

Rapid Reliable Sulphur Determination in Gases and Liquefied Gases (LPG)

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The possible applications of gases are just as versatile as the requirements for instrument technology. The properties of this matrix type affect the safety, the required effort, the completeness of sample digestion and thus the quality of the results. High precision metering technology and intelligent safety functions integrated into the instrument, such as the Self Check System, are therefore essential. With the GSS/LPG module and the analysis system multi EA® 5000 gases and liquefied gases can be analysed in the shortest possible time without any sample preparation

Gas analysis – a wide field of application

Gaseous hydrocarbons increasingly gain in importance. They are valuable source materials for synthesis processes, fuels, energy carriers or auxiliary materials in pharmaceuticals and cosmetics. Their purity plays an important role. In addition to the general composition, the quality control also focuses on their content of undesirable components – especially sulphur compounds.

For the use as propellant gas freedom from sulphur is a must ($c < 100$ ppb). The same applies to the use for the synthesis of high molecular compounds (e. g. polyethylene). Here, sulphur compounds cause catalyst contamination, undesirable byproducts and increased production costs. To detect sulphur traces with precision, powerful metering technology, quantitative combustion and highly sensitive detectors are important requirements.

For the use of fuels (LPG, CNG) other guidelines apply. Of course, the limits applicable to sulphur must not be exceeded. In addition it must be ensured, by adding sulphurous odorants, that escaping gas is detected immediately. To guarantee optimum product quality and instant process optimisation, the rapid detection of high sulphur content is required.

Many Possible Applications for a Single Analysis System

Using an elemental analyser of the multi EA® 5000 series, equipped with GSS/LPG gas sampler, the entire spectrum of sulphur analysis can be covered. The analysis system meets the requirements of ASTM D 6667 and D 7551.

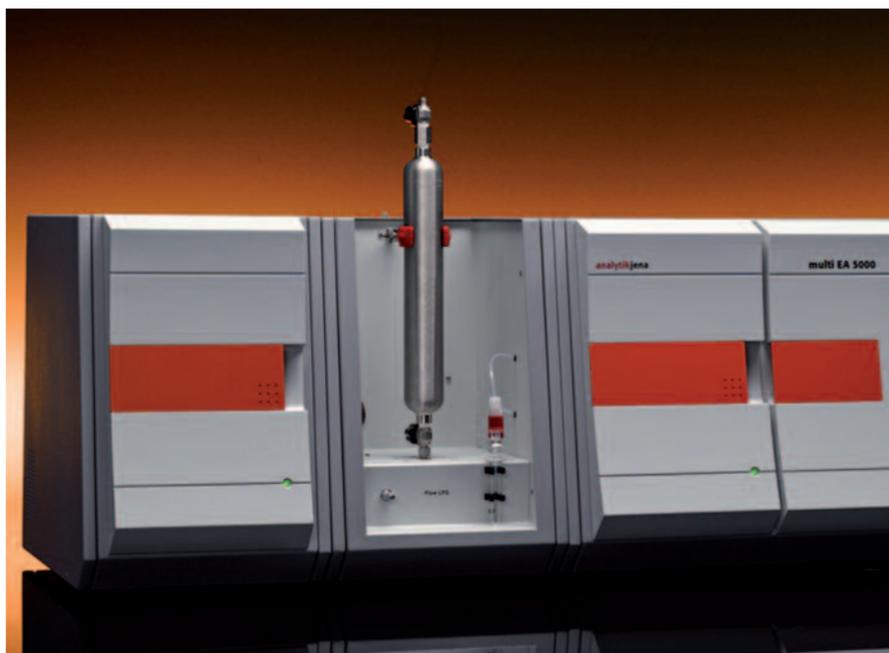


Fig. 1: multi EA® 5000 with GSS/LPG module

The GSS/LPG module can be used extremely flexibly for the automatic metering of gases and liquefied gases at different pressures. The sample volume can be varied by the user within the range of 1–50 µl (LPG) or 1–20 ml (gas).

Liquefied gases can already expand with a minimum of pressure reduction (e. g. sampling). This results in a non-reproducible metering of the sample at excessive speeds which leads to strongly scattered results and sooting of the analysis system. To prevent this, the sample pressure is increased using an auxiliary gas. Thanks to the cooled sampling valve in the GSS/LPG module, this is no longer required. Even liquefied gases at lowest pressure (e. g. butadiene at 2.1 bar) can be metered with good reproducibility.

Prior to being transferred to the combustion module the samples pass through a heated evaporation chamber where all components (inhibitors etc.) are quantitatively converted into the gaseous aggregate state. This prevents memory effects and the related incorrect measurements. The quantitative transfer of the now gaseous samples to the combustion system takes place using Perma Purge, a powerful inert gas flushing. There, the complete oxidation takes place in a two-phase process at 1050°C. The generated SO₂ is introduced to the UV fluorescence detector after drying the measuring gas. This sensitive detector can measure lowest sulphur contents (detection limit: 5 ppb S = 0.2 ng S) without difficulty and without time-consuming enrichment procedures (trap and release). Thanks to excellent reproducibility, replicate measurements are kept to a minimum.

Table 1: Reproducibility of sampling in the example of a LPG

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 %									

Flexible Calibration Strategies

The use of alternative calibration strategies not only simplifies the work but also permits obtaining the best possible, most reliable result every time, independent of the sulphur content to be detected. This applies in particular to analyses in the trace and ultra-trace range, where no suitable calibration gases are available.

The calibration of the system can be achieved using a calibration gas (Fig. 2a) as well as calibration kits of liquid standards at different concentrations (here dibenzothiophene in iso-octane) (Fig. 2b). This is possible because the combustion with the multi EA® 5000 is quantitative. For the detector it does not matter whether the SO₂ originates from the combustion of a liquid, solid or gas sample. Independent of this, 1 ng sulphur always produces the same amount of SO₂ during quantitative combustion and thus always an integral of the same size, even if the measuring graphs may look different.

The daily factor function additionally helps ensuring the long-term stability of the respective calibration and thereby best results without laborious recalibration of the system.

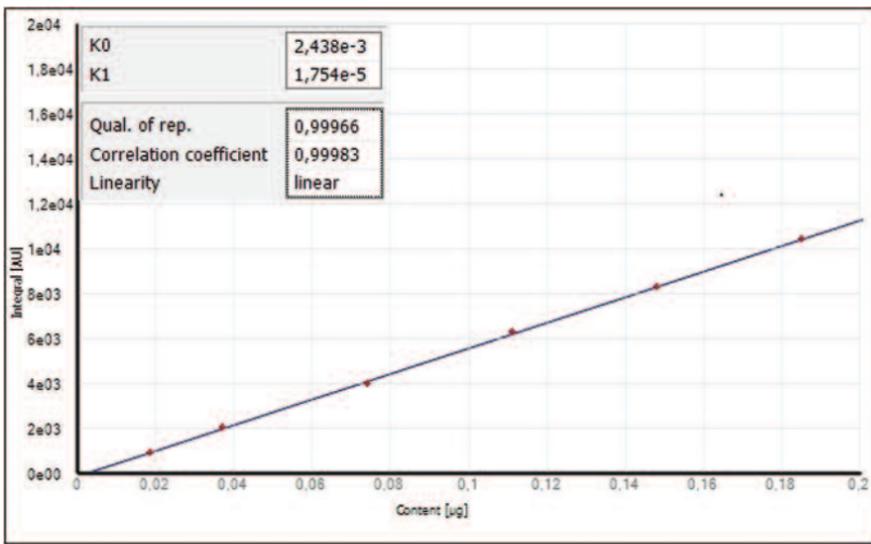


Fig. 2a: Calibration using an LPG standard

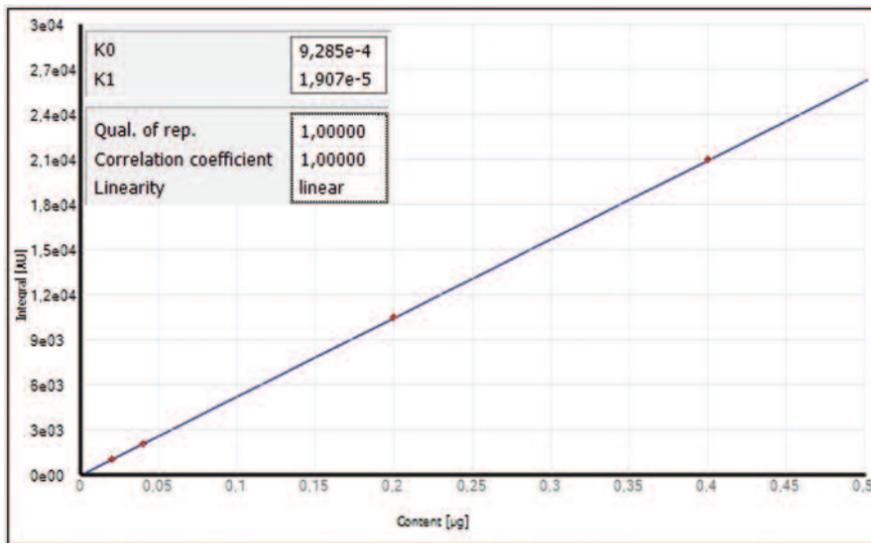


Fig. 2b: Calibration using liquid standards

Table 2: 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 sulphide in propane)	3.73 ± 0.03 mg/l	3.73 ± 0.03 mg/l
LPG (specimen)	579.59 ± 5.10 µg/l	571.62 ± 5.55 µg/l

Rapid Best Results Thanks to Optimum Process Control

The analysed samples were contained in gas cylinders, the sample pressure varied within the range of 1.2–85 bar.

Table 3: Sulphur contents of the examined gas and liquefied gas samples

Sample	Sample Type	c _S	SD
Butadien (1)	LPG	0.02 mg/l	< 0.01 mg/l
6.56 mg/l S in butane (2)	LPG	6.56 mg/l	0.11 mg/l
3.70 mg/l S in propane (3)	LPG	3.73 mg/l	0.03 mg/l
10 mg/l S in methane (4)	gas	10.1 mg/m ³	0.24 mg/m ³
Propene (5)	gas	438 µg/m ³	19.0 µg/m ³
Natural gas (6)	gas	7.88 mg/m ³	0.07 mg/m ³

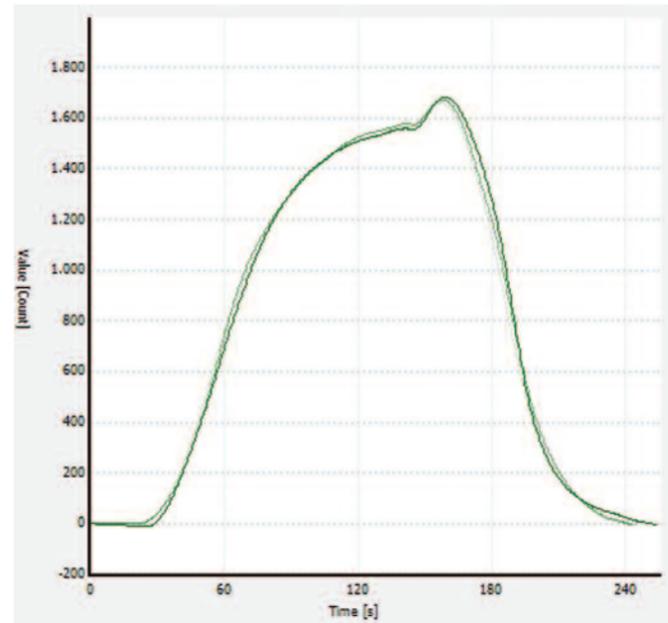


Fig. 3a: Sample 3 – LPG

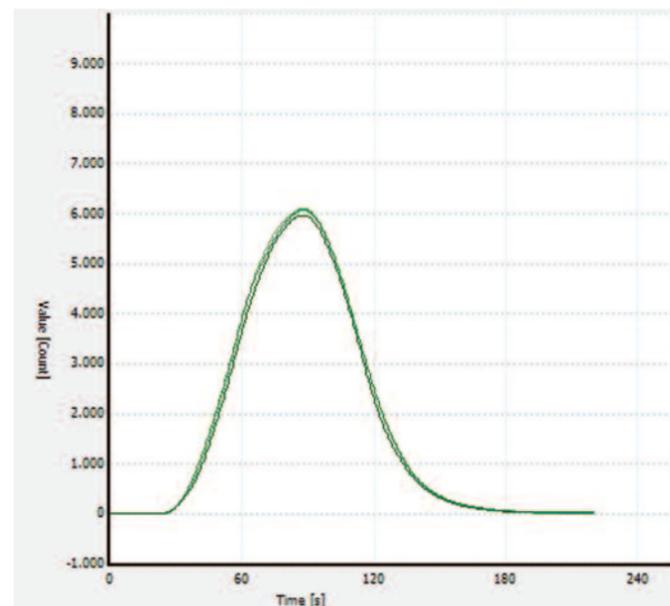


Fig. 3b: Sample 4 – gas

For the liquefied gases (2) and (3) a volume of 20 µl was dosed. In consideration of the high purity of the sample (1) it was increased to 50 µl in order to achieve the best possible results. For the gases (4) and (6) 5 ml each and for (5) 20 ml were dosed.

To optimise the analysis process the sample volume can be adjusted flexibly to the expected sulphur contents in order to achieve the optimal result in the shortest time. Thanks to the high precision of the metering technology, the change to the next sample is possible after a minimum of replicate measurements. Thereby the sample throughput can be increased greatly.

Figures 3a and 3b show typical measuring graphs. The measuring duration depends on the sulphur content and metering volume and is between 150–420 seconds.

Reliably Simple – Simply Reliable

The sulphur detection using the multi EA® 5000 provides results of the highest precision independent of the sample pressure and element content. Variable sample volumes and an optimum combustion lead to short measuring times. The easy to operate multiWin® software with a rich library of ASTM and DIN compliant methods prevents operating errors and dangerous situations already in advance.

Additional functions, such as the integrated filter system and the purge tool for preventative care, significantly minimise the maintenance effort. The easy to operate hardware and top safety standards permit the use during shift operations and in analysis centers with the highest possible sample throughput.

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