

Compound Specific Stable Sulfur Isotope Analysis ($\delta^{34}\text{S}$ and $\delta^{33}\text{S}$) of Organic Compounds Using Gas Chromatography Hyphenated with Multiple Collector Inductively Coupled Plasma Mass Spectrometry (GC-MC-ICPMS)

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Compound Specific Stable Sulfur Isotope Analysis

Isobaric interferences and background

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- Isobaric interferences (e.g. $^{16}\text{O}^{16}\text{O}^+$, $^{32}\text{SH}^+$) can falsify signals of ^{32}S and ^{33}S
- Normally avoided by separation of sulfur masses from interferences by operating in medium or high resolution; not possible in low resolution → thus, investigations concerning isobaric interferences carried out in medium resolution
- GC-MC-ICPMS → dry plasma conditions → significant reduction of interferences → main factor influencing interference intensity and signal sensitivity of ^{32}S and ^{33}S is sample gas flow → sample gas flow adjusted to maximal signal to noise ratio (Fig. 1A) and not to maximum sensitivity (Fig. 1B)
- Result: $^{16}\text{O}^{16}\text{O}^+$ only a minor abundance, $^{32}\text{SH}^+$ was insignificant

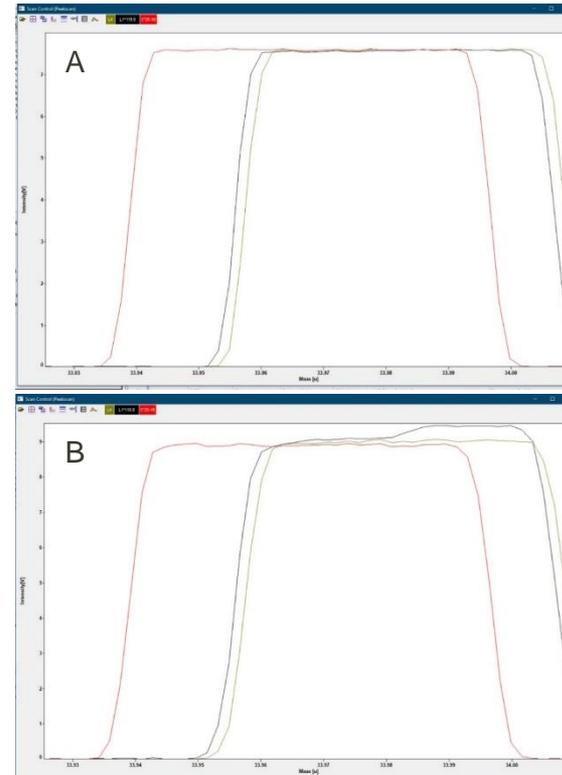


Figure 1: Mass scans of ^{32}S (black), ^{33}S (green) and ^{34}S (red) at medium resolution during inhalation of SF_6 . A: mass scan at a sample gas flow of 1.31 L/min. At this flow the signal-to-noise ratio was highest and interferences at mass 32 are very small. B: mass scan at a sample gas flow of 1.4 L/min. The signal is close to maximum and interferences are visible on mass 32 (but not 33).

Compound Specific Stable Sulfur Isotope Analysis

Analytical precision

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- Tested from 60 to 1500 pmol S injected on-column → signal sizes of 15 to 350 V for mass 32
- Precision (low and medium mass resolution) ranged from <0.25 mUr (^{33}S) and <0.1 mUr (^{34}S) for 60 pmol S to <0.1 mUr (^{33}S) and <0.05 mUr (^{34}S) for 400 pmol of S (ca. 100 V signal)
- Precision for ^{34}S similar to previous reports¹
- Precision for ^{33}S of CSIA method not yet been reported but achieved precision of <0.1 mUr for ^{33}S only requires 400 pmol S which may be sufficient for multiple applications

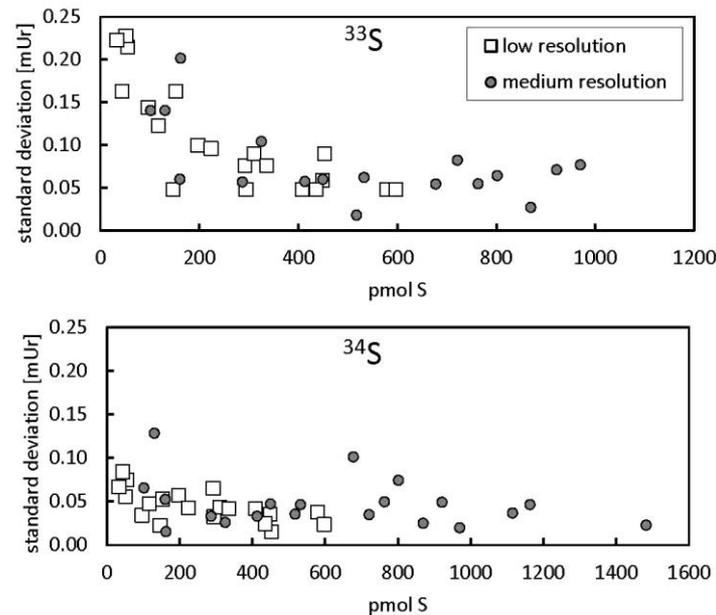


Figure 2: Analytical precision for ^{33}S and ^{34}S for different amounts of sulfur given in pmol. Each data point indicates the standard deviation of five replicate measurements.

Compound Specific Stable Sulfur Isotope Analysis

Linearity

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- $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ showed a linear relationship with a slope of about 0.004 and 0.008, respectively \rightarrow average change of 0.4 mUr ($\delta^{33}\text{S}$) and 0.8 mUr ($\delta^{34}\text{S}$) per 100 V measured for mass 32 (Fig. 3A)
- To avoid linearity effects \rightarrow usage of internal reference compounds SF_6 (gas phase analyses) and thiophene (dissolved organics)
- Internal reference compound was adjusted to analyte \rightarrow similar signal sizes of internal reference and analyte (maximum difference $\pm 20\%$)
- Internal reference compound was set to zero at each peak size and analyte of same peak size was referenced against them (Fig. 3B)

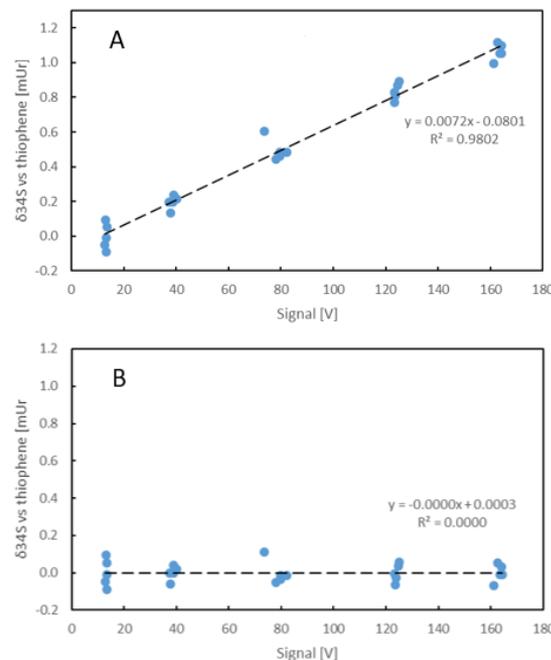


Figure 3: Relationship between signal size and isotopic composition ($\delta^{34}\text{S}$ versus signal).
A: All isotopic ratios of tetrahydrothiophene (THT; signal sizes of 17 to 170V) were referenced against the isotopic ratio of thiophene (internal reference compound) with a 17 V signal size \rightarrow consequence: linear relationship between signal size and $\delta^{34}\text{S}$ of THT. $\delta^{34}\text{S}$ shifts by about 1.2 mUr from signal sizes of 17 to 170V.
B: THT is referenced against thiophene of similar signal sizes only \rightarrow consequence: $\delta^{34}\text{S}$ become independent of signal size within analytical uncertainty.

Compound Specific Stable Sulfur Isotope Analysis

Method evaluation and referencing of compounds versus V-CDT

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- Characterization of organics versus V-CDT done by two point normalization using international reference materials IAEA-S2 and IAEA-S3 (Ag_2S) converted to SF_6 ; quality of normalization was confirmed by analyzing IAEA-S1 as SF_6 (low and medium resolution were tested)
- Needed, because adequate organic sulfur standards not available; additional problem \rightarrow no $\delta^{33}\text{S}$ consensus values of IAEA standards are yet assigned, but there are $\delta^{33}\text{S}$ values available in literature²
- Result: no significant difference between $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ obtained at low and medium resolution and good quality of the normalization (Tab. 1)

Table 1: $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of international reference materials (IAEA) and industrially produced organic compounds.

| Compound | $\delta^{33}\text{S}$ [mUr] normalized | $\delta^{33}\text{S}$ [mUr] published | $\delta^{34}\text{S}$ [mUr] normalized | $\delta^{34}\text{S}$ [mUr] consensus |
|---------------------------|--|---------------------------------------|--|---------------------------------------|
| IAEA-S1 | -0.07±0.18 | -0.05 ² | -0.16±0.10 | -0.30 ² |
| IAEA-S2 | 11.57±0.12* | 11.57 ² | 22.62±0.08* | 22.70 ³ |
| IAEA-S3 | -16.61±0.16* | -16.61 ² | -32.49±0.09* | -32.30 ³ |
| SF_6 (in-house) | 1.16±0.15 | - | 1.87±0.10 | - |
| Dimethyl disulfide (DMDS) | 8.60±0.17 | - | 16.97±0.07 | - |
| Thiophene (THI) | -1.74±0.18 | - | -3.35±0.07 | - |
| Diethyl sulfide (DES) | 6.36±0.20 | - | 12.54±0.17 | - |
| Tetrahydrothiophene (THT) | 4.13±0.17 | - | 7.82±0.15 | - |

$\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ include values measured at low and medium resolution which were indistinguishable. Isotopic reference materials used as anchors for two point normalization to V-CDT scale are indicated with an asterisk.

2 Ding, T. et al. Geochim Cosmochim Acta, 2001; 65: 2433-2437

3 Mann, J. et al. Rapid Commun. Mass Spectrom, 2009; 23: 1116-1124