CO Detection in SF_6 Using Quartz-enhanced Photoacoustic Spectroscopy

ABSTRACT

Researchers from China and Italy have developed a highly sensitive and selective optical sensor using quartz-enhanced photoacoustic spectroscopy (QEPAS) for carbon monoxide (CO) detection in sulfur hexafluoride (SF_6) decomposition. High-voltage apparatuses, utilizing SF_6 as gas-insulating medium, require rapid and continuous monitoring. Detecting CO as one of the SF_6 decomposition products allows early diagnosis of apparatus failure. With the spectrophone consisting of an 8 kHz T-shaped quartz tuning fork and a pair of resonator tubes for photoacoustic detection, a quantum cascade laser (QCL) with central wavelength of 4.61 μm is used as the light source of the optical sensor. This novel design achieved a minimum detection limit of 10 ppb at 10 seconds of signal integration time for CO detection in SF_6 decomposition.

INTRODUCTION / SF_6

Sulfur hexafluoride (SF_6) is commonly used in electrical power plants and apparatuses with high-voltages (**Figure 1**). Because of its dielectric strength, heat transfer capacity, and ability to interrupt electric arcs, SF_6 is a popular insulating gas in electrical equipment such as electrical switches and gas circuit breakers. It is especially useful for high-voltage systems as SF_6 is non-flammable, non-toxic, and relatively low cost.

The only problem that can cause hesitation with SF_6 as the insulating medium for these devices is the high global warming potential. SF_6 is a potent greenhouse gas and can trap heat in the atmosphere if not contained. It is important to monitor and maintain all systems and apparatuses that use SF_6 as the gas-insulating medium.

When SF_6 coexists with metal and decomposes, it can break down into SF_2, SF_4, SF_5, and S_2F_{10}. If no impurities are present these products recombine and return to their original shape and composition. However, they can react with O_2 and H_2O impurities and produce chemically active products such as SO_2, SOF_2, SO_2F_2, CO, and CF_4.[1] Measuring these decomposition products of SF_6 can provide an efficient and precise method to detect failures and overheating problems in gas-insulated switchgears (GISs) and other SF_6-insulated systems.

Carbon monoxide (CO) is the best candidate for monitoring the maintenance of the GISs. With regulated working levels for 8-hour shifts of around 20-50 parts-per-million (ppm), it can be used to provide an early diagnosis on the health of the GISs. A good detection system would have a minimum detection limit of ~1 ppm for real-time, in-situ operation in SF_6 environments.[1]

Figure 1. High-Voltage Gas-Insulated Switchgear (GIS) in Utility Substation.

PHOTOACOUSTIC SPECTROSCOPY

Researchers have reported many different methods to detect decomposition products of SF_6, among them are: gas chromatography, electrochemical methods, metal-oxide semiconductor sensors, and tube detection methods. Unfortunately, these method usually contain large amounts of background noise as well as low stability and are not consumption free regarding the material.[2] These drawbacks prevent real-time and in-situ monitoring of the decomposition products of SF_6 in GISs. However, in the past few years, optical methods have been reported to detect CO at the ppm level and even at the parts-per-billion (ppb) level.[1]

Optical methods are ideal techniques for avoiding electromagnetic noise in high-voltage systems and can be useful for measuring CO contents in SF_6 gas matrices.[1] The two main techniques for optical CO detection are tunable diode laser spectroscopy (TDLAS) and photoacoustic spectroscopy (PAS). While both methods can achieve the minimal detection limits required for GISs monitoring, PAS does not require a multipass gas cell and is used in this research experiment.

A new method makes a slight change to PAS to provide better accuracy. A quartz tuning fork (QTF) can replace the microphone in PAS to act as a sharp photoacoustic transducer. The piezoelectric properties of the QTF allow the prong motion, generated by pressure waves from the absorbing molecules, to be transduced into an electrical signal. This electrical signal can be amplified using a transimpedance or voltage amplifier to produce the signal spectrum.[1] This method is known as quartz-enhanced photoacoustic spectroscopy (QEPAS). In QEPAS, the QTF is acoustically coupled with a pair of resonator tubes to amplify the acoustic pressure waves from the excited gas. The system- the QTF, and the resonator tubes, is called the QEPAS spectrophone, and it can provide high resonance quality-factor, compact size, and strong insensitivity to ambient acoustic noise.[1] QEPAS allows for wavelength-independent operation, useful with lasers from UV to THz range with custom QTFs, and it can be utilized for multi-gas detection.[1]

METHOD

Researchers from China and Italy have developed a custom QEPAS spectrophone for CO monitoring in SF_6 decomposition for use in SF_6 high-voltage applications. A custom QTF was designed for a better sensor detection limit by taking into account the effect of the SF_6 matrix.

Figure 2 shows the CO absorption cross section and SF_6 absorption cross section simulation. It is important to select a wavelength that has a high CO absorption property as well as a narrow spectral overlap with the tail of the SF_6 absorption feature in the lower graph. The fundamental roto-vibrational absorption band of CO is located in the mid-infrared (MIR) range from 4.5 µm to 4.9 µm. In this MIR range, SF_6 exhibits a weak and wide absorption feature with a longer tail toward the 4.7 µm range. The most intense CO absorption line, 4.60 µm, was selected, and this line exhibits a cross section of 2.0×10^{-18} cm^2/mol. At this wavelength, SF_6 exhibits an absorption cross section of < 10^{-22} cm^2/mol.[1]

It is crucial that this spectral overlap between the CO and SF_6 absorption does not affect the detection of the CO gas. How CO, SF_6, and other decomposition gases from SF_6 behave, regarding roto-vibrational energy levels, will determine the shape, features, materials, and characteristics of the tuning forks as well as resonator tubes.

Because different molecules and gases are characterized by different vibrational energy levels, the relaxation time of CO in the SF_6 matrix needs to be known. SF_6 does not act as a relaxation promoter when existing with CO, but it does provide both vibration-to-translational and vibration-to-vibrational collisions. This leaves an effective relaxation time of CO in the SF_6 matrix equal to τ = 33 ms·Torr.[1] Standard QTFs have resonance frequencies of 32 kHz, but this exceeds the CO-SF_6 collision rate and cannot be used.

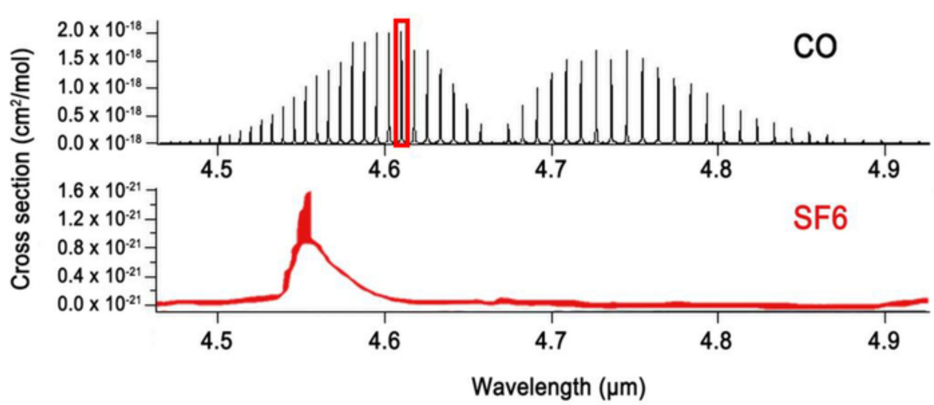

Figure 2. CO absorption cross section (black line) and SF_6 absorption cross section (red line) simulated using PNNL database. The red rectangle points at the CO feature targeted for the detection.[1]

A recent custom QTF uses rectangularly shaped prongs with resonance frequency of 15.2 kHz to detect CO in standard air in the ppb range (Li2019). However, to decrease the resonance frequency even further, the prong's thickness can be decreased. This does add a problem of decreased QTF quality factor, however. A new QTF geometry is required to maintain quality factor and reduce resonance frequency. Here, researchers have designed a T-shaped QTF with carved grooves to modify the resonance frequency without affecting the quality factor. The schematic and parameters of the custom T-shaped QTF can be seen in **Figure 3**.

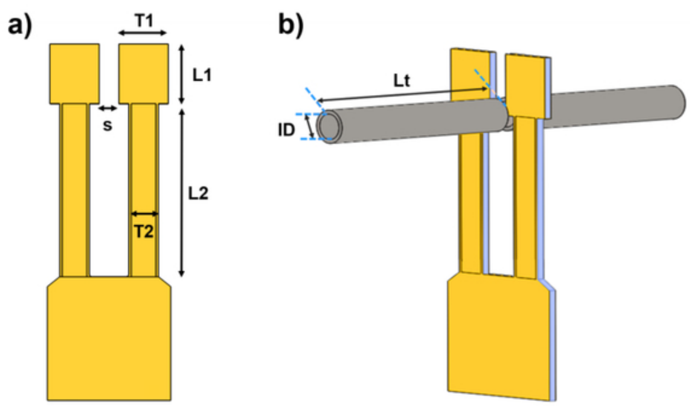

Figure 3. (a) Schematic diagram of the T-shaped grooved QTF, with geometrical parameters. T1 = 2.0 mm; T2 = 1.2 mm; L1 = 2.4 mm; L2 = 7.0 mm; s = 0.8 mm. Carved grooves on the QTF prong are 50 µm deep. (b) Schematic diagram of the QEPAS spectrophone.[1]

The above QTF has resonance frequency of f_{air} = 8070.0 Hz and f_{SF6} = 8066.7 Hz in air and in the SF_6 matrix, respectively. Because the molar mass of SF_6 is nearly five times higher than the molar mass of air, the damping effects of the surrounding medium on the prongs' vibration is slightly different, causing the resonance frequencies to not be identical. The quality factor, *Q*, is also affected by whatever gas surrounds the QTF. The measured *Q* for the 8 kHz QTF is 10900 and 5700 in air and SF_6, respectively. The standard 32.7 kHz QTF in SF_6 only has *Q* = 3700 in SF_6, solidifying the improvements of the new QTF.[1]

The rest of the QEPAS sensor can be seen in **Figure 4**, including the laser with current control, acoustic detection module (ADM), and waveform generator.

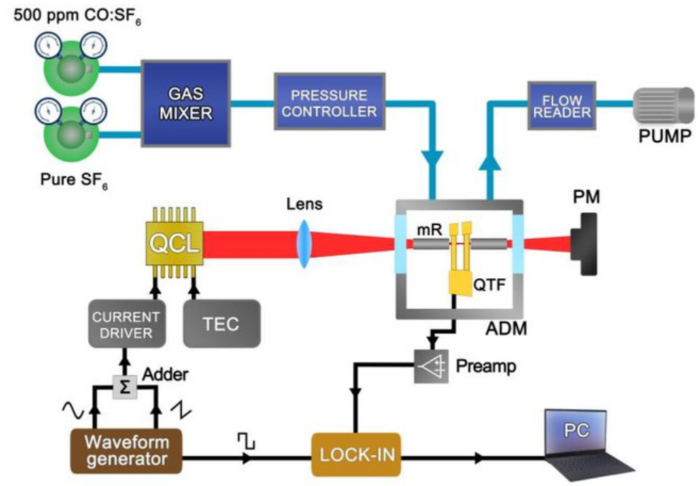

Figure 4. Schematic of the QEPAS sensor for CO detection in the SF_6 matrix. TEC, thermo-electric cooler; ADM, acoustic detection module; PM, power meter; DAQ, data acquisition; PC, personal computer.[1]

An airtight chamber contains the QTF and the resonator tubes for acoustic detection. A distributed feedback (DFB) quantum cascade laser (QCL) was used for transmitted radiation into the gas chamber. This laser has a central wavelength of 4.61 µm, targeting the high absorption range of CO. With a QCL driver from Wavelength Electronics, the laser source was controlled to the selected absorption line at 2169.2 cm^{-1} with an injection current of 214 mA. This corresponds to an output optical power of 20 mW as well as ensures the highest absorption of light in CO gas. The emitted light from the QCL can pass through windows on the ADM and through the resonator tubes with diameter of 1.0 mm, while only being absorbed by the gas inside the chamber and not touching the resonator tubes. The gas mixer and pressure controller optimize the gas concentrations inside the ADM at any given time and can provide different gas mixtures with different CO concentrations in SF_6.

The QCL current driver also enabled the laser to perform a modulation signal at half the QTF resonance frequency from a waveform generator. An analog adder superimposed a triangular ramp to scan the laser wavelength and the second harmonic ($2f$) modulation at half the resonance frequency. The preamplifier can then detect the signals from the QTF and send to the PC for storage and analysis. A lock-in integration time of 1 second was set for this system.[1]

Initial testing was performed to maximize the QEPAS signal by calibrating the current modulation amplitude, operating pressure, and other operating conditions for CO detection.

RESULTS

Initial tests determined the optimal pressure and modulation depth of the QEPAS signal for CO detection. The results are shown in **Figure 5**.

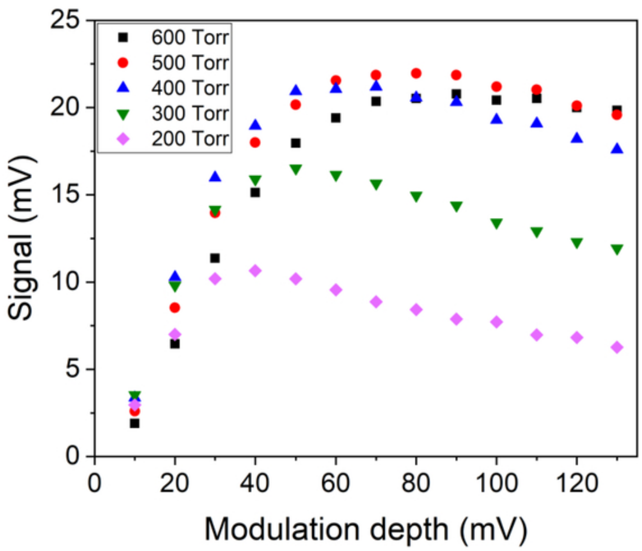

Figure 5. QEPAS signal of a certified 500 ppm CO:SF_6 mixture, as a function of the modulation depth set on the waveform generator. Operating pressure varied from 200 Torr to 600 Torr.[1]

From the plot above, the highest QEPAS signal was recorded when the operating pressure was 500 Torr and the modulation depth was 80 mV. With these parameters, different concentrations and mixtures of CO in SF_6 were generated and analyzed. Starting from the verified 500 ppm mixture, the concentration was diluted down to 15 ppm. By varying the injection current to target just SF_6 and CO, an offset of 40 μV was calibrated for the SF_6 gas. Tuning the laser current at the CO absorption peak of 214 mA, the QEPAS signal was plotted as a function of CO concentration after removing the SF_6 offset in **Figure 6**. A linear fit was added to the data as seen in the graph inset, resulting in a slope of 45.1 μV/ppm. To determine the detection limit of the sensor, the background noise was measured to be 4.6 μV (1σ value) at 1 s of integration time. The minimum detection limit (MDL) was then calculated where the CO concentration corresponds to a signal-to-noise ratio of 1. The MDL calculated for this custom QEPAS sensor resulted in 90 ppb, making this sensor a reliable and high precision system for CO detection in many applications.

The stability of the sensor was acquired with long-term measurement with the laser injection current locked at 214 mA. The results are shown in **Figure 7**.

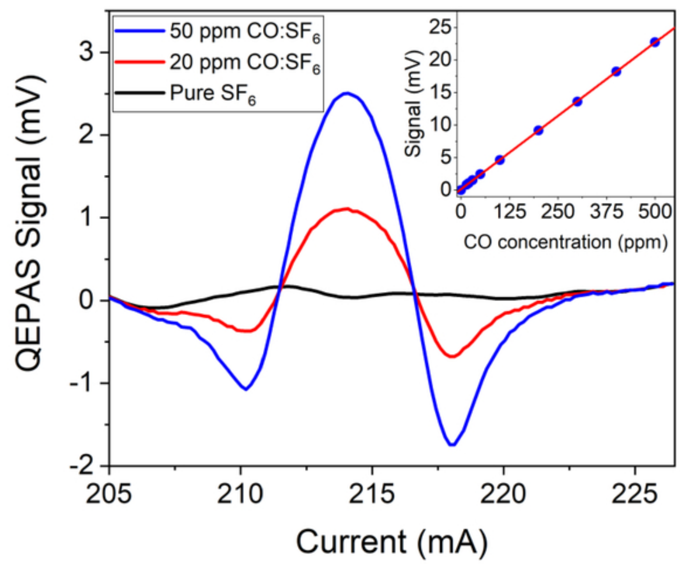

Figure 6. QEPAS signals acquired at different concentrations of CO in SF_6 mixture and QEPAS signal of pure SF_6 as a function of the laser injection current. (inset) CO peak signals acquired at different CO concentrations (blue dots) and the corresponding linear fit (red line).[1]

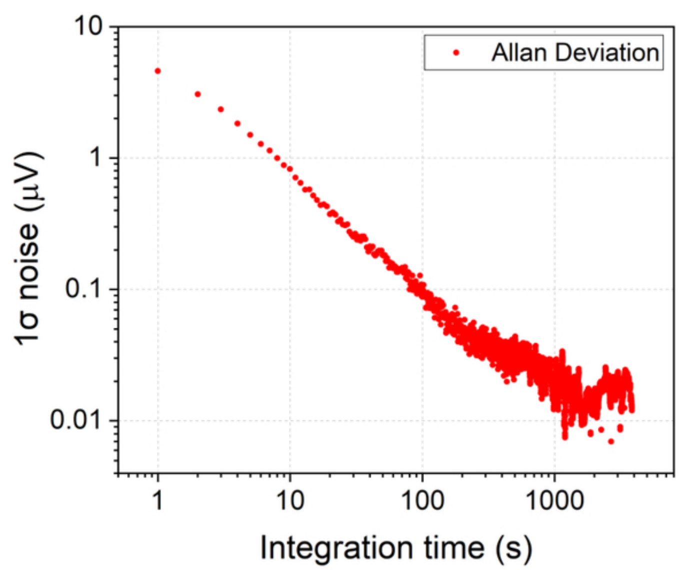

Figure 7. 1σ noise of QEPAS signal as a function of the lock-in integration time as result of Allan-Werle deviation analysis.[1]

Because the sensor 1σ noise level decreases as the integration time increases, an estimated MDL of 10 ppb can be calculated from an integration time of 10 s. This makes the compact QEPAS sensor with custom T-shaped QTF an essential tool for CO monitoring in GISs with real-time tracking and in-situ CO detection in the ppb range.

WAVELENGTH'S ROLE

Detecting CO gas by means of wavelength modulation, second harmonic modulation, and photoacoustic techniques requires high precision and stable control of the quantum cascade laser in the QEPAS sensor. Wavelength Electronics' QCL driver, the QCL2000 LAB, enabled sensitive measurements with minimal electronic noise from the laser for narrow linewidth from the QCL. The driver also allows analog modulation of up to 2-3 MHz for wavelength modulation and second harmonic modulation in the QEPAS sensor. This allowed the QEPAS sensor to achieve a minimum detection limit of 90 ppb which can be decreased down to 10 ppb using an integration time of 10 s, indicating the long term stability of the QCL2000 LAB current driver

The stability of the QCL is critical for exact excitation of the gas molecules detected by the quartz tuning fork. Wavelengths' low noise, high stability QCL driver, QCL2000 LAB, can precisely deliver up to 2 A to the laser. This benchtop QCL driver instrument exhibits noise performance of 1.3 µA RMS up to 100 kHz with an average current noise density of 4 nA/√Hz. Additional features, such as the intuitive touchscreen interface, USB and Ethernet connections, rack mountability, and adjustable output current and compliance voltage enable custom setup in any design. Brown-out, overvoltage, key switch, turn-on delay, and current ramp protect the user and the QCL from potential damage and electrical faults.

The QCL2000 LAB QCL driver instrument enables CO detection at parts-per-billion levels with low noise and stable laser output. This makes the developed QEPAS a reliable tool for CO monitoring inside gas-insulated switchgears and other high-voltage apparatuses using SF_6 as the gas-insulating medium.

PRODUCTS USED
QCL2000 LAB

KEYWORDS
Photoacoustic spectroscopy, quartz tuning fork, sulfur hexafluoride, carbon monoxide, gas sensing, quantum cascade laser, gas-insulated switchgears, QCL, QEPAS, SF6, CO, QTF, GIS

REFERENCES

1. Andrea Zifarelli, Pietro Patimisco, Stefano Dello Russo, Angelo Sampaolo, Marilena Giglio, Bo Sun, Hongpeng Wu, Lei Dong, and Vincenzo Spagnolo "Quartz-enhanced photoacoustic spectroscopy for CO detection in SF6 decomposition", Proc. SPIE 11693, *Photonic Instrumentation Engineering VIII*, 116930H (2021); https://doi.org/10.1117/12.2577619
2. Bo sun, Andrea Zifarelli, Hongpeng Wu, Stefano Dello Russo, Shangzhi Li, Pietro Patimisco, Lei Dong, and Vincenzo Spagnolo "Mid-Infrared Quartz-Enhanced Photoacoustic Sensor for ppb-Level CO Detection in a SF6 Gas Matrix Exploiting a T-Grooved Quartz Tuning Fork", Anal. Chem. 13922-13929 (2020); https://doi.org/10.1021/acs.analchem.0c02772

USEFUL LINKS

- QCL2000 LAB **Product Page**

PERMISSIONS

Figures 2, 3, 4, 5, 6, & 7 and data used for this case study were obtained from Reference 1. Permission was granted for use of the images and data from SPIE and the corresponding author(s) of Reference 1.

No changes were made to the images or the captions. They are presented here in their original form.

REVISION HISTORY

Document Number: CS-LD05

REVISION	DATE	NOTES
A	March 2022	Initial Release