Challenge

Fast, safe and reliable matrix-independent analysis of LPG samples of a wide concentration range and pressure spectra.

Solution

Direct sample dosing from liquid phase, controlled complete combustion and result evaluation using liquids calibration mode.

Intended audience

Analytical labs and professionals in the oil & gas, petrochemical, and fuel industries focused on sulfur trace analysis in LPG and gaseous hydrocarbons.

Determination of total volatile sulfur in gaseous hydrocarbons and liquefied petroleum gases by ultraviolet fluorescence according to ASTM D6667 resp. ASTM D7551

Introduction

This application note describes different application methods for the fast and reliable determination of widely varying sulfur contents by means of UV fluorescence with a minimum effort for calibration and sample preparation. Gaseous hydrocarbons are valuable source materials for synthesis processes, fuels, energy carriers or auxiliary materials in pharmaceutics and cosmetics. Their quality and composition, especially their sulfur content, play an important role. To use them as propellant gas, they need to be free from sulfur (c < 100 ppb). The same applies to their use in the synthesis of high molecular compounds (e.g., polyethylene), since sulfur compounds may cause catalyst contamination, undesirable byproducts and increased production costs. A reliable sulfur trace detection in such matrices requires precise and safe metering technology, quantitative combustion and highly sensitive detectors.

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 sulfurous odorants 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. LPG analysis confronts the operator with two main challenges: 1) the sample digestion, including introduction and combustion quality and 2) the analysis evaluation, including calibration strategies and quality assurance of results.

Due to widely varying pressures, safe and controlled handling and dosing of LPG into the analysis system 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 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. Inert coating (e.g. SilcoNert) of relevant parts thereby supports the detection of the tiniest TS impurities without falsifying component losses. Still, a quantitative sample conversion does not necessarily lead to correct analysis results. These strongly depend on a suitable and correct calibration strategy. In general, the system is calibrated either by just one certified standard using a single point calibration or by doing an error-prone and laborious dilution line for one standard material. The first approach can deliver suitable results when high element contents must be analyzed and the blank need not be considered. For analysis in the trace and ultra-trace range, where there are no suitable calibration gases available, this strategy will deliver results that are false, because they are too low. Here, the use of a dilution line is recommended but requires a dedicated and skilled operator as it bears a high risk of error (changing blank, adsorption loss, cross-contamination, pressure effects, etc.).

The problems discussed here can be easily avoided by applying alternative calibration strategies. These simplify lab work and make it possible to obtain reliable results independent of the operator's skills and experience. System calibration can be achieved using a calibration gas with variable injection volumes, as well as calibration kits of liquid standards at different concentrations and constant injection volume. This is possible because the multi EA 5100 provides a quantitative detection. Detection of the SO2 is the same originating from the combustion of a liquid, solid or gaseous sample. Furthermore, the daily factor function helps to ensure the long-term stability of the respective calibration resulting in best results without laborious re-calibration of the system.

Materials and methods

Samples and reagents

- 3.70 mg/L TS standard (dimethyl sulfide in propane)
- LPG (butane/propane mix)

Sample preparation

The samples were contained in LPG cylinders. The sample pressure varied within a wide range. The LPG samples and standards were analyzed directly without sample pretreatment.

Calibration

The analysis system was calibrated in advance applying two different strategies to confirm the suitability of alternative calibration strategies compared to the common method. The calibration of the system using one calibration gas with variable injection volumes is shown in Figure 1 a. The calibration by means of liquid standards at different concentrations (here dibenzothiophene in iso-octane) is shown in Figure 1 b. The received calibration functions already indicate the comparability of both strategies.

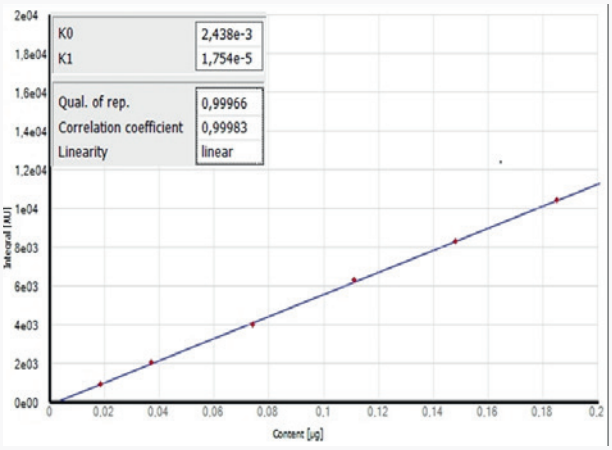

Figure 1 a: Calibration using a LPG standard

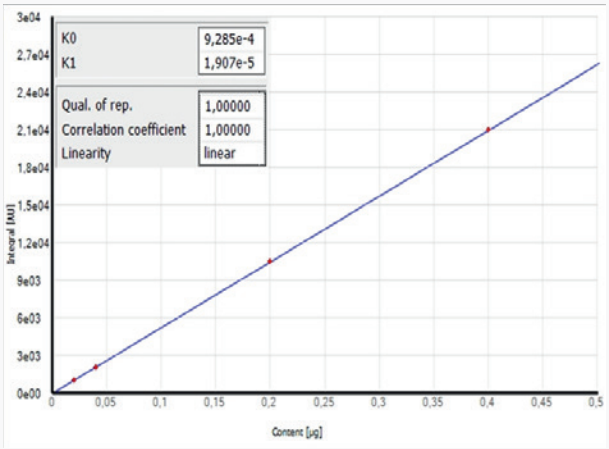

Figure 1 b: Calibration using liquid standards

Instrumentation

The analysis was performed on the elemental analyzer multi EA 5100 in vertical operation mode. The system was equipped with an LPG 2.0 high pressure LPG sampling system for the direct introduction of liquefied pressurized gases up to 34 bar, compliant with ASTM D6667 and D7551 and DIN EN 17178.

The LPG 2.0 module 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).During the analysis 10 µL sample volume (liquid phase) were injected for each LPG measurement.

LPGs can expand even with a minimum of pressure reduction (e.g., sampling). This results in a nonreproducible analysis of the sample at excessive speeds which leads to strongly scattering results and sooting of the analysis system. To prevent this, the sample pressure is normally increased using an auxiliary gas. Thanks to the cooled sampling valve of the LPG 2.0, this is no longer required. Even liquefied gases at lowest pressure (e.g., butadiene at 2.1 bar) can be analyzed with good reproducibility.

Prior to the transfer to the combustion module, the samples pass through a heated evaporation chamber where all components (inhibitors etc.) are quantitatively converted into the gaseous state. This prevents memory effects and hence incorrect measurements. The quantitative transfer of the gaseous samples to the combustion system is done using Perma Purge, a powerful inert gas flushing. The catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1,050 °C. In the first process phase, evaporation of volatile sample components in an inert gas stream takes place, followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier sample components and formed pyrolysis products are quantitativelyoxidized in pure oxygen. Thereby the quartz pyrolyzer ensures a uniform evaporation, modulates the combustion process, and prevents incomplete combustion. This establishes the best conditions for a reproducible and fast analysis. The implemented Auto-Protection System guarantees highest operational safety, including a particle and aerosol trap, and a complete transfer of the formed SO2 into the ultraviolet fluorescence detector (UVFD) after a sufficient drying of the reaction gases. The multi EA 5100 enables a detection limit of as low as 5 µg/L S, without time-consuming enrichment procedure (trap and release). To check the system performance, a fivefold analysis of a standard LPG was performed 10 times over a period of 24 hours. The deviation of the single analysis is less than 2%. Due to this excellent reproducibility, replicate measurements can be reduced to a minimum.

Figure 2: LPG 2.0 module

Table 1: Reproducibility test of LPG analysis

Measurement	1	2	3	4	5	6	7	8	9	10
c_S in mg/L	3.78	3.60	3.69	3.71	3.68	3.69	3.61	3.66	3.69	3.56
Average value	3.67 mg/L									
SD	0.06 mg/L									
RSD	1.77%									

Method parameter

Standard method settings for vertical operation stored in the method library are applied. The parameter settings for the combustion process are summarized in the following table. The quartz combustion tube was equipped with a quartz wool plug in the inner tube.

Table 2: Process parameters

Parameter	Specification for liquid calibration	Specification for LPG analysis and calibration
Furnace temperature	1050 °C	1050 °C
Second combustion	60 s	60 s
Ar flow (first phase)	150 mL/min	100 mL/min
O_2 main flow	200 mL/min	200 mL/min
O_2 flow (second phase)	150 mL/min	100 mL/min
Draw up	2 µL/s	automatically by LPG 2.0
Injection	0.5 µL/s	automatically by LPG 2.0

Evaluation parameters

Standard method settings from the method library are applied. They are summarized in the following table.

Table 3: S detection parameters

Parameter	Specification S
Max. integration time	240 s
Start	1.0 ppb
Threshold	1.1 ppb
Stability	7

Results and discussion

The results of the analysis of two different LPG samples and one standard material are summarized in Table 1, 4 and 5. They are either averages of five (Table 1) or three replicate analyses (Table 4–5). Due to the matrix-optimized combustion, a threefold determination is sufficient to achieve results within 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 of the analysis system and suitability of the applied alternative calibration strategy (adaptation of liquids calibration) was confirmed by analyzing a TS standard material with known concentration (see Table 4).

Table 4: Comparison of different calibration strategies

Sample	c_S [mg/L] LPG calibration	c_S [mg/L] Liquid calibration
3.70 mg/L TS standard (dimethyl sulfide in propane)	3.73 ± 0.03 mg/L	3.73 ± 0.03 mg/L
LPG (butane/propane mix)	579.59 ± 5.10 µg/L	571.62 ± 5.55 µg/L

For the liquefied gases (2) and (3) a volume of 20 µL was dosed. With regards to the high purity of the sample (1), the volume was increased to 50 µL in order to achieve the best possible results.

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.

Figure 3 shows a typical TS analysis curve. The duration of the measurement depends on the sulfur content and metering volume and is between 150 and 420 seconds.

Table 5: Sulfur contents of the examined gas and liquefied gas samples

Sample	c_S [mg/L]	SD [mg/L]
Butadiene (1)	0.02	< 0.01
6.56 mg/L S in butane (2)	6.56	0.11
3.70 mg/L S in propane (3)	3.73	0.03

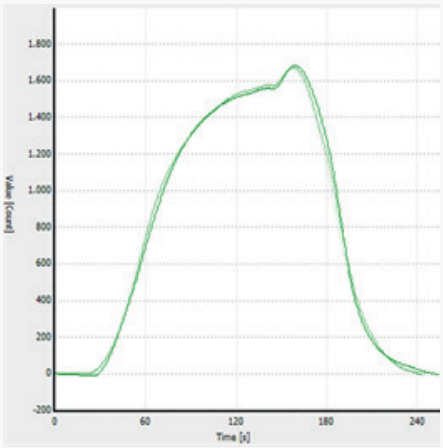

Figure 3: TS analysis curve for propane (LPG)

Figure 4: multi EA 5100

Summary

By applying liquids calibration, a high quality of the analysis results can be achieved in less time with minimum effort and costs compared to the classical calibration methods (one-point LPG or LPG dilution line). The results achieved using both strategies are equivalent. Especially in trace and ultra-trace analysis, the use of liquids calibration is superior, as it allows a sufficient blank correction, and reliable liquid standards are available in concentration levels as low as ppb-level.

With the LPG 2.0 and the analysis system multi EA 5100, liquefied gases can be analyzed independent of their matrix properties and pressure in the shortest possible time without any sample pretreatment. High-precision metering technology and intelligent safety functions integrated into the instrument, such as the Self Check System, ensure complete sample digestion and thus a high quality of the results.
Additional functions, such as the integrated filter system and the purge tool for preventative care, significantly minimize the maintenance effort. The easy-to-operate hardware and top safety standards permit use in shift operation and in analysis centers with the highest possible sample throughput. Due 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 easily achieved. The optimal sample digestion and the efficient Auto-Protection System, including a high capacity membrane dryer, enable excellent reproducibility.

Recommended device configuration

Table 6: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 5100	450-300.011	Elemental analyzer for determination of sulfur, nitrogen, carbon
C/N/S High-performance drier kit	450-300.012	Efficient reaction gas drying for CNS analysis
S module basic	450-300.021	Extension for sulfur determination by UV-fluorescence detection
LPG module 2.0	450-900.465	Autosampler for LPGs
multiWin software	450-011.803	Control and evaluation software, incl. method library

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