Abstract: Laser Raman spectroscopy is a powerful analytical technique that is used in a variety of applications for the compositional analysis of solid, liquid and gaseous samples. This whitepaper looks at some examples of how Raman systems can be used to quantitatively measure the composition of gas mixtures with high measurement precision, sensitivity and trueness.

When monochromatic photons interact with a molecular sample, the photons can be scattered either elastically or inelastically. When the spectrum of the scattered light is observed, each of the elastically scattered lines is accompanied by one or more inelastically scattered lines. This phenomenon of inelastic scattering is commonly known as Raman scattering. The displacement of the Raman lines from the excitation wavelength is characteristic of the scattering substance used. This means that Raman scattering can be used to determine the nature of the molecular sample and is known as Raman spectroscopy.

Additionally, the intensity of the measured Raman lines is proportional to the molecular composition. This means that Raman spectroscopy cannot only be done qualitatively, but also for quantitative analysis. It is routinely used in a range of applications for the compositional analysis of solid and liquid samples. The advancement of photonics technology has seen an increase in the popularity of Raman spectroscopy of gases in recent years. It has the additional advantage that it is a non-contact, inline multi-species gas analysis technique.

An example of this is the laser Raman group at the Tritium Laboratory Karlsruhe (TLK), it has set up and utilised a series of Raman systems for gas analysis applications over the past decade to measure the composition of various mixtures of gaseous hydrogen isotopologues. A variety of systems have been developed in both 90° and 180° scattering configurations using Laser Quantum’s excel 532, gem 532, opus 532 and finesse 532 lasers as the excitation source. Laser light is focused into the gas cell connected to the TLK gas processing systems and the scattered light is collected and imaged into a spectrometer/CCD detector combination optimised for detecting very faint signals. The Raman analysis is performed in real time using the groups integrated acquisition and analysis routine LARASoft, which enables the analysis to be performed in parallel to measurements with an analysis time of less than half a second. The software outputs the peak intensities and concentrations immediately after every spectral recording enabling real time feedback as required in process control applications.

An example of a measured, background subtracted Raman spectrum of hydrogen isotopologues is shown in figure 1. The Raman signal for each observed component is extracted from the spectrum as either the area under the spectral branch or the maximum intensity (peak height) of the spectral branch. The Raman signal is then monitored over time to assess the change in the composition of the system. An example of this is shown in figure 2 where a Raman system was used to monitor the filling and catalytic mixing of hydrogen isotopologues.

To accurately measure the composition of gas mixtures, a Raman system has to be calibrated. A high trueness of the calibration factors of better than 3% has been obtained at the TLK using two complimentary calibration approaches. The first is a gas sampling technique and the second uses a combination of theoretical Raman intensities, calculated from quantum theory, and the measured spectral sensitivity of the system. Using these approaches, along with the analysis software, the composition of the gas mixture can be monitored in real time.

The figure shows that it is possible to monitor the change in composition of each component separately and in real time using Raman spectroscopy during the evacuation, filling and catalytic mixing process.

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Quantitative laser Raman spectroscopy of gases

Stable and precise long term operation of the Raman systems to monitor the composition of gas mixtures with a precision of <0.1% with measurement periods of several weeks has been demonstrated.

To quantify the sensitivity of a Raman system, the limit of detection (LOD) needs to be calculated. The limit of detection is calculated from the signal-to-background-noise ratio (SNR) and the pressure (p) of the gas in the measurement system as

\[ \text{LOD} = \frac{3p}{\text{SNR}} \]

To allow a better comparison of LODs the number here is stated for an acquisition time of 1 s and for an excitation laser power of 1 W i.e. the units are mbar/s/W.

In the standard 90° implementation, an LOD of less than 5 mbar/s/W has been obtained for the hydrogen isotopologues. This is deemed to be fairly close to the ultimate reachable limit when using this implementation.

To increase the detection limit beyond that of the 90° implementation enhancement techniques need to be considered to either increase the effective excitation laser power and/or increase the number of interacting molecules with the laser radiation. An elegant approach to increase the number of interacting molecules whilst maintaining decent light collection properties is to use a metal lined hollow glass fibre (capillary) as the Raman gas cell. The fibre is contained inside a stainless steel tube and connected to a gas circulation system, so different gas mixtures can be passed through the cell as required. The setup was optimised to maximise the Raman signal and minimise the fluorescence emitted from the glass within the system.

Direct comparison measurements between the capillary setup and the conventional 90° setup were performed using ambient air by taking the signal amplitude as the maximum intensity (peak height) of the Q, branch of N₂ with the background subtracted. This demonstrated that a signal enhancement of ≈170x was achieved. However, the capillary measurement configuration exhibits substantially increased noise from the increased fluorescence background when compared with the virtually fluorescence free 90° setup. This limits the improvement in the detection limit to ≈10x that of the conventional 90° setup.

To further improve the sensitivity of the enhanced approach, a range of fluorescence reducing approaches were investigated and implemented in a prototype setup including the rearrangement of optical components and the replacement of glass components (including the capillary itself) by metal alternatives. This practically eliminated the fluorescence from the enhanced setup whilst maintaining a substantial signal enhancement over the conventional 90° setup. This leads to a further improvement in the detection limit to ≈7x that of the original capillary setup. Using this enhanced approach combined with a rolling average LODs 0.07 mbar/s/W was achieved. Even without the rolling average a LOD of 0.185 mbar/s/W was achieved for N₂ using the prototype setup.

The implementations discussed here show that Raman spectroscopy can be used for in-situ, fast, precise and true compositional analysis of gas mixtures in process flow or static configurations. With enhancement approaches implemented, it is also a promising approach where trace gas analysis or rapid process control is required. When combined with the integrated acquisition and analysis routine, Raman systems can be integrated into process control systems that require real time (automated) feedback. This is not only advantageous in process control at the TLK, but it would be useful in many different applications where inline, non-contact multi species gas analysis is required e.g. bio gas plants.

Raman spectroscopy of gases requires stable laser excitation sources to minimise the uncertainties in the analysis caused by drift in the laser power over time. The excel 532, gem 532, opus 532 and finesse 532 lasers used in this work all have stabilities of <1% RMS and noise levels <0.8% RMS which are ideal for long term, quantitative compositional analysis. Additionally, the lasers all have a good pointing stability (<10 µrad/°C) which ensures the beam pointing to the scattering region remains consistent over time, without the need to realign the beam pointing to maximise the efficiency of the system. Raman spectroscopy depends on the ability to resolve spectral lines to identify the substances in the sample. The observed Raman spectral linewidth is dependent on the linewidth of these lasers and the bandwidth of these lasers is <30 GHz (0.028 nm at 532 nm). This is much narrower than the linewidth of the vibrational (Q₁) branch of the hydrogen isotopologues that have spectrometer resolution limited linewidths >1 nm, so the lasers will not limit the resolution of the Raman measurement here.

Finally, all the Laser Quantum lasers used in this experiment can be controlled and monitored via an RS232 interface and using LabVIEW drivers which are incorporated into the LARAsoft acquisition and analysis routine enabling one to monitor the laser power and laser temperature at the same time as the Raman intensities and gas compositions, which is another valuable parameter for process control applications.

Acknowledgements: Thanks to Dr. Tim James from Laser Quantum, Dr Magnus Schlösser, Karlsruhe Institute of Technology, Karlsruhe, and the TLK Laser Raman group.

References:

Figure 3: Laser Quantum’s gem 532 which has power stability of <0.8% RMS, excellent for long term analysis.
Figure 4: Laser Quantum’s finesse 532, which has an exceptional noise level of <0.1% RMS.