The Analysis of Sulfur Components in Various LPGs

Coen Duvekot, Edwin Hollebrandse
Varian, Inc.

Introduction

The low level analysis of sulfur containing components such as H_2S, COS and mercaptanes is challenging. First of all the system has to be inert; stainless steel adsorbs H_2S and other sulfur containing components. Secondly, the column used must be able to separate the component of interest. Although a highly selective pulsed flame photometric detector is used in sulfur mode, the matrix tends to quench the PFPD signal.

The Varian Custom Solutions office therefore developed a two-channel configuration for this type of analysis. Both channels were equipped with a PFPD. Injection was performed using two sample loop fitted valves fed by a micro gasifier. The whole sample path was UltiMetal™ deactivated ensuring an inert system and no adsorption of sulfur components.

The two columns/channels approach permitted the analysis of all components of interest in one run. If the matrix was propane, H_2S was analyzed on CP-Sil 5 CB. COS was analyzed on PoraBOND Q. The other mercaptans can be analyzed on both columns. If the matrix was butane the methylmercaptane was analyzed on PoraBOND Q as it co-eluted with butane on the CP-Sil 5 CB.

Instrumentation

The two channel system was set up according to the scheme in Figure 1.

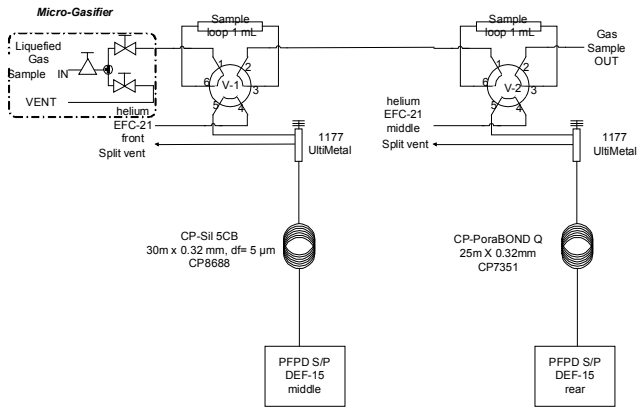

Figure 1. Plumbing scheme for the two channel system.

Technique: Varian 450-GC Gas Chromatograph
Injection: Gas sampling valve
Detection: Pulsed flame photometric detection
Software: Galaxie™ Software for GC control and data handling

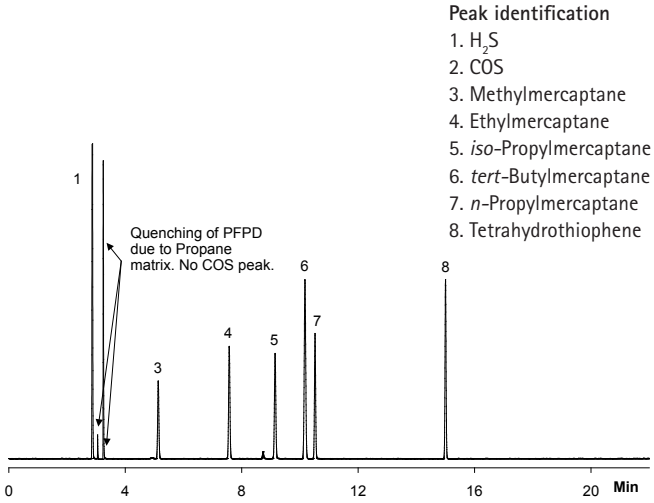

Figure 2. Sulfur components in propane front channel.

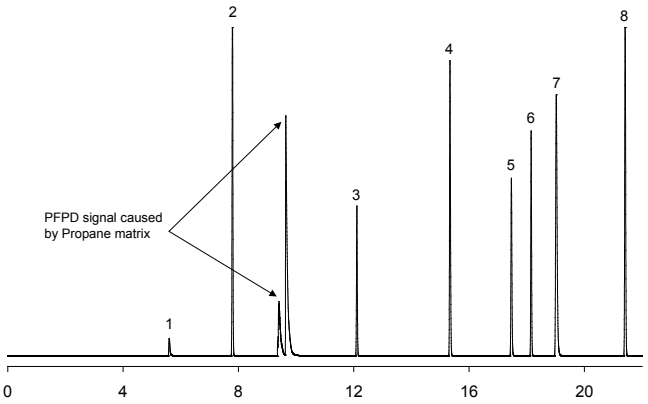

Figure 3. Sulfur components in propane middle channel.

Materials and Reagents

Column front channel: CP-Sil 5CB, 30 m x 0.32 mm, df = 5 µm (CP8688)
Column middle channel: CP-PoraBOND Q, 25 m x 0.32 mm (CP7351)

Conditions

Injection:	Front, 220 °C, split 1:30
	Middle, 220 °C, split 1:20
Oven:	35 °C @ 12 °C/min to 250 °C (1.25 min)
Carrier Gas:	Helium, 2 mL/min (both columns)
Large valve oven:	100 °C

Table 1. PFPD settings (both detectors).

Temperature	200 °C
Air 1	17 mL/min
H_2	13 mL/min
Air 2	10 mL/min
Trigger level	200 mV
Tube voltage	510 V
Sampling delay	4 ms
Sample width	10 ms

Results and Discussion

Figures 2 and 3 show chromatograms obtained in a propane matrix. The CP-Sil 5CB column from the front channel showed co-elution of propane and COS. H_2S and the mercaptanes were very well resolved and perfectly placed for quantification. The CP-PoraBOND Q column from the middle channel revealed no co-elution and here the COS could be analyzed, as well as the mercaptanes.

Figures 4 and 5 show the analysis of sulfur components in a butane matrix.

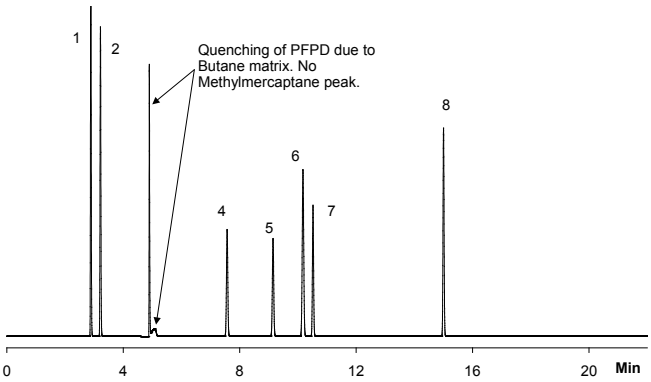

Figure 4. Sulfur components in butane, front channel.

On the CP-Sil 5CB column butane co-eluted with methylmercaptane causing quenching of the PFPD. In this case methylmercaptane was analyzed on the CP-PoraBOND Q of channel 2. H_2S and COS were analyzed on the CP-Sil 5 CB and the higher mercaptanes could be determined on both channels.

Peak identification

1. H_2S
2. COS
3. Methylmercaptane
4. Ethylmercaptane
5. *iso*-Propylmercaptane
6. *tert*-Butylmercaptane
7. *n*-Propylmercaptane
8. Tetrahydrothiophene

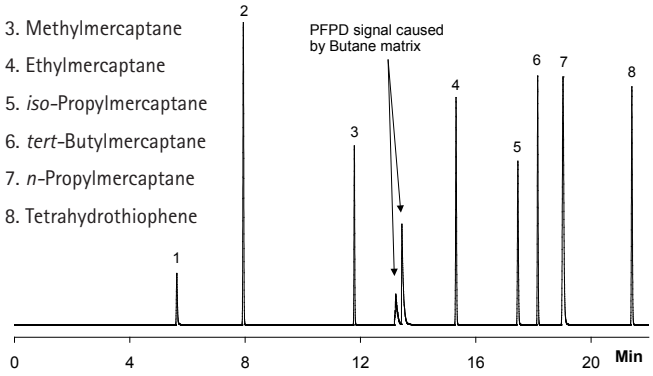

Figure 5. Sulfur components in butane, middle channel.

In order to check the system suitability a calibration gas was analyzed several times (Tables 2 and 3, Figures 8 and 9). Chromatograms obtained for both channels are shown in Figures 6 and 7.

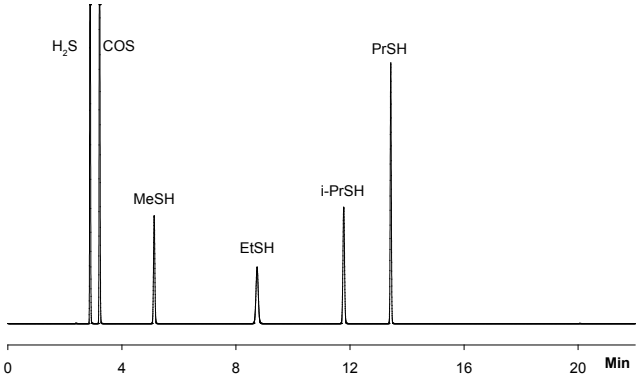

Figure 6. Calibration standard, front channel.

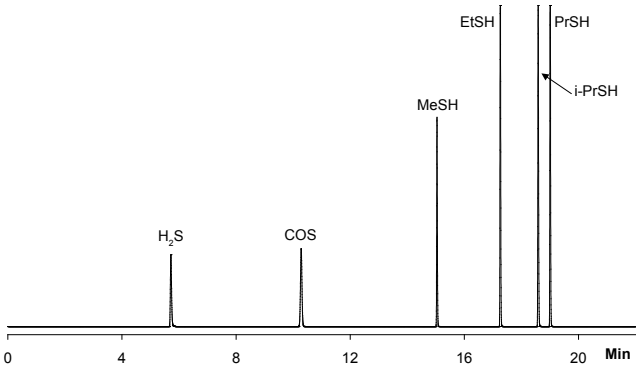

Figure 7. Calibration standard, middle channel.

As the matrix of this calibration gas was nitrogen, no co-elution and thus no PFPD quenching occurred. All components could be analyzed on both channels.

Table 2. Repeatability data, front channel.

Run	H_2S	COS	MeSH	EtSH	i-PropSH	n-PropSH
1	1215606.3	918906.1	327885.5	294361.1	404067.8	633667.2
2	1254247.2	935745.6	328676.4	298573.8	425777.5	628583.6
3	1239701.4	943248.3	332392.1	300741.5	419172.7	646792.3
4	1274377.5	948168.4	335002.5	296092.8	425079.8	617067.9
5	1243905.3	924323.5	339181.4	299545.4	426836.1	618301.7
6	1285375.9	937870.1	338153	299489.2	433642.5	648997.8
7	1228259.2	964881	335008.9	298247.3	424477.3	623803.7
8	1291765.5	939708.7	335746.5	299883	413520.7	625519.5
9	1275769.5	964139.7	341015.7	302964.7	437842.4	651128.1
10	1278718.3	979071.4	341822.9	299994.6	430573.7	641596.1
11	1273792.2	970358.1	335826.6	305985.7	432967.4	638664.9
12	1236413.7	949311.9	330519.5	297651.2	434679.3	655548.5
13	1235316.2	919577.2	329218.5	291020.7	423661.2	632948
14	1225871.1	908744	322353.2	292466.9	415694.5	661764.1
15	1237258.7	926689.7	320472.2	289775.8	416483	662962.1
N	15	15	15	15	15	15
Average	1253071.9	942049.6	332885.0	297786.2	424298.4	639156.4
Std Dev	24620	20763	6360	4406	9218	15062
Rsd %	1.96	2.20	1.91	1.48	2.17	2.36

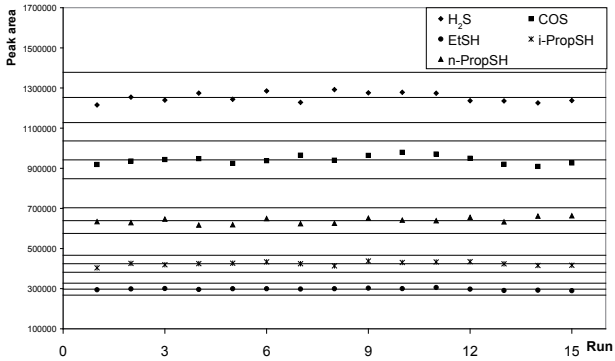

Figure 8. Visualized repeatability of data from Table 2.

Table 3. Repeatability data, middle channel.

Run	H_2S	COS	MeSH	EtSH	i-PropSH	n-PropSH
1	545461.5	687804.9	827494.9	1594183.6	1424798.9	1628308.1
2	538183.8	677330.1	824772	1583902.8	1439569.1	1642324.8
3	532202.8	693216.6	846290.1	1612155.3	1463528.6	1634376.8
4	544055.3	703603.8	839708.8	1596014.7	1466332.1	1658114.8
5	548043.4	702749.4	843958.2	1588910	1433280.3	1641331.9
6	542476.3	695695	847345.9	1601312.8	1494174.8	1672709.2
7	552342.1	713600.7	856817.4	1665891.4	1532624.5	1706859.5
8	538958.8	702749.5	844759.3	1629821.6	1461747.7	1667079
9	541759.1	697076.7	850349.6	1633218	1489507.5	1678310
10	518533.6	699978.8	844821.8	1617187.6	1494334.3	1665749.2
11	538677.4	684485	829601.1	1574631.6	1430748.3	1651975.7
12	525474.5	702033	840279.8	1613473.7	1498360.8	1691345.9
13	525826.5	708638.9	834847.8	1573162.2	1491257.2	1648297.2
14	521070.8	711786.3	830655.5	1615305.1	1457386.4	1634290.4
15	518329.3	702761.6	833949	1605378.4	1446364.9	1633788.8
N	15	15	15	15	15	15
Average	535426.3	942049.6	839710.1	297786.2	1468267.7	1656990.8
Std Dev	11104	9988	9223	24335	30926	23141
Rsd %	2.10	1.4	1.1	1.5	2.1	1.4

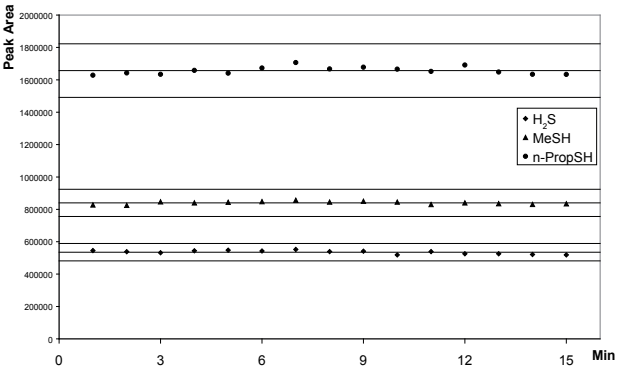

Figure 9. Visualized repeatability of data from Table 3.

Conclusion

This custom configured GC offers a number of benefits. The micro-gasifier enables the direct coupling of an LPG stream to the GC. No sample pre-treatment is required. The UltiMetal™ sample path ensures a trouble free analysis of sulfur-containing components at low concentrations. The two-channel approach allows for increased flexibility with regard to the matrix that contains the sulfur components. Two different columns, each equipped with a PFPD, ensure maximum flexibility and separation power for components such as H_2S, COS, methylmercaptane, ethylmercaptane, propylmercaptane, iso-propylmercaptane, tert-butylmercaptane and tetrahydrothiophene. Repeatability data show that the system is perfectly suited for the analysis of these low level, sulfur-containing components.

These data represent typical results.
For further information, contact your local Varian Sales Office.

Varian, Inc.
www.varianinc.com
North America: 800.926.3000 – 925.939.2400
Europe: *The Netherlands*: 31.118.67.1000
Asia Pacific: *Australia*: 613.9560.7133
Latin America: *Brazil*: 55.11.3238.0400

Application Note SI-01589