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Safe LPG injection for trace Sulfur and permanent gas analysis

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INTRODUCTION

LPG (Liquefied Petroleum Gas) has many industrial as well as domestic applications. It is used as ignition fuel for vehicles, as domestic fuel, as replacement for Chlorine and Fluor containing refrigerants, as chemical feedstock for e.g. polymers and for many other purposes. Safe LPG sample handling is an important issue in every laboratory. Due to the high pressure nature of this sample type, special precautions have to be taken to guarantee high laboratory safety.

This poster describes the exercises followed on risk analysis for the Sample Securitiser from Global Analyser Solutions, using HAZOP study methodology, verifying PED (Pressure Equipment Directive) and ATEX Directives. Apart from safety, the accurate analysis of LPG is of great importance as well. Besides hydrocarbon composition, also trace amounts of other present species need to be known for the various usage of the LPG. This poster focusses on the analysis of Sulfur compounds and permanent gases at ppb/ppm level, using customised analysers with (Pulsed) Flame Photometer Detector and Pulsed Discharge Detector.

SAFE INJECTION OF LPG

LPG contains primarily Propane and Butane and has a vapor pressure up to 8 bar at room temperature because of the components low boiling points (resp. -1 and -42 °C). In case of liquid LPG injection, pressures up to 20 bar are used to secure the liquid state of the sample. Applying such high pressures in the daily laboratory routine requires thorough risk analysis.

RISK ANALYSIS

Handling of LPG needs careful treatment. Both the high pressure cylinders and the flammability of LPG can create hazardous situations. For this reason compliance with adequate directives is required.

Figure 1
Sample Securitiser for safe LPG sample handling.

At least the Pressure Equipment Directive (PED 97/23/EC) and the ATEX Directive (94/9/EC) are compulsory.

PED

The Sample Securitiser has been tested against PED 97/23/EC, and is categorised under Clause 3 sub 3, which is according this directive below specified pressure and volume thresholds. The directive states that specified equipment and assemblies accordingly must (1) be safe, (2) be designed and manufactured according sound engineering practice, and (3) bear specified markings. To make sure that our LPG injection instruments are compliant with the directive, harmonised standard EN13445 is used for product design, and all possible risks are taken into consideration. Several safety measurements like relief and check valves are used, and each instrument is extensively tested and delivered with a certificate of test compliance.

ATEX

Equipment and safety systems for use in potentially explosive atmospheres should be designed in such a way that ignition of the surrounding atmosphere is impossible. The Sample Securitiser will be used in non-hazard laboratories, but explosive substances might be released at certain moments. Therefore the unit does not have any ignition sources by design, however some subcomponents are utilised with ATEX approval. For this reason the Sample Securitiser is fully compliant with directive 94/9/EC.

SAFETY CENTERED DESIGN: SCD

We have performed several dedicated risk assessments. Virtually all potentially hazardous circumstances have been taken into consideration in close contact with specialised safety consultancies. We also organised HAZOP assessments with representatives of expert laboratories on LPG analysis, and all possible situations and requirements were taken into account. Besides being compliant to the safely directives, also a user friendly device was designed in this way.

Figure 2
High priority on safety because of the involved high pressure and flammability

Figure 3
Compliance with ATEX directive

Figure 4
LPG analyser with LSV and Sample Securitiser

ANALYTICAL PERFORMANCE

There are two injection methods available for LPG analysis: injection as gas or as liquid. In case of gas injection, the sample is vaporised first, followed by injection though GSV (Gas Sampling Valve). This method works well for the analysis of permanent gases and hydrocarbons up to C4/C5.
When the sample contains higher boiling components as well, liquid injection is preferred to avoid loss of the heavier compounds. The liquid sample is injected through LSV into a heated Split injector for fast evaporation before entering the analysis column. For reliable quantitative results, complete filling of the sample loop is essential, and partial evaporation prior to injection must be avoided. This is achieved by applying a controlled pressure that is set above the sample pressure (10-20 bar). At this point the Sample Securitiser proves its importance by delivering high pressure resulting in good analytical performance under safe conditions.

LPG is analysed for several components, dependent on its usage. Measurement of hydrocarbon impurities is quite common, but especially when LPG is used as a feedstock in production which involve catalysts, analysis of trace impurities is of great importance. In this poster the analysis of ppb/ppm Sulfur components and permanent gases is shown.

❶ LOW LEVEL SULFUR

Figure 5 shows the analysis of various Sulfur species in liquid Propylene, according to ASTM D6228, D5303 or 5504. PFPD (Pulsed Flame Photometer Detector) is applied for ppb detection limit. Figure 6 shows the chromatogram of a calibration standard; figures 7, 8 and 9 show excellent repeatability, linearity and detection limit.
The system has a highly inert sample path, which is a strict requirement for obtaining good peak shape and low detection limit. FPD (Figure 10) is also available at lower costs, when higher (about 5 times) LOD is sufficient.

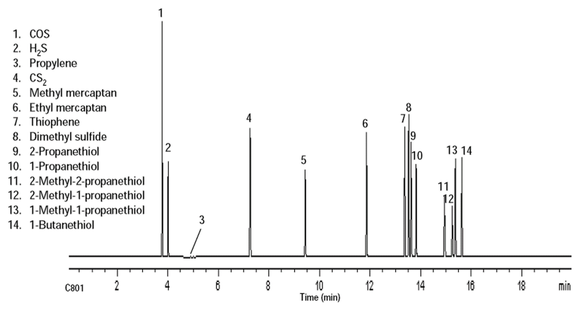

Figure 5
Sulfur components in Propylene at ppb level using PFPD detection.

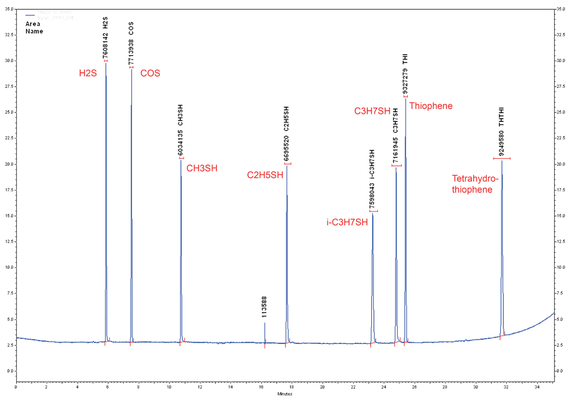

Figure 6
Calibration standard of Sulfur components in N_2 (5 ppm each). Injection GSV; detection: PFPD.

GC-PFPD ID	H2S Area	COS Area	CH3SH Area	C2H5SH Area	i-C3H7SH Area	C3H7SH Area	THI Area	THTHI Area
PFPD_071	7653680	7716514	6026713	6764998	7612207	7096988	9317300	9228699
PFPD_072	7575351	7695225	5928568	6794046	7631111	7204149	9296086	9213385
PFPD_073	7648397	7698897	6013745	6725392	7641811	7193838	9352864	9246370
PFPD_074	7608142	7713938	6034135	6695520	7598043	7161945	9327279	9249580
Min:	7575351	7695225	5928568	6695520	7598043	7096988	9296086	9213385
Max:	7653680	7716514	6034135	6794046	7641811	7204149	9352864	9249580
Mean:	7621393	7706144	6000790	6744989	7620793	7164230	9323382	9234509
Std Dev:	36820	10646	48880	43352	19489	48294	23569	16811
%RSD:	0.48	0.14	0.81	0.64	0.26	0.67	0.25	0.18

Figure 7
Repeatability at 5 ppm concentration level. PFPD detection

Component	LOD (ppb)
H_2S	17
COS	18
CH_3SH	25
C_2H_5SH	27
i-C_3H_7SH	39
C_3H_7SH	30
Thiophene	22
Tetrahydrothiophene	30

Figure 8
LOD Sulfur components (3*noise).
PFPD detection

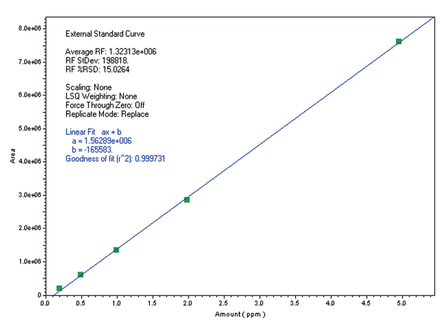

Figure 9
Linearity curve of H_2S: r^2 = 0.9997 for 100ppb - 5 ppm. (r^2 > 0.995 for all components)

Figure 10
FPD Instant Connect Detector Module (Thermo Trace 1300 GC) is available when 100 ppb detector limit for Sulfur species is sufficient as an alternative for the more expensive PFPD.

❷ LOW LEVEL SULFUR using COMPACTGC$^{4.0}$

Figure 11 shows the measurement of low level Sulfur in hydrocarbon matrices by CompactGC$^{4.0}$, a fast 19" MicroGC, equipped with PFPD for this purpose (Figure 12). Two analytical channels with different columns are used for best possible separation. Both channels share the same PFPD. Components like H2S, COS and Mercaptans are analysed at ppb level in this way. Additional channels are available for hydrocarbons and permanent gases with FID, TCD and PDD detectors. The instrument is calibrated using a gas standard, which can be diluted by the MK5 Calibrator module for multi-level calibration (Figure 13). This module can be equipped with permeation tubes with Sulfur components as well, avoiding the use of a calibration gas.

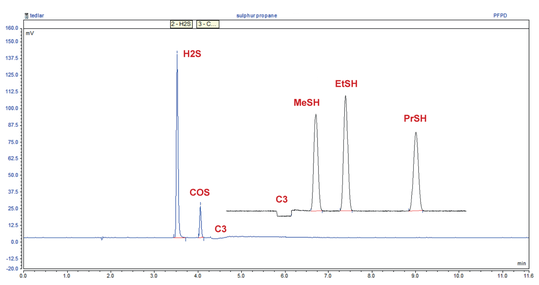

Figure 11
Analysis of H_2S, COS and Mercaptans by CompactGC$^{4.0}$
1 ppm level; PFPD detection

Figure 12
CompactGC $^{4.0}$ 19" GC equipped with PFPD

Figure 13
Calibrator module for generating/diluting calibration gases

❸ LOW LEVEL PERMANENT GASES

Figure 14 shows the chromatogram of low level permanent gases in LPG, according to ASTM D2504, using PDD (Pulsed Discharge Detector). A second channel for CO_2 and other components according to ASTM D2505 is available as well.
After vaporising, the sample is injected by GSV. The LPG matrix is effectively back flushed, and therefore not seen in the chromatogram. Figure 16 demonstrates the lowest detection limits of the instrument, which are in the low ppb range. A very low background level is mandatory in achieving such low LOD values, which is realised thanks to the use of diaphragm valves with internal purge option (Figure 15).

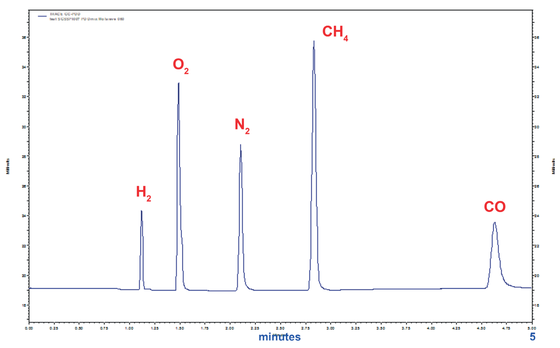

Figure 14
Analysis of permanent gases in LPG. Calibration standard at 10 ppm level. Detector: PDD

Figure 15
Thermo Trace 1300 GC with auxiliary valve oven, diaphragm valves and Pulsed Discharge Detector

Component	LOD (ppb)
H_2	<20
O_2	<15
N_2	<15
CH_4	<15
CO	<25

Figure 16
LOD of permanent gases (at 3*noise) in LPG

SUMMARY

The Sample Securitiser from Global Analyser Solutions guarantees high laboratory safety and complies with Pressure Equipment Directive 97/23/EC and ATEX Directive 94/9/EC. Besides high safety, accurate results are achieved as well. GAS offers dedicated solutions for low Sulfur species and permanent gases in LPG.

For more information, please visit www.gassite.com

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