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Mid-infrared quartz-enhanced photoacoustic sensor for ppb-level CO detection in SF6 gas matrix exploiting a T-grooved quartz tuning fork

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ABSTRACT: An optical sensor for highly sensitive detection of carbon monoxide (CO) in sulfur hexafluoride (SF6) was demonstrated by using quartz-enhanced photoacoustic spectroscopy (QEPAS) technique. A spectrophone composed by a custom 8 kHz T-shaped quartz tuning fork (QTF) with grooved prongs and a pair of resonator tubes, to amplify the laser-induced acoustic waves, was designed aiming to maximize the CO photoacoustic response in SF6. A theoretical analysis and an experimental investigation of the influence of SF6 gas matrix on spectrophone resonance properties for CO detection have been provided, and the performances were compared with the standard air matrix. A mid-infrared quantum cascade laser with central wavelength at 4.61 μm, resonant with the fundamental band of CO, and optical power of 20 mW was employed as light excitation source. A minimum detection limit of 10 ppb at 10 s of integration time was achieved and a sensor response time of ~3 minutes was measured.

Sulfur hexafluoride (SF6) is a non-toxic, non-flammable and thermally stable gas with excellent heat transfer and arc-quenching capability.† The latter comes from the ability of SF6 molecules to rapidly recombine after dissociation during an electrical discharge, providing a strong dielectric recovery strength. Therefore, SF6 is widely used as a gas-insulating medium in several high-voltage apparatus, including gas-insulated switchgears (GISs), gas circuit breakers (GCBs) and gas-insulated transformers (GItS). These devices have become the main equipment of electrical power stations due to their high insulation reliability, low failure rate and small footprint.‡ However, due to the aging, internal diagnosis and rapid maintenance are essential to improve the reliability of its power supply, especially for large-scale GIS equipment. Several kinds of local insulation defects existing in GISs, such as spark and arc discharges, can cause decomposition reactions of SF6.†‡ Although its decomposition temperature is 500 °C, when SF6 coexists with metals, different decompositions may occur also at 200 °C to generate a variety of low-fluorine sulfides such as SF4, SF2, S2F10.†‡ These low-fluoride sulfides react with moisture and oxygen and generate chemically active by-products such as CO, SO2, H2S, CF4, etc.,§ with different contents and ratios. Thus, the detection of SF6 gas decomposition products can be an efficient method for equipment failure detection, especially if the detection technique is not affected by electromagnetic noise and mechanical vibrations, making it suitable for in-situ detection. The early detection of partial discharges could allow predicting overheating faults, as well as to check whether the internal insulation materials in electrical equipment are qualified.§ Among these decomposition products, carbon monoxide (CO) is a trace characteristic component that can be used as an indicator gas to identify low temperature overheating insulation defects in GIS equipment. Excessive CO generated inside the equipment also poses a threat to personnel safety issues. When the CO concentration is within 20 part-per-million (ppm), it means that the GIS is working in a safe state.†§ When it exceeds this range, the equipment should be maintained in time. Therefore, it is crucial to develop and design a compact, highly stable and sensitive CO gas sensor for GISs that can detect the CO concentration in SF6 matrix with a detection limit below 1 ppm in real time. Some methods for measuring the content of decomposition products of SF6, such as gas chromatography,†¹ electrochemical method,†² metal-oxide semiconductor sensors,†³ and tube detection method†⁴ have been reported. However, these methods suf-
fer from poor stability, long stabilization time, large background noise and material consumption. Recently, optical methods have been used for the detection of decomposition products of SF₆, and several CO optical sensors in SF₆ have been reported. In 2018, a tunable diode laser absorption spectroscopy (TDLAS) sensor employing a diode laser emitting at 2.33 μm and a 14.5-nm multi-pass gas cell (MGC) allowed CO detection at ppm level. In 2019, a photoacoustic spectroscopy (PAS) sensor was developed to detect the CO content in SF₆ in real time. Employing a DFB laser emitting at 1.56 μm together with a 10 W fiber amplifier, a minimum CO detection limit of ~120 ppb was achieved.¹⁵

Quartz enhanced photoacoustic spectroscopy (QEPAS) has established itself as an enhanced version of traditional PAS,¹⁶ with further advantages of low-cost, high immunity to external noise and small compact volumes,¹⁷⁻¹⁹ in which the wideband microphione of traditional PAS is replaced with a ultra-narrowband quartz tuning fork (QTF) to detect sound waves generated when the gas absorbs modulated light. The QTF is acoustically coupled with a pair of millimeter-size resonator tubes, aligned on both sides of the QTF in a way that the laser beam can be focused between QTF prongs while passing through both tubes, without touching them.²⁰⁻²² When the laser beam is modulated at the resonance frequency of one in-plane flexural mode of the QTF, a standing wave vibrational pattern is created within the resonator tubes which directs the two prongs in opposite directions, exciting QTF piezoelectrically-active, anti-symmetrical flexural mode. Thus, an electrical signal proportional to the absorbed analyte concentration is generated. From 2002, several QEPAS sensors have been realized and more than 30 different analytes have been detected by using various wavelength laser sources, spanning from UV-visible to Terahertz range, in most cases with ultimate detection limits in part-per-billion range.²⁰

The QTF resonance frequency rules the modulation of the absorbed light, which in turn determines the efficiency of the energy relaxation, i.e. the efficiency of sound generation.²³ With a commercial QTF having a frequency as high as 32.7 kHz, the energy relaxation occurring in the absorbing gas cannot be fast enough to follow the intensity light modulation, resulting in low radiation-to-sound conversion efficiency. In fact, CO has a relatively slow vibration-to-translational (V-T) energy transfer rate, which lead to a weak QEPAS signal output when a 32.7 kHz QTF is employed. These issues promote the research of the QTF with lower resonance frequencies.²⁴⁻²⁵ In all sensors reported in literature, trace analyte was detected in N₂ or air matrix. A CO QEPAS sensor in air matrix was demonstrated by exploiting a custom-made 15.2 kHz-QTF with grooves carved on both prongs’ surfaces. With water vapor as the catalyst for vibrational energy transfer, the QEPAS sensor reached a minimum detection limit of 7 ppb for a 1 s averaging time.²⁶ When the gas matrix changes, two considerations should be taken into account. First, the main energy dissipation mechanism occurring in a vibrating prong is the damping by the surrounding fluid.²⁷ Thus, matrix composition and its thermodynamic parameters affects the QTF quality factor. Since the QEPAS signal is proportional to the QTF quality factor, the ultimate sensor sensitivity will be dependent on the matrix composition. For gas matrices composed by molecules with heavy molecular weight, as the SF₆ matrix, the drop of the QTFs’ quality factor due to damping effects may strongly affects the sensor performances. The second consideration regards the geometrical parameters of resonator tubes, in particular, the internal diameter and the length of the two tubes l, that influence the sensor performance.²¹,²² The length of the two tubes is correlated with the sound wavelength \( \lambda = \frac{\nu_s}{f_0} \), where \( \nu_s \) is the sound speed in the matrix and \( f_0 \) is the QTF resonance frequency. Since \( \nu_s \) depends on matrix temperature and composition, the tubes length must be optimized for SF₆ matrix to match the acoustic field inside the tubes. All these considerations suggest that the QEPAS spectrophone composed by the QTF and resonator tubes must be properly designed and optimized for an efficient CO detection in SF₆ matrix.

In this paper, a custom T-shape QTF with grooves carved on prong surface was designed with a resonance frequency of 8 kHz, 4 times lower than the standard QTF, and a quality factor of ~11,000 in air, at atmospheric pressure. By means of this QTF, the QEPAS technique was applied to the measurement of CO in SF₆ environment. The geometric parameters of tubes were studied to ensure high sound amplification in SF₆ matrix. The QEPAS spectrophone performance was analyzed both in standard air and in SF₆ matrix. A mid-infrared distributed-feedback (DFB) quantum cascade laser (QCL) with a center wavelength of 4.61 μm was chosen as the light source to photoacoustically excite the CO molecules.

**EXPERIMENTAL SECTION**

**CO relaxation dynamics in SF₆ matrix.** CO is a heavy diatomic molecule with a low density of vibrational energy levels. Therefore, the CO molecule is characterized by a slow V-T energy transfer rate in the collisional de-excitation process with another CO molecule as well as in the collision with a N₂ molecule. Indeed, QEPAS sensor based on commercial 32.7 kHz-QTF allowed ultimate detection limit of CO at part-per-billion concentration level but with a wall-level excitation source.²⁸ Furthermore, SF₆ has a high density of vibrational levels available for multi-channel resonant energy transfers via consecutive multi-step relaxation processes. For this reason, SF₆ has been widely used as a promoter for slow-relaxing gases, such as N₂O and CO₂, in order to speed up the relaxation processes and increase the QEPAS sensor response. Although it is efficient in case of N₂O and CO₂, SF₆ does not significantly promote vibrational de-excitation of CO.²⁹ Thus, the SF₆ does not act as a relaxation promoter for CO. The CO QEPAS signal can be expressed as:

\[
S = \frac{S_0}{\sqrt{1 + \left(\frac{f_0}{f}\right)^2}}
\]

where \( f \) is the QTF resonance frequency, \( r \) is the gas sample effective relaxation time, \( P \) is the operating pressure and \( S_0 \) is the photoacoustic signal for instantaneous V-T transfer, i.e. where \( f_0/P << 1 \). The CO relaxation time \( r \) in a SF₆ matrix depends on the different collision channels with the different types of molecules in the mixture.

The excited CO molecules can relax in a non-radiative way by V-T collisions with another CO molecule (identified by a characteristic relaxation time \( r_{V-T} \)) or, alternatively, by V-V (vibrational to vibrational) interaction with an SF₆ molecule \( (r_{V-V}) \), which will be in turn excited. This excited SF₆ molecule will consequently de-energize by V-T collisions with other SF₆ molecules \( (r_{V-T, SF₆}) \). The potential relaxation pathways of the laser-excited CO energy level are shown in Figure 1.
The relaxation time values reported in literature are $\tau_{V-T,SF_6} = 42 \mu s \cdot Torr$,$^{20}$ $\tau_{V-V} = 33 ms \cdot Torr$,$^{31}$ and $\tau_{V-T} = 1.52 ms \cdot Torr$.$^{32}$ $\tau_{V-V}$ is three orders of magnitude smaller than that $\tau_{V-T}$, and therefore V-T collisions between SF$_6$ molecules can be considered as instantaneous. The relaxation rate $1/\tau$ is then given by the sum of the relaxation rates of every possible energy transfer pathway, weighted by the concentrations of CO and SF$_6$ molecules, $C_{CO}$ and $C_{SF6}$ respectively, in the mixture by:\textsuperscript{33}

$$1/\tau = \frac{C_{CO}}{\tau_{V-T}} + \frac{C_{SF6}}{\tau_{V-V}}$$

(2)

The effective relaxation time of CO in SF$_6$ matrix is $\tau = 33 ms \cdot Torr$. With such a high value, the ratio $S/S_0$ is $\sim 0.11$ when a standard 32 kHz QTF is employed at atmospheric pressure but can increase up to $\sim 0.42$ if the QTF resonance frequency is reduced to 8 kHz.

**Figure 1.** Relaxation pathways following optical excitation (represented by red wavy arrow) of excited level of CO molecule.

**Design and test of QEPAS spectrophone.** In Ref. 26, a custom 15.2 kHz-QTF with rectangular grooves was used for the spectrophone of QEPAS sensor for CO detection in air. The prong length $l$, width $w$, thickness $t$, and prong spacing $g$ of the 15.2 kHz-QTF are 9.4 mm, 2 mm, 0.25 mm, and 0.8 mm, respectively. In addition, four 50 μm-deep rectangular grooves were carved on both surfaces of the two QTF prongs, in order to decrease the QTF electrical resistance.$^{34}$ The fundamental mode at 15,243 Hz reaches a quality factor of 15,020 at atmospheric pressure, in air. Moving to low resonance frequencies by varying the ratio $t/l$ following Euler-Bernoulli equation for rectangular prongs, the $Q$-factor decreases. In particular, QTFs with a resonance frequency lower than 10 kHz cannot ensure $Q > 10,000$, at atmospheric pressure. A further reduction of resonance frequency with slight modifications of the overall quality factor requires a change of prong geometry. T-shaped prongs have been proposed to accomplish both requirements, with a further increase of stress field distribution along vibrating prongs with respect to rectangular prongs, beneficial for piezoelectric charge generation when prongs are deflected.

To investigate the resonance properties of a T-shaped grooved QTF, a finite-element-analysis (FEA) using COMSOL Multiphysics was performed. T1 represents the width of the T-shaped prong head and T2 represents the width of the T-shaped prong body (see Figure 2a). The influence of the ratio T2/T1 on the resonance frequency was investigated. T1, L1 and L2 were kept constant to 2.0 mm, 2.4 mm and 7.0 mm, respectively, as for 15.2 kHz-QTF in Ref 26, while T2 was reduced. 50 μm-deep grooves were carved on both sides of each prong, as sketched in Figure 2a. The simulation was performed in vacuum environment to avoid the influence of the surrounding medium and the results are shown in Figure 2b. T2/T1 = 0.5 was set as lower limit for the simulation.

The simulation results clearly indicate a linear trend of the fundamental resonance frequencies with respect to the T2/T1 ratio, with a $R^2$ value of 0.9998. Ratios lower than 0.7, i.e. T2 smaller than 1.4 mm, lead to resonance frequencies lower than 10 kHz. However, the lowering of the resonance frequency through reduction of T2/T1 ratio is in competition with the mechanical stability of the QTF. Low T2/T1 ratio would not guarantee a stable oscillation of the QTF prong due to the low moment of inertia. Moreover, prong oscillations would be highly influenced by the surrounding medium damping leading to high viscous losses that in turn negatively affect the quality factor.$^{27}$ For these reasons, the ratio T2/T1 = 0.6 was chosen, corresponding to T1 = 2.0 mm and T2 = 1.2 mm. The predicted fundamental resonance frequency in vacuum is equal to 7,903 Hz.

Based on this simulation, we realized a QTF as reported in ref.$^{23}$ The resonance properties of the QTF fundamental mode were measured by using the electric excitation experimental setup (Figure S1 of the Supporting Information, SI). The QTF is mounted in an airtight chamber, connected with a gas line that included a pressure controller, a valve system, and an oil-free pump. In this way, it is possible to select and fix the gas pressure

**Figure 2.** (a) Schematic diagram of the T-shaped grooved QTF, with geometrical parameters. (b) COMSOL Multiphysics simulation of fundamental resonance frequency of T-shaped grooved QTF as a function of the T2/T1 ratio.

**Figure 3.** Measured fundamental resonance frequency for QTF in ambient air (red circles) and in pure SF$_6$ (blue squares), as a function of the QTF operating pressure.
in the chamber in the range between 50 and 700 Torr. For each pressure, resonance curves were acquired by varying step-by-step the frequency of the function generator. Each resonance curve was fitted by a Lorentzian function to determine the resonance frequency, i.e., the peak value of the Lorentzian fit function and the full-width-half-maximum (FWHM). The ratio between the resonance frequency and the FWHM value gives the QTF quality factor. The resonance curves at different pressures were acquired with two different gases flowing in the chamber, standard air and pure SF₆. The resonance frequencies f₀ are plotted as a function of the pressure in Figure 3, when standard air (red circles) or pure SF₆ (blue squares) flows in the chamber.

For both gases, the QTF resonance frequency linearly decreases as the pressure increases. The dependence of the resonance frequency on the surrounding gas pressure can be determined by the assumption that the gas effect on prong vibrations damping increases the inertia of the prong. Thus, the Euler-Bernoulli equation describing the motion of vibrating prongs requires an additional term corresponding to the reactive part, which attributes additional inertia to the vibrating prong.\(^\text{23,35}\)

\[
EI \frac{\partial^2 y(z,t)}{\partial x^4} + \left( \rho A + u \right) \frac{\partial^2 y(z,t)}{\partial t^2} = 0
\]

where \(E\) is the quartz Young modulus, \(I\) is the moment of inertia of the prong, \(A\) is the cross sectional area of the prong, \(u\) is the added mass, \(\rho\) is the quartz density, \(t\) is the time and \(y(z)\) is the prong displacement function. eq 3 can be solved by imposing clamped-free boundary conditions (i.e. one prong end is free to oscillate while the other end is clamped to the quartz base) and eigenfrequencies \(f\) can be estimated as:\(^\text{35}\)

\[
f = f_0 \left( 1 - \frac{1}{2} \frac{u}{\rho I} \right)
\]

where \(f_0\) is the resonance frequency in vacuum, i.e. the first eigenfrequency (referred to the fundamental flexural mode) of Eq. 3 when \(u=0\). The exact derivation of the added mass \(u\) is a complicated problem even for simple prism structures. In Ref. 36, the added mass per unit length of a thin beam of width \(w\) has been found to be proportional to gas density \(\rho_0\). By using the ideal gas law, the gas density can be expressed by:

\[
\rho_0 = \frac{MP}{RT}
\]

where \(M\) is molar mass, \(P\) is the gas pressure (in Torr unit), \(R = 62.3637\) m⁴·torr·k·mol is the gas constant and \(T\) is the quartz temperature (in K). Thus, the frequency shift of the QTF resonance frequency due to a pressure change depends on the molar mass of the gas mixture, if the temperature is fixed. Following these considerations, the data points of Figure 3 have been fitted by a linear function, resulting in \(f = 8070.65 - k_{SF_6}P\) and \(f = 8070.63 - k_{SF_6}P\) when the gas matrix is air or pure SF₆, respectively, with \(k_{SF_6} = 9.05 \times 10^4\) Hz/torr and \(k_{SF_6} = 4.15 \times 10^4\) Hz/torr. The intercept values are almost identical and represent the resonance frequency in vacuum, namely \(f_0\) in Eq. 4, while different slope values have been recorded. The discrepancy between measured \(f_0\) (8070.6 Hz) and the related FEA prediction (7903 Hz) can be ascribed to small deviations in geometry between the modeled and the real QTF and to additional weight due to the electrode gold layers, as well as to dependence of the elasticity modulus of quartz on the crystallographic axes orientation. The molar mass of SF₆, \(M_{SF_6}\) is 146.06 g/mol and that of the air, Mair is 28.96 g/mol. According to Eq. 4 and Eq. 5 the ratio \(k_{SF_6} / k_{air} = 4.6\) is comparable with \(M_{SF_6}/M_{air} = 5.0\), demonstrating that the QTF frequency shift as a function of the pressure are mainly dominated by the mass of the surrounding gas, which is a bulk property.

The \(Q\)-factor of a resonance mode is a measure of energy loss of prongs while it is vibrating.\(^\text{21,37}\) It has been demonstrated that the QTF mainly loses energy via the interaction with the surrounding viscous medium. The air damping mechanism can be modeled by using an analytical expression derived by Hosaka et al.\(^\text{38}\) leading to a formulation of the \(Q\)-factor contribution related to gas damping:

\[
Q_{gas} \approx \frac{4\mu T 2w^2 f}{3\mu_0 + 4\pi^2 \mu \rho_0 f^2}
\]

where \(\mu\) is the gas viscosity. By combining Eq. 3 and Eq. 4 and using experimental resonance frequency values reported in Figure 3, \(Q_{gas}\) has been plotted as a function of the gas pressure both for air (\(\mu = 1.81 \times 10^{-5}\) kg/m·s) and SF₆ (\(\mu = 1.4 \times 10^{-4}\) kg/m·s) in Figure 4a. The same trend has been also simulated for standard 32.7 kHz in SF₆ (\(T = 300\) μm, \(w = 350\) μm and assuming a pressure-independent resonance frequency of 32.78 kHz). In Figure 4b, the measured quality factors are reported for the custom 8 kHz-QTF, in air and SF₆, and for standard 32.7 kHz-QTF.

The dependence of the measured \(Q\)-factors on gas pressure follows the trend of \(Q_{gas}\), confirming that the dominant loss mechanism is gas damping, both for air and SF₆. Due to the heavy molecular weight of SF₆, for 8 kHz-QTF vibrating in SF₆, the quality factor is reduced in the overall pressure range with respect to the QTF immersed in air, while maintaining the same trend. When a standard 32.7 kHz-QTF is employed in SF₆, the quality factor values are well below the 8 kHz-QTF trend: in particular, at 500 torr the quality factor is below 5000, not an optimal condition for a QTF to be used in a QEPAS sensor.

The QTF is not used as a standalone in a QEPAS sensor but it is acoustically coupled with a pair of millimeter-size resonator tubes, typically located on both sides of the QTF. (Figure S2) Resonator tubes act as an acoustic resonator.\(^\text{21,22}\) the standing wave vibrational pattern within tubes enhances the intensity of the acoustic field between the QTF prongs up to 60 times.\(^\text{24}\) The QTF coupled with a pair of resonator tubes constitutes the QEPAS spectrophotograph and represents the core of any QEPAS detection module.
When acoustically coupled with a QTF, the internal diameter (ID) of tubes and their length influence the enhancement of the sound wave between QTF prongs. The optimal tube diameter can be estimated by considering the theoretical model proposed in Ref. 22, in which the acoustic coupling between two tubes is expressed in terms of the amount of the acoustic field transferred from one tube to the other one. As result, the optimal tube radius strongly depends on the sound wavelength $\lambda$, and prong spacing $g$. With an 8 kHz-QTF ($\lambda = \nu / f_0 = 16.7 \text{ mm}$, where the speed of sound in the SF$_6$ gas is $\nu = 136 \text{ m/s}$ and $g = 800 \mu\text{m}$) the theoretical model predicts an optimal ID = 1.0 mm. The optimal tube length can be estimated by considering the open-end correction, which assumes that the antinode of a standing sound wave in an open-ended resonator is located outside the tube end, due to an impedance mismatch between the acoustic field inside the resonator and outside. The optimal tube length $l$ depends on the tube ID and the sound wavelength by the relation:

$$ l = \frac{\nu}{2f_0} - \frac{81D}{3\pi} $$

For ID = 1.0 mm, the optimal theoretical length is 7.5 mm. These latter parameters will be used to assemble a dual-tube QEPAS spectrophone with the 8 kHz-QTF optimized to detect CO molecules in SF$_6$ matrix.

**Experimental set up.** A schematic of the QEPAS sensor for CO detection in SF$_6$ matrix is depicted in Figure 5. A mid-infrared distributed-feedback QCL (AdTech optics, Model HHIL-17-62) with a central wavelength of 4.61 $\mu\text{m}$ was chosen as the light excitation source (For the selection process of the CO absorption line and the selection of the light excitation source, see Supplementary Material, discussion S1, Figure S5). A temperature controller (Thorlabs, Model TED200C) and a current driver (Wavelength Electronics, Model QCL2000LAB) were used to fix the operating temperature and the injected current in the QCL, respectively. According to the HITRAN database, the R(6) CO absorption line located at 2,169.2 cm$^{-1}$ with a line-strength of $4.5 \times 10^{-19}$ cm/mol was selected in the fundamental band. To target the selected R(6) line, the temperature and the current of the DFB QCL were set to $37 \, ^{\circ}\text{C}$ and 214 mA, respectively: in these conditions, an optical power of 20 mW was measured. The QEPAS spectrophone composed by 8 kHz-QTF and a pair of resonator tubes ($l = 7.5 \text{ mm}$ and ID = 1.0 mm) was mounted in a stainless steel gas chamber with a volume of 114 cm$^3$, equipped with two CaF$_2$ windows with a diameter of 25 mm, and gas inlet and outlet connectors. The laser beam was focused into the gas cell by using a CaF$_2$ lens, in order to pass through resonator tubes without touching them. A power meter was placed after the ADM both to align the laser beam and to monitor optical power in real time. The QCL scanned the selected CO absorption line by applying a slow (10 mHz) ramp from 202 mA to 222 mA to the current driver. The QEPAS sensor operated in wavelength modulation and 2f-detection: the laser current was modulated at half of the QTF resonance frequency and the QTF signal was demodulated by using a lock-in amplifier (Stanford Research System, Model SR830) at the QTF resonance frequency. The integration time of the lock-in amplifier were set to 1 s with filter slope = 12 dB/oct. The corresponding detection bandwidth was 0.25Hz. Starting from two certified gas cylinders containing pure SF$_6$ and a mixture of 500 ppm of CO in SF$_6$, different CO concentrations in SF$_6$ were generated by using a gas dilution system. A diaphragm pump, a system of valves, a pressure controller and a flow meter were used to fix pressure and measure the gas flow rate within the gas line.

![Figure 5. Schematic of the QEPAS sensor for CO detection in SF$_6$ matrix. CD, current driver; TEC, thermo-electric cooler; ADM, acoustic detection module; NV, needle valve.](image)

**RESULTS AND DISCUSSION**

Assessment of QEPAS sensor performance. The performance of a QEPAS sensor depends on the amplitude of the sinusoidal modulation applied to the laser driver and on the gas pressure. The current modulation amplitude depends on the gas pressure since the full width half maximum (FWHM) of the absorption line suffers from the pressure broadening. Thus, for each gas pressure an optimal current modulation amplitude can be expected. The QEPAS signal is proportional to the QTF quality factor, which increases as the pressure decreases (see Figure 4b). However, a reduction of the pressure results in a decrement of the number of molecules, negatively affecting the sound generation efficiency within the gas. These two opposite trends identify an optimal operating gas pressure.

The certified 500 ppm CO:SF$_6$ gas mixture was used to investigate the QEPAS signal as a function of the peak-to-peak modulation amplitude, for representative gas pressure values ranging from 700 torr to 100 torr. For each spectral scan, the maximum value was extracted (Figure S3). The gas flow rate was fixed to 60 standard cubic centimeters per minute (sccm), for each measurement. At fixed pressure, the QEPAS signal rapidly increases as the modulation depth increases until it reaches a maximum value; then it slightly decreases. A modulation depth maximizing the QEPAS signal is well identifiable for each pressure. As the pressure decreases, the modulation depth maximizing the QEPAS signal clearly shifts toward lower values, as expected because the FWHM value of the CO absorption feature decreases as the pressure is reduced. Thus, the trend of the QEPAS signal as a function of the gas mixture pressure can be extracted. As a result of the investigation, the optimal modulation depth and gas pressure are 80 mV and 500 Torr, respectively.

Starting from the certified 500 ppm CO in SF$_6$ mixture, different CO concentrations in SF$_6$ were generated by using a gas dilution system, down to 15 ppm of CO in SF$_6$. High-resolution QEPAS spectral scans of CO:SF$_6$ mixtures with different concentrations are shown in Figure 6a, together with the spectral scan acquired when pure SF$_6$ flows in the QEPAS sensor.
As expected, when CO flows in the line, the acquired QEPAS scan clearly resemble the second-derivative of the Lorentzian-like R(6) CO absorption line with distortions on negative lobes caused by the residual amplitude modulation effect. When pure SF₆ flows in the sensor, the spectral scan is not zero-flat but a weak structureless absorption feature is observed, this result agrees with the observation of a flat, continuous and weak SF₆ absorption background around 4.61 μm which is discussed in the supplementary material discussion S1. Assuming it as a background, the pure SF₆ QEPAS scan was subtracted from the CO scans to filter out SF₆ absorption interference. In detail, at the QCL current of 214 mA, i.e. where the maximum of CO absorption spectrum is located, the pure SF₆ signal amplitude is ~40 μV. The CO QEPAS scans after the background subtraction are shown in Figure 6b. For each spectral scan, the QEPAS peak signal was extracted and plotted as a function of the CO concentration in Figure 7.

The sensor response curve was obtained by imposing a linear fit to the experimental data-points, characterized by a R² value equal to 0.99995 and a slope equal to 45.1 μV/ppm. A 1σ noise of 4.6 μV was measured at 1 s of integration time, thus a minimum detection limit of 90 ppb was estimated, corresponding to a normalized noise equivalent absorption coefficient (NNEA) of 1.8 ×10⁻⁷ W·cm⁻¹·Hz⁻¹/².

The long-term stability of the CO-QEPAS sensor was investigated by performing an Allan-Werle variance analysis. Pure SF₆ was flushed into the gas line with the QCL wavelength locked at the CO absorption peak while the measurement was continued in ppb unit by using the sensor response curve is plotted as a function of the signal integration time, with both horizontal and vertical axis in logarithmic scale (Figure S4). For a lock-in integration time of 10 seconds, a minimum detection limit as low as 10 ppb was achieved. This detection sensitivity reaches the single ppb level by increasing the integration up to 100 second.

The sensor response time is the last parameter to be determined. For CO real-time monitoring in GIS, the faster the response time of the system, the earlier the failure conditions in the equipment can be known and handled. A gas cell volume as low as few cm³, allows a rapid exchange of gas. In addition, a fast flow rate of SF₆ can positively affects the response time. However, with flow rates > 60 sccm the noise level increases, and the sensor performance deteriorates. Thus, the gas flow rate was fixed to 60 sccm. The sensor response time was determined as follows. First, the QCL current was fixed to 214 mA, corresponding to the maximum of the CO absorption line. Starting from pure SF₆ flowing in the sensor gas line, 100 ppm CO:SF₆ mixture was rapidly introduced into the system. The rise time was measured as the time required for QEPAS signal to rise from background level to 100% of its steady value. After stabilization, the gas dilution system quickly switches again to pure SF₆ in order to measure the fall time, defined as the time required for QEPAS signal to decrease from steady state value to background level. Figure 8 depicts the measurement of the rise and fall response times of the CO QEPAS signal. An average rise and fall time of 3 min was estimated. The...
measurements were repeated several times and no hysteresis effects or time delays were observed.

CONCLUSIONS

A sensitive and compact QEPAS gas sensor for detection of CO in SF₆ matrix was demonstrated, employing a spectrophone composed by custom T-shaped grooved QTF and a pair of resonator tubes. The QTF was designed to achieve a low resonance frequency of 8 kHz and a high quality factor of 6000 in SF₆ matrix, at atmospheric pressure. This allowed an efficient detection of the CO photoacoustic response in SF₆, providing the highest QEPAS signal at an operating pressure of 500 Torr. A strong CO spectral feature located at 4.61 μm was targeted by means of a compact DFB-QCL with emission power of 20 mW. The SF₆ absorption contribution results in a weak structureless background that can be easily subtracted. The linearity of CO sensor response was demonstrated in the range 0–500 ppm and a minimum detection limit of 90 ppb at 1 s of integration time was achieved, corresponding to a NNEA of 1.8 × 10⁻⁷ W cm⁻¹ Hz⁻¹/². A sensor response time of ~3 minutes was measured when the gas flow rate is 60 sccm. The overall performances match the requirements for real-time monitoring of GIS discharge, offering a compact and reliable alternative to the bulky instruments currently employed to accomplish the task.

ASSOCIATED CONTENT

Supporting Information

Supporting Information Available: The following files are available free of charge.
Supporting Information.docx contains Circuit diagram for QTF characterization; Schematic diagram of the employed QEPAS spectrophone; QEPAS signal of 500 ppm of CO:SF₆ under different pressures and different modulation depths; Allan-Werle deviation plot for CO-QEPAS sensor with 8 kHz-QTF in SF₆ environment; Selection of CO absorption line.

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REFERENCES

Sensors-basel 2013, 13, 14764–14776.


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