Fuel 277 (2020) 118118



Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Quartz-enhanced photoacoustic spectroscopy for hydrocarbon trace gas detection and petroleum exploration



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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords: Quartz-enhanced photoacoustic spectroscopy Trace gas sensing Methane Ethane Propane Hydrocarbons Methane isotopes

ABSTRACT

Quartz-enhanced photoacoustic spectroscopy represents a valuable candidate for natural gas analysis in the oil & gas field. The core element of this spectroscopy technique is a quartz tuning forks, employed as high quality-factor optoacoustic transducers, capable of operating in a wide range of temperatures and pressures. The robustness and compactness of these sensors, together with the possibility to avoid the use of optical detectors, open the way to the development of a new generation of small-sized gas spectrometers to be potentially employed downhole for source rock characterization and estimation of oil & gas properties. We report here on the realization of a shoe-box sized quartz-enhanced photoacoustic spectroscopy system capable of: i) selective detection of methane and ethane in the parts-per-billion range, and propane in the parts-per-million range, by employing a single interband cascade laser emitting at 3.345 μ m; ii) selective detection of ¹²CH₄ and ¹³CH₄ isotopes at the parts-per-billion sensitivity level by employing a quantum cascade laser operating around 7.73 μ m.

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https://doi.org/10.1016/j.fuel.2020.118118

Received 2 March 2020; Received in revised form 23 April 2020; Accepted 14 May 2020 0016-2361/@ 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Trace gas sensing systems are extensively applied in petroleum exploration, petrochemical industry, environmental monitoring and biomedical testing and treatments. Several chemical and optical techniques have been proposed and the optimum choice depends on the involved gas species, the gas concentration range, the required spectral resolution, the sensitivity, the specificity, the response time, the operating environment (such as temperature and presence of interfering species), the size and the cost [1-3]. Laser-based infrared (IR) trace gas sensing is a powerful tool for applications such as fire and explosion prevention, indoor air quality control, food production, environmental monitoring, industrial process control, petrochemical production and medical diagnostics [2-6]. Indeed, laser-based optical techniques represent a suitable solution for the analysis of gas compositions, since they exploit the laser's narrow spectral resolution and allow for unambiguous and real-time measurements of trace gas mixtures [2]. To date it has been demonstrated that trace gas species can be optically detected with detection sensitivities down to parts-per-quadrillion concentration levels [7-9]. Thus, laser-based techniques are excellent candidates for a large number of applications requiring high specificity and detection sensitivity as well as real-time response. A recent interest in the petrochemical and oil & gas industry is hydrocarbon detection in gas phase. An optical system analyzing the natural gas mixture at a well site can offer near-instantaneous readings. Therefore, the acquisition time is substantially determined by the time needed to transport the gaseous sample at the surface [10]. For this purpose, suction lines using a constant flow of air as a carrier bring the gas from the gas trap, located in the shaker shale, to the logging unit. The primary instrument devoted to the analysis of the samples extracted from the drilling mud is a flame ionization detector (FID). The basic function of a FID is the measurement of the background gas concentrations, usually ranging from a few ppm to per cent depending on the formation process and circulating conditions, to determine the baseline of the curve plotted by the total gas [10]. A significant increase in the gas detected, which reflects the richness of hydrocarbon and/or the improvement of reservoir quality, constitutes a gas show. When a gas show occurs, the mud logger triggers an automated cycle of more systematic and precise analysis of the oil and gas quantities, starting from the separation of the gas flow into different fractions based on their molecular weight operated by a gas chromatograph. The cycle time can last up to several minutes. The analysis performed by the gas chromatograph essentially returns the composition of the gas mixtures in terms of concentrations of the lightest alkanes: methane (C1), ethane (C2), propane (C3), butane (C4) and pentane (C5). The geochemical evaluation of the gas mixtures allows the characterization of the drilling fluid. The quantity of the recovered gas, the composition and the ratios among different molecule concentrations are useful in predicting properties of reservoir fluids and identifying zones of producible oil or gas [11].

Besides the gas composition, isotopic ratio can be used as a fingerprint and an indicator for many processes involving isotopic fractionations. A measurement of the isotopic ratio of carbon and hydrogen of methane helps to identify the thermogenic or biogenic origin of natural gases, their sources and history [12]. For example, the isotopic distributions and isotopic fractionation processes are evaluated to estimate the global quantity of methane, as well as for investigations on a regional scale. The production of biogenic methane represents a major process mediated by anaerobic methanogens, most likely involving syntrophic bacteria. The isotopic ratios in methane, ethane and propane are usually evaluated to gather the evolution of gas formation [13].

For all these reasons, a breakthrough innovation for the oil & gas field could be represented by a new generation of ruggedized sensors able to selectively target hydrocarbon species, work properly in harsh environments and/or allow easy deployment and transportation from one site to another [14,15].

Quartz enhanced photoacoustic spectroscopy introduces a compact/ rugged sensing method for molar gases and their isotopes. The possibility to employ custom tuning forks as sharply resonant sound wave detectors that can operate in extreme conditions, eliminates the need of using any kind of photodetector. Moreover, the QTFs are acoustically isolated from the environment and very small amounts of gas sample are required thanks to the compactness of the acoustic detection modules. These characteristics enable the design of a downhole system including a QEPAS spectrometer coupled with a sampling tool, to be positioned along a drill string within a wellbore formed in a subterranean zone of a hydrocarbon formation, as described and illustrated in [16].

A plurality of quantities and ratios of a corresponding plurality of hydrocarbons in the sample can be determined to evaluate and map a hydrocarbon formation. The analysis can be used to guide well placement, also referred to as geo-steering, so that the wellbore remains within a zone of interest or in the most economically productive portion of a reservoir.

2. Quartz-enhanced photoacoustic spectroscopy

All spectroscopic techniques are based on optical absorption, which is governed by Beer–Lambert's law:

$$I = I_0 e^{-\alpha l} \tag{1}$$

where I is the light transmitted through a cell containing the gas sample, I_0 is the light incident on the gas sample, α is the absorption coefficient of the gas sample at a specific laser wavelength and *l* is the optical pathlength. The absorption coefficient α depends on the gas concentration and the strength of the selected absorption line. Starting from this principle, gas sensing techniques based on measurement of optical absorption at specific wavelengths have been developed. Among them, the optical sensors that have proved to be effective for trace gas detection can be divided in three major groups: i) direct absorptionbased sensors; ii) cavity-enhanced based sensors; iii) photoacoustic (PAS) or quartz enhanced photoacoustic and photothermal based sensors [2]. Considering that the highest detection sensitivity is most desirable, the choice of a specific technique is mainly determined by the final application requirements and constraints. Minimum detection limits are usually quantified as the noise equivalent concentration (NEC). The convention adopted is that the NEC is the gas target concentration giving a signal equal to the $1-\sigma$ standard deviation of the signal variations. Furthermore, it is also important to take into account the available optical laser power P_{0} , the strength of the selected absorption line and the signal integration time t used for the gas concentration measurements. In this case, the normalized noise equivalent absorption parameter (NNEA), represents the best indicator to compare the performances of different sensors with respect to a specific gas target detection. The NNEA is defined as:

$$NNEA = \frac{\alpha_{min}P_0}{\sqrt{t}}$$
(2)

being α_{\min} is the minimum detectable absorption coefficient.

In Fig. 1 the performance of several gas detection techniques in terms of NNEA versus the effective optical pathlength are reported. Tunable diode laser absorption spectroscopy exploiting multi-pass cells is the most representative approach among the direct absorption-based techniques. The laser beam experiences multiple reflections at different points on two large diameter focusing mirrors which compose the multipass cell. In this way, the optical pathlength can be as high as 100 m even if the gas cell length is in the order of tens of cm.

The alignment is critical to preserve the pattern of laser beam reflections between the two mirrors of the cell. Indeed, the signals are strongly affected by fringe-like noise patterns when misalignments occur. Nevertheless, many robust portable sensors employing multipass



Fig. 1. NNEA for gas sensors based on optical spectroscopic techniques as a function of the effective optical path-length. Key: CEAS—cavity-enhanced absorption spectroscopy, PAS photoacoustic spectroscopy, QEPAS—Quartz-enhanced photoacoustic spectroscopy, TDLAS—tunable diode laser absorption spectroscopy.

cells were demonstrated and developed over the last years [17,18]. In the cavity-enhanced absorption spectroscopy, the gas cell is composed of a high finesse optical cavity. Extremely long pathlength cells can be obtained by using mirrors with high reflectivity (R > 99.99%), achievable using dielectric coatings. Resonant cavities are formed in the manner of a high finesse Fabry-Perot etalon. The cavity enhancedbased techniques suffer from misalignment, since the linewidth and spectral purity of longitudinal cavity modes can be deteriorated by a non-optimal matching between the laser beam path outside and the light propagation through the cavity itself. The requirement of laser beams with high spatial quality and narrow linewidth is mandatory. The cost that this kind of techniques have to pay for a lower NNEA and higher sensitivity - down to part per quadrillion [7-9] - is a significant increase in the optical pathlengths as well as the overall size of the sensors. Both multi-pass cells and optical cavities must be necessarily employed in combination with optical detectors. The use of widely tunable laser sources, or array of lasers, for analyzing gas mixtures potentially containing many broadband absorbers is generally precluded, for CEAS based sensors in particular.

The main strengths of the photoacoustic spectroscopy (PAS) are that no optical detectors are needed, and sound wave detectors are wavelength insensitive [19]. In the photoacoustic wave generation, the laser light can be modulated in intensity or in wavelength creating a sequence of absorption/release of the accumulated energy, i.e. heat, thus resulting in a process of rise/fall of the gaseous molecules' spatial density. The propagation of molecular density variations in space gives rise to a sequence of sound waves. In traditional PAS, gas cells are used to i) contain the mixture to be analyzed, ii) provide the interaction pathlength between the laser light and target analyte molecules, iii) amplify the sound waves produced at a frequency resonant with the fundamental acoustic mode of the cell, typically in the range 1-4 kHz [19]. The quality factor *Q*, defined as the ratio between the stored energy and the energy losses per cycle, usually does not exceed the value of 200. In order to detect sound waves in the photoacoustic cell, highly performing microphones are employed, which however do not provide any frequency selectivity and makes the acoustic and mechanical isolation of the sensor from the surrounding environment a critical issue. Recently a rugged methane sensor designed to be insensitive to the incoherent external acoustic noise, by implementing a cumulative average of the demodulated signal, was developed [20].

In the perspective of reducing the dimension of the acoustic cell and exploiting an intrinsic immunity to the environmental noise, a quartzenhanced photoacoustic spectroscopy (QEPAS) approach was subsequently developed, employing quartz tuning forks (QTF) as resonators and piezoelectric transducers [21–24]. In this configuration, the laser beam is focused between QTF prongs and the acoustic waves, generated by the modulated absorption of the target analyte molecules, make the QTF prongs oscillate. The laser modulation frequency has to be resonant with one of the in-plane anti-symmetrical flexural modes of the tuning fork. The photoacoustic signal

$$S \sim Q \cdot P \cdot \alpha \cdot \varepsilon$$
 (3)

is proportional to the quality factor of the resonator Q, the radiation-tosound conversion efficiency ε , the available optical power P and the absorption coefficient α . Since the invention of QEPAS in 2002 standard tuning forks (S-QTFs) used in electronic watches for timepiece applications have been used in QEPAS with a resonance frequency close to $f_0 \sim 32,768$ (i.e. 2^{15}) Hz [21,22]. The excited mode corresponds to the fundamental, anti-symmetric, in-plane flexural vibration mode, which exhibits *Q*-factors in the order of 100,000 under vacuum and higher than 10,000 at atmospheric pressure. At this resonance frequency, QEPAS sensors are immune to background acoustic noise since the $\sim 1/f$ ambient acoustic noise spectral density is very low at frequencies in the order of magnitude of tens of kHz. Moreover, for the piezoelectric signal demodulation, the use of lock-in amplifiers and/or narrow filters in general allow a further noise reduction on the signal component extracted at the modulation frequency, or one of its harmonics.

The prong length of S-QTFs is 3 mm, the width and thickness are 0.35 mm and 0.34 mm respectively, while the separation between the prong is 0.3 mm. In order to enhance the pressure of the sound wavefront impacting on the internal surface of the prongs and the effective interaction pathlength between the laser beam and the gas molecules, acoustic resonator tubes can be applied to form, combined with the tuning fork, a QEPAS dual tube spectrophone. In the on-beam configuration, a pair of tubes are aligned perpendicular to the OTF plane, with the tube axes at the same height of the fundamental vibration mode antinode and at a distance of tens of micron from the QTF of tens, typically. Thus, when the modulated laser radiation propagates through the dual tube system, a standing soundwave is generated, with its pressure peak pressure occurring at the vibrational antinode between the prongs. The optimum tube dimensions maximizing the SNR for the S-QTF, were demonstrated to be \sim 4 mm of length and 0.8 mm of internal diameter, with an external diameter not lager than 1.2 mm [25]. Even though the alignment of the laser beam with respect the spectrophone structure can be relatively easy to preserve, a particular care must be taken so that the light does not directly irradiate the QTF prongs or the internal walls of the resonator tubes, otherwise a photothermal undesired noise contribution would arise to limit the ultimate detection sensitivity, represented by the QTF thermal noise [26,27]. To overcome alignment issues and make the sensor architecture more robust, a novel configuration based on the photoacoustic excitation generated by evanescent waves was demonstrated, in which a tapered fiber was coupled with a standard spectrophone [28]. A QEPAS sensor operating in the THz range was demonstrated for the first time in 2013, exploiting a custom made QTF and a quantum cascade laser emitting at 3.93 THz to target a rotational transition of methanol [29,30]. The extension of the photoacoustic spectroscopy to the THz range could only be pursued by employing a quartz resonator with an enlarged prong spacing, because of the high divergence, large beam waist e poor spatial quality characterizing the THz radiation. During the last years, many other QTF designs were investigated. The custom spectrophones were then tested and installed in QEPAS sensor with successful results. [23,24,31-34]. QEPAS sensors employing powerful near-IR fiber amplified lasers, or mid-IR distributed-feedback QCL arrays were also demonstrated thanks to a new generation of custom resonators designed on purpose for the specific application, with prongs spacing spanning from 0.4 to 1.5 mm [35-36]. The possibility to improve the dual tube on-beam configuration in a more efficient acoustic

amplification system, in which a single tube is directly placed between the QTF prongs, was also demonstrated thanks to the custom geometries and large prongs spacing. [37–38].

In Fig. 2 the best noise equivalent concentrations, for a selection of gas species investigated so far with QEPAS, are reported as a function of the employed laser wavelength [22,23,39,40].

The short optical pathlength and capability to reach high detection sensitivity represent the main distinct advantages that make QEPAS the leading-edge technique mature for out-of-laboratory operation, targeting in-situ applications such as environmental monitoring and leak detection [41–43]. Furthermore, QEPAS spectrophones are particularly suited in hard environments, such as hydrocarbon detection for exploration and production applications. In fact, the high compactness of QEPAS sensing module, the high frequency stability of the QTF's resonance (with frequency shifts of ~0.04 ppm/T² in the temperature range T from -40 °C to 90 °C) [36] and the QTF immunity to environmental noise make the downhole deployment of QEPAS sensors an applicable task.

In this work, the detection strategies and performances of two QEPAS sensors are reported: the first one is based on a S-QTF and exploits an interband cascade laser (ICL) to study the natural gas composition; the second one employs a custom QTF (C-QTF) and a quantum cascade laser (QCL) for monitoring the methane ${}^{13}C/{}^{12}C$ isotopic ratio.

3. Detection of methane, ethane and propane

Like all the other hydrocarbons, C1, C2 and C3 are characterized by the C–H bond. The fundamental bands of the vibrational levels due to C–H bond stretching fall in the 3–4 μ m spectral window. The most efficient laser sources operating in such a spectral range are the ICLs [44]. The exact values of transition energies and linewidths are determined by the boundary conditions related to the chemical structure of a specific hydrocarbon compound. The largest absorption cross-sections for both methane and ethane correspond to C–H stretching which lies in the spectral range 2900–3200 cm⁻¹ [45]. The ICL employed for C1/ C2/C3 detection was fabricated by Nanoplus and has a central emission wavelength at 3345 nm. The schematic of the QEPAS sensor employing the ICL as the light source is reported in Fig. 3.

The laser beam emerges collimated from the TO66 package and it's focused, by means of a ZnSe AR-coated lens (L1 in Fig. 3(b)) with a 7.5 cm focal length, into the dual-tube spectrophone composed of a S-QTF and a pair of resonator tubes having a length of 4.0 mm, inner and outer diameter of 0.6 mm and 0.8 mm, respectively. The spectrophone is housed in an acoustic detection module composed of a vacuum-thigh cell with gas-in and -out connector designed for spectroscopic analysis of both static and flowing gas, and equipped with two ZnSe windows treated with a 3-12 µm anti-reflection coating. The pressure and flow rate of the sample gas through the cell are controlled externally using a pressure controller and gas flow meter (MKS Instruments Type π PC). A gas mixer (MCQ Instrument Gas Blender 1003) generates different gas target concentrations in N2, starting from a certified concentration of the gas target and a cylinder containing the gas carrier. A constant water concentration of 1.7% was provided by inserting a Nafion humidifier in the gas line. The light exiting the gas cell is re-collimated by means of another AR-coated lens (L2 in Fig. 3(b)) with a 7.5 cm focal length and directed onto a power meter for alignment purposes. By measuring the optical power after the gas cell with the pyroelectric detector, it was verified that more than 98% of the focused laser beam passes through the sensing module.

The QTF has dynamic resistance $R = 62.6 \text{ k}\Omega$, a quality factor Q = 2100 and resonance frequency $f_0 = 32,741.5$ at the atmospheric pressure. The piezocurrent collected from the QTF is processed and transformed into a voltage signal by a transimpedance amplifier (TA, gain factor 30). In collaboration with THORLABS GmbH, we packaged all the sensing system, i.e. the laser source, the pyroelectric detector, the TA electronic, the two ZnSe lenses (L1, L2) and the ADM into a

30 cm \times 10 cm \times 20 cm case as shown in Fig. 3(e).

In order to retrieve the QEPAS signal with zero background, we implemented a wavelength modulation approach and 2f-detection by applying a sinusoidal modulation to the ICL current at half of the QTF resonance frequency $f_0/2$ and demodulating the QTF response at f_0 by means of a lock-in amplifier. In addition, to scan the laser wavelength over the targeted absorption features, a low-frequency ramp was applied to the driving current. With this approach, the QEPAS scan of a Lorentzian-like absorption feature resembles the second derivative of the Lorentzian function itself. The demodulated signal is acquired by an USB data acquisition card (National Instruments DAQ-Card USB6008) and analyzed via a LabVIEW-based software.

The ICL central emission wavelength was chosen in order to target a Lorentzian-like absorption line of C2 located at 2986.25 cm⁻¹ and three partially merged lines of C1 with the strongest absorption peaked at 2988.8 cm⁻¹. The cross-sections for these absorption features were simulated by using the HITRAN database [46] for pure C1 and C2 at 200 Torr and are reported in the lower panel of Fig. 4. A spectral separation larger than 2 cm^{-1} avoids any absorption interference and sets the basis for a selective detection of both gas species. When N2 is used as the gas carrier, the gas pressure maximizing the QEPAS response for both C1 and C2 was 200 torr. At this pressure value, the absorption linewidths are mainly determined by the collisional broadening due to the gas pressure, and thus the 2f-QEPAS peaks are also dependent on the $f_0/2$ modulation depth A_m . The QEPAS response for both C1 and C2 was optimized when $A_m = 130$ mV. In the upper panel of Fig. 4 are displayed the QEPAS signals acquired at 200 Torr, at a lock-in integration time of 0.1 s for a sequence of two ICL current scans, the first in the range 44.5–51 mA and the second in the range 64–70 mA, with the ICL temperature fixed at T = 15 °C. The mixture analyzed was composed of 990 ppm-C1 and 10 ppm-C2 in pure N₂. The 2nd derivative of the three-fold C1 structure in the QEPAS spectrum, recorded during the first current scan window, is clearly recognizable.

Likewise, in the second scan window, the 2*f*-profile of the C2 absorption line can be identified. Starting from a certified mixture of 1000 ppm of C1 in N_2 and 1000 ppm of C2 in N_2 , two calibration curves were determined by evaluating the QEPAS sensor response at different C1 and C2 concentrations, obtained by diluting the certified concentrations in N_2 . We measured a detection sensitivity of 0.46 mV/ppm and 5.54 mV/ppm for C1 and C2, respectively. In order to evaluate the ultimate detection limit and the long-term stability of the QEPAS sensor for C1 and C2 detection, an Allan-Werle deviation analysis was



Fig. 2. Best NEC results obtained with the QEPAS technique for a selection of gas species plotted as a function of employed laser wavelength, in the UV–Vis, near-IR, mid-IR and THz spectral ranges.



Fig. 3. Schematic of the experimental apparatus divided in three main building blocks: (a) a gas handling system including a 3 channels MCQ Instrument Gas Blender 1003, b) a sensing system and (c) an electronic unit. (d) is a picture of the ADM: acoustic detection module including the QTF and the acoustic micro-resonator tubes (mR). L1 and L2 are AR-coated ZnSe lenses, TA is the transimpedance amplifier. The sensing system has been embedded into a shoe box sized case (sizes $30 \text{ cm} \times 10 \text{ cm} \times 20 \text{ cm}$) shown in the picture (e).

performed [47]. The laser current was firstly locked to 48.5 mA, which corresponds to a laser emission resonant with the C1 strongest peak. The QEPAS signal was then acquired as a function of the time, while pure N_2 was flowing through the cell. For C2, the same procedure was adopted by locking the laser current to 66.5 mA. In Fig. 5 the Allan-Werle Deviation plots for C1 (black dots) and C2 (blue dots) are displayed as a function of the lock-in integration time.

Both trends closely follow a $1/\sqrt{t}$ dependence over the entire duration of the measurement series without base line or sensitivity drift up to 100 s, indicating that QTF thermal noise is the dominant noise source.

The two-windows scheme for C1/C2 detection is simple and effective. In fact, with two fast and narrow scans across the target

features, the concentrations of both species can be independently retrieved in the ppb range. The measurement reliability is not affected by unbalanced mixtures like natural gas, where C1 concentration is expected to be found more than 10 times higher with respect to C2.

For the analysis of natural gas, spectroscopic measurements are usually not performed on single gas component samples but on multicomponent mixtures. Relatively small molecules such as C1 or C2 present well defined Lorentzian-like absorption features, while mixtures of larger molecules are often characterized by strongly overlapping and broadened spectra.

The absorption spectrum of propane (C3) is available from the HITRAN database only in the spectral range 700–800 $\rm cm^{-1}$



Fig. 4. Upper panel: 2*f*-signal is reported for a mixture of 990 ppm of methane, 10 ppm of ethane in pure N_2 ; Lower panel: absorption cross-sections from the Hitran database [38] of methane and ethane simulated in the spectral range 2986–2989.5 cm⁻¹, corresponding to an ICL injected current scan from 45 to 70 mA.



Fig. 5. Allan-Werle Deviation Analysis (in ppb) for methane (black dots) and ethane (blue dots). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(12.5–14.3 µm). Recently, widely tunable optical parametric oscillators have been employed to reconstruct the C3 absorption band in the 3–4 µm spectral range [48]. In this spectral region at the atmospheric pressure, three different transitions, the v_{10} and v_{15} stretch of the CH₃ groups and the v_{23} stretch of the CH₂ group merge together into a sharp intense absorption peak located at 3369.76 nm. According to the PNNL spectral database, C3 cross sections are almost five times lower in intensity with respect to C2 within the ICL tuning range at atmospheric pressure [49]. Nevertheless, the linewidth broadening and the high spectral density cause multiple absorption lines to merge together, resulting in a spectrum composed of well-separated features. The QEPAS broadband spectrum of C3 acquired at atmospheric pressure for a certified mixture of 400 ppm C3 in N₂ is shown in Fig. 6.

The spectrum was obtained by scanning the laser current from 25 mA to 65 mA at T = 15 °C and employing an optimized current modulation amplitude $A_m = 300$ mV. The linearity of photoacoustic response was evaluated and verified by fitting the QEPAS spectra at different C3 concentrations in pure N₂, ranging from 1000 ppm down to 100 ppm, with a function $Y = aX_{1\%}^{C3}$, where $X_{1\%}^{C3}$ is the reference C3-QEPAS spectrum at 1000 ppm and *a* is a fit parameter. The *a* parameter multiplied by 1000 ppm provides the measured C3 concentration in pure N2. Once verified that the whole C3 QEPAS spectrum scales linear with the concentration, we provided an estimation of the detection sensitivity for propane by performing an Allan deviation analysis, with the ICL current fixed in correspondence of the 2f-like absorption feature peaked at I = 61.3 mA (red oval in Fig. 6). The calibration curve of the peak value at I = 61.3 mA returns a linearity coefficient of 0.019 mV/ ppm, leading to a minimum detection limit of \sim 3 ppm at 1 s of integration time [40].

For real downhole natural gas samples, in which the background absorption rises up from C2, C3 and the heavier molecules (C4, C5, etc.), a selective identification of distinct components and their concentration is difficult to obtain due to the strong overlap of absorption features belonging to different gas species. Identifying an approach to discriminate contributions from different overlapping broadband absorbers in quasi-real time measurements represents a priority for applications in exploration and assisted drilling. In this case, each hydrocarbon molecule must be spectrally characterized in order to generate a reference spectrum as a function of the laser wavenumber λ at a fixed concentration. Then, a linear combination of reference spectra can be constructed:

$$Y(\lambda) = \sum_{i=0}^{n} a_i X(\lambda)_i$$

= $a_1 X(\lambda)_{C1} + a_2 X(\lambda)_{C2} + a_3 X(\lambda)_{C3} + a_4 X(\lambda)_{C4} + a_5 X(\lambda)_{C5} + \cdots$
(4)

which can be used as a fitting function for the analysis of a 2*f*-QEPAS spectrum obtained for an unknown mixture. A first validation test for this multi-gas detection approach was made using several mixtures composed of C2 and C3 concentrations ranging from 100 ppm to 1000 ppm in a gas matrix of pure N_2 [40].

In Fig. 7 the results obtained by analyzing a representative mixture of 500 ppm of C2 and 500 ppm of C3 in pure N_2 are displayed. The green and blue curves represent, respectively, the C2 and C3 individual contributions to the QEPAS spectrum, while the red dash-dot line is their sum, which matches perfectly the measured QEPAS spectrum of the mixture (black line). For all the mixtures analyzed, the differences between the fitting parameters from Eq. (4), i.e. the calculated C2, C3 concentrations, and the nominal concentrations expected, were found to be below 5% [33]. These first reliable results set the basis for an accurate and more extended investigation of the broadband absorption characteristics of complex hydrocarbons, with the aim of quantifying their contribution to the absorption in natural gas mixtures.

In Table 1 is reported a performance comparison among the QEPAS spectrometer described above and the more representative, reliable and field proven technologies for light hydrocarbon molecules detection.

All three sensors are portable devices and take advantage of a fairly low response time, thus allowing for measurements in real-time and/or in a continuous monitoring mode. The outstanding precision in the parts-per-trillion range provided by the TILDAS sensor, limits on the other hand the detection range, relegating the employment of this device mainly to environmental concentration monitoring of C1 and C2. The QEPAS spectrometer shows comparable performances in terms of precision with respect to the CRDS sensor, in addition the QEPAS prototype can provide also C3 concentration with a precision in the ppm range.

4. Detection of methane isotopes

In laser spectroscopy, high precision isotopic ratio measurements with individual ro-vibrational lines require a spectral separation at a given pressure, which is large enough to avoid absorption interference. In the case of methane isotopes, both ¹²CH₄ and ¹³CH₄ are spherical rotors, that show similar vibrational–rotational line patterns, shifted by 10 cm⁻¹ due to the C mass difference [12]. Therefore, the location of the strongest ¹³CH₄ isotopic lines will be relatively close to those of the parent ¹²CH₄ species.



Fig. 6. 2*f*-QEPAS spectrum measured for a C3 concentration of 400 ppm in pure N_2 at atmospheric pressure. A 300 mV modulation depth and a slow triangular ramp were imposed to the ICL current, scanning its central value from 25 to 65 mA.



Fig. 7. *2f*-signal acquired for a mixture C2-500 ppm, C3-500 ppm, rest of pure N_2 (black line); *2f*-signal acquired for C2-500 ppm (green line), C3-500 ppm (blue line) and their sum (dash-dot red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For ${}^{13}\text{CH}_4/{}^{12}\text{CH}_4$ features having comparable line-strengths, the isotopic ratio measurement is affected by the large dynamic range expected for the different isotopic abundances (~1/100). In order to compensate the absorption cross-sections, the most suited target consists of a pair of ${}^{13}\text{CH}_4$ - ${}^{12}\text{CH}_4$ lines in which the ${}^{13}\text{C}$ isotope transition has an oscillator strength approximately two order of magnitude higher with respect to the ${}^{12}\text{C}$ transition. Attention must be also given regarding the possible large dependence that a ratio in intensity has on the temperature through ground-state energies and broadening coefficients. Based on the available laser sources, the pair of absorption features that better fulfill the requirements listed above is composed of two lines at 1296.12 cm⁻¹ and 1296.03 cm⁻¹ for ${}^{12}\text{CH}_4$ and ${}^{13}\text{CH}_4$, respectively, characterized by a temperature coefficient of the cross-section ratio of $-6.7\%/^{\circ}\text{C}$.

The laser source selected for this investigation is a distributed-feedback QCL produced by Corning and emitting at 7.73 μ m, in the middle of the absorption bands of the C–H bond bending [46]. Since the QCL beam waist at the focal point has a FWHM of ~ 300 μ m, a custom C-QTF with a prong spacing of 0.8 mm was used. The resonance properties of the custom QTF was investigated in detail in [34]. The measured resonance frequency is 12,461.22 kHz with a quality factor of 42,000 at 50 Torr. The custom C-QTF was acoustically coupled with a pair of micro-resonator tubes (inner diameter of 1.52 mm, length of 9.5 mm) in an *on-beam* configuration and housed in a gas cell.

One of the strengths of a QEPAS sensor consists in its modularity. In fact, the ease of alignment and the versatility of the shoe box sized sensor architecture allowed us to easily replace the ICL with the QCL and swap the two ADMs containing the S-QTF and the C-QTF, while keeping the rest of the experimental setup depicted in Fig. 3 unaffected.

In the lower panel of Fig. 8 are plotted the absorption cross-sections for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4,$ simulated at 50 Torr by using the HITRAN

database [40].

The absorption cross-section takes into account the natural abundance of each isotope (~98.82% $^{12}\mathrm{CH}_4$, 1.11% $^{13}\mathrm{CH}_4$). The cross-section ratio at 20 °C is $\sigma_{13}/\sigma_{12} \sim 0.06$, with a temperature coefficient of -6.7%/°C, which represents a negligible correction with respect to the gas temperature variations expected during the experiment. As shown in the lower panel of Fig. 7, at 50 Torr the spectral separation between the two lines is more than 7 times larger than their full width half maximum (~0.012 cm^{-1}), so that no overlap occurs between the two Lorentzian-like absorption profiles. In order to verify the validity of all the assumptions made and demonstrate the sensor capability in detecting methane isotopes, a gas sample of standard methane was analyzed.

In the upper panel of Fig. 7, the QEPAS spectra acquired at 50 Torr for different standard methane concentrations (from 50 ppm to 1000 ppm) in N₂ are displayed. The 242.6 mA – 252.6 mA QCL injected current scan corresponds to a wavenumber tuning from 1296 cm⁻¹ to 1296.15 cm⁻¹. The modulation depth was set at 7.5 mV. As shown in the upper panel of Fig. 7, the two features related to the isotope ¹²CH₄ and ¹³CH₄ are perfectly distinguishable. The 1000 ppm mixture of standard methane was then diluted with N₂ down to 50 ppm. We verified that there is a perfect linearity of the 2*f*-QEPAS signal peaks versus the methane concentration for both isotopes ¹²CH₄ and ¹³CH₄ (see upper panel in Fig. 7).

For all the concentrations, the ratio between the QEPAS peak signals S_{13}/S_{12} was verified to be ~ 0.06. This result is in excellent agreement with the cross-section ratio simulated by the HITRAN database for a standard abundance ratio and consistent with the proportionality between the QEPAS signal and the absorption coefficient expressed by Eq. (3) [46]. The standard deviation of the noise level is 0.1 mV, while the ¹³CH₄-QEPAS signal peak for a concentration of 11 ppm resulted ~ 10 mV. This corresponds to a minimum detection limit of ~ 110 ppb achievable at 0.1 s of lock-in integration time. In the same way, the ¹²CH₄ minimum detection limit at the same operating conditions was 600 ppb. The sensor capability in measuring variation of the ¹³C/¹²C abundance ratio can be calculated starting from the deviation $\delta^{13}C$ of $1^{13}C/^{12}C$ in the sample with respect to a standard ratio:

$$\delta^{13}C = \left[\left(\frac{^{13}C}{^{12}C} \right)_{\text{sample}} / \left(\frac{^{13}C}{^{12}C} \right)_{\text{standard}} - 1 \right] \times 1000\%$$
(5)

The $\delta^{13}C$ variations $\Delta\delta^{13}C$, calculated from (5) through the propagation of error, for a mixture of 1000 ppm of methane in N₂ results proportional to signal fluctuations and inversely proportional to the S¹² peak signal. Considering that the 1- σ fluctuations of S¹² and S¹³ peak signals were measured as low as of 0.1 mV, at 0.1 sec of integration time $\Delta\delta^{13}C$ is calculated slightly below 10%.

Table 2 is reported a comparison among the preliminary results obtained with our QEPAS spectrometer re-modulated for targeting a pair of ¹²CH₄, ¹³CH₄ absorption lines at \sim 7.73 µm, and the performance of a couple of well established and field proven methane isotope analyzers.

As it can be noticed, the essential requirement for providing valuable and reliable methane isotopic ratio deviations are the capability to sense $\delta^{13}C$ variation with a precision of 1‰ or lower in a detection range as wide as possible.

Table 1

Performance comparison among the most representative optical sensors for light hydrocarbon detection.

	CRDS Picarro G4302 GasScouter [50]		TILDAS Mini Tra Gas Monitor [51	TILDAS Mini Trace Gas Monitor [51]		QEPAS Spectrometer [40]		
	CH ₄	C_2H_6	CH ₄	C_2H_6	CH ₄	C_2H_6	C_3H_8	
Precision Range Response Time	30 ppb @1s 1–5000 ppm < 1s	10 ppb @1s 0-500 ppm < 1s	300ppt @1s 0-100 ppm < 1s	50ppt @1s 0–50 ppm < 1s	90 ppb @1s 0–1000 ppm < 1s	7 ppb @1s 0–1000 ppm < 1s	3 ppm @1s 10–1000 ppm < 1s	



Fig. 8. Lower panel: absorption cross-section for ${}^{12}\text{CH}_4$ (black line) and ${}^{13}\text{CH}_4$ (red line) absorption features at 50 Torr; Upper panel: *2f*-QEPAS signal recorded for standard methane at concentration levels varying from 1000 ppm down to 50 ppm in pure N₂ at a pressure of 50 Torr. The QCL injected current scan in the upper panel corresponds to the wavelength tuning reported in the lower panel (1296–1296.15 cm⁻¹). In the inset a zoom on the ${}^{13}\text{C}$ peak is shown.

For a methane gas mixture in the per cents concentration scale, typical of natural gas samples, and at an integration time in the order of magnitude of tens of seconds, the $\Delta \delta^{13}C$ for the QEPAS spectrometer is expected to reach a value well below the 1‰ as well. Further improvements in precision can be achieved by implementing differential measurements with two ADMs, also combined with a modulation cancellation approach [54].

5. Conclusions

In this paper, we demonstrate that the QEPAS technique can be considered as a reliable tool to implement an in-situ and real time analysis of natural gas samples, opening the way to the development of ruggedized sensors for downhole and well-site measurement in the oil & gas field. Initially, a QEPAS sensor based on a 3.3 μ m ICL for hydro-carbon composition analysis is described here. The demonstrated detection sensitivities of 90 ppb and 7 ppb at 1 sec of integration time for C1 and C2, respectively, are well below the concentration scales in natural gas samples. Despite the lack of resolved C3 absorption spectra in the 3–4 μ m spectral range on the HITRAN database, we demonstrate the possibility to employ a wavelength modulation detection strategy at the atmospheric pressure that leads to a detection sensitivity of 3 ppm at 1 s of integration time. Dealing with the broadband characteristics of propane sets the basis for a more comprehensive and robust approach in

which overlapping bands from different absorbers (C4, C5, etc.) can be analyzed. Thus, the contributions from each hydrocarbon can be determined by fitting the QEPAS signal acquired for a given gas sample mixture with a linear combination of reference spectra.

The possibility to detect ¹²C and ¹³C isotopes of methane is also demonstrated by substituting the ICL and the standard spectrophone used for C1/C2/C3 setup with a OCL emitting at 7.73 μ m and a custom QTF-based spectrophone. A standard methane sample is tested and the standard abundances of \sim 98.82% 12 CH₄ and 1.11% 13 CH₄ are verified by comparing the absorption cross section ratio related to the selected lines with the QEPAS signals ratio. The detection sensitivity measured for both isotopes allowed us to estimate a $\Delta \delta^{13}C$ in the order of magnitude of 10‰. Both prototypes have been integrated into a ruggedized sensor conceived for deployment at well-site. A new version of the shoebox sized sensor including a digital lock-in amplifier, a laser current driver and a waveform generator is currently under test. The next step for a more sensitive detection of C1/C2/C3, heavier molecules like C4, C5 and also other concerned non-hydrocarbon components (e.g., H₂S, CO₂) in natural gas, is the implementation of partial least squares or multivariate analysis. While, for methane isotope sensing, a rigorous calibration performed by means of certified ¹³C and ¹²C concentrations will be needed to validate the promising results obtained with the analysis of the standard methane sample and estimate the $\delta^{13}C$ achievable at different integration times.

Table 2

	CRDS PICARRO G2132-i [52]		OA-ICOS LOS GATOS Methane Carbon Isotope Analyzer [53]		QEPAS Spectrometer	QEPAS Spectrometer [this work]	
	¹² CH ₄	¹³ CH ₄	¹² CH ₄	$^{13}\text{CH}_4$	¹² CH ₄	¹³ CH ₄	
Precision Precision $\delta^{13}C$	50 ppb @30 s < 0.4‰ @1h	10 ppb @30 s	< 0.2‰ @300 s < 1‰ @300 s	< 0.2‰ @300 s	600 ppb @ 0.1 s < 10‰ @0.1 s	110 ppb @0.1 s	
Range	10–100 ppm	10-100 ppm	1 ppm-100%	1 ppm-100%	50-1000 ppm	50–1000 ppm	

Funding

The authors from Dipartimento Interateneo di Fisica di Bari acknowledge financial support from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie project OPTAPHI, grant No. 860,808 and from THORLABS GmbH, within the joint-research laboratory PolySense. Welch Foundation (C0568); National Natural Science Foundation of China (NSFC) (61622503, 61575113, 61805132); Ministry of Education of the People's Republic of China, 111 project (D18001).

CRediT authorship contribution statement

Angelo Sampaolo: Methodology, Writing - original draft, Conceptualization, Data curation. Giansergio Menduni: Methodology, Writing - original draft, Conceptualization, Data curation. Pietro Patimisco: Conceptualization, Data curation, Writing - review & editing. Marilena Giglio: Conceptualization, Data curation, Writing review & editing. Vittorio M.N. Passaro: Conceptualization, Writing review & editing. Lei Dong: Conceptualization, Writing - review & editing. Hongpeng Wu: Conceptualization, Writing - review & editing. Frank K. Tittel: Conceptualization, Writing - review & editing. Vincenzo Spagnolo: Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support from THORLABS GmbH, within the joint-research laboratory PolySense is acknowledge. The authors from Dipartimento Interateneo di Fisica di Bari acknowledge dr. Verena Mackowiak, dr. Hubert Rossmadl and dr. Christian Brehm from THORLABS GmbH for helping in packaging the sensor system into a shoe box sized enclose. Authors also acknowledge Gianfranco Carrieri, Specialty & Pure Gases Specialist di Rivoira Gas S.r.l. part of Nippon Gases Europe, for providing the certified gas mixtures and Dr. Giuseppe Canuti for providing the Gas Blender GB100.

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