

# Whitepaper | Oil & Gas

## New paths for LPG analysis

Faster and safer analyses thanks to new calibration strategies and analyzer technologies



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## Who should read this whitepaper?

The whitepaper addresses lab managers and technicians in quality, control, and contract laboratories in the petrochemical, chemical, and polymer industries, who have to analyze LPG samples on a daily basis.

We are presenting a new method for LPG analysis that greatly improves the safety in your lab and the quality of your analysis results. The analysis times are also much shorter. Even non-specialist personnel can thus safely and quickly measure LPG samples. The method only has to be integrated once.

The presented alternative strategy for LPG analysis is suitable for the detection of nitrogen, sulfur, carbon, and chlorine compounds.

## Key Learnings

- New calibration strategies for faster, more reliable trace and ultra-trace measurement results
- Avoidance of complex sample preparation
- Increased safety and analytical quality in the laboratory
- Faster workflows – even for non-specialist users
- New analyzer concepts for C/N/S/X analysis

## 1. A new approach to LPG analysis is urgently needed

The industrial importance of gaseous hydrocarbons as additives and propellants in the pharmaceutical and cosmetic industries has grown steadily in recent years. In addition, they are increasingly being used as fuels, and are valuable starting material for synthesis processes. Their composition – i.e. their quality – plays an essential role for the quality and properties of subsequent products.



Above all, a high sulfur content has a negative effect: For the use of gaseous hydrocarbons as fuels or combustibles in the form of LPG (Liquefied Pressurized Gases) or CNG (Compressed Natural Gas), the active legal limit values (e.g. 10 ppm S in the EU) for fuels must be adhered.

The same applies to the synthesis of high molecular weight composites such as polypropylene. Excessively high levels of sulfur cause catalyst contamination, unwanted byproducts and thus high production costs.

To ensure optimal product quality and a time and cost-effective process, LPG samples must be analyzed quickly.

Therefore reliable and safe analyzers are required, based on quantitative combustion and high sensitivity of detection.

There are two hurdles to overcome here: Sample digestion/introduction and the evaluation of the analysis results.

To help you overcome these hurdles and make your analysis process safer, faster, and more sensitive, read this whitepaper.

We wish you many valuable insights.  
Your Analytik Jena Team

## 2. Challenges faced by LPG analysis

In a laboratory there are many factors that potentially influence the analysis process and thus the quality of the results. Analyzing LPGs is particularly challenging. Almost every step of the work process has pitfalls that a user needs to consider - from sample dosing to digestion to evaluation of the results. Essentially, two issues cause problems for control and quality laboratories.

### 2.1 Elaborate sample preparation and safety risks

Due to changing pressure conditions, the controlled and safe handling and dosing of LPG in an analytical system is difficult. The samples tend to change very quickly from the liquid to the gaseous state. This not only leads to inferior analysis results, but also involves major safety risks in the laboratory - for example, due to soot formation, incomplete combustion, and above all a risk of explosion.

There are two basic approaches to overcome these hurdles. On the one hand, many laboratories initially convert the LPG into a pressureless, gaseous state, in order to then feed it relatively safely and simply to the analyzer. However, other complications occur during this procedure. Condensation or adsorption losses - to name only two - occur, which also have a negative impact on the analysis (results too low). Quantitative sample conversion does not necessarily give good results. On the other hand, a high additional pressure is applied to the cylinder with the LPG sample with the aid of an inert support gas. This counteracts a premature decompression of the sample and associated, strongly scattering analysis results. However, this strategy also carries its risks. The application process requires a skilled user so as not to change the original sample and the support gas itself has quite an effect on the determined element content (type of gas, quality, moisture content, etc.).

### 2.2 Stability and suitability of LPG standards for the ultra-trace range

For the analysis of LPG samples, analyzers are generally calibrated by single-point calibration using a commercial, certified LPG standard. Another possibility is to create a complex and, depending on the abilities and experience of the user, more or less error-prone dilution series to cover a wider concentration range.

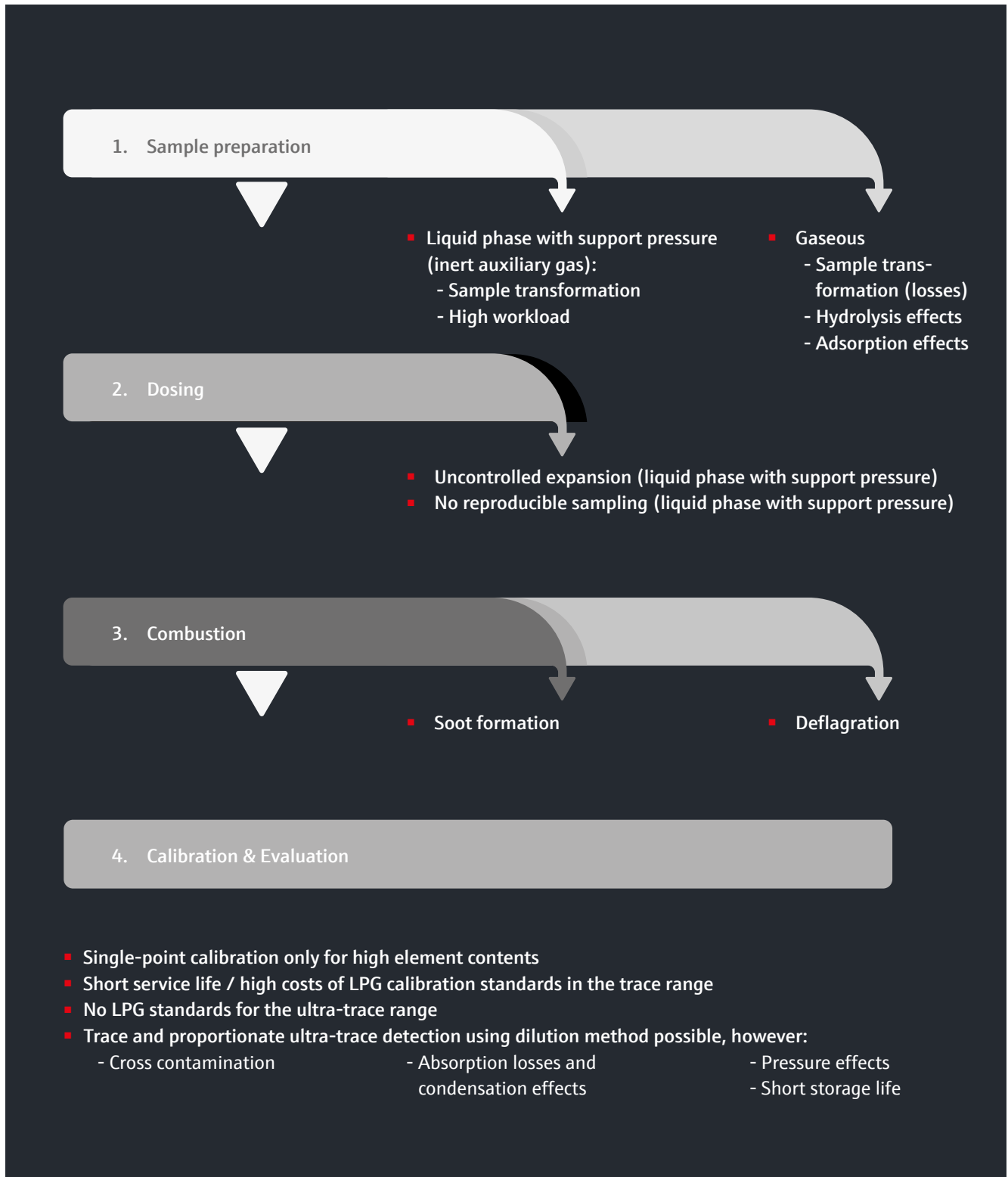
The first way can lead to acceptable results, as long as only a high element content in the ppm range (ppm = parts per million) has to be analyzed. The detection of trace or

ultra-trace elements is a different matter. The low detection limits in the ppb (parts per billion) range needed to reliably determine such small traces of elements is simply too low for the commercially available LPG standards. In addition, the required blank value correction is not possible due to the lack of the original matrix. This results in incorrect and far too low measured values.

Although it is possible to determine trace elements with the „home-made“ dilution method mentioned above, the risk of error is very high. Fluctuating blank values, cross-contamination, adsorption losses, pressure effects, and other factors make this work mode very difficult.

But there is some good news: There are now solutions for both the time-consuming preparation of samples and sometimes hazardous dosing into the combustion system, as well as the generation of trustworthy and sensitive calibrations for the determination of low-trace levels. The difference was made by an innovative dosing technique that extracts the sample aliquot to be dosed directly from the untreated liquid phase of the original sample and new calibration strategies based on a matrix-independent, quantitative conversion of all sample components. The analysis of LPGs thus becomes a routine task - even for non-specialist personnel in the laboratory. How this works in detail is explained in the next section.

### 2.3 Hurdles of LPG analysis



### 3. The alternative approach



#### 3.1 Alternative calibration strategies using liquid standards

Instead of calibrating using only one certified calibration gas, calibration kits with different liquid standards, different concentrations and a constant injection volume, can also be used. A particular advantage of this strategy: The calibrations generated in this way are blank value-corrected, which enables precise/correct working in the ultra-trace range (ppb) and thus significantly improve the quality of the analysis. Compared to classic single-point calibration or an LPG dilution series, laboratories using this calibration strategy can achieve reliable results in less time and at lower cost – and irrespective of the user's level of experience.

The prerequisite for this is an analyzer that quantitatively digests standards and samples, irrespective of the matrix type. For the analysis of sulfur, for example, it is irrelevant to the detector whether the  $\text{SO}_2$  to be measured originates from the combustion of liquid, solid, or gaseous samples.

One nanogram of sulfur always produces the same amount of  $\text{SO}_2$  when the combustion is quantitative. Even if the shape of the measured curves may look different process-related, the integration provides identical results.

The effectiveness of the method compared to conventional calibration is illustrated by the following example of the measurement of TS (total sulfur) in LPG samples using different starting matrices, pressures and concentrations. Figure 1 shows the calibration using a certified calibration gas and varying injection volumes. Figure 2 shows the new method using liquid standards in different concentrations (in this case dibenzothiophene in isooctane). The following table again demonstrates the robustness of the method compared to conventional calibration strategies.

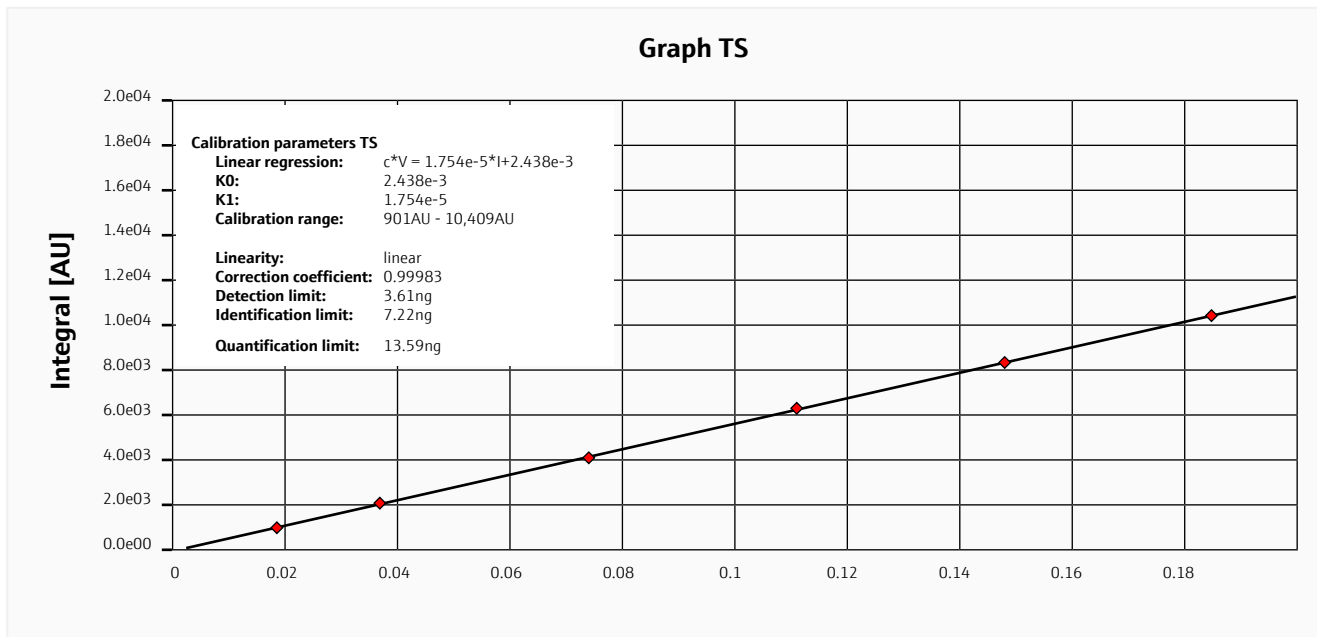


Figure 1 a: Calibration using a single LPG standard and different injection volumes

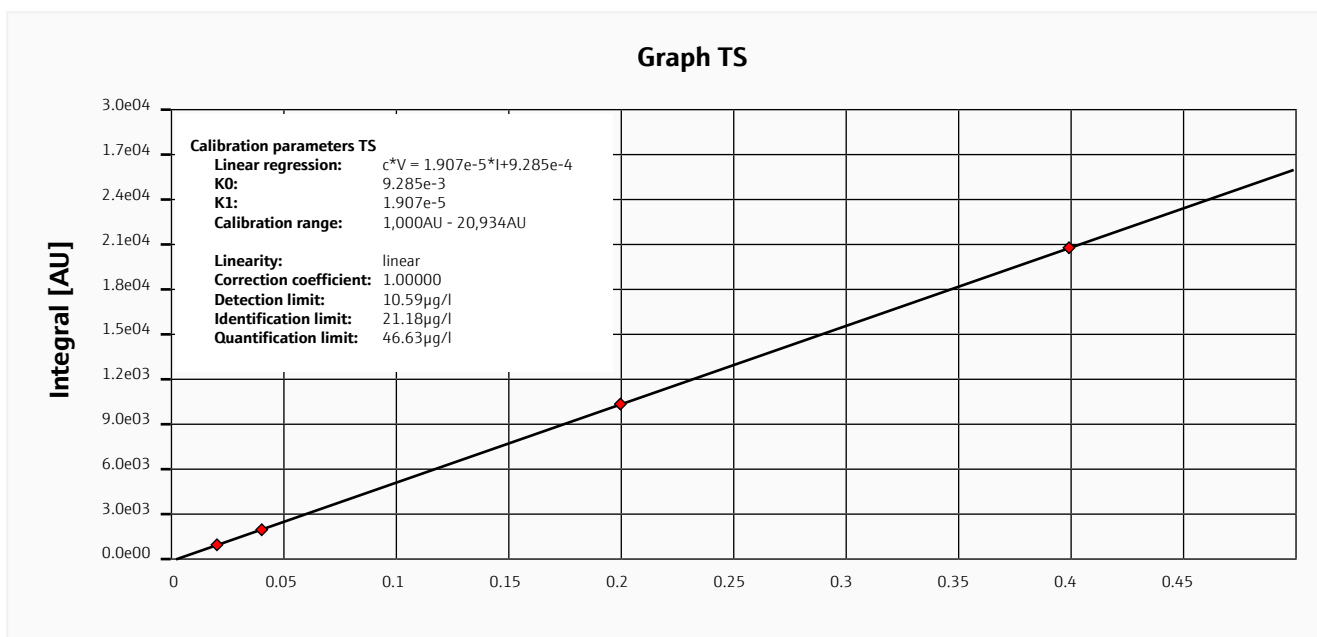


Figure 1 b: Calibration using liquid standards with different concentration levels

Sample	$c_s \pm SD$ [mg/L] LPG calibration	$c_s \pm SD$ [mg/L] Liquid calibration
3.70 mg/l TS standard (dimethyl sulfide in propane)	$3.73 \pm 0.03$ mg/L	$3.74 \pm 0.03$ mg/L
LPG (butane/propane mix)	$579.59 \pm 5.10$ µg/L	$571.62 \pm 5.55$ µg/L

Table: Comparison of different calibration strategies





### 3.2 Sample preparation and dosing

With the help of matrix-optimized dosing systems, it is now possible to analyze LPGs regardless of their pressure or their matrix properties. The LPG 2.0 module from Analytik Jena is one such system, which allows a number of Analytik Jena's elemental analyzers to be upgraded for simplified LPG analysis. Effort and time are reduced considerably, since a sample pre-treatment is superfluous – the workflow is thus simplified.

Liquefied gases can be injected directly into the combustion system using the LPG 2.0 module. It has a heated evaporation chamber, which converts all matrix components into a gaseous state in a very short time. Memory effects during the measurements are thus impossible. These – now gaseous – samples are then quantitatively transferred with the aid of an inert gas into the combustion system, where they are completely oxidized at 1050 °C in a two-phase process.

### 3.3 Improved analyzer technology

An essential prerequisite for the successful calibration of the system using liquid standards is the matrix-independent, quantitative combustion. This is guaranteed by optimal process control (gas flows, evaporation rate, combustion temperature, etc.).

In combination with the HiPerSens detection system, a uniquely wide concentration range can thus be covered. These detectors combine the highest detection sensitivity in ultra-trace analysis with far-reaching linearity, even in the highest working range. Samples with, for example, high and low element contents can be processed together in one measurement sequence using only one method. High concentration samples can be analyzed directly without dilution.

In addition to the detectors, further innovations ensure simplified analysis. In elemental analyzers of the current generation, there are many small features that make a big difference in total. For example, in modern dosing systems, analytically relevant components are coated with SilcoNert®, which minimizes adsorption losses. In addition, there are improvements with regard to combustion and device safety, such as the high-precision and stable control of the gas flows, integrated pressure sensors, and the automatic leak check. Thanks to these technologies, you get reliable results after just a few repeat measurements and significantly reduce maintenance work.

### 3.4 Overview of advantages

#### Preconditions

- Loss-free dosing
- Safe, quantitative sample digestion
- Highly sensitive detection

#### 1 Calibration using liquid standards

- Complete, matrix-independent combustion
- Cost-effective
- Long-term stable
- Simply and quickly available
- Also for the trace and ultra-trace range
- Matrix blank value to correct the calibration (inclusive)

#### 2 Technological innovations

- Low detection limits without trap-and-release
- One sampler for high and low concentrations
- SilcoNert® coating against adsorption losses
- Variable dosing volume
- No too early sample decompression thanks to cooled sampling valve
- Particle filter for component protection
- Purge tool for preventive cleaning of the dosing valve



## 4. LPG analysis as a routine application in every laboratory

Calibration using liquid standards not only provides excellent analysis results, but also saves time, cost and effort compared to traditional LPG single-point and dilution methods.

The advantages of the method are particularly evident in the detection of trace and ultra-trace elements. In addition to the possibility of extremely important blank value correction, reliable liquid standards with concentrations in the low ppb range are also commercially available at a reasonable cost.

State-of-the-art analyzer technology is another step towards process efficiency in LPG analysis. Complete combustion, highly sensitive detection, intelligent safety features, libraries with proven, standard-compliant methods, predictive maintenance, and many other small optimizations save additional time and effort.

Technology and the right calibration strategy together make the difference and the analysis of LPGs a safe and efficient routine application.

## Annex

### LPG 2.0-Modul

Analytik Jena is extending its range of elemental analyzers for nitrogen, sulfur, carbon, and chlorine determination in LPG samples with the LPG 2.0 sampling system.

The module enables direct dosing of LPGs up to 34 bar. It can be used flexibly for the automatic dosing of liquefied gases at different pressures. The sample volume can be freely adjusted by the user in a wide range from 1  $\mu\text{L}$  to 50  $\mu\text{L}$ .

The LPG 2.0 sampling system complies with ASTM D6667, ASTM D7551, and DIN EN 17178.



### Analyzers that can be equipped with the LPG 2.0 module



#### compEAct TN/TS analyzer

- High throughput with up to 160 samples per day
- Independent operation 24/7
- Minimal maintenance / predictive maintenance functions
- Minimal space requirement



#### multi EA 5100 C/N/S/X analyzer

- C/N/S/X analysis without device conversion
- Highly sensitive detection systems
- One analyzer for solid, liquid, and gaseous samples
- Maximum operational safety
- Future-proof due to modular design

## Application examples

**Application Note · compEAct**



**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.

**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 <math>< 100\text{ ppb}</math>, 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 solvents (e.g., mercaptan) added for safety reasons must be at the appropriate level. To guarantee optimum product quality and instant

### Application Note · compEAct

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

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**Application Note · multi EA 5100**



**Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence According to ASTM D6667 resp. ASTM D7551**

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

**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 pharmaceuticals 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 (<math>< 100\text{ ppb}</math>). The same applies to their use in the synthesis of high molecular compounds, (e.g., polyethylene), since sulfur compounds may cause catalyst contamination,

### Application Note · multi EA 5100

Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence According to ASTM D6667 resp. ASTM D7551

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### Links

- Industrial solutions → **Oil & Gas**
- C/N/S/X analysis → **multi EA 5100**
- C/N/S/Cl analysis → **compEAct**

## Get a free consultation

You want to improve your LPG analysis?

Analytik Jena's application team is here to support you.  
Your optimized workflow is just a few clicks away.

**Request  
consultation**

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