

Quartz-Enhanced Photoacoustic Sensors for Detection of Eight Air Pollutants

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A quartz-enhanced photoacoustic spectroscopy sensor architecture capable of detecting eight different air pollutants (CH_4 , NO_2 , CO_2 , N_2O , CO , NO , SO_2 , and NH_3) is reported. Each analyte is targeted using the same sensor components (acoustic detection module, quartz-tuning fork, etc.) and a dedicated laser source. Both interband cascade lasers and quantum cascade lasers are employed to target a well-resolved and isolated absorption feature from each investigated gas, in a wavelength ranging from 3.35 to 9.06 μm . The sensor is calibrated with certified concentrations of each gas species, in a wet nitrogen matrix. For each analyte, the optimal pressure is determined. Minimum detection limits of 40, 13, 800, 230, 450, 78, 18, and 5.8 ppb are obtained for CH_4 , NO_2 , CO_2 , N_2O , CO , NO , SO_2 , and NH_3 , respectively, at 100 ms of integration time.

1. Introduction

The first decade of the 21st century can be labeled as the “Sensor Decade.” Gas sensors for air pollution detection will be the key to a sustainable future for different applications,^[1] from the monitoring of environmental conditions of fragile ecosystems to the control of pollutant emissions from various industrial activities.^[2] Sustainable environmental monitoring systems require low-power consuming gas sensors capable of communicating

in an efficient way, adaptable to address several challenges that still need to be faced. Air pollution sensors can be separated into two main categories, those measuring the concentration of gas phase species and those quantifying particulate matter (PM) mass concentrations and diameters of particles.^[3,4] Usually, primary pollutants are directly emitted from a definite process, while secondary pollutants are produced in air as a product of primary pollutants’ reaction or interaction. The major primary pollutants are nitrogen oxides (NO_x), emitted from high-temperature combustion;^[5] carbon monoxide (CO), a product of incomplete combustion of fuel such as natural gas, coal,

wood, or vehicular exhaust;^[6] carbon dioxide (CO_2), a nontoxic greenhouse gas associated with ocean acidification, emitted from sources such as combustion, cement production, and respiration;^[7] methane (CH_4) and nitrous oxide (N_2O), the most important non- CO_2 greenhouse gases characterized by global warming potential 25 and 265 times higher than CO_2 ;^[8,9] ammonia (NH_3), mainly emitted from agricultural processes;^[10] sulfur oxides (SO_x), especially sulfur dioxide (SO_2) which is produced in various industrial processes in the combustion of coal and petroleum.^[11]

The selection of appropriate and reliable sensors is always a challenging goal. Low-cost sensor technology, as that provided by electrochemical gas sensors, can potentially revolutionize the area of air pollution monitoring, but exhibit variable performance in real outdoor (uncontrolled) conditions. Indeed, the measurement quality of electrochemical gas sensors is usually susceptible to changes in ambient air temperature and relative humidity, and to cross-interference of various gases.^[12] Reliable air pollutant measurements have been carried out with analytic instruments using optical spectroscopy or gas chromatography/mass spectrometry (GC-MS). These instruments can give a precise analysis but they can seldom be used in real-time and in-field applications.^[13] GC-MS sensors generally remain confined to academic research laboratories due to their operational complexity and prohibitively high cost.

Laser absorption-based optical spectroscopy uses narrow-band light sources operating in the infrared (IR) wavelength range, a gas cell, and a photodetector.^[14] The compactness and robustness, that define the capability of the sensor of operating in-field, are determined by the employed gas cell and the capacity of preserving the optical alignment between the laser beam and the gas

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DOI: 10.1002/adpr.202200353

cell over long times. The most used gas cells that guarantee high stability and long effective path lengths are the multipass cells.^[15] They trap laser beam into multiple reflections between two large diameter focusing mirrors. Effective optical path lengths as high as several tens of meter can be reached with gas cell lengths of few tens of centimeters. Highly performant multipass cells are commercially available; however, they are too expensive, delicate, and labor-intensive. Moreover, they must be used with expensive and fast photodetector to reach highly sensitive sensor and they can be used in narrow wavelength ranges.

To overcome constraints imposed by the gas cell size, indirect absorption techniques can be exploited. They measure the effect that an optical absorption produces within a gas sample when it is photothermally excited by a light source. Photoacoustic spectroscopy is one of them: the absorption of light is measured indirectly via the heat waves created when the gas sample is irradiated with intensity-modulated light.^[16] In quartz-enhanced photoacoustic spectroscopy (QEPAS),^[17] a quartz tuning fork (QTF) coupled with a pair of millimeter-sized resonator tubes, acting as organ pipes, is placed within the gas cell to detect the sound waves.^[18] The laser beam passes through the resonator tubes and between the prongs of the QTF, and is modulated at the QTF resonance frequency or at one of its subharmonics. Due to photoacoustic effect, the sound wave generated between the prongs of the QTF puts them into vibration: the prongs' mechanical deflection is converted into an electrical signal thanks to the piezoelectricity of the quartz. Thus, the gas cell only serves to separate the gas to be analyzed from the external ambient, allowing volumes as small as few centimeters. QEPAS can fulfill the requirements of performing reliable measurements of different gases employing a modular and compact design whose most important components are the laser source, a focusing lens, and the detection module. As such, QEPAS gas sensors can offer an unmatched and effective solution for air pollutants detection with high sensitivity: they are compact, robust, with versatile applications at low cost.^[19,20] High-quality, customized, rugged, and lightweight QEPAS detection module can be efficiently produced in large quantities. Moreover, they can embed with electronics, pressure, and temperature sensors as well as heaters to reduce condensation, thus reducing assembly cost and paving the way for cost-efficient production.

In this work, we investigated the potentiality to use QEPAS technology to detect eight different air pollutants, namely CH₄, NO₂, N₂O, NO, CO, CO₂, SO₂, and NH₃, with the same acoustic detection module and interchangeable laser sources,

to prove the modularity of the technique as well as the adaptability to different laser sources. Thus, the architecture of the QEPAS sensor remained the same as the laser sources were alternated. The targeted absorption features, and thus the laser wavelengths, have been selected with defined criteria taking into account the absorption cross-section, the interference with other gas species and the laser type, and the latter assessed in terms of the electrical power consumption and the emitted optical power.

2. Experimental Section

2.1. Selection of Target Wavelengths

The advantage and strength of gas sensing in the mid-IR wavelength region lie in its extreme sensitivity and specificity for detecting traces of molecular gases. The detection sensitivity strongly depends on the intensity of the absorption lines of the molecular gases of interest and on the laser power. For each of the eight air pollutants, the fine structure of the infrared absorption bands has been simulated by using the online database HITRAN.^[21] Within the mid-IR range, the convenient absorption bands have been selected by using the two following criteria: 1) When absorption bands with comparable intensity are available for a target analyte, those falling in the spectral region 3.0–5.5 μm have been preferred due to the availability of low power consumption interband cascade lasers (ICLs) as compared to quantum cascade lasers (QCLs). 2) Bands of different analytes that are spectrally near were given high priority due to the possibility to target two different analytes with one single laser source.

Within the chosen bands, target single spectral lines not spectrally interfering with the absorption spectrum of air and water have been identified. The absorption cross-sections for the spectral bands of interest have been reported in **Figure 1**. All simulations are at room temperature.

Based on the simulation in **Figure 1**, **Table 1** summarizes for each target analytes the selected wavelengths, the laser type, and its provider.

For NO₂, the interferent-free absorption band peak at 2891.3 cm^{-1} has a low line strength, thus we also selected the strongest absorption band peak at 1599.9 cm^{-1} reachable with the QCL technology. The 4.57 μm -ICL is capable to target both the N₂O and CO absorption features at 2190.3 and 2190.0 cm^{-1} , respectively.

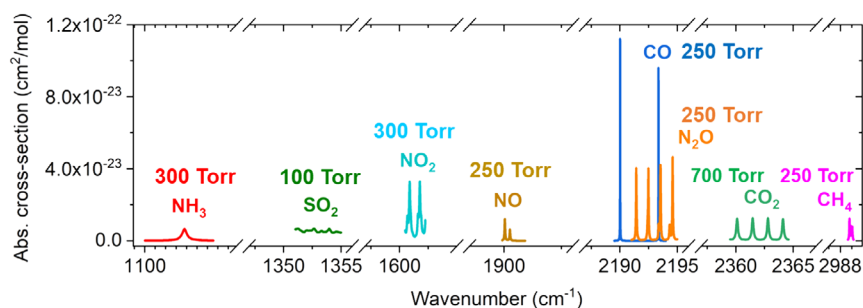


Figure 1. Simulation of the absorption cross-section of the selected absorption bands for each gas analyte. The NO₂ absorption band centered at 2,891 cm^{-1} is not shown since its line strength is much lower than those of the other analytes.

Table 1. Selected absorption features wavelengths and corresponding selected laser sources.

Wavelengths and laser sources				
Analyte	Absorption wavenumber [cm ⁻¹]	Absorption wavelength [μm]	Type of laser	Provider
CH ₄	2988.8	3.35	ICL	Nanoplus
NO ₂	2891.3	3.46	ICL	Nanoplus
	1599.9	6.25	QCL	Thorlabs
CO ₂	2361.5	4.23	ICL	Nanoplus
N ₂ O	2190.3	4.57	ICL	Nanoplus
CO	2190.0	4.57	ICL	Nanoplus
NO	1900.0	5.26	ICL	Nanoplus
SO ₂	1354.0	7.39	QCL	Thorlabs
NH ₃	1103.5	9.06	QCL	Thorlabs

2.2. Architecture of the QEPAS Sensors

All QEPAS sensors share the same architecture depicted in Figure 2.

The laser was used as the light source exciting the molecules within the acoustic detection module (ADM; Thorlabs ADM01). The ADM is composed of a spectrophone enclosed in a stainless-steel housing with inlet and outlet connector for gas flowing. The spectrophone consists of a T-shaped QTF acoustically coupled with a pair of resonator tubes. The geometry and sizes of the T-shaped QTF are reported in Patimisco et al.^[18] The two tubes were mounted on both sides of the QTF at a distance of 200 μm, perpendicular to the QTF plane, and with the tube center 2 mm below the QTF top. Both tubes have a length of 12.4 mm, an internal and external diameter of 1.59 and 1.83 mm, respectively. In Figure 2b, a picture of the QEPAS spectrophone is shown. The resonance frequency and the quality factor of the fundamental flexural mode of the spectrophone are plotted as a function of the air pressure, as shown in Figure 3.

The laser beam was focused into the ADM, fixed on a five-axis stage for alignment purposes, by using a 50 mm focal length ZnSe lens with a 3–12 μm antireflection coating. Such a focal length was chosen to achieve a trade-off between the need for a small-diameter beam focused between the QTF prongs and a small numerical aperture of the beam passing through the 12.4 mm-long dual-tube resonator. A ≈2 mm diameter pinhole was placed between the lens and the acoustic detection module

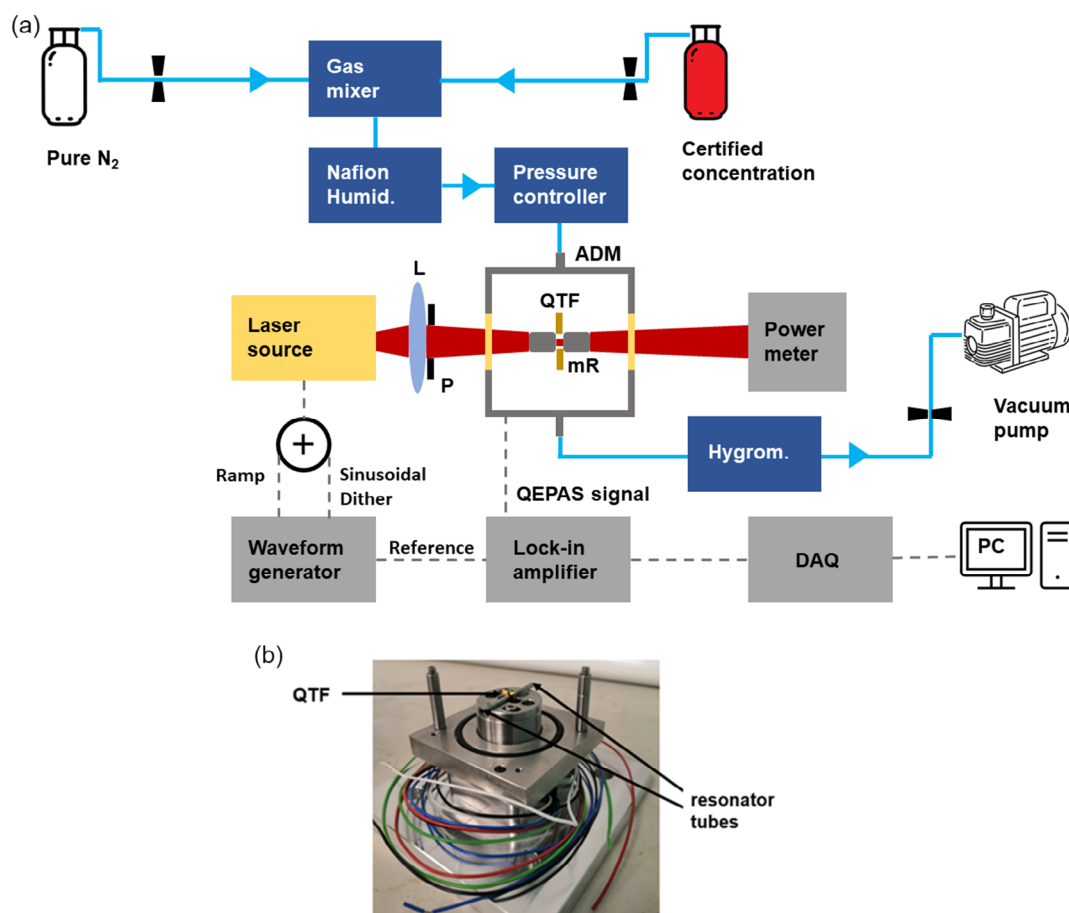


Figure 2. a) Schematic of the employed setup; QTF, quartz tuning fork; ADM, acoustic detection module; mR, millimeter-size resonator tubes; L, focusing lens; P, pinhole; DAQ, data acquisition board; PC, personal computer. b) Picture of the spectrophone mounted within the ADM, with black arrows indicating the QTF and resonator tubes.

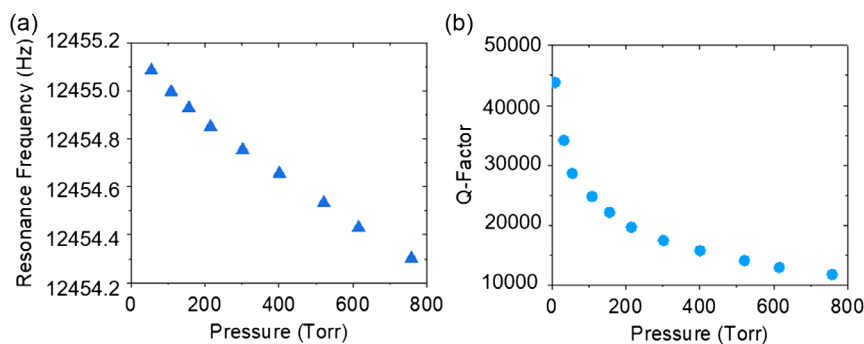


Figure 3. a) Spectrophone resonance frequency as function of the pressure. b) Spectrophone Q-factor as function of the pressure.

to cut laser beam tails that could hit the resonator tubes and/or the quartz tuning fork prongs, avoiding the generation of a nonzero background that would worsen the sensor's ultimate detection level. The far-field spatial intensity distribution of the laser beam was acquired using a pyroelectric camera (Spiricon PY-III-HR-C-A Pro, pixel size $100 \times 100 \mu\text{m}$, Ophir). A $\approx 7\%$ reduction of the laser power after passing through the ADM was measured, for all employed laser sources. The lasers' emission wavelengths were measured by using a Fourier transform optical spectrum analyzer operating in the range of $1\text{--}12 \mu\text{m}$ (OSA207C, Thorlabs). QEPAS measurements were performed using the wavelength modulation and dual-frequency detection method: a sinusoidal dither matching half of the QTF resonance frequency of the employed spectrophone was applied to the QCL current driver (ITC4002QCL, Benchtop Laser Driver and Temperature Controller, Thorlabs) and the transduced QTF signal was demodulated by the lock-in amplifier (MFIA 500 kHz Lock-in Amplifier, Zurich Instruments) at the QTF resonance frequency. The lock-in time constant was set at 100 ms. The demodulated signal was thus digitalized and stored on a personal computer by means of a data acquisition board, with the sampling time set at three times the lock-in time constant. The pressure of the gas mixture flowing inside the ADM was regulated using a pressure controller (MKS Type 649), while the flow rate was set by the gas mixer (MCQ Instruments, Gas Blender 103). A Nafion humidifier (PermSelect PDMSXA 1 cm^2) was placed after the gas mixer to

humidify the gas samples, fixing the water vapor concentration at 1% for all measurements. The humidity level within the gas line was verified using a capacitive hygrometer.

3. Calibration of QEPAS Sensors

Eight laser sources have been interchanged in the QEPAS setup depicted in Figure 2 to target the selected absorption features, as reported in Table 1. The QEPAS signal depends on the gas pressure. As the pressure changes, there are two trends to be considered: 1) the Q factor of the spectrophone decreases with increasing pressure (see Figure 3b);^[22,23] 2) the energy transfer of photoexcited molecules energy via nonradiative relaxation processes are faster at higher pressures (because each molecule can count on more nearest neighbors to interact), resulting in a more efficient generation of the sound wave.^[24] This suggests that the QEPAS signal can be optimized as a function of pressure, as a trade-off between these two opposite trends. Thus, for each gas species, the gas pressure was varied to obtain the largest QEPAS signal. The QEPAS peak signal of the selected absorption features reported in Table 1 is shown in Figure 4, as a function of the gas pressure.

The QEPAS peak signal of the selected absorption features reported in Table 1 is shown in Figure 4, as a function of the gas pressure, for all gas species apart SO_2 .

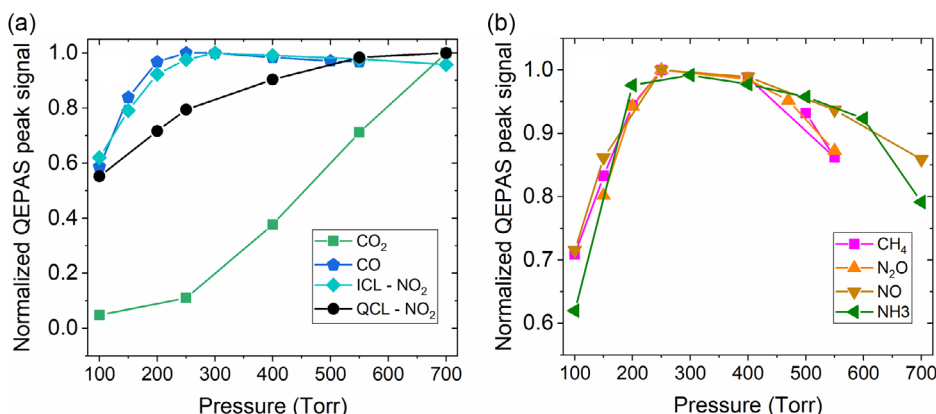


Figure 4. a) Normalized QEPAS peak signals as a function of pressure for CO_2 (green squares), CO (blue hexagons), ICL-detected NO_2 (light blue diamonds), and QCL-detected NO_2 (black dots). b) Normalized QEPAS peak signals as function of pressure for CH_4 (pink squares), N_2O (orange triangles), NO (yellow triangles), and NH_3 (green triangles). Solid lines are a guide for the eye.

A slightly different analysis was performed for SO₂ detection, since in the 7.39 μm QCL current dynamic range the SO₂ absorption spectrum is dense of lines (see Figure 1). By increasing the pressure, an absorption line merging is expected. **Figure 5** shows the absorption spectrum acquired with 1000 ppm of SO₂:N₂ (humidified mixture) at three different pressure values, namely, 100, 300, and 500 Torr.

The two most intense peaks occur around 225 mA (corresponding to 1,353.4 cm^{-1}) and around 270 mA (corresponding to 1,352.7 cm^{-1}). As shown in **Table 2**, these peak values extracted from scans in **Figure 6** are reported at different pressures.

Even if the highest signal was recorded at 100 Torr, we selected 300 Torr as the operating pressure, since it is more feasible for in-field operation and similar to the optimal values measured for the gas species reported in Figure 5b.

The absorption lines selected for detection using the ICLs sources are shown in **Figure 7**.

The QEPAS scans of the selected absorption lines have been acquired by using certified concentrations of the analytes in N₂, at their optimal pressures, as extracted from Figure 4. The gas target-N₂ mixture was then humidified at 1% water content by the Nafion humidifier.

The QEPAS scans of the NO₂ and NH₃ absorption features acquired by using QCL sources (see Table 1) and certified concentrations in humidified N₂ are reported in Figure 6.

For the NO₂, as shown in Figure 6a, in the QCL current dynamic range, the strongest absorption feature is targeted at a QCL current of 259 mA, corresponding to a laser emission at 1,600.9 cm^{-1} . For NH₃, the absorption line at 1,103.5 cm^{-1} was targeted by operating the QCL source at 319 mA

Table 2. QEPAS signal of the two most intense SO₂ peaks measured at different pressures.

SO ₂ QEPAS sensor	<i>P</i> = 100 Torr	<i>P</i> = 300 Torr	<i>P</i> = 500 Torr
Peak@225 mA	651.4 mV	584.1 mV	570.9 mV
Peak@270 mA	1051.2 mV	914.8 mV	563.9 mV

(see Figure 6b). For SO₂, the absorption line at 1,352.7 cm^{-1} was targeted by operating the QCL source at 270 mA (see Figure 6c).

Each QEPAS sensor was then calibrated, by acquiring the gas target spectral scan while diluting the certified mixture with humidified N₂. Then, the peak values have been extracted from each spectral scan and plotted as a function of the analyte concentration, as shown in **Figure 8**, together with related best linear fits.

The slope of the linear fit corresponds to the sensitivity, and it can be used together with the noise level to estimate the ultimate detection limit. This is usually expressed in terms of noise equivalent concentration (NEC) and is strictly defined as the concentration of the gas to be detected whose signal equals the noise level. In other words, the NEC is estimated at a signal-to-noise ratio of 1. The noise level is calculated as the standard deviation (1σ) of the sensor response in the condition of no optical absorption, namely when pure N₂ flows within the ADM. The 1σ noise can be lowered by further averaging the signal over longer times. An Allan–Werle deviation analysis was performed with the aim of estimating the 1σ noise (and thus the achievable minimum

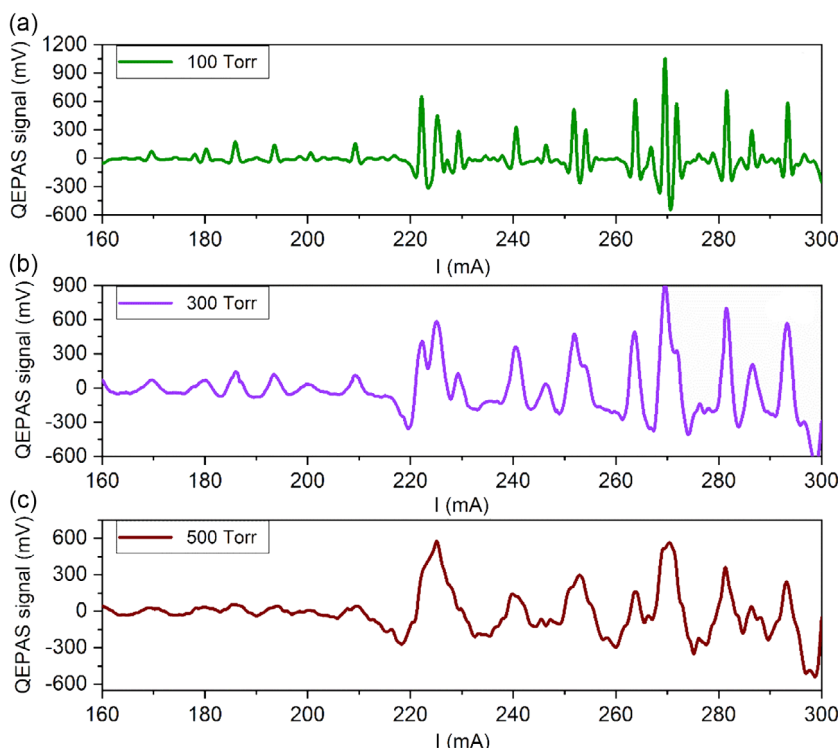


Figure 5. Absorption spectrum of 1,000 ppm of SO₂:N₂ (humidified mixture) at a) 100 Torr, at b) 300 Torr, and c) 500 Torr.

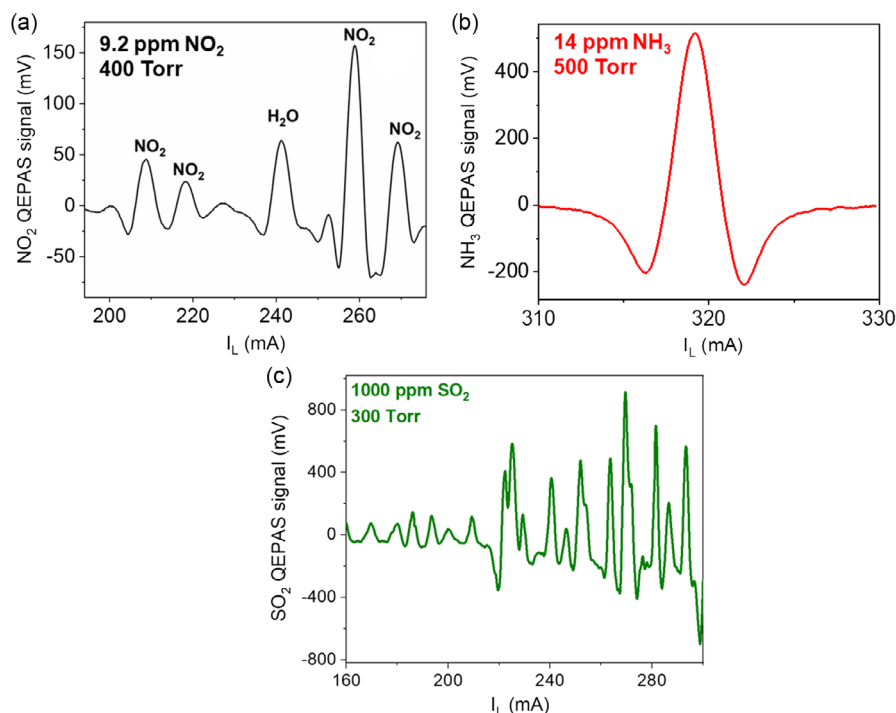


Figure 6. a) QCL-detected NO_2 QEPAS spectral scan together with a close H_2O absorption feature. b) QCL-detected NH_3 QEPAS spectral scan and c) QCL-detected SO_2 QEPAS spectral scan.

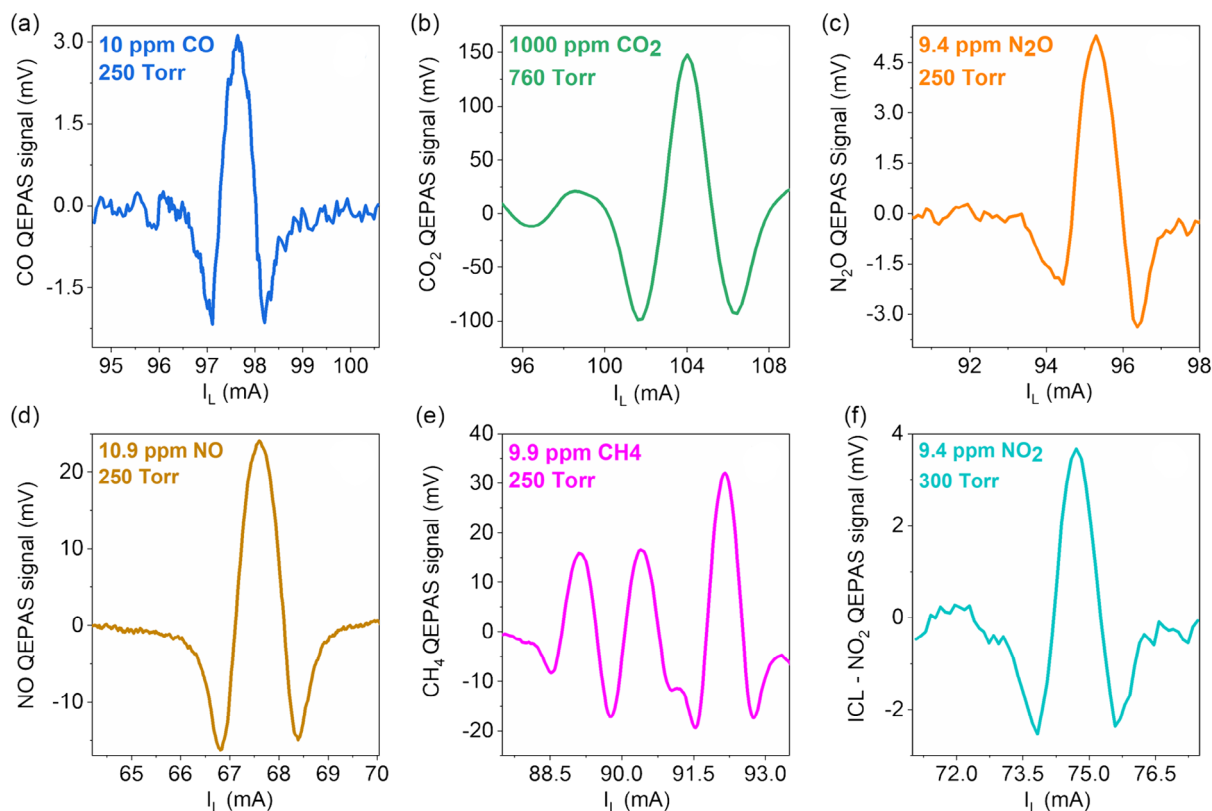


Figure 7. a) QEPAS spectral scan of 10 ppm $\text{CO}:\text{N}_2$; b) QEPAS spectral scan of 1000 ppm $\text{CO}_2:\text{N}_2$; c) QEPAS spectral scan of 9.4 ppm $\text{N}_2\text{O}:\text{N}_2$; d) QEPAS spectral scan of 10.9 ppm $\text{NO}:\text{N}_2$; e) QEPAS spectral scan of 9.9 ppm $\text{CH}_4:\text{N}_2$; f) QEPAS spectral scan of 9.4 ppm $\text{NO}_2:\text{N}_2$.

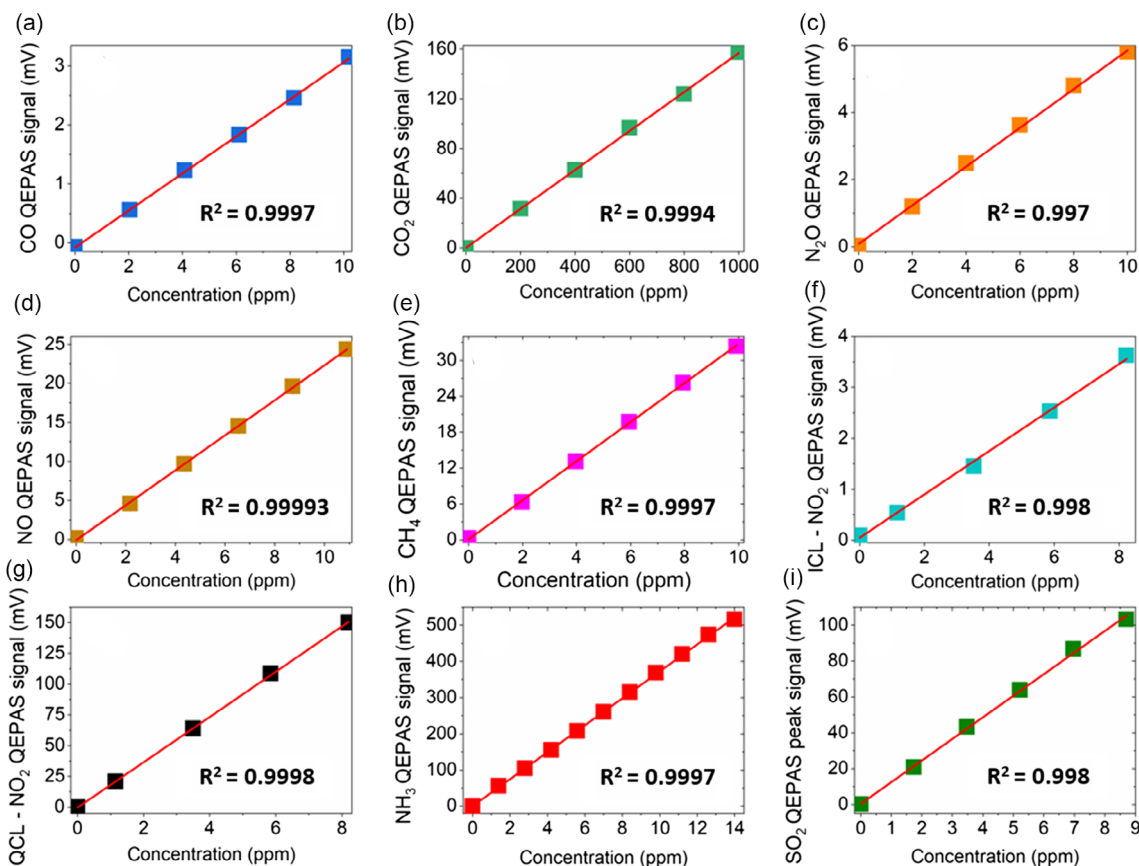


Figure 8. a) QEPAS peak signals (data points) as a function of the analyte concentration for the investigated analytes: (a) CO, b) CO₂, c) N₂O, d) NO, e) CH₄, f) NO₂, QCL-detected g) NO₂, h) NH₃, and i) SO₂. For each panel, the red solid line is the best linear fit of the data points.

detection limit, MDL) as a function of the lock-in integration time.^[25] The Allan–Werle deviation plot was calculated for each laser source. As a representative, the Allan–Werle plot acquired when the 4.23 μ m ICL is mounted in the QEPAS sensor (for CH₄ detection) is reported in **Figure 9**.

The 1σ noise of 0.13 mV at 0.1 s of signal integration time can be lowered down to 36 μ V if the lock-in integration time is set to

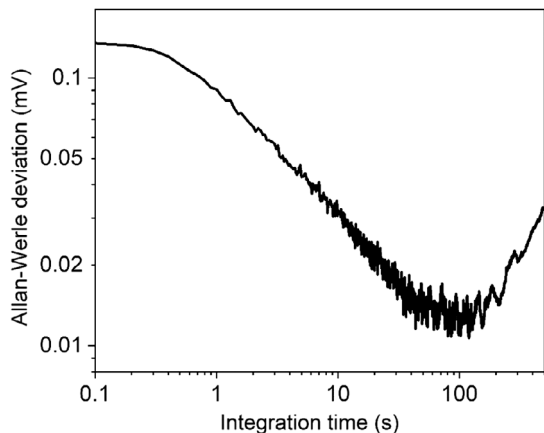


Figure 9. Allan–Werle deviation plot for the CH₄ sensor.

10 s. The Allan deviation analysis shows that for integration times <100 s, the QEPAS noise level follows the inverse of the square root of the integration time, demonstrating that the QTF thermal noise dominates. At 100 s, a turnover point appears: the noise level deviates from the thermal noise trend, and it starts to deteriorate for longer integration times. This can be mainly ascribed to the occurrence of other long-term effects, such as laser and mechanical instabilities as well as temperature drifts.^[25] The Allan deviation analysis for the other gas species follows the same trend as that one showed for CH₄ for integration times <10 s, since the dominant noise contribution is the thermal noise of the QTF.^[26,27]

4. Summary and Discussion

Table 3 summarizes the performance obtained for each QEPAS sensor. The typical natural abundance^[28,29] for each gas species is also reported.

Nearly all QEPAS sensors allow the detection of air pollutants with an ultimate detection limit well below their typical natural abundance in air, even when the signal integration time is as low as 0.1 s. The minimum detection limit of CO₂ is negatively affected by the strong absorption of light in open path because of its strong cross-section.^[26,27] In other words, a small fraction

Table 3. Summary of performance for air pollutants detection using the developed QEPAS sensors. The typical natural abundance of each gas species is listed in the last column. MDL – minimum detection limit. The reported optical powers are those measured at the laser output and with the source locked to the selected absorption lines (see Figure 1).

Performance of QEPAS sensors										
GAS	Absorption peak [cm ⁻¹]	Cross section [cm ² mol ⁻¹]	Pressure [Torr]	Power [mW]	Sensitivity [mV ppm ⁻¹]	Noise [mV]	MDL @0.1 s [ppb]	MDL @10 s [ppb]	NNEA [Wcm ⁻¹ Hz ^{-1/2}]	Natural abundance
CH ₄	2988.8	1.33 E-18	250	14.8	3.25	0.13	40	9.3	1.55 E-08	few ppm
NO ₂	2891.0	2.36 E-19	300	10.5	0.43	0.18	410	105	2.40 E-08	<100 ppb
CO ₂	2360.1	1.15 E-17	760	4.2	0.157	0.13	800	150	2.31 E-06	>400 ppm
N ₂ O	2191.4	4.39 E-18	250	3.1	0.58	0.14	230	65	6.17 E-08	<400 ppb
CO	2190.0	4.63 E-18	250	3.3	0.32	0.14	450	128	1.35 E-07	<1 ppm
NO	1900.1	1.81 E-18	250	4.5	2.24	0.17	78	25	1.25 E-08	<100 ppb
NO ₂	1600.9	3.37 E-18	400	29.0	18.37	0.24	13	4	4.00 E-08	<100 ppb
SO ₂	1353.4	6.66 E-19	300	73.0	9.64	0.19	18	7.8	2.07 E-08	<100 ppb
NH ₃	1103.4	2.65 E-18	500	59.0	37.22	0.21	5.8	1.4	3.57 E-08	<30 ppb

of the laser beam power reaches the ADM. A huge increase in detection sensitivity can be reached by using a fiber-coupled ICL source. For all sensors, improved performance can be achieved when the signal integration time is increased to 10 s. The performances of the realized sensors are competitive with results reported in the literature for QEPAS detection of the target analytes. Y. Ma et al. reported about QEPAS detection of CO and NH₃ with MDLs of 11.2 and 418 ppb,^[30,31] which are significantly higher than those achieved in this work both at 0.1 and 1 s integration time. A similar comparison can be drawn between the results reported by Breitegger et al.,^[32] Zhang et al.,^[33] Shi et al.,^[34] Wacławek et al.,^[35] the MDLs reported in these works are, respectively, 21 ppb for NO₂, 79 ppm for CH₄, 120 ppb for NO, and 100 ppb for SO₂. These MDLs are all above those reported in Table 3 at 0.1 s integration time for the same target species. Lower MDLs for CO₂ and N₂O than those obtained in this article are reported by Zifarelli et al. and Elefante et al., respectively.^[36,37]

The sensitivity S of the QEPAS sensor is proportional to P_L is the laser power, σ is the absorption cross-section, ϵ is the radiation-to-sound conversion efficiency which affects the acoustic waves generation within the gas

$$S = K \cdot P_L \cdot Q \cdot \sigma \cdot \epsilon \quad (1)$$

where K is the sensor constant. It is mainly determined by the transfer rate of the vibrational energy of excited analyte molecules into kinetic energy (translation) of the surrounding molecules (V–T relaxation). For all gas species, water vapor in the gas mixtures acts as a fast-relaxing promoter, thereby enhancing the target analyte relaxation rate and the QEPAS detection sensitivity.^[38–40] A water concentration as high as 1% corresponds to a saturation of the relaxation effect of the promoter on the analyte, thus ϵ can be imposed equal to 1 for all analytes. The sensor constant K can be supposed to be the same for all analytes since it is related to geometrical and material properties of the ADM. With these assumptions, the QEPAS sensitivity is proportional to the product $P_L \cdot Q \cdot \sigma$. By using laser powers and cross-section values listed in Table 3 and Q -values of

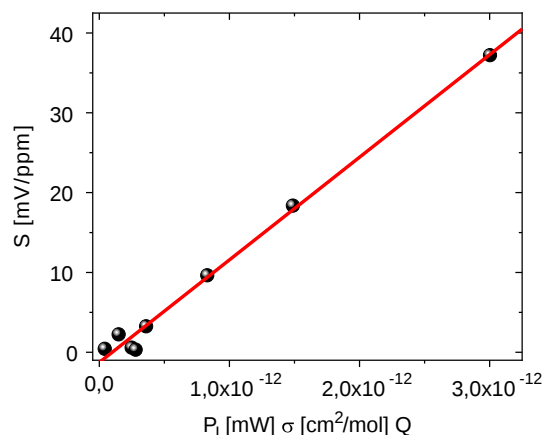


Figure 10. Experimental plot of the QEPAS sensor sensitivity S (black dots) and the corresponding best linear fit (red line).

Figure 3b at the pressure values in Table 3, the sensitivities in Table 3 have been plotted as a function of $P_L \cdot Q \cdot \sigma$ in Figure 10.

A linear fit was imposed on the data points, and its slope of 1.29×10^{13} represents the sensor constant K , in the unit of measure defined by those used for the physical quantities reported in Figure 10. Therefore, it can be concluded that by knowing K , the sensitivity of a QEPAS sensor per unit of milliwatt can be predicted for any gas species by only simulating the cross-section of the selected absorption feature.

5. Conclusion

In this work, eight QEPAS sensors for the detection of eight different air pollutants employing the same acoustic detection module and interchangeable laser sources were realized. This approach demonstrates that the QEPAS technology is well suited for the realization of compact, robust, and low-cost gas sensors for environmental monitoring. The sensors targeted a resolved absorption feature for each of the following species: CH₄,

NO₂, CO₂, N₂O, CO, and NO using six different ICLs and SO₂, NO₂, and NH₃ with three different QCLs. The developed sensors were calibrated in a wet N₂ matrix with H₂O concentration fixed at 1%. Performing several dilutions of each analyte, the linear response of the sensors to the target gas concentration was demonstrated for each gas species, achieving minimum detection limits below the natural abundance.

Acknowledgements

All authors acknowledge funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 101016956 PASSEPARTOUT, in the context of the Photonics Public Private Partnership. MG acknowledges POR PUGLIA FESR-FSE 2014/2020—Asse X—Azione 10.4. Research for Innovation—REFIN.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

R.W., V.S., and P.P.: Conceptualization; R.D.P., A.E., A.Z., A.S., M.G., and P.P.: methodology; R.D.P., A.E., G.B., F.P., R.W., and V.V.: validation; R.D.P., A.E., G.B., and F.P.: formal analysis; R.D.P., A.E., G.B., F.P., and P.P.: data curation; R.D.P., A.E., V.V., and P.P.: writing—original draft preparation; R.D.P., A.Z., A.S., M.G., and V.S.: writing—review and editing; P.P., V.S., and M.G.: funding acquisition. All authors have read and agreed to the published version of the manuscript.

Keywords

air pollutants, environmental monitoring, QEPAS

Received: December 16, 2022

Revised: February 25, 2023

Published online: April 14, 2023

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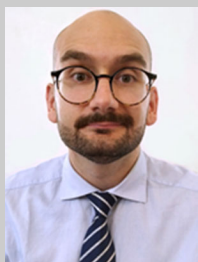
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