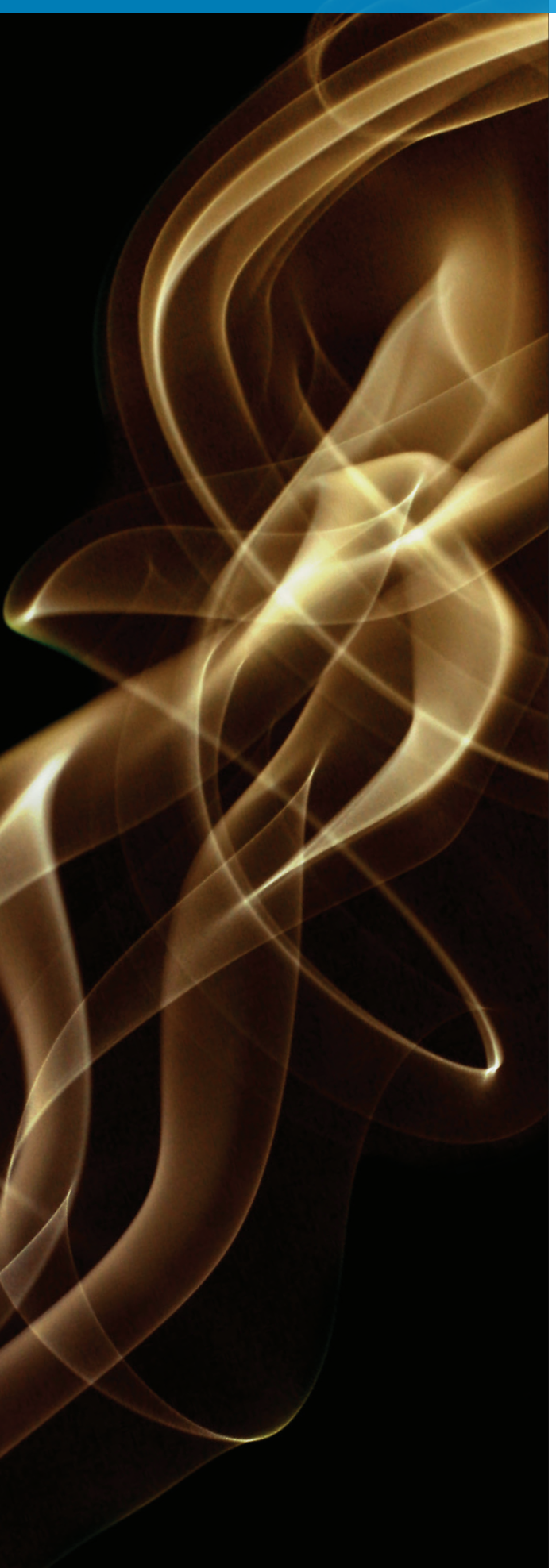
RELIABLE AND ROUTINE TRACE LEVEL SULPHUR ANALYSES IN LPG AND GASEOUS SAMPLES IN COMPLIANCE WITH ASTM D6667

Liquefied Petroleum Gas (LPG) is a group of hydrocarbon gases typically compromising three or four carbon atoms. The most common forms of LPG are propane (C3H8), propylene (C3H6), butane (C4H12) and butylenes (C4H8).



Being colourless and odourless necessitates the addition of odourants to LPG to aid detection. These odourants are normally the sulphur containing compounds mercaptanes, which are added at an approximate concentration of less than 10 ppm. Measurement of the total sulphur (TS) content in natural gas streams is important both in avoiding sulphur related pipeline corrosion and for the determination of precise quantity of odorant that must be added to the LPG.

LPG and other light hydrocarbons are also finding use as feedstocks for a variety of new refining technologies. The need for low sulphur measurements in this part of the industry is of growing importance. Furthermore, LPG is increasingly used as an automotive fuel and must therefore comply with legislation concerning the sulphur content of automotive fuels, the limits of which are decreasing.

The total sulphur analysis of LPG by combustion UV-Fluorescence detection method is governed by ASTM D6667 [1] and is applicable to samples containing 1.0 – 100 mg/kg of sulphur. This article describes a direct sampling and injection technique, which is fully compliant with ASTM D6667, for measuring low level sulphur in LPG using the TSHR TS 7000 Total Sulphur Analyser in conjunction with the TSHR GM 7000 Gas & LPG Sample introduction module. The principle and performance of this technique makes it applicable towards other LPG and gas samples applications for the determination of the trace level total nitrogen and chlorine content.

Experimental

The LPG sample was introduced into the Combustion Elemental Analyser using a Gas and LPG sample introduction module containing a rotary valve fitted with two sample loops (one for gas samples and one for LPG samples). The sample loops allowed for the delivery of known quantities of Gas or LPG sample into the Combustion Elemental analyser, with the gas loop delivering 10 ml per loop and the LPG loop delivering 100 ul sample volume.

The multiple sample loop injection feature, controlled by software operation, results in a fully automatic calibration and sample analysis for trace level Total Sulphur content in such gas and LPG samples with the Total Sulphur analyser used for this analysis.

The Gas and LPG sample introduction module was used to introduce several loops of di-butylsulphide doped butane LPG, with a sulphur concentration of 1 ppm w/w, into the analyser. The total sulphur content, as a function of the number of loops, was then measured in triplicate to calibrate the analyser prior to determining the sulphur content of LPG samples with unknown sulphur concentrations.

The gas/LPG sampling, sample introduction, high temperature oxidation (combustion) and SO2 detection process was controlled using TSHR's Athena software. Within the software a method with typical system parameters and control of the Gas and LPG sample introduction module has been pre-defined in accordance with ASTM D6667, which resulted in the system parameters shown in Table I.

The LPG was vapourised within the Gas and LPG sample introduction module and mixed with argon carrier gas to drive the injection volume towards the inlet of the Total Sulphur analyser. Complete oxidation of the sample occurred in the oxygen-rich environment of the high temperature furnace. Combustion products were dried using a permeable membrane drying tube contained within the Total Sulphur analyser and the total sulphur content was determined by pulsed UV-Fluorescence detection.

Table I: System parameters used on the TSHR TS 7000 Total Sulphur analyser for determination of total sulphur by ASTM D6667

Parameter	System value
Argon flow (GM 7000)	250 ml/min
Argon flow (furnace)	25 ml/min
Oxygen primary flow	300 ml/min
Oxygen secondary flow	50 ml/min
Temperature Furnace I	975 °C
Temperature Furnace II	1050 °C
Sample loop volume	100 ul

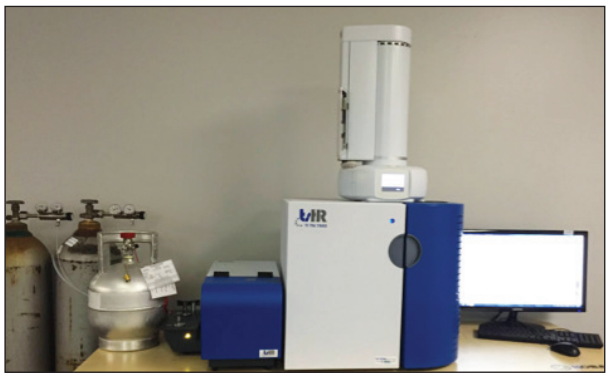


Figure 1: TS 7000 with GM 7000 set-up

Results

Presented in Table II are the results of injecting known quantities of sulphur-containing butane LPG into the Total Sulphur analyser. The data was used to generate a linear calibration plot for the instrument, which is shown in Figure 2. Representative peaks shapes for a typical analysis of two times 100 uL sample loop injection are shown in Figure 3.

Table II: Sulphur concentrations resulting from known quantities of sulphur-containing butane LPG.

Concentration S (mg/kg)	Replicate 1 concentration mg S/kg	Replicate 2 concentration mg S/kg	Replicate 3 concentration mg S/kg	Mean concentration mg S/kg	SD mg S/kg	RSD (%)
2,0	2,02	2,06	2,05	2,04	0,021	1,0%
4,0	4,09	4,08	3,93	4,03	0,090	2,2%
6,0	5,99	5,73	6,00	5,91	0,153	2,6%
12,0	12,1	12,2	12,1	12,1	0,061	0,5%

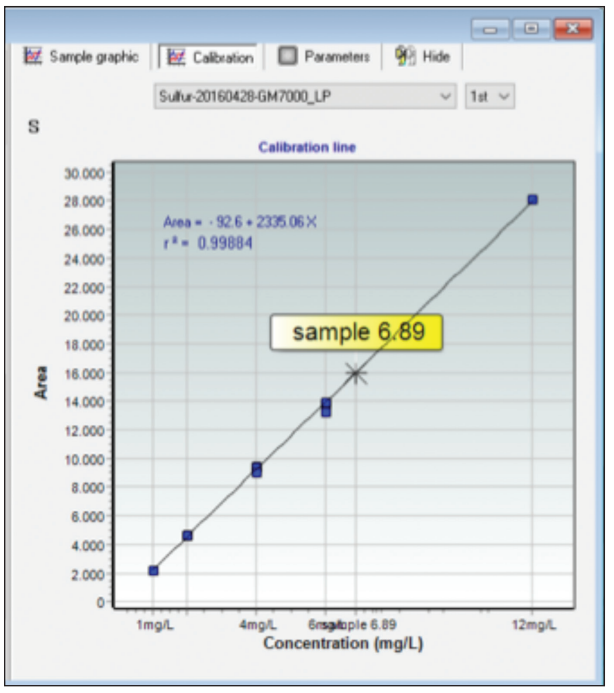


Figure 2: First order calibration line for the TSHR TS 7000 Total Sulphur analyser with GM 7000 Gas and LPG sample introduction module. The signal response of the sulphur detector exhibits excellent linearity with R2 = 0,99884

Sulphur analyser with GM 7000 Gas and LPG sample introduction module. The signal response of the sulphur detector exhibits excellent linearity with R2 = 0,99884

Finally, a few LPG samples were analysed for the sulphur content using the calibration data presented in Figure 1. The results of the analyses are presented in Table III and shows the calculated the average total sulphur concentrations and standard deviation for the three samples.

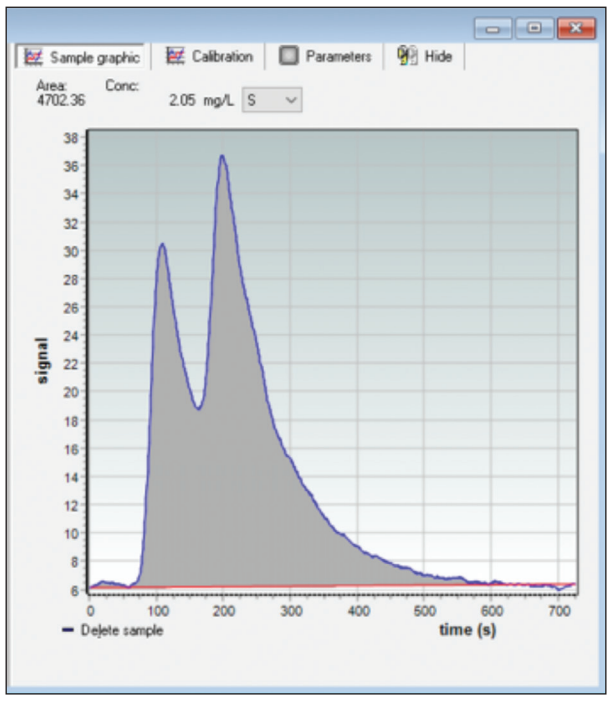


Figure 3: Peak shapes arising from the sampling, injection and detection of two loops of dibutylsulfide in n-butane LPG. The total sulphur content was 2 mg/kg. The high degree of repeatability was typical for measurements and is consistent with the low RSD's presented in Table II.

Table III. Total Sulphur analysis data of 3 LPG samples with GM 7000 and TS 7000 configuration.

Sample	Replicate 1 concentration mg S/kg	Replicate 2 concentration mg S/kg	Replicate 3 concentration mg S/kg	Mean concentration mg S/kg	SD mg S/kg	RSD (%)
LPG 1	6,98	6,93	7,00	6,97	0,036	0,5%
LPG 2	4,35	4,51	4,4	4,42	0,082	1,9%
LPG 3	8,6	8,72	8,69	8,67	0,062	0,7%

Discussion

The analysis of trace level sulphur content in LPG samples with the above written set-up shows reliable and reproducible performance data without extended handling or user maintenance.

The principle of multiple loops injection of a LPG/gas sample controlled through software reduces cost of ownership, improves productivity and precision of the test result.

The procedure supported by TSHR's Athena software is fully compliant with ASTM D6667 method, and ASTM D7551 method as well, and results in a customised solution for both routine and R&D laboratories. The sensitivity of the used pulsed UV-Fluorescence detector in the Total Sulphur analyser, provides enhanced capabilities to measure down to ppb level sulphur content in a wide range of gaseous and liquid hydrocarbon based samples. The analysis of the given LPG samples shows relative standard deviation values of less than 2% which is a solid performance indicator about the accuracy of the sampling and analysing process configuration.

References

[1] ASTM D6667 Standard Test Method for Determination of Total Sulphur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence detection.

[2] ASTM D7551 Standard Test Method for Determination of Total Volatile Sulphur in Gaseous Hydrocarbons and Liquefied Petroleum Gases and Natural Gas by Ultraviolet Fluorescence

Author Contact Details

Arthur van Strien, Global Sales & Marketing Manager, TSHR International, Netherlands