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Mid-Infrared Laser based Trace Gas Sensor Technologies: Recent Advances and Applications

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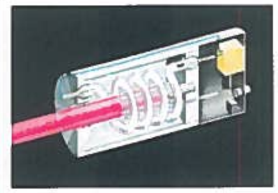
- Development of robust, compact, highly sensitive & selective mid-IR trace gas sensor technology based on high performance interband cascade lasers (ICLs) & quantum cascade lasers (QCLs) for medical diagnostics, environmental monitoring, atmospheric chemistry and industrial process control
- Development of Laser Absorption Spectroscopy (LAS)
- Photoacoustic Spectroscopy (PAS), Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) and I-QEPAS based trace gas sensor systems
- Future development of trace gas sensors for monitoring broadband absorbers, such as acetone (C_3H_6O), propane (C_3H_8), benzene (C_6H_6) & acetone peroxide-TATP ($C_6H_{12}O_4$)
- Drone based sensor systems

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation as well as sub-awards ARPA-E from AERIS Technologies & Maxion-Thorlabs and DOD-SCOUT from JPL is acknowledged

LASER is an acronym for: Light Amplification by Stimulated Emission of Radiation



Charles H. Townes (Columbia University) and Arthur L. Schawlow (Stanford University) conceived the laser in 1960. Theodore Maiman (Hughes Aircraft Company) demonstrated the first laser: a flash-pumped ruby laser in the same year. Gordon Gould was a graduate student of Prof. Townes, and first used the acronym "LASER."

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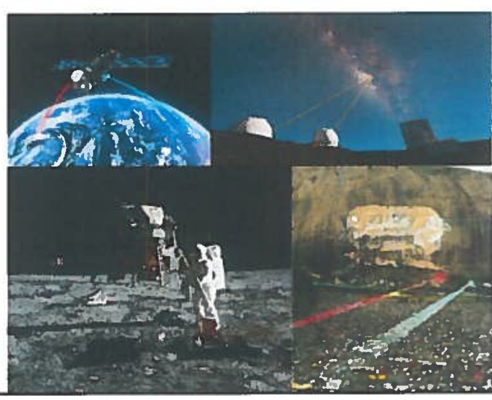
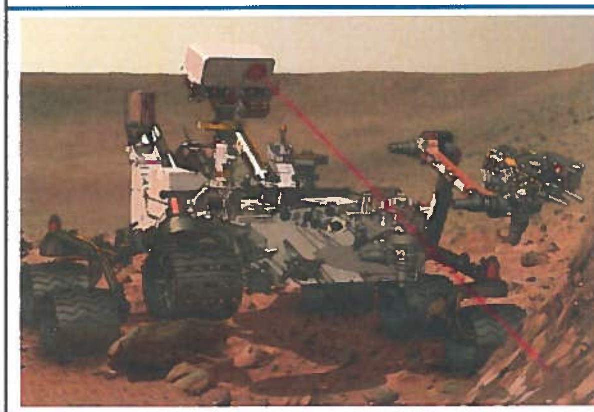
High-Power Lasers in Space



"Curiosity" landed on Mars on August 6, 2012



Main applications of gas sensing

Industrial process control
- Chemical analysis
- Monitoring combustion processes
- Quantification of gas leaks

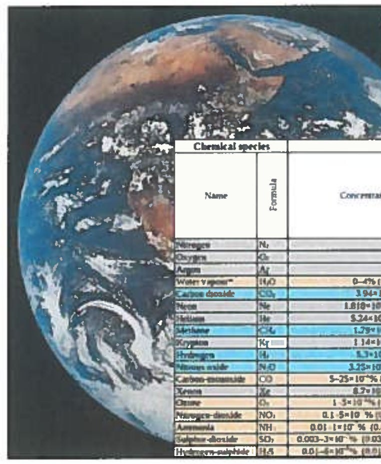
Health and Life Sciences
- Breath analysis
- Biomedicine

TRACE GAS SENSING APPLICATIONS

Environmental Monitoring
- Air pollution monitoring
- Detection of toxic gases
- Eco-sustainability

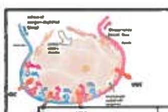
Law Enforcement
- National Security
- Defense

Trace gas in the atmosphere



Chemical species				Sources				
Name	Formula	Concentration	Residence time	Biogenic	Anthropogenic	Photochemical	Volcanic	Radiogenic
Nitrogen	N_2	78.084%	1.6×10^7 years	✓			✓	
Oxygen	O_2	20.946%	3×10^3–10^4 years	✓				
Argon	Ar	0.934%						✓
Water vapour*	H_2O	0–4% (0–40 000 ppm)	10 days	✓	✓		✓	
Carbon dioxide	CO_2	3.94×10^{-2}% (394 ppm)	20–150 years	✓	✓		✓	
Neon	Ne	1.818×10^{-3}% (18.18 ppm)					✓?	
Helium	He	5.24×10^{-4}% (5.24 ppm)	10^7 years					✓
Methane	CH_4	1.79×10^{-4}% (1.79 ppm)	10 years	✓	✓			
Krypton	Kr	1.14×10^{-4}% (1.14 ppm)						✓
Hydrogen	H_2	5.3×10^{-5}% (0.53 ppm)	2 years	✓	✓			
Nitrous oxide	N_2O	3.25×10^{-5}% (0.325 ppm)	150 years	✓	✓			
Carbon monoxide	CO	5–25$\times10^{-6}$% (0.05–0.25 ppm)	0.2–0.5 year	✓	✓			
Xenon	Xe	8.7×10^{-6}% (0.087 ppm)						
Ozone	O_3	1–5$\times10^{-6}$% (0.01–0.05 ppm)	weeks – months			✓		
Nitrogen dioxide	NO_2	0.1–5$\times10^{-6}$% (0.001–0.05 ppm)	8–10 days	✓	✓	✓		
Ammonia	NH_3	0.01–1$\times10^{-6}$% (0.0001–0.01 ppm)	~5 days	✓	✓			
Sulphur dioxide	SO_2	0.003–3$\times10^{-4}$% (0.03–30$\times10^{-4}$ ppm)	~2 days		✓	✓	✓	
Hydrogen sulphide	H_2S	0.01–6$\times10^{-6}$% (0.01–0.6$\times10^{-4}$ ppm)	~0.5 days	✓	✓		✓	

Trace gases in human breath



Molecule	Formula	Biological/Pathology Indication	Center wavelength [μm]
Pentane	C_5H_{12}	Inflammatory diseases, transplant rejection	6.8
Ethane	C_2H_6	Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)	6.8
Carbon Dioxide isotope ratio	$^{13}CO_2/^{12}CO_2$	Helicobacter pylori infection (peptic ulcers, gastric cancer)	4.4
Carbonyl Sulfide	COS	Liver disease, acute rejection in lung transplant recipients (10-600 ppbv)	4.8
Carbon Disulfide	CS_2	Disulfiram treatment for alcoholism	6.5
Ammonia	NH_3	Liver and renal diseases, exercise physiology	10.3
Formaldehyde	CH_2O	Cancerous tumors (400-1500 ppbv)	5.7
Nitric Oxide	NO	Nitric oxide synthase activity, inflammatory and immune responses (e.g. asthma) and vascular smooth muscle response (6-100 ppb)	5.3
Hydrogen Peroxide	H_2O_2	Airway inflammation, oxidative stress (1-5 ppbv)	7.9
Carbon Monoxide	CO	Smoking response, lipid peroxidation, CO poisoning, vascular smooth muscle response	4.7
Ethylene	C_2H_4	Oxidative stress, cancer	10.6
Acetone	C_3H_6O	Ketosis, diabetes mellitus	7.3

A North Dakota Oil Facility in 2016.

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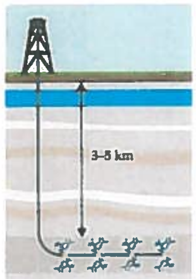
Typical Oil & Gas Production Site near Houston, TX



This figure depicts the result of a sequence of four fracking injections obtained by directional drilling which creates horizontal production in the target stratum.

A DOE-ARPA-E methane detection project at 3 327 µm started at an ARPA-E CSU site in 2017

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Laser-Based Absorption Spectroscopy

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Gas Cell (e.g Astigmatic Herriot - Aerodyne, Aeris DoE Monitor Bow-Tie)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector or back scattering from topographic target): Standoff and Remote Detection
  - Fiberoptic & Wave-guide Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

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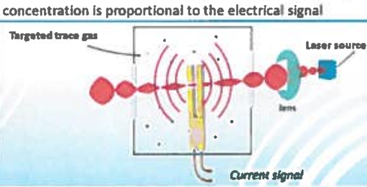
Quartz-Enhanced Photoacoustic Spectroscopy Introduction and Basic Operation

- Optical radiation is focused between the prongs of a quartz tuning fork
- Trace gases absorb optical energy at characteristic frequencies
- A pressure (sound) wave is generated by modulating the laser power
- Resonant mechanical vibration is excited by the sound waves
- The mechanical vibration is converted to an electrical signal via the piezoelectric effect
- The trace gas concentration is proportional to the electrical signal



P. Patimisco, A. Sampaolo, L. Dong, F.K. Tittel, V. Spagnolo, Appl. Phys. Rev. 5, 011106, 2018
P. Patimisco, A. Sampaolo, H. Zheng, L. Dong, F.K. Tittel, V. Spagnolo, Adv. Phys. X 2, 169, 2016
P. Patimisco, G. Scamarcio, F.K. Tittel and V. Spagnolo, Sensors 14, 6165-6206, 2014.

Quartz-Enhanced Photoacoustic Spectroscopy Merits and main characteristics

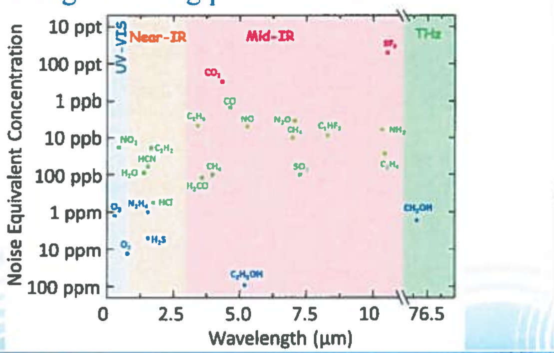
- Small sensing module and sample volume (a few cm^3)
- Wavelength independent
- Optical detector is not required
- Wide dynamic range (from % to ppt)
- Immune to environmental acoustic noise
- Acoustic micro-resonator(s) to enhance the QEPAS signal

- Sensitivity scales with laser power
- Cross sensitivity issues
- Alignment (no light must hit the QTF or micro-resonators)
- Responsivity depends on the molecular energy transfer processes

Record sensitivity: 50 part-per-trillion
$\lambda = 10.54\, \mu m$ (mid – IR), SF_6

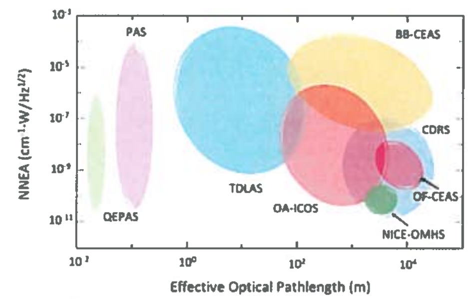
P. Patimisco et al., Applied Physics Review 5, 011106, 2018
P. Patimisco et al., Sensors 14, 6165, 2014
V. Spagnolo et al., Optics Letters 37, 4461-4463, 2012

QEPAS gas sensing performance



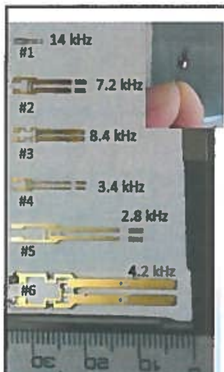
P. Patimisco, et al., Applied Physics Review, 5, 011106, 2018
P. Patimisco et al., Sensors, 14, 6165-6206, 2014

Gas sensing techniques performances (Mid-IR)



NNEA for categories of gas detection techniques as a function of optical path-length. Key: BB-CEAS—broadband cavity-enhanced spectroscopy, CRDS—cavity ring-down spectroscopy, OA-ICOS—off-axis integrated cavity output spectroscopy, OF-CEAS—optical feedback cavity-enhanced absorption spectroscopy, NICE-OHMS—noise-immune cavity-enhanced optical heterodyne spectroscopy, PAS photoacoustic spectroscopy, QEPAS—Quartz-enhanced photoacoustic spectroscopy

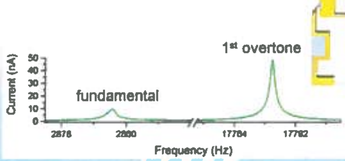
Custom QTF 2nd generation

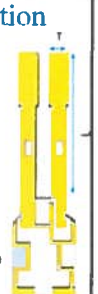


Euler-Bernoulli Equ.

$$f_n = \frac{\pi T}{8\sqrt{12}L^2}\sqrt{\frac{E}{\rho}}\,n^2 \qquad n_{fund} = 1.19 \quad n_{overt} = 3$$

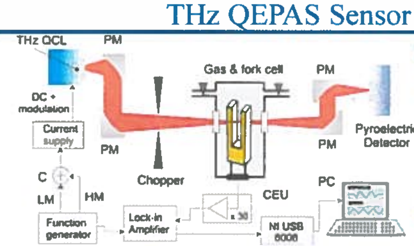
$$f_{1st\ overtone} \sim 6.2 \cdot f_{fundamental}$$

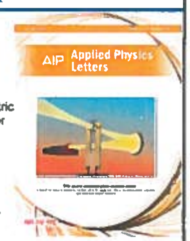




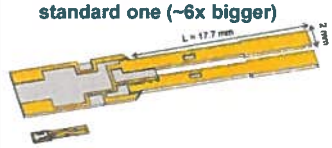
P. Patimisco, et al., Applied Physics Review, 5, 011106, 2018
P. Patimisco et al., Sensors and Actuators B Chemical, 227, 539-546, 2016

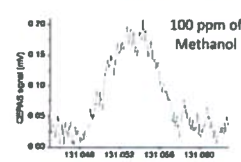
THz QEPAS Sensor

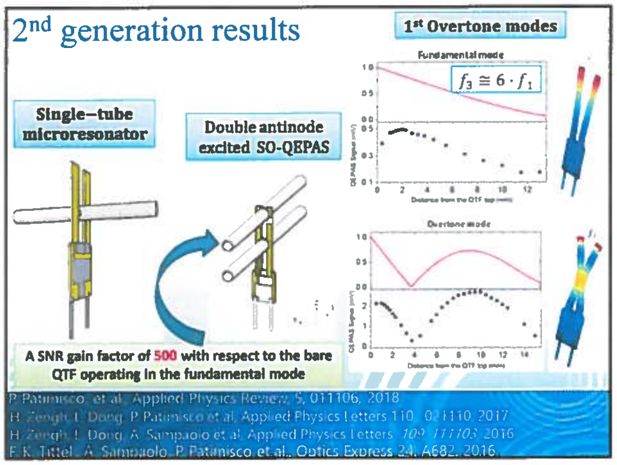


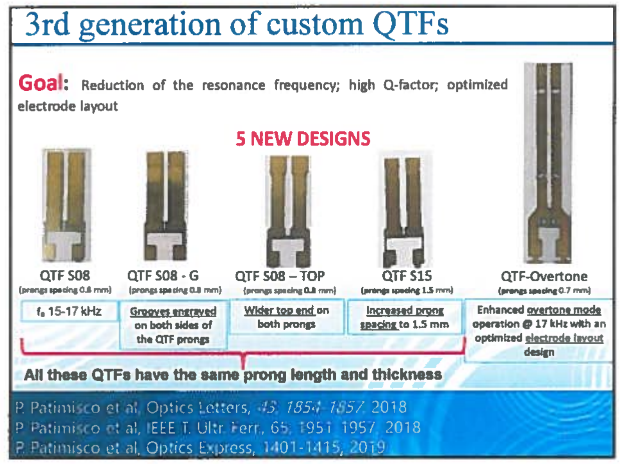


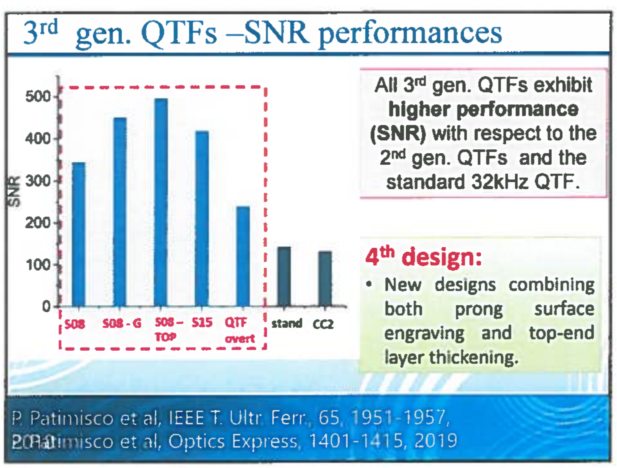
QTF with same geometry of standard one (~6x bigger)



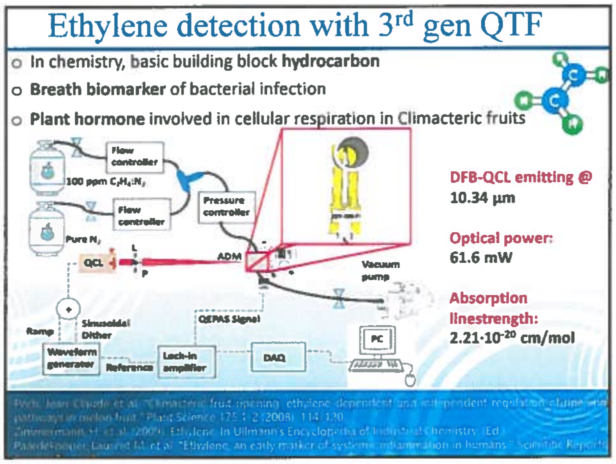


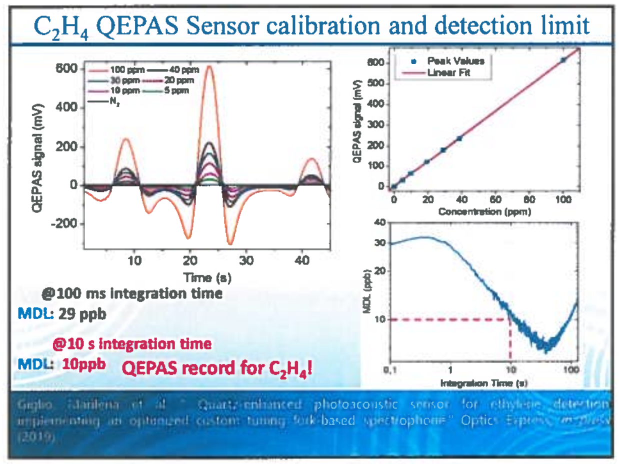

2nd generation results
1st Overtone modes
Single–tube microresonator
Double antinode excited SO-QEPAS
Fundamental mode
$f_3 \cong 6 \cdot f_1$
Overtone mode
A SNR gain factor of 500 with respect to the bare QTF operating in the fundamental mode
P. Patimisco et al, Applied Physics Review, 5, 011106, 2018
H. Zeng, L. Dong, P. Patimisco et al, Applied Physics Letters 110, 021110, 2017
H. Zeng, L. Dong, A. Sampaolo et al, Applied Physics Letters 109, 111103, 2016
F. K. Tittel, A. Sampaolo, P. Patimisco et al., Optics Express 24, A682, 2016


3rd generation of custom QTFs
Goal: Reduction of the resonance frequency; high Q-factor; optimized electrode layout
5 NEW DESIGNS
QTF S08 (prongs spacing 0.8 mm)
QTF S08 - G (prongs spacing 0.8 mm)
QTF S08 – TOP (prongs spacing 0.8 mm)
QTF S15 (prongs spacing 1.5 mm)
QTF-Overtone (prongs spacing 0.7 mm)
f_0 15-17 kHz
Grooves engraved on both sides of the QTF prongs
Wider top end on both prongs
Increased prong spacing to 1.5 mm
Enhanced overtone mode operation @ 17 kHz with an optimized electrode layout design
All these QTFs have the same prong length and thickness
P. Patimisco et al, Optics Letters, 43, 1854-1857, 2018
P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, 2018
P. Patimisco et al, Optics Express, 1401-1415, 2019


3rd gen. QTFs –SNR performances
SNR
500
400
300
200
100
0
S08
S08 - G
S08 – TOP
S15
QTF overt
stand
CC2
All 3rd gen. QTFs exhibit higher performance (SNR) with respect to the 2nd gen. QTFs and the standard 32kHz QTF.
4th design:
• New designs combining both prong surface engraving and top-end layer thickening.
P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, 2018
P. Patimisco et al, Optics Express, 1401-1415, 2019


New QEPAS Acoustic Detection Module with 3rd gen. QTF–available in the market in 2019
THORLABS


Ethylene detection with 3rd gen QTF
In chemistry, basic building block hydrocarbon
Breath biomarker of bacterial infection
Plant hormone involved in cellular respiration in Climacteric fruits
Flow controller
100 ppm C2H4:N2
Flow controller
Pure N2
Pressure controller
QCL
ADM
Vacuum pump
QEPAS Signal
Ramp
Sinusoidal Dither
Waveform generator
Reference
Lock-in amplifier
DAQ
PC
DFB-QCL emitting @ 10.34 µm
Optical power: 61.6 mW
Absorption linestrength: 2.21·10-20 cm/mol
pathways in melon fruit." Plant Science 175.1-2 (2008): 114-120
In Ullmann's Encyclopedia of Industrial Chemistry (Ed.)
"Ethylene: an early marker of systemic inflammation in humans." Scientific Reports


C2H4 QEPAS Sensor calibration and detection limit
100 ppm
40 ppm
30 ppm
20 ppm
10 ppm
5 ppm
N2
QEPAS signal (mV)
Time (s)
Peak Values
Linear Fit
QEPAS signal (mV)
Concentration (ppm)
MDL (ppb)
Integration Time (s)
@100 ms integration time
MDL: 29 ppb
@10 s integration time
MDL: 10ppb
QEPAS record for C2H4!
"Quartz-enhanced photoacoustic sensor for ethylene detection implementing an optimized custom tuning fork-based spectrophone." Optics Express
(2019)


Visit by Frank Tittel to Thorlabs Booth at Photonics West Feb. 2018
First commercial Ethylene QEPAS prototype
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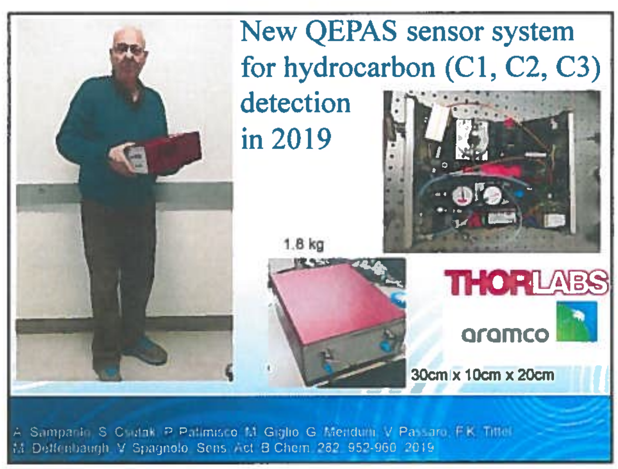
New QEPAS sensor system for hydrocarbon (C1, C2, C3) detection in 2019
1.8 kg
THORLABS
aramco
30cm x 10cm x 20cm
A. Sampaolo, S. Csutak, P. Patimisco, M. Giglio, G. Menduni, V. Passaro, F.K. Tittel, M. Deffenbaugh, V. Spagnolo, Sens. Act. B Chem. 282, 952-960, 2019

Future development of a Drone mounted QEPAS Chemical Sensor System

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Summary, Conclusions and Future Developments

- Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICLs & QCLs for environmental monitoring, atmospheric chemistry, industrial process control and medical diagnostics
- Realization of QTFs 3rd generation all showing improved performances with respect to standard and 2nd gen. QTFs.
- Demonstration of an Ethylene QEPAS sensors employing 3rd generation QTF resulted in a minimum detection limit of 10 ppv for a 10 sec integration time aimed at breath sensing applications.
- Future development of QEPAS on drone sensors for monitoring of carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6) in collaboration with Aramco, Houston, TX
- Future development of a QEPAS sensors for hydrocarbon isotopes detection