

Bosch Optical Gas Spectrometer - A New Dimension in Gas Measurement with Raman Spectroscopy

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Abstract. Analysing the composition of a gas is a complex challenge. Depending on the use case and considering thermodynamic constraints such as gas temperature, gas pressure, and flow rate, various technologies are available. Specific sensors are usually straightforward to use. However, they often have limited concentration ranges and require more or less complex calibration. More sophisticated techniques, such as mass and absorption spectroscopy or gas chromatography, each have their own limitations. Some require ambient pressure, dedicated probe extraction, or time-consuming analysis processes. Raman spectroscopy appears to overcome many of these limitations. However, the Raman effect is so weak that complex and expensive setups are required. To overcome these problems, Bosch developed the BOGS (Bosch Optical Gas Spectrometer). Raman gas spectroscopy is now extremely easy. Gas concentrations as low as 100 ppm can now be detected, and even lower concentrations when the pressure is higher (up to 40 bar) and the detection time is increased from seconds to minutes.

1 Raman Spectroscopy

Raman spectroscopy, an inelastic light scattering, is an effective method for measuring all molecular gases. This means that all species besides noble gases have a specific Raman signal. As stated in the publication by the discoverers [1], the Raman effect is very weak, especially for gases due to their low density. This is one of the main reasons why Raman spectroscopy is not often used to analyse gases in industry. It is mainly because a complex and expensive laboratory setup is required. The challenge in introducing Raman spectroscopy as a measurement device lies in overcoming the sensitivity issue and making the setup more industrialised. The BOGS (Bosch Optical Gas Spectrometer) is a significant step towards achieving that goal.

1.1 Technical Setup

We have chosen the classic 90-degree setup, as shown in Figure 1. The Raman excitation is done by a high-power laser diode with constant approx. 3.5 W at 450 nm. The scattered light passes through a long-pass filter to reduce disturbing Rayleigh light, before being detected by a Czerny-Turner spectrometer with a 512-pixel CCD detector. A Raman shift from approximately 395 to 5050 cm^{-1} can thus be detected. The spectral range above 3500 cm^{-1} is not often available and enables measurements of molecules such as water vapour at approximately 3650 cm^{-1} and hydrogen at approximately 4150 cm^{-1} .

The gas to be measured passes through a stainless-steel pipe containing sapphire windows, through which

the laser beam is guided, and the scattered light is collected. As with Raman spectroscopy in general, no carrier gas is required. Nor is gas flow necessary.

1.2 Bosch Optical Gas Spectrometer

The BOGS (Figure 1) is a newly developed gas analyser based on Raman spectroscopy. We have industrialised this technology and integrated it into a compact tabletop device, with a 19-inch housing.

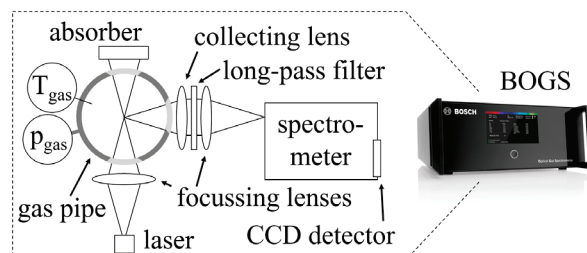


Fig. 1. Sketch of a classic 90-degree Raman setup, which is integrated into the gas pipe of the BOGS and additionally equipped with a gas pressure and gas temperature sensor. The gas is supplied from the rear (not shown). There is a pipe inlet and outlet connection.

One of the most significant advancements is the substantial improvement in sensitivity compared with today's gas Raman systems, as illustrated in Figure 2.

As is known from laboratory setups using a solid-state laser (compare CO_2 spectra in e.g. [2, 3]), the spectral resolution is mainly limited using a laser diode. Nevertheless, this is sufficient for a lot of applications.

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In summary, depending on the test conditions and anticipating the next chapter, the BOGS can measure concentrations ranging from 100 ppm to 100 vol%, and it can operate at gas temperatures of up to 40 °C and pressures of up to 40 bar, as well as sub-ambient pressures. Thanks to its highly sensitive Raman signal, even evaporated liquids can be studied.

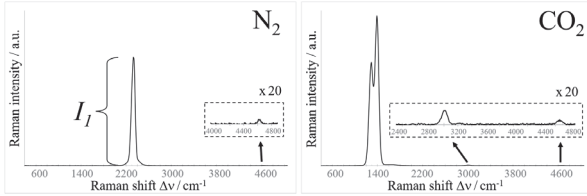


Fig. 2. With BOGS measured Raman spectra of pure nitrogen and carbon dioxide, shown as the median of three 5-second measurements at 3500 hPa. At 20x magnification, the second-order Raman lines can be clearly seen. I_1 is here an evaluation example of the peak height as an indicator of the nitrogen intensity.

1.3 Gas Concentration & Calibration

The radiation flux Φ_l of one Raman signal (at wave-number ν_l) is strong linear to the gas density, respectively to the gas particles N_l in the observed volume V [2, 3]:

$$\begin{aligned} \Phi_l(\nu_l) &= N_l/V \cdot \partial\sigma(\nu_l)/\partial\Omega \cdot \Omega \cdot l \cdot P_L \\ &= a_l \cdot N_l/V. \end{aligned} \quad (1)$$

Table 1. Formula symbols at section 1.3 that have not been described in the text

$\partial\sigma(\nu)/\partial\Omega$	differential cross-section
Ω	solid angle of observation
l	length of scattering volume
P_L	laser power
a, b	constants
α	Raman sensitivity factor/constant
k	Boltzmann constant

This enables the evaluated intensity I_l (see Figure 2) to be calibrated at a single point, depending on the exposure respectively detection time t of the measurement:

$$\begin{aligned} I_l &= b_l \cdot \Phi_l(\nu_l) \cdot t = b_l \cdot a_l \cdot N_l/V \cdot t \\ &= \alpha_l \cdot N_l/V \cdot t. \end{aligned} \quad (2)$$

The concentration c_l (in vol%) according to ISO 14912 with $c_l \stackrel{\text{def}}{=} V_l/V$ and $c = \sum_i V_i = I$ of a gas species can be calculated by measuring the gas pressure p , the gas temperature T and applying the ideal gas law

$$p \cdot V = N \cdot k \cdot T \Rightarrow N = p \cdot V / (k \cdot T) \quad (3)$$

finally by

$$c_l = I_l / (\alpha_l \cdot t) \cdot k \cdot T / p. \quad (4)$$

Therefore, to calculate the gas concentration, the Raman sensitivity or calibration factor α of the Raman peak of each species must be known. There are many ways to determine or calibrate this factor. Some of these methods are presented in the following section.

2 Measurements & Use Cases

The in following shown measurements, taken using the Raman spectroscopic system implemented in the BOGS, typically are normalised spectra at a standard pressure of 1013.25 hPa, a temperature of 20 °C and an exposure time of 1s. They are calculated using equation (3), which uses the ratio of the measured gas pressure and temperature to the standard and the exposure time ratio to 1 s. The advantage here is that it allows the same evaluation algorithm to be used in different conditions relating to gas pressure, temperature, and exposure time. It also makes it easier to compare the important signal-to-noise ratio. A ratio of more than 3:1 is usually required for a significant detection threshold.

2.1 Fundamentals

Figure 3 shows the normalised spectra obtained by measuring dry and ambient air.

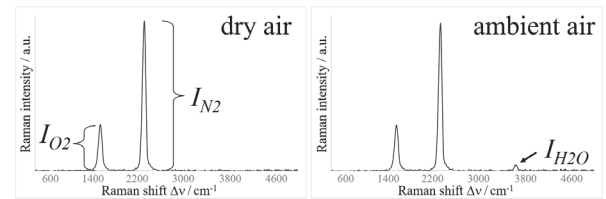


Fig. 3. Raman spectra of dry air and ambient air (including moisture) measured over 10 s at 1150 hPa, 32 °C and 0.4l/min gas flow.

At altitudes of up to around 80 km, the composition of dried ambient air is constant to 78.09 vol% nitrogen, 20.95 vol% oxygen and 0.96 vol% other gases (e.g. argon and carbon dioxide) [4]. This data can be used to calibrate α_{N_2} and α_{O_2} from equation (4), with the intensity I_{N_2} and I_{O_2} being calculated either from the peak height or, for better repeatability, from the peak area of the single, positioned Raman peaks. Furthermore, measuring ambient air afterwards gives the nitrogen and oxygen concentrations, which has been reduced by moisture. The same ratio was used to reduce the concentrations of the other gases. The final difference to 100 vol% is than the water vapour concentration, which is 1.85 (abs.) vol% here. Therewith the α_{H_2O} can be calculated by the water Raman peak intensity evaluation (German patent application DE 10 2023 211 698 A1).

The BOGS software includes these and more options for Raman signal evaluation and gas concentration calibration.

One of most important topic is the accuracy of a measurement. Depending on the definition used for different use cases, we can provide data on repeatability

here. Each gas species has different sensitivities (e.g. methane is 10 times more sensitive than nitrogen), a longer detection time (limited by the CCD detector dynamic), and a higher pressure will increase the signal-to-noise ratio. Overlapping Raman lines require more complex evaluation algorithms. This means that no single repeatability value can be defined. Nevertheless, we will provide two examples: An absolute and a relative gas concentration evaluation.

A repetition measurement of a single gas (here hydrogen), also comparable of a single component in an unknown mixture, gives a standard deviation of the hydrogen concentration of $\sigma_{n-1} = 0.12$ vol%. This was calculated by evaluating the peak area of the vibrational Raman line from a median average of five measurements taken every 15 minutes over 60 repetitions: see Figure 4 (left).

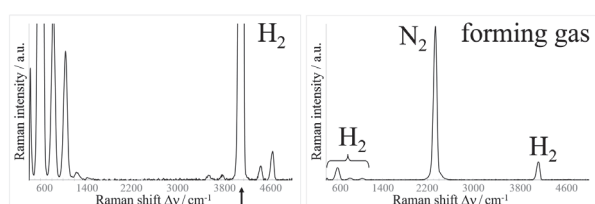


Fig. 4. Zoomed-in view of the Raman spectrum of hydrogen 5.0 (99.999) and 4 vol% nitrogen in hydrogen 5.0 (\pm forming gas) measured over 5 s at hydrogen, 10 s at forming gas, and 1150 hPa, 32 °C, 0.4 l/min for both. The peak marked on the left is the vibrational; all the others are the rotational hydrogen Raman lines.

If the gas matrix is known, as with forming gas (see Figure 4 on the right), repeatability increases significantly. This means that the total concentration of all known components can be normalised to 100 vol%. Minor influences, such as pressure and temperature measurement deviations or gas flow disturbances, will be eliminated. The results in Table 2 were obtained by initially calibrating the peak area with the forming gas, followed by 40 repetitions at 15-minute intervals. The above-described evaluation also normalises the gas concentration to 100 vol%.

Table 2. Result of a relative/normalised gas concentration evaluation of a repetition measurement taken 40 times at nearby ambient air pressure.

gas species	gas concentration / vol%	measured mean value / vol%	standard deviation / vol%
N ₂	96.00	95.98	0.03
H ₂	4.00	3.99	0.02

In summary, an absolute measurement results in a standard deviation of around 0.1 vol%, whereas a relative evaluation results in a value one order of magnitude lower, at around 0.01 vol%. That is at ambient pressure. Increasing the gas pressure will improve repeatability even further. We are not yet able to provide any concrete results, but we will do so as soon as we are able. Increasing the exposure time is here not possible. Due to the limited CCD detector dynamic, we

have chosen the 5 and 10 s as the maximum possible Raman signal height.

2.2 Hydrogen & ISO 14687

In [5], a good overview of the measurement possibilities for impurities, in accordance with ISO 14687, is provided. No Raman technology was used at that time. Figure 5 shows our initial approaches with BOGS.

At approximately 5000 hPa, the two most significant impurities can be detected with a required signal-to-noise ratio of 3:1. Please note that the ISO limit value of 100 ppm methane would already be reached at ambient pressure.

And, at a typical electrolyser working pressure, oxygen and water can also be observed in situ. The minimum detectable concentration, which is also limited by the shown Raman peak overlap, is now under development.

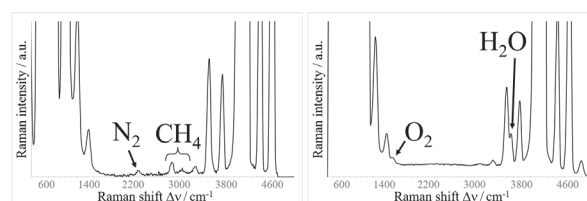


Fig. 5. Zoomed-in view of the median average of five hydrogen spectra, with 288 ppm of nitrogen and 98 ppm of methane impurities, is shown on the left, measured over 60 seconds at 5000 hPa and 32 °C. On the right is the hydrogen measured at an electrolyser with approximately 600 ppm of oxygen and 200 ppm of water vapour impurities, measured over 30 seconds at 4 MPa and 32 °C.

Finally, two questions remain. Firstly, is it possible to measure the other constituents according to ISO 14687, and if so, at what detection limit? For that purpose, we started a research project in cooperation with the institute Laseranwendungstechnik at Ruhr-University Bochum and Linde Gase at Munich with the public funding project HyQ2Ra. This is sponsored by the German Federal Ministry for Economic Affairs and Energy. The project has ended in December 2025. Preliminary results are shown in [6, 7]. Anticipating the report: Most of the constituents have Raman lines in the hydrogen-free spectral area (see Figure 4 on the left: 1700 - 3500 cm⁻¹), making them easier to evaluate. Increasing the gas pressure above the current 4 MPa achieved with BOGS also helps to increase sensitivity. The known Raman line broadening and shifting seem to be negligible up to 10 MPa, or even higher.

2.3 Natural Gas & THC

The knowledge of the gas compensation of natural gas is essential (billing, gas motor control, ...). Today, gas chromatography is usually considered to be state of the art. The advantages of Raman technology include the ability to take measurements at higher pressures (for example, at the transport grid, pressures can reach up to 10.5 MPa) without having to extract the probe and the

speed of the process (less than a few minutes). A first approach with a classic Raman spectroscopic setup is given in [8].

We have developed an optimised evaluation algorithm using the BOGS by fitting the previously measured spectra of pure gas substances to those of a natural gas mixture. Figure 6 shows the spectra of the alkanes that are included in the evaluation. Isomers have different spectra and can therefore be distinguished. By the way, isotopes, such as those from hydrogen, are also different. Additional, for the natural gas evaluation, nitrogen, oxygen, carbon dioxide and hydrogen are included.

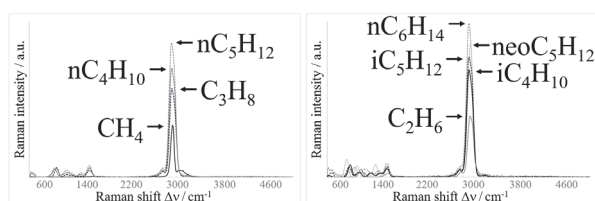


Fig. 6. Raman spectra of alkanes and their isomers from methane (CH_4) to n-hexane (nC_6H_{14}), scaled to the same gas concentration. The higher the atoms in the molecule, the higher the Raman signal/sensitivity.

To verify the algorithm and ensure consistency with the OIML R 140 and ISO 6967 standard, special calibration gases must be tested. Figure 7 shows a typical measurement of a calibration gas called '9M'.

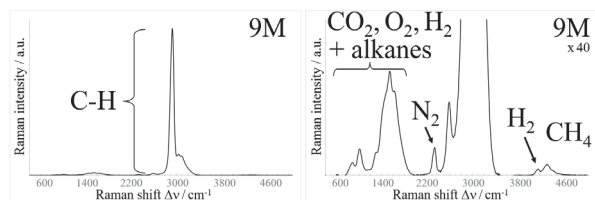


Fig. 7. Raman spectrum of the 9M calibration gas for natural gas. The (normalised) spectrum was created using higher detection times outside the dominant Raman C-H vibration area ($2400 - 3500 \text{ cm}^{-1}$) to improve the signal-to-noise ratio. The zoom-in view on the right shows the areas of interest outside the C-H vibration. The median average of five measurements taken over a period of 21 seconds at a pressure of 3500 hPa and a temperature of $26 \text{ }^\circ\text{C}$ is shown.

The results of the normalised concentration evaluation, as described in the 'Fundamentals' section, are shown in Table 3. The difference between the measurement and the certification is very small. With a calorific value deviation of -0.43% , it is below the $\pm 0.5\%$ limit. This demonstrates the accuracy of the measurement, and repeating the measurement (not shown) produces the same result.

Further calibration gases are currently under investigation. However, the initial results demonstrate the significant potential of Raman spectroscopy, even when dealing with more complex spectra featuring overlapping peaks and numerous gas components.

Figure 6 shows the Raman spectra of the alkanes. There is one more thing we can learn from these spectra. All hydrocarbons have a very sensitive Raman signal in

the 3000 cm^{-1} area; this is due to the C-H vibration of the molecules. If a significant signal is detected here (with a signal-to-noise ratio of more than 3:1), then hydrocarbons are present in the gas. This can be used as a detection threshold for determining the presence of THC (total hydrocarbons). It is, at a minimum, methane because the Raman signal for the hydrocarbon is the lowest.

Table 3. Gas concentration and measurement of the 9M calibration gas in vol%

gas species	9M gas certification	9M BOGS measurement
N_2	04.00	04.07
H_2	00.20	00.14
CO_2	02.48	02.37
O_2	00.40	00.57
CH_4	89.03	89.29
C_2H_6	02.49	02.30
C_3H_8	01.00	00.96
nC_4H_{10}	00.20	00.12
iC_4H_{10}	00.20	00.12
nC_5H_{12}	00.00	00.00
iC_5H_{12}	00.00	00.00
$\text{neoC}_5\text{H}_{12}$	00.00	00.00
nC_6H_{14}	00.00	00.06

2.4 Biogas

Lastly, as a further example of evaluation, we can consider a typical biogas Raman spectrum: Figure 8. The main components of this mixture are methane and carbon dioxide, along with small amounts of hydrogen and residual moisture. Although the Raman peaks of carbon dioxide and methane overlap slightly, the classic evaluation of peak area with the left half assigned to carbon dioxide and the right half to methane is sufficient for the required accuracy in the $0.5 \text{ vol}\%$ range. The small amount of hydrogen sulfide positioned directly on a side peak of methane is more complex. In addition to the above-described algorithm for natural gas, a simple fit of pure methane in the spectral area of $2600 - 3600 \text{ cm}^{-1}$ can be used as a background to determine the residual hydrogen sulfide.

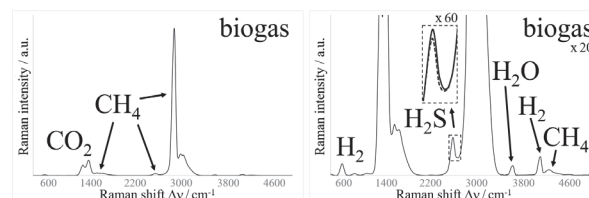


Fig. 8. Raman spectrum of biogas at ambient pressure. The two main components are $40 \text{ vol}\%$ carbon dioxide and $58 \text{ vol}\%$ methane, as shown on the left. In the zoomed-in view on the right, there is $1 \text{ vol}\%$ hydrogen and residual moisture. The $60\times$ magnification shows the presence of 1000 ppm of hydrogen sulfide (black line) compared to its absence (dotted line).

One of the next steps in our investigation is to determine the detectable hydrogen sulfide concentration limit below 1000 ppm , which also depends on the gas pressure.

3 Summary & Outlook

The BOGS brings a new dimension to Raman spectroscopy for gases. We have demonstrated its various applications here. Many new applications, as well as previously impossible ones, are now achievable. While it does not overcome all limitations, it provides additional capabilities, particularly for molecules such as nitrogen, oxygen and hydrogen. In-situ and online applications at higher pressure can now also be easily implemented without any problems.

We have demonstrated classic and more sophisticated algorithms for quantitative spectral analysis. In addition to natural gas analysis, which involves separating overlapping Raman peaks to enable quantified measurements, more advanced evaluation algorithms are required. This is particularly important for applications involving low-concentration gas species.

According to ISO 14687, the public funding project HyQ2Ra evaluated increasing the pressure and using specific algorithms. In anticipation of the final report, it is thought that gas concentration in the one or two-digit ppm range can be achieved at higher pressures, potentially up to 10 MPa.

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