

# A Unified Approach for the Measurement of Individual or Total Volatile Organic Sulfur Compounds in Hydrocarbon Matrices by Dual-Plasma Chemiluminescence Detector and Low Thermal Mass Gas Chromatography

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## Abstract

A novel gas chromatographic technique has been developed, offering dual-analytical capability of either speciation or rapid measurement of total volatile sulfur compounds in hydrocarbon matrices using the same hardware. The technique employs a pressurized liquid injection system for the delivery of volatile liquid hydrocarbons, low thermal mass gas chromatography, and a dual-plasma sulfur chemiluminescence detector to enable this dual capability with a high degree of sensitivity and selectivity towards sulfur-containing compounds. Using the technique described, a detection limit in the range of 20 ppb sulfur and less than 30 s analysis is attained. Response is linear over five orders of magnitude, with a high degree of repeatability.

## Introduction

The analysis of trace sulfur in hydrocarbons is crucial in the petrochemical and chemical industries. At low levels, sulfur compounds create odor problems; at high level, they can be highly corrosive and hazardous. Many hydrocarbon products such as ethane, propane, propylene, butane, and 1,3-butadiene have specifications on the maximum allowable level of sulfur (1,2).

Common approaches in analyzing sulfur-containing compounds in hydrocarbons have been made using selective detectors such as the flame photometric detector and its variants, the atomic emission detector, the amperometric sulfur detector, the differential mobility detector, and the sulfur chemiluminescence detector.

A novel analytical technique has been developed, which combines advanced sample introduction technique, such as the pressurized liquid injection system (PLIS) with low thermal mass gas

chromatography (LTMGC) and the proven, highly selective, and sensitive dual plasma sulfur chemiluminescence detector (DP-SCD) for the measurement of individual volatile sulfur compounds in hydrocarbons. By using appropriate experimental conditions, the versatility of this hardware can be leveraged to measure total volatile sulfur compounds (total sulfur) with a high degree of accuracy. This report summarizes the results obtained.

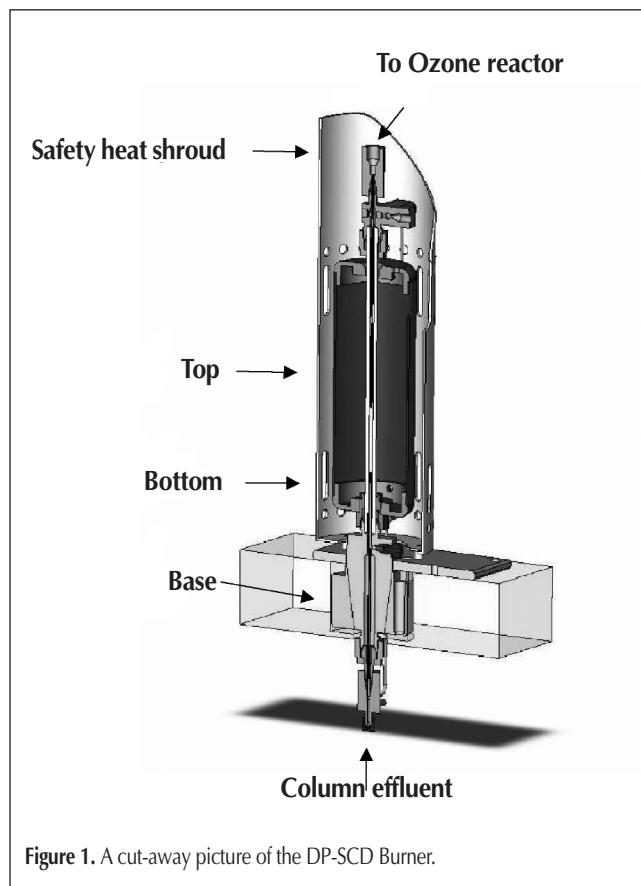


Figure 1. A cut-away picture of the DP-SCD Burner.

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## Experimental

An Agilent HP-6890N gas chromatograph (Wilmington, DE) equipped with two split/splitless injectors, a flame ionization detector, and a DP-SCD (Agilent Technologies, Boulder, CO) was used for the application development. A RVM LTM-68A LTMGC

**Table I. Equi-Molar Response and Short-term Precision for Volatile/Semi-Volatile Sulfur Compounds Analysis by PLIS-LTMGC-DP-SCD ( $n = 10$ )**

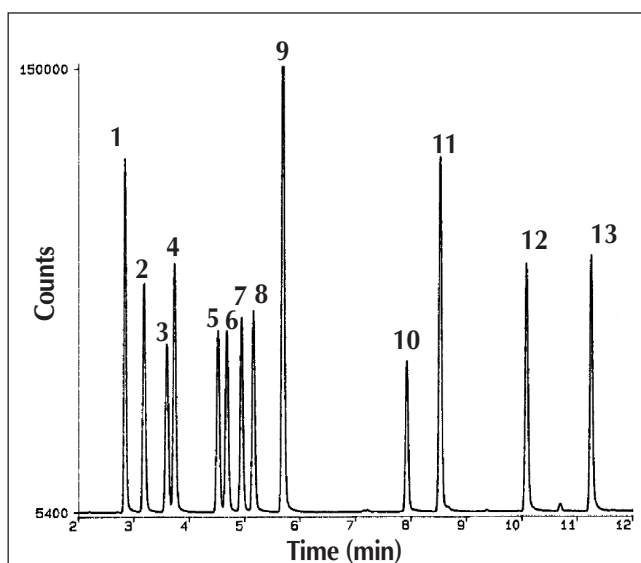
ID*	RT (min) <sup>†</sup>	ppm wt Sulfur	%RSD <sup>‡</sup>	EQM <sup>§</sup>
1	2.84	263	1.01	1.01
2	3.18	213	1.42	1.00
3	3.59	171	0.99	1.01
4	3.73	213	0.89	1.01
5	4.51	178	1.08	1.03
6	4.67	178	0.89	1.02
7	4.94	179	1.12	1.02
8	5.15	180	1.25	1.03
9	5.69	429	1.13	1.00
10	7.92	137	2.12	1.02
11	8.52	314	1.12	1.00
12	10.08	242	1.12	0.99
13	11.25	270	1.08	0.98

\* 1, Dimethyl sulfide; 2, Isopropyl mercaptan; 3, Tert-butyl mercaptan; 4, Propyl mercaptan; 5, Sec-butyl mercaptan; 6, Iso-butyl mercaptan; 7, Diethyl sulfide; 8, Butyl mercaptan; 9, Dimethyl disulfide; 10, Dipropyl sulfide; 11, Diethyl disulfide; 12, Diisopropyl disulfide; 13, Dipropyldisulfide.

<sup>†</sup> Retention time

<sup>‡</sup> % Relative Standard Deviation

<sup>§</sup> Equi-Molar Response



**Figure 2.** The detection of sulfur compounds by PLIS-LTMGC-DP-SCD. Peak numbers are: 1, Dimethyl sulfide; 2, Isopropyl mercaptan; 3, Tert-butyl mercaptan; 4, Propyl mercaptan; 5, Sec-butyl mercaptan; 6, Iso-butyl mercaptan; 7, Diethyl sulfide; 8, Butyl mercaptan; 9, Dimethyl disulfide; 10, Dipropyl sulfide; 11, Diethyl disulfide; 12, Diisopropyl disulfide; 13, Dipropyldisulfide.

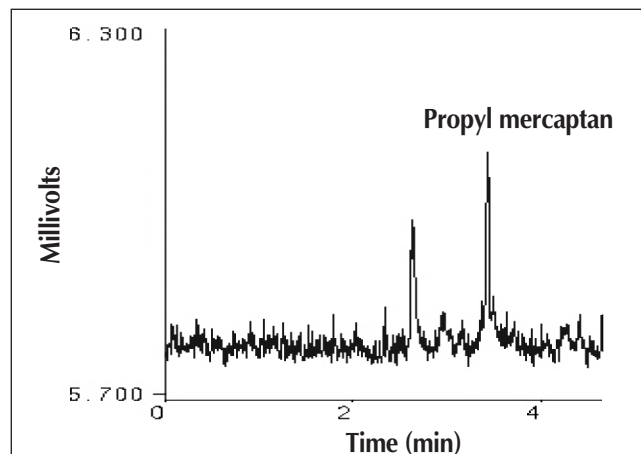
module (RVM Scientific, Santa Barbara, US) was used for the application described. Volatile liquid hydrocarbons such as ethane, ethylene, propylene, propylene, and 1,3-butadiene were introduced into the analytical system by using a PLIS (Transcendent Enterprise, Edmonton, Alberta, Canada). Sulfur standards were obtained from Aldrich Chemicals (Oakville, Ontario, Canada), while solvents used were obtained from Fisher Scientific (Edmonton, Alberta, Canada). Hydrocarbon samples used for the testing were obtained from the local hydrocarbon production plant. For the speciated sulfur measurement, the gas chromatographic conditions used were: 30°C, held for 2 min, increased at 30°C/min to 250°C, and held for 2 min with the injector at 250°C in split mode with a split ratio of 5:1. Separation of solutes was conducted with a 18-m, 0.25-mm i.d., 0.25- $\mu$ m Varian VF-1ms column using helium carrier gas at an average carrier gas linear velocity of 45 cm/s. For the analysis of total sulfur measurement, all conditions were kept the same except the column temperature, which was kept isothermally at 250°C. In both cases, the sample injection size was 2  $\mu$ L.

## Discussions

### PLIS-LTMGC-DP-SCD

While GC is often viewed as a mature technique, significant breakthroughs are being made in areas like sample introduction (such as in the case of PLIS) and high throughput (in the case of low thermal mass gas chromatography).

PLIS proved to be a reliable and practical sample introduction system for volatile liquid hydrocarbons such as ethane, ethylene, propane, propylene, and 1,3-butadiene (3). LTMGC leverages advantages of many of the key fundamental principles in high-speed GC, such as resistive heating, rapid heating and cool-down, and low power consumption, to deliver unsurpassed chromatographic performance. LTMGC as a technology has been described earlier by Luong et al. (4). The capability of rapid heating and cooling time provide LTMGC with the capability to either collapse the separation power of the analytical column in the case of total sulfur analysis, or to maximize its separation in



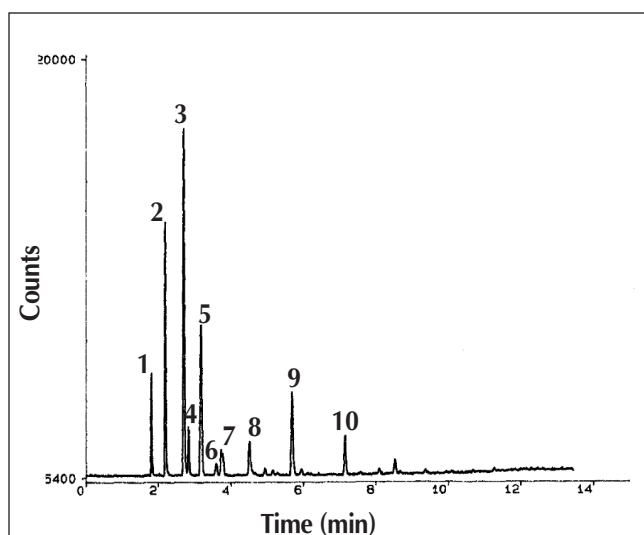
**Figure 3.** A chromatogram of 20 ppb (w/w) of sulfur (from propyl mercaptan) using the analytical system described.

the case where speciation is needed, making the chromatographic application highly flexible.

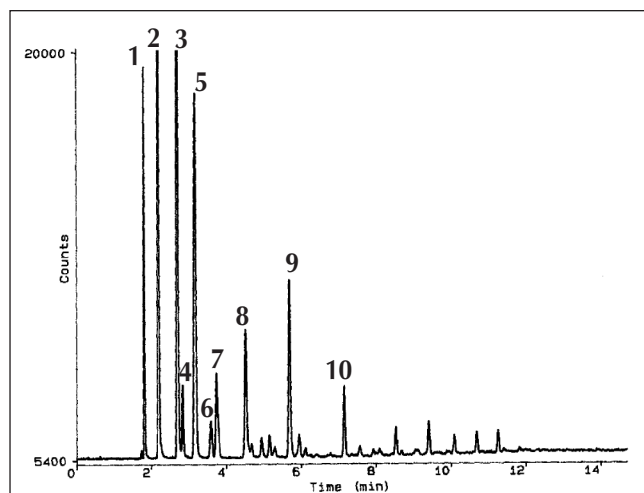
Amongst selective detectors used for sulfur measurements, the sulfur chemiluminescence detector has become widely applied within petroleum, petrochemical, and chemical laboratories. This specific detector has been described previously in detail (5,6).

The high degree of selectivity, sensitivity, equi-molar response, respectable linear dynamic range, and the absence of hydrocarbon interferences of the SCD is well-established (7,8).

Simply stated, detection of sulfur compounds in the SCD is based on a two-step mechanism shown below:



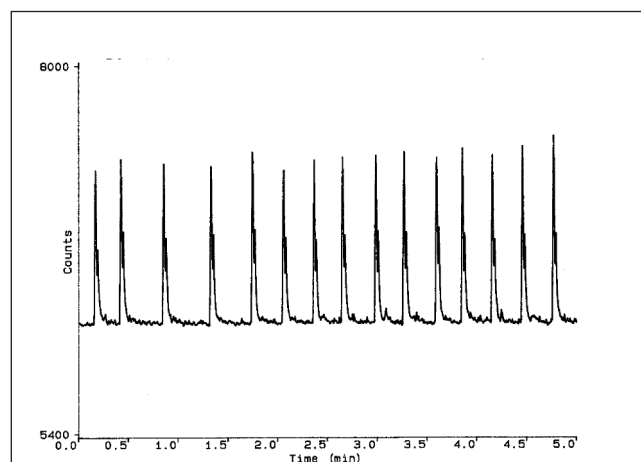
**Figure 4.** Sulfur compounds in C<sub>2</sub>+ hydrocarbons in speciated mode. Peak numbers are: 1, carbonyl sulfide; 2, methyl mercaptan; 3, ethyl mercaptan; 4, dimethyl sulfide; 5, isopropyl mercaptan; 6, tert-butyl mercaptan; 7, propyl mercaptan; 8, sec-butyl mercaptan; 9, diethyl sulfide; 10, dimethyl disulfide.



**Figure 5.** Sulfur compounds in C<sub>3</sub>+ hydrocarbons in speciated mode. Peak numbers are the same as in Figure 4.

In equation 1, sulfur-containing compounds are combusted to sulfur monoxide (SO), sulfur dioxide (SO<sub>2</sub>), and other products. In the second reaction, light energy in the blue region of the spectrum is emitted from the chemiluminescent reaction of SO with ozone.

The mechanism of the dual plasma sulfur chemiluminescence detector (DP-SCD) is basically the same as described earlier, except that two flames are employed instead of one. The purpose of the first flame is to eliminate potentially interfering matrix components. Sulfur combustion products from the first flame are transferred to the second, hydrogen-rich flame. There, sulfur species are converted to sulfur monoxide, which is subsequently detected by its chemiluminescence with ozone (6). In the case of the DP-SCD, a quartz-based heater is enclosed in a low thermal mass metal housing to form the heated portion of the reactor burner. As a safety feature, an outside shroud is used to prevent



**Figure 6.** A chromatogram of 15 successive injections of a 12.3 ppm (w/w) sulfur standard derived from four sulfur compounds: dimethyl sulfide, propyl mercaptan, dimethyl disulfide, and diethyl disulfide at 100°C—Note the partial separation of the compounds.

**Table II. The Concentration of Total Organic Sulfurs Detected in Various Light Hydrocarbon Feed Stocks, Demonstrating the Usefulness of the Technique to Track the Level of Sulfurs in these Streams**

Sample Identification	Number of Runs (n)	ppm (w/w) Sulfur	%RSD
Crude propane			
January 31	10	438	1.9
February 11	10	789	4.6
C2 and heavier hydrocarbons			
January 1	10	119	4.3
February 28	10	336	0.8
C2 and heavier hydrocarbons			
March 1	10	150	2.4
C3 Plus, Shell Scottford, Alberta			
March, 1	10	1.5	3.3

the possibility of accidental burns to the users. A heated block on the base of the reactor burner is used to compensate for the temperature gradient created by temperature programming, or to prevent water condensation from combustion products in the first flame. These improvements lead to the delivery of a detector with enhanced selectivity, and sensitivity for the measurement of lower sulfur levels without hydrocarbons interference.

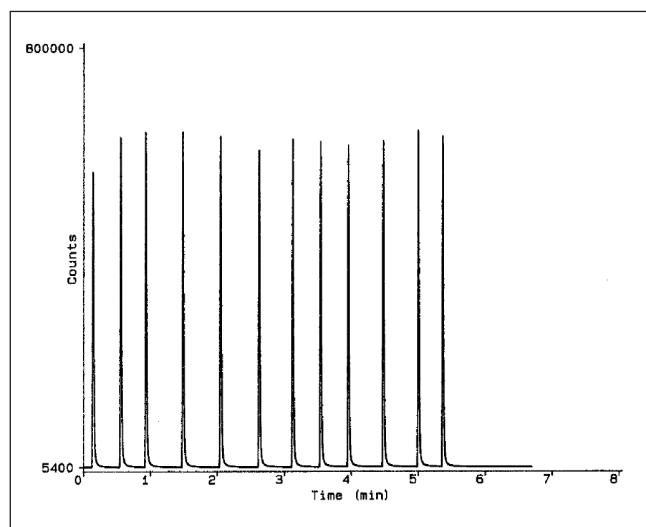
Figure 1 shows a cut-away picture of the reactor with the top and bottom burners clearly illustrated.

### Speciation for sulfur-containing compounds

A mixed sulfur standard of 13 common volatile and semi-volatile sulfur compounds such as mercaptans, sulfides, and disulfides with concentrations ranging from 170 to 300 ppm w/w of sulfur in hexanes was used to demonstrate equi-molar response and short-term precision, as shown in Table I. Clearly, the system demonstrates good short-term precision, with most compounds yielding a relative standard deviation of response less than 2.2% ( $n = 10$ ). In terms of equi-molar response, the results show that the system has less than  $\pm 3\%$  error, meaning sulfur response is equivalent regardless of the molecules involved. This is a highly sought attribute because it allows quantitative measurement of unknown sulfur compounds, or where an exact standard cannot be obtained or is too toxic to use. The equi-molar response simplifies the calibration process. Figure 2 shows a chromatogram of 13 sulfur compounds using the technique described, while Figure 3 shows a chromatogram of a 20 ppb (w/w) sulfur from propyl mercaptan using the system described. Figures 4 and 5 show the presence of various sulfur compounds in different matrices, such as commercially available  $C_2+$  and  $C_3+$  hydrocarbons.

### Analysis for total sulfur in hydrocarbon matrices

With proper optimization of the LTMGC module, it is possible to measure total volatile sulfur as a single discrete peak. Factors affecting peak symmetry include sample size, the degree of volatility of the hydrocarbon matrix, the column used, and the

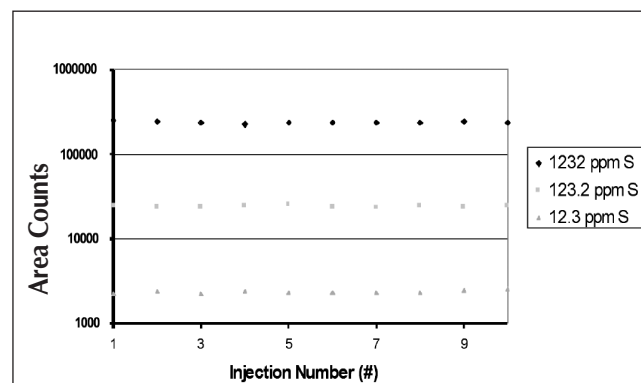


**Figure 7.** A chromatogram of 12 successive injections of 12.3 ppm (w/w) sulfur standard derived from four sulfur compounds: dimethyl sulfide, propyl mercaptan, dimethyl disulfide, and diethyl disulfide at 100°C.

temperature of the module. As an example, the effect of module temperature is illustrated by using a 12.3 ppm (w/w) sulfur standard derived from four sulfur compounds, namely dimethyl sulfide, propyl mercaptan, dimethyl disulfide, and diethyl disulfide. At 100°C, partial separation of these compounds was observed resulting in split peak as shown in Figure 6, while at 250°C, discrete Gaussian peak was achieved as illustrated in Figure 7.

For the measurement of total volatile sulfur, the effect of split ratio of the GC injector was carefully optimized so that no hydrocarbon interference was observed while obtaining maximum selectivity and sensitivity. Under the conditions used, the optimum condition was found to be at 5:1 split ratio. A higher split ratio will not have an impact on selectivity, but will negatively impact system detectability for sulfur. Figure 8 shows a plot of ten injections of 12.3, 123.2, and 1232 ppm (w/w) sulfur. A relative standard deviation of less than 4% was obtained ( $n = 10$ ), illustrating the high degree of reproducibility of the technique. The detection limit obtained from the technique in the total sulfur mode was approximately 20 ppb sulfur for a signal-to-noise ratio of 3:1. Figure 9 shows that a linear response to total sulfur is obtained with the system over a concentration range from 1.2 ppm to 1200 ppm, with a correlation coefficient of greater than 0.9999 and y-intercept basically at zero. A y-intercept at zero reaffirms that there is no positive or negative interference from the hydrocarbon matrix. Figures 10 and 11 show run-to-run repeatability of commercially available crude propane with concentration of total sulfur ca. 440 ppm (w/w) of sulfur and commercially available crude butane with concentration of total sulfur ca. 1.5 ppm (w/w) of sulfur. Note the high throughput nature of the methodology of less than 30 seconds per analysis. In Figure 10, the very slight decrease in response with successive injections was caused by the accumulation of the PLIS valve's Teflon seal debris in the sampling groove, which reduced the mass of sample being injected. This issue was rectified by replacing the prototype non-radius injection stem of the PLIS valve with an improved sampling stem that has a 35° angle radius on the sampling groove. With this modification, respectable precision and reliable performance were attained, as shown in Figure 11.

The high throughput nature of the total sulfur method was found to be quite effective not only for trend analysis, but for



**Figure 8.** Reproducibility of total sulfur over a various range of concentrations.

troubleshooting the performance of an operating plant and to provide a rapid assessment of the presence of organic sulfur compounds in hydrocarbon feed stocks. Table II lists the concentration of organic sulfur compounds detected in various light hydrocarbon feed stocks, demonstrating the usefulness of the technique to track the sulfur levels in these streams.

In addition to the application described, the technique has shown to be quite effective in measuring sulfur in other matrices, such as in the case of tertiary dodecyl mercaptan (TDM) isomers in emulsion polymers. Figure 12 shows a chromatogram of 1000 ppm (w/w) of TDM in iso-octane extract.

Some of the constraints encountered with the method are described in the following. First, because this is a technique based on GC, only sulfur compounds that can be successfully chromatographed are measured. The use of the technique against high molecular weight sulfur compounds with low volatility that might not elute from the column should be

checked with a complementary technique, such as XRF, to ensure that the accuracy of the method has not been compromised. It should be noted, however, that this technique exhibits superior sensitivity when compared to most other sulfur detection methods. A second constraint is that the resolving power of the analytical column must be carefully chosen and optimized for the intended application. For the application described in this paper, an 18-m, 0.25-mm i.d., 0.25- $\mu$ m polydimethyl siloxane column provides an optimum performance in that adequate separation for the individual sulfur compounds can be conducted when speciation is required, yet they can easily be thermally compressed into one discrete peak at 250°C for total sulfur measurement.

The advantage of using the LTMGC approach is that LTM can easily yield speciated or total sulfur (one peak) results without the changes of hardware involved. That is, only the temperature of the GC module is changed for a particular analysis.

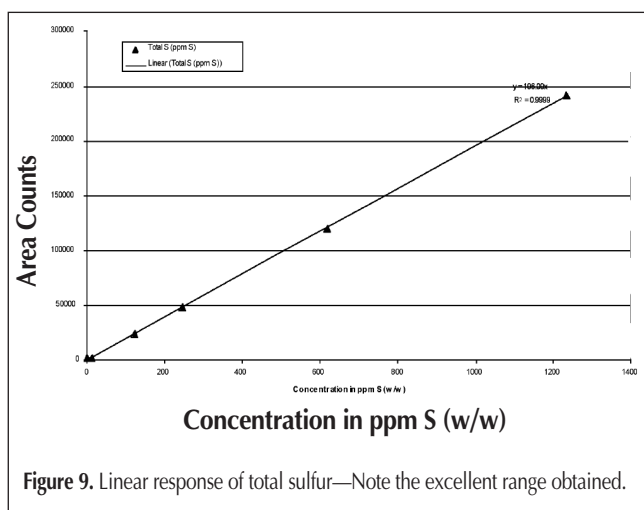


Figure 9. Linear response of total sulfur—Note the excellent range obtained.

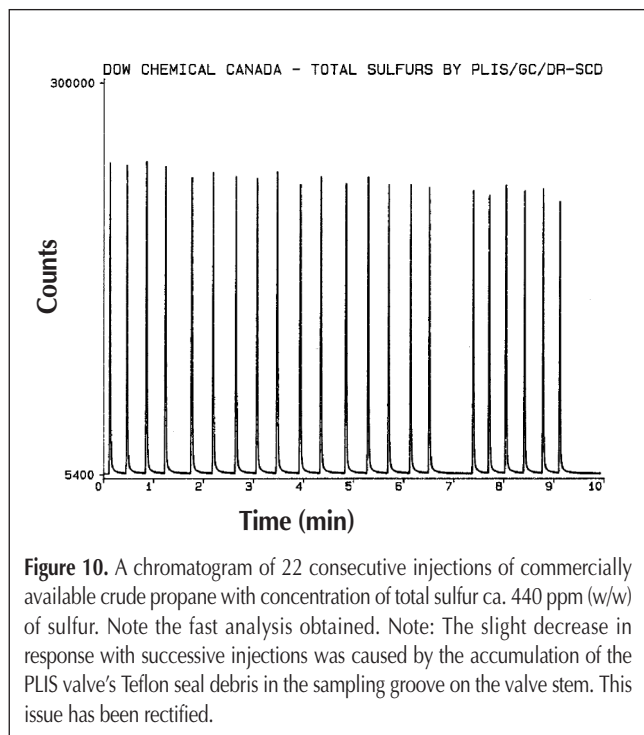


Figure 10. A chromatogram of 22 consecutive injections of commercially available crude propane with concentration of total sulfur ca. 440 ppm (w/w) of sulfur. Note the fast analysis obtained. Note: The slight decrease in response with successive injections was caused by the accumulation of the PLIS valve's Teflon seal debris in the sampling groove on the valve stem. This issue has been rectified.

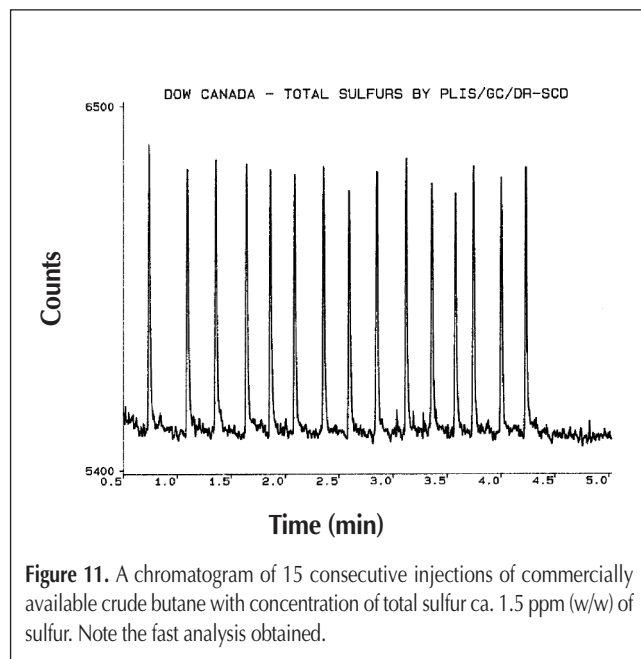


Figure 11. A chromatogram of 15 consecutive injections of commercially available crude butane with concentration of total sulfur ca. 1.5 ppm (w/w) of sulfur. Note the fast analysis obtained.

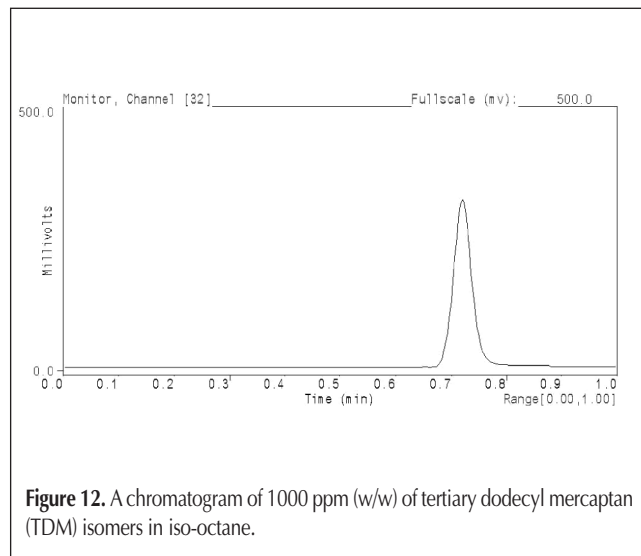


Figure 12. A chromatogram of 1000 ppm (w/w) of tertiary dodecyl mercaptan (TDM) isomers in iso-octane.

## Conclusions

When a highly selective and sensitive sulfur detector, such as the DP-SCD, is combined with LTMGC and an appropriate means for sample introduction, such as the PLIS, a versatile analytical method is created to allow both the speciation and fast detection of total sulfur in hydrocarbon matrices without changing any hardware.

In the total sulfur mode, a complete total sulfur analysis can be conducted in less than 30 s, making the technique ideal for screening hydrocarbon feed stocks, or for plant troubleshooting. There is merit in having a rapid method to determine total volatile organic sulfur in hydrocarbons because speciation is desirable but not always necessary.

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VF-1ms is a trademark of Varian Inc., Middelburg, The Netherlands. LTM is a trademark of RVM Scientific, Santa Barbara, California, USA. PLIS is a trademark of Transcendent Enterprises, Edmonton, Alberta, Canada. Teflon is a trademark of Dupont de Nemours, Wilmington, Delaware, USA.

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