SECOND YEAR PHD REPORT

Nell'ambito della borsa di dottorato aggiuntiva del Programma Operativo Nazionale Ricerca e Innovazione 2014-2020 (CCI 2014IT16M2OP005), Fondo Sociale Europeo, Azione I.1 “Dottorati Innovativi con caratterizzazione Industriale”

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CUP	H92H18000100006
Titolo Progetto	DEVELOPMENT OF INNOVATIVE OPTICAL SENSORS FOR INDUSTRIAL AND BIOMEDICAL APPLICATIONS

In piena coerenza con le attività previste dal progetto nell’ambito del quale è stata finanziata la borsa di dottorato, si presenta la relazione annuale dell’attività svolta.

OGGETTO: Relazione di secondo anno di dottorato

Data:

12/02/2020

Arianna Elefante

Second year PhD Report

During the second year of PhD, the reseach activity has been conducted at the Thorlabs company in Dachau, Germany. It has been focused on the development of gas sensors based on the Quartz Enhanced PhotoAcoustic Spectroscopy (QEPAS). QEPAS technique offers high sensitivity and selectivity, fast response time and compactess that are needed for industrial applications requiring real time and in situ monitoring.
In particular, the research activity of this year has been focused on:

- The design, realization and charaterization of a compact QEPAS sensor for the detection of SF_6;
- The design of an innovative Acoustic Detection Module containing two quartz tuning forks for applications requiring the detection of gases in a wide concentration range (from few ppm to the percentage);
- The characterization and the study of the stability of a compact QEPAS sensor for the detection of methane in air.

Finally, a preliminary study on the influence of water vapor on the QEPAS signal of the methane has been performed to calibrate the methane sensor with respect to the water concentration.

SF_6 compact QEPAS sensor

The aim of this research activity is the development of a QEPAS sensor for the detection of SF_6. SF_6 is used as trace gas to detect leakage in mechatronic systems. This industrial application requires the development of a compact sensor to be implemented in a test station for the leakage detection. During this year of PhD, the sensor was designed and realized at Thorlabs in Dachau and will be then tested at the MASMEC company.
Results obtained by the Polysense group for the detection of SF_6 using the QEPAS spectroscopy, reaching a sensitivity of 50 ppt for 1s integration time, have been used as starting point. The typical apparatus of a QEPAS sensor (shown in Fig. 1a) was modified to be inserted in the box, as shown in Fig 1b.

a) b)

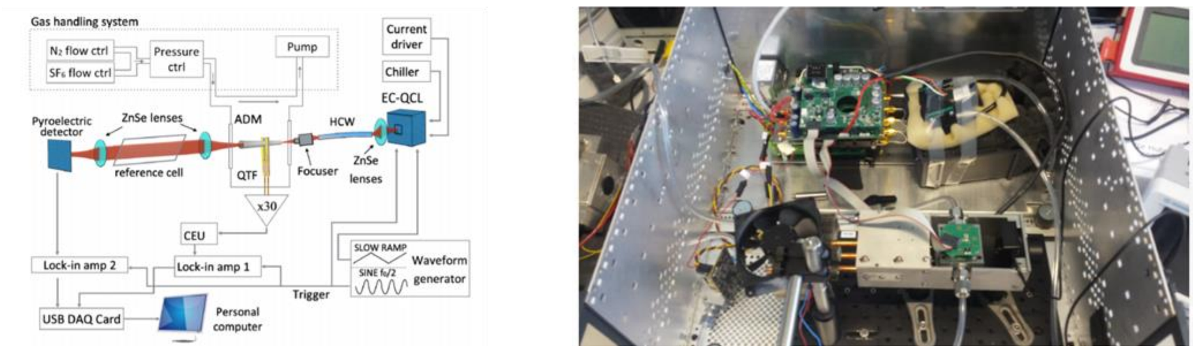

Figure 1 a) Typical QEPAS setup. b)QEPAS sensor for the detection of SF6 developed at Thorlabs, with all the components inside the box.

In the box, the following components have been placed:

- The mechanical structure where the laser, the ADM and the power meter are installed is shown in Fig. 2.

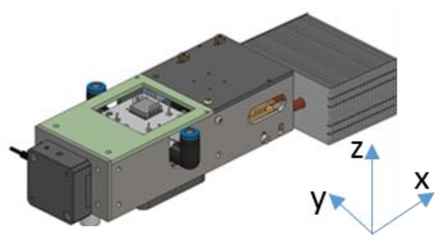

Figure 2: Prototype of the mechanics structure containing the laser, the ADM and the power meter.

The laser is a DFB QCL in HHL housing. It has an emission wavelength at 10.54 µm, where the strongest absorption lines of the SF_6 with linestrength up to 10$_{.20}$ cm/mol are present. The laser is mounted on a heat spreader connected to heat pipes. A cooling fan facilities the heat dissipation.
The beam is focused into the acoustic detection module (ADM) using a ZnSe BiConvex E3 coated lens of focal length 40 mm.
The ADM consists of a QTF having prongs length 9.4 mm, thickness of 0.5 mm, and are spaced by 0.8 mm. The fundamental mode frequency is 12457,6 Hz at 80 Torr. The QTF is coupled with a pair of microresonator tubes having length of 12.4 mm and internal diameter of 1.51 mm to enhance the sensitivity of the sensor. The ADM contains four miniature cartridge heating elements to regulate its temperature and a thermistor is used to monitor it. The pressure, temperature and humidity of the gas inside the ADM are monitored using an integrated PHT

sensor. It is composed by a piezo-resistive sensor providing pressure and temperature and by a capacitive-type humidity sensor.
The alignment procedure is realized as follows: the laser beam height and tilt in the *z*-direction, and the ADM *y*-position and tilt in the *xy*-plane can be adjusted using two different pair of screws. The lens is mounted on a cage system to focus the laser beam between the prongs of the QTF. These mechanic parts have been designed to realize a rugged sensor capable to hold the alignment.
The sensor has been enclosed in foam for protection and acoustic isolation.

- The laser current and temperature are controlled using an OEM laser driver and a miniature temperature controller shown in Fig. 3. On the laser driver board, the needed compliance voltage and laser current limit can be set by changing the value of two potentiometers. These values were set to 12 V and 860 mA.
  The temperature of the laser is controlled using the MTD1020T Miniature Temperature controller. The evaluation board MTDEVAL1 is used to perform an oscillation test and set the correct PID parameters. While I and D are set to 0, the critical gain P was found as the minimum value at which the system oscillate without damping. Once the initial value for the P parameter is set, the firmware calculate the final PID parameters.

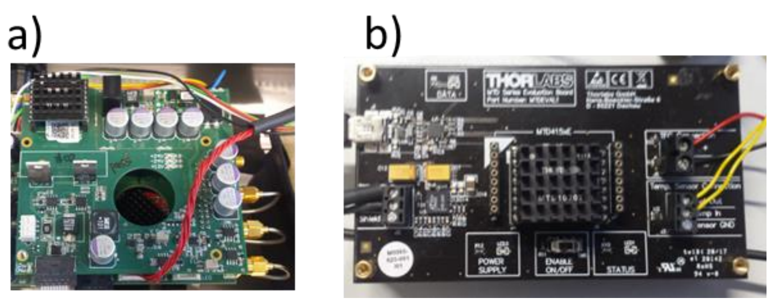

Figure 3: a) Laser driver board; b) Evaluation board used for setting the PID parameters.

- The electronic for the generation and the acquisition of the QEPAS signal (waveform generator and analogic lock-in amplifiers) is substituted by the RedPitaya board shown in Fig. 4. and a mainboard. The mainboard provides different power supply voltages for the laser driver, the pump, the PHT sensor, the pressure controller and the flow meter and connects RedPitaya to the accessories.

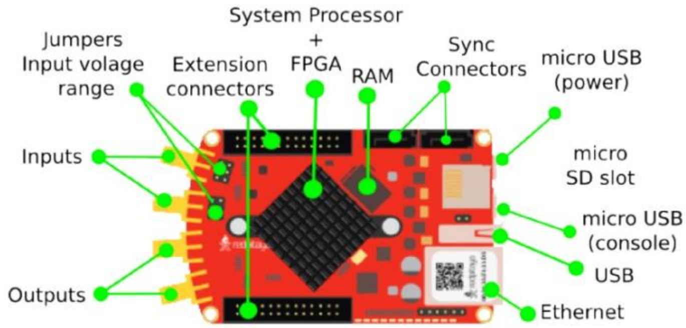

Figure 4: RedPitaya board

The lock in amplifiers is implemented on the field programmable gate array (FPGA) device on the RedPitaya board; the reference signal in the form of a sinusoidal wave is internally generated by the board. The QTF signal is acquired by using an analog input, while the analog output is used to both sinusoidally excite the QTF and modulate the laser current.

- The gas line consists of a diaphragm pump, the pressure controller Alicat, a flow meter and a needle valve. The pressure can be set using a Labview program and the speed of the pump can be adjusted to reach the desired pressure and flow within the gas line.

Fig. 5. shows a comparison between the absorption cross section of the SF_6 at 80 Torr simulated using the HITRAN database and the QEPAS scan measured for 20 ppm of SF_6. The laser operating temperature was set to 30°C and the laser current was swept in the range [770, 810] mA. The modulation amplitude was set to 9 mV.

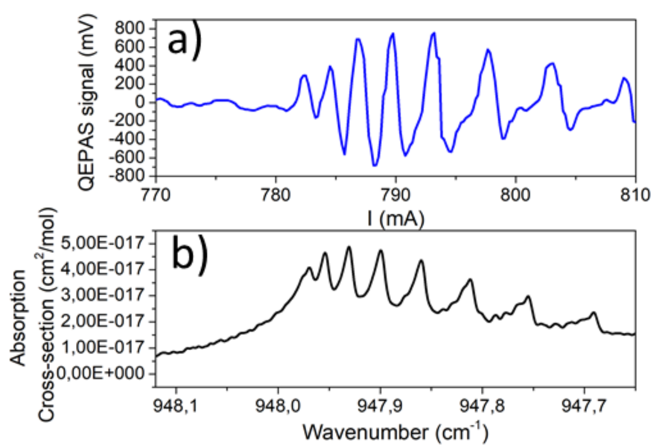

Figure 5: Comparison of a) QEPAS spectral scan measured for 20 ppm of SF_6 at 75 Torr and b) Hitran simulation of the absorption cross-section for pure SF_6 at 75 Torr

The sensor was calibrated acquiring the QEPAS signal of the SF_6 absorption line at 947.93 cm^{-1} for different concentrations of SF_6. The mixtures were realized starting from a certified concentration of 20 ppm of SF_6 and diluting with N_2 using a gas mixer. Fig. 6 shows the QEPAS peak signals as a function of SF_6 concentration. A calculated R^2 value of 0.996 confirms the linearity of the QEPAS signal with the SF_6 concentration. For a 1σ noise level of 0.36 mV and a peak value of 740 mV a signal-to-noise ratio of 2055 was estimated for the 20 ppm of SF_6, corresponding to a minimum detection limit of 10 ppb at 8 ms integration time.

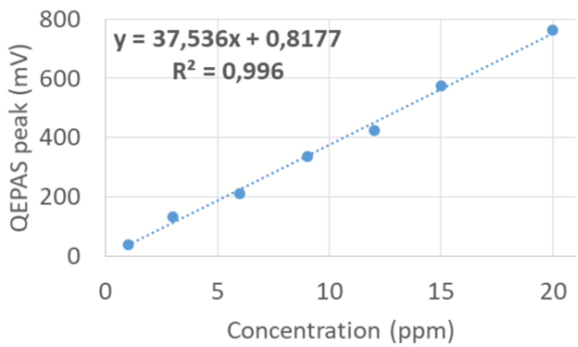

Figure 6: Calibration curve

Dual QTF Acoustic Detection Module

When dealing with high concentration gas mixtures, non-linearity effects can occur and influence the linear response of the QEPAS signal with the concentration. The variation of the gas matrix from few ppm to the percentage range causes a variation of both the gas target no-radiative relaxation dynamics and the sound speed, which affects the acoustic micro-resonator AmR enhancement factor. Since the QEPAS signal is proportional to both these factors, the non-linear effects must be taken into account for a reliable estimation of the concentration of the gas species.

For applications that require a wide dynamic range in concentration, a new design of acoustic detection module was developed. The idea is to design a spectrophone consisting of a bare QTF S1 aligned with a QTF + AmR tubes S2. The bare QTF does no benefit of the enhancement factor due to AmR tubes; however, it is not affected by the variation of the speed of sound when higher concentrations are used. By combining signals detected with the two QTFs, an accurate and precise measurement of gas concentrations can be retrieved.

Fig. 7. shows the design for the acoustic detection module of the dual QTF system.

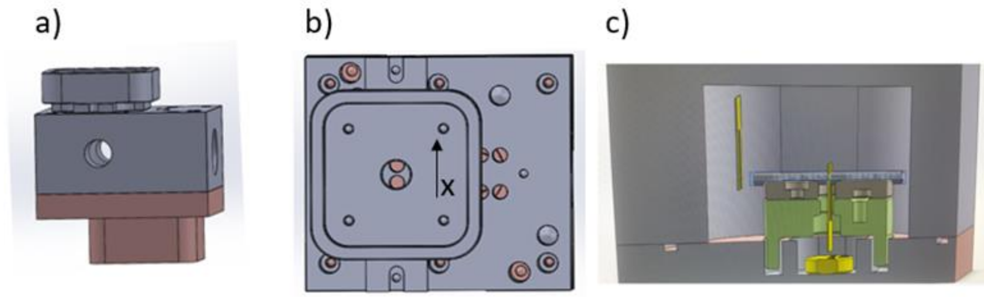

Figure 7: a) External and b) top view of the dual QTF ADM; the upper adaptor is used to insert the QTF1 from the top and align it with respect to the QTF2. C) Inside view of the ADM.

The QTF2 has prong length of 9.4 mm, thickness of 0.5 mm, and spacing of 0.8 mm. It is coupled with tubes of length of 12.4 mm and inner diameter of 1.51 mm, to guarantee the best sensitivity of the QEPAS sensor, since QTF2 will be used for the detection of low concentration. Since the laser beam will be focused between the prongs of QTF2, QTF1 must have larger prong spacing to accommodate the laser beam and to allow the alignment of the laser without touching the prongs. QTF2 has prong spacing of 1.5 mm. It is placed 5 mm far from the window to minimize the direct absorption of the laser radiation before the QTF1. QTF1 will be inserted from the top of the ADM and will be mounted on the adapter shown in Fig. 7. The adapter contains the preamplificator of the QTF1 and can be moved in the x-direction (see Figure 7b) to align QTF1 with respect to QTF2. The overall ADM is 55.6 mm long, 50.6 mm wide and 32.6 mm high.

The ADM will be mounted in the mechanical system shown in Fig. 8.

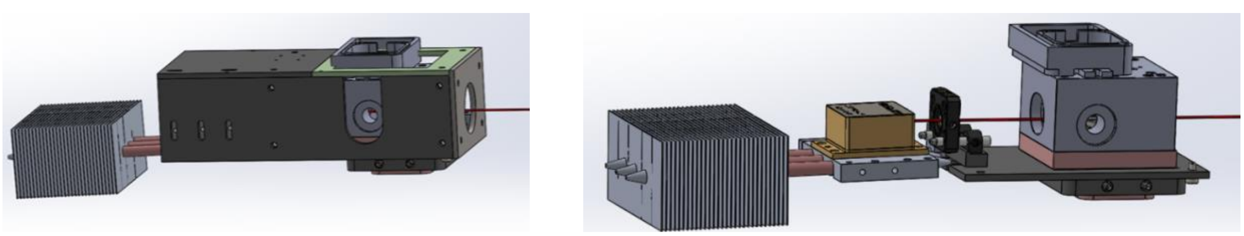

Figure 8 Mechanics containing the laser, the focusing lens with the pinhole and the ADM.

The laser is mounted on a heat spreader connected to heat pipes. The laser beam is focused between the prongs of QTF2 using a lens of focal length 70 mm. A pinhole can be inserted before the lens to cut the beam tails that could hit the mR tubes and/or the quartz tuning fork prongs. The total length of the prototype is 22 mm.

<u>Compact QEPAS sensor for the detection of methane in air</u>

A QEPAS sensor for the detection of methane in air was presented at the LASER World of PHOTONICS Traid Fair in Munich.

Methane is an odourless, flammable gas present in the atmosphere with an average concentration of 1.8 ppm. Its monitoring and highly sensitive detection is of great importance since it is a greenhouse gas causing global warming and climate change.

All the component of the sensor are contained in the box shown in Fig. 9.

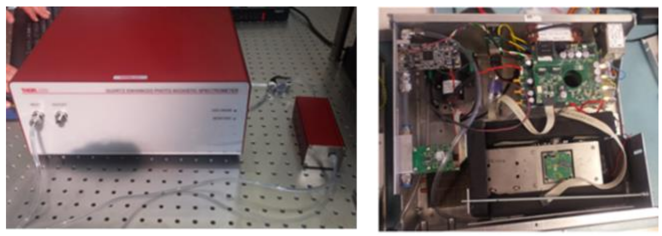

Figure 9. QEPAS sensor for the detection of methane in air presented at the LASER World of PHOTONICS Traid Fair in Munich. The air from the room is humidified using the Permselect contained in the little red box on the right.

The laser used as excitation source is a Mid-IR ICL emitting at 3.345 µm, where the fundamental vibration band of the CH_4 molecules with the strongest absorption coefficient is located. The laser is capable of detecting a methane triplet at 2988.8 – 2988.9 -2989.02 cm^{-1} and a water line at 2988.6 cm^{-1}, as shown in the Hitran database simulation in Fig. 10.

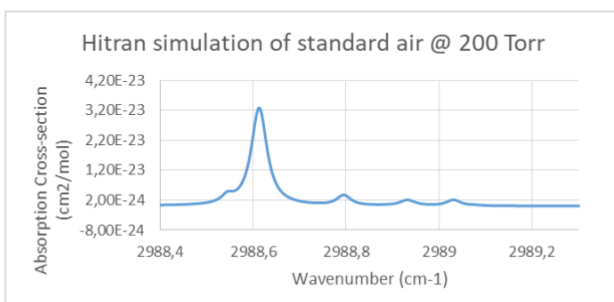

Figure 10: Hitran simulation of standard air at 200 Torr in the spectral range emitted by the ICL.

The water molecules present in the air act as a promoter of the vibrational to translational relaxation of methane; as a result, the variation of water concentration in air causes a variation of the QEPAS methane signal which is not due to a change of CH_4 concentration. To guarantee a reliable CH_4 measurement, we used a Permselect humidifier to provide a constant concentration of water vapour. The humidifier was inserted in the gas line, just before the ADM. The laser temperature was set to 25°C and the laser current to 118.5 mA to detect the methane absorption line at 2988.8 cm^{-1}. The measurement of methane concentration in the laboratory air was performed for 7 h. Fig. 11 shows the acquired QEPAS signal as a function of time.

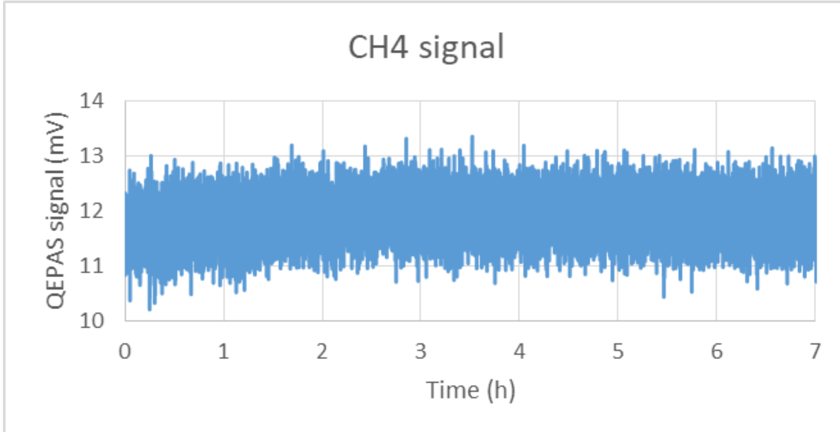

Figure 11: QEPAS signal of the methane line at 2988.88 cm^{-1} acquired during the trade.

A 1σ noise level of 0.38 mV and a peak value of 11.84 mV were measured at 8 ms integration time, corresponding to a minimum detection limit of 57 part-per-billion. An Allan deviation analysis was performed to estimate the ultimate detection limit of the sensor, corresponding to 2 ppb at 6 s integration time, as shown in Fig. 12.

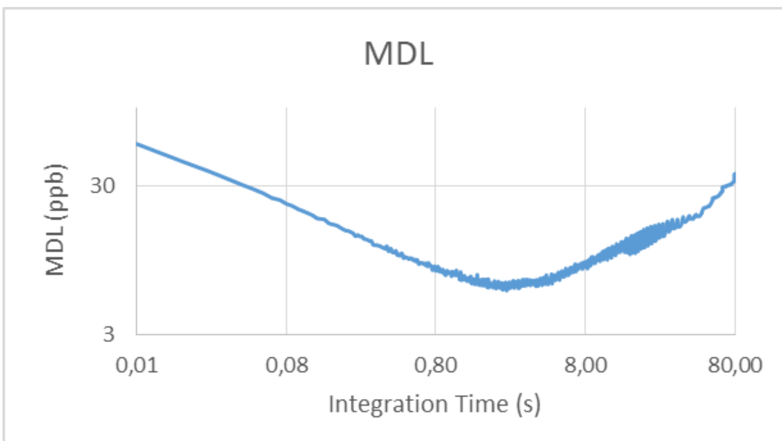

Figure 12: Allan-Werle deviation plot of the QEPAS signal as a function of the integration time.

Calibration of the methane sensor

An alternative approach for the detection of methane in air is a calibration of the methane signal with respect to the water vapour concentration. The experimental setup used for this study is shown in Fig. 13.

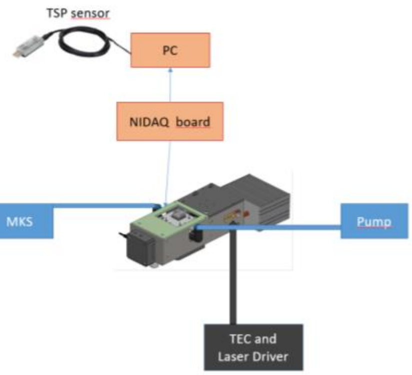

Figure 13: Schematic of the QEPAS sensor for the detection of methane in air.

The laser is a ICL emitting at 3.345 µm, capable of detecting a triplet of CH_4 absorption lines at 2988.9 cm^{-1} and a water line absorption at 2988.6 cm^{-1} . The laser beam was focused in the acoustic detection module by using a 40 mm focal length lens. The acoustic detection module contains a custom quartz tuning fork having frequency 124656.9 Hz at 200 Torr, acoustically coupled with two 12.4 mm-long tubes with internal diameter of 1.51 mm. QEPAS measurements were performed using the wavelength modulation and dual frequency detection method. The laser current and temperature were controlled using the Thorlabs ITC TEC and laser driver. A data acquisition board of the National Instrument and a dedicated Labview program were used to generate the modulation signals for the laser and the QTF and to acquire and demodulate the QTF signal.
The temperature and relative humidity of the air in the lab was also monitored using the Thorlabs sensor TSP01.
The measurement of water vapour and methane in the air of the lab was performed for 62 h. Fig. 14 shows the spectral scan acquired by setting the temperature of the ICL to 25°C and scanning the laser current in the range [226, 232] mA. The modulation amplitude was set to 40 mV. The pressure and the flow of the air inside the ADM were 200 Torr and 25 sccm, respectively.

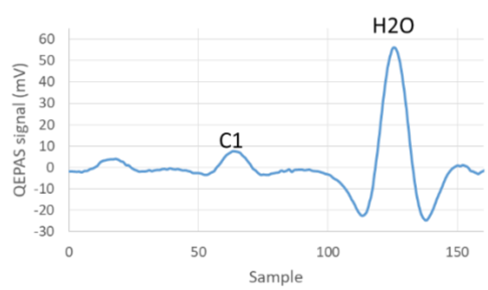

Figure 14: QEPAS spectral scan of air.

Figs 15 a) and b) show the QEPAS peak signals of methane and water extracted from the spectral scans, while Fig. 15 c) shows the absolute humidity calculated from the temperature and relative humidity measured by the TSP sensor. In Fig. 15 d), the three signals are normalized and overlapped.

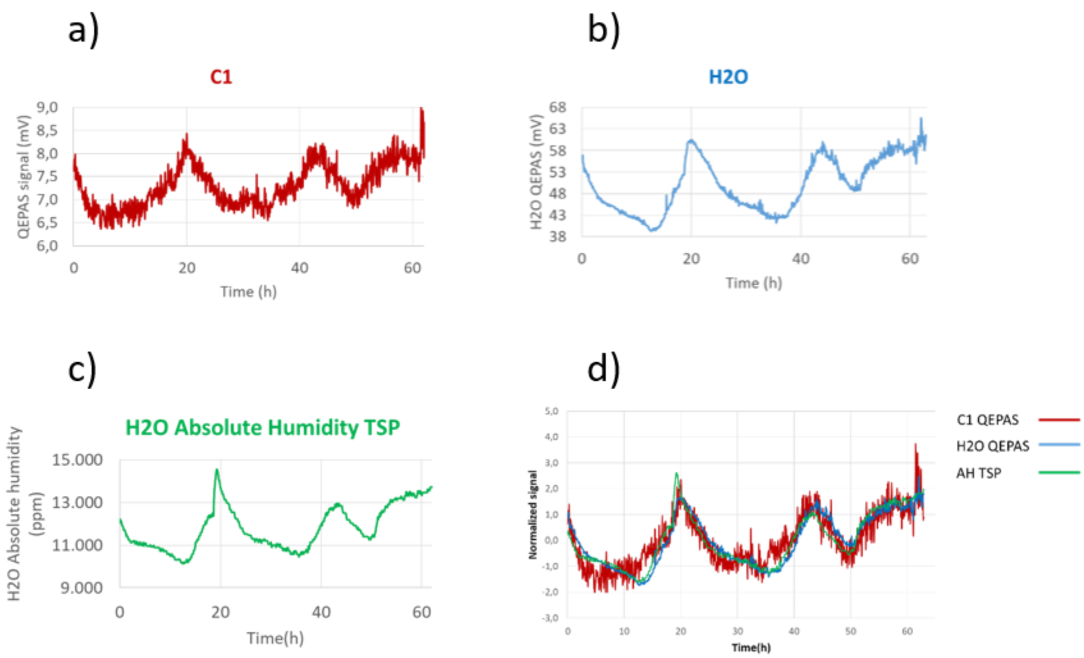

Figure 13: QEPAS signal of a) methane and b) water vapour; c) Absolute humidity calculated from the temperature and relative humidity detected with the TSP; d) Normalized signals.

The QEPAS signal of the water absorption line and the absolute humidity measured from the TSP sensor show the same trend; plotting the H_2O QEPAS signal as a function of the absolute humidity AH (Fig. 16) the sensor is calibrated for water detection. In Fig. 16, the red line is the calibration curve, having a slope of 0.006 mV/ppm with R_2 of 0.99.

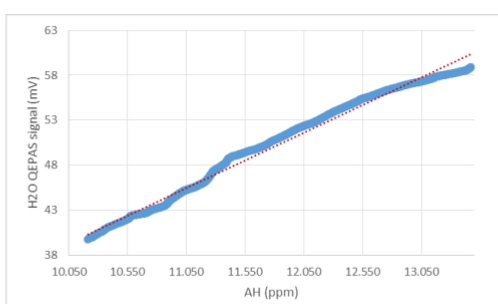

Figure 14: H_2O QEPAS signal as a function of the absolute humidity of the air measured with the TSP sensor.

The water vapour act as a promoter for the CH4 relaxation rate, as shown in Fig. 15 d), where the CH4 QEPAS signal variations follow the absolute humidity variations. The CH4 QEPAS signal amplitude measured for 1.8 ppm concentration can be linearly fitted as a function of the absolute humidity, that varies from 1.1% to 1.4% (Fig. 17 a)). The slope of the linear fit m=0.0004 mV/ppm can be used to normalize the influence of the water concentration in air on the CH_4 no-radiative relaxation. Fig. 17 b) shows the corrected CH_4 QEPAS signal.

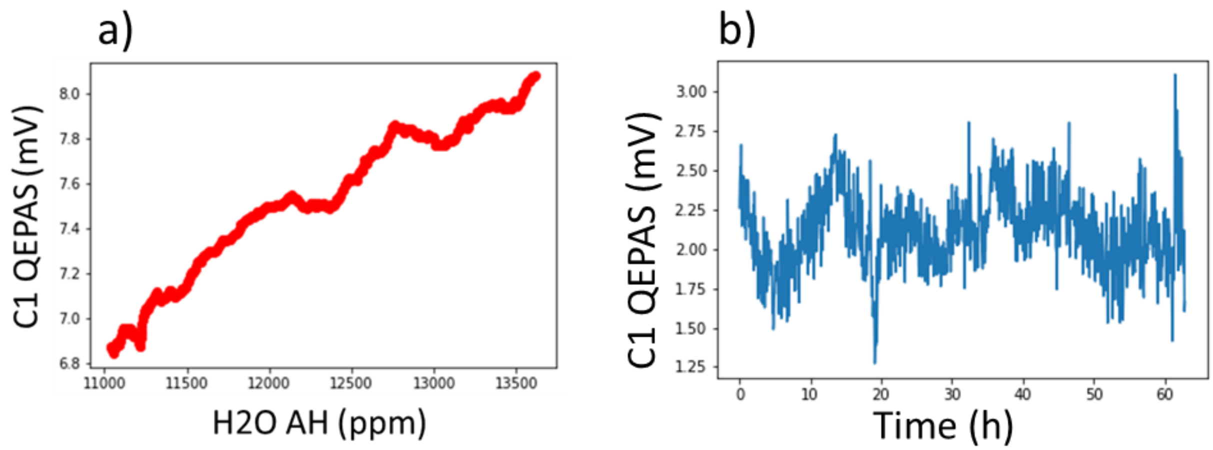

Figure 157: a) QEPAS signal of the methane in air in function of the absolute humidity of the air measured with the TSP sensor; b) Methane QEPAS signal after the correction with the absolute humidity.

A second set of measurements has been acquired and is shown in Fig. 18: the red line is the normalized CH4 QEPAS signal, while the green one is the absolute humidity acquired with the TSP sensor.

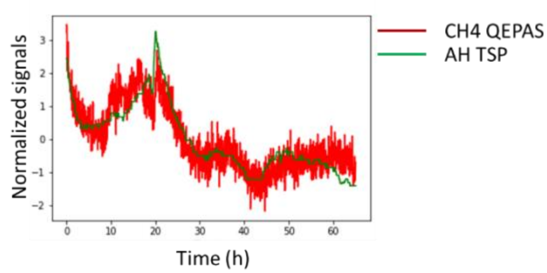

Figure 16: Normalized methane QEPAS signal (red line) and absolute humidity signal (green line)

The linear fit of the CH4 QEPAS signal as a function of the AH gives the same slope m= 0.00049 mV/ppm obtained with the first set of measurement. Using this slope the C1 signal (Fig. 18 a)) has been normalized with respect to the water concentration, giving the results shown in Fig. 18 b).

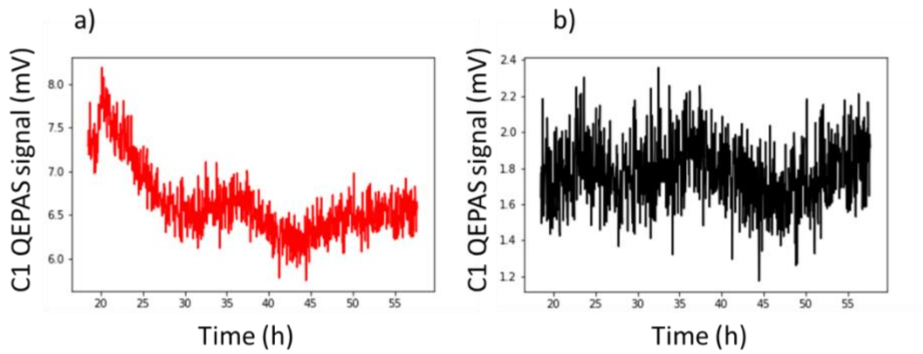

Figure 17: a)Methane signal acquired with the QEPAS sensor; b) Methane QEPAS signal after the calibration.

The stability of the signal and the 1σ=0.18 mV confirm the possibility to calibrate the sensor using the measurement of the TSP.

Third year goals

- Implementation of the SF_6 QEPAS sensor in test station for the leakage detection at Masmec;
- Assembling and testing of a QEPAS sensor with the dual QTF ADM for the detection of methane from the ppm to the percentage range.

Publications

- M. Giglio, A. Zifarelli, A. Sampaolo, G. Menduni, **A. Elefante**, R. ,Blanchard, C. fluegl,M.F. Witinski, D. Vakhshoori, H. Wu, V.M.N. Passaro, P. Patimisco, F.K. Tittel, L. Dong, V. Spagnolo, "Broadbanddetection of methane and nitrous oxide using a distributed feedbackquantum cascade laser array and quartz-enhanced photoacousticsensing", Photoacoustics 17, 100159 (2020).
- **A. Elefante**, M. Giglio, A. Sampaolo, G. Menduni, P. Patimisco, V. M.N. Passaro, H. Wu, H. Rossmadl, V. Mackowiak, A. Cable, F.K. Tittel, L. Dong and V. Spagnolo, "Dual-Gas Quartz-Enhanced Photoacoustic Sensor for Simultaneous Detection of Methane/Nitrous Oxide and Water Vapor", Anal. Chem. 91, 12866-12873 (2019).

Conference Proceedings

- Partial least squares regression as novel tool for gas mixtures analysis in quartz-enhanced photoacoustic spectroscopy, Andrea Zifarelli, Univ. degli Studi di Bari Aldo Moro (Italy); Pietro Patimisco, Angelo Sampaolo, Marilena Giglio, Giansergio Menduni, Politecnico di Bari (Italy); **A. Elefante**, Univ. degli

Studi di Bari Aldo Moro (Italy); Vittorio M. N. Passaro, Politecnico di Bari (Italy); Frank K. Tittel, Rice Univ. (USA); Vincenzo Spagnolo, Politecnico di Bari (Italy), *SPIE OPTO, San Francisco, 2020*.

- Measurement of non-radiative gas molecules relaxation rates by using quartz-enhanced photoacoustic spectroscopy, Stefano dello Russo, Univ. degli Studi di Bari Aldo Moro (Italy); Pietro Patimisco, Angelo Sampaolo, Marilena Giglio, Giansergio Menduni, Politecnico di Bari (Italy); **A. Elefante**, Univ. degli Studi di Bari Aldo Moro (Italy); Vittorio M. N. Passaro, Politecnico di Bari (Italy); Frank K. Tittel, Rice Univ. (USA); Vincenzo Spagnolo, Politecnico di Bari (Italy), *SPIE OPTO, San Francisco, 2020*.

- Fiber-coupled quartz-enhanced photoacoustic sensor for methane and ethane trace detection, Fabrizio Sgobba, Univ. degli Studi di Bari Aldo Moro (Italy); Giansergio Menduni, Angelo Sampaolo, Pietro Patimisco, Marilena Giglio, Politecnico di Bari (Italy); **A. Elefante**, Univ. degli Studi di Bari Aldo Moro (Italy); Vittorio M. N. Passaro, Politecnico di Bari (Italy); Frank K. Tittel, Rice Univ. (USA); Vincenzo Spagnolo, Politecnico di Bari (Italy), *SPIE OPTO, San Francisco, 2020*.