

## **SECTION F: CODES**

### **1. CODES FOR ACID SULFATE SOIL ANALYTICAL METHODS**

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#### **1.1 INTRODUCTION**

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

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

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

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

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

### **ACIDITY METHODS**

- KCl pH ( $\text{pH}_{\text{KCl}}$ ) & Titratable Actual Acidity (TAA)
- Peroxide pH ( $\text{pH}_{\text{OX}}$ ), Titratable Peroxide Acidity (TPA) and Excess acid neutralising capacity ( $\text{ANC}_{\text{E}}$ ) after peroxide oxidation

#### ***Calculated parameter—from acidity measurements***

- Titratable Sulfidic Acidity (TSA)

### **SULFUR METHODS**

- Total Sulfur ( $\text{S}_{\text{T}}$ )
- Chromium Reducible Sulfur ( $\text{S}_{\text{CR}}$ )
- Acid Volatile Sulfur ( $\text{S}_{\text{AV}}$ )
- Acid Volatile Sulfur, diffusible ( $\text{S}_{\text{DAV}}$ )
- Disulfide Sulfur ( $\text{S}_{\text{D}}$ )
- Elemental Sulfur ( $\text{S}_{\text{E}}$ )
- Peroxide Sulfur ( $\text{S}_{\text{P}}$ )
- 1 M KCl Extractable Sulfur ( $\text{S}_{\text{KCl}}$ )
- 4 M HCl Extractable Sulfur ( $\text{S}_{\text{HCl}}$ )
- Peroxide Residual Acid-Soluble Sulfur ( $\text{S}_{\text{RAS}}$ )

#### ***Calculated parameters—from sulfur measurements***

- Total Oxidisable Sulfur ( $\text{S}_{\text{TOS}} = \text{S}_{\text{T}} - \text{S}_{\text{HCl}}$ )
- Peroxide Oxidisable Sulfur ( $\text{S}_{\text{POS}} = \text{S}_{\text{P}} - \text{S}_{\text{KCl}}$ )
- Net Acid-Soluble Sulfur ( $\text{S}_{\text{NAS}} = \text{S}_{\text{HCl}} - \text{S}_{\text{KCl}}$ )

### **COMBINED METHOD**

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

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

- ANC: Back Titration ( $\text{ANC}_{\text{BT}}$ )
- Carbon: Inorganic ( $\text{C}_{\text{IN}} = \text{C}_{\text{T}} - \text{C}_{\text{TO}}$ )

#### ***Calculated parameters—from alkali cation measurements***

- Ca – Additional released by SPOCAS method ( $\text{Ca}_{\text{A}}$ )
- Mg – Additional released by SPOCAS method ( $\text{Mg}_{\text{A}}$ )
- Ca – Net Acid Soluble by HCl ( $\text{Ca}_{\text{NAS}} = \text{Ca}_{\text{HCl}} - \text{Ca}_{\text{KCl}}$ )
- Mg – Net Acid Soluble by HCl ( $\text{Mg}_{\text{NAS}} = \text{Mg}_{\text{HCl}} - \text{Mg}_{\text{KCl}}$ )

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

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

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

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

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

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

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

**SUPPLEMENTARY FINISHING STEP CODES**

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

**Table F1.3. Supplementary finishing codes for SPOCAS (Method 23) and S<sub>HCl</sub> (Method 20B).**

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

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

**1.4 TOTAL SULFUR (S<sub>T</sub>) – METHOD CODE 20A****Table F1.4. Analytical method codes for total sulfur.**

<i>Method Code</i>	<i>Symbol &amp; Units</i>	<i>Analysis and description</i>
20A	S <sub>T</sub> (%)	Total Sulfur
a-20A	a-S <sub>T</sub> (mol H <sup>+</sup> /t)	Total Sulfur ( <i>expressed in acidity units</i> ) (assumes all S is sulfide)

**Table F1.5. Finishing codes for Method 20A—Total sulfur (S<sub>T</sub>).**

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

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

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

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

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

#### **SUPPLEMENTARY FINISHING STEP CODES FOR 4 M HCl EXTRACT**

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

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

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

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

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

## 1.6 ACID NEUTRALISING CAPACITY – METHOD CODE 19

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

Method Code	Symbol & units	Analysis and description
<b>Acid Neutralising Capacity (ANC)–Acid reacted &amp; back titration methods</b>		
19A1 <sup>#</sup>	ANC <sub>BT</sub> (%CaCO <sub>3</sub> )	<b>Acid Neutralising Capacity</b> (Back Titration after 1 M HCl treatment – <b>not recommended for ASS</b> )
19A2	ANC <sub>BT</sub> (%CaCO <sub>3</sub> )	<b>Acid Neutralising Capacity</b> (Back Titration after 0.1 M HCl treatment – Lewis and McConchie 1994) ( <i>expressed in equivalent %CaCO<sub>3</sub> units</i> )
a-19A2	a-ANC <sub>BT</sub> (mol H <sup>+</sup> /t)	(19A2 x 199.8) (ANC <sub>BT</sub> <i>in equivalent acid neutralising units</i> )
s-19A2	s-ANC <sub>BT</sub> (%S)	(19A2 / 3.121) (ANC <sub>BT</sub> <i>in equiv. % pyrite S it will neutralise</i> )
<b>Leco™ Carbon Methods</b>		
6B4	C <sub>T</sub> (%)	<b>Carbon: Total</b> (Leco™) (Method 6B4 from Revised Rayment <i>et al.</i> (In Press))
6B5	C <sub>TO</sub> (%)	<b>Carbon: Total Organic</b> (Leco™) (Method 6B5 from Revised Rayment <i>et al.</i> (In Press))
19C1	*C <sub>IN</sub> (%)	<b>Carbon: Inorganic</b> [Method 6B4 minus 6B5]
a-19C1	a-C <sub>IN</sub> (mol H <sup>+</sup> /t)	(19C1 x 1665) (C <sub>IN</sub> <i>calculated in equivalent acid neutralising units</i> )
s-19C1	s-C <sub>IN</sub> (%)	(19C1 x 2.67) (C <sub>IN</sub> <i>in equiv. % pyrite S it will neutralise</i> )
<b>Net acid soluble Ca and Mg</b>		
19F1	Ca <sub>NAS</sub> (%)	<b>Calcium: Net acid soluble</b> (Net Ca released by 4 M HCl) [Method 20E minus 23V]
a-19F1	a-Ca <sub>NAS</sub> (mol H <sup>+</sup> /t)	(19F1 x 499.0) (Ca <sub>NAS</sub> <i>calculated in equivalent acid neutralising units</i> )
19G1	Mg <sub>NAS</sub> (%)	<b>Magnesium: Net acid soluble</b> –(Net Mg released by 4 M HCl) [Method 20F minus 23S]
a-19G1	a-Mg <sub>NAS</sub> (mol H <sup>+</sup> /t)	(19G1 x 822.6) (Mg <sub>NAS</sub> <i>calculated in equivalent acid neutralising units</i> )

Table notes:

<sup>#</sup>similar to Rayment and Higginson (1992)\*C<sub>IN</sub> can also be expressed in ANC units of equivalent %CaCO<sub>3</sub> (ie. ANC<sub>C</sub>)

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

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

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

<b>Method Code</b>	<b>Symbol &amp; Units</b>	<b>Analysis and description</b>
<b>pH measurements</b>		
21A	pH <sub>KCl</sub>	pH of filtered 1:20 1 M KCl extract, overnight shake (TAA)
21Af	pH <sub>F</sub>	pH done in the field on saturated soil sample using pH probe
21B	pH <sub>OX</sub>	pH of filtered 1:20 1 M KCl after peroxide digestion
21Bf	pH <sub>FOX</sub>	pH measured in the field – 30% peroxide reaction, pH probe
<b>Sulfur methods</b>		
21C	S <sub>KCl</sub> (%)	KCl extractable S (additional codes added for S determination)
21D	S <sub>P</sub> (%)	Peroxide sulfur after peroxide digestion
21E	S <sub>POS</sub> (%)	Peroxide oxidisable S [21D minus 21C]
<b>Acidity methods</b>		
21F	TAA (mol H <sup>+</sup> /t)	Total Actual Acidity in 1 M KCl titrated to pH 5.5
21G	TPA (mol H <sup>+</sup> /t)	Total Potential Acidity in 1 M KCl peroxide digest titrated to pH 5.5
21H	TSA (mol H <sup>+</sup> /t)	Total Sulfidic Acidity [21G minus 21F]
21J	S <sub>TAA</sub> (%)	TAA <i>calculated as equivalent</i> pyrite S % for comparison and arithmetic purposes
21K	S <sub>TPA</sub> (%)	TPA <i>calculated as equivalent</i> pyrite S % for comparison purposes
21L	S <sub>TSA</sub> (%)	TSA <i>calculated as equivalent</i> pyrite S % for comparison with 21E using the same units
<b>Calcium values from POCASm to estimate additional Ca from acid-shell/carbonate reaction</b>		
21V	Ca <sub>KCl</sub> (%)	Ca extracted in 1 M KCl (TAA)
21W	Ca <sub>P</sub> (%)	Ca in peroxide digest (TPA)
21X	Ca <sub>A</sub> (%)	Ca reacted with acid generated by peroxide digest [21W minus 21V]
<b>Magnesium values from POCASm to estimate additional Mg from acid-shell/dolomite/carbonate reaction</b>		
21S	Mg <sub>KCl</sub> (%)	Mg extracted in 1 M KCl (TAA)
21T	Mg <sub>P</sub> (%)	Mg in peroxide digest (TPA)
21U	Mg <sub>A</sub> (%)	Mg reacted with acid generated by peroxide digest [21T minus 21S]
<b>Sodium values from POCASm</b>		
21M	Na <sub>KCl</sub> (%)	Na extracted in 1 M KCl (TAA)
21N	Na <sub>P</sub> (%)	Na in peroxide digest (TPA)
21P	Na <sub>A</sub> (%)	Na difference (21N minus 21M)
<b>Neutralising methods</b>		
21Q	NQ (% CaCO <sub>3</sub> )	Quick residual neutralising capacity
21R	NQ <sub>S</sub> (S <sub>R</sub> %)	Quick residual neutralising capacity 21Q, calculated as equivalent pyrite %S

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

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

## 1.8 MOISTURE CODES

**Table F1.9. Acid sulfate soil moisture codes.**

<i>Method Code</i>	<i>Symbol &amp; units</i>	<i>Analysis and description</i>
<i>Moisture content methods from Rayment and Higginson (1992)</i>		
2B1	W <sub>105</sub> (%)	As received moisture content 105 °C
<i>Methods to be added to Rayment et al. (In Press)</i>		
2B2	W <sub>85</sub> (%)	As received moisture content 85 °C

## 1.9 ACID SULFATE SOIL LIMING CONVERSIONS

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

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

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

Notes on Table F1.10

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

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

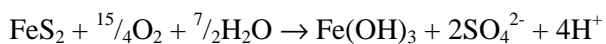
\*Assumes a bulk density of 1.0 g/cm<sup>3</sup> or 1 t/m<sup>3</sup> (the bulk density range can be 0.7–2.0 and as low as 0.2 for peats). Where bulk density is >1 g/cm<sup>3</sup> then the factor will increase for lime rates/m<sup>3</sup> soil (eg. if BD = 1.6, then 1 m<sup>3</sup> of soil with 1.0%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

\*\*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<sub>3</sub>) with a neutralising value of 100. Where the neutralising value is less than 100, the factor

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

### 1.10 EXPLANATION OF CALCULATIONS AND EXAMPLES

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



1 mole pyrite (FeS<sub>2</sub>) → 4 moles acid (H<sup>+</sup>)

1 mole sulfur (S) → 2 moles acid (H<sup>+</sup>)

Examples:

#### A) Converting %S to mol H<sup>+</sup>/t

A soil has a S<sub>CR</sub> value of 1.23 %S, which in other words is 1.23 g sulfur (as pyrite) per 100 g of oven dry soil.

The first step is to convert grams of sulfur to moles of sulfur. The molar mass of sulfur (ie. the weight of 1 mole of sulfur) is 32.066 g/mol.

$$1.23 \text{ \%S (or g S/100 g soil)} \div 32.066 = 3.836 \times 10^{-2} \text{ mol S/100 g soil}$$

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

$$3.836 \times 10^{-2} \text{ mol S/100 g soil} \times 2 = 7.672 \times 10^{-2} \text{ mol H}^+/\text{100 g soil}$$

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

$$7.672 \times 10^{-2} \text{ mol H}^+/\text{100 g soil} \times 10\,000 = 767 \text{ mol H}^+/\text{t.}$$

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

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

#### B) Calculating net acidity from laboratory results

Calculate the Net Acidity (in units of equivalent % pyrite S) for a soil (analysed by the SPOCAS suite) which has a pH<sub>KCl</sub> of 3.3, a TAA of 73 mol H<sup>+</sup>/t, an S<sub>POS</sub> of 0.13 %S and an S<sub>RAS</sub> of 0.45 %S.

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

We have an estimate of the potential acidity already in the correct units: S<sub>POS</sub> = 0.13 %S

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

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

$\therefore$  Net Acidity =  $0.13 + 0.12 + 0.34 = 0.59 \%S$

### C) Calculating net acidity and lime requirement from laboratory results

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

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

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

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

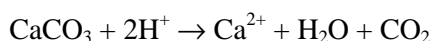
Now we must decide which units we want to use for the ABA. In this case, we will use units of mol  $\text{H}^+$ /t. The chromium reducible sulfur result ( $S_{\text{CR}}$ ) is in units of %S, which needs to be converted to a- $S_{\text{CR}}$  (in units of mol  $\text{H}^+$ /t). The TAA is already in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

Potential Sulfidic Acidity:  $a\text{-}S_{\text{CR}} = S_{\text{CR}} \times 623.7 = 2.2 \times 623.7 = 1372 \text{ mol H}^+$ /t

Actual Acidity : TAA = 26 mol  $\text{H}^+$ /t

Net Acidity: Potential Sulfidic Acidity + Actual Acidity =  $1372 + 26 = 1398 \text{ mol H}^+$ /t

**Step 2:** We now want to work out the weight of pure  $\text{CaCO}_3$  needed to neutralise this Net Acidity. We use the stoichiometry of the reaction showing the acid dissolution of  $\text{CaCO}_3$  which shows that each mole of  $\text{CaCO}_3$  neutralises 2 moles of  $\text{H}^+$ .



Hence 1398 mol  $\text{H}^+$ /t is neutralised by  $1398 \div 2 = 699 \text{ mol CaCO}_3$ /t

To convert to g  $\text{CaCO}_3$ /t, multiply by molar mass of  $\text{CaCO}_3$  (100.087 g/mol), then divide by 1000 to get to kg  $\text{CaCO}_3$ /t.

$699 \text{ mol CaCO}_3$ /t  $\times 100.087 \div 1000 = 69.97 \text{ kg CaCO}_3$ /t.

Hence, to convert **from mol  $\text{H}^+$ /t to kg  $\text{CaCO}_3$ /t**:  $\text{mol H}^+$ /t  $\div 2 \times 100.087 \div 1000$ , or **divide by 19.98**

**Step 3:** We now need to consider the neutralising value of the Ag Lime and the application of a suitable safety factor. The neutralising value of pure  $\text{CaCO}_3$  is 100 and that of the Ag Lime is 96, hence to convert from kg  $\text{CaCO}_3$ /t to kg Ag Lime/t we need to multiply by (100/96).

$69.97 \text{ kg CaCO}_3$ /t  $\times (100/96) = 72.88 \text{ kg Ag Lime}$ /t

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

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

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

109.3 kg Ag Lime/t x 1.3 t/m<sup>3</sup> = 142.1 kg Ag Lime/m<sup>3</sup>

**So for 5 m<sup>3</sup> we need a total of 710.6 kg of Ag Lime.**

#### **D) Calculating net acidity from verification testing results**

(i) Some acid sulfate soil has been treated with agricultural lime (using the 1.5 safety factor). Samples have been collected for verification testing (ie. to ensure the appropriate amount of lime has been used and that there will be no net acidity) using the SPOCAS suite of analysis and the following results were obtained:

pH<sub>KCl</sub> = 8.6                      pH<sub>OX</sub> = 7.5

S<sub>POS</sub> = 0.67 %S

ANC<sub>E</sub> = 5.51 %CaCO<sub>3</sub>

(TAA and S<sub>RAS</sub> did not need to be determined as pH<sub>KCl</sub> >6.5 and there was no jarosite found in the initial investigation).

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

Potential Sulfidic Acidity: S<sub>POS</sub> = 0.67 %S

Acid Neutralising Capacity: s-ANC<sub>E</sub> = ANC<sub>E</sub>/3.121 = 5.51/3.121 = 1.77 %S

We can now calculate net acidity using the following equation (as outlined in Table A3.5):

Net Acidity = Potential Sulfidic Acidity – measured ANC/FF

$$= S_{POS} - [(S_{POS} + s-ANC_E^1) / 1.5]$$

$$= 0.67 - [(0.67 + 1.77) / 1.5]$$

$$= 0.67 - 1.63$$

$$= -0.96 \%S$$

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

(ii) Some acid sulfate soil has been treated with agricultural lime (using the 1.5 safety factor). The soils had not oxidised before treatment (ie. no jarosite was present in the soil). Samples have been collected for verification testing (ie. to ensure the appropriate amount of lime has been used and that there will be no net acidity) using the Chromium suite of analysis and the following results were obtained:

pH<sub>KCl</sub> = 8.5

S<sub>CR</sub> = 0.41 %S

ANC<sub>BT</sub> = 4.19 %CaCO<sub>3</sub>

(TAA and S<sub>RAS</sub> did not need to be determined as pH<sub>KCl</sub> >6.5 and there was no jarosite found in the initial investigation).

<sup>1</sup> In the SPOCAS suite, the acid neutralising capacity result to be substituted into the ABA equation is comprised of both the excess acid neutralising capacity, plus the ANC that was already spent in neutralising the acid released by the peroxide oxidation of sulfides (which is equivalent to S<sub>POS</sub>; hence ANC = (S<sub>POS</sub> + ANC<sub>E</sub>)/1.5).

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

Potential Sulfidic Acidity: S<sub>CR</sub> = 0.41 %S

Acid Neutralising Capacity: s-ANC<sub>BT</sub> = ANC<sub>BT</sub>/3.121 = 4.19/3.121 = 1.34 %S

We can now calculate net acidity using the following equation (as outlined in Table A3.6):

$$\begin{aligned} \text{Net Acidity} &= \text{Potential Sulfidic Acidity} - \text{measured ANC/FF} \\ &= S_{\text{CR}} - (s\text{-ANC}_{\text{BT}}/1.5) \\ &= 0.41 - (1.34/1.5) \\ &= 0.67 - 0.89 \\ &= -0.22 \%S \end{aligned}$$

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

### References

- Lewis DW, McConchie D (1994) 'Analytical Sedimentology'. (Chapman and Hall: New York)
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- Vogel AI (1978) 'Vogel's Textbook of Quantitative Inorganic Analysis.' 4<sup>th</sup> Edn. (Longman: London)

***SECTION G: MISCELLANEOUS RESEARCH METHODS***

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

## **SECTION H: FIELD TESTS**

### **1. ACID SULFATE SOIL FIELD pH TESTS**

*KM Watling, CR Ahern and KM Hey*

#### **1.1 INTRODUCTION**

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

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

#### **1.2 FIELD pH TEST ( $\text{pH}_F$ )**

The procedure for the field pH test ( $\text{pH}_F$ ) is outlined below:

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

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

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

### 1.3 *FIELD PH PEROXIDE TEST ( $\text{pH}_{\text{FOX}}$ )*

It is recommended that 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) be used in the  $\text{pH}_{\text{FOX}}$  test. 30%  $\text{H}_2\text{O}_2$  is highly corrosive and care should be taken when handling and using the peroxide. Safety glasses and gloves should be worn when handling and using peroxide. All chemical bottles should be clearly labelled and Material Safety Data Sheets (MSDS) should be kept with the chemicals at all times. Appropriate health and safety precautions should be adhered to. Peroxide should be kept in the fridge when not in use.

The procedure for the field pH peroxide test ( $\text{pH}_{\text{FOX}}$ ) is outlined below:

- ❑ **Adjust the pH of the hydrogen peroxide to pH 4.5–5.5 before going into the field.** This can be done by adding a few drops of dilute NaOH stirring and checking the pH with the electrode regularly until the correct range is reached. NaOH is highly caustic so safety precautions must be exercised. NaOH can raise the pH quickly or slowly, so the pH needs to be monitored. Recheck the pH after allowing the peroxide to stand for 15 minutes. Do NOT buffer a large quantity of hydrogen peroxide at one time. Only buffer the amount to be used in the field for about a month. This must be kept in a fridge, well labelled with only small quantities to be taken into the field at one time. This will ensure the longevity of the peroxide. Further, over time, the pH of the peroxide that has already been buffered may change. It is important to check the pH of the peroxide in the morning before departing to the field. Having a small quantity of NaOH in the field kit is recommended so the peroxide can be buffered if required.
- ❑ **Calibrate battery powered field pH meter** according to manufacturer's instructions.
- ❑ **Prepare the test tubes in the test tube rack as for  $\text{pH}_F$  test.** Make sure the rack is marked with the depths so there is not confusion about the top and bottom of the profile. Use of separate racks for the  $\text{pH}_F$  and  $\text{pH}_{\text{FOX}}$  tests is recommended as contamination may occur when the  $\text{pH}_{\text{FOX}}$  reactions are violent. It is important to use **heat-resistant test tubes** for the  $\text{pH}_{\text{FOX}}$  test as the reaction can generate considerable heat (up to  $90^\circ\text{C}$ ). It is recommended that a tall, wide tube be used for this test as considerable bubbling may occur, particularly on highly sulfidic or organic samples.
- ❑ **Conduct  $\text{pH}_{\text{FOX}}$  tests at intervals on the soil profile of 0.25 m or at least one per horizon** whichever is lesser.
- ❑ **From the teaspoon of soil previously collected for the  $\text{pH}_F$  test, place approximately ½ teaspoon of the soil into the  $\text{pH}_{\text{FOX}}$  test tube** for the corresponding depth test. It is important that these two sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
- ❑ **Add a few millilitres of 30%  $\text{H}_2\text{O}_2$  (adjusted to pH 4.5–5.5) to the soil** (sufficient to cover the soil with peroxide) **and stir the mixture.** Do NOT add the peroxide to the test tube in which the  $\text{pH}_F$  test was conducted, that is, the  $\text{pH}_{\text{FOX}}$  test tube should not have any deionised water in it. Beakers can be used, however glass is usually easily broken when conducting field work, and when multiple tests are being conducted it is difficult to handle large beaker

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

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

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

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

**Table H1.1. Soil reaction rating scale for the pH<sub>FOX</sub> test.**

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

#### ***1.4 INTERPRETATION OF FIELD pH TESTS***

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

- Ahern CR, Ahern MR, Powell B (1998). 'Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998'. pp. 28–30 (Queensland Department of Natural Resources: Brisbane)
- Ahern CR, Stone Y, Blunden B (1998). Acid Sulfate Soils Assessment Guidelines. In 'Acid Sulfate Soils Manual 1998'. pp. 56–58 (Acid Sulfate Soil Management Advisory Committee: Wollongbar, NSW)
- Hey KM, Ahern CR, Watling KM (2000) Using Chemical Field Tests to Identify Acid Sulfate Soils Likelihood. In 'Acid Sulfate Soils: Environmental Issues, Assessment and Management, Technical Papers.' (Eds CR Ahern, KM Hey, KM Watling, VJ Eldershaw) pp. 16/9–16/12 (Queensland Department of Natural Resources: Brisbane)
- Hey KM (Ed) (2002). 'Field Testing, Sampling and Safety for Acid Sulfate Soils'. pp. 12–16 (Queensland Department of Natural Resources and Mines: Brisbane)

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

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

The procedure for the fizz test is outlined below:

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

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

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

### References

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

**SECTION I: APPENDIX**

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

Table II.1. Suggested Chromium suite report format.

Field morphology summary						Laboratory Results										
Borehole No/ID	Soil Texture	Field pH			Sample depth (m)	Lab No/ID	pH <sub>KCl</sub>	S <sub>OR</sub>	TAA	S <sub>HCl</sub>	S <sub>KCl</sub>	S <sub>NAS</sub>	ANC <sub>BT</sub>	C <sub>T</sub>	C <sub>To</sub>	C <sub>N</sub>
		Depth	pH <sub>F</sub>	pH <sub>Fox</sub>												
		(m)					%S	mol H <sup>+</sup> /t		%S	%CaCO <sub>3</sub>	%C				
						23A	22B	23F	20B	23C	20J	19A2	6B4	6B5	19C1	



## 2. GLOSSARY

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

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

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

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

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

**ANC<sub>BT</sub>:** Acid neutralising capacity by back titration. Acid neutralising capacity measured by acid digest followed by back titration of the acid that has not been consumed.

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

**Ca<sub>A</sub>:** Reacted calcium. The calcium soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. (Ca<sub>P</sub> – Ca<sub>KCl</sub>). It can be used (in combination with Mg<sub>A</sub>) to provide an estimate of the soil carbonate content, but may be an underestimate if the HCl-titration to pH 4 has not been performed as part of the TPA/ANC<sub>E</sub> procedure.

**Ca<sub>HCl</sub>:** Calcium soluble in 4 M HCl, which includes soluble and exchangeable calcium as well as calcium found in certain carbonate minerals (eg. dolomite, calcite, aragonite).

**Ca<sub>KCl</sub>:** Potassium chloride extractable calcium measured following the TAA analysis, which includes soluble and exchangeable calcium as well as calcium from gypsum.

**Ca<sub>NAS</sub>:** Net acid soluble calcium. The calcium soluble in 4 M HCl that is not soluble in 1 M KCl. (Ca<sub>HCl</sub> – Ca<sub>KCl</sub>). It can be used (in combination with Mg<sub>NAS</sub>) to provide an estimate of the soil carbonate content, but may be an overestimate if calcium is dissolved from non-carbonate or non-acid-neutralising minerals.

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

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

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

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

**$C_{\text{T}}$ :** Total carbon. A measure of the total carbon content of the soil, encompassing both organic and inorganic forms.

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

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

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

**$\text{Mg}_{\text{A}}$ :** Reacted magnesium. The magnesium soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. ( $\text{Mg}_{\text{P}} - \text{Mg}_{\text{KCl}}$ ). It can be used (in combination with  $\text{Ca}_{\text{A}}$ ) to provide an estimate of the soil carbonate content, but may be an underestimate if the HCl-titration to pH 4 has not been performed as part of the TPA/ $\text{ANC}_{\text{E}}$  procedure.

**$\text{Mg}_{\text{HCl}}$ :** Magnesium soluble in 4 M HCl, which includes soluble and exchangeable magnesium as well as magnesium found in certain carbonate minerals (eg. dolomite, magnesite).

**$\text{Mg}_{\text{KCl}}$ :** Potassium chloride extractable magnesium measured following the TAA analysis, which includes soluble and exchangeable magnesium.

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

**$\text{Mg}_{\text{P}}$ :** Peroxide magnesium. Magnesium measured following the TPA analysis, which includes soluble and exchangeable magnesium, as well as magnesium (eg. from carbonates) dissolved as a result of acid produced due to oxidation of sulfides by peroxide.

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

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

**pH<sub>F</sub>:** Field pH. Field determination of pH in a soil:water paste.

**pH<sub>FOX</sub>:** Field peroxide pH. Field determination of pH in a soil:water mixture following reaction with hydrogen peroxide.

**pH<sub>KCl</sub>:** Potassium chloride pH. pH in a 1:40 (W/V) suspension of soil in a solution of 1 M potassium chloride measured prior to TAA titration.

**pH<sub>OX</sub>:** Peroxide oxidised pH. pH in a suspension of soil in a solution after hydrogen peroxide digestion in the SPOCAS method.

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

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

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

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

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

**S<sub>HCl</sub>:** Sulfur soluble in 4 M HCl which includes soluble and adsorbed sulfate, sulfate from gypsum, as well as sulfate from hydroxy-sulfate minerals such as jarosite and natrojarosite.

**S<sub>KCl</sub>:** Potassium chloride extractable sulfur measured following the TAA analysis, which includes soluble and adsorbed sulfate as well as sulfate from gypsum.

**S<sub>NAS</sub>:** Net acid soluble sulfur. (S<sub>HCl</sub> – S<sub>KCl</sub>). The sulfur soluble in 4 M HCl that is not soluble in 1 M KCl. It provides an estimate of the sulfate contained in jarosite and similar low solubility hydroxy-sulfate minerals (and can be used to estimate retained acidity).

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

**S<sub>POS</sub>:** Peroxide oxidisable sulfur from the SPOCAS method. The sulfur soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. (S<sub>P</sub> – S<sub>KCl</sub>). It provides an estimate of the soil sulfide content, but is affected by the presence of organic sulfur.

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

**S<sub>T</sub>:** Total sulfur. A measure of the total sulfur content of the soil, encompassing both organic and inorganic forms.

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

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

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

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

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

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

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