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# THE MEASUREMENT OF $\delta^{34}\text{S}$ IN ENVIRONMENTAL SAMPLES BY CONTINUOUS FLOW MASS SPECTROMETRY (CFMS).

*John Dighton, Richard Cresswell, Andrew Herczeg and  
Steve Welsh*

**CRC LEME OPEN FILE REPORT 185**

**February 2005**

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## Executive Summary

In our attempts to describe, characterise and understand the regolith we take for granted the production of thousands of geochemical analyses that we manipulate to provide clues on the formation of minerals, the dispersion of metals, the origins of salts, and other processes. Increasingly, isotopes are being used to help constrain models of the evolution and reaction pathways of elements in the regolith and hydrosphere. Key amongst these are the isotopes of sulphur, which show significant fractionation effects (up to 100‰) as sulphur-bearing minerals are dissolved, precipitated and re-dissolved; transformed from reduced to oxidised species, and undergo bacterial reduction from sulphate to sulphide, all depending on the prevailing redox potential, the pH and elemental concentrations in the fluids in their environment. Sulphur is present in nearly all natural environments and occurs in a number of oxidation states, from sulphides to elemental sulphur, to sulphates. It is obviously of great interest in studies of the regolith.

Behind all these analyses, however, extreme care needs to be exercised by the providers of the numbers. Precision and accuracy are vital if the conclusions gleaned from models are to be believed. So, we have an arena where we require increasing numbers of analyses to populate our models, balanced by a requirement for increased accuracy and precision as we attempt to disentangle the sometimes complex histories these models suggest.

The highly reactive nature of sulphur and the use of oxidised species ( $\text{SO}_2$ ) for analyses, however, has meant that, until recently, large amounts of sample and stringent cleaning procedures were required to prevent severe fractionation effects occurring during the analyses themselves.

The development of continuous flow mass spectrometry (CFMS) in the 1990s has alleviated these problems, but is generally performed on purpose-built spectrometers. This report describes a novel, but generic, CFMS procedure that can routinely, relatively cheaply, determine the sulphur isotopic ratio for dissolved sulphates from water samples and from sulphur-bearing minerals with an accuracy and precision of 0.3‰. By combining an elemental analyser with a standard mass spectrometer we can now also resolve the different combustion products produced during preparation, an important aid in determining potential sources of analytical error.

Sulphur isotope analyses have never been so easy, nor so useful!

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## ABSTRACT

This report describes a novel method for the measurement of the isotopic ratio of  $^{34}\text{S}$  to  $^{32}\text{S}$  of dissolved sulphate from groundwater and sulphur minerals, at natural abundance levels, using a mass spectrometer and elemental analyser combination (CFMS), set up primarily to measure C and N isotopes using the  $\text{SO}^+$  ion beam, as a proxy for  $\text{SO}_2$ .  $\text{SO}_2$  is separated from other combustion gases using a gas chromatography column specifically designed for the purpose of analysing sulphur gases. The Supelco “Supelpak- S” GC column has proven to be a satisfactory alternative to the propriety column supplied with the instrument. The isotopic ratio is determined from the integrated peak areas of  $^{32}\text{SO}^+$  and  $^{34}\text{SO}^+$  ions produced in the source. The amount of sulphur required for analyses is about 30  $\mu\text{g}$ , with a precision of 0.3‰. The major advantages being the PTFE construction and the ability to resolve the combustion products of the elemental analyser - an important aid in determining potential sources of analytical error. The data for IAEA S2 and S3, which lie within the ranges reported from inter-laboratory comparisons of primary standards (IAEA Vienna), are used to calibrate a series of internal standards.



## INTRODUCTION

Sulphur has four stable isotopes-  $^{32}\text{S}$  with a relative abundance of 95.02%,  $^{33}\text{S}$  (0.75%),  $^{34}\text{S}$  (4.21%), and  $^{36}\text{S}$  (0.02%). The range of the isotopic ratio of the most abundant pair  $^{34}\text{S}/^{32}\text{S}$ , in the natural environment, is about 100‰. Generally, this variability is referenced to an international standard, based on the isotopic composition of Troilite (FeS) in the Canyon Diablo Meteorite (V-CDT). For comparison, the  $\delta^{34}\text{S}$  of the ocean is about +21‰ relative to V-CDT.

Prior to the development of continuous flow mass spectrometry (CFMS) techniques in the early 1990s, mass spectrometric determination of the sulphur compounds was performed following “off-line” sample preparation techniques. These required the conversion of the solid sample to  $\text{SO}_2$  or  $\text{SF}_6$ , (Rees, 1978), through a number of steps that included the cryogenic purification of the gas. At each of these steps, meticulous care was needed to ensure that there was no isotopic fractionation due to incomplete recovery (Raleigh distillation effect). Subsequent mass spectrometry of the gas was performed by the dual inlet method. This method required instrument modification that included the fitting of heating tapes to all inlet stainless steel tubing and to the source housing, in an attempt to eliminate memory effects associated with residual molecules of the previous sample “sticking” to tubing walls. Sample size requirements were, depending on the method, usually several milligrams. With the development of the CFMS method (Haystead, 1990; Giesemann et al, 1994) many of these difficulties have been overcome, and sample size requirements have been reduced to about 30  $\mu\text{g S}$ .

This report describes a CFMS method, which can be used to produce  $\text{SO}_2$ , without isotopic fractionation, from a range of sulphur bearing materials (including sulphates, sulphides and organic matter) using an elemental analyser. The ratio  $^{34}\text{S}$  to  $^{32}\text{S}$  in the gas is determined from the analysis of  $\text{SO}^+$  ions produced in the mass spectrometer source. Sample to sample reproducibility is about 0.3%.

The following methodology describes a procedure for the determination of dissolved sulphate in water samples. It has been developed using the Europa Scientific Ltd Geo 2020 isotope ratio mass spectrometer coupled to the ANCA-SL elemental analyser ( Welsh S. Sercon Ltd, Crewe, Cheshire, UK. pers comm. ). It is sufficiently generic to apply to any elemental analyser/isotope ratio mass spectrometer combination.

### Sample preparation

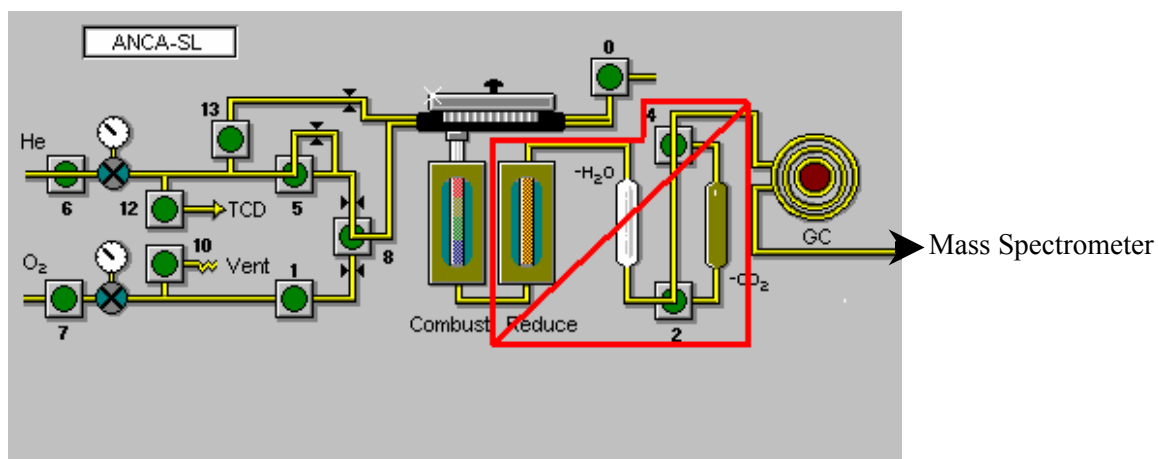
The target weight of sample required for a single analysis is equivalent to about 30  $\mu\text{g S}$ . Samples are collected in the field by filtering about 40 ml of sample through a 0.45  $\mu\text{m}$  syringe filter, into a 50 ml centrifuge tube (falcon type). Three “drops” of concentrated HCl are then added using a Pasteur pipette and the tube capped and shaken vigorously to purge any dissolved inorganic carbon and to assist in the degassing of  $\text{H}_2\text{S}$ . Approximately 10 ml of saturated  $\text{BaCl}_2$  is then added to precipitate

dissolved SO<sub>4</sub> as BaSO<sub>4</sub>. Any dissolved organic matter will co-precipitate with the BaSO<sub>4</sub> at this stage. Samples are then centrifuged (3500 rpm for 10 minutes) in the laboratory. The supernatant is aspirated using a pipette attached to a liquid trap at a reduced pressure supplied by a vacuum pump. Hydrogen peroxide (30% v/v) is then added to the remaining pellet and the solution gently heated with a hot air gun to release any organic S. Final purification is achieved by a further two steps of re-suspension in de-ionised water, centrifugation and aspiration. The resultant precipitate is dried in an oven at 105°C for 3 hours and then ground to a fine powder in situ in the falcon tube with a round bottom glass rod.

For mass spectrometry analysis, approximately 0.2 mg of precipitate is placed into a tin foil capsule. An additional 2-5 mg of Vanadium pentoxide is added and the capsule closed and formed into a ball. For details on the preparation of other sample types for mass spectrometry, refer to Carmody et al. (1998).

## apparatus

The system consists of an elemental analyser designed and manufactured by Europa Scientific Ltd. This instrument, when coupled to a Europa Scientific Ltd Geo 2020 stable isotope ratio mass spectrometer, is used primarily for the determination of the carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotopic composition of both organic and inorganic samples.

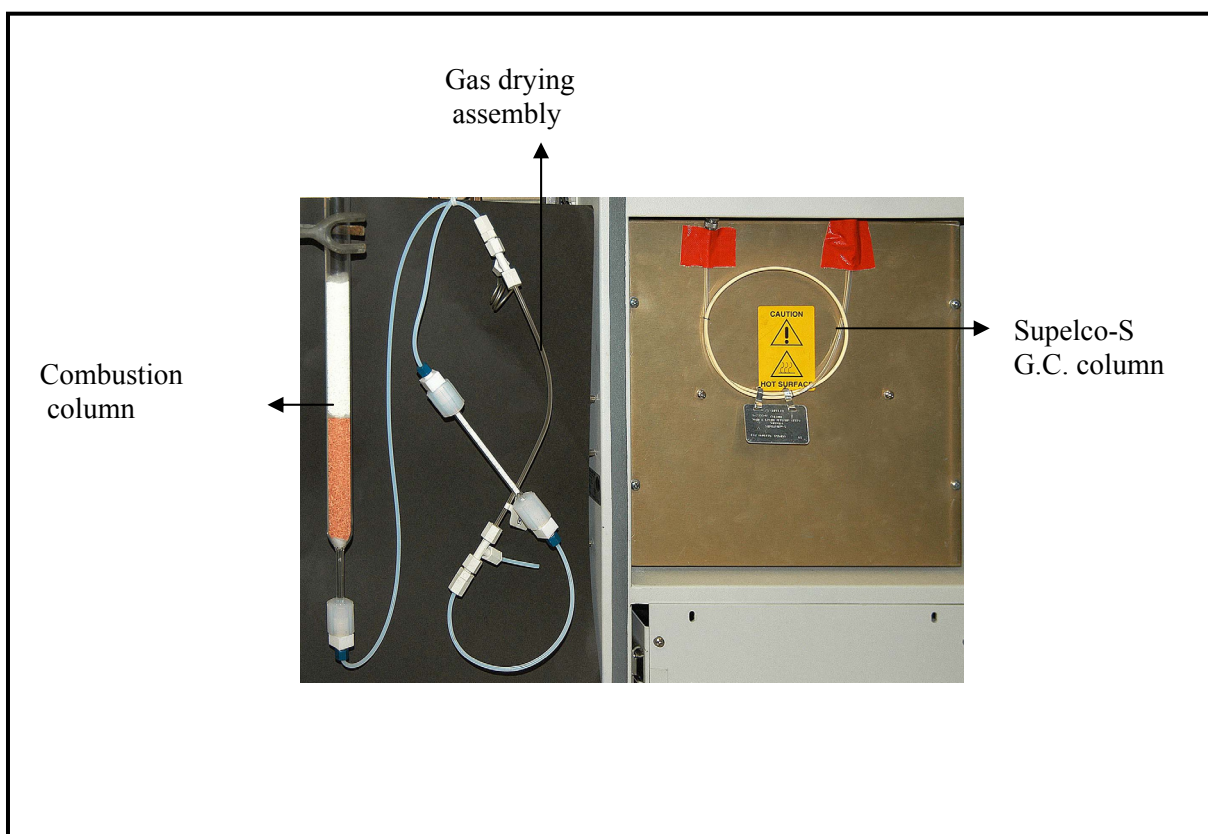


**Figure 1.** Valve and Column configuration

Figure 1 shows the schematic configuration of the valves and columns in this elemental analyser when used for the isotopic analyses of samples containing nitrogen and carbon compounds. The section outlined in red, is redundant for sulphur. This is replaced with the combustion column and gas drying assembly described in Figure 2.

## procedure

There are two key steps to precisely measure  $\delta^{34}\text{S}$  in any sulphur bearing samples. First, the complete conversion of S in the samples to  $\text{SO}_2$  gas by combustion must be achieved. Secondly,  $\text{SO}_2$  must be completely separated from other combustion gases. Figure 2 shows the three simple components required to achieve these aims.



**Figure 2.** Sulphur Dioxide sample preparation and purification assembly

### Combustion column

The Combustion column consists of a transparent silica tube (part number C1040 supplied by Sercon Australia Pty Ltd). It is filled with (from the bottom) a 20 mm wad of quartz wool followed by about 80 mm of reduced high purity copper wires; a further 5 mm of quartz wool separates 90 mm of tungstic oxide supported on zirconium. The overall length of the packing is about 200 mm. This places

the top of the reagents in the hottest zone of the furnace. A silica tube packed with a 5 mm wad of quartz wool is inserted into the top. This tube collects the residual ash from the combusted samples.

The Combustion column is inserted into the furnace and the carousel is attached. The bottom connection is NOT made at this point. The column must be conditioned over two hours by gradually increasing the furnace temperature to 1080 °C. A considerable amount of water vapour is released and any droplets forming on the bottom tube must be wiped away.

The gas drying assembly, consisting of PTFE Swagelok fittings, a Nafion membrane and a small length of glass tube packed with  $\text{Mg}(\text{ClO}_4)_2$ , is only connected to the bottom of the tube and to the inlet to the GC column after conditioning. The purge valve (valve 12; Figure 1) to the non-existent thermal conductivity detector (TCD) is switched on, to provide a counter-flow of helium to the Nafion dryer. This flow rate is set to about 100 ml/min. Note that all tubing between the bottom of the column to the GC is PTFE to minimise memory effects and tailing due to  $\text{SO}_2$  absorption.

### **Gas chromatography column set-up**

A Supelco “Supelpak- S” G.C. column (Supelco Bulletin 722P Sigma-Aldrich) is used to separate  $\text{SO}_2$  from other combustion products. The column consists of 76 cm of 3 mm diameter PTFE tube packed with 45 cm of factory prepared Porapak QS material. The column was chosen specifically for its ability to resolve  $\text{SO}_2$  from other S gases, in particular,  $\text{CH}_3\text{SH}$  (methanethiol) at trace levels. The column is conditioned at 200°C for 16 h with a carrier gas flow rate (UHP He) of 60 ml/min. Note that during conditioning the outlet of the column must be disconnected from the mass spectrometer to prevent any volatile compounds from entering the source. After conditioning, the column temperature is set to 40°C, the flow stabilised at 60 ml/min and reconnected to the mass spectrometer.

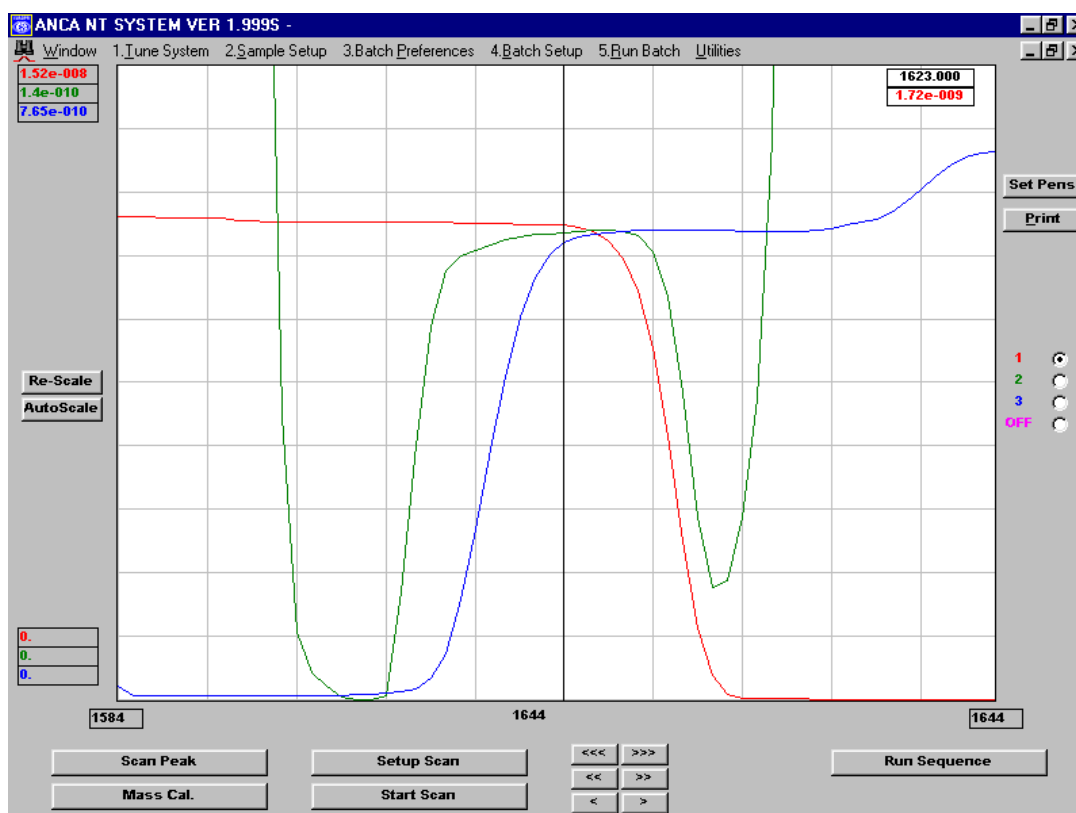
After checking for leaks the system is ready for S analyses.

### **Tuning the mass spectrometer**

In this method, the mass spectrometer is not set up in the usual configuration with a cylinder of reference  $\text{SO}_2$  gas to optimise the source parameters. Instead, a capsule of reference material is combusted and the resulting  $\text{SO}_2$  is contained within a trapping loop. The valves in this loop activated just as the major beam reaches the maximum intensity.

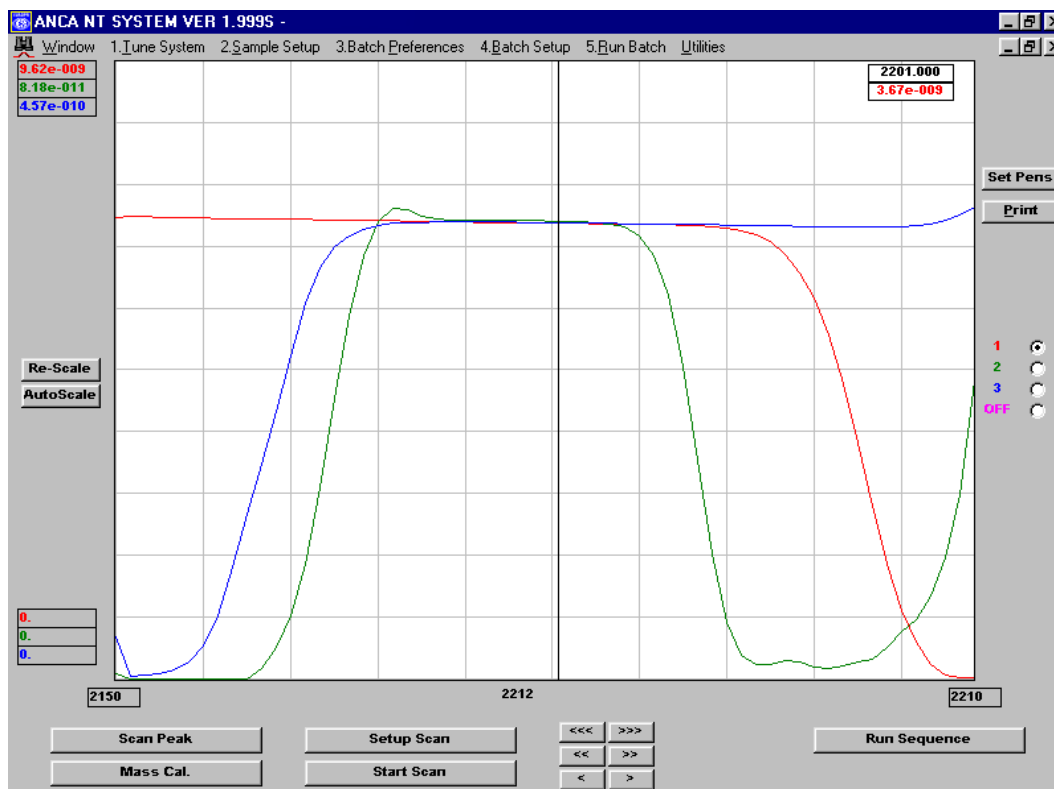
The isotopic ratios of  $\text{SO}_2$  have traditionally been determined using dual inlet isotope ratio mass spectrometry (IRMS) by measuring  $\text{SO}_2^+$  ions at atomic ratios of masses (AMU) 64, 65 and 66. Figure 3 shows the beam shapes for these masses when the ion optics (magnet position in particular) for this mass spectrometer are optimised for carbon and nitrogen isotopes. The resulting peak shapes and widths are narrow, resulting in poor results from drift and noise when in CFMS mode. Whilst it is

possible to retune the instrument to optimise for SO<sub>2</sub>, the overall system would be compromised for subsequent carbon and nitrogen isotopic analyses.



**Figure 3.** Ion beam (amu 64,65,66) peak shapes for SO<sub>2</sub><sup>+</sup>.

However after entering the mass spectrometer, SO<sub>2</sub> is ionised in the source with about 1/3 “cracking” to SO<sup>+</sup>, without isotopic fractionation. The peak shapes for this molecule (at masses 48,49 and 50) are broader and flatter than the SO<sub>2</sub> peak (Figure 4).



**Figure 4.** Ion beam (amu 48,49,50) peak shapes for  $\text{SO}^+$ .

Tuning the mass spectrometer to  $\text{SO}^+$  overcomes the instability problem associated with possible peak drift due to the source power supply. A sample containing  $30 \mu\text{g}$  of S gives a primary beam current (mass 48) of about  $2e^{-9}$  A.  $\delta^{34}\text{S}$  is determined from the ratio of mass 50 to mass 48. The other advantage of using the  $\text{SO}^+$  beams instead of the  $\text{SO}_2^+$  beams is that the molecular weights of its isotopes are closer to those of  $\text{CO}_2$ , thus requiring less adjustment of the tuning parameters.

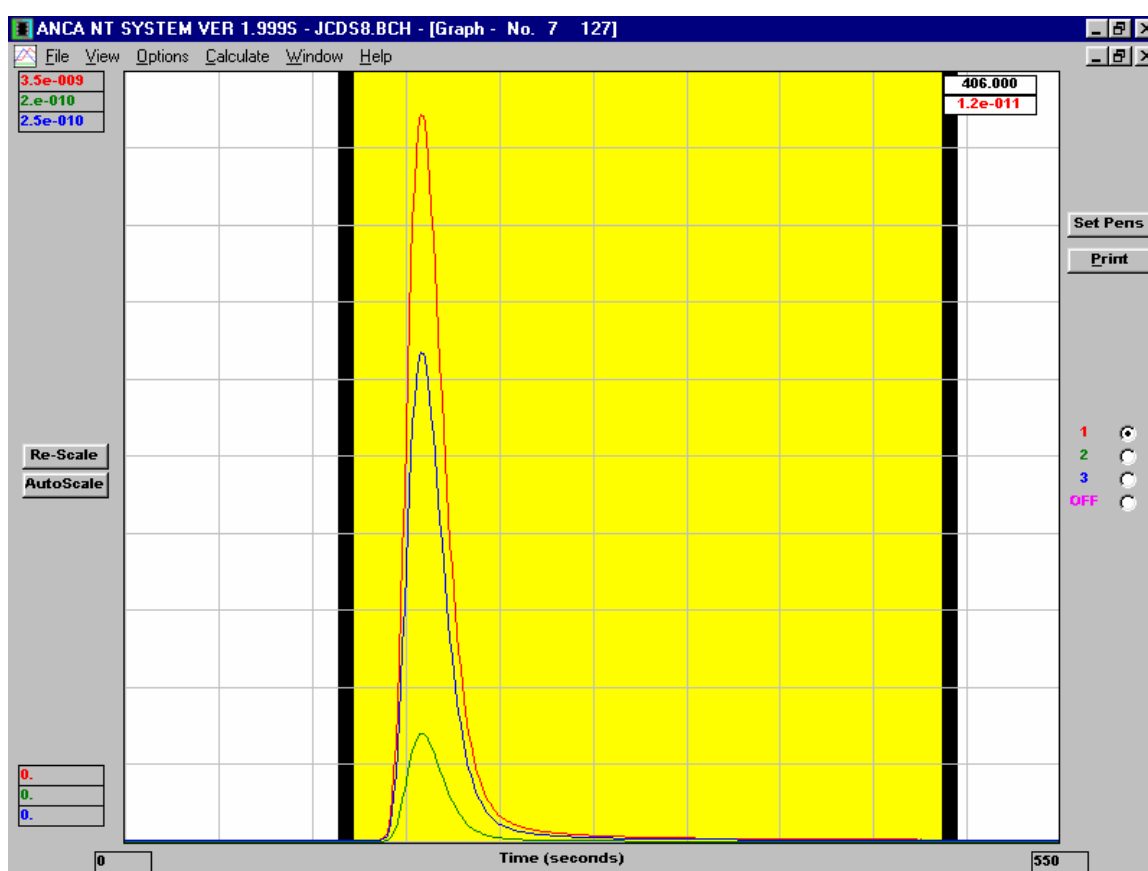
### Measurement of isotopic ratios in samples and standards

Under ideal conditions, the conversion of the solid sample to  $\text{SO}_2$  is complete when the capsule instantly and explosively ignites as it reaches the top of the column. The combustion of the tin capsule is exothermal, with the local temperature rising in excess of  $1800^\circ\text{C}$ . The dissociation of  $\text{V}_2\text{O}_5$  provides an additional source of  $\text{O}_2$  and a point for catalysis, enhancing the combustion of the sample to gas. In practice, the combustion never reaches completion, with a mixture of  $\text{SO}_x$  species forming. This gas mixture is then swept through the reactants by the ultra high purity He carrier gas, resulting in the complete catalytic oxidation of the  $\text{SO}_x$  to  $\text{SO}_2$  and the removal of excess  $\text{O}_2$ . Figure 5 shows the ideal results of these reactions.

Figure 5 shows a typical isotopic chromatogram from which reproducible data can be obtained indicating that the elemental analyser is operating at maximum efficiency.

The isotopic ratio is calculated from the area under each curve within the integration window. The time set for each analyses is 550 seconds for this procedure. The actual timing sequences for the oxygen pulse and carousel action are dependant on the type of elemental analyser used and must be carefully adjusted at the time of the initial set up.

In addition to the off-line conditioning, a newly packed column must be conditioned on-line before samples are analysed. This is achieved by including 10 dummy samples (empty capsules) at the beginning of the first batch run.



**Figure 5.** Expected relative peak shapes and tailing for  $\text{SO}^+$ . Each curve represents the change in beam current (nA) as detected by the mass spectrometer collectors for each ion or ion combinations. The yellow box represents the integration period (240 s).

### Batch set-up

To reduce measurement error (described in Section 6 Quality control), batch runs are designed to consist of no more than fifty samples including standards. These are arranged in a sequence consisting of two standards for every ten unknown samples. Included in the batch must be at least 3 internal

standards, each to be analysed in triplicate. These should be placed randomly within the batch. The ash collector is exchanged before the next batch run. The combustion column is replaced after about one hundred capsules have been combusted.

## calculations and data processing

### Standards

The stable isotopic composition is reported as the ratio of  $^{34}\text{S}/^{32}\text{S}$  relative to the standard V-CDT (Vienna-Canyon Diablo Troilite). The original troilite standard no longer exists and in practice, values are reported relative to a defined V-CDT through the International Atomic Energy Agency (IAEA) standards S1, S2 and S3 and the US National Institute of Standards and Technology (NIST) SRM8557 (NBS123 Sphalerite) and SRM8558 (NBS127 Barium Sulphate). The range of values for S2 and S3, shown in **Table 1**, are those reported from the results of a number of inter-laboratory comparison studies.

**Table 1: The primary reference standards for  $\delta^{34}\text{S}$  analyses**

Matrix	Code	Concentration in $\delta^{34}\text{S}_{\text{V-CDT}} \text{‰}$
Sphalerite	SRM8557	+17.1
Silver Sulphide	IAEA-S-3	range [- 30.7 ..... -32.1]
Silver Sulphide	IAEA-S-2	range [+21.4 ..... + 21.7]
Silver Sulphide	IAEA-S-1	-0.30
Barium Sulphate	SRM8558	+20.3

### Calibration

All calculations are dependant upon the values of the defined reference  $\delta^{34}\text{S}_{\text{REF}}$  for each batch. This reference standard is entered with the  $\delta^{34}\text{S}$  defined relative to the international standard but with the  $\delta^{18}\text{O}$  value set to zero. There will be slight drift in the measured isotopic composition between a reference standard at the beginning of a batch and that of the measured value at the end of the batch. This is due to a number of factors including combustion efficiency and depletion of reagents. All manufacturers routinely include a software algorithm to correct for this drift. In order to eliminate the need to make any correction for the oxygen isobaric interference, the drift corrected results for the



reference values were used to calibrate the instrument run (Table 2). This was done in a spreadsheet using the assigned values as listed in Table 1 and the standard methods, universally adopted for instrument calibration.

**Table 2** shows the format of the spreadsheet,

**Table 2: Data processing to convert the measured drift corrected values to values relative to the international standard.**

Step 1: Standard curve between measured and expected drift corrected $\delta^{34}\text{S}_{\text{REF}}$			Step 2: Conversion of the drift corrected results to $\delta^{34}\text{S}_{\text{V-CDT}}$ using the calibration values from Step 1.		
Name	Measured $\delta^{34}\text{S}_{\text{REF}}$	Assigned $\delta^{34}\text{S}_{\text{V-CDT}}$	Name	Measured $\delta^{34}\text{S}_{\text{REF}}$	Corrected $\delta^{34}\text{S}_{\text{V-CDT}}$
IAEA S1	-0.3	-0.3	check	-0.3	-0.4
IAEA S1	0.1	-0.3	s1	0.1	0
IAEA S1	-0.3	-0.3	127	21.6	20.2
IAEA S1	-0.2	-0.3	127	21.7	20.3
NBS 127	21.6	20.3	127	21.9	20.4
NBS 127	21.7	20.3	123	18.3	17.1
NBS 127	21.9	20.3	123	18.3	17.1
NBS 123	18.3	17.1	123	18.3	17.1
NBS 123	18.3	17.1	s2	22.7	21.3
NBS 123	18.3	17.1	s2	22.8	21.3
slope	0.9383		s2	22.8	21.3
intercept	-0.1053		s3	-33.1	-31.1
			s3	-33	-31.1
			s3	-33.4	-31.5
			alh	21.4	19.9
			alh	21.6	20.2
			alh	21.6	20.2
			ma	7.1	6.6
			ma	7.1	6.6
			ma	6.7	6.1
			s1	-0.3	-0.4
			check	-0.2	-0.3

**Table 3** presents a summary of all the calibration data for the internal laboratory standards alh, ( $\text{BaSO}_4$ , precipitated from sea water collected from the jetty at Port Noarlunga, Gulf St Vincent, South Australia) and ma, ( $\text{BaSO}_4$ , precipitated from a solution of Merck reagent grade  $(\text{NH}_4)_2\text{SO}_4$ ). Included, are the results of IAEA- S2 and IAEA-S3 analysed during the same time period and over different sample runs as alh and ma.

**Table 3: Summary of all  $\delta^{34}\text{S}_{\text{V-CDT}}$  calibration samples**

	alh	ma	IAEA-S2	IAEA-S3
Average ‰	20.2	6.6	21.3	-31.1
n	52	47	14	14
stdev	0.2	0.3	0.2	0.4
Range ‰	19.7 to 20.8	6.0 to 7.3	21.0 to 21.7	-31.6 to -30.1

The data for S2 and S3, which lie within the range for those reported from inter-laboratory comparisons of primary standards calibration methods conducted by the Isotope Hydrology section of the IAEA Vienna, confirm and validate the calibrated values and methods described.

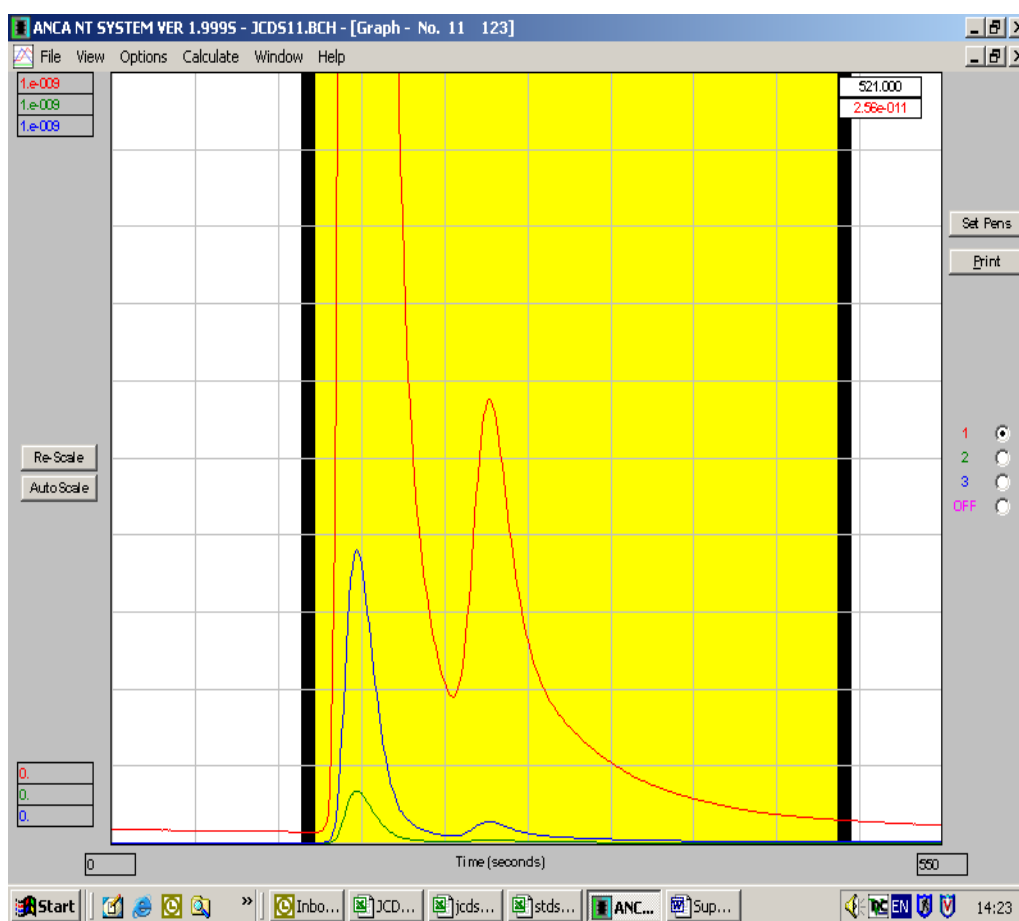
#### **quality control – column degradation**

Analytical errors occur with the gradual build up of ash (metal oxides) from preceding samples resulting in the capsule dropping into a cooler part of the column. This causes a “slow” burn that may last for more than 3 seconds, or, there can be two separate processes observed. The result of this process is shown in an extreme form in Figure 6. The initial flash as the tin capsule oxidises, is followed by a longer reduction process. This is characterised by a reduced temperature “glow” that continues for an extended period. The two pulses of  $\text{SO}_2$  are then flushed through the combustion column and the GC, separated by the carrier gas and eluting at the same rate at which the combustion occurred. Whilst the two peaks probably represent the complete conversion of the sample to  $\text{SO}_2$ , peak tailing is excessive and the software is unable to integrate the beam currents.

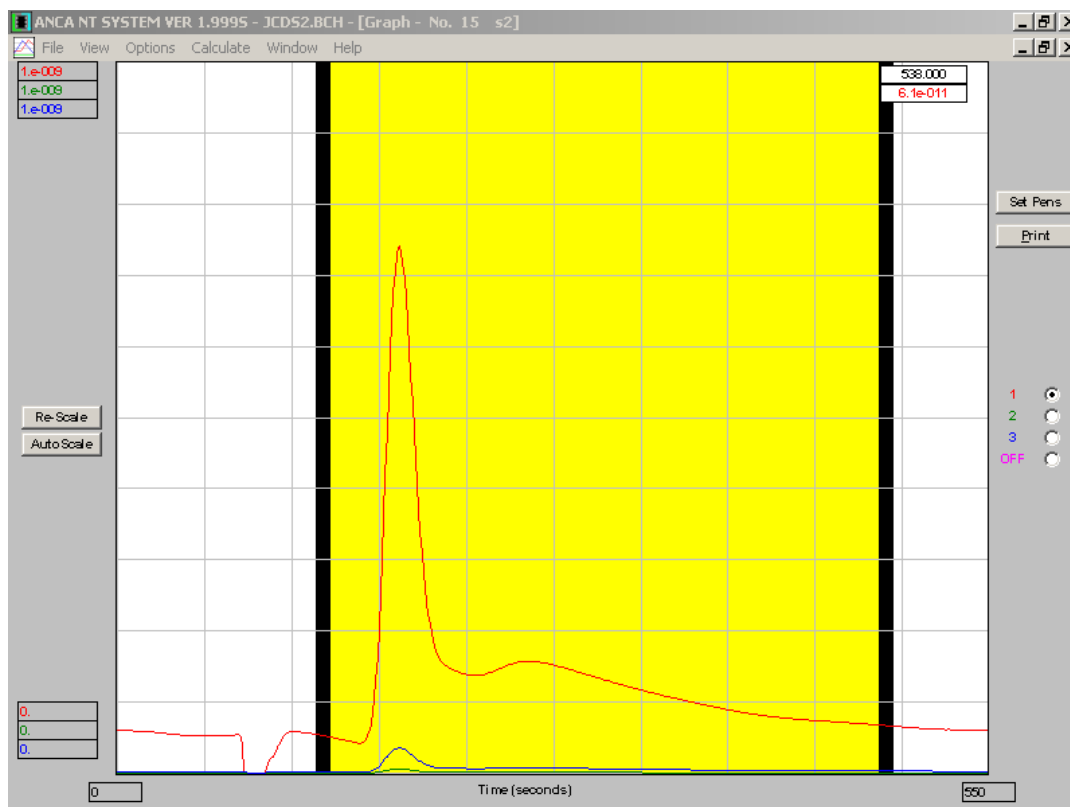
The ageing and surface contamination of the reactants by vaporised Pb, Ag and V and the oxidation of the reduced copper wires show similar effects, that also include a gradual reduction in overall peak heights until no  $\text{SO}_2$  is produced due to adsorption in the hydrated  $\text{Mg}(\text{ClO}_4)_2$  trap. Removal of the quartz ash collector at this stage, will show this build up with the top layers consisting of a very hard conglomerate of cemented oxides and probably, partially reacted sulphur compounds. The combustion column shows that the reduced copper is almost completely converted to CuO (at least on the surface), and the tungstic oxide is contaminated.

Fry et al. (1996) reported that the addition of a carbon source in the form of dextrose enhances the combustion process, particularly for some recalcitrant samples (sediments). The resulting gas mixture

when produced with this type of combustion column, contains considerable amounts of CO species, which when coupled with gradually depleted combustion chemicals, results in the formation of CH<sub>3</sub>SH. This molecule elutes from the GC at a similar time to SO<sub>2</sub> and is ionised to amu 48 contributing to the overall integrated beams. This additional signal and the increased peak tailing causes in the analytical error shown in Figure 7. Note that this molecule is not resolved in the GC column supplied by the manufacturer of the elemental analyser, and it's presence as a source of analytical error has only been detected by using the Supelco "Supelpak- S" column. The negative peak in the major beam shown before the integration window is CO<sub>2</sub><sup>+</sup>.



**Figure 6.** Effect of incomplete conversion, exhausted reagents and ash build up, with this type of combustion column, on the production of SO<sub>2</sub>. (measured  $\delta^{34}\text{S}_{\text{REF}}$  = 18.9‰, true value = 17.3‰)



**Figure 7.** The effects of C and contaminated reagents on the production of  $\text{SO}_2$ , with this type of combustion column set up. The negative peak at about 90 s is  $\text{CO}_2^+$ . ( $\delta^{34}\text{S}_{\text{REF}} = 18.9\text{‰}$ , true value =  $21.3\text{‰}$ )

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