APPLICATION NOTE PA201

Quantum cascade laser photoacoustic spectroscopy (QCL-PAS) measurement of SF_6 and NF_3

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_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 the commercial SF_6 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.

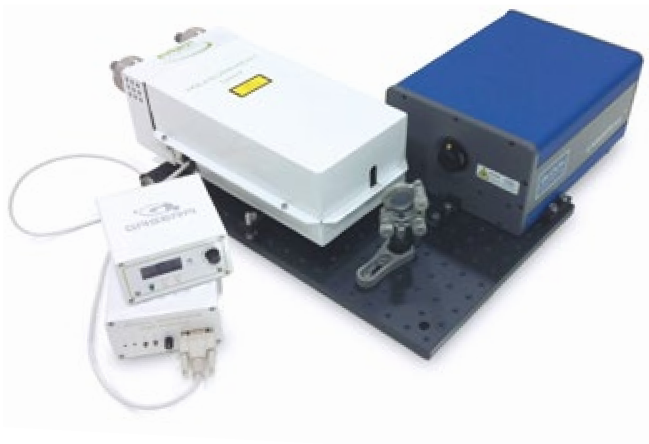

Fig. 1. PA201 photoacoustic detector (Gasera Ltd.) and LaserTune widely tunable EC-QCL (Block Engineering LLC).

Application

SF_6 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_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 to 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 the emissions but also the 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 is also a greenhouse gas with 17,900 times greater GWP than CO_2, second only to SF_6. NF_3 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 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_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 even over 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 Fig. 1. The components were mounted on an optical table for a stable alignment of the laser beam. Measurement parameters are presented in Table 1.

Table 1. Measurement parameters.

Laser power	0.5 - 1.5	mW
Laser tuning range	770 - 1320	cm^{-1}
Laser linewidth	< 1	cm^{-1}
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_6 and 10 ppm NF_3 mixture. Also, 10000 ppm H_2O 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}. Fig. 3 shows the time series of N_2 sample (zero-gas) at 910 and 948 cm^{-1}. 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 measurement time. NF_3 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.

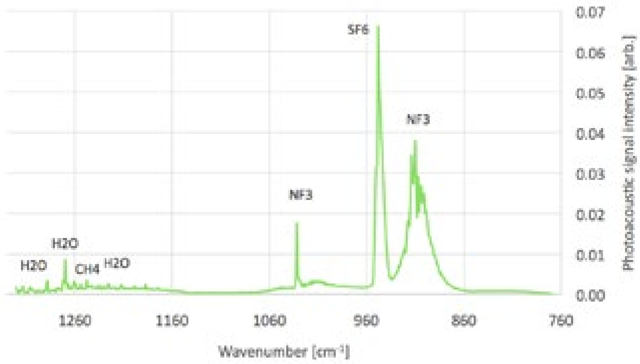

Fig. 2. The photoacoustic signal of PA201 photoacoustic gas cell from a mixture of 1 ppm SF_6, 10 ppm NF_3, 10000 ppm H_2O, and 2 ppm CH_4 was recorded over the full tuning range of the LaserTune EC-QCL.

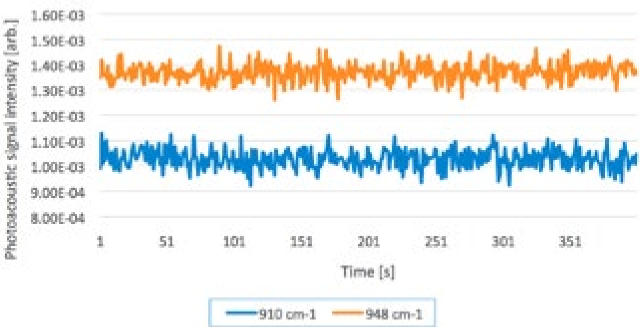

Fig. 3. N_2 background signal at 910 cm^{-1} (NF_3) and 948 cm^{-1} (SF_6) demonstrating the low noise in the measurement