Video Article

Measurement of H_2S in Crude Oil and Crude Oil Headspace Using Multidimensional Gas Chromatography, Deans Switching and Sulfur-selective Detection

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Abstract

A method for the analysis of dissolved hydrogen sulfide in crude oil samples is demonstrated using gas chromatography. In order to effectively eliminate interferences, a two dimensional column configuration is used, with a Deans switch employed to transfer hydrogen sulfide from the first to the second column (heart-cutting). Liquid crude samples are first separated on a dimethylpolysiloxane column, and light gases are heart-cut and further separated on a bonded porous layer open tubular (PLOT) column that is able to separate hydrogen sulfide from other light sulfur species. Hydrogen sulfide is then detected with a sulfur chemiluminescence detector, adding an additional layer of selectivity. Following separation and detection of hydrogen sulfide, the system is backflushed to remove the high-boiling hydrocarbons present in the crude samples and to preserve chromatographic integrity. Dissolved hydrogen sulfide has been quantified in liquid samples from 1.1 to 500 ppm, demonstrating wide applicability to a range of samples. The method has also been successfully applied for the analysis of gas samples from crude oil headspace and process gas bags, with measurement from 0.7 to 9,700 ppm hydrogen sulfide.

Video Link

The video component of this article can be found at https://www.jove.com/video/53416/

Introduction

Accurate analysis of crude oil is essential for the oil and gas industry, as health and safety regulations and economics are functions of oil quality. In order to protect transporters of crude samples, it is necessary to determine the properties of crude samples to develop safety regulations to be implemented in the event of a release or spill. In particular, quantification of hydrogen sulfide (H_2S) is important, due to its high toxicity in the gas phase; exposures as low as 100 ppm can be fatal (http://www.cdc.gov/niosh/idlh/7783064.html)[1,2]. Dissolved H_2S in crude samples is generally considered to be corrosive[3,4], and can deactivate catalysts used to treat the oil[5-7]. Removal of H_2S from crude oil streams is ideal, but without a method to measure dissolved H_2S, it is difficult to assess the success of removal treatments. For these reasons, this protocol was developed to measure dissolved H_2S in heavy crude oil samples such as Canadian oil sands crudes.

A number of standard methods exist for quantification of H_2S in lighter petroleum or fuel based samples, but none have been validated for use with the heavier crudes commonly extracted from the Canadian oil sands. H_2S and mercaptans are determined using a titration technique by Universal Oil Products (UOP) method 163[8], but this method suffers from user-interpretation bias that results from manual reading of titration curves. Institute of Petroleum (IP) method 570 uses a specialty H_2S analyzer that heats fuel oil samples[9], and benefits from simplicity and portability, but lacks accuracy with heavier samples[10]. The American Society for Testing and Materials (ASTM) method D5623 uses gas chromatography (GC) with cryogenic cooling and sulfur selective detection to measure H_2S in light petroleum liquids[11,12]. This standard could be improved to use an ambient separation and also be applied to heavier crude oils, therefore it was used as the basis for the protocol discussed herein.

GC is a heavily used technique for the analysis of petroleum samples. Samples are vaporized in a hot inlet, and separations occur in the gas phase. The gas phase separation makes GC ideal for the analysis of H_2S, as it is easily liberated from the liquid sample during heating in the inlet. GC methods can be created and tailored for different samples, depending on the temperature programs used, columns implemented, and the use of multidimensional chromatography[13-15]. There have been a number of recent developments for the measurement of H_2S using GC. Luong *et al.* demonstrated H_2S and other light sulfur compound measurement in light and middle distillates using multidimensional GC and Deans switching, but the method has not yet been applied to heavier crudes[16]. Di Sanzo *et al.* also quantified H_2S in gasoline using GC, however it also has not been used on heavier crudes, and requires sub-ambient cooling[17]. The method presented here demonstrates considerable time saving over these previous methods, with a completed analysis time of 5 min, compared to 10 min (Luong) and 40 min (Di Sanzo). Unfortunately, implementation of these methods in our lab to compare accuracy was not possible due to equipment and time restrictions.

Multidimensional GC allows the user to exploit the selectivity of two columns, rather than a single column. In conventional GC, separation occurs on one column. In the case of multidimensional GC, the sample is separated on two different columns, enhancing the separation and selectivity. The Deans switch is one device used to employ a two-dimensional column configuration. The switch uses an external valve to direct gas flow from an inlet on the switch to one of two outlet ports[18-20]. Effluent from the first column can be directed in either direction; in this case, light sulfur gases are “heart cut”[21] from the first separation to a porous layer open tubular (PLOT) column for secondary separation, which has been shown to be excellent for the separation of H_2S from other light sulfur gases (http://www.chem.agilent.com/cag/cabu/pdf/gaspro.pdf)[22-24]. A sulfur chemiluminescence detector is used for detection, providing selectivity for sulfur compounds and eliminating possible interference from any other light gases that may have been transferred to the PLOT column during the heart cut. Hydrocarbons from the crude oil sample are retained on the first dimension column and are removed during a backflush procedure; this protects the PLOT column from any contamination[25-27]. This approach has also been successfully implemented for the analysis of oxidation inhibitors in transformer oils[28].

Herein, a two-dimensional GC method is employed for the analysis and quantification of dissolved H_2S in heavy crude oil samples. The method is shown to be applicable over a wide range of H_2S concentrations, and can also be used to measure H_2S in gas phase samples.

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS) for materials before using. In particular, CS_2 is highly flammable and should be stored and handled appropriately. H_2S gas is highly toxic, and any containers or gas bags containing H_2S should not be opened or handled outside of a properly vented fumehood. Work with crude oil samples should only be done with full personal protective equipment (gloves, safety glasses, lab coat, pants and closed-toe shoes), and all crude samples should be opened, transferred and handled in a fumehood. Certified gas standards will be delivered from the manufacturer with an expiry date, and for the most accurate results care should be taken to use standards that have not expired.

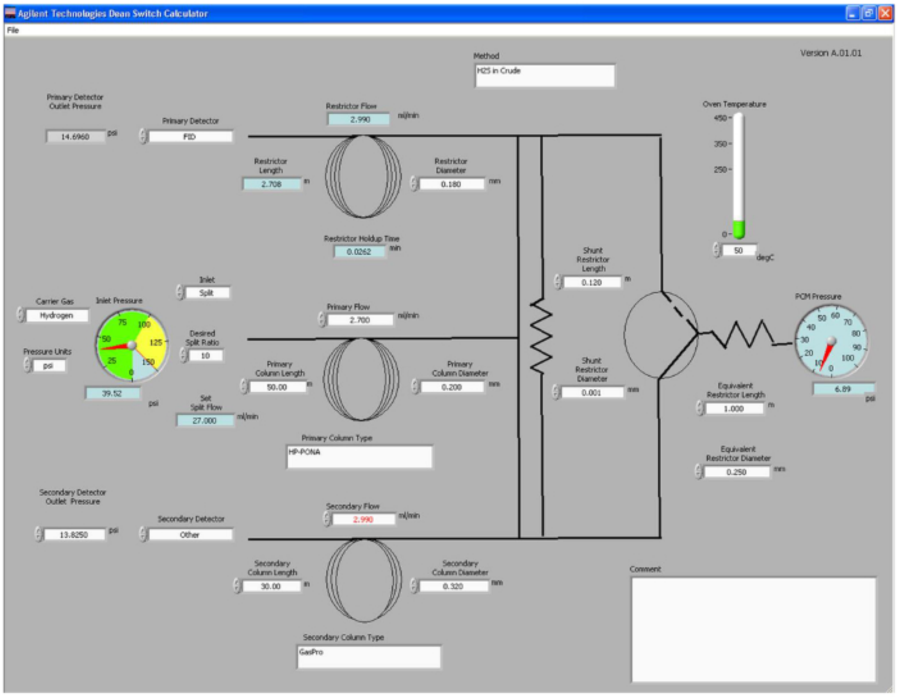
1. Preparation of Standards

1. Liquid standards
    1. Using an automatic pipette, dispense 10 µl of carbon disulfide (CS_2) into a 50 ml volumetric flask. Fill the volumetric flask to the marked line with HPLC (high performance liquid chromatography) grade toluene. Cap the flask and mix the solution by inverting and swirling a minimum of five times; this is the 500 ppm stock calibration solution.
    2. On each day of analysis, prepare four vials of CS_2 for calibration. Label four 1.5 ml autosampler vials and place them in a vial tray.
    3. Using an automatic pipette, dispense 200 µl of the 500 ppm stock CS_2 solution into each vial. Using a second automatic pipette, dispense 800 µl of HPLC grade toluene into each of the four vials. Cap each vial immediately after dispensing the CS_2 and toluene, and invert three times to mix; these are the 100 ppm calibration standards.

2. Gas standards
    1. Move a gas cylinder of certified calibration gas to a vented fumehood, and attach a regulator that is fitted for attachment to a gas bag.
    2. Open the nozzle on an empty gas bag and attach the gas bag to the regulator on the gas cylinder.
    3. With the regulator closed, open the gas cylinder by turning the knob on top counterclockwise.
    4. Turn the knob on the regulator counterclockwise until a steady flow of gas fills the gas bag. When the gas bag is full, turn the regulator knob clockwise to shut off the gas flow.
    5. Close the nozzle on the gas bag and detach it from the regulator. Close the gas cylinder by turning the knob on top clockwise. Open the regulator to purge any remaining gas and release pressure, closing it again when the regulator no longer has any gas it in it.

2. Instrument Set-up

1. Method parameters
    1. Using the following procedure, configure the Deans switch according to the columns installed in the gas chromatograph, as each system will have unique pressure settings.
    2. Open a Deans switch calculator program on a computer, and input the column dimensions, carrier gas, temperature, desired flow rates and detectors used (see **Figure 1**).The calculator will define the pressures needed for the inlet and pressure control module (PCM), and the length of restrictor tubing needed for installation between the Deans switch and the flame ionization detector (FID). Note these pressures and input them into the method file.
    3. Using the information from the Deans switch calculator and the information in **Table 1**, program the method file with the correct parameters for either gas or liquid analysis. Save the method file.



Method: H2S in Crude
Primary Detector Outlet Pressure: 14.6960 psi
Primary Detector: FID
Restrictor Flow: 2.990 ml/min
Restrictor Length: 2.708 m
Restrictor Diameter: 0.180 mm
Restrictor Holdup Time: 0.0262 min
Oven Temperature: 50 degC
Shunt Restrictor Length: 0.120 m
Inlet: Split
Carrier Gas: Hydrogen
Inlet Pressure: 39.52 psi
Pressure Units: psi
Desired Split Ratio: 10
Set Split Flow: 27.000 ml/min
Primary Flow: 2.700 ml/min
Primary Column Length: 50.00 m
Primary Column Diameter: 0.200 mm
Shunt Restrictor Diameter: 0.001 mm
PCM Pressure: 6.89 psi
Equivalent Restrictor Length: 1.000 m
Equivalent Restrictor Diameter: 0.250 mm
Primary Column Type: HP-PONA
Secondary Detector Outlet Pressure: 13.8250 psi
Secondary Detector: Other
Secondary Flow: 2.990 ml/min
Secondary Column Length: 30.00 m
Secondary Column Diameter: 0.320 mm
Secondary Column Type: GasPro
Comment:

Figure 1. Deans switch calculator. Screenshot of the Deans switch calculator program. User-adjustable parameters are shown in white boxes, and output parameters are shown in blue boxes. Please click here to view a larger version of this figure.

2. Column installation
    1. Ensure that the instrument, oven and inlet are at RT. Turn off the gas flow to the inlet and PCM supplying flow to the Deans switch.
    2. Following the manufacturer's instructions, install the dimethylpolysiloxane column between the split/splitless inlet and the Deans switch, the PLOT column between the Deans switch and the sulfur chemiluminescence detector (SCD), and the restrictor tubing (length determined in step 2.1.2) between the Deans switch and the FID.
    3. Using the gas chromatograph software, turn on the carrier gas flow to the inlet and PCM, and test the system for leaks by passing an electronic leak detector in close proximity of the fittings at the end of each column and at the Deans switch; leaks are indicated by a light and/or sound notification on the detector.
        1. If leaks are present, gently tighten fittings and re-test with the electronic leak detector. Close the oven door and turn on the gas chromatograph oven and inlet heater.

    4. Perform a bake-out of the columns and restrictor tubing by increasing the oven temperature to the upper temperature limit of the PLOT column (found on the column documentation); allow the oven to sit at this temperature for a minimum of 3 hr.
    5. When the bake-out is complete, cool the oven to RT and re-test the connections inside the oven for gas leaks with the electronic leak detector, tightening where necessary.
    6. Load the pre-programmed method file using the software controlling the gas chromatograph; the instrument is ready for analysis.

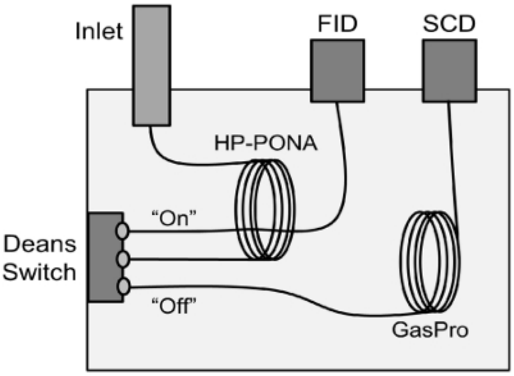


Figure 2. Gas chromatograph oven. Configuration of the column arrangement in the GC oven. FID: flame ionization detector, SCD: sulfur chemiluminescence detector. Please click here to view a larger version of this figure.

3. Determining proper Deans switch timing
    1. As the Deans switch is controlled by a valve in the gas chromatograph; locate the valve timing point section in the method parameters. In the software, set the switch to "on", and create time events for the valve that controls the Deans switch, beginning with the valve

turning "off" at 0.5 min, and a second event that turns the valve "on" again at 3.0 min. The "off" position in this description corresponds to the direction in which column effluent will be carried to the SCD.

2. Place a gas bag containing the calibration gas (known amount of H_2S in helium) in the fumehood, and place a rubber nipple or equivalent penetrable cover on the nozzle of the gas bag. Open the nozzle on the gas bag.
3. Using a 250 µl gas-tight glass syringe, puncture the rubber nipple on the top of the bag and withdraw 250 µl of calibration gas. Cap the syringe with an inlet septa, and transport the syringe to the gas chromatograph.
4. Remove the septa cap from the syringe; manually and swiftly inject the calibration gas into the gas chromatograph, simultaneously starting the software acquisition. The H_2S will appear as a peak on the SCD signal trace; record the retention time of this peak. .
5. Begin decreasing the time of the heart-cut window, one side at a time (*i.e.,* decrease the valve "on" event by 0.1 min for sequential injections); continue in this manner until the H_2S peak disappears from the chromatogram. Add 0.2 min to this time and note it as the upper limit of the heart-cut window.
6. Perform the same procedure on the lower end of the time window, gradually increasing the time of the valve "off" event for sequential injections until the peaks are no longer visible. Subtract 0.2 min from this time and note it as the lower limit of the heart-cut window.
7. Save the valve "on"/"off" commands into the method file.

3. Instrument Calibration

1. Liquid
    1. Ensure that a liquid autosampler is installed on the split/splitless inlet of the gas chromatograph. Place the four previously prepared calibration vials in vial positions 1-4 on the autosampler tray.
    2. Using a glass pipette, fill a vial with HPLC grade toluene and place it in the vial position for the wash solvent on the autosampler tray. Ensure that the waste vial or reservoir on the autosampler tray is empty.
    3. Load the method configured for liquid phase analysis on the software connected to the gas chromatograph; ensure that both detectors are turned on and that the gas chromatograph is in a ready state.
    4. Use the gas chromatograph software to perform one injection per vial according to the method, and integrate the CS_2 peak in each chromatogram using the software provided with the gas chromatograph.
    5. Using a spreadsheet program, calculate an average response factor for the SCD by dividing the area counts of the CS_2 peak by the concentration of the calibration solution (100 ppm), and then dividing this by two to give response per one atom of sulfur.

2. Gas
    1. Ensure that the liquid autosampler tower has been removed from the gas chromatograph, and load the appropriate method for gas analysis. Ensure that both detectors are turned on, and that the gas chromatograph is in a ready state.
    2. Inject the calibration gas as described in steps 2.3.2 to 2.3.4.
    3. Repeat the manual injection of calibration gas a minimum of three times.
    4. Use the gas chromatograph data analysis software to integrate the H_2S peaks in the three injections and, using a spreadsheet program, calculate an average response factor for H_2S by dividing the average area of the H_2S peaks by the concentration of H_2S in the gas bag.

4. Sample Analysis

1. Liquid
    1. Assess crudes for injection by transferring a small amount (<1 ml) with a glass pipette. If the crude is transferred with no significant residue left in the glass pipette, the crude can be injected neat. If the crude leaves a significant amount in the glass pipette, dilute as described in 4.1.2. For crudes that can be injected neat, transfer ~1 ml of the crude into a gas chromatograph autosampler vial, and cap the vial.
    2. Dilute high viscosity crudes by transferring 0.75 ml of crude with an automatic pipette to an autosampler vial, and adding an equal volume of HPLC grade toluene. Cap and invert the vial with shaking to adequately mix the solution.
    3. Place the filled vials in the autosampler tray, and load the liquid analysis method on the gas chromatograph software.
    4. Using the gas chromatograph software and the previously configured method (**Table 1**), use the automatic sampler to perform three replicate injections per vial.

2. Gas
    1. Headspace
        1. Fill a 500 ml amber glass bottle with 450 ml of the crude to be analyzed. Attach a septum-topped cap to the top of the bottle. Perform any crude transfer steps in a vented fumehood.
        2. Place the bottle(s) to be analyzed in a temperature controlled environment (*i.e.,* a water bath at 30 °C). Note: Crude oil samples may become volatile at elevated temperatures and care should be exercised depending on the samples used.
        3. Using a 1 ml glass gas tight syringe, puncture the septum top and leave the syringe in the top of the bottle to provide an avenue for pressure release if the gas in the headspace should build up.
        4. Leave the bottle(s) in the temperature controlled environment for 24 hr, gently lifting and shaking the bottles once an h to equilibrate the H_2S between the liquid and headspace.
        5. To analyze the headspace gas, puncture the septum top and withdraw µl of gas into a gas tight glass syringe.
        6. Cap the syringe end with a piece of inlet septa and transport the syringe to the gas chromatograph. Manually and swiftly inject the gas into the inlet, simultaneously starting the software to begin data collection.

    7. Repeat this procedure to obtain a minimum of three replicate injections of gas. If the H_2S peak is too concentrated and not on the scale of the detector (see **Figure 3**), perform the procedure with a smaller syringe of gas to bring the peak on scale; *i.e.,* 100 µl or 25 µl.

2. Gas bags
    1. Place a rubber nipple or equivalent penetrable cover on the nozzle of the gas bag to be analyzed, and place the gas bag in a vented fumehood.
    2. Ensure the correct method for gas analysis is loaded on the gas chromatograph software, and that the gas chromatograph is in the ready state.
    3. Open the nozzle on the gas bag, and puncture the top of the nipple with a 250 µl gas tight syringe. Fill the syringe with 250 µl of gas, withdraw the syringe, and close the nozzle on the gas bag.
    4. Cap the syringe end with a piece of inlet septa and transport the syringe to the gas chromatograph, and manually inject the gas into the inlet, simultaneously starting the software to begin data collection.
    5. Repeat this procedure to obtain a minimum of three replicate injections of gas. If the H_2S peak is too concentrated and is not on the scale of the detector (see **Figure 3**), perform the procedure with a smaller syringe of gas to bring the peak on scale; *i.e.,* 100 µl or 25 µl.

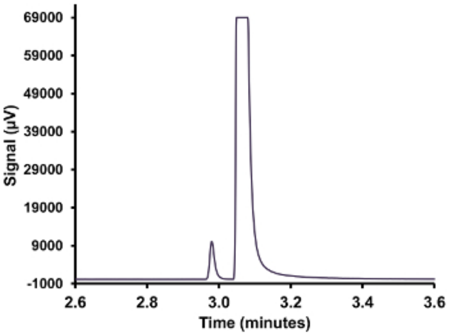


Figure 3. A gas chromatogram with an overloaded H_2S peak. A gas injection from the headspace of a liquid crude sample held at 30 °C, demonstrating an overloading of the SCD. Please click here to view a larger version of this figure.

5. Data Analysis

1. Liquid
    1. Determining H_2S peak retention time (only needs to be repeated if instrument configuration changes)
        1. Use a glass pipette to fill a GC autosampler vial with a liquid crude that does not require dilution and cap the vial.
        2. Load the appropriate method for liquid analysis on the gas chromatograph software, and ensure the liquid autosampler tower is installed.
        3. Place the liquid crude sample in the autosampler tray, and perform one injection of the crude.
        4. Fill a glass gas-tight syringe with 750 µl of H_2S-containing gas (2.5% in helium). Remove the vial from the autosampler tray and puncture the septa on the cap of the vial with the syringe filled with gas, and place the end of the syringe below the surface of the sample in the vial. Depress the plunger on the syringe to bubble the gas through the crude sample.
        5. Place the vial back in the autosampler tray and use the software to direct the autosampler to perform a single injection of the spiked sample.
        6. Using the software accompanying the gas chromatograph, compare the chromatograms before and after the H_2S spike. A large peak should be present in the second chromatogram that was not present in the first chromatogram; record the retention time of this peak (see **Figure 4**).
    2. Analysis
        1. Use the data analysis software accompanying the gas chromatograph to integrate the peak area for H_2S (identify using the retention time noted in step 5.1.1.6) in each chromatogram (**Figure 5**), and calculate the average peak area for each sample with a spreadsheet program.
        2. Using the response factor determined in Section 3.1, divide the average peak area for the sample by the response factor to give the amount of H_2S present in ppm. For samples that were diluted, multiply the concentration by the correct dilution factor to give the amount of H_2S in the undiluted sample (**Figure 6**).

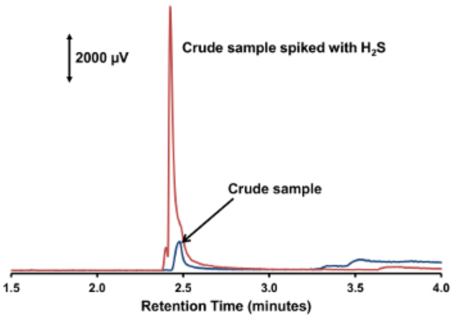
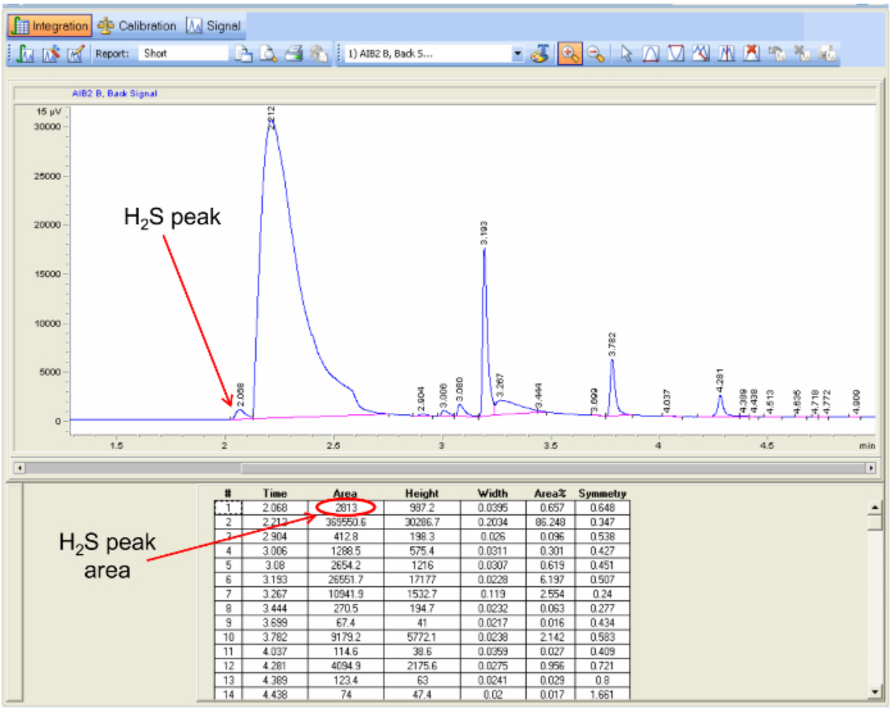
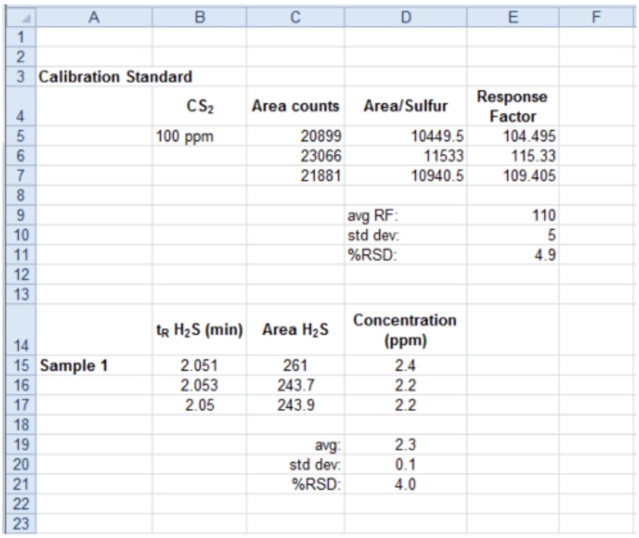


Figure 4. Crude sample spiked with H_2S. Two overlaid chromatograms illustrating the change expected when spiking a crude sample with H_2S. Please click here to view a larger version of this figure.



#	Time	Area	Height	Width	Area%	Symmetry
1	2.068	2813	987.2	0.0395	0.657	0.648
2	2.212	369550.6	30286.7	0.2034	86.248	0.347
3	2.904	412.8	198.3	0.026	0.096	0.538
4	3.006	1288.5	575.4	0.0311	0.301	0.427
5	3.08	2654.2	1216	0.0307	0.619	0.451
6	3.193	26551.7	17177	0.0228	6.197	0.507
7	3.267	10941.9	1532.7	0.119	2.554	0.24
8	3.444	270.5	194.7	0.0232	0.063	0.277
9	3.699	67.4	41	0.0217	0.016	0.434
10	3.782	9179.2	5772.1	0.0238	2.142	0.583
11	4.037	114.6	38.6	0.0359	0.027	0.409
12	4.281	4094.9	2175.6	0.0275	0.956	0.721
13	4.389	123.4	63	0.0241	0.029	0.8
14	4.438	74	47.4	0.02	0.017	1.661

Figure 5. Gas chromatogram data analysis. A screenshot of a data analysis program highlighting the location of an H_2S peak in a sample and the peak area to be used to determine the concentration of H_2S. Please click here to view a larger version of this figure. Please click here to view a larger version of this figure.



	A	B	C	D	E	F
1						
2						
3	**Calibration Standard**					
4		**CS_2**	**Area counts**	**Area/Sulfur**	**Response Factor**	
5		100 ppm	20899	10449.5	104.495	
6			23066	11533	115.33	
7			21881	10940.5	109.405	
8						
9				avg RF:	110	
10				std dev:	5	
11				%RSD:	4.9	
12						
13						
14		**t_R H_2S (min)**	**Area H_2S**	**Concentration (ppm)**		
15	**Sample 1**	2.051	261	2.4		
16		2.053	243.7	2.2		
17		2.05	243.9	2.2		
18						
19			avg:	2.3		
20			std dev:	0.1		
21			%RSD:	4.0		
22						
23						

Figure 6. Sample spreadsheet for data analysis. A screenshot of a spreadsheet program showing an example of how to calculate the concentration of H_2S using the area of the calibration standard peak and the area of the sample peak. Please click here to view a larger version of this figure.

2. Gas
    1. Identify the H_2S peak in each chromatogram by matching the retention time of the H_2S peak used to calibrate in Section 3.2.
    2. Use the data analysis software accompanying the gas chromatograph to integrate the peak area for each H_2S peak in the collected data, and calculate the average peak area for each sample.
    3. Using the response factor determined in Section 3.2, divide the average peak area for the sample by the response factor to give the amount of H_2S present in ppm. For samples that used a smaller syringe volume, multiply the concentration by the correct dilution factor to give the amount of H_2S that would be present in a 250 µl syringe (*i.e.,* (250 µl/25 µl for a 25 µl syringe).

Representative Results

In order to obtain reliable quantification of H_2S for both liquid and gas samples, proper calibration is necessary. For calibration injections and sample injections, the H_2S peak should not be overlapping with neighboring peaks and should have a reproducible peak area. **Figure 3** shows an injection of a gas sample where the gas is too concentrated for this method. It was found that gas concentrations of greater than 500 ppm using a 250 µl syringe overloaded the detector. This issue was not encountered for liquid samples, as gas phase concentrations of H_2S were generally much higher than in the liquid. The overloading issue was addressed by injecting a smaller volume of gas. It was found that adjusting other parameters such as split ratio degraded the chromatographic performance, whereas smaller injection volumes were the most reproducible. For both liquid and gas injections the first injection often had a different peak area than the three subsequent injections, and was regularly discarded. The SCD was also calibrated at the beginning of each day of analysis.

Figures 7 and **8** illustrate typical chromatograms achieved using this method. The H_2S peak is close to, but does not coelute with, neighboring peaks. Other peaks in the chromatograms were not identified, as the focus of the protocol was H_2S. Proper timing and balancing of the Deans switch is essential for achieving and maintaining good separation and chromatography of H_2S. An improperly timed switch will be indicated by small, variable peak areas, or intermittent loss of peaks. If pressures are not balanced properly, the H_2S gas will be split between both detectors, or will not be heart cut properly to the PLOT column, resulting in an absence of peaks. Backflushing occurs after the separation, and should not interfere with H_2S measurement. Regular blank injections of toluene should indicate no carryover or system contamination.

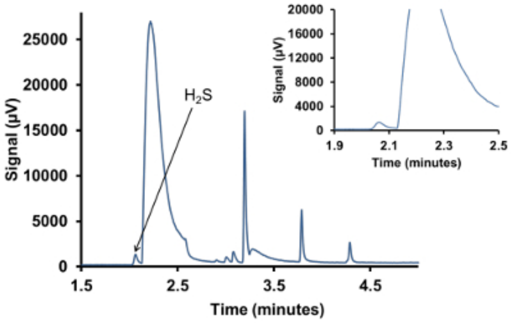


Figure 7. Representative liquid crude chromatogram. A chromatogram of a liquid crude sample that contains 26.3 ppm of dissolved H_2S. The H_2S peak is identified with an arrow. Please click here to view a larger version of this figure.

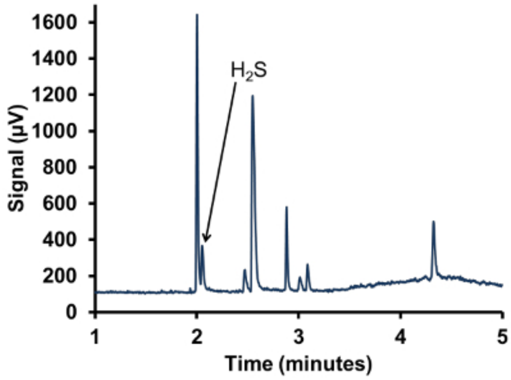


Figure 8. Representative gas chromatogram. A chromatogram of a gas sample taken from the headspace of a liquid crude sample held at 30 °C. The arrow identifies the H_2S peak; this gas sample contains 9.03 ppm of H_2S. Please click here to view a larger version of this figure.

	Carrier gas		H_2
Oven			

	Oven program		50 °C for 2 min, then 100 °C/min to 250 °C for 1 min
	Run time		5 min
	Post run*		250 °C for 16 min
Split-Splitless Inlet			
	Liner		Deactivated glass wool
	Mode		Split
	Temperature		250 °C
	Pressure		40 psi
	Total flow[§]		30.778 ml/min
	Septum purge flow		1 ml/min
	Split ratio[#]		10:1
HP-PONA Column			
	Initial pressure		40 psi
	Flow		2.7071 ml/min
	Pressure program		40 psi for 5 min
	Post run *		1 psi for 16 min
GasPro column			
	Initial pressure		6.89 psi
	Flow		2.9859 ml/min
	Pressure program		6.89 psi for 5 min
	Post run*		39.405 psi for 16 min
Fused silica transfer line			
	Initial pressure		6.89 psi
	Flow		5.1837 ml/min
	Pressure program		6.89 psi for 5 min
	Post run*		39.405 psi for 16 min
FID			
	Temperature		250 °C
	H_2 Flow		40 ml/min
	Air flow		450 ml/min
	Makeup flow		20 ml/min
Deans switch			
	Off		0.7 min
	On		2.3 min
Liquid autosampler*			
	Syringe size		10 µl
	Injection volume		1 µl
	Pre-injection washes		1
	Post-injection washes		2
	Wash volume/sample wash volume		8 µl
	Sample washes		2
	Sample pumps		6
	Solvent/sample wash draw speed		300 µl/min
	Solvent/sample wash dispense speed		6,000 µl/min

	Injection dispense speed		6,000 µl/min
	Viscosity delay		6 sec
* Omitted for gas analysis			
§ 111.99 ml/min for gas analysis			
# 40:1 for gas analysis			

Table 1. Gas chromatograph method parameters for both liquid and gas analysis.

Discussion

In order to achieve optimum measurement of H_2S, this method employs a Deans switch, backflushing and a sulfur chemiluminescence detector (SCD). A dimethylpolysiloxane column is used as the first dimension GC column, and serves to retard the movement of heavier hydrocarbons present in the sample so that they do not contaminate the PLOT column. This effect is enhanced by a cool (50 °C) initial separation. Light gases pass through the first dimension column and are captured by the PLOT column during the heart-cut for further separation. The SCD only responds to compounds containing sulfur, adding an additional layer of selectivity, and preventing interference by any hydrocarbons or other light gases[29,30]. The column configuration used in this method is shown in **Figure 2**. The use of the PLOT column makes backflushing essential when injecting liquid crude samples. During the backflush, the columns are heated and gas flow is reversed out the inlet, removing hydrocarbons from the column and preventing their transfer to the PLOT column during subsequent injections[25-27]. The process of backflushing will result in a buildup of material in the inlet liner of the GC, and the liner will require cleaning and/or replacement approximately every 50 injections. Regular blank injections indicated that no sample carryover occurred between injections, and monitoring of chromatographic performance showed that hydrocarbon contamination was not an issue for the PLOT column. The limits of detection and quantification for this method were calculated using the signal/noise relationship of blank samples[31]. For gas samples, the limits of detection and quantification were calculated to be 0.2 ppm and 0.6 ppm, and 0.5 ppm and 1.6 ppm for liquid samples, respectively. The liquid values are comparable to the limits of quantification listed for standard methods ASTM D5623[11] and UOP 163[8] (1.0 ppm), and somewhat greater than IP 570[9] (0.5 ppm).

H_2S is a light gas that will easily escape to the ambient air. When working with gas bags, they need to be monitored for leaks, and emptied and refilled when the area of the calibration peaks begins to change between day-to-day analyses. For this same reason, vials of crude oil for analysis were prepared on the day of, and not reused for a second day to mitigate evaporative losses. Obtaining the lowest relative standard deviation (%RSD) for manual injection also depends on user technique. Consistent practice using a gas tight syringe to manually inject samples improved %RSD for samples to consistently achieve <10% variation for samples, and <5% variation for standard calibration. Retention time variation was less than 1% for manual injection. When generating response factors for quantitation, a new response factor should be calculated on each day of analysis. While this limits the number of analyses that can be completed in a day, it was found to be optimal for the best accuracy, as instrument response varied by up to 10% over extended periods of use. Liquid samples that are diluted may require optimization; in our sample set, a 1:1 dilution with toluene was sufficient to preserve the H_2S, but any greater dilution resulted in a loss of the H_2S peak. The CS_2 stock solution used for liquid calibration was stored at ambient temperature in a flammable storage cabinet, and was found to produce a consistent response over 6 months of use. The use of CS_2 as a calibration standard is possible because the SCD provides a uniform response toward sulfur, and any stable sulfur-containing compound can be used.

Programming and balancing the Deans switch can present a challenge. The use of available software for determining inlet and PCM pressures greatly reduces the time required to implement switching (**Figure 1**). Prior to optimizing the heart-cut window, it was useful to inject the gaseous H_2S calibration standard directly through the columns with no heart-cutting. This gave a baseline to which performance could be compared, and the H_2S peak area after heart-cut optimization was compared to the peak area without heart cutting to ensure the peak was fully captured. This process should be done with a pure gas standard, and not with a spiked liquid crude, as contamination of the PLOT column with hydrocarbons will degrade chromatographic performance[24]. The system can also be modified from that recommended in this study. Other hydrocarbon columns have been successfully used in place of the 100% polydimethylsiloxane column, and helium as a carrier gas has been implemented as well. It is also possible to install short (<60 cm) fused silica connectors between the columns and the detectors if so desired; using 0.250 mm inner diameter fused silica reduces any additional backpressure, and does not require modification of the method.

The method described herein demonstrates the applicability of Deans switching for the analysis of targeted compounds in heavy crude oil. It is expected that the principle of this experiment could be applied to the analysis of other light gases present in crude oil, especially when the use of a selective detector is practical. To the best of our knowledge, this method is the only available technique that is capable of accurately measuring dissolved H_2S in heavy crudes, and that does not employ the use of sub-ambient cooling. Samples ranging in density from 0.74 to 0.94 g/ml were analyzed without difficulty. Dissolved H_2S was successfully quantified from 1.1 - 500 ppm in liquid samples, and gas phase H_2S was quantified from 0.7 - 9,700 ppm. It is hoped that this work will serve as an excellent complement to previously established methods whose focus is on lighter crude oil streams and fuels.

Disclosures

The authors have nothing to disclose.

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References

1. Guidotti, T. L. Hydrogen sulphide. *Occ. Med.* **46**, 367-371 (1996).
2. Reiffenstein, R. J., Hulbert, W. C., & Roth, S. H. Toxicology of Hydrogen Sulfide. *Annu. Rev. Pharmacol. Toxicol.*, 109-134 (1992).
3. Qi, Y. *et al.* Effect of Temperature on the Corrosion Behavior of Carbon Steel in Hydrogen Sulphide Environments. *Int. J. Electrochem. Sci.* **9**, 2101-2112 (2014).
4. Ma, H. *et al.* The influence of hydrogen sulfide on corrosion of iron under different conditions. *Corros. Sci.* **42**, 1669-1683 (2000).
5. Kallinikos, L. E., Jess, A., & Papayannakos, N. G. Kinetic study and H_2S effect on refractory DBTs desulfurization in a heavy gasoil. *J. Catal.* **269**, 169-178 (2010).
6. Liu, B. *et al.* Kinetic investigation of the effect of H_2S in the hydrodesulfurization of FCC gasoline. *Fuel.* **123**, 43-51 (2014).
7. Si, X., Xia, D., Xiang, Y., & Zhou, Y. Effect of H_2S on the transformation of 1-hexene over NiMoS/γ-Al_2O_3 with hydrogen. *J. Nat. Gas Chem.* **19**, 185-188 (2010).
8. *UOP 163-10, Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration.* ASTM International, West Conshohocken, PA (2010).
9. *ASTM D7621-10, Standard Test Method for Determination of Hydrogen Sulfide in Fuel Oils by Rapid Liquid Phase Extraction.* ASTM International, West Conshohocken, PA (2010).
10. Lywood, W. G., & Murray, D. H_2S in Crude Measurement Report. *Canadian Crude Quality Technical Association.* March 21, (2012).
11. *ASTM D7621-10, Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection.* ASTM International, West Conshohocken, PA (2009).
12. Liu, W., & Morales, M. *Detection of Sulfur Compounds According to ASTM D5623 in Gasoline with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) and an Agilent 7890A Gas Chromatograph.* Agilent Technologies, (2008).
13. Barman, B. N., Cebolla, V. L., & Membrado, L. Chromatographic Techniques for Petroleum and Related Products. *Crit. Rev. Anal. Chem.* **30**, 75-120 (2000).
14. Rodgers, R. P., & McKenna, A. M. Petroleum Analysis. *Anal. Chem.* **83**, 4665-4687 (2011).
15. Nizio, K. D., McGinitie, T. M., & Harynuk, J. J. Comprehensive multidimensional separations for the analysis of petroleum. *J. Chromatogr. A.* **1255**, 12-23 (2012).
16. Luong, J., Gras, R., Shellie, R. A., & Cortes, H. J. Tandem sulfur chemiluminescence and flame ionization detection with planar microfluidic devices for the characterization of sulfur compounds in hydrocarbon matrices. *J. Chromatogr. A.* **1297**, 231-235 (2013).
17. Di Sanzo, F. P., Bray, W., & Chawla, B. Determination of the Sulfur Components of Gasoline Streams by Capillary Column Gas Chromatography with Sulfur Chemiluminescence Detection. *J. High Res. Chromatog.* **17**, 255-258 (1994).
18. Deans, D. R. A new technique for heart cutting in gas chromatography. *Chromatographia.* **1**, 18-22 (1968).
19. Hinshaw, J. V. Valves for Gas Chromatography, Part III: Fluidic Switching Applications. *LC GC N. Am.* **29**, 988-994 (2011).
20. Seeley, J. V., Micyus, N. J., Bandurski, S. V., Seeley, S. K., & McCurry, J. D. Microfluidic Deans Switch for Comprehensive Two-Dimensional Gas Chromatography. *Anal. Chem.* **79**, 1840-1847 (2007).
21. Tranchida, P. Q., Sciarrone, D., Dugo, P., & Mondello, L. Heart-cutting multidimensional gas chromatography: A review of recent evolution, applications, and future prospects. *Anal. Chim. Acta.* **716**, 66-75 (2012).
22. Armstrong, D. W., Reid III, G.L., & Luong, J. Gas Separations: A Comparison of GasPro™ and Aluminum Oxide PLOT Columns for the Separation of Highly Volatile Compounds. *Curr. Sep.* **15**, 5-11 (1996).
23. Ellis, J., Vickers, A. K., & George, C. Capillary Column Selectivity and Inertness for Sulfur Gas Analysis in Light Hydrocarbon Streams by Gas Chromatography. *Fuel Chemistry Division Preprints.* **47**, 703-704 (2002).
24. Ji, Z., Majors, R. E., & Guthrie, E. J. Porous layer open-tubular capillary columns: preparations, applications and future directions. *J. Chromatogr. A.* **842**, 115-142 (1999).
25. Luong, J., Gras, R., Shellie, R. A., & Cortes, H. J. Applications of planar microfluidic devices and gas chromatography for complex problem solving. *J. Sep. Sci.* **36**, 182-191 (2013).
26. Hildmann, F., Kempe, G., & Speer, K. Application of the precolumn back-flush technology in pesticide residue analysis: A practical view. *J. Sep. Sci.* **36**, 2128-2135 (2013).
27. Gray, B. P., & Teale, P. The use of a simple backflush technology to improve sample throughput and system robustness in routine gas chromatography tandem mass spectrometry analysis of doping control samples. *J. Chromatogr. A.* **1217**, 4749-4752 (2010).
28. Hayward, T., Gras, R., & Luong, J. Characterization of selected oxidation inhibitors in transformer oils by multidimensional gas chromatography with capillary flow technology. *Anal. Methods.* **6**, 8136-8140 (2014).
29. Hutte, R. S., Johansen, N. G., & Legier, M. F. Column Selection and Optimization for Sulfur Compound Analyses by Gas Chromatography. *J. High Res. Chromatog.* **13**, 421-426 (1990).
30. Yan, X. Unique selective detectors for gas chromatography: Nitrogen and sulfur chemiluminescence detectors. *J. Sep. Sci.* **29**, 1931-1945 (2006).
31. Araujo, P. Key aspects of analytical method validation and linearity evaluation. *J. Chromatogr. B.* **877**, 2224-2234 (2009).