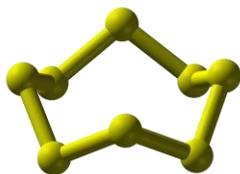


## Analysis of Sulphur, Elemental and Otherwise - A review of testing options

## TECHNICAL BULLETIN

Sulphur is ubiquitous in the environment, abundantly present in the earth's crust at 0.1%. Because of its presence in fossil fuels and in metal sulphide deposits, impact from various forms of sulphur has increased over time. Sulphur is a multivalent non-metal and may be frequently available in elemental form. Sulphur is often associated with the rotten egg smell, which is due to the hydrogen sulfide ( $\text{H}_2\text{S}$ ) form. In its elemental form, it is a tasteless and odorless, brittle yellow solid that is easily oxidized or reduced, depending on the environment.

Sulphur is present in soils in various forms, from sulphate ( $\text{SO}_4^{2-}$ ) and sulphite ( $\text{SO}_3^{2-}$ ) to sulfide ( $\text{S}^{2-}$ ) and elemental sulphur, predominately  $\text{S}_8$  and to a lesser extent  $\text{S}_6$ . Although in soils the majority of sulphur is in organic form (i.e. bound to nitrogen, oxygen or carbon), the predominant form of inorganic sulphur is sulphate ( $\text{SO}_4^{2-}$ )<sup>1</sup>. In surface and groundwaters, dissolved sulphur is primarily in sulphate form ( $\text{SO}_4^{2-}$ )<sup>1</sup>.



Elemental sulphur ( $\text{S}_8$ ) is present in soil due to natural (i.e. tidal swamps, poorly drained waterlogged soils and organic horizons) and anthropogenic (i.e. sour gas processing, pulp and paper, fertilizers and polymers) sources.  $\text{S}_8$  is insoluble in water and poorly soluble in organic solvents.

The purpose of this Technical Bulletin is to provide a review of available analytical testing options, the differences and applicability of each depending on chemical species required.

### ***Elemental Sulphur ( $\text{S}_8$ ) - Colorimetric method of analysis***

This is the standard method of measuring  $\text{S}_8$  in soil, sediment, solids and vegetation samples. Sulphur is extracted from pre-weighed soil samples using ACS grade acetone. The sulphur contained in the extract reacts with sodium cyanide to produce thiocyanate. When mixed with ferric chloride, the thiocyanate displaces the chloride ion and forms a red complex (ferric thiocyanate). The absorbance of the complex is measured with a spectrophotometer at a wavelength of 465 nm.

Although economically accessible and a relatively easy method of analysis, this test is prone to interferences of the colored complex from the presence of naturally occurring organic materials in soils. If dealing with soil that is high in organic content, a more specific method for  $\text{S}_8$  analysis should be used. The Reporting Detection Limit (RDL) for this method is 300 mg/kg, therefore making this method unsuitable for baseline monitoring.

<sup>1</sup> Brown, K. A.. **Sulphur in the Environment: A Review**. *Environmental Pollution (Series B)*. 3 (1982). 47-80.

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Matrix	Container	Amount	Hold Time	Preservation
Wet / As Received Soil	Various sized bags or jars	125 mL	30 days as received	Store at 4 ± 2°C
Dried and Ground Soil	Bags	10 grams		Store at ambient temperature
Soil Extracts	50mL centrifuge tubes	10mL	7 days	Store at ambient temperature

## **Elemental Sulphur (S<sub>8</sub>) - HPLC method of analysis (elemental Sulphur)**

Maxxam was contracted by Alberta Environment and Parks to develop a High Performance Liquid Chromatography (HPLC) analytical method for quantitation of elemental sulphur in soils. This method is superior to the standard colorimetric method described above, implementing newer technology, eliminates the risk of interferences from organic material and provides a significantly lower RDL at 10 mg/kg.

In this method, after drying and grinding to < 2 mm, soil samples are extracted with either acetone or dichloromethane (DCM). These solvents extract all forms of elemental sulphur from the soil matrix up to concentrations limited by the solubility of S<sub>8</sub> in the solvent. The extract is separated from the soil residue and analyzed by High Performance Liquid Chromatography (HPLC) using a methanol-water mobile phase and UV detection at 220 nm.

Matrix	Container	Amount	Hold Time	Preservation
Soil Extract	40 mL amber glass vials		14 days	Store at 4 ± 2°C
Soil	Wide mouth glass jars (recommended*), plastic bags or polyethylene containers of various sizes.	125 mL	30 days as received; 7 days to analyze extract	Store at 4 ± 2°C
Dried and Ground Soil	Glass	10 grams	Indefinite***	Store at room temperature

\* S<sub>8</sub> may tend to adhere electrostatically to plastic surfaces

\*\* Soils should be dried and ground as soon as possible after receipt in order to minimize biological degradation of S<sub>8</sub>. Freezing as-received samples may be used to extend hold time.

\*\*\* Maxxam recommendation.

## **Sulphur, all forms - ICP-OES method of analysis**

This method determines all forms of sulphur by ICP-OES. An acid digested water or soil is aspirated into an inductively coupled plasma which converts all sulphur compounds to sulphur ions in an excited state. When they return to the ground state they emit energy at characteristic wavelengths which are detected and quantitated. It is applicable to soils and aqueous sample types, including ground waters, surface waters, wastewaters and potable waters. Groundwater samples that have been pre-filtered and acidified will not need acid digestion but must be matrix matched with the standards. Surface waters, effluents and soils are typically subject to strong acid leachable method (SALM) prior to analysis.

The results are reported as a single value for sulphur. Although the ICP-OES method of analysis can be adapted to also measure elemental sulphur, Maxxam's method does not include the solvent extraction step for elemental sulphur prior to acid digestion. Therefore, **the data reported for sulphur by Maxxam using the**

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ICP scan should not be considered as representative of elemental sulphur. The RDL for soils is 50µg/g and for waters it is 0.5 mg/L (dissolved or total).

Matrix	Container	Amount	Hold Time	Preservation
Water	120 mL HDPE	Minimum 50 mL	60 days (O.Reg. 153; 30 days (MISA); 14 days (SDWA); 180 days (CCME)	HNO <sub>3</sub> , Ambient temperature
Soil / Sediment	100 mL glass jar	Minimum 10 g	180 days as received; indefinite when lab dried (O.Reg. 153/04, CCME)	None
Water Digest	50 mL tube	Minimum 25 mL	7 days	Ambient temperature
Soil Digest	15 mL tube	Minimum 5 mL	7 days	Ambient temperature

## Total Sulphur - LECO Furnace method of analysis

This procedure can be used to determine total sulphur (organic and inorganic species) in soil/sediment. Accelerator materials are added to the dried and homogenized sample and it is heated in the presence of oxygen and a catalyst to a high temperature. The combustion gases are converted to SO<sub>2</sub> and swept up to the IR cell for quantification. The RDL is 500mg/kg.

Matrix	Container	Amount	Hold Time	Preservation
Soils	100 mL glass jars	10 grams	180 days (as received); Indefinite for dried and ground samples.	None

## SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> - Ion Chromatography method of analysis

This method is used for the analysis of major anions in soil and water samples, including sulphate (in soils and waters) and sulphite (in waters), the latter form of sulphur being more unstable of the two. Sulphite is not typically present in natural water systems because it readily oxidizes to sulphate, however, it can be found in oxygen depleted environments where sulphate reducing bacteria proliferate. The aqueous extract is injected through a set of ion exchangers where the ions of interest are separated based on the relative affinities to the anion exchangers. The anions are then converted to their highly conductive acid forms and the parameters are measured by conductivity. Identification is completed by retention time and quantified by measurement of peak area. The RDL for sulphate in water samples is 1mg/L and in soil sample it is 20mg/L. The RDL for sulphite in water samples is 0.5mg/L.

Matrix	Container	Amount	Hold Time	Preservation
Waters	250mL or 500mL HDPE	50mL	28 days	Store at 4 ± 2°C
Soil / Sediment	100mL glass jar	50g	Indefinite when dried	Store at 4 ± 2°C
Soil Extract	Falcon tube	50mL	28 days	Store at ambient temperature

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## $\text{SO}_4^{2-}$ - Automated turbidimetry method of analysis

This method is used for the analysis of sulphate in water and soil matrices. The sulphate ion is precipitated in an acidic environment with barium, forming crystals of uniform size. The precipitating reagent contains gelatin, which maintains the crystals in suspension. The precipitated sample is measured using a photometer at a wavelength of 420nm. The concentration of sulphate is proportional to the amount of light scattered by the incident beam. The RDL in water samples is 1mg/L and in soil samples it is 10mg/L.

Matrix	Container	Amount	Hold Time	Preservation
Waters	1L, 500mL or 250mL HDPE	25mL	28 days	Store at $4 \pm 2^\circ\text{C}$
Soils	Plastic bag or 120ml, 250mL glass jar	125g	30 days as received; indefinite if dried	Store at ambient temperature
Soil extract	Glass or plastic tube	25mL	28 days	Store at $4 \pm 2^\circ\text{C}$

## $\text{HS}^{1-}$ and $\text{H}_2\text{S}$ - Ion selective electrode or Colorimetric method of analysis

This method is used to analyze dissolved sulphide in water samples using an ion selective electrode (ISE) from an automated PC-Titrate System. A silver / sulphide ISE is used to determine the activity from the sulphide ion in solution. The  $\text{HS}^{1-}$  and  $\text{H}_2\text{S}$  forms are converted to  $\text{S}^{2-}$  ions using an alkaline anti-oxidant reagent, which also provides a constant pH environment. The electromotive force produced in the electrode varies with the logarithm of sulphide concentration. The RDL is 0.02mg/L.

Matrix	Container	Amount	Hold Time	Preservation
Waters	250mL HDPE	40mL	7 days	1mL 50% NaOH + 1mL 22% $\text{ZnC}_2\text{H}_3\text{O}_2$ Store at $4 \pm 2^\circ\text{C}$

Sulphide in water samples can also be determined using a colorimetric technique, which is slightly more sensitive than the ISE method described above. The water sample is preserved with a combination of zinc acetate and sodium hydroxide solution, resulting in a white zinc sulphide precipitate. An acidic oxalate reagent is added (N, N-dimethyl-p-phenylenediamine) which converts all forms of sulfide into  $\text{H}_2\text{S}$ . The subsequent addition of ferric chloride results in the formation of a deep blue colour that is measured at 665nm. The RDL is 0.0019mg/L.

Matrix	Container	Amount	Hold Time	Preservation
Waters	250mL HDPE	40mL	7 days	2mL NaOH + 2mL $\text{ZnC}_2\text{H}_3\text{O}_2$ Store at $4 \pm 2^\circ\text{C}$

## $\text{S}_2\text{O}_3^-$ and $\text{SCN}^-$ - Ion chromatography method of analysis

This method is used to measure thiosulphate ( $\text{S}_2\text{O}_3^-$ ) and thiocyanate ( $\text{SCN}^-$ ) in various water matrices. Thiosulfate is used in a variety of industrial activities, including pulp and paper, smelting and textiles. Thiosulfate may be tested for in drinking water systems as it is an effective dechlorinating agent and could therefore lower intended residual chlorine levels. Thiocyanate may be a by-product of mining operations and is used as a building block in the manufacture of certain insecticides and herbicides. The release of

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thiocyanate into nearby waters can cause toxic effects to ecological receptors. Thiocyanate is also tested for as a background check prior to analysis for cyanide, since it causes a biased result.

A small portion of homogenized sample material is injected in an ion chromatography system with an organic modifier. The ions in solution partition in the column based on varying degrees of affinity to the stationary phase and elute at different times. The ions are measured using conductivity and identified based on retention time and comparison to standards. The RDL in water for both thiosulphate and thiocyanate is 0.2mg/L.

Matrix	Container	Amount	Hold Time	Preservation
Waters	1L, 500mL or 250mL HDPE or glass	30mL	28 days	Store at 4 ± 2°C

## HS<sup>1-</sup> and H<sub>2</sub>S – Acid Volatile Sulphide method of analysis (soils and sediments)

This method is used to analyze acid volatile sulphide in soils and sediments. Sulphide in the sample is first converted to hydrogen sulphide by acidification with hydrochloric acid, passed through a micro-distillation tube and the H<sub>2</sub>S is purged and trapped in sodium hydroxide solution. The trapped sulphide is then measured colorimetrically at 664nm, following the addition of the oxalate and ferric chloride reagents as described above.

Matrix	Container	Amount	Hold Time	Preservation
Soils or sediments	125mL glass jar	50g	7 days	none