Quantum Cascade Laser Photoacoustic Spectroscopy (QCL-PAS) Measurement of SF$_6$ and NF$_3$

By Jaakko Lehtinen, Ph.D.

Abstract
The Gasera PA201 research photoacoustic gas cell combined with a widely tunable mid-infrared quantum cascade laser (QCL) source proved to be a powerful tool in the detection of SF$_6$ and NF$_3$. The detection limit for SF$_6$ in 15 seconds was 0.5 ppb, which is at least an order of magnitude lower than the detection limits varying from 5 ppb to 1 ppm in commercial SF$_6$ infrared detectors. The combination of photoacoustic spectroscopy (PAS) and QCL technologies provides high sensitivity and selectivity, and enables the downscaling of the system ultimately to hand-held size.

Application
SF$_6$ (sulfur hexafluoride) is mainly used in gas insulated switchgear (GIS) and circuit breakers, but also in, for example, cables, tubular transmission lines and transformers. Switchgear typically use SF$_6$ as the insulator gas to prevent arcing when the circuit breaker is activated. SF$_6$ itself is non-toxic, but it can decompose into toxic by-products due to discharges or arcing.

SF$_6$ is a greenhouse gas with a 23,900 times greater global warming potential (GWP) than CO$_2$ and an atmospheric life of 3,200 years. Therefore, even a relatively small amount of SF$_6$ can have a significant impact on the climate. Because SF$_6$ cannot be replaced with another less harmful gas in the power utility, its emissions have to be minimized. Roughly 80% of all SF$_6$ produced worldwide is used by the electric power industry.

Leaking GIS causes unnecessary SF$_6$ emissions but also induces costs in maintenance and leak testing. Measurement of leak rates prevents failures, extends equipment life, reduces maintenance costs, and increases personnel safety. By accurately measuring the leaks, not only emissions but also costs can be reduced. All SF$_6$-insulated equipment leaks to some degree and SF$_6$ gas is always present in the GIS surrounding air, at concentrations varying typically between 20 and 100 ppb.

NF$_3$ (nitrogen trifluoride) is also a greenhouse gas with 17,900 times greater GWP than CO$_2$, second only to SF$_6$, and is used, for example, in plasma or thermal cleaning and silicon dioxide etching, and is considered as an environmentally preferable substitute for SF$_6$ in some applications.

Technology
The measurement setup consisted of Gasera’s PA201 cantilever-enhanced research photoacoustic gas cell combined with the LaserTune, a widely tunable external cavity (EC) QCL source by Block Engineering LLC. Cantilever-enhanced PAS has several advantages over the more conventional transmission-based infrared techniques:

- PAS is a so-called zero-background technique. The advantage that comes from a zero-background is the high stability and repeatability of the measurement. In practical use, this also means infrequent calibration.
- PAS does not require long absorption path lengths familiar with the Fourier Transform Infrared (FTIR) spectrometers or non-dispersive infrared (NDIR) systems. Therefore, a photoacoustic detector can be constructed in a compact size without compromising high sensitivity.
- The cantilever sensor-based optical microphone provides ultimate sensitivity when compared to condenser microphones, which are traditionally used in PAS.
- The response of the cantilever is highly linear, resulting in a wide linear dynamic range. This enables the monitoring of trace levels and high concentrations of SF$_6$ with the same system without range adjustments.

Widely tunable EC-QCLs enable data acquisition over a broad spectral range in the mid-infrared region. Previously, this has been limited to standard FTIR spectrometers. Widely tunable EC-QCLs are superior to FTIR spectrometers in optical power and spectral radiance. Also, the high optical power can be combined with high resolution, which cannot be done in FTIR spectrometers. At present, the
tuning range of an EC-QCL can be up to 1000 cm$^{-1}$, which enables a number of possibilities for multi-component analysis. The EC-QCL can be electronically amplitude modulated, which excludes the use of any additional moving parts, e.g. optical choppers.

**Measurement Results**

The measurement setup is shown in Figure 1. The components were mounted on an optical table for a stable alignment of the laser beam. Measurement parameters are presented in Table 1.

![Figure 1. PA201 photoacoustic detector (Gasera Ltd.) and LaserTune widely tunable EC-QCL (Block Engineering LLC)](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser power</td>
<td>0.5 – 1.5 mW</td>
</tr>
<tr>
<td>Laser tuning range</td>
<td>770 – 1320 cm$^{-1}$</td>
</tr>
<tr>
<td>Laser linewidth</td>
<td>&lt; 1 cm$^{-1}$</td>
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<tr>
<td>Modulation frequency</td>
<td>70 Hz</td>
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<td>PA cell pressure</td>
<td>1000 mbar</td>
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<tr>
<td>PA cell temperature</td>
<td>50 °C</td>
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<tr>
<td>PA cell length</td>
<td>100 mm</td>
</tr>
</tbody>
</table>

**Table 1. Measurement parameters**

Figure 2 shows the measured photoacoustic spectrum of 1 ppm SF$_6$ and 10 ppm NF$_3$ mixture. Also, 10,000 ppm H$_2$O and 2 ppm CH$_4$ were present in the sample during the measurement. SF$_6$ has a strong peak around 950 cm$^{-1}$, and NF$_3$ has two peaks around 910 and 1030 cm$^{-1}$. Figure 3 shows the time series of a N$_2$ sample (zero-gas) at 910 cm$^{-1}$ and 948 cm$^{-1}$ for NF$_3$ and SF$_6$ respectively. The noise of the system and the background signal were calculated from these measurements. The detection limit (2 x RMS) for SF$_6$ was determined to be 0.5 ppb in 15 seconds of measurement time. The NF$_3$ detection limit was 7.5 ppb in 15 seconds.

![Figure 2. The photoacoustic signal of PA201 photoacoustic gas cell from a mixture of 1 ppm SF$_6$, 10 ppm NF$_3$, 10,000 ppm H$_2$O, and 2 ppm CH$_4$ was recorded over the full tuning range of the LaserTune EC-QCL.](image)

Figure 3. N$_2$ background signal at 910 cm$^{-1}$ (NF$_3$) and 948 cm$^{-1}$ (SF$_6$) demonstrating the low noise in the measurement.

_Jaakko Lehtinen, Ph.D., attended the University of Turku in Finland, and received a Master’s degree in 2010 and a Doctoral degree in 2014 in Physics. Both his Master’s and Doctoral Theses concerned the use of cantilever-enhanced photoacoustic spectroscopy. During his doctoral studies, Lehtinen worked as a Project Researcher and doctoral student between 2011 and 2013 at the University of Turku. He joined Gasera Ltd. in 2011 as a part-time Application Scientist. Currently he is working at Gasera as a Client Partner._

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