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Short communication

Gas chromatographic sulphur speciation in heavy crude oil using a modified standard D5623 method and microfluidic Deans switching

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ABSTRACT

A modification to American Society for Testing and Materials (ASTM) method D5623 is proposed to enable successful and repeatable analysis of heavy crude oil samples. A two-dimensional gas chromatography configuration was implemented, with separation of sulphur compounds occurring on two columns. A Deans switch is used to enable heart-cutting of volatile sulphur compounds onto a DB-Sulfur stationary phase, and separation occurs concurrently with the backflushing of the primary column. The use of a sulphur-selective detector increases selectivity, and 22 volatile sulphur species are quantified in less than 15 min, which is almost half the time of the original ASTM method. Samples ranging from light distillation cuts to whole crudes (boiling from 100 °C to >750 °C) were analyzed with minimal sample preparation. The calculated limit of detection was 0.7 mg/kg, repeatability was 3% relative standard deviation (RSD), and a linear range of 1–250 mg/kg was obtained, with an R^2 value of 0.994 or better, depending on the compound.

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1. Introduction

The need for accurate characterization of sulphur compounds in petroleum samples is well known, due to desulphurization requirements for the production of low and ultra-low sulphur transportation fuels. Sulphur content in crudes can impact market prices, and high sulphur is considered to be undesirable in downstream processing [1–3]. Sulphur compounds can be aggressive catalyst poisons [4–6], affecting the efficiency of some petroleum refining processes. From an environmental point of view, sulphur released as emissions can upset surrounding ecosystems [2,5,7], and easily liberated hydrogen sulphide (H_2S) can be toxic at very low concentrations [8,9].

The oil and gas industry is currently faced with challenges when characterizing petroleum, as the need for analysis has progressed from lighter, lower boiling samples to heavier, higher boiling crudes. Gas chromatography (GC) remains as one of the best techniques to speciate hydrocarbon compounds in crude samples, owing to its high separation efficiencies and quick analysis times. In recent years, both GC [10–12] and two-dimensional GC (GC × GC) [12–15] have been employed for the analysis of sulphur species in crude oil. However, GC methods are often limited by boil-

ing point, and chemists are now challenged to analyze heavy oil samples using established standard methods that were designed for conventional or light oil samples. As more heavy petroleum reserves are being developed across the world, methods capable of analyzing higher boiling oil samples are becoming even more important, especially since heavier crudes generally have higher sulphur content [16,17].

ASTM method D5623, *Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection*, is a useful and widely adopted method for separating and quantifying sulphur species in samples with boiling points under 230 °C [18,19]. The ASTM method uses a methylsilicone stationary phase, sulphur-selective detection and cryogenic cooling to separate and quantify volatile sulphur compounds. In order to apply this approach to crudes that boil above 230 °C, the two-dimensional methodology developed in our previous work was adapted to enable analysis of multiple sulphur species in heavy crudes [20,21]. The use of two columns, backflushing, and selective heart-cutting Deans switching allows for repeatable analysis of heavy crudes; the benefits and mechanics of this approach have been previously described, and will not be repeated here [21–25].

While there have been some recently published papers reporting analysis of sulphur using microfluidics and multiple GC columns [21,24], the present method is designed specifically to apply ASTM D5623 to higher boiling crudes, with no additional information sought. The implementation of this adaptation is relatively sim-

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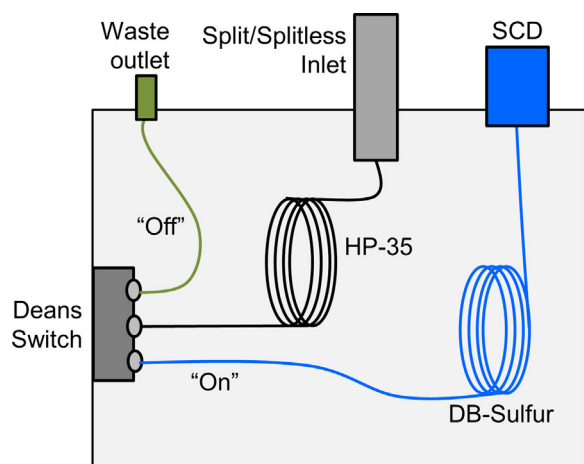


Fig. 1. Configuration of columns in the GC oven. When the Deans switch is in the “On” position, gas flow carries through the HP-35 column to the DB-Sulfur column, and finally to the SCD detector. When the Deans switch is in the “Off” position, gas flow exits to waste, preventing contamination of the DB-Sulfur column with high-boiling hydrocarbons. A fused silica capillary connects the Deans switch to the waste outlet. SCD: sulphur chemiluminescence detector.

ple, requiring only one single detector and one microfluidics flow switching device, without cryogenic cooling. Other similar work may generate more information, with the use of two microfluidic devices and two detectors, but is inherently more complex and difficult to implement, with a longer analysis time [24]. Analysis of lower boiling samples (IBP (initial boiling point) -200°C) by the present method has shown that it is not limited to higher boiling oils, and could replace the original ASTM method in labs where a wide range of sample types are analyzed.

Herein, the method is described in detail, with results shown for both calibration standards and oil samples. Repeatability, limits of detection, and limits of quantification are reported. Limitations of the method are discussed, along with the benefits of the chromatographic system design.

2. Materials and methods

An Agilent 7890 gas chromatograph was used in this work. The instrument was equipped with a split-splitless inlet, a Deans switch with pneumatics control module (Agilent, PN G2855A), and a Sievers 355 sulphur chemiluminescence detector (SCD) (Agilent, Mississauga, ON, Canada). System control and data analysis were performed using Agilent's ChemStation software, version B.04.01.

The oven was run under a temperature program, starting at 35°C with a hold time of 2 min, and then ramped at $25^{\circ}\text{C}/\text{min}$ to 250°C . A temperature of 250°C was then held for 5 min, followed by a 15 min post-run backflush at 250°C . Diluted samples were injected at a volume of $1\ \mu\text{L}$, with a 6 s viscosity delay, into a split-splitless inlet at 250°C , with a split ratio of 20:1. The primary column was an HP-35 column (Agilent, Mississauga, ON, Canada) with dimensions of $30\ \text{m} \times 320\ \mu\text{m} \times 0.25\ \mu\text{m}$, and the secondary column was a DB-Sulfur column (Agilent, Mississauga, ON, Canada) with dimensions of $40\ \text{m} \times 320\ \mu\text{m} \times 0.75\ \mu\text{m}$. The oven configuration is illustrated in Fig. 1, where the HP-35 is connected between the inlet and the Deans switch, the DB-Sulfur column is connected to the Deans switch and SCD, and a fused silica capillary connects the second Deans switch outlet to a waste port. The Deans switch was set to the “Off” position, and programmed to turn to the “On” position between 1.5 and 9.5 min. Helium was used as the carrier gas and the system was run in constant flow mode, with the HP-35 column at $4.9\ \text{mL}/\text{min}$ and the DB-Sulfur column at $7.5\ \text{mL}/\text{min}$.

Table 1
Characteristic retention times of sulphur standards under the defined conditions.

#	Compound	Retention time (min)
1	Hydrogen sulphide/carbonyl sulphide	2.91
2	Methyl mercaptan	3.18
3	Ethyl mercaptan	3.61
4	Dimethyl sulphide	3.72
5	Carbon disulphide	3.87
6	Isopropyl mercaptan	3.96
7	Tert-butyl mercaptan	4.24
8	N-propyl mercaptan	4.43
9	Ethyl methyl sulphide	4.48
10	Sec-butyl mercaptan	5.00
11	Isobutyl mercaptan	5.12
12	Thiophene	5.17
13	Diethyl sulphide	5.38
14	n-butyl mercaptan	5.54
15	Dimethyl disulphide	6.29
16	2-methyl thiophene	6.47
17	3-methyl thiophene	6.53
18	Ethyl disulphide	8.05
19	Benzothiophene	10.80
20	5-methyl benzothiophene	11.61
21	3-methyl benzothiophene	11.69
22	Diphenyl sulphide	14.05

Samples were prepared by diluting the oil samples with toluene (HPLC grade, Fisher Chemicals, Fairlawn, NJ, USA) at a ratio of approximately 12:1 (toluene:oil) by weight. This ratio was found to be sufficient to reduce the viscosity for injection via an autosampler; any dilution that is appropriate for the sample may be used. The samples analyzed ranged from naphtha distillation cuts (IBP– 200°C) to whole crudes, with final boiling points (FBP) exceeding 750°C . Retention times and detector response were calibrated using ASTM D5623 standards from DCG Partnership (Pearland, TX, USA), and from o2si Smart Solutions (Charleston, SC, USA). The standards from DCG Partnership were used as-is (concentrations were approximately $100\ \text{mg}/\text{kg}$), and the standard from o2si Smart Solutions was diluted with toluene from the stock concentration of $2000\ \text{mg}/\text{kg}$ to $100\text{--}150\ \text{mg}/\text{kg}$. In cases where peak identity needed to be confirmed by a single compound standard, sulphur standards from Sigma-Aldrich (Oakville, ON) were used, prepared in toluene at a concentration of approximately $100\ \text{mg}/\text{kg}$.

3. Results and discussion

In order to separate volatile sulphur compounds in higher boiling crude oils, the use of backflushing is necessary. When two columns are used with a device capable of backflushing, such as a Deans switch, separation of desired light boiling components can occur on the secondary column, while undesired high boilers can be pushed off the head of the primary column [26]. In this work, an HP-35 column was used as the primary column, and a DB-Sulfur column was used as the secondary column (Fig. 1). DB-Sulfur is a stationary phase specifically manufactured for the separation of sulphur compounds, and is an ideal choice for the D5623 method, especially when paired with an SCD. The use of the HP-35 column, with the (35%–phenyl)–methyl polysiloxane stationary phase, provided the best separation of early eluting sulphur compounds when paired with the DB-Sulfur column. The moderate polarity of the HP-35 column is not necessarily orthogonal to the polydimethylsiloxane in the DB-Sulfur, but enhances and improves separation of the more polar sulphur species. In order to transfer the sulphur species to the secondary column, it is necessary to program the Deans switch to switch into the “On” position for an appropriate amount of time. If one wishes to extend the range of compounds analyzed, the Deans switch timing points only need to be increased to a larger window. This approach was shown to be successful in our

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