Speciation and δ^{34}S analysis of volatile organic compounds in crude oil by GC-MC-ICP-MS using the Thermo Scientific GCI 300 Interface

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Keywords

Neptune Plus ICP-MS, GCI 300 Interface, Gas Chromatography, Speciation, Sulfur, δ^{34}S, Isotope Ratio, Crude Oil, Medium Resolution

Goal

To demonstrate the utility of the Thermo Scientific™ Neptune Plus™ Multicollector ICP-MS, when coupled with the Thermo Scientific™ Trace™ 1310 GC via the Thermo Scientific™ GCI 300™ Interface, for isotopic sulfur analysis of individual compounds within a series of crude oil samples.

Introduction

As the 10th most abundant element on Earth, sulfur is a common constituent of many organic compounds.[1] Redox transitions of sulfur can result in large isotopic fractionations. By measuring the δ^{34}S of individual compounds within a sample, information can be derived about the source of the sample and the processes it has undergone. Amrani *et al* (2009)[2] first explored the coupling of gas chromatography (GC) to a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) for determining the δ^{34}S of individual components in crude oil, which can contain weight percentage levels of sulfur. Subsequent GC-MC-ICP-MS has confirmed δ^{34}S fractionation between benziothiophenes and dibenzothiophenes as indicative of petroleum samples which have undergone thermochemical sulfate reduction.[3–5]

The GCI 300 Interface is a simple, lightweight, flexible transfer line, facilitating easy coupling between the Thermo Scientific Trace 1300 GC and Thermo Scientific Neptune Plus MC-ICP-MS. The homogenous temperature profile helps maintain excellent GC peak definition, aiding compound identification and quantification, vital for a complex mixture such as crude oil.

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Method

Gas Chromatography

A Thermo Scientific TRACE 1300 GC was coupled to the Thermo Scientific Neptune Plus MC-ICP-MS via the GCI 300 Interface. A T-insert (Figure 1), inserted between the ICP injector and the interface, created a port for the introduction of reference gases to the plasma.
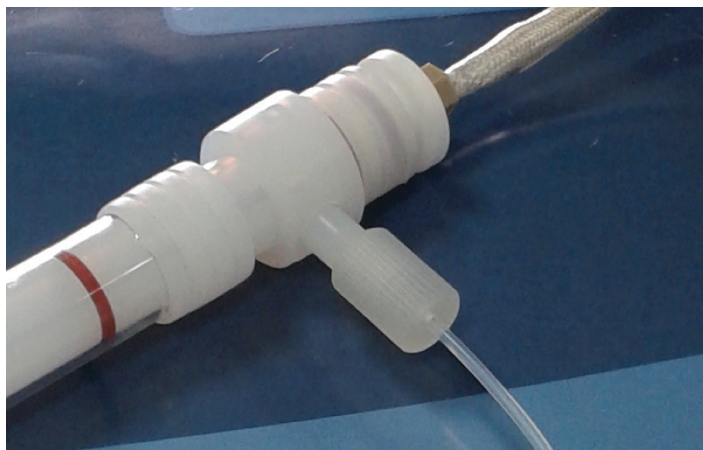

Figure 1. Connection of GCI 300 Interface to semi-demountable torch and injector. SF_6 gas could be added via the T-inlet.

The GC operational parameters (Table 1) were optimized for peak definition, $^{34}S/^{32}S$ ratio stability and run time. Optimization was performed with a mixture of four sulfur containing compounds, 3-hexylthiophene (eluting at 140 °C), hexyl sulfide (eluting at 145 °C), dibenzothiophene (eluting at 182 °C) and 1-octadecanethiol (eluting at 210 °C) in toluene. The elution times covered the expected range of the sulfur-containing compounds within crude oil (Figure 2).
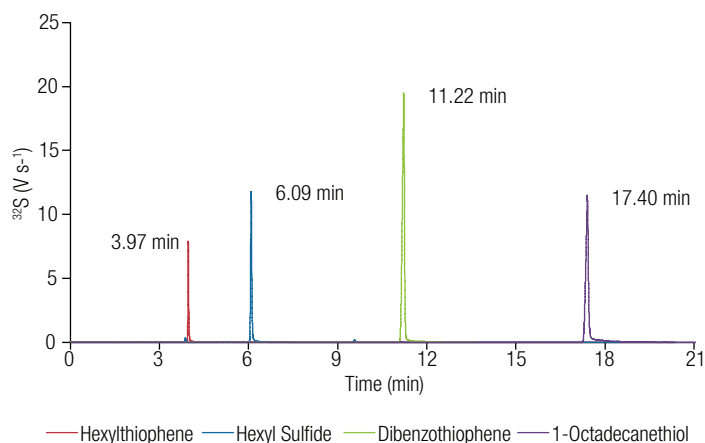

Figure 2. Combined chromatogram of all four external standards, with retention times.

Table 1. Instrument configuration and operation parameters.

GC Parameters	Value
Oven Program	Initial temp of 100 °C, ramp at 10 °C/min, 300 °C (2 min)
Column	30 m × 0.25 mm × 0.25 µm (P/N 26098-1420)
Injection Volume	1 µL
Carrier Gas	He
Injection Mode	PTV, splitless
Injection Port Temperature	Initial temp of 80 °C, ramp at 14.5 °C/min to 300 Clean at 305 °C between runs
Flow Rate	3 mL min^{-1}
Septum Purge Flow	5 mL min^{-1}
Purge Flow	50 mL min^{-1} at 1.5 min
Transferline	195 °C (corresponding to 290 °C)

ICP-MS Parameters	Value
Interface	Ni-sampler (Std) Ni-skimmer (H)
Resolution	Medium
RF Power	1200 W
Transferline Gas Flow	Ar at 1.5 L min^{-1}
Add Gas	SF_6 in He at 3 mL min^{-1} (Tune)
Cup Configuration	L3 – ^{32}S L1 – ^{33}S, C – Mass 33.65, H1 – ^{34}S
Integration Time	131 ms
Duration	21 min

Mass Spectrometry

Tuning and calibration of the Neptune Plus MC-ICP-MS operating parameters (Table 1) required a stable sulfur signal. During tune 3 mL min^{-1} of SF_6, a colorless and inert gas, diluted in He was continuously introduced through the T-inlet. To separate the sulfur isotopes from O_2-based interferences requires at least medium resolution, or a $\Delta m/m$ value of ≈5,000. As the GC-MC-ICP-MS interface produced a very dry plasma, no O_2-based interferences were detected by a mass scan (Figure 3). However, as the presence of interferences during sample analysis could not be ruled out, an O_2^+ interferent was deliberately introduced by injection of methanol (2 µL) into the GC. The resulting mass spectra was used to position the centre mass away from interfering ions (Figure 4).
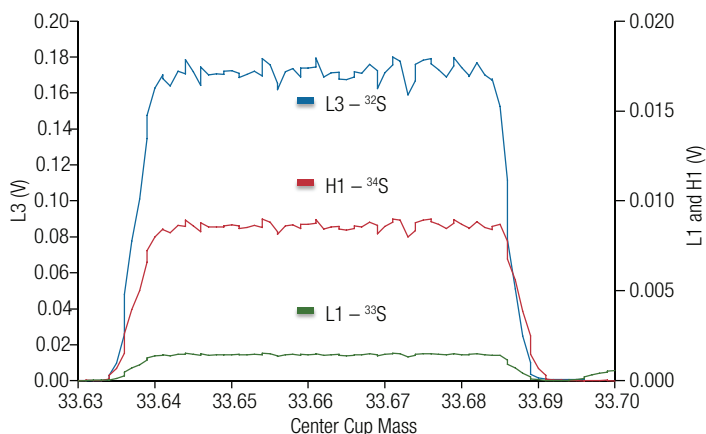
Figure 3. Mass scan of three sulfur isotopes in SF$_6$ tune gas. In dry conditions there is no evidence of O$_2^+$ interferences.
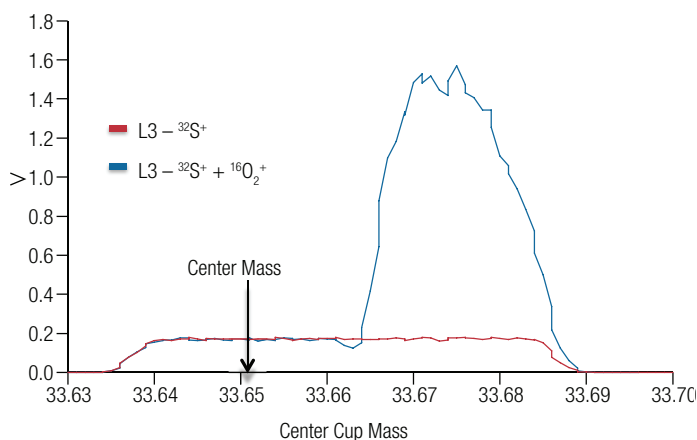

Figure 4. Mass scan across ^{32}S$^+$, before and after the introduction of MeOH. Center Cup Mass positioned away from O$_2^+$ interferences.

Sample preparation

Four crude oil samples (Bryan Mount, Basrah Light, Saudi Light and Saudi Medium) were prepared in a 1:200 mixture with hexane and passed through a 20 μm PTFE syringe filter prior to injection. 1 μL of an internal standard, 3-hexylthiophene, was added to 1000 μL of each oil/hexane mixture. Five replicate analyses were run for each sample.

Data analysis

Investigations into the utility of GC-MC-ICP-MS have reported significant isotope ratio drift across peaks,[6] hampering accurate and precise measurement. In gas chromatography the retention times of the different isotopologues of a molecule can differ, causing isotope ratio drift. Additionally MC-ICP-MS analysis of short transient signals can result in isotope ratio drift, due to different tau responses on the Faraday cup amplifiers assigned to each isotope. A mechanism to correct for isotope ratio drift, based on a linear relationship between isotope ratio and the rate of signal change,[7–9] was necessary.

Data (from Thermo Scientific™ Multi Collector Software SP 3.2.1.15) analysis was performed using an in-house data processing application, "GC Neptune Evaluation", produced on the Shiny™ platform from R-Studio™. Each chromatographic peak was identified through retention time. The background signal was ideally determined from 10-20 points directly preceding each peak, but in practice that was not always possible due to the complex GC spectra. In this case the nearest background area was selected.

Corrections for isotope ratio drift were determined and applied within selected areas (Figure 5).
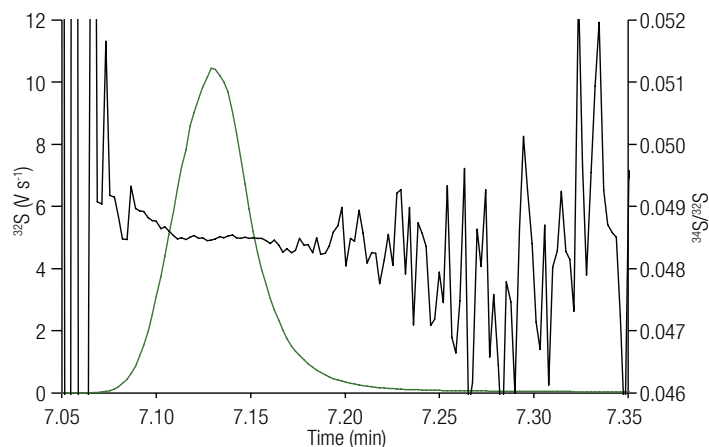

Figure 5. Isotopic drift corrected ^{34}S/^{32}S ratio across a hexyl sulfide chromatographic peak.

In order to calibrate and report the raw isotope ratios in the conventional $\delta^{34}S_{VCDT}$ notation, the $\delta^{34}S_{VCDT}$ values of each of the four external standards, 3-hexylthiophene (4.14±0.66‰), hexyl sulfide (4.71±0.47‰), dibenzothiophene (13.74±0.19‰) and 1-octadecanethiol (6.63±0.13‰), were determined against calibrated reference materials (IAEA-S-1, IAEA-S-2 and IAEA-S-3) by EA-IRMS using the Thermo Scientific™ EA IsoLink™ IRMS System. The calibrated $\delta^{34}S_{VCDT}$ EA-IRMS values were plotted against the corresponding GC-MC-ICP-MS values to produce a normalization curve (Figure 6). The resulting external correction was used in combination with the added 3-hexylthiophene internal standard to calculate calibrated $\delta^{34}S_{VCDT}$ results for each compound identified within the crude oil samples.
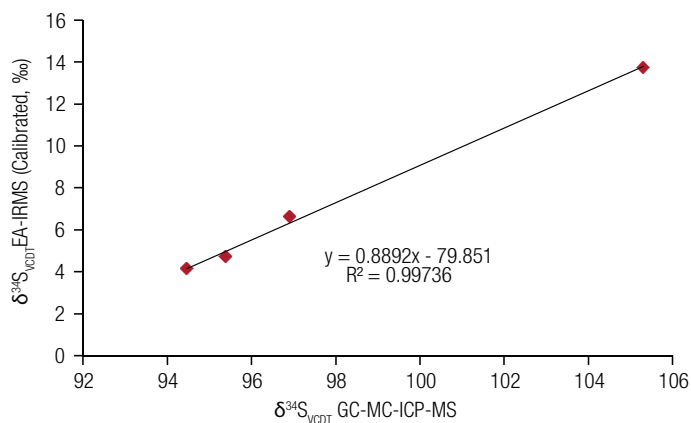

Figure 6. $\delta^{34}S_{VCDT}$ normalization curve for GC-MC-ICP-MS produced from four external standard materials.

Results

The GC-MC-ICP-MS chromatogram for Bryan Mount crude oil was representative of all 4 crude oil samples (Figure 7). Crude oil is a challenging matrix, containing numerous sulfur-containing compounds. However, alongside the internal standard, 11 major component peaks were identified for each sample (12 for Saudi Medium).
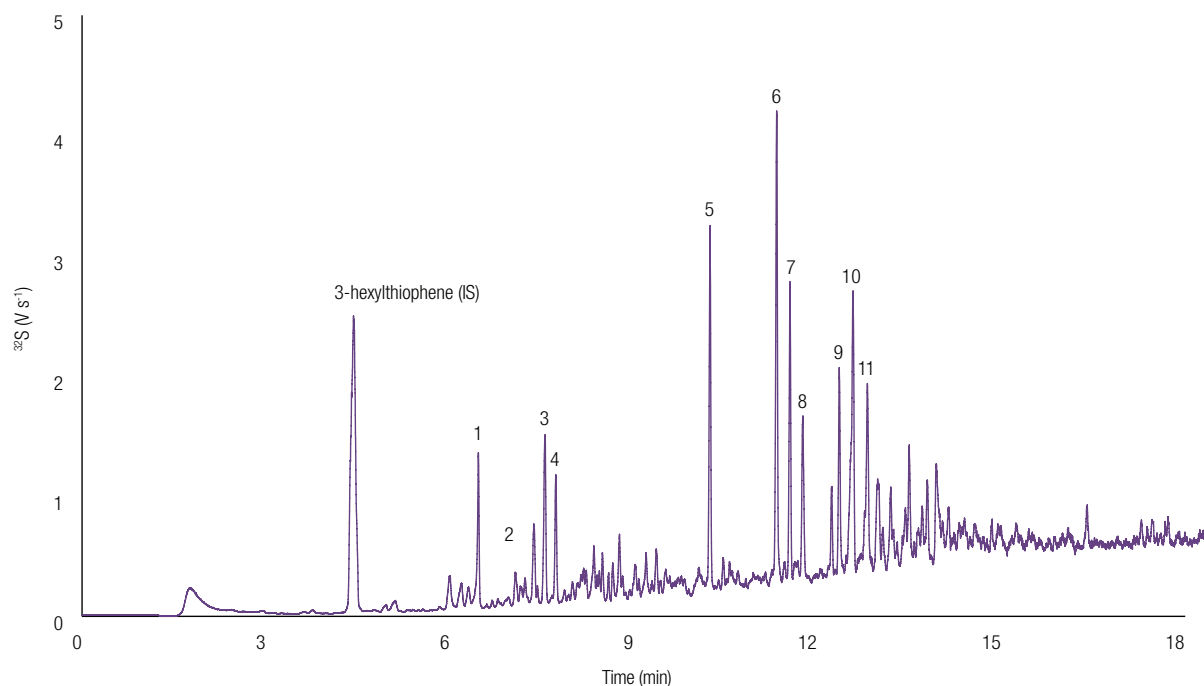

Figure 7. ³⁴S Chromatogram of Bryan Mount crude oil and 3-hexylthiophene internal standard. $\delta^{34}S_{VCDT}$ values determined for 11 major peaks.

Only one of the peaks (number 5, dibenzothiophene) could be identified by comparing its retention time to the standard. Compounds with retention times longer than dibenzothiophene were likely also dibenzothiophenes, containing additional alkyl groups at postitions C1-C4. Conversely, compounds with retention times less than dibenzothiophene were expected to be either benzothiophenes or alkyl-thiophenes. Therefore, the δ^{34}S values of peaks 1–4 were compared to peak 5–11 as potential evidence of a thermochemical sulfate reduction. A shift of between 2–3‰ (Table 2) was observed for all four crude oils, significant, but insufficient to suggest a major thermochemical sulfate reduction had occurred.

Individual peaks exhibited larger shifts in δ^{34}S, over 5‰ between peak 2 and peak 10 for Saudi Light (Figure 8). The distribution of δ^{34}S values were similar for each crude oil, suggesting a strong correlation between sulfur isotopic composition and the organic molecular structure of each compound.

Table 2: Average δ^{34}S$_{VCD}$T (‰) values of five replicates for 11 major peaks within 4 crude oil samples. Each peak was identified by retention time.

Peak	Bryan (‰) Mount δ^{34}S$_{VCDT}$	Basrah (‰) Light δ^{34}S$_{VCDT}$	Saudi (‰) Light δ^{34}S$_{VCDT}$	Saudi (‰) Medium δ^{34}S$_{VCDT}$
1	5.32 ± 1.71	-7.82 ± 0.69	0.01 ± 0.11	-4.63 ± 0.37
2	2.97 ± 0.38	-8.45 ± 0.80	1.38 ± 0.47	-4.78 ± 0.46
3	4.84 ± 0.98	-8.89 ± 0.46	-0.93 ± 0.21	-6.03 ± 0.20
4	4.79 ± 0.50	-8.93 ± 0.60	-0.87 ± 0.29	-5.74 ± 0.38
5	2.33 ± 0.22	-9.87 ± 0.35	-2.42 ± 0.41	-6.99 ± 0.27
6	1.42 ± 0.43	-10.93 ± 0.37	-3.62 ± 0.17	-8.49 ± 0.22
7	2.16 ± 0.42	-10.41 ± 0.16	-3.42 ± 0.45	-7.97 ± 0.26
8	2.79 ± 0.39	-9.77 ± 0.61	-1.97 ± 0.42	-6.92 ± 0.27
9	0.79 ± 0.24	-11.34 ± 0.48	-3.93 ± 0.27	-8.92 ± 0.45
10	1.36 ± 0.14	-11.53 ± 0.72	-4.41 ± 0.18	-9.23 ± 0.15
11	2.55 ± 0.48	-10.87 ± 0.35	-3.09 ± 0.23	-8.07 ± 0.26

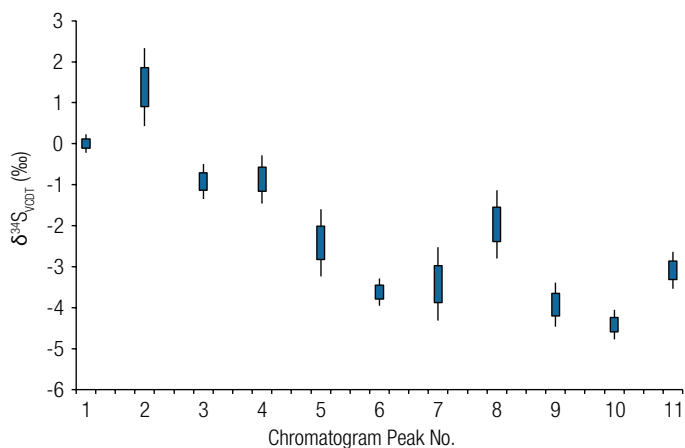Figure 8. Boxplot of δ^{34}S$_{VCDT}$ for 11 major peaks in Saudi Light crude oil. Box denotes 1σ, line 2σ, distribution.

The different geological source of each crude oil was reflected in their δ^{34}S compound values. The $\delta^{34}$$_{SVCDT}$ (2σ) of dibenzothiophene could be used to identify each crude oil (Figure 9).
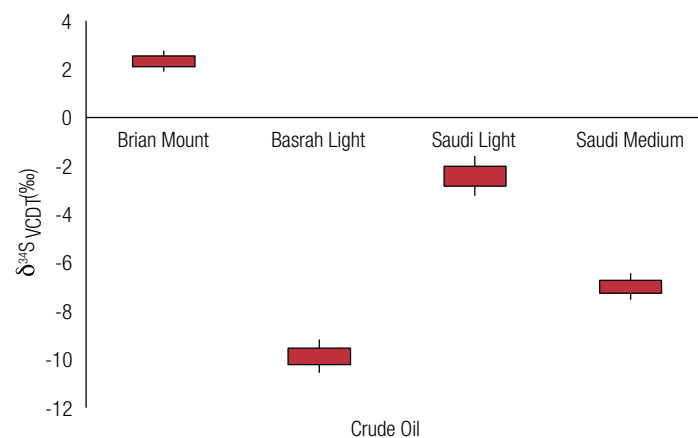

Figure 9. Boxplot of δ^{34}S$_{VCDT}$ of dibenzothiophene in four different crude oils. Box denotes 1σ, line 2σ distribution.

Conclusion

The GCI 300 interface was successfully applied to the isotopic analysis of sulfur containing compounds in crude oil. Highly reproducible, compounds could be identified via retention time, improving confidence in speciation analysis.

GC-MC-ICP-MS can provide evidence of both the source of crude oil samples, and evidence of thermochemical sulfate reduction reactions in the paleoenvironment.

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