

ANALYSIS OF SULPHUR COMPOUNDS IN VARIOUS LIQUEFIED PETROLEUM GASES

Introduction

Liquefied Petroleum Gas (LPG) are a group of hydrocarbon gases constituting three or four carbon atoms. The most common LPGs are Propylene, Propane, Butylene and Butane. LPGs are odourless and colourless gases which require the addition of odourants for detection. Commonly these odourants are sulphur containing mercaptans. It is vital that the total sulphur content is measured and regulated to not only avoid pipeline corrosion but to determine the quantity of odourant that is added. New refining technologies commonly use LPGs as feedstocks. The requirement for low level sulphur composition is vital for the refinery industry. When used as a fuel source, there are global regulations for the maximum level of sulphur present in the LPGs.

The low-level analysis of sulphur containing components such as Hydrogen Sulphide (H_2S), Carbonyl Sulphide (COS) and mercaptans, in 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. SCION Instruments developed a method for the detection of eight sulphur based compounds in LPG via GC-dual PFPD.

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

The analytical conditions for this application were as follows: sample loop 100 μ L. S/SL Channel A 220 $^{\circ}$ C with 1:30 split with S/SL Channel B 220 $^{\circ}$ C with 1:20 split. The column flow was set at 2mL/min with helium. Both columns were operated with a time program of 35 $^{\circ}$ C, 12 $^{\circ}$ C/min to 250 $^{\circ}$ C (hold 1.25min). Both PFPDs were operated at 200 $^{\circ}$ C with Air 1 at 17mL/min, Air 2 at 10mL/min and H_2 at 13mL/min. Samples included sulphur calibration standards prepared in nitrogen and bulk analysis of propane and butane.

Results

To validate the performance of the system, a calibration mixture was used. It is vital that the nitrogen does not quench either channel for sulphur components. Figure 2 shows the dual chromatogram from the sulphur 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. Figure 3 shows the dual chromatograms of the bulk propane analysis.

Using both PFPD channels, it was possible to successfully identify all target sulphur compounds. Due to PFPD quenching of COS on Channel A, Channel B (BOND Q column), was used for identification. Figure 4 shows the dual chromatograms of bulk butane analysis.

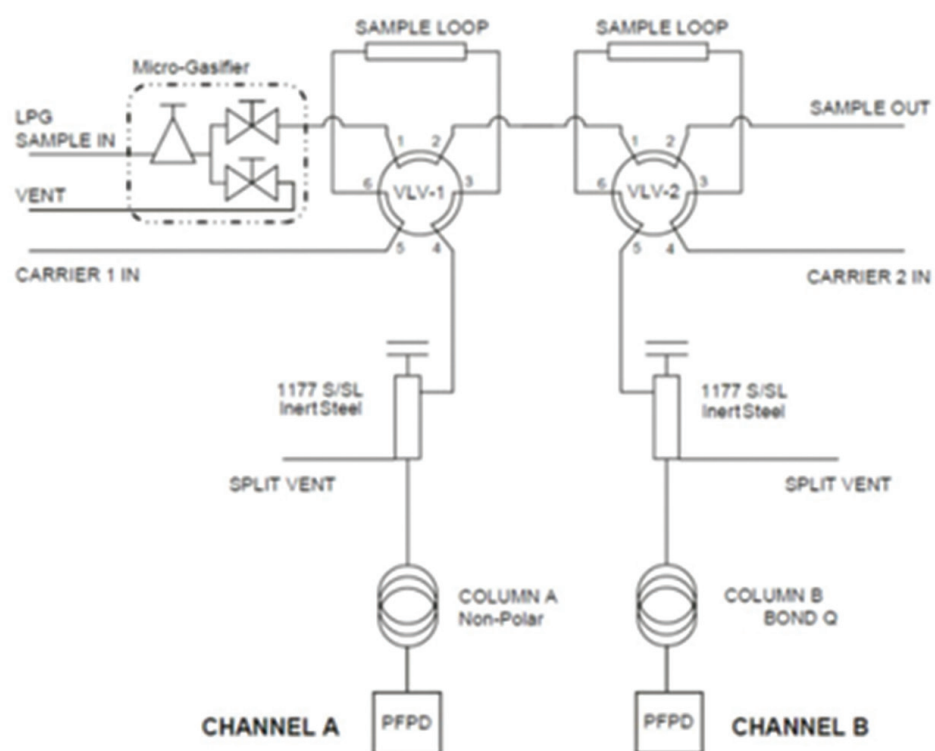


Figure 1. Schematic of GC-PFPD Sulphur Analyser

When using the non-polar column, on Channel A, the bulk butane co-elutes with the methyl mercaptan causing quenching of the PFPD. Methyl mercaptan is therefore analysed using the BOND Q column on Channel B.

Repeatability data was collected with validation of the method using 15 consecutive injections of the sulphur calibration standard. Excellent repeatability was observed for all target compounds with the values shown in Table 1.

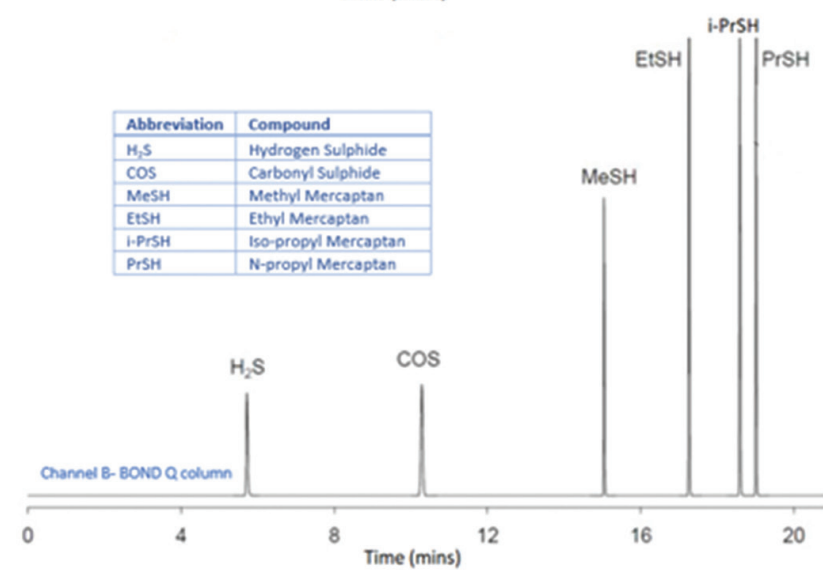
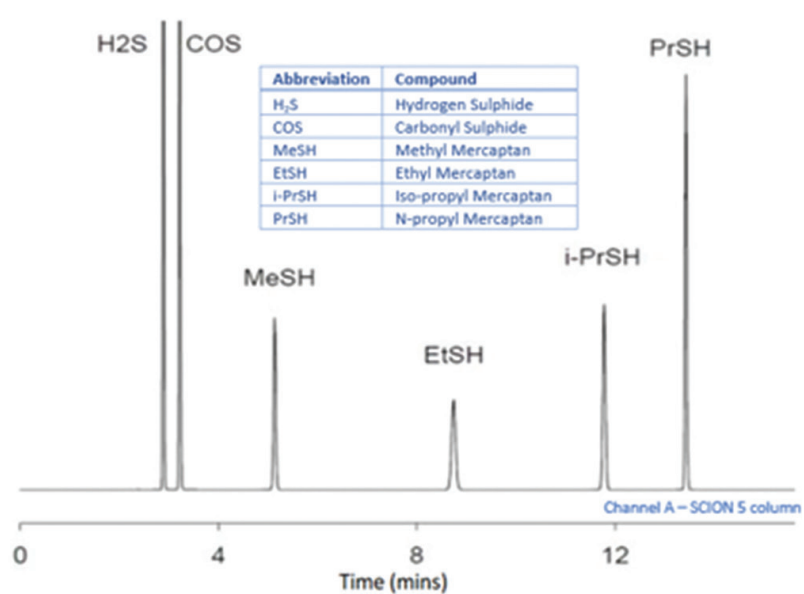


Figure 2. Dual Chromatogram of Sulphur Calibration Standard

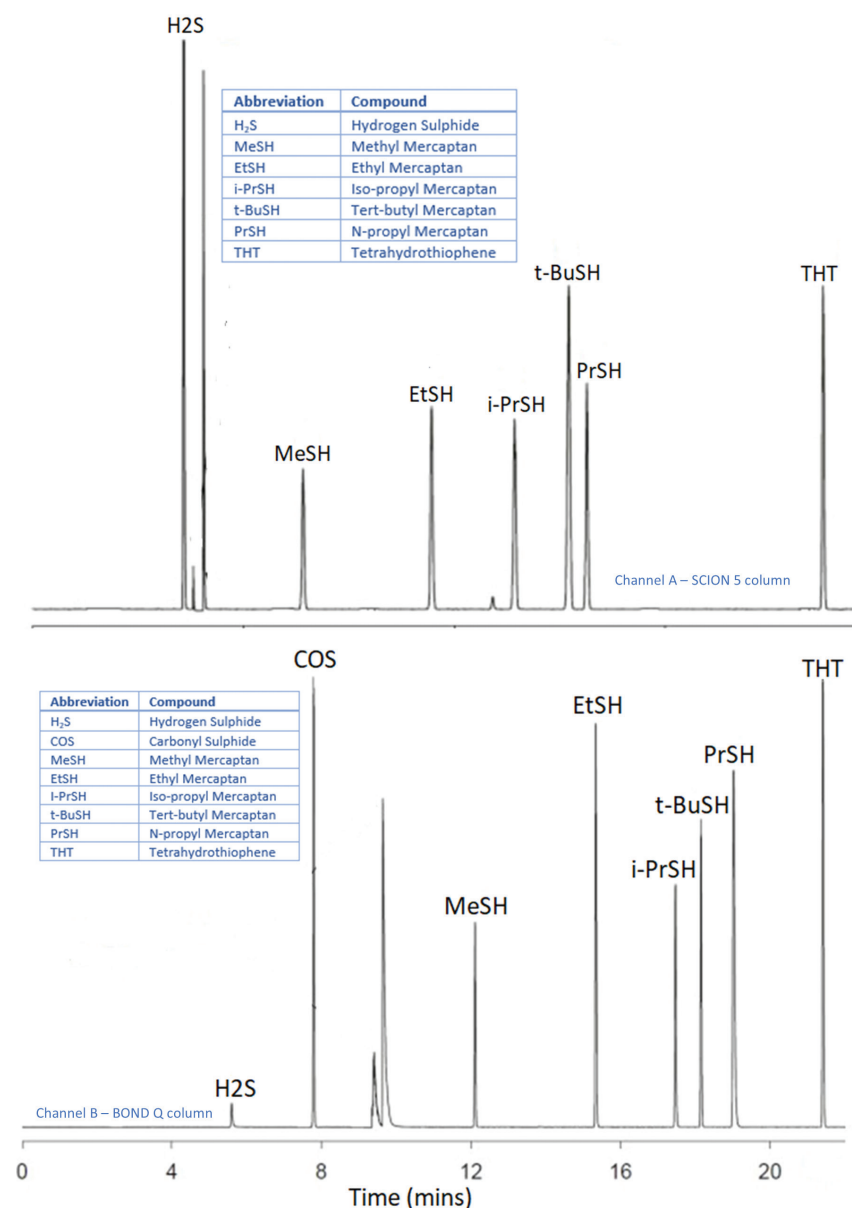


Figure 3. Dual Chromatograms of Bulk Propane Analysis

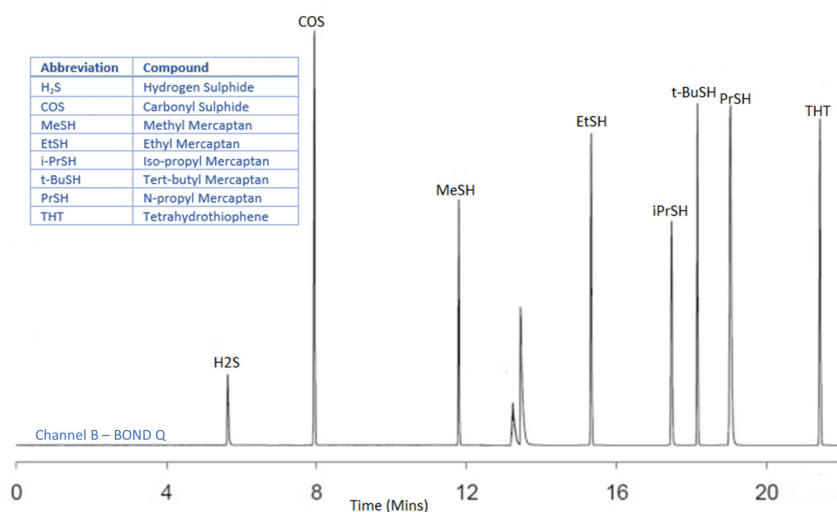
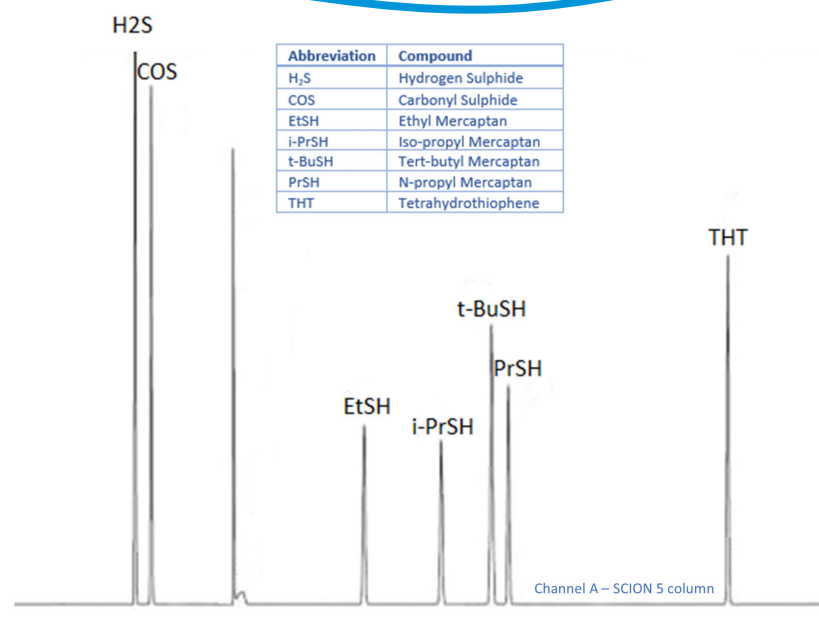


Figure 4. Dual Chromatograms of Bulk Butane Analysis

Table 1. Repeatability of sulphur calibration standard (n=15)

Channel A	H ₂ S	COS	MeSH	EtSH	i-PrSH	PrSH
Ave. Area	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
Channel B	H ₂ S	COS	MeSH	EtSH	i-PrSH	PrSH
Ave. Area	535426	698901	839710	1606970	30926	15062
Std Dev	11104	9988	9223	24335	30926	15062
RSD%	2.1	1.4	1.1	1.5	2.1	2.4

Conclusion

The custom configured SCION 456 GC offers numerous benefits for the analysis of sulphur components in Liquefied Petroleum Gas. The micro-gasifier enables direct coupling of an LPG stream to the GC, eliminating the needs for sample pre-treatment. The Ultimetal sample path ensures a trouble free analysis of sulphur containing compounds at low concentrations. Increased flexibility with a regard to different samples types 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 Hydrogen Sulphide, Carbonyl Sulphide and Mercaptans. Repeatability data shows that the system is perfectly suited for the analysis of these low level sulphurs.

Author Contact Details

Ashleigh Mellor. SCION Instruments UK,

- Livingston Business Centre, Livingston. EH54 7FA
- Tel: +44 7534 742406
- Email: ashleighm@scioninstruments.com
- Web: scioninstruments.com



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