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## Application Note SI-01365

### Analysis of Total Sulfur in Light Petroleum Liquids by GC and Pulsed Flame Photometric Detection

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#### Introduction

The pollution emitted by diesel engines contributes greatly to air quality problems. Therefore, new standards (EPA and others) require a major reduction in the sulfur content of diesel fuels and emission levels from diesel engines and vehicles. To meet the standards, the petroleum industry is producing Ultra Low Sulfur Diesel (ULSD), a cleaner-burning fuel. The move to lower sulfur levels in diesel is global but maximum levels of sulfur allowed in automotive diesel vary in different countries. These levels in general are between 10 and 100 ppm or mg/kg sulfur. The ASTM D 5623 method covers the determination of volatile sulfur-containing compounds in light petroleum liquids.

The test method is applicable to the determination of individual sulfur species at levels of 0.1 to 100 mg/kg. Detector response to sulfur is linear and essentially equimolar for all sulfur compounds within the scope of this method. Therefore, both unidentified and known individual compounds are determined. Coincidentally, the total sulfur content of samples is estimated from the sum of the individual compounds determined.

#### Instrumentation

Varian 450-GC Gas Chromatograph  
Column: Varian CP-Sil™ 5 CB, 30 m x 0.32 mm x 3 μm (pn: CP8687)  
Injector: Varian 1177 Split/Splitless Injector, full EFC control  
Detection: PFPD, full EFC control  
Injector: 250 °C, split 1:50  
Oven: 50 °C (1 min isothermal) @ 10 °C/min to 300 °C (5 min isoT)  
Detection: 300 °C

Software  
GC Control and Data Handling: Galaxie™ Software from Varian

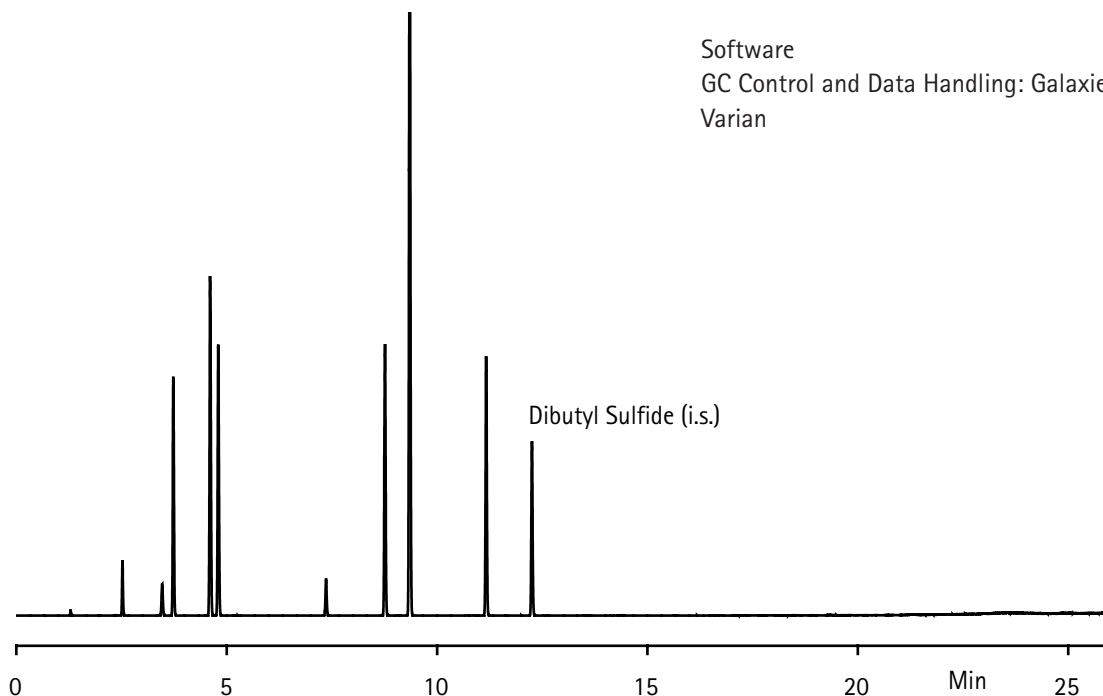


Figure 1. Sulfur compounds in spiked diesel.

Table 1. PFPD settings.

Trigger Level	200 mV
Tube Voltage	570 V
Sampling delay	6 ms
Sampling width	20 ms
Combustion 1 (Air 1)	17.0 mL/min
Combustion (H2)	13.0 mL/min
Combustion 2 (Air 2)	10.0 mL/min

## Results and Discussion

Commercially available diesel and other fuels show very low sulfur content. In order to show the significance of this method two spiked diesel samples were analyzed as well as a plain diesel sample. A chromatogram of a spiked diesel (approx. 130 mg/kg total sulfur) is shown in Figure 1. The repeatability was tested, with the results given in Table 2 and Figure 2.

Table 2. Repeatability data 100 mg/kg sample

Run	Total S (mg/kg)	Run	Total S (mg/kg)
1	101.7	14	96.41
2	103.96	15	98.87
3	104.59	16	101.49
4	101.25	17	102.96
5	101.23	18	103.99
6	101.47	19	104.99
7	103.73	20	102.34
8	97.17	21	97.8
9	105.87	22	99.14
10	100.89	23	96.68
11	100.17	24	100.28
12	98.44	25	102.72
13	101.17		
	N		25
	Mean		101.17
	Std Dev		2.64
	Rsd %		2.61

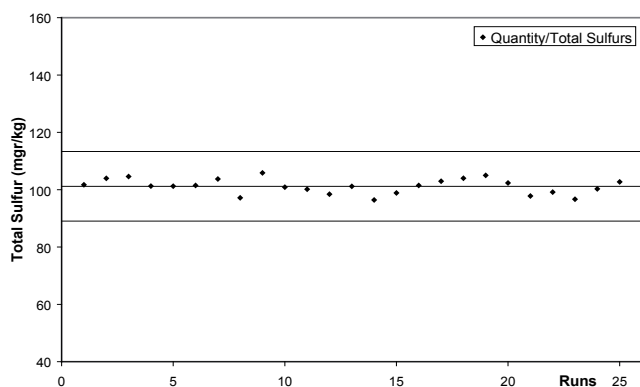


Figure 2. Repeatability chart 100 mg/kg total sulfur.

Figure 2 shows the repeatability data and the limit specified by the method. In this case, it is  $0.12\%[C]$ . Subsequent values may exceed these limits only once every 20 analyses. From these data, it can be concluded that the Varian system is well suited to this type of analysis in this concentration range as no value exceeds the limits.

In Figure 3, a chromatogram is shown of a Euro 95 gasoline. As the concentration of the individual sulfur containing components is low, it is critical that a sulfur specific detector is used. To illustrate this, the PFPD and the FID signal are plotted. The FID will never be able to identify the sulfur components in the matrix.

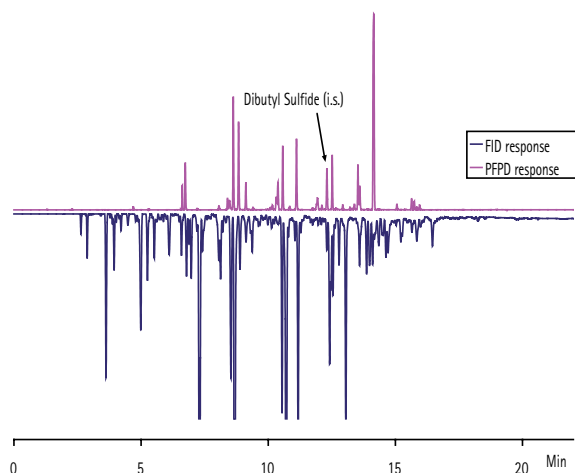


Figure 3. PFPD and FID signal of Euro 95 gasoline.

Total sulfur in this gasoline is about 240 mg/kg. The repeatability data of this analysis are presented in Figure 4. The area between the horizontal lines represents the limit specified in the method. From the data it can be concluded that the system runs perfectly. In Table 3 the individual results are shown as well as the calculated average and RSD.

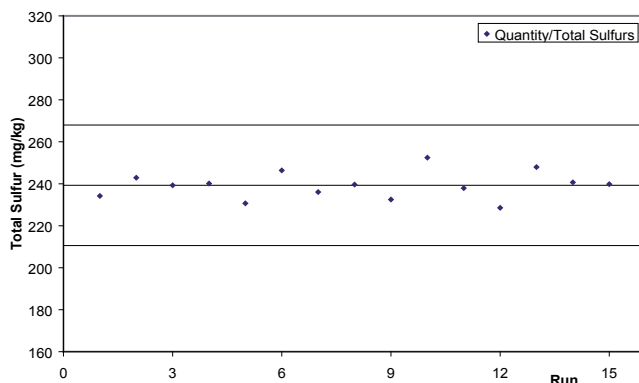


Figure 4. Repeatability chart, sulfur in Euro 95 gasoline.

Table 3. Repeatability data Euro 95.

Run	Total S (mg/kg)	Run	Total S (mg/kg)
1	234.22	9	232.52
2	242.88	10	252.45
3	239.29	11	237.93
4	240.14	12	228.55
5	230.67	13	247.98
6	246.39	14	240.67
7	236.07	15	239.83
8	239.62		
	N		15
	Mean		239.28
	Std Dev		6.48
	RSD %		2.71

The repeatability data are well within the limits required by the ASTM D 5623 method. Low sulfur containing gasolines were also tested. Figure 5 shows the repeatability data of a Euro 95 gasoline containing 17 mg S/kg.

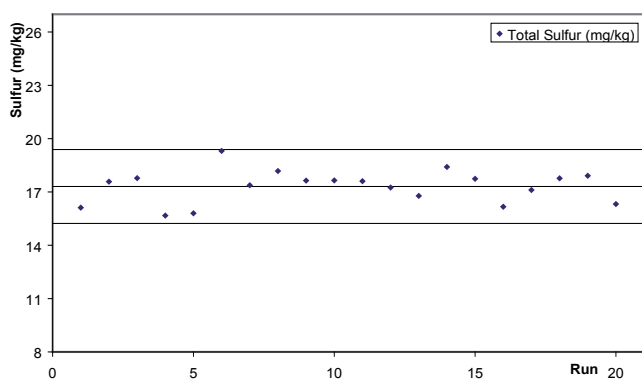


Figure 5. Repeatability data of a Euro 95 gasoline containing 17 mg S/kg.

The total sulfur as well as an individual sulfur containing component were also analyzed. The data are again presented in charts (Figures 5 and 6) and Table 4. The results are once more well within the limits specified by ASTM D 5623.

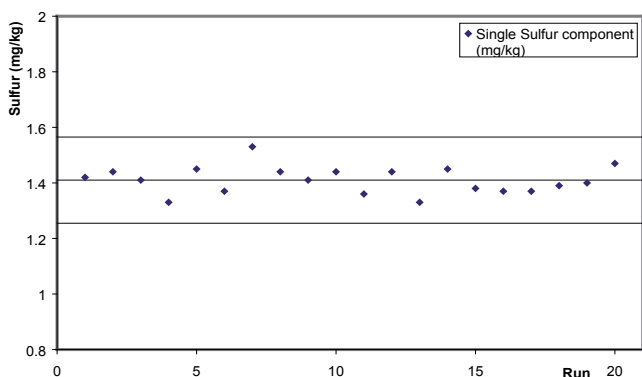


Figure 6. Repeatability data per component on 1 mg S/kg level.

Table 4. Repeatability data low sulfur Euro 95.

Run	Total S (mg/kg)	S component (mg/kg)	Run	Total S (mg/kg)	S component (mg/kg)
1	16.12	1.42	11	17.61	1.36
2	17.58	1.44	12	17.25	1.44
3	17.78	1.41	13	16.78	1.33
4	15.67	1.33	14	18.41	1.45
5	15.8	1.45	15	17.74	1.38
6	19.31	1.37	16	16.17	1.37
7	17.38	1.53	17	17.11	1.37
8	18.18	1.44	18	17.77	1.39
9	17.64	1.41	19	17.91	1.4
10	17.65	1.44	20	16.32	1.47
	N			20	20
	Mean			17.309	1.41
	Std Dev			0.93	0.049
	RSD (%)			5.36	3.50

### Conclusion

The Varian 450-GC Gas Chromatograph equipped with a Pulsed Flame Photometric Detector (PFPD) is perfectly suited to the total sulfur analysis of light petroleum liquids. In this application note, these light petroleum liquids are diesel (spiked to 130 mg S/kg), high sulfur (240 mg S/kg) containing Euro 95 and low sulfur (17 mg S/kg) containing Euro 95. The PFPD detects only the sulfur containing components and is not influenced by the hydrocarbon matrix. Total sulfur and individual sulfur containing components, in the concentration range of low to high ppm, were analyzed with good repeatability. The specifications stated in ASTM D 5623 were met.

### References

ASTM Standard D 5623, 1994, "Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection", ASTM International, West Conshohocken, PA, www.astm.org

These data represent typical results.  
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