Quantification of elemental sulfur in acid sulfate soils and sediments

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INTRODUCTION

Elemental sulfur (S^0) is an important part of the global sulfur cycle and potentially has important implications for our understanding of sulfide formation and oxidation processes in acid sulfate soil (ASS) environments. Elemental sulfur typically forms during the incomplete oxidation of pore water sulfide by oxygen, other oxidising species (*e.g.* Fe^{3+}, Mn^{4+}), or both (Morse *et al.*, 1987; Aller and Rude, 1988). Elemental sulfur is also a known product of iron monosulfide oxidation (Burton *et al.*, 2009), and may form during the initial stages of pyrite oxidation (White and Melville, 1993). While elemental sulfur is generally a minor component of the reduced inorganic sulfur fraction in ASS materials, it has been found at appreciable proportions in monosulfidic black oozes (MBOs) (e.g. Burton *et al.*, 2006a; 2006b; Ward *et al.*, 2010; Sullivan *et al.*, 2018a).

A number of organic solvents (including acetone, chloroform, toluene and methanol) have been used over the past decade to extract elemental sulfur from sulfidic soil materials (e.g. Burton *et al.*, 2006b; 2007; 2011; Johnston *et al.*, 2014). The extracted elemental sulfur has then been measured using a number of analytical techniques including chromium reduction (e.g. Burton *et al.*, 2006a; 2006b), colorimetric determination after cold cyanolysis (e.g. Burton *et al.*, 2007; MDBA, 2010; Ward *et al.*, 2010) and high-performance liquid chromatography (HPLC) (e.g. Burton *et al.*, 2011; Johnston *et al.*, 2014). The extraction of elemental sulfur by either toluene or methanol, followed by HPLC analysis, is now the most frequently used method to determine the concentration of elemental sulfur in ASS materials. Cold cyanolysis is not recommended for routine use as the cyanide used in this procedure is highly toxic.

The elemental sulfur method outlined below is designed as part of a sequential extraction procedure (i.e. acid volatile sulfur – S_{AV}, elemental sulfur – S_E, disulfide sulfur – S_D). Elemental sulfur is extracted from the soil material after initial S_{AV} determination (NLM-6.1 or NLM-6.2; Sullivan *et al.*, 2018b). However, if elemental sulfur is the only fraction required, care must be taken to prevent any dissolved sulfide or iron monosulfide oxidation; oxidation of these components may increase the elemental sulfur concentration. The soil moisture content also needs to be measured alongside this procedure (NLM-1.1; Sullivan *et al.*, 2018b).

The following method uses methanol as a solvent to extract elemental sulfur from the soil material. Toluene can be used instead of methanol, however, toluene is slightly more toxic and considerably more expensive.

REAGENTS

Methanol, Toluene, Acetone and Ethanol are all hazardous and highly flammable. Methanol is also toxic. Refer to Safety Data Sheets.

Methanol

Toluene

Elemental sulfur standard (500 ppm): *Dissolve 0.5 g of sublimed sulfur in 700 mL of toluene. Make up to 1 L with toluene and store in a Schott bottle.*

Acetone

Ethanol

APPARATUS

50 mL centrifuge tubes, vortex mixer, sample rack, orbital shaker, 2 mL syringes (without rubber gaskets), 0.22 µm hydrophobic syringe filters, capped glass vials (e.g. PTFE/silicone caps), HPLC, 1 L Schott bottle, and 100 mL volumetric flasks. Analytical balance (500 g ± 0.01 g) also required if not part of a sequential extraction procedure.

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PROCEDURE

The procedure outlined below is designed to be used as part of a sequential extraction procedure. The elemental sulfur concentration is determined after S_{AV} (NLM-6.1 or NLM-6.2; Sullivan *et al.*, 2018b) and is followed by disulfide analysis (NLM-2.1; Sullivan *et al*, 2018b). The sample preparation steps required following S_{AV}, and prior to S_{CR} analysis, are given below.

a) *Preparation of sample following acid volatile sulfide analysis*

- Fill centrifuge tube containing sample to 50 mL mark with deionised water, and mix using a vortex mixer for a few seconds.
- Centrifuge samples for 10 min at 4000 rpm, and decant the deionised water.
- Freeze sample if not immediately proceeding to the next step.

b) *Extraction of elemental sulfur*

- Add 20 mL of methanol to each sample. If samples were frozen, allow the samples to defrost before adding methanol.
- Place samples in a sample rack and cover with cling wrap.
- Place the centrifuge tubes on their side on an orbital shaker for 16 h at 150 rpm.
- Centrifuge samples for 10 min at 4000 rpm.
- Filter approximately 1.5 mL of sample into glass vials suitable for HPLC analysis using a 2 mL syringe, without a rubber gasket, through a 0.22 µm hydrophobic syringe filter.
- Cap immediately to prevent any volatilisation. As a precaution store all samples in a refrigerator to prevent losses due to volatilisation.
- Carefully decant the remaining methanol into a suitable waste container.

c) *Analysis of elemental sulfur by HPLC*

- Using the elemental sulfur standard (500 ppm) make up an appropriate range of standards in a 100 mL volumetric flask (e.g. 0, 5, 10, 25, 50, 100 and 250 ppm). Make standards up to volume with methanol.
- Analyse the standards and samples using HPLC. An example of the HPLC system requirements (for a Dionex UltiMate 3000 system) includes: mobile phase = 95% methanol; column = reverse-phase C18; flow rate = 2 mL per min; column temp. = 40 °C; UV detection at 254 nm (Johnston *et al.*, 2014).

d) *Preparation for disulfide analysis*

To prepare the samples for disulfide analysis, all samples must be washed a total of four times to remove any remaining elemental sulfur.

- Add 40 mL acetone to each sample and mix using a vortex mixer for a few seconds.
- Place samples in a sample rack and cover with cling wrap.
- Place the centrifuge tubes on their side on an orbital shaker for 10 min at 150 rpm.
- Centrifuge samples for 10 min at 4000 rpm.
- Carefully decant the remaining solvent into a suitable waste container.
- Repeat this process for a total of three times, and then repeat with 40 mL of ethanol.
- The samples are now ready to be analysed using the chromium reducible sulfur method (S_{CR} – NLM-2.1; Sullivan *et al.*, 2018b).
- Freeze samples if not immediately proceeding with analysis.

CALCULATIONS

The concentration of elemental sulfur (S_E) in % S is calculated as follows:

$$S_E\,(\%) = \frac{(A \text{ x } 20) / m}{10\,000}$$

Where:

A = The elemental sulfur concentration (in **mg/L**)
m = The oven dried mass of soil (in **g**)

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