Express results on dry soil basis as peroxide sulfur (S_P%) **(Method 21D)** and indicate the method of sulfur determination in the code using Table 3.1 and 3.2**.**

(iv) If ICP is used, then calcium (**Method 21Wh**) and magnesium (**Method 21Tm**) can usually be determined on the same aliquot at little extra cost. See 'Section 4.3'.

f. Peroxide digest, Total Potential Acidity (TPA) titration

(i) Measure and record pH_{OX} **(Method 21B)** of aliquot prior to 'TPA' titration.

(ii) **If the pH_{OX} is >5.5** after peroxide oxidation then the TPA is zero and the Quick Residual Neutralising Capacity **(Method 21Q** – NQ $CaCO_3$ %) may be determined (*see Section 4.2 h*)

(iii) If pH_{OX} is less than 5.5, titrate a 25 mL aliquot of solution with 0.05M NaOH (for sands and expected low pyrite soils) or 0.25M NaOH (on suspected highly pyritic soils/muds) to pH 5.5 with stirring. Once again record pH and volume of alkali at a pH near to but below pH 5.5 for interpolation purposes.

Note: Where prior knowledge of expected sulfide levels of the soil is not available, the value of pH_{OX} in combination with soil texture can be used to assist in estimating the concentration of NaOH used in the titration. Marine clays and clayey soils usually have good buffering capacity, so a low pH_{OX} indicates that a large volume of titrant is needed. On the other hand, sandy soils have little buffering capacity and usually require a small volume of titrant compared to clays for the same low pH_{OX} values. Additionally, sandy soils are usually low in sulfide content. As a general rule, sands and samples with a pH_{OX} of ≥ 3 should be titrated with lower concentration NaOH.

(iv) Record the volume and concentration of alkali used.

(v) '**Double oxidation' Step** - immediately add an aliquot (2.5 mL) of 30 % peroxide with stirring and record this pH. (If you are using 5 g of sample add a 5 mL aliquot of peroxide). If pH drops below 5.5, titrate with stirring back to pH 5.5 with NaOH. If using an auto-titrator, 0.05M NaOH can be used even if 0.25 M NaOH has been used in the first part of the titration. Once again record pH and alkali volume just below endpoint.

Note: The 'double oxidation' step developed by Dent and Bowman, (1996) is required to ensure complete iron oxidation and subsequent acid generation. Complete oxidation of Fe^{2+} to Fe^{3+} is inhibited by very low pH after peroxide treatment.

(vi) Record the volume of alkali added. Add this to the volume used in the first part of the titration (checking that the two molarities are compatible).

(vii) Use the blank result to correct titrations according to the volume of peroxide used in each particular sample. Use of analytical grade peroxide usually results in negligible blanks.

Note: Some laboratories have found substantial blanks using technical grade peroxide which is generally unreliable, variable between containers and may be stabilised with phosphoric or sulfuric acid. The pH and sulfur content of each container of peroxide must be checked. Generally AR grade peroxide has a pH of >4 and a change of supply should be considered if substantial blanks occur. Stock peroxide should be stored in the refrigerator and decanted into smaller containers for laboratory use. This does not remove the need for having a blank in every batch of samples.

(viii) Calculate the TPA result and express as mol H^+/tonne of dry soil **(Method 21G)** or TPA equivalent S_{TPA} % **(Method 21K)** assuming that all acidity generated is from pyrite.

g.

Modifications to sample weight for sandy material

As a general rule for sandy material with low organic content, a minimum sample of 5 g fine-ground (<0.5mm) or 10 g (<2mm) is required to provide an adequate volume for titration of low analysis samples.

Variation 1 'TPA' procedure for 5 g of fine-ground sample

(i) Add 12.5 mL 2M KCl initially and proceed with oxidation

(ii) When oxidation is complete, add 37.5 mL (3 × 12.5 mL) 2M KCl and sufficient deionised water to make total volume approximately 100 mL.

(iii) After heating to remove excess peroxide, cool and add deionised water until the weight of flask and contents equals original flask + sample + weight of 100 mL 1M KCl.

(iv) Titrate a 75 mL aliquot for the TPA and add 5 mL peroxide for the **'**double oxidation' step.
Note: Sluiced sands with a very low sulfide content, may require 5 g or 10 g of fine-ground sample to a final volume of 50 mL ie. a 1:10 or 1:5 ratio of soil to extractant to improve the lower limit of detection. With these exceptions, the extraction ratios on samples must be kept at 1:20 for comparability.

Variation 2 'TPA' procedure for 10g coarse-ground sample

(i) Add 25 mL 2M KCl initially and proceed with oxidation

(ii) When oxidation is complete, add 75 mL (6 × 12.5 mL) 2M KCl and add sufficient deionised water to make total volume approximately 200 mL.

(iii) After boiling to remove excess peroxide, cool and add deionised water until the weight of flask and contents equals original flask + sample + weight of 200 mL 1M KCl.

(iv) Titrate a 150 mL aliquot for the TPA and add 5 mL peroxide for the **'**double oxidation' step
Note: Calculations will need to be adjusted accordingly.

h. Quick Residual Neutralising Capacity

If pH is >5.5 after peroxide oxidation then an **optional step** is to determine residual quick neutralising capacity (Dent and Bowman, 1996).

(i) titrate the 25 mL aliquot (V9) with standardised HCl (0.05M) (M4) to pH 5.5 while stirring and record the titre (T5)

(ii) calculate the result and express as $CaCO_3$ % **(Method 21Q).**
NQ ($CaCO_3$ %) = (V5/V9) x M4 x T5 x (100.087 x 0.05/W2)

for **0.05M HCl** and suggested weights, volumes and dilutions this reduces to
NQ ($CaCO_3$ %) = T5 x 0.2002

Step 3. Peroxide Oxidisable Sulfur (S_{POS}) and Total Sulfidic Acidity (TSA)

This step involves calculating the differences between the determinations on the peroxide extract (Step 2) and the KCl extract (Step 1). The result for the **sulfur trail** and the **acid trail** can be compared when converted to the same units.

i. Peroxide Oxidisable Sulfur (S_{POS} %)

Peroxide oxidisable sulfur is the difference between the sulfur determined in the peroxide digest **(Method 21D)** and the sulfur extracted by 1M KCl (**Method 21C**).

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

or

Method 21E = Method 21D – Method 21C

Note: Peroxide oxidisable sulfur results should yield similar values to the often used POSA method of Lin and Melville (1993). The essential difference is that the POCAS method uses a KCl solution instead of water to displace adsorbed and soluble sulfates in the extraction stage. Also samples with high gypsum content or those containing excess lime/shell and produce substantial gypsum during the peroxide digest are better catered for in POCAS because of the greater extraction ratio (1:20).

j. Total Sulfidic Acidity (TSA)

Total sulfidic acidity is the acidity attributed to the complete oxidation of all the remaining sulfidic compounds in the soil by hydrogen peroxide. The existing acidity or TAA from previous oxidation does not contribute to TSA . TSA is calculated as:

TSA = TPA - TAA (mol H^+ / tonne)

or

Method 21H = Method 21G – Method 21F

Note: TSA values by this method should give values similar to the double oxidation method of Dent and Bowman (1996) although the POCAS method employs KCl instead of NaCl as extractant and uses filtered or centrifuged solutions rather than titration of the soil suspension. Additionally, POCAS results are expressed on a dry weight basis (mol H^+ / tonne) rather than an as sampled (wet) volumetric basis (mol H^+ / m^3).

4.3

General comments on the POCAS method

a. What methods to use?

It should be noted that no single method (including this combined method) will provide all the answers to the complex chemistry involved in reactions of acid sulfate soils. For some samples, it can be expected that various methods may give different results due to partially oxidised or complex salts, gypsum, organic matter or neutralising materials. Organic matter in the environment is variable in composition and its effects on both the sulfur and acid trail are difficult to quantify.

The peroxide sulfur trail can overestimate the complete acid generating potential in partially oxidised layers. The common, pale yellow partial oxidation product, jarosite, $K(Fe)_3(OH)_6(SO_4)_2$ is not extracted by 1M KCl but may be analysed in S_P% (**Method 21D**) under very acid conditions and hence included in the peroxide oxidisable sulfur (S_{POS}%) result (**Method 21E**). One mole of jarosite slowly oxidises to produce only one mole H^+.

Significant shell or neutralising material lowers the acidity trail result but does not affect the sulfur trail (unless saturated solutions of gypsum are formed). In such cases (unless the shell in the original unground sample is very fine), the acidity trail can substantially underestimate the potential environmental risk. All the shell in the fine ground laboratory sample is likely to react with any significant acid produced by peroxide treatment, reducing the TPA or S_{TPA}% result. In contrast, in the actual soil environment most shells become coated with gypsum or insoluble iron compounds preventing short-term neutralising action. At disturbed sites, highly acidic water has been found running past and through substantial pockets of shell with a neutralising capacity many times that required to account for all potential acid production from pyrite (without significant consequent neutralisation). The proposed volumetric procedure does not suffer as much from the effect of shell as no grinding is involved, but achieving representative samples using a 10 mL syringe in soils with appreciable shell is likely to be a problem.

Determination of calcium, magnesium or sodium on the KCl extract (**Method 21V, 21S, 21M**) and peroxide digest (**Method 21W, 21T, 21N**) can assist calculations on the amount of shell or lime that may have reacted with the acid produced by peroxide oxidation of pyrite. This is an easy, low cost addition when analysing for sulfur on the same extract using some ICP instruments. Analysis 21X, the difference between 21W and 21V (when multiplied by 0.8 to convert Ca % to equivalent S %), often accounts for the difference between the acidity trail (21L) and sulfur trail (21E) when all results are expressed in the equivalent S units (eg. S %). Sometimes the magnesium result also needs to be taken into account (factor = 1.319). The 1:20 extraction with 1M KCl for Ca, Mg, and Na gives an estimate of soluble plus exchangeable cations.

The calcium result of **Method 21W** and the sulfur result of **Method 21D** also allow for easy checking on whether calcium and sulfate concentrations are approaching the solubility product of gypsum for a 1:20 KCl extract (≈3.15 % S, 3.9 % Ca; McElnea and Baker 1998). A repeat analysis using more dilute extraction/digestion ratio such as 1:50 is required as a precaution when this occurs, because the sulfur trail can be underestimated when gypsum ($CaSO_4.2H_2O$) precipitates out of solution.

b. Sample size

For fine-ground homogenous samples (<0.5mm), 2.5 g is recommended as the minimum sample weight. Fine-ground samples will give more reproducible results, and possibly faster and more complete peroxide oxidation. Where ground material principally <2mm is available, 5 g is the minimum sample weight required and the soil:extractant ratios must remain at 1:20.

c. Extraction ratio

The 1:20 ratio is a compromise and balances the need to keep extractions as close as practicable to saturated soil solution ratios with the need to obtain sufficient volumes of extract for laboratory analysis and the dissolution of sulfate salts. It should be noted that for soils with high gypsum levels (>5 % gypsum - equivalent to >1 % S) the gypsum content of the soil may exceed the amount that can be dissolved in a 1:20 extract. In such cases, the procedure may need to be repeated using a wider extraction ratio (eg. 1:50) to determine the sulfate before and after oxidation. The titrated TAA and TPA values should be taken from the 1:20 extraction procedure. Where electrical conductivity (EC) and chloride values of a 1:5 soil:water extract are available, high EC together with low chloride indicate the possible presence of substantial sulfate salts.

d. Molarity of titrants

The molarity of NaOH or HCl used for the various titrations may be altered to suit individual equipment (auto-titrators, etc.) or batches of sample being analysed. In general, the use of the higher molarity titrants on low acidity samples will be accompanied by an increase in error and loss of precision. This should be balanced against the potential confusion to operators of recording volumes of different molarity solutions and the possibility of gross errors in the calculations. A well-designed laboratory recording sheet and spreadsheet software would minimise these risks and simplify calculations and the reporting of results.

e. Titration end point

Results from the comparison of a range of soil samples from Queensland and New South Wales (Table 1, Attachment 1 of Ahern *et al*. 1996) show that slightly lower TAA, TPA and TSA values are generally obtained from the clear solution (centrifuged or filtered) than from the suspension (soil + extractant). Greater proportional differences and variation occurred with the TAA determinations than with TPA determinations.

Advantages of the clear solution titrations were a sharp end-point (Figure 1, Ahern *et al.* 1996b). In contrast, the TAA titrations on suspensions have poor end-points and drift substantially over time. Re-titrating 24 hours later is considered an impost by many routine laboratories and has been overcome by Dent and Bowman's, 1996 modification of a 24 hour stand. However, it has been suggested that a 24 hour stand has the potential to allow some minor pyrite oxidation (yet to be proven) and possible carbon dioxide effects. The 1 hour shake and overnight stand (16 hour) for the TAA procedure is somewhat of a compromise, which may not guarantee immunity from these potential complications.

TAA titration curves (Attachment, Fig 1, Ahern *et al*. 1996) of 1M NaCl and 1M KCl extracts showed a general trend of KCl_{Susp} > $NaCl_{Susp}$ > KCl_{Clear} >$NaCl_{Clear}$. This clearly illustrates the necessity of a standard approach for acid sulfate soils methods throughout Australia for environmental samples. Standardised techniques assist regulators and consultants to avoid confusion between results supplied by the many laboratories using a myriad of permutations on the POSA, TPA, TAA and TSA methods. The NSW EPA (1995) guidelines and the 'Interim Acid Sulfate Soils Analytical Methods, June 1996' of the NSW Acid Sulfate Soils Advisory Committee (ASSMAC) were a significant step in the standardisation process. This combined peroxide method builds on that process and takes advantage of most recent findings on laboratory methods.

f. Difficult materials

Care should be exercised in interpreting results of samples from peaty soils, high organic material, coffee rock and indurated sands. Pyrite commonly occurs inside old root channels and its formation is usually closely associated with organic matter, which if abundant enough, may form sulfidic peats.

However some positive results, by both the sulfur and acid trail, have been found in samples with no identifiable mineral pyrite under the electron microscope. The positive oxidisable sulfur result in such cases may be attributed to high organic sulfur content in the organic matter. Such organic sulfur compounds are not expected to produce significant amount of acid on disturbance and hence pose little to no environmental risk. Research to find a more appropriate method for use on these difficult samples is continuing.

Coffee rock is expected to be fully oxidised due to its pedological and geomorphic history (Bowman pers. comm.). While the chief reason for positive TSA results is claimed to be insufficient oxidation with peroxide (Dent and Bowman, 1996), positive results by both the acid and sulfate trail have been recorded on a number of low lying (ie. below watertable) coffee rock samples from the Sunshine Coast, Queensland. As sulfidic layers are usually associated with such occurrences, this coffee rock and its significance is being further investigated. In the mean time, it should **not** be assumed that all coffee rock has no environmental risk. If significant quantities of the monosulfide (Fe_xS_y) are expected (such as can occur in sediments from drains, lakes and estuaries) then analyses of freeze dried samples may be required as the monosulfides and other compounds such as greigite (Fe_3S_4) are likely to rapidly oxidise on oven drying.

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4.4

Outline of POCAS method for laboratory use

REAGENTS

2M Potassium Chloride (KCl)
Dissolve 149.1 g of AR grade potassium chloride and make up to 1.0 L with deionised water.

1M Potassium Chloride (KCl)
Dissolve 74.55 g of AR grade potassium chloride and make up to 1.0 L with deionised water or make up 500 mL of 2M KCl to 1.0 L with deionised water.

0.25M Sodium Hydroxide (NaOH)
Dissolve 10.0 g A.R. sodium hydroxide (NaOH) pellets in deionised water and make up to 1.0 L. Standardise against potassium hydrogen phthalate ($KHC_8H_4O_4$) using a similar procedure to Method 4D1 (Rayment and Higginson, 1992). Alternatively make up stock solution from ampoule, standardise and dilute accurately to final concentration. Special precautions to exclude carbon dioxide prior to standardisation and for storage are necessary.

Method for Standardisation of 0.25M Sodium Hydroxide

- *Dry primary standard grade potassium hydrogen phthalate (F.W. 204.223) in an oven at 110 ℃ for 2 hours and store in a desiccator.*

- *Weigh accurately three samples of between 0.45 and 0.50 g (analytical balance) solid potassium hydrogen phthalate and dissolve each in ~ 25 mL deionised water. Add 3 drops of phenolphthalein indicator solution. Titrate with sodium hydroxide solution until endpoint is reached. Between 8.8 and 9.8 mL of ~ 0.25M NaOH should be required. Calculate actual concentration of sodium hydroxide using titre values.*

0.05M Sodium Hydroxide (NaOH)
Accurately dilute recently standardised 0.25M NaOH. Alternatively, accurately diluted standardised stock solution made from ampoule. Use immediately, do not store.

0.05M Hydrochloric Acid (HCl)
Commercial standard solutions may be used or add 5 mL of AR grade concentrated hydrochloric acid (10M) to deionised water and make volume to 1.0 L. Standardise against sodium tetraborate ($Na_2B_4O_7.10H_2O$) using a similar procedure to Method 7A1 (Rayment and Higginson, 1992).

30 % Hydrogen Peroxide (H_2O_2)
Use only AR grade hydrogen peroxide. Check the pH of the peroxide and determine a blank TPA and blank sulfur content before use. Blanks should be virtually negligible. Technical grades are not recommended as they are usually acid stabilised and vary considerably between bottles in both sulfur content and pH.

Step 1. KCl Extractable Sulfur (S_{KCl}) and Acidity (TAA)

a. KCl Extraction

(i) weigh accurately a minimum of 2.5 g (W_1) of fine-ground (<0.5 mm) oven-dry sample
(ii) make 1:20 suspension with 50 mL (V_1) of 1M KCl; prepare a blank
(iii) extract solution on reciprocal or end-over end shaker for 1 hour and let stand overnight (16hr)
(iv) re-shake briefly after overnight standing then filter the suspension or centrifuge at an appropriate speed to obtain a clear solution. Take a 25 mL aliquot (V_2) for titration of acidity and a 10 mL initial aliquot (V_3) for sulfur determination (the aliquot size depends on sulfur method employed).

b. KCl extractable Sulfur determination

(i) Determine KCl extractable sulfur (generally sulfate) by making up the aliquot (V_3) to suitable volume (V_4) for sulfate determination. This final volume will depend on your technique and/or equipment for measuring sulfate.
(ii) By using an appropriate range of standards for the method employed, calculate sulfur (S_1) (mg S/L). Also determine S on a blank (S_2). Indicate using codes from Table 3.2 which sulfur finishing step was employed. Calculate KCl extractable S (**Method 21C**) as below:

$$S_{KCl}\ (\%) = (S_1-S_2)\ (\text{mg S/L}) \times (V_4/V_3) \times (V_1/W_1) / 10000$$

Note: Calcium and magnesium may be determined on the same solution (Methods 21V, 21S) and is strongly recommended for samples containing shell material, carbonate or gypsum. Sodium may also be determined on the extract (Method 21M).

c. KCl extractable acidity -TAA Titration:

(i) Measure and record pH_{KCl} (**Method 21A**) of the aliquot prior to 'TAA' titration.
(ii) If pH_{KCl} is greater than 5.5, then TAA is zero
(iii) If pH_{KCl} is less than 5.5, titrate 25 mL aliquot (V_2) with standardised 0.05 M NaOH (or NaOH prepared from an ampoule according to manufacturer's instructions) to pH 5.5 with stirring.
(iv) Record molarity (M_1) and titre (T1, mL) of alkali added in titration to reach pH 5.5.
(v) Titrate a blank sample (T_2) using the same molarity NaOH
(vi) Calculate result and express as mol H^+ / tonne of dry soil (**Method 21F**)

$$\text{TAA (mol } H^+ \text{ / t)} = (V_1/V_2) \times (T_1-T_2) \times M1 \times (1000/W_1)$$

for NaOH molarity M_1 = 0.05M, zero blank and suggested weights/volumes/dilutions as above, this reduces to

$$\textit{TAA (mol } H^+ \textit{ / t)} = 40 \times T_1$$

Step 2. Peroxide oxidation Sulfur (S_P) and Acidity (TPA)

d. Peroxide digest (oxidation)

(i) weigh accurately a minimum of 2.5 g (W_2) of fine-ground (<0.5 mm) oven-dry sample into a conical flask.

(ii) record the total weight of flask plus sample, for later use in accurately making up final volume of extractant.

(iii) make an homogenous 1:5 suspension with 12.5 mL 2M KCl. A 1:5 ratio is initially selected to enhance peroxide oxidation but the final ratio is 1:20 as in the TAA titration.

(iv) completely oxidise samples with 5 mL aliquots of analytical grade (or equivalent) 30 % hydrogen peroxide (H_2O_2). Care needs to be taken to avoid samples bubbling/frothing-over when the initial aliquot of peroxide is added. If the reaction is too vigorous, add more deionised water to the sample. It is recommended that after addition of the initial aliquot of peroxide, samples should be left standing at room temperature for at least 2 hours before they are gently heated.

(v) swirl, and if necessary, gently heat (max. 55-60 ^oC) samples between additions of peroxide aliquots until oxidation is complete. Record the number (or total volume) of H_2O_2 aliquots used, for calculating blank corrections where necessary.

(vi) When oxidation is complete add 12.5 mL 2M KCl and if total volume is < 50 mL add sufficient deionised water to make volume approximately 50 mL.

(vii) Remove excess peroxide by heating between 85 and 95°C until bubbling has stopped and solutions have cleared. If total volume exceeds 50 mL (1:20 ratio) reduce volume of sample, by further heating. Boiling will remove excess volume quickly but precautions to prevent potential loss of solution are needed.

(viii) Allow to cool to room temperature. Weigh flask plus contents and add de-ionised water until weight coincides with original weight + a constant weight (equivalent to the weight of 50 mL of 1M KCl) to give a final volume of 50 mL (V_5) .

(ix) Filter the suspension or centrifuge at a sufficient speed to obtain a clear solution. Take a 25 mL aliquot (V_6) for titration of acidity (TPA) and a 10 mL aliquot (V_7) for sulfate determination. (The aliquot depends on sulfur method employed).

e. Peroxide digest, Sulfur determination (S_P)

(i) Determine total solution sulfur after oxidation by diluting an aliquot (V_7) to suitable volume (V_8) for sulfate determination (S_3) (mg/L). The final volume will depend on the technique and equipment for measuring sulfate.

(ii) Determine sulfate on the blank (S_4) and use an adjusting factor (F_1) if necessary, for the volume of peroxide used for each sample compared to volume used in the blank.

(iii) Calculate results as sulfur percentage (S_P %) (**Method 21D**) as shown below:

$$S_P\ \% = (S_3 - F_1 \times S_4) \times (V_8/V_7) \times (V_5/W_2) / 10000$$

*Note: Optionally, calcium and magnesium may be determined on the same solution (**Methods 21W, 21T**) and is strongly recommended for samples containing shell material or gypsum. Sodium may also be determined on the extract (Method 21N).*

f. Peroxide digest, TPA Titration:

(i) Measure and record pH $_{OX}$ (**Method 21B**) of aliquot prior to 'TPA' titration

(ii) If pH is >5.5 after oxidation then the TPA is zero and quick neutralising capacity may be determined *see Section 4.5 g).*

(iii) If pH $_{KCl}$ is less than 5.5, titrate aliquot of solution with 0.05M NaOH (M_2) for sands and expected low pyritic soils or 0.25M NaOH (M_3) on suspected highly pyritic soils/muds to pH 5.5 while stirring the solution.

(iv) Record the titre and molarity of alkali used.

(v) **'Double oxidation' step -** immediately add an aliquot (2.5 mL) of 30 % peroxide with stirring and note pH. If pH drops below 5.5, titrate with stirring back to pH 5.5 with NaOH.

(vi) Record the total titre (T_3) and molarity (M_2 or M_3) of alkali added. Use the blank (T_4) result to correct titration volumes according to the volume of peroxide used in each particular sample (factor F_1).

(vii) Calculate TPA result and express as mol H^+/tonne of soil **(Method 21G)**.

$$\text{TPA (mol } H^+ \text{ /t)} = (V_5/V_6) \times (M_2 \text{ or } M_3) \times (T_3 - F_1 \times T_4) \times (1000/W_2)$$

*for **0.05M NaOH** (M_2), zero blank, suggested weights, volumes and dilutions this reduces to*

$$\textit{TPA (mol } H^+ \textit{ /t)} = 40 \times T_3$$

*for **0.25M NaOH** (M_3), zero blank, suggested weights, volumes and dilutions this reduces to*

$$\textit{TPA (mol } H^+ \textit{ /t)} = 200 \times T_3$$

g. Quick Residual Neutralising Capacity

If pH is >5.5 after peroxide oxidation then an **optional step** is to determine residual quick neutralising capacity (Dent and Bowman, 1996).

- titrate the 25 mL aliquot (V9) with standardised HCl (0.05M) (M_4) to pH 5.5 while stirring and record the titre (T_5)
- calculate the result and express as $CaCO_3$% **(Method 21Q).**

  $$NQ\ (CaCO_3\ \%) = (V5/V9) \times M_4 \times T_5 \times (100.087 \times 0.05/W_2)$$
- for **0.05M HCl** and suggested weights, volumes and dilutions this reduces to

  $$NQ\ (CaCO_3\ \%) = T_5 \times 0.2002$$

Step 3. Peroxide Oxidisable Sulfur (S_{POS}) and Total Sulfidic Acidity (TSA)

h. Peroxide Oxidisable Sulfur (S_{POS})

Peroxide oxidisable sulfur is the difference between the sulfur determined in the peroxide digest (Method 21D) and the sulfur extracted by 1M KCl (Method 21C).

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

or

Method 21E = Method 21D - Method 21C

i. Total Sulfidic Acidity (TSA)

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

TSA = TPA - TAA (mol H^+ / tonne)

or

Method 21H = Method 21G - Method 21F

5. TOTAL OXIDISABLE SULFUR

TOS - METHOD 20

CR Ahern, A. McElnea and DE Baker

Introduction

The Total Oxidisable Sulfur (TOS) method[2] is aimed at providing a standardised, low-cost measure of total oxidisable sulfur for evaluation of the potential environmental risk from acid produced by the oxidation of sulfides, predominantly pyrite or iron disulfide (FeS_2). The main approach recommended is determination of total sulfur minus 4M HCl extractable sulfur to give what is termed 'total oxidisable sulfur' (TOS). This term is used to distinguish it from peroxide oxidisable sulfur (Method 21E).

The TOS method is a useful screening approach to determine pyrite levels in soils providing a low cost measure of pyrite content but gives no estimate of 'actual soil acidity' from previous or partial oxidation of sulfides. The method's main disadvantages are that it follows only the sulfur trail, usually has higher detection limits and does not provide as much data on the sample. For this reason, a percentage of samples should be analysed by POCAS (method 21) to assist interpretations, particularly in partially oxidised soil layers. Also the soil should be checked for any significant neutralising capacity. The TOS method is generally not suitable for accurate determinations on soils with low sulfidic levels, for example sands. The XRF and LECO instruments usually have higher detection limits than the POCAS method.

Codes compatible with the '*Green Book' Australian Laboratory Handbook of Soil and Water Chemical Methods* (Rayment and Higginson 1992) have been allocated for the various individual components of the TOS method (Tables 3.3 -3.5). These codes define the procedures followed, and allow concise reference and use in databases or reporting formats. They should be strictly adhered to and new codes should not be invented without the agreement of ASSMACTC and the authors of Rayment and Higginson (1992).

5.1 Overview of the TOS method

There are two recommended procedures:

a. Method 20 C - Difference between total sulfur and extractable sulfur

Step 1. Determination of total soil S by one of a number of approved methods including X-Ray fluorescence (XRF), Laboratory Equipment Corporation (Leco) Sulfur Analyser as well as other rigorous chemical methods. *(Method 20 A)*

Step 2. Extraction of the soil with 4M HCl to remove soluble and exchangeable sulfates and sparingly soluble sulfates such as gypsum ($CaSO_4.2H_2O$) and jarosite, $KFe_3(SO_4)_2(OH)_6$. *(Method 20B)*

Step 3. Calculating the difference between total sulfur and extractable sulfur to measure total oxidisable sulfur (S_{TOS}%), *(Method 20C).* The result can used to predict the potential acid risk from oxidation of pyrite.

b. Method 20 D - Direct determination

Pre-treated with 4M HCl to remove HCl soluble sulfur and water washed to remove the HCl followed by direct determination of total sulfur on the remaining sample, usually by Leco .

[2] The comparative work of Lin et al. (1996) is acknowledged. S. Dobos, G. Lancaster, B. Blunden, M. Melville, I. Willett, P. Mulvey and NSW ASSMAC Technical Committee members provided valuable discussion and comment.

5.2 Method 20 C - Difference between total sulfur and extractable sulfur

Step 1. Method 20A - Determination of total soil sulfur - Total S (S_T%)

For determination of total S in soils, the various sulfur forms are converted to a single form (usually 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.

a. Method 20A1 - X-Ray Fluorescence

The XRF is a suitable technique for routine total S determination in soils. However, Brown and Kanaris-Sotiriou (1969) reported that a correction for matrix effects needs to be applied for organic soils (soils with loss on ignition > 30%). Darmody *et al.* (1977) noted that the mineralogical and the 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.

(i) **Preparation of pellet for X-ray fluorescence (XRF)**

Oven dry (at 65 ^oC) approximately 10 g of previously dried and 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 minutes, or until soil particle size is <2 μm. Pellet approximately 2 g of the above soil mix (<2 μm) into a 45 mm diameter disc with a H_3BO_3 backing, using a hydraulic press of around 25 tonne total force.

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).

(ii) **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). 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.

b. Method 20A2 - Leco Furnace with infrared detection

Originally Laboratory Equipment Corporation (Leco) Sulfur Analyser was designed to determine sulfur in steel using low weights <1g, though recently models are now available for soils which can take up to 3g of soil. Older model Leco's were designed on the assumption that the technique quantitatively converted S to SO_2. The titration procedure did not however, recover S 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.

Preferably, a resistance furnace should be used which employs a horizontal open ended combustion tube heated by silicon carbide elements. Samples of up to 3 grams are placed in reusable ceramic boats then into the hottest part of the furnace. A stream of oxygen is passed over the sample and the gas evolved is measured by an infra-red detector.

Note: Kaplan et al. (1963) found that 'Leco' did not give reproducible results for total S of marine sediments. They also found Leco results were lower than those obtained by a wet combustion method. Moreover, Lowe (1969) found that Leco resulted in poor recovery of total soil S and had poor precision, especially for samples of low S content. Fortunately, the Leco instrument has changed considerably in recent times.

c. Method 20A3 - Combustion with titration end point

The manufacturer's instructions for the particular model of equipment should be consulted to optimise procedures for the range of sulfur values expected. Samples are heated to about 1600 °C in an induction furnace in a stream of pure oxygen, liberating SO_2. The sulfur dioxide evolved is collected in dilute HCl containing starch, KI and a trace of KIO_3 and titrated with standard KIO_3 solution.

Note: The technique assumed that the combustion process quantitatively converted S to SO_2, however, conversion to SO_3 is possible which was not recovered by the titration (Tabatabai and Bremner 1970, Tabatabai 1982).

d. Method 20A4, - Combustion with conversion to sulfate

Various techniques exist for high temperature combustion with dry ashing/fusion with sodium carbonate (or sodium bicarbonate) combined with an oxidising agent to form sulfate, see dry ashing 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.

e. Method 20A5 - Oxidation with sodium hypobromite

This technique involves the alkaline sodium hypobromite NaOBr oxidation followed by hydriodic acid reduction (Tabatabai and Bremner, 1970).

f. Method 20A6 - Mixed acid digest

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

g. Method 20A7 - Bromine - nitric acid oxidation

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

h. Method 20A9 - Total S by summation of $S_{TOS} + S_{HCl}$

This method involves the calculation of total sulfur by the summation of acid washed Leco sulfur (method 20D) and acid soluble sulfur if the washings are collected and analysed similarly to Method 20B. The method saves having to do another Leco sulfur on a non-acid treated sample. It is mainly used where the sulfur is determined on the Leco after pre-washing with HCl and water. A pre-wash with HCl is required to remove carbonate before determining organic carbon. (See comments in Section 5.3 as to why some laboratories may do LECO sulfur after acid treatment).

Step 2. Method 20 B - HCl (4M) acid extractable Sulfur (S_{HCl} %)

To get a measure of oxidisable S (principally as pyrite S) an indirect method is used. The sulfate/sulfur extracted by 4M HCl is subtracted from the total S determined on a separate sub-sample. Begheijn *et al.* (1978) used successive extractions of 0.1 M EDTA.3Na (3 hours) (to remove water soluble + exchangeable and gypsum sulfate) and hot 4M HCl (to remove jarosite). Lin *et al*. (1996) found that a single boiling 4M HCl extraction achieved very similar results to the slower EDTA-HCl process.

Providing a wide extraction ratio is used (eg. 1:40) strong HCl will dissolve gypsum and jarosite. Ahern *et al* (1998) compared sulfur extracted by boiling 4M HCl with that extracted by overnight shaking at room temperature, for a range of samples (including; reduced, oxidised, gypsic and jarositic acid sulfate soils and mine spoil). No significant difference ($P< 0.05$) using F and *t* tests were found between the two treatments. Thus the cold extraction overnight (16 hr.) has been adopted as a convenient routine method for removing the common non-sulfidic sulfate sources except organic sulfur.

Highly organic or peaty soils may contain significant amounts of organic S in a variety of organic compounds, which will not all be extracted by HCl. Thus Total Oxidisable Sulfur (S_{TOS} %) results may contain an organic sulfur component. This may be significant for peaty soils, which if fresh water peats, may not contain any detectable pyrite. The test is not suitable for low analysis samples particularly sandy soils as the detection limit on total analysis methods is usually too high.

Hydrochloric acid will digest the so-called acid volatile sulfides (AVS) or iron monosulfides such as amorphous FeS, mackinawite ($FeS_{0.9}$) and greigite (Fe_3S_4) (partially) evolving hydrogen sulfide gas (H_2S) which may then be lost (a fume cupboard should be used for safety as H_2S is highly poisonous). While marine sediments from the bottom of some lakes may contain some monosulfides and elemental S, sulfidic soils usually contain quantities too small to be significant (Bloomfield and Coulter, 1973). These monosulfides are metastable and oxidise rapidly on air exposure, thus are lost in the drying process anyway. Freeze drying or volumetric sampling (method 22) may be more appropriate for samples containing monosulfides.

The hydrochloric acid will also dissolve carbonates, fine shell material, and any gypsum ($CaSO_4.2H_2O$) adhering to it. Thus, if Ca and Mg are determined on the extract some upper estimates of carbonate content or potential neutralising material can be made. These estimates will be best on non- gypseous samples or low salinity samples (indicated by electrical conductivity, EC).

As potassium is usually a minor constituent of salts in soils, determination of potassium in the HCl extract, in addition to sulfur, will give an upper estimate on jarosite content of the sample. Potassium content of jarosite is 7.81 % and the K:S ratio is 1:1.64 by weight.

i.

Extraction and determination of sulfur/sulfate

(i) Weigh accurately a minimum of 2.5 g fine-ground oven dried sample into an acid resistant plastic extraction container. With <2 mm ground samples use a minimum of 5 g and a correspondingly larger volume to keep the extraction ratio at 1:40.

(ii) Make 1:40 soil suspension with 100 mL of 4M HCl (prepared by diluting AR concentrated HCl 2.5 times)

(iii) Extract on reciprocal or end-over-end shaker overnight (16 hours)

(iv) Obtain a clear extract by filtering, or centrifuging at an appropriate speed

(iv) Treat sample accordingly for laboratory's sulfur/sulfate method used

Methods for sulfate determination

The samples may require dilution or pH adjustment before following a standard sulfate method such as:

a. Turbidimetric determination
b. Gravimetric determination
c. Automated colour
d. Ion chromatography
e. ICPAES
f. Automated turbidimetric
g. Indirect - precipitation with barium and reading remaining barium by AAS

(iv) Subtract the contribution of the blank run with samples

(vii) Calculate percentage S in oven dry soil

j. Finishing steps for Ca, Mg, Na and K determination

A recommended step is the measurement of calcium, magnesium and optionally other elements soluble in 4M HCl in the extract and coded as per Chapter 3, Table 3.4. When combined with similar data from the POCAS method some coarse fractionating of potential neutralising material can be made.

Calcium	
h	calcium, ICPAES
j	calcium, atomic absorption (AAS)
k	calcium, titration EDTA
Magnesium	
m	magnesium, ICPAES
n	magnesium, atomic absorption (AAS)
p	magnesium, titration EDTA
Sodium	
s	sodium, ICPAES
t	sodium, atomic absorption
u	sodium, flame emission
Potassium	
v	potassium, ICPAES
w	potassium, atomic absorption (AAS)
x	potassium, flame emission

Step 3. Method 20 C - Total Oxidisable Sulfur (S_{TOS}%) by difference

The determination of the total oxidisable sulfur can be made by subtracting the 4M HCl extractable sulfur from the total sulfur.

Calculate: $S_{TOS}\ \% = S_T\ \% - S_{HCl}\ \%$
or
Method 20C = Method 20A – Method 20B

5.3 Method 20 D - Total Oxidisable Sulfur (S_{TOS}%) pre-treated 4M HCl

This approach is useful for removing carbonates from samples before determining Total S and Total C on the Leco instrument. It gives a single result $S_{TOS}\ \%_{directly}$ without the need to determine sulfur on the HCl and deionised water leachate.

The same codes as Method 20A and 20B apply

1	X-ray fluorescence (similar to method 10A1 Rayment and Higginson 1992)
2	Leco (the older model Leco furnace is unsuitable)
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	Acid oxidation using nitric, perchloric, phosphoric, hydrochloric acids (Arkley, 1961)
7	Bromine - nitric acid oxidation (Vogel 1978)

For example Method 20D2 is Total oxidisable sulfur by Leco, pre-treated HCl

Note: Care must be exercised with this method as it is less suited to routine laboratories that the "Difference" method because of the need to ensure no loss of clay particles during sample pre-treatment with 4M HCl and subsequent washing, filtering/centrifuging and drying. In addition substantial leaching/washing times are required on some dispersed soils. Where samples contain significant quantities of acid soluble salts such as jarosite and gypsum or carbonates (eg. in mine spoils or calcareous soils) this component will be dissolved and removed in the leachate. This reduces the sample weight and effectively concentrates the pyrite in the remaining sample resulting in inflated S % values.

Any acid volatile sulfides will also be lost by this procedure. Use of a fume cupboard for the leaching step is recommended due to the possibility of some poisonous H_2S gas emissions.

It is also possible to determine sulfur on the combined HCl and water leachate, $S_{HCl}\ \%$ (Method 20B) and by addition of $S_{TOS}\ \%$ (Method 20D) to calculate total sulfur ($S_T\ \%$) (Method 20A7).
The procedure has not been detailed here as it may differ from lab to lab due to instrument requirements.

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6. ACID NEUTRALISING CAPACITY METHODS

METHOD 19

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Introduction

At this stage the methods for acid neutralising capacity (ANC) are less developed for application in acid sulfate soils. As a result, the methodology, to some extent, has been left to the discretion of the laboratory.

The amount of acidity leached to the environment depends not only on the amount of acid generated but also on the acid neutralising capacity (ANC) of the soil and of the environment (Dent and Bowman, 1993). Coarse shell fragments in the soil may have little neutralising capacity due to its small surface area to volume ratio. Therefore, methods of measuring acidity and neutralising capacity in sediments must not involve the crushing of coarse shell material in the sample preparation. Consequently, a separate large, unground sample is necessary for credible ANC analysis. This is rarely practised by routine laboratories and such samples are hard to homogenise.

Methods that add acid very slowly, producing a titration curve, are more likely to correlate to field reactivity than those that add excess strong acid and back titrate. As slow titration curves are rarely produced commercially, the common ANC data supplied is usually an overestimate and may be of limited value.

Until further research is completed on the reactivity of shells and soil carbonates, ASSMACTC have not approved the use of acid sulfate soils risk analysis based solely on the calculation of Net Acid Generation Potential (NAGP). Whether ANC (adjusted to the same units) can be subtracted from the oxidisable sulfur result need to be considered on a site by site basis, taking into account fineness and distribution of shell or carbonate in the soil profile. Confirmatory pilot projects or kinetic studies may also be necessary to confirm the ANC calculations.

In general, risk analysis and management approaches based on adding neutralising agents should be based on calculations using the sulfur trail initially, with arguments for the reduction of management requirements based on soil and site characteristics. In developing the overall site management plan, the following factors are a legitimate basis for negotiating a reduction in the neutralising requirement calculated from the sulfur analysis only:

- Data on differences between the sulfur and acid trail (if shown by POCAS analysis)
- No risk indicated by the acid trail (TPA or TSA = 0)
- Significant ANC results (with data and comment on neutralising material's effectiveness)
- NAGP calculations or acid base accounting.

The acid neutralising capacity of the soil is usually expressed as $\%CaCO_3$ equivalent or kg $CaCO_3$/tonne soil. If bulk density is known this can be converted into kg $CaCO_3 / m^3$.

6.1 Carbonate rapid titration of $CaCO_3$ equivalent - Method 19A1

The ANC method *19A1* described in Rayment and Higginson (1992) is applicable, though dilute titrants may be required for soils with low carbonate concentrations. 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 HCI 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.

Reagents
1M Hydrochloric Acid

0.5M Sodium Hydroxide
Dissolve 20.0 g sodium hydroxide (NaOH pellets) in deionised water and make to 1.0 L
Standardise against potassium hydrogen phthalate ($KHC_8H_4O_4$) as described in Method 4D1 of Rayment and Higginson (1992). Special precautions to exclude carbon dioxide (CO_2) prior to standardisation are unnecessary.

Phenolphthalein Indicator 0.1%)
Dissolve 100 mg phenolphthalein ($C_{20}H_{16}O_4$) in 100 mL, ethanol (C_2H_5OH).

a. Procedure:

(i) Weigh 5.0 g dry soil (<2 mm) into a 250 mL wide-mouth plastic extracting bottle. Include two blanks (no soil) plus either a reference sample or 0.5 g $CaCO_3$ powder. Use 2.5 g air-dry soil (<2 mm) if the soil is known to contain >30% carbonate.

(ii) Add 100 mL 1 M HCI and swirl. Cover in a manner that permits release of any CO_2 and swirl occasionally for 1 h at 25°C. Allow to stand overnight, cap securely, then mechanically shake for 2 h. Let the suspension settle, then filter or centrifuge.

(iii) Take 10 mL supernatant into a 100 mL Erlenmeyer flask and add 25 mL deionised water. Add 2-3 drops phenolphthalein indicator and titrate with standard 0.5M NaOH.

(iv) Report $CaCO_3$ equivalent (%) on an oven-dry (85^0C) basis.

b. Calculation

$$\% \ CaCO_3 \text{ equivalent} = \frac{M \times (a - b) \times 50}{S}$$

where
a = mL standard 0.5M NaOH used for blank (mean of 2 blanks).
b = mL standard 0.5M NaOH used for sample.
S = weight (mg) of dry soil.
M = molarity of standard NaOH (usually 0.5M).
$50 = 50 \times 10^{-3} \times 10 \times 100\%$ (where $50 \approx$ equivalent wt of $CaCO_3$).

6.2

Carbonate content (inorganic carbon) - Method 19A2

This procedure was developed by Lewis and McConchie (1994) and modified by the use of weaker acid.

(i) Crush dried sample material to <300µm (remove large shells first) and weigh 1.0g into a 250 mL flask. Weigh out three sub-samples (the analysis should be carried out in triplicate).

(ii) Add 50 mL of analytical grade water and 25 mL of standardised 0.1M HCI to each flask.

(iii) Prepare a blank (water and acid only) and a pure 0.1 g calcium carbonate reference.

(iv) Boil all flasks for two minutes, cool to room temperature, and add a few drops of phenolphthalein indicator.

(v) Titrate the unused acid in the flasks with pre-standardised 0.1M sodium hydroxide solution (ie. colour change to pink or pH 9). The blank should require 25 mL of sodium hydroxide solution and the calcium carbonate reference, 0.1 g of pure calcite ($CaCO_3$) reacts with 20 mL of 0.1M HCI.

(vi) Determine the volume of acid used as:
25 mL - the volume of sodium hydroxide used.

(vii) Calculate the calcium carbonate equivalent of the sample as:

$$\%CaCO_3 \text{ equivalent} = \frac{0.5 \times \text{volume of acid used (mL)}}{\text{sample weight}}$$

Note: The $CaCO_3$ standard should give 100% $CaCO_3$ equivalent when calculated

Soil suspensions will probably need filtering through GFA to detect endpoint or preferably use a pH meter to detect pH change (ie. pH 7 titration). Negative results (recorded as 0% $CaCO_3$ equivalent) are not unusual with acid sulfhate soils due to the actual acidity of soils.

The reduced acid strength also allows an increased detection limit of 0.05% $CaCO_3$ equivalent but a maximum detection of 10% $CaCO_3$ equivalent with the 1g sample weight. In some circumstances the 1M acid/ hydroxide may be more suitable.

When using 1M HCI and NaOH use the following calculation:

$$\%CaCO_3 \text{ equivalent} = \frac{5 \times \text{volume of acid used (mL)}}{\text{sample (or standard) weight}}$$

6.3

Carbonates manometric method - Method 19B1

This method developed by GE Rayment and FR Higginson (1992) is a manometric procedure with the ability to give satisfactory results for both calcitic and dolomitic minerals (Martin and Reeve 1955, Skinner and Halstead 1958, Skinner *et al*. 1959). The approach performed well in slightly modified form in comparative tests of four methods for soil carbonates (McKeague and Sheldrick 1976).

This method is based on measurement of pressure change with time (constant temperature) in a closed system, as CO_2 is evolved following the reaction of carbonate with a solution of HCl-$FeCl_2$. The ferrous chloride ($FeCl_2$) is incorporated to prevent interference from reactions of manganese dioxide (MnO_2) with organic matter in the presence of HCl (Martin and Reeve 1955). Calcite (or limestone) can be estimated separately from dolomite because the reaction rate of the former is more rapid. For full method description refer to pages 207-209 Rayment and Higginson (1992).

6.4 Neutralising gravimetric loss of carbon dioxide (NG) - Method 19C1

(Under development)

6.5 Neutralising curve (titration) (NC) - Method 19D1

(Under development)
This approach is based on slow titration of a soil with mineral acid. The titration curve is used to estimate the neutralising capacity of the soil. This approach generally gives a lower neutralising value than the traditional adding of excess acid and back titrating the excess, unreacted acid with alkali. The titration curve approach better reflects the pH values found in field soils and hence the solubility of neutralising materials such as shells.

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7. MOISTURE CONTENT, BULK DENSITY, SPECIFIC GRAVITY, PORE SPACE RELATIONSHIPS

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Introduction

Mass-based measurements can be converted to volumetric measures for contractors (eg. m^3) by dividing by the bulk density. Additionally, a measure of moisture content is often required for calculations.

7.1 'As received' moisture content dried at 105^{0}C - Method 2B1

The 'as received' moisture content of soils dried at 105^{0}C can be easily calculated by the addition of two weighings to the drying procedure. A representative sub-sample is placed in a dish of known mass and weighed before and after drying. The sample dried at 105^{0}C is normally discarded and not used for further analysis

Procedure:

(i) Confirm the mass of each clean, dry weighing/drying container (W_1 g). Place the sub-sample 10-50 g 'as received' soil into the container and record mass (W_2 g). With lids removed, dry at 105°C to constant mass then quickly transfer to a dry desiccator (no desiccant) to cool.

(ii) When cool, replace relevant lids and re-weigh (W_3 g).

To calculate mass of water (W_4 g) = ($W_2 - W_3$)

$$\text{As received moisture content } (105^0\text{C}) \ (\%) = \frac{\text{Wt of water (g) x 100\%}}{\text{Wt of dry soil (g)}}$$

$$= \frac{W_4 \text{ x } 100\%}{(W_3 - W_1)}$$

(iii) Report as received moisture content (105^{0}C).

7.2 As received' moisture content dried at 85^{0}C - Method 2B2

If as received moisture content (85^{0}C) of the soils is required, take the entire sample and place in a large dish of known mass and proceed as Section 7.1 above, noting that the laboratory oven is set at 85°C instead of 105°C or use. The sample dried at 85^{0}C can be used for normal acid sulfate soils analysis. Alternatively, take a sub-sample and follow the same procedure.

7.3 Laboratory bulk density and gravimetric water content

The pore space relationship (PSR) of soil is a description of the volumetric proportions of a soil material. The determination of PSR requires the measurement of the bulk density, the gravimetric water content, and the specific gravity of the soil solids. The first two of these measurements are made together, the third can be approximated or measured using the material from the second measurement.

The determination of bulk density and gravimetric water content requires the measurements of the mass of water and the mass of oven-dried soil (105^{0}C) in a measured volume of the soil. Three

methods are possible. If sampling from a pit or in surface soil, stainless steel coring rings are suitable for determining the soil volume after trimming and then measure the water content.

Approximate bulk density: In very uniform sand or soil, a bulk excavation of a precisely measured volume of soil can be weighed and the gravimetric water content of a subsample measured after oven-drying at 105^0C. An approximate bulk density on soft moist samples may be achieved by sampling with a large bore plastic syringe (with a cut off end.) or other appropriate push sampler of known volume. The known volume of soil and sample container is weighed wet, oven dried at 105^OC to constant mass, (normally 48 hours) and re-weighed. Subtractions are made for container mass and the bulk density is calculated by:

bulk density (g/cm^3) = [oven-dry mass of sample] / volume of sample

Measurements of Pore Space Relationships (PSR) in very soft materials (eg. clay gels) or saturated material from below the watertable is often a problem. Such materials can be sampled without significant disruption of their PSR (eg. by compaction) from samples taken below the watertable in an auger hole using a Russian D-section corer of diameter > 100mm. The material from this corer can be wrapped in plastic film and transported to the laboratory in split PVC tubing. Large bulk blocks of soil can also be taken from below the watertable in a pit after pumping or bailing out the water and ensuring all necessary safety precautions against wall-collapse are met.

Assume that we have an irregular-shaped sample of soil or clay gel in the laboratory, say about 30 cm^3, with minimal compaction or water loss. About half the soil is used to determine the gravimetric water content by weighing before and after the drying at 105^0C. This oven-dried soil can be retained for measuring the specific gravity (see later). The bulk density is then measured on the other part of the original irregular-shaped block.

Procedure:

(i) Attach cotton thread to the block of soil and weigh the block.

(ii) Quickly dip the block in and out of molten paraffin wax held at a temperature just above its melting point. The sample must be completely sealed with the wax; any small holes left after dipping can be sealed with molten wax from a glass rod.

(iii) Re-weigh the waxed block to determine the mass of wax that has been added. The density of this wax should have been measured by applying Archimedes' Principle, noting that since its density (≈ 0.9 g/cm ^{3}) is less than that of water, it will tend to float. The mass and density give the volume of wax added (i.e. V = mass/density).

(iv) Half fill a 600 mL beaker with water and note total mass.

(v) Suspend the wax block in the water without allowing it to touch the sides or the base of the beaker. The apparent increase in mass (g) equals the volume of the waxed block (cm^3) (i.e. applying Archimedes' Principle).

(vi) The volume of the waxed block less the volume of the wax gives the volume (cm^3) of the part sample prior to its waxed coating.

(vii) The mass of oven dried soil in this part block is calculated from its original wet mass and the gravimetric water content measured on the other part of the original block.

oven-dry mass (g) in block = wet mass of block / [1+ gravimetric water content (g/g)]

The bulk density is calculated by:

bulk density (g / cm^3 or tonnes / m^3) = [oven-dry mass of block] / volume of block

7.4 Specific gravity of soil

The oven-dry soil after having been used for determining the gravimetric water content can be used to measure specific gravity of soil. If air-dry soil is used, its gravimetric water content must be known so as to determine the oven-dry mass of a measured air-dry mass.

Procedure:

(i) Add about 50 g of oven-dry soil to a clean, dry 250 mL beaker and determine its exact mass.

(ii) Add approximately 100mL of deionised water to the soil and boil the contents for several minutes until the soil is completely disrupted and any entrapped air is removed.

(iii) Weigh a clean, dry 250 mL volumetric flask. Choose one with a large neck opening to better enable filling with the soil slurry. Assume that the contained volume up to the mark is exactly 250 mL but this can be checked by weighing and using de-aired, deionised water.

(iv) Quantitatively add the cooled beaker contents to the 250 mL volumetric flask using a large orifice funnel and caution to allow air escape while pouring in the soil slurry.

(v) Wash all contents into the volumetric flask and make up volume with distilled water exactly to the mark. If froth obstructs this measurement add a couple of drops of butyl alcohol to the flask neck.

(vi) Weigh the flask and its contents. The volume of the soil equals the volume of water displaced by the soil, which equals the mass of water displaced by the soil.

$$\text{Volume of soil solids } (cm^3) = 250 + \text{mass of flask} + \text{oven-dry soil mass} - (\text{mass of flask} + \text{slurry})$$

(vii) Specific Gravity (g/cm^3) = oven dry soil mass / volume of soil solids

Note: The measured specific gravity will usually lie between 2.5 and 2.7 g/cm^3 and could be assumed equal to that of quartz (2.65 g/cm^3).

7.5 Calculation of Pore Space Relationship (PSR)

The measured values of gravimetric water content, the bulk density and the specific bulk density are used to calculate the PSR (volume proportions of solid, liquid and gas phases).

(i) % solid (by volume) = [bulk density/specific gravity] x 100

(ii) % water (by volume) = gravimetric water content (g/g) x bulk density x 100

(iii) % air = 100 - (i) - (ii)

8. ACID VOLATILE SULFUR

S_{AV} - METHOD 22A

Miscellaneous Research Methods

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Introduction

Acid volatile sulfur is far more reactive than pyrite (Bloomfield 1972) and its presence in acid sulfate soils has important implications for soil and land management (Bush and Sullivan, 1998). Additionally, acid volatile sulfur minerals such as greigite (Fe_3S_4), mackinawite ($FeS_{0.94}$) and amorphous sulfide (FeS) are important in the formation of pyrite (FeS_2)(Sweeney and Kaplan 1973; Rickard 1975; Schooner and Barnes 1991; Wang and Morse 1996) and the oxidation of acid sulfate soils (Bloomfield 1972; Evangelou 1995). The sulfur in these minerals is readily reduced to H_2S by hydrochloric acid and is referred to as 'acid volatile sulfur', whereas a stronger reducing reagent like acidified chromous chloride, (see Sullivan *et al*. Chapter 9 this book) is required to reduce pyrite (FeS_2) and elemental sulfur (S^o).

Most acid volatile sulfur methods are based on the decomposition of sulfur to H_2S by a HCl solution; the evolved H_2S is carried by a nitrogen gas flow into a trapping solution where it is precipitated as a metal sulfide. The metal sulfide in the trapping solution is quantified by iodometric titration, potentiometric titration, colorimetric spectrophotometry, or gravimetrically. Morse and Cornwell (1987) examined the selectivity of numerous acid volatile, sulfur distillation procedures for synthetic minerals and found cold 6N HCl best discriminated acid volatile sulfur from pyrite. They favoured this technique because stronger reducing procedures (eg. heating with HCl and/or the addition of catalysts) resulted in some pyrite reduction (ie. < 5 % total pyrite). Where high pyrite and low acid volatile sulfur concentrations occur, the contribution of sulfur from even a small fraction of pyrite could result in a significant over-estimation of acid volatile sulfur.

For Australian acid sulfate soil materials tested so far we have found cold 12N HCl extracts far more acid volatile sulfur than does 6N HCl and yet does not recover any pyrite sulfur. Therefore, we recommend distillation with cold 12N HCl. However, only 75% acid volatile sulfur is recovered with HCl, the difference remaining in the reaction vessel as elemental sulfur, formed by the oxidation of H_2S by ferric iron (III) liberated from the dissolution of iron oxides and greigite (Morse and Cornwell 1987). Therefore, acid volatile sulfur concentrations extracted using HCl need to be corrected for iron (III) interference.

Acid volatile sulfur requires special pre-cautions to ensure the preservation of these materials during sampling and sample preparation. Freezing samples immediately in the field with liquid nitrogen followed by freeze-drying can preserve acid volatile sulfur (Bush and Sullivan 1997). Oven drying procedures recommended for pyrite preservation (Ahern *et al.* 1996) enhance the oxidation of acid volatile sulfur minerals and should be avoided (Bush and Sullivan 1997). Our experience shows that normal sample grinding procedures can cause substantial loss of acid volatile sulfur (eg. up to 50 % losses) and therefore, only a gentle hand crush is recommended. An additional advantage of freeze-drying over other sample dehydration techniques is that freeze-dried sediments tend to shatter readily making freeze-dried samples easy to crush.

Alternatively, field analysis of wet samples or laboratory analysis of frozen samples thawed in a N_2 atmosphere can avoid the oxidation of sulfides during storage and drying. However, soil pore waters can contain considerable amounts of dissolved H_2S (eg. up to 10 mM H_2S (Rickard 1997)) which may erroneously contribute to the acid volatile sulfur mineral fraction when field wet samples are used. For this reason freeze-drying is recommended. Duplicate analyses using 5g of sample is recommended to minimise error due to heterogeneous acid volatile sulfur distribution.

Reagents

Ethanol (95 %) (wetting agent)

12N Hydrochloric acid (concentrated HCl)(digesting solution)

3% Zinc Acetate / 25% Ammonium Hydroxide (trapping solution)
Dissolve 60 g of zinc acetate in 1.5 L of deionised water. Add 200 mL of concentrated (28%) ammonium solution and make volume up to 2 L with deionised water.

Standard 0.025N 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 6M NaOH and make to volume with deionised water.

Starch Indicator
Dissolve 2g starch and 0.2g salicylic acid in 100 mL hot deionised water.

Iodine solution
Dissolve 22.500g of potassium iodide in water and add 3.2g iodine. After the iodine has dissolved, dilute to 1.0 L with deionised water and standardise against the standard 0.025M $Na_2S_2O_3$ solution using the starch solution as an indicator. Standardisations should be performed daily.

8.1 Procedure:

(i) Weigh 5g of sample into the digestion flask and add 10 ml of ethanol solution to wet the sample.

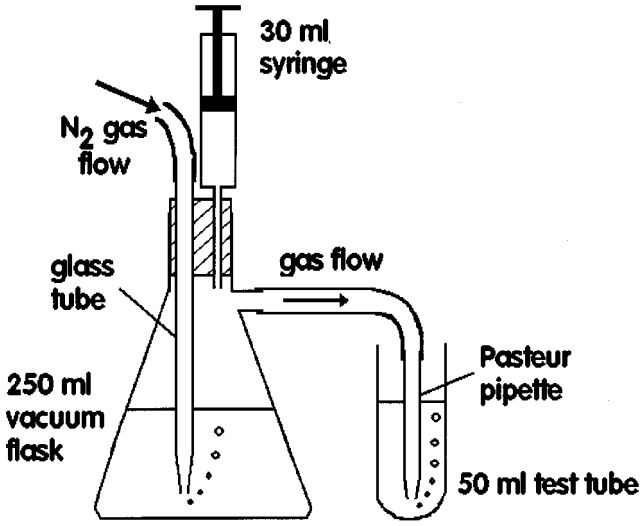
(ii) Attach the stopper to the flask, ensuring an airtight seal. Attach the pipette to the vacuum outlet. Put the pipette in a 40 mL test tube containing 30 mL of the zinc acetate/ammonium hydroxide trapping solution.

(iii) Draw 20 mL 12N HCl into the syringe and attach syringe to a prepared port in the stopper. Start the N_2 gas source and adjust gas flow rate 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 (around 3 minutes).

(iv) Inject the HCl solution from the syringe into the flask and carefully agitate the contents by swirling 2-3 times. Leave digesting for 1 hour, repeat agitation every 10 minutes.

(v) Remove the test tube and wash any ZnS on the pipette into the test tube. Transfer the solution for the test tube into a 100 mL Erlenmeyer flask and add 1 mL of the starch indicator solution. Add 20 mL of 6M HCl via a pipette and titrate the trapping solution using the standardised iodine solution to a permanent blue end-point

Figure 8.1 Schematic representation of the apparatus used for the determination of acid volatile sulphur



8.2 Calculation of the Acid Volatile Sulfur (S_{AV} %) content

The concentration of acid volatile sulfur (S_{AV}) % (w/w) is given by the following equation:

$$S_{AV}\ \% = \frac{(A - B) \times C \times 1600 \times 1.33(\text{correction for } Fe^{III})}{\text{Soil mass (mg)}}$$

Where:

A = The volume of iodine (mL) used during the titration of the zinc acetate trapping solution following soil digestion.

B = The volume of iodine (mL) used for the titration of the zinc acetate trapping solution following a blank digestion.

C = The molarity of the iodine solution as determined by the titration of this solution with the standard 0.025M Sodium Thiosulfate ($Na_2S_2O_3.5H_2O$) solution as below:

$$C = \frac{0.025 \times \text{titration volume of standard } Na_2S_2O_3.5H_2O \text{ solution (mL)}}{\text{Volume of iodine solution used for the titration (mL)}}$$

8.3

General comments

a) Detection limits

Using a micro-burette (ie. 0.01 mL graduations), and assuming typical C values of 0.025, the theoretical detection limit of method is around 0.001%S.

b) Correction factor for iron (III) interference

Only around 75 % of AVS is recovered when using pure HCl reactant (Morse and Cornwell 1987) because Fe (III) from the dissolution of iron oxides (Fe_2O_3) and from greigite oxidises H_2S to elemental sulfur, preventing it from being liberated. Stannous chloride has been used to eliminate iron (III) interference, however, such additions also cause the recovery (eg. 10 – 18 % (Morse and Cornwell 1987)) of pyrite sulfur. Therefore, to account for around 25% H_2S loss from iron (III) interference, acid volatile sulfur results obtained using 12 M HCl are corrected upward by a factor of 1.33.

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9. CHROMIUM REDUCIBLE SULFUR

S_{CR} - METHOD 22B

Miscellaneous Research Methods

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Introduction

The use of chromium reduction to measure reduced inorganic sulfur compounds in sediments was proposed by Zhabina and Volkov (1978). It 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 (e.g. 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 in acid sulfate soil 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 (e.g. greigite and mackinawite). The chromium reduction method can be made specific to the iron disulfide fraction if pre-treatments are used to remove the acid volatile sulfides and elemental sulfur fractions.

Reagents

Zinc Acetate solution
Dissolve 60 g of zinc acetate in 1.5 L of deionised H_2O. Add 200 mL of 28% ammonia solution and make up to 2 L with deionised H_2O.

Standard 0.025M 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 H_2O in a 1.0 L volumetric flask. Add 1.5 mL 6M NaOH and make to volume with deionised water.

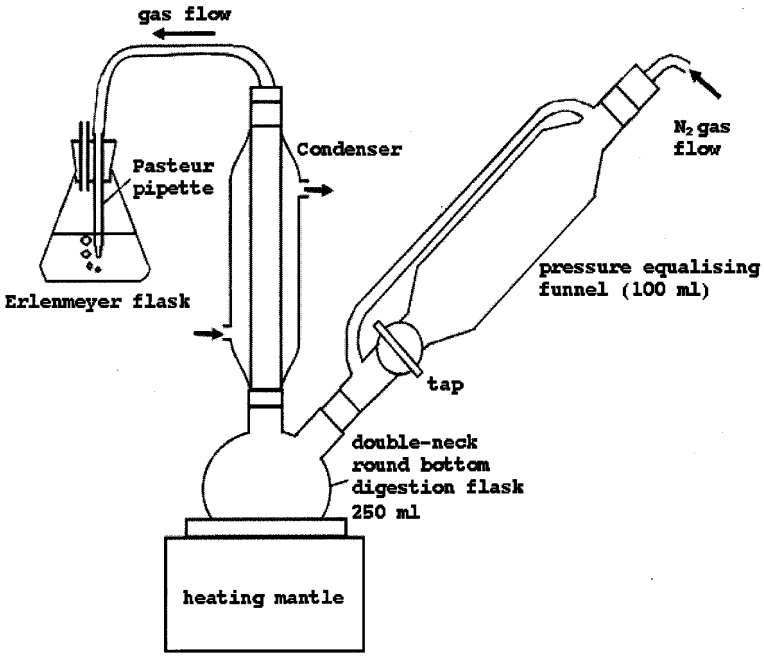
Starch solution
Dissolve 2 g starch and 0.2 g salicylic acid in 100 mL of hot deionised water.

Iodine solution
Dissolve 22.500 g of potassium iodide in water and add 3.2 g iodine. After the iodine has dissolved, dilute to 1 L with deionised H_2O and standardised against the standard 0.025M $Na_2S_2O_3$ solution using the starch solution as an indicator. Standardisations should be performed daily.

Chromium Reducible Sulfur is an alternative measure to Peroxide Oxidisable Sulfur (Method 21D) and, unlike Peroxide Oxidisable Sulfur, is not subject to significant interference from sulfur in either organic matter or sulfate minerals (e.g. gypsum). This is especially important for sediments with low concentrations of reduced inorganic sulfur compounds where an erroneous estimate of the reduced inorganic sulfur content may lead to the recommendation of costly and/or inappropriate and environmentally-damaging management practices.

Our experience with the chromium reduction method indicates that it is a quick, accurate and low-cost method for measuring reduced inorganic sulfur compounds in sediments and soils.

Figure 9.1 Schematic representation of the apparatus used in the chromium reduction method for determination of reduced inorganic sulphur



9.1 Procedure:

(i) Weigh 1 gram of sample into a double-neck round-bottom digestion flask. (See discussion below for suggested optimum sample weights). Add 2.059g of Chromium powder and then 10 mL ethanol (95% concentration) to digestion flask and swirl to wet sample. Place digestion flask in heating mantle and connect to lower condenser. Digestion apparatus should be set up in a fume cupboard.

(ii) Attach pressure equalising funnel making sure the gas flow arm is facing the condensers and the solution tap is shut. Attach pasteur pipette to top hose. Place 50 mL Erlenmeyer flask containing 40 mL zinc acetate solution into position and lower the pasteur pipette into this solution.

(iii) Turn on the water flow around the condensers. Make sure that all ground glass fittings are tight to avoid losses. Add 60 mL of 5.65M HCl to the glass dispenser. Connect the N_2 flow to the pressure equalising funnel and adjust gas flow rate 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 (around 3 minutes).

(iv) Slowly release the 5.65M HCl from the dispenser. (Note: the 5.65M HCl should be added to the sediment and chromium powder very slowly in a fume cupboard). Wait for 2 minutes before turning on the heating mantle and adjust the heat so that a gentle boil is achieved. Check for efficient reflux in the condensers. Allow to digest for 60 minutes.

(v) 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 5.65M HCl down the pipette into the solution. (N.B. Care should be exercised when using the 5.65M HCl). Add 1 mL of the starch indicator solution to the zinc acetate solution and gently mix on a magnetic stirrer. Titrate the zinc acetate trapping solution with the iodine solution to a permanent blue end-point.

9.2 Calculation of the Chromium Reducible Sulfur (S_{CR} %) content

The concentration of Chromium Reducible Sulfur (S_{CR}) in % is calculated as follows:

$$S_{CR}\ \% = \frac{(A - B) \times C \times 1600}{\text{mass soil (mg)}}$$

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 as determined by titration of this solution with the standard 0.025M $Na_2S_2O_3$ solution (see below).

$$C = \frac{0.025 \times \text{titration volume of standard } Na_2S_2O_3 \text{ solution (in mL)}}{\text{volume of iodine solution titrated (in mL)}}$$

9.3 Comments on the quantiry 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:

(i) 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 or (more likely) the need to use excessive amounts of iodine titrant.

(ii) if too little reduced inorganic sulfur is digested then only very small quantities (if any) 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 likely reduced inorganic sulfur contents can be assessed we have found the following guidelines useful for determining the optimum sediment weights to use.

Note:

- *For samples with likely reduced inorganic sulfur contents >1%, about 500 mg of dry powdered sample is recommended.*
- *For samples with likely reduced inorganic sulfur contents of <1% but > 0.5%, 1 g of dry powdered sample is recommended.*
- *For samples with likely reduced inorganic sulfur contents of < 0.5%, 3 g of dry powdered sample is recommended.*

A guide to the likely reduced inorganic sulfur contents can be gained by the total oxidisable sulfur method (**Method 20C**). (The total oxidisable sulfur is the difference between the total sulfur content (**Method 20A**) and the acid extractable sulfur content (**Method 20B**)). Of course, total oxidisable sulfur includes some organic sulfur as well as reduced inorganic sulfur. If the likely reduced inorganic sulfur content is not known then at least 1 g of dry powdered sample should be used to ensure adequate analytical precision. Although Canfield *et al*. (1986) recommended the use of 10% ammonium hydroxide in the zinc acetate solution, we have found that a 2.8% concentration of ammonium hydroxide in this solution produces clearer iodometric titration endpoints without compromising H_2S trapping efficiency.

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10. VOLUMETRIC PEROXIDE METHODS

To be developed

At the stage of printing this document, development and evaluation of some proposed volumetric methods and a volumetric variation of POCAS are incomplete.