



Fast and Reliable TS Determination in Liquefied Pressurized Gases (LPG) according to ASTM D6667, ASTM D7551, and DIN EN 17178

Challenge

Fast and matrix-independent analysis of LPG samples of a wide concentration and pressure range.

Solution

Fast, safe, and reliable analysis of the LPG by direct sample dosing from the liquid phase followed by controlled complete combustion of all LPG components.

Introduction

Gaseous compounds in the liquefied pressurized state are valuable source materials for chemical synthesis or polymerization, but are also increasingly utilized as energy carrier for heating, power generation and transportation purposes. The concentration of sulfur compounds is a key parameter for their quality and usability, for example as propellant gas or as starting material in polymer production (e.g., polyethylene). Because sulfur compounds may cause catalyst poisoning and undesirable byproducts, their content should be <100 ppb, to avoid increased production costs. For the use as combustible or fuel (LPG, CNG), different requirements and standards apply. Here emission limits for sulfur must not be exceeded and the odorants (e.g., mercaptan) added for safety reasons must be at the appropriate level. To guarantee optimum product quality and instant process optimization, the rapid detection of ultra-low and high sulfur contents is required in LPG analysis.
Analysis of an LPG is more challenging than any other sample matrix due to two big challenges. The first is the sample metering and dosing into the analyzer, the second the safe and complete combustion of this vigorously reacting matrix.

Due to widely varying pressures, safe and controlled handling and quantitative dosing of LPG into the combustion zone is challenging. Samples tend to evaporate too early, affecting analysis quality and operating safety due to deflagration, explosion, soot formation or incomplete combustion. When expanding the LPG to allow a more controlled handling, the samples undergo changes due to adsorption

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loss, condensation, etc., which clearly influences the analysis quality. Direct LPG analysis out of the liquefied phase followed by stepwise evaporation in controllable safe small volumes is one approach to overcome these challenges. Sulfinert™ coating of relevant system parts and the PermaPurge function help to avoid adsorption losses of reactive TS compounds.

Materials and Methods

Samples and Reagents

- 3.71 mg/l S, certified LPG standard
- LPG 1 sample (propylene matrix)
- LPG 2 sample (butane/propane mixed matrix)

The samples and the standard were contained in LPG cylinders. The sample pressures varied within a wide range from 5 to 17 bar.

Sample Preparation

The LPG samples and the LPG standard were analyzed directly without sample pretreatment. The adaptation of the sample pressure by adding an inert gas, to increase the sample pressure to a certain level, is not necessary.

Calibration

The analysis system was calibrated prior to the actual determination. Therefore one certified LPG standard, based on dimethyl sulfide in propane, was used. To cover a broad concentration range, different volumes of this LPG standard were injected to generate a wide-range calibration. Figure 1 and 2 depict typical calibration curves and performance parameters of an LPG calibration.

calibration range	1
measurement range [µg]	0,01855 - 0,1855
measurement range [AU]	9,264 - 79,860
k_0	1,876,5
k_1	422,562,5
coefficient of determination, R^2	0,99960
calculation volume, V_{Cal} [µl]	50
calculation density, ρ_{Cal} [-]	-
detection limit [µg/l]	107,59
quantification limit [µg/l]	439,82
method standard deviation [µg/l]	36,91
method coefficient of variation [%]	2,21
linearity	linear

Fig.1: TS calibration for the trace range

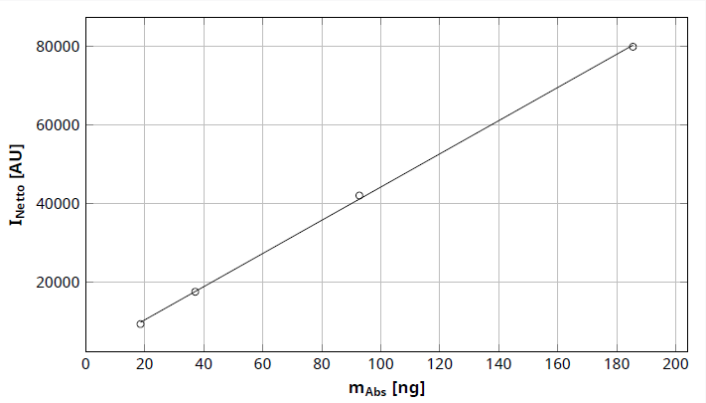


Fig.2: Typical calibration curve of the HiPerSens UVFD detector

Instrumentation

The analysis was performed on a compEAct S elemental analyzer. The system was equipped with HiPerSens UVFD detector, and the LPG 2.0, a matrix-optimized dosing system for liquefied pressurized gases. It enables the safe and controlled automatic dosing of liquefied pressurized gases (LPG) with sample pressures up to 34 bar, in compliance with ASTM D6667, ASTM D7551, and DIN EN 17178.

The LPG 2.0 is equipped with a cooled sampling valve to avoid an uncontrolled and too early evaporation of the liquefied pressurized sample. The integrated evaporation chamber ensures the quantitative evaporation of all sample components in shortest time, even of such heavy compounds as inhibitors or odorants. The standard Sulfinert™ coating for all relevant components, in combination with the PermaPurge feature, effectively avoids adsorption loss and thereby undesired memory effects.

The LPG 2.0 can be used very flexibly for the automatic metering of liquefied gases at different pressures. The sample volume can be varied by the user within the range of 1–50 µl (liquid phase). For the analyzed samples and the standard injection volumes between 5 and 50 µl (taken directly from the liquid phase) were used.



Fig. 3: LPG 2.0 module with sample cylinder

To ensure that this process is fast and completely matrix-independent, a specially designed quartz glass reactor including a quartz-pyrolyzer was used. The sophisticated management if process gases allows lighter sample components to evaporate quickly and safely in a pure inert carrier gas atmosphere. Heavier components are pyrolyzed quickly and controlled on the active surface of the quartz-pyrolyzer. This way only the volatized components enter the combustion zone in the first stage of the process. In the second stage, the formed pyrolysis products as well as other heavier sample components, which were retained by the quartz-pyrolyzer, are digested quantitatively in the presence of pure oxygen at 1050 °C.

Before entering the detection system, the combustion gases are cleaned and dried. The remaining SO_2 is detected by means of UV fluorescence. With its high sensitivity, the device allows a detection limit as low as 5 ppb S (0.2 ng S absolute) without time-consuming enrichment procedures (trap-and-release).

Method Parameters

Standard method settings for vertical operation provided in the library method for LPG analysis (e.g., ASTM D6667) are applied. The parameter settings for the combustion and sample introduction process are summarized in Table 1. The evaluation parameters for the detection of sulfur are given in Table 2.

Table 1: Process parameters

Parameter	Specification
Furnace temperature	1050 °C
Second combustion	60 s
Ar flow (first phase)	200 ml/min
O_2 main flow	100 ml/min
O_2 flow (second phase)	100 ml/min

Table 2: Detection parameters - UVFD

Parameter	Specification
Max. integration time	300 s
Start	0.5 cts
Threshold	0.5 cts

Results and Discussion

The results of the analysis of two different LPG samples and one standard material are summarized in Table 3 and 4. They are either averages of ten (Table 3) or three replicate analyses (Table 4). Due to the matrix-optimized combustion, a threefold determination is sufficient to achieve results far below 3 % RSD. This is remarkably affecting the sample processing time and therefore generates a higher sample throughput. The analysis results and their reproducibility depict the high quality of the digestion process. The proper performance and stability of the analysis system was confirmed by analyzing a TS standard material with known concentration (see Table 3).

Table 3: Reproducibility test with 3.71 mg/l S LPG standard

Analysis	1	2	3	4	5	6	7	8	9	10
c_S in mg/l	3.70	3.69	3.71	3.73	3.65	3.70	3.66	3.67	3.69	3.72
Average value	3.69 mg/l									
SD	0.02 mg/l									
RSD	0.54 %									
Nominal value	3.71 mg/l									
Deviation	0.49 %									

The deviation of the single analysis from the average as well as the deviation of the average result from the certified nominal value is less than 1 %.

Table 4: Results of the sulfur determination for the LPG samples and LPG standard

Measurement	c_S	SD	RSD
LPG 1	4.25 mg/l	< 0.01 mg/l	0.13 %
LPG 2	5.23 mg/l	0.05 mg/l	0.96 %
LPG Standard 3.71 mg/l S	3.70 mg/l	0.02 mg/l	0.63 %

To optimize the analysis process the sample volume can be adjusted flexibly to the expected sulfur contents in order to achieve the optimal result in the shortest time. Thanks to the high precision of the metering technology, the next sample can be analyzed after a minimum of replicate measurements resulting in high sample throughput.

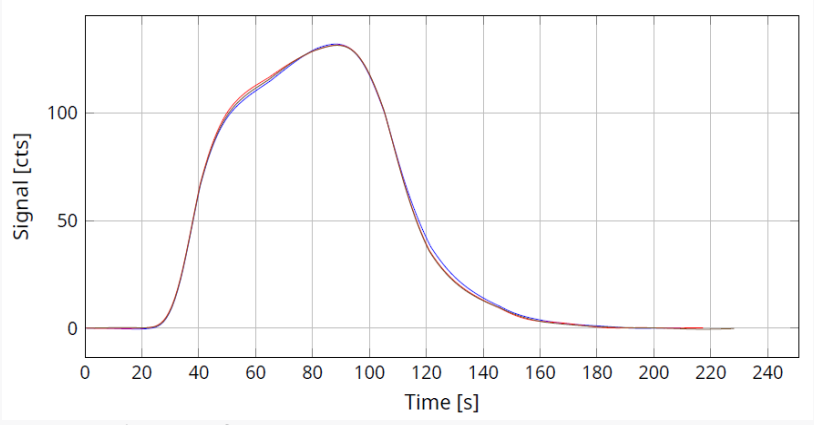


Fig. 4: TS analysis curve for LPG 1

Figure 4 and 5 show the TS analysis curves of both LPG samples. The duration of the measurement depends on the sulfur content and metering volume, and is in average between 150 and 240 seconds.

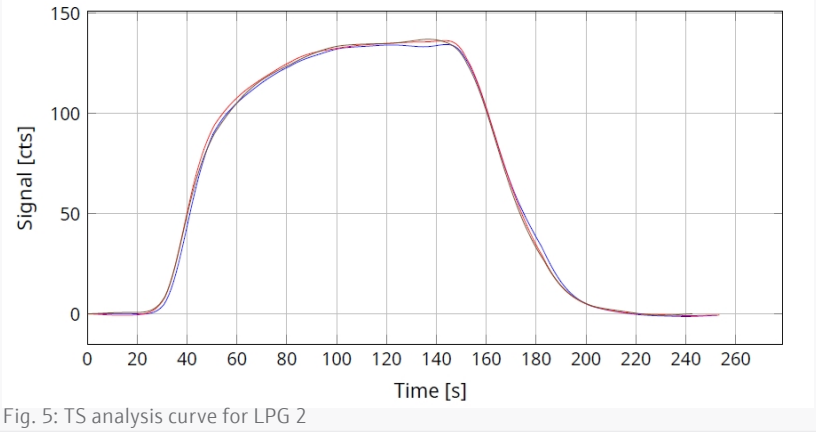


Fig. 5: TS analysis curve for LPG 2

Conclusion

The compEAct S together with the LPG 2.0 sample supply system provides a fast and reliable solution for the precise determination of widely varying sulfur contents in liquefied pressurized gases (LPG). The system can handle the samples independent of their initial pressure, a time-consuming and error-prone pre-treatment (resp. pressurization with argon, expansion into gas bags) is not necessary.

High-precision metering technology and intelligent safety functions integrated into the instrument, such as the Auto-Protection and Self Check Systems, ensure complete sample digestion and thus a high quality of the results. In addition, the integrated filter system, the Sulfinert™ coating of the relevant sample paths, and the purge tool for preventative care, significantly minimize the maintenance effort and downtime. The easy-to-operate hardware and top safety standards permit use in shift operation and in analysis centers with the highest possible sample throughput.
Thanks to the unique HiPerSens technology, a measuring range of up to 10,000 mg/l starting at a limit of detection as low as 5 µg/l of sulfur can be achieved easily.

If needed, the analysis system can be extended for the determination of TS in liquid or gaseous matrices (e.g., diesel, HEL, methane) by adding one of the optional sampling systems for liquids or gases.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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