



# Matrix-Optimised Analysis of Gases and LPG Samples

Dr. Angela Gröbel, Product Specialist Elemental Analysis, Analytik Jena AG Konrad-Zuse-Str. 1, 07745 Jena / Germany,  
Tel.: +49/(0)3641/ 777 191 Fax: +49/(0)3641/ 77 92 79 Email: info@analytik-jena.de www.analytik-jena.com

Determination of nitrogen, sulfur and chlorine content in a broad concentration range. The analysis of gaseous matrices in routine analytics still presents a real challenge even today. No matrix type is so versatile in its behavior and the requirements for the sample feed and the combustion process. This makes it difficult to quickly gain precise and reliable analysis results. Thanks to the outstanding flexibility of the elemental analyzer multi EA 5000, combined with application-optimised sample gas systems, liquid gases, highly pressurised gases, but also gases relaxed to normal pressure, such as ambient air, can be analysed for element contents in the range of ultratraces up to percentages. In only one single cycle, the sulfur, nitrogen and carbon content is determined simultaneously, and chlorine is determined sequentially.

## Introduction

Gaseous matrices are analysed for their sulfur, nitrogen and chlorine content for numerous reasons.

When used as raw material for the synthesis of higher hydrocarbons and their oxygenic homologs or as raw material for the production of highly molecular organic compounds (e.g. polypropylene, polyethylene), the contained contaminants sulfur, nitrogen and chlorine lead to lower-quality end products due to undesired secondary reactions. In addition, organic sulfur and chlorine compounds, as catalyst contaminants, lead to an insufficient production yield and significantly increased production costs. Furthermore, in combination with moisture, hydrolysis-sensitive organic chlorine compounds can quickly react to hydrogen chloride, which may cause corrosion and thus lead to premature aging of reactors and metallic components. Also, if gases are used as energy carriers for heat production and as fuel (LPG, NG, biogas, etc.), strict limit values apply that must be observed.

To avoid exceeding the set limits and thus avoid undesired reactions, a reliable monitoring of the gaseous matrices used is essential.

As the field of application for gaseous matrices (liquid gases, relaxed gases) is very diverse, so are the requirements for the analysis technology used.

Liquid gases, including LPG, are gas matrices liquefied under pressure. They are chiefly composed of C3 and C4 hydrocarbons with single or double bonds (e.g. propylene, butane, propane, etc.) that can be easily liquefied even at room temperature and pressures above 5 bar. Even a minimal decrease in the sample pressure, e.g. when taking the sample, can lead to sudden relaxation. This leads to the sample being taken much too quickly and therefore to a non-quantitative combustion with soot formation.

For a safe analysis of such critical sample matrices, a special dosing technology is required that ensures stable, easily reproducible and hazard-free sampling. An optimal sampling module has been designed for this purpose. It enables the precise dosing of gases that have been liquefied under pressure and ensures a safe transition from the liquid to the gaseous state.

A flexible sampling module that enables pressure-independent dosing of the gases has been developed for feeding matrices at diverse pressures. It facilitates both direct dosing of liquid gases from cylinders at up to 200 bar and introducing relaxed gases in Tedlar™ bags. During the process, the operator can adjust the volume and speed to the matrix that is to be analysed as needed.

## Instrumentation

### Analysis system

All measurements were performed with an elemental analyser of the multi EA series (Fig. 1) in the following configuration:

- multi EA 5000 – basic device with double furnace in the vertical operating mode
- Chemoluminescence detector for nitrogen determination
- UV fluorescence detector for sulfur determination
- Chlorine module with "high sensitive" cell for the coulometric determination of trace-level chlorine contents
- LPG module for the precise dosing and evaporation of liquid gases
- GSS module with adapter box for the safe dosing of unpressurised and pressurised gases



Figure 1: The multi EA 5000 analysis system with gas sampling system for liquid gases

### Sample analysis

#### Liquid gases:

The liquid gas samples examined were contained in gas cylinders (sample pressure from 5 to 17.5 bar). Since, when relaxed, liquid gases return to the gaseous state as soon as the temperature exceeds 0°C, a special, Peltier-cooled sample loop must be used. This is the only way to avoid a premature transition to the gaseous state and ensure even sample dosing. For the sulfur and nitrogen determination, the sample volume was varied in the range of 2-50 µl to ensure optimum adjustment to the element content of the sample. For the chlorine analyses, 50 µl were dosed by default. Since liquid gases are highly combustible and lead to an explosive combustion if dosed too quickly, controlled dosing is absolutely essential. Therefore, the dosing was performed at a constant speed of 0.4 µl/s. Prior to the transfer to the combustion module, the sample passes through a heated evaporation chamber. This is where the controlled transition from the liquid to the gaseous state occurs. Tempering is necessary to counteract the condensation of sample components and thus scattering measurement values and lower results. By means of an inert gas stream, the now gaseous sample is transferred to the combustion system, where it is quantitatively digested in a 2-phase process at 1000 °C, in an oxygen stream, without the use of a catalyst.

#### Gases:

The examined gaseous samples were contained in gas cylinders (sample pressure from 38-100 bar) or in Tedlar™ bags (normal pressure).

The GSS module with adapter box used enables the pressure-independent dosing of the most diverse gaseous matrices.

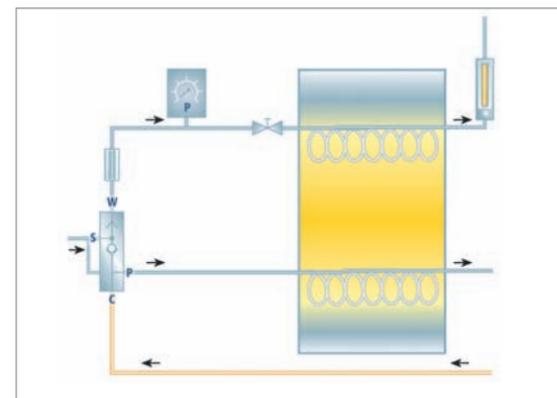


Figure 2: Functional diagram of the sampling module for liquid gases

The permissible preliminary pressure of the samples can vary over a broad range, from normal pressure up to 200 bar. The system automatically relaxes the pressurized matrices to normal pressure. The samples are taken from the relaxed, gaseous phase. This ensures optimum reproducibility. For the sulfur and nitrogen determination, the sample volume was varied in the range of 20-100 ml to ensure optimum adjustment to the element content of the sample. For the chlorine analyses, 100 ml were dosed by default.

Since organic gases are highly combustible and lead to the formation of cracking products and soot due to incomplete combustion if dosed too quickly, a dosing speed adapted to the reaction behavior is essential. (Fig. 3)

The sampling speed is highly flexible and can be adjusted to the specific requirements of the respective gas matrix. An inert gas stream is used for the quantitative transfer of the gaseous samples into the combustion system. The sample digestion is performed in the same manner as for the analysis of the liquid gases.

The gaseous reaction products SO<sub>2</sub>, NO<sub>x</sub> and HCl formed during combustion are fed into the respective detection systems after the measuring gas drying process. The sulfur and nitrogen content can be determined simultaneously and time-effectively.



Figure 3: GSS module – autosampler for pressurised and relaxed gases

The duration of a determination was approx. 300 s. The analysis of the chlorine content was performed subsequently and took approx. 600 s per determination. Thanks to the excellent reproducibility of the method, even with lowest element contents, a three-fold determination was sufficient in most cases.

#### Calibration

For the determination of the trace concentrations in the range of 0-0.5 mg/l for sulfur and nitrogen, and in the range of 0.1-10 mg/l for chlorine, the system was calibrated using standard kits. The values displayed in Fig. 4 represent the results of the nitrogen and sulfur calibration. The detection limits of the method were determined from the calibration curves according to the calculation instructions of DIN 32645.

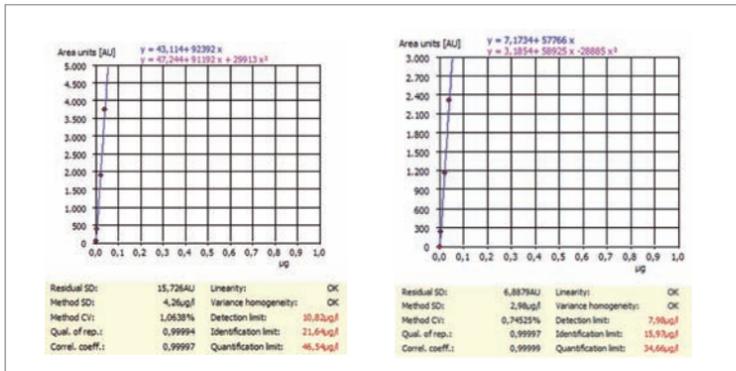


Figure 4: Calibration curves for the elements nitrogen and sulfur at trace level

## Results and discussion

Samples 1-3 are C3–C4 hydrocarbons that were liquefied under pressure, samples 4-8 are pressurized gases, and samples 9-13 are unpressurized gas samples relaxed in Tedlar bags™. The results of the sulfur and nitrogen determination displayed in tables 1-3 are mean values from three-fold measurements. The values displayed for the chlorine determination result from five-fold measurements.

Table 1: Element contents of the examined liquid gas samples, samples 1-3

Sample	$c_S$ [mg/l]	$c_N$ [mg/l]	$c_{Cl}$ [mg/l]
Propylene_M	$0.008 \pm 0.0007$	$0.8 \pm 0.05$	$0.17 \pm 0.028$
Butane	$3.84 \pm 0.04$	$7.78 \pm 0.04$	nd*
Butane / propane mix	$1.89 \pm 0.03$	$4.65 \pm 0.05$	nd*

\* not detectable      \*\* not analysed

For the determination of the element chlorine, the sample volume was 50 µl. For the first liquid gas, a trace content near the lower detection limit (0.1 mg/l) of the method could be determined; for samples 2 and 3, chlorine was not detectable (nd). For the determination of sulfur and nitrogen, the dosing volume for samples 2 and 3 was 20 µl; for sample 1, it was increased to 50 µl because of the low element contents.

Table 2: Element contents of the pressurized gases (gas cylinders), samples 4-8

Sample	$c_S \pm SD$ [mg/m <sup>3</sup> ]	$c_N \pm SD$ [mg/m <sup>3</sup> ]	$c_{Cl} \pm SD$ [mg/m <sup>3</sup> ]
Ethene	$0.05 \pm 0.008$	--- **	nd*
Butane / butylene mix	$1.13 \pm 0.03$	$1.73 \pm 0.08$	$0.22 \pm 0.04$
Methane_M	$7.78 \pm$	--- **	nd*
Butane_C	$70 \pm 0.25$	$18.24 \pm 0.24$	$0.17 \pm 0.04$
CO <sub>2</sub>	$0.01 \pm 0.001$	--- **	nd*

\* not detectable      \*\* not analysed

For the determination of sulfur and nitrogen, a volume of 20 ml was dosed for samples 5 and 6; a volume of 5 ml was dosed for sample 7. To increase the detection sensitivity, the volume for samples 4 and 8 was increased to 100 ml.

For the determination of chlorine, the dosing volume was always 100 ml. For samples 4, 6, 8 and 13, chlorine was not detectable (nd).

For the determination of sulfur and nitrogen, a volume of 100 ml was dosed for samples 10 and 11; for sample 9, it was reduced to 2 ml for process optimisation, and to 5 ml for sample 13.

Exemplary for all measurements, figures 5-7 display the curves of a three-fold determination for the elements sulfur, nitrogen and chlorine.

The final examination of the results shows that the N, S, Cl determination with the multi EA 5000 and its matrix-optimised gas sampling systems can be performed quickly, easily and with high precision.

Table 3: Element contents of the unpressurized gases (Tedlar bags™), samples 9-13

Sample	$c_S \pm SD$ [mg/m <sup>3</sup> ]	$c_N \pm SD$ [mg/m <sup>3</sup> ]	$c_{Cl} \pm SD$ [mg/m <sup>3</sup> ]
Biogas	$637 \pm 1.91$	$0.45 \pm 0.06$	$2.83 \pm 0.34$
Butane / propane mix	$0.102 \pm 0.009$	$16.98 \pm 0.016$	$0.396 \pm 0.038$
Propene_UT	$0.438 \pm 0.019$	$0.527 \pm 0.06$	$0.117 \pm 0.026$
Hydrogen 99.9 %	nd*	--- **	$0.078 \pm 0.023$
Natural gas	$7.88 \pm 0.07$	--- **	nd*

\* not detectable      \*\* not analysed

Table 4: Reproducibility of the sampling with the LPG module, using the example of a sulfur standard ( $c_S$ : 3.78 mg/l)

Measurement	1	2	3	4	5	6	7	8	9	10
$c_S$ in mg/l	3.79	3.73	3.81	3.81	3.74	3.72	3.83	3.78	3.76	3.78
Mean value	3.78 mg/l									
SD	0.04 mg/l									
RSD	0.98 %									

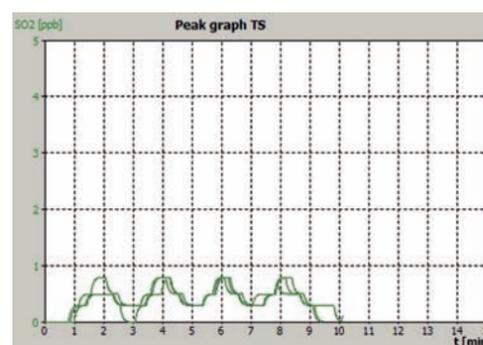


Figure 5: Sample no. 4, measurement curve for sulfur determination

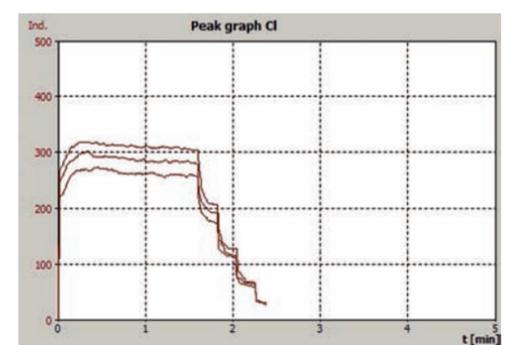


Figure 6: Sample no. 9, measurement curve for chlorine determination

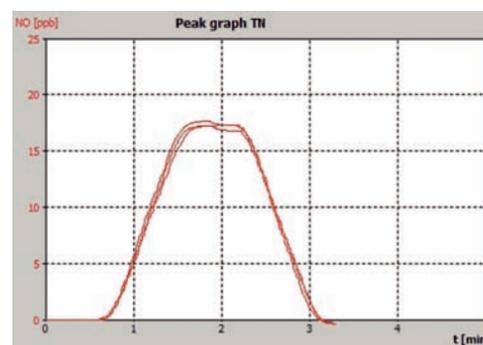


Figure 7: Sample no. 5, measurement curve for nitrogen determination

## Summary

In the analysis of gases, the sample pressure has a significant influence on the entire analysis process, the measurement result and especially on occupational safety.

In addition to reliable combustion systems that ensure safe and quantitative oxidation of the entire spectrum of gas matrices, high-precision dosing technology and device-integrated safety features like those offered by the Self Check System are essential for meeting the analytic requirements of gas matrices.

The multi EA 5000 offers all of this. With the simultaneous / sequential C/N/S/Cl determination, it combines short measurement times and minimal maintenance requirements with convenient, user-friendly hardware and software which prevents operator errors in advance. This guarantees trouble-free use in shift operation as required in modern labs. Thanks to the modular design, it is also possible to use the same analysis system for analysing other organic matrices, such as solids and liquids. This enables an additional increase of effectiveness.