

## APPLICATION NOTE **PA201**

Quantum cascade laser photoacoustic spectroscopy (QCL-PAS)  
measurement of SF<sub>6</sub> and NF<sub>3</sub>



Gasera PA201 research photoacoustic gas cell combined with widely tunable mid-infrared QCL source proved to be a powerful tool in the detection of SF<sub>6</sub> and NF<sub>3</sub>. The detection limit for SF<sub>6</sub> 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 the commercial SF<sub>6</sub> infrared detectors. The combination of PAS and QCL technologies provides unmatched sensitivity and selectivity, and enables the downscaling of the system ultimately to hand-held size.

### Application

SF<sub>6</sub> is mainly used in gas-insulated switchgear (GIS) and circuit breakers, but also in e.g. cables, tubular transmission lines and transformers. Switchgear typically use SF<sub>6</sub> as the insulator gas to prevent arcing when the circuit breaker is activated. SF<sub>6</sub> itself is non-toxic, but it can decompose into toxic by-products due to discharges or arcing.

SF<sub>6</sub> is a greenhouse gas with a 23,900 times greater global warming potential (GWP) than CO<sub>2</sub> and an atmospheric life of 3,200 years. Therefore, even a relatively small amount of SF<sub>6</sub> can have a significant impact to the climate. Because SF<sub>6</sub> cannot be replaced with another less harmful gas in the power utility, its emissions have to be minimized. Roughly 80% of all SF<sub>6</sub> produced worldwide is used by the electric power industry.

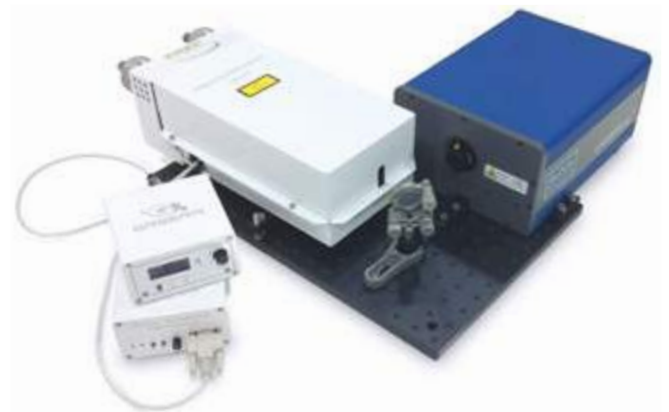


Fig. 1. PA201 photoacoustic detector (Gasera Ltd.) and LaserTune widely tunable EC-QCL (Block Engineering LLC).

Leaking GIS causes unnecessary SF<sub>6</sub> 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 the emissions but also the costs can be reduced. All SF<sub>6</sub>-insulated equipment leaks to some degree and SF<sub>6</sub> gas is always present in the GIS surrounding air, at concentrations varying typically between 20 and 100 ppb.

NF<sub>3</sub> is also a greenhouse gas with 17,900 times greater GWP than CO<sub>2</sub>, second only to SF<sub>6</sub>. NF<sub>3</sub> is used for example in plasma or thermal cleaning and silicon dioxide etching, and is considered as an environmentally preferable substitute for SF<sub>6</sub> 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 against 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<sub>6</sub> 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 even over 1000 cm<sup>-1</sup>, 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 Fig. 1. The components were mounted on an optical table for a stable alignment of the laser beam. Measurement parameters are presented in Table I.

Table I. Measurement parameters.

Laser power	0.5 - 1.5	mW
Laser tuning range	770 - 1320	cm <sup>-1</sup>
Laser linewidth	< 1	cm <sup>-1</sup>
Modulation frequency	70	Hz
PA cell pressure	1000	mbar
PA cell temperature	50	°C
PA cell length	100	mm

Fig. 2 shows the measured photoacoustic spectrum of 1 ppm SF<sub>6</sub> and 10 ppm NF<sub>3</sub> mixture. Also, 10000 ppm H<sub>2</sub>O and 2 ppm CH<sub>4</sub> were present in the sample during the measurement. SF<sub>6</sub> has a strong peak around 950 cm<sup>-1</sup>, and NF<sub>3</sub> has two peaks around 910 and 1030 cm<sup>-1</sup>. Fig. 3 shows the time series of N<sub>2</sub> sample (zero-gas) at 910 and 948 cm<sup>-1</sup>. The noise of the system and the background signal were calculated from these measurements. The detection limit (2 × RMS) for SF<sub>6</sub> was determined to be 0.5 ppb in 15 seconds measurement time. NF<sub>3</sub> detection limit was 7.5 ppb in 15 seconds.

Fig. 2 also shows the multi-component potential of widely tunable EC-QCLs. While the mixture consisted of four different compounds, most of the available spectral range is still unused, and can be applied for a simultaneous measurement of wide range of other gases of interest.

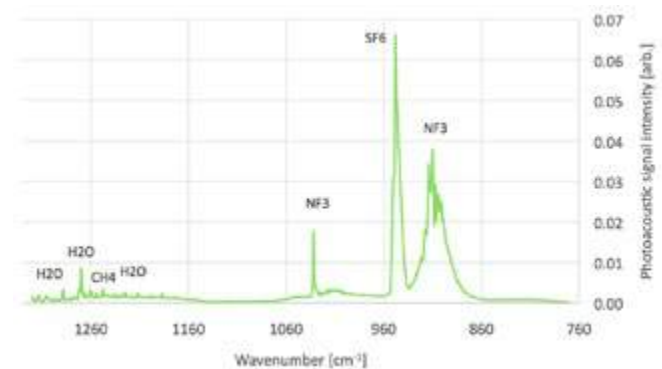


Fig. 2. The photoacoustic signal of PA201 photoacoustic gas cell from a mixture of 1 ppm SF<sub>6</sub>, 10 ppm NF<sub>3</sub>, 10000 ppm H<sub>2</sub>O, and 2 ppm CH<sub>4</sub> was recorded over the full tuning range of the LaserTune EC-QCL.

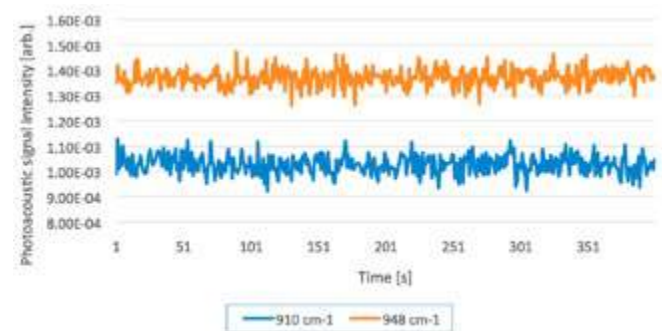


Fig. 3. N<sub>2</sub> background signal at 910 cm<sup>-1</sup> (NF<sub>3</sub>) and 948 cm<sup>-1</sup> (SF<sub>6</sub>) demonstrating the low noise in the measurement