BEYOND MEASURE

Analysis of Sulphur Compounds in Various Liquefied Petroleum Gases

Application Note

INTRODUCTION

The low-level analysis of sulphur containing components such as Hydrogen Sulphide (H_2S), COS (carbonyl sulphide) and mercaptans, in liquified petroleum gas (LPG), is challenging. First of all, the system has to be inert; stainless steel adsorbs H_2S and other sulphur containing components. Secondly, the column used must be able to separate the components of interest. Although a highly selective pulsed flame photometric detector (PFPD) is used in sulphur mode, the bulk hydrocarbons tends to quench the PFPD signal.

EXPERIMENTAL

The LPG type samples are injected as a gas via two gas sampling valves, in series. A micro-gasifier in front of the injection valves ensures a fully gaseous sample state. The complete sample path is Ultimetal deactivated ensuring an inert system preventing adsorption of the sulphur components.

If the bulk sample is mainly propane, H_2S is analysed on the non-polar column from Channel A. The COS is analysed on the BOND Q column from channel B. The mercaptans can be analysed on both columns. However, if the bulk is mainly butane, the methyl mercaptan is analysed on BOND Q from channel B as it co-elutes with butane on the non-polar column of channel A. Analytical parameters of the analysis can be found in table 1.

SCION Instruments developed a two-channel configuration for this analysis with both channels being equipped with a PFPD, as shown in Figure 1.

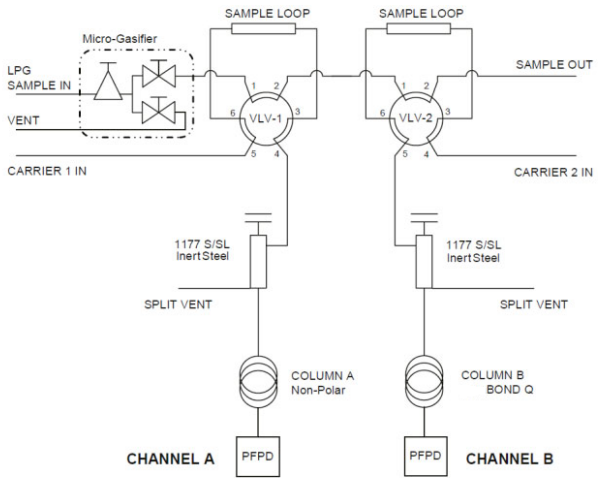

Fig 1. Schematic for the two-channel system

Table 1. Analytical parameters

Sample loop	100µL
Channel A	220˚C, Split 1:30
Channel B	220˚C, Split 1:20
Oven	35˚C, 12˚C/min to 250˚C (1.25min)
Column A	SCION-5, 30m x 0.32mm x 5µm
Column B	BOND Q 25m x 0.32mm
Carrier	Helium, 2mL/min
PFPD	200˚C
Air 1 & 2	17mL/min, 10mL/min
H2	13mL/min

Samples included a sulphur calibration standard in nitrogen. Bulk analysis was also performed on propane and butane

RESULTS

To validate the performance of the system, a calibration mixture was used. It is vital that the nitrogen must not quench either channel for sulphur components. Figures 2 and 3 show the chromatograms from the calibration standard on both channels.

The non-polar column from channel A shows co-elution of propane and COS. H_2S and the mercaptans are very well resolved and perfectly placed for quantification. Figures 4 shows the chromatogram of the bulk propane analysis on channel A.

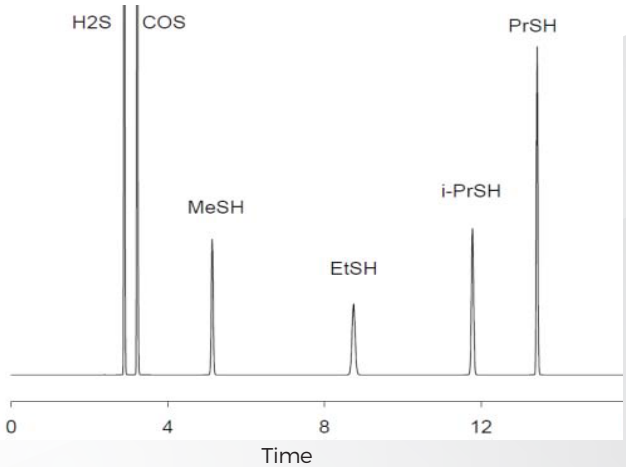

Fig 2. Sulphur components in calibration standard – non-polar

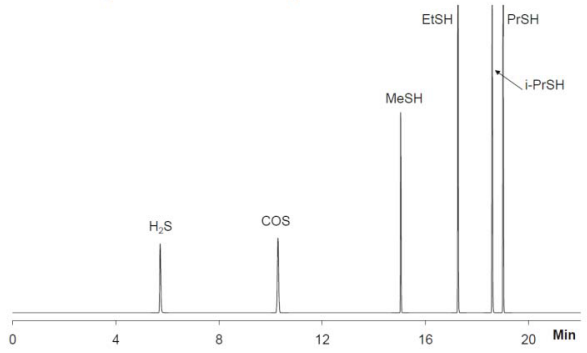

Fig 3. Sulphur components in calibration standard – BOND Q

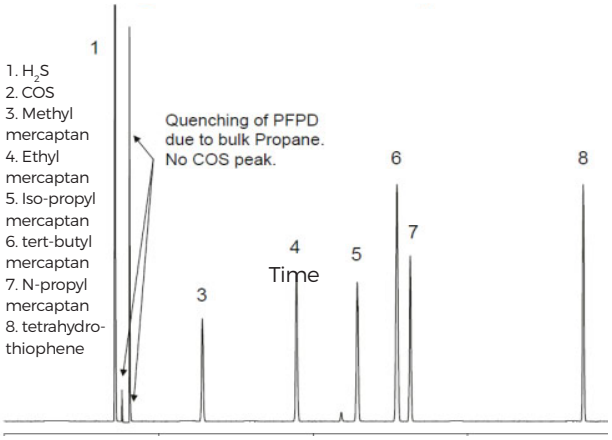

Fig 4. Sulphur components in propane- non polar

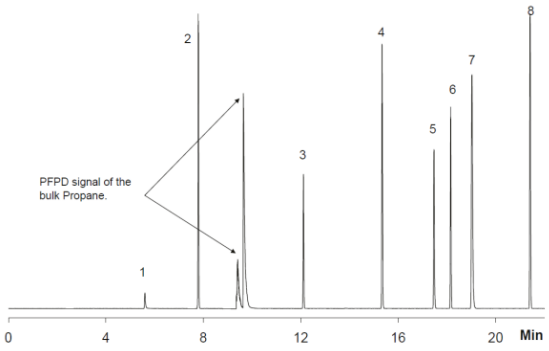

Fig 5. Sulphur components in propane - BOND Q

Analysis of sulphur components in bulk butane can be found in Figures 6 and 7. On the non-polar column in channel A, the bulk butane co-elutes with methyl mercaptan causing quenching of the PFPD. Methyl mercaptan is therefore analysed on the BOND Q column, on channel B.

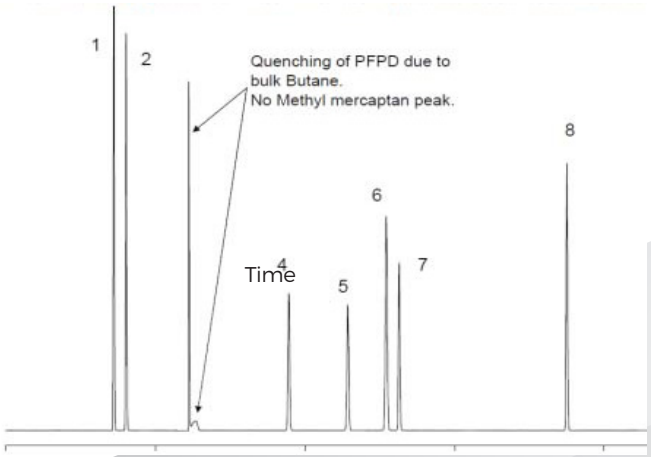

Fig 6. Sulphur components in butane - non-polar

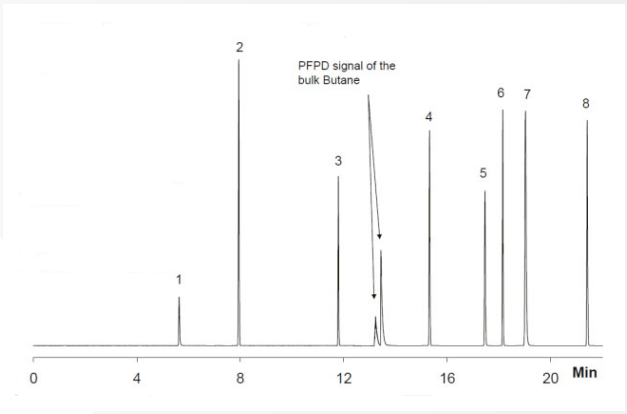

Fig 7. Sulphur components in propane - BOND Q

The calibration mixture was analysed 15 times for validation. The validation data can be found in Tables 2 and 3, in the appendix. Figures 8 shows the repeatability from channel A.

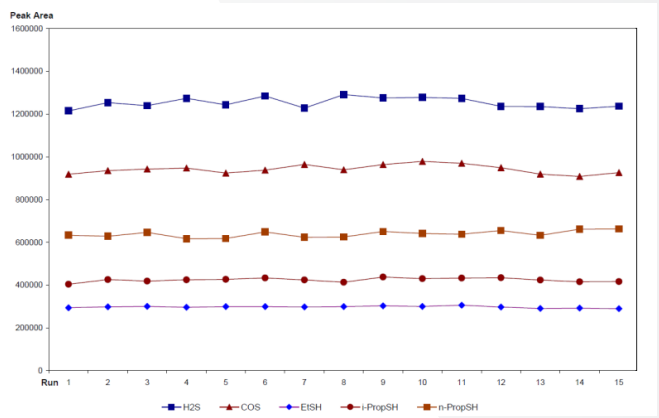

Fig 8. Repeatability data from channel A

CONCLUSION

The custom configured SCION 456 GC offers numerous benefits for the analysis of sulphur components in LPG. The micro-gasifier enables the direct coupling of an LPG stream to the GC, eliminating the need for sample pre-treatment. The Ultimetal sample path ensures a trouble-free analysis of sulphur containing components at low concentrations. Increased flexibility with regard to the different samples is achieved via a two-channel approach. Two different columns, each equipped with a PFPD detector, ensures excellent separation independent of the bulk components to analyse H2S, COS and mercaptans. Repeatability data shows that the system is perfectly suited for the analysis of these low level, sulphur containing components.

Appendix

Table 2. . Repeatability data of channel A

Run	H2S	COS	MeSH	EtSG	i-propSH	n-propSH
1	1215606	918906	327886	294361	404068	633667
2	1254247	935746	328676	298754	425778	628584
3	1239701	943248	332392	300742	419173	646792
4	1274378	948168	335003	296093	425080	617068
5	1243905	924324	339181	299545	426836	618302
6	1285376	937870	338153	299489	433643	648998
7	1228259	964881	335009	298247	424477	623804
8	1291766	939709	335747	299883	413521	625520
9	1275770	964140	341016	302965	437842	651128
10	1278718	979071	341823	299995	430574	641596
11	1273792	970358	335827	305986	432967	638665
12	1236414	949312	330520	297651	434679	655549
13	1235316	919577	329219	291021	423661	632948
14	1225871	908744	322353	292467	415695	661764
15	1237259	926690	320472	289776	416298	662962
Ave	1253092	942050	332885	297786	424298	639156
Std Dev	24587	20763	6360	4406	9218	15062
RSD%	2.0	2.2	1.9	1.5	2.2	2.4

Table 3. Repeatability data of channel

Run	H2S	COS	MeSH	EtSG	i-propSH	n-propSH
1	54562	687805	827495	1594184	1424799	1628308
2	538184	677330	824772	1583903	1439569	1642325
3	532203	693217	846290	1612155	1463529	1634377
4	544055	703604	839709	1596015	1466332	1658115
5	548043	702749	843958	1588910	1433280	1641332
6	542476	695695	847346	1601313	1494175	1672709
7	552342	713601	856817	1665891	1532625	1706860
8	538959	702750	844759	1629822	1461748	1667079
9	541759	697077	850350	1633218	1489508	1678310
10	518534	699979	844822	1617188	1494334	1665749
11	538677	684485	829601	1574632	1430748	1651976
12	525475	702033	840280	1613474	1498361	1691346
13	525827	708639	834848	1573162	1491257	1648297
14	521071	711786	830656	1615305	1457386	1634290
15	518329	702762	833949	1605378	1446365	1633789
Ave	535426	698901	839710	1606970	1468268	1656991
Std Dev	11104	9988	9223	24335	30926	15062
RSD%	2.1	1.4	1.1	1.5	2.1	2.4

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