

# Simultaneous Detection of Methane, Ethane, and Propane by QEPAS Sensors for On-Site Hydrocarbon Characterization and Production Monitoring

Pan Luo,\* Jonathan Harrist,\* Giansergio Menduni, Rabah Mesdour, Nathan StMichel, and Angelo Sampaolo\*



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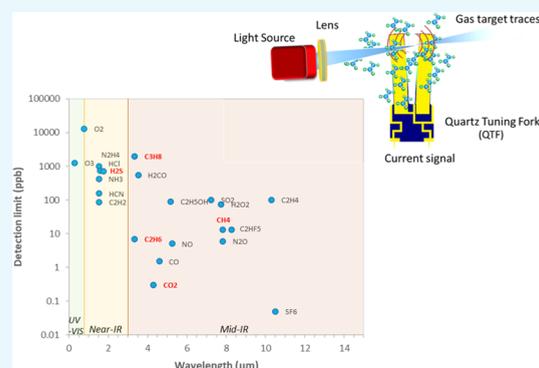
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**ABSTRACT:** Natural gas is sampled and produced throughout the lifespan of a petroleum field. Gas composition and isotope data are critical inputs in the exploration and field development, such as gas show identification, petroleum system analysis, fluid characterization, and production monitoring. On-site gas analysis is usually conducted within a mud gas unit, which is operationally unavailable after drilling. Gas samples need to be taken from the field and shipped back to the laboratory for gas chromatography and isotope-ratio mass spectrometry analyses. Results are usually without sufficient resolution to fully characterize the heterogeneity and dynamics of fluids within the reservoir and the production system. In addition, it often takes a considerable time to obtain the results using the traditional method. A novel QEPAS (quartz-enhanced photoacoustic spectroscopy) sensor system was developed to move gas composition analyses to field for quasi-real-time characterization and monitoring. With respect to previously reported QEPAS prototypes for trace gas detection, the new system realized measuring concentrations of methane (C1), ethane (C2), and propane (C3) in gas phase within the percentage range that is typically encountered in natural gas samples from oil and gas fields. A gas mixing enclosure was used to dilute the natural gas-like mixtures in nitrogen gas (N<sub>2</sub>) to avoid the saturation of QEPAS signals. An iterative analysis based on multilinear regression of QEPAS spectra was developed to filter out the influence of gas matrix variation from multiple hydrocarbon components. The advance in simultaneous measuring hydrocarbon gases and expanded linearity range of QEPAS, with previously reported detection of H<sub>2</sub>S, CO<sub>2</sub>, and gas isotopes (<sup>12</sup>CO<sub>2</sub>/<sup>13</sup>CO<sub>2</sub>, <sup>13</sup>CH<sub>4</sub>/<sup>12</sup>CH<sub>4</sub>), opens a way to use the advanced sensing technology for in situ and real-time gas detection and chemical analysis in the oil industry.



## 1. INTRODUCTION

Gas is ubiquitous in the subsurface, as free gas in porous space, adsorbed gas on kerogen/mineral surface, or dissolved gas in water and oil. Gas is sampled or produced throughout the lifespan of a field, including mud gas logging, formation and well testing, and production. Detecting and measuring gas is a basic analysis in the oil industry that provides gas composition and properties for petroleum system analysis, formation evaluation, PVT study, reservoir simulation, production monitoring, safety, and economic evaluation.<sup>1–3</sup>

QEPAS (quartz-enhanced photoacoustic spectroscopy) is a laser-based optical absorption spectroscopy for gas sensing, relying on quartz tuning forks (QTFs) as sound-to-current transducers. This technique was invented at Rice University and reported in 2002.<sup>4</sup> These first prototypes employed standard 32 kHz tuning forks, normally used for time keeping. The Jet Propulsion laboratory, NASA, was involved very quickly in the development mainly for early fire warning.<sup>5,6</sup> NASA still have active R&D and application of QEPAS sensors

in trace gas sensing (e.g., CH<sub>4</sub>, HCl, NO<sub>2</sub>, H<sub>2</sub>CO, SO<sub>2</sub>, and CO<sub>2</sub>) relevant to spacecraft environmental monitoring and advanced life support (<https://isda.jsc.nasa.gov/experiment/exper/9272>). QEPAS was proposed to the oil industry in the 2008 Offshore Technology Conference<sup>7,8</sup> for monitoring hydrogen sulfide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>), and methane (C1) inside the annulus of flexible risers because the presence of the sour gases can dramatically influence corrosion fatigue levels and may cause safety issues in operation. Based on our best knowledge and investigation in the market, the proposal has not been applied in the field and commercialized in the

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market. Starting from 2013, the Polysense Laboratory in the Polytechnic University of Bari developed custom resonators on purpose for gas sensing applications.

In a collaboration between the Polysense Laboratory, Rice University, and Saudi Aramco,<sup>10–13</sup> a new generation of a QEPAS spectrometer has been designed and prototyped in a cake box size as a portable gas analyzer for multiple hydrocarbon components. The sensor box demonstrated the capability of the QEPAS technique in measuring concentrations of C1 and ethane (C2) in ppb sensitivity level and propane (C3) in ppm level by employing a single interband cascade laser (ICL) emitting at 3.345  $\mu\text{m}$ , and the potential to detect  $^{12}\text{CH}_4$  and  $^{13}\text{CH}_4$  isotopologues at ppb level by using a quantum cascade laser (QCL) operating around 7.730  $\mu\text{m}$ . This paper aims to introduce QEPAS technology to the oil industry, illustrate the realization of a QEPAS-based gas analysis and calibration system, and summarize benching testing results and performance. This paper discusses the advantages and limits of the new technique and some potential applications in the laboratory and oil and gas fields.

## 2. GAS SENSING AND CHEMICAL ANALYSIS

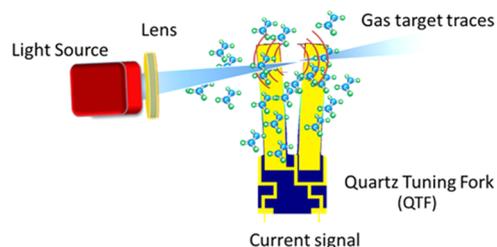
There are many types of gas sensors (detectors/monitors/analyzers), which are mainly categorized into four groups based on the detection technology: semiconductor, electrochemical, analytical (gas chromatography (GC), spectrometry), and laser optical absorption sensors.<sup>9,14</sup> In the oil industry, for operation safety, infrared point and catalytic bead (pellistor) as two major sensors are used for monitoring combustible (hydrocarbon) gas, and electrochemical sensors are used for  $\text{H}_2\text{S}$  detecting and warning. These sensors usually detect single gas component/species in ambient air, suffering from drift, cross-response to other gases, and changing humidity levels.<sup>15</sup> Therefore, semiconductor and electrochemical sensors are not suitable for quantitative and chemical analysis in downhole, flow line, and laboratory analytics environments.

During drilling, exploration, reservoir characterization, and production monitoring, fluid (gas) samples are taken from drilling mud, reservoir formation, wellhead, or separator. The samples are usually injected into GC, connecting with alternative detectors for chemical composition analysis. The most common detectors are flame ionization detectors (FIDs) for hydrocarbons, and a thermal conductivity detector (TCD) for non-hydrocarbon gases (e.g.,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_2$ ,  $\text{H}_2$ , He, and Ar).<sup>1,16</sup> Recently, a quadrupole mass spectrometer (QMS) was developed for rapid and direct analysis of C1–C10 hydrocarbons and common inorganic volatiles in mud gas logging.<sup>17</sup> Isotope ratios (e.g.,  $^{13}\text{C}/^{12}\text{C}$ , D/H) of each gas component, as geochemical fingerprints, are commonly determined by GC connected with isotope ratio mass spectrometry (GC-IRMS).<sup>18</sup> These are quite big and delicate instruments, requiring stable and strict laboratory conditions and sophisticated experts for operation and maintenance. Consequently, such high precision laboratory analyzers (GC/MS/IRMS) are incompatible with a tough and dynamic downhole environment and well site conditions. Transporting field fluid samples to a laboratory provides delayed, sparse, and sometimes unrepresentative data, which do not help in near real-time and high economic value decisions for drilling, formation/well testing, and on-site troubleshooting.<sup>19,20</sup> In addition, the sampling, transporting, sample preparation, and routine laboratory analysis are expensive operations, which are

not a pragmatic workflow to generate high resolution/time-lapse data for fluid heterogeneity and dynamics studies.

Laser-based optical absorption technology offers non-contact, fast response, minimal drift, high specificity, low maintenance requirements, and continuous monitoring, for gas detection and chemical analysis.<sup>15,21,22</sup> Several techniques, based on the Lambert–Beer law, measuring the optical absorption at specific wavelength are developed, including non-dispersive infra-red, spectrophotometry, tunable laser absorption spectroscopy (TLAS)/tunable diode laser absorption spectroscopy (TDLAS), cavity ring down spectroscopy (CRDS)/cavity-enhanced absorption spectroscopy (CEAS)/integrated cavity output spectroscopy (ICOS), and photoacoustic spectroscopy (PAS).

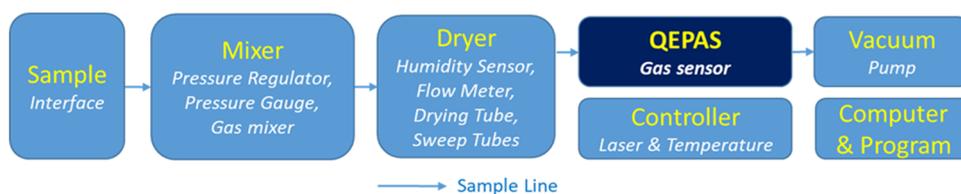
PAS, based on the photoacoustic effect discovered by Alexander Graham Bell in 1880, is an indirect optical absorption technique that does not require an optical detector and has a laser wavelength-independent responsivity. As shown in Figure 1, when a modulated laser output is absorbed by a



**Figure 1.** Schematic diagram shows the principal of PAS for gas detection and the use of QTF to enhance the photoacoustic spectroscopy (QEPAS).

target gas, the absorbed laser energy at characteristic wavelengths induces heating and expansion to create a vibration of gas molecules at the resonant frequency, subsequently resulting in the generation of an acoustic wave. A microphone transduces the pressure wave into an electrical signal proportional to the concentration (mol %, vol %) of the target gas. QEPAS is an improved approach to photoacoustic detection by replacing the microphone with a piezoelectric QTF as a sharply resonant acoustic transducer to detect weak photoacoustic excitation, allowing the sensor to be made in an extremely small size.<sup>9,11</sup>

Among the main optical sensors, QEPAS has been proven to be a leading-edge technique for out-of-laboratory detection for trace gas because of extremely high sensitivity (down to ppb/ppt), level of compactness, immunity to environmental noise and its proven reliability, ruggedness, and in-situ operation.<sup>9,11,14,23,24</sup> In a similar way to PAS, QEPAS does not require an optical detector; it reaches high detection sensitivity within the short optical pathlength, and the sound wave detection by the tuning fork is insensitive to the laser wavelength used for exciting the optical transition. These factors, together with the modularity of the whole system, represent the main advantages with respect to other laser-based techniques, such as TDLAS, CRDS/CEAS, and other multipass based spectroscopy.<sup>9,11,15,25</sup> The core part of a QEPAS sensor is the tuning fork (QTF), whose dimensions are pretty comparable with a coin, and the whole sensor could be made very compact, for example, fitting into a 2-inch internal diameter pipe for downhole operations.<sup>10,11</sup> The resonance of QTF presented high frequency stability (with frequency shift



**Figure 2.** Enclosures and sample line for the QEPAS gas analyzer system.

of  $\sim 0.035\text{ppm}/\text{C}^2$  in the temperature from  $-40$  to  $90$  °C),<sup>13</sup> suggesting that QEPAS sensors may operate in a large temperature range. In addition, the QEPAS technique has proved that it can detect multiple gas species and their isotopes.<sup>13,26</sup> The performances of the QEPAS spectrometers are also continuously improving in terms of precision, accuracy, detection limits, and response time. Furthermore, the spectral range of operation has reached the THz region, where other concerned non-hydrocarbon components such as  $\text{H}_2\text{S}$  can be more easily discriminated by the absorption bands of the alkane molecules.<sup>27</sup> Therefore, QEPAS may overcome the abovementioned disadvantages for conventional gas sensors and laboratory-based instruments and be applied in oil and gas fields for in-situ and real-time gas detection and chemical analysis.

### 3. QEPAS GAS ANALYZER SYSTEM

The QEPAS gas analyzer system consists of five major components (Figure 2): sample introduction enclosure, sample mixing enclosure, sample drying enclosure, QEPAS sensor and laser controller enclosure, and PC with QEPAS specific software.

The QEPAS spectrometer fits in a  $30\text{ cm} \times 10\text{ cm} \times 20\text{ cm}$  box (Figure 3a), containing the optical components, an ICL

operating in the spectral range  $3342\text{--}3349\text{ nm}$ , the acoustic detection module (ADM), the gas line, the pressure meter and a power meter for alignment purposes. The ADM is composed of a standard  $32\text{ kHz}$  QTF equipped with a dual tube resonator system for sound wave amplification. A PCIe-6363 NI-DAQ provides the modulation signal to the ICL and acquires the QTF signal. A LabVIEW-based software was implemented to manage the current driver/temperature controller (Thorlabs ITC4002QCL) and monitor the values of both the pressure meter and the power meter. A dedicated sub-routine of the software acts as a lock-in detector for the QEPAS signal demodulation at different integration times.

The sensing system was complemented with a gas sample control system, composed of components for sample drying, quantitative mixing (dilution) and handling the common gas samplers (cylinder and isotube) used in the industry. All components were mounted in a rack (Figure 3b) as a prototype of the gas analyzer for benching tests.

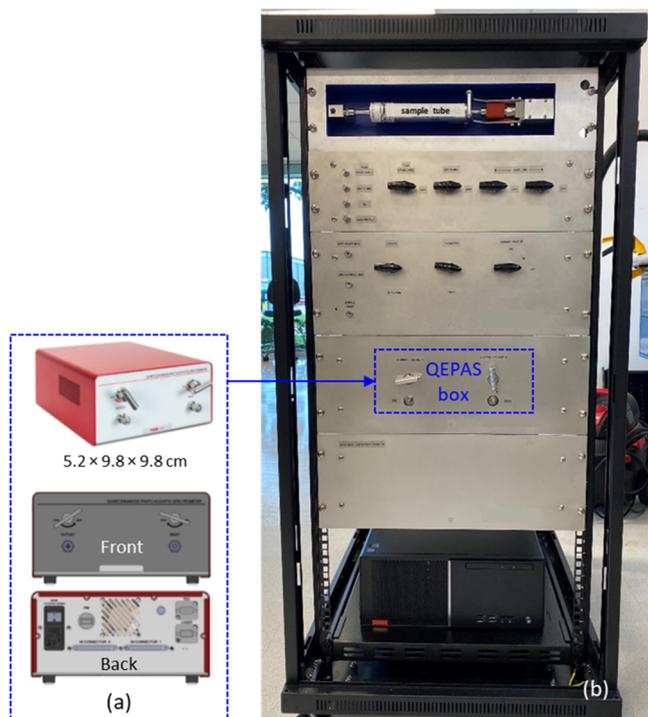
The system was designed to meet the following design parameters:

- 1) measuring major hydrocarbon gas components in typical concentrations in the natural gas field (C1: 70–100%, C2: 1–10%, and C3: <2%);<sup>1,3</sup>
- 2) handling common gas cylinders (including isotube);
- 3) preparing gas samples that need to be diluted with dry nitrogen ( $\text{N}_2$ ) and dehumidified to the level of water vapor less than 300 ppm;
- 4) calculating and reporting gas concentrations, ratios of hydrocarbons and sample pressure.

**3.1. Sample Introduction.** The QEPAS prototype system can be connected to a gas cylinder or an isotube through the sample introduction enclosure. Any common type of a gas cylinder can be connected to the QEPAS with a pressure regulator and appropriate adapters. In order to provide a driving force to fill the sensor chamber, it is necessary to pressurize the gas sample to 80 psi.

**3.2. Gas Mixing Enclosure.** The gas sample flows through the gas mixing enclosure that dilutes 1-part of the sample with 9-parts of  $\text{N}_2$ . Considering the high hydrocarbon concentration range under investigation, the gas sample needs to be diluted to avoid gas direct absorption, thus lowering the optical power available to stimulate the photoacoustic effect, and the saturation of electronic components. The dilution also helps the detection such that they do not to exceed the linearity range set by the gain of the transimpedance amplifier. This enclosure uses a commercially available gas blender to mix gas from the sample port with  $\text{N}_2$  from an external cylinder.

**3.3. Gas Drying Enclosure.** The gas sample needs to be dried before entering the QEPAS chamber to minimize the effect of moisture. In fact,  $\text{CH}_4$  may rapidly relax the energy through collisions with water vapor molecules, thus the photoacoustic generation efficiency strongly depends on  $\text{H}_2\text{O}$  concentration variations in the  $3\text{ }\mu\text{m}$  wavelength range.<sup>11</sup> The



**Figure 3.** Realization of a QEPAS-based gas analysis system. (a) QEPAS sensor box; (b) QEPAS, sample preparation enclosures and PC are assembled in a rack.

drying enclosure uses a monotube dryer to dehumidify gas samples down to 300 ppm of water vapor. The monotube dryer uses a Nafion tube to transfer moisture from the sample line to a purging line surrounding the Nafion tube.

**3.4. QEPAS Sensor with a Laser Controller.** QEPAS measures the absorption of a gas sample via photoacoustic excitation, by focusing a tunable laser beam between the prongs of a tuning fork. The laser wavelength is modulated across the absorption peak of the target gas. The gas modulated absorption generates a pressure wave. The modulation frequency matches the vibrational fundamental mode of the QTF. The quartz piezoelectric property allows the pressure wave to be converted into an electric signal. The amplitude of the signal from the QTF is proportional to the gas concentration.<sup>14</sup> The ADM houses a standard QTF resonant at  $f_0 = 32\,767$  Hz and the cylindrical acoustic resonators. A mid-infrared ICL emitting at a central wavelength of 3345 nm was employed. An optical power meter is used to align the beam through the acoustic resonator and between the QTF prongs. The alignment is improved, minimizing the noise acquired in the QEPAS scan.

**3.5. QEPAS Software.** Two programs are developed for operating the QEPAS gas analyzer. The first program is developed by Aramco Houston Research Center for monitoring the sample preparation system. PolySense Lab developed a LabVIEW-based software to both control the laser source and acquire and process the QTF data, employing a PCIe-6363 NI-DAQ. The modulation frequency provided to the laser is  $f_0/2$ . A dedicated subroutine is implemented to acquire the QTF signal and retrieve its  $f_0$  component. This  $2f$ -detection allow for the acquisition of a background-free signal.<sup>14</sup>

#### 4. LABORATORY TESTING, CALIBRATION, AND PERFORMANCE

In a previous study, a QEPAS sensor capable of detecting C1, C2, and C3 in a nitrogen-based mixture was reported.<sup>12,13</sup> The hydrocarbon concentrations ranged from 1 to 1000 ppm and the measurements demonstrated a good linearity between the QEPAS signal and the concentration of each individual component in the range (Table 1). The Allan deviation analysis showed that for 1 s integration time the detection limit for C1, C2, and C3 is  $\sim 90$ ,  $\sim 7$  ppb, and  $\sim 3$  ppm, respectively. The detection limit achieved for C2 made a record for the QEPAS technique, and measuring C3 added a new capability to the technique. These limits are well below the sensitivity needed for a sensor aiming at hydrocarbon detection in petroleum exploration and engineering, where concentrations of hydrocarbon gases are expected to be generally much above the ppm scale (usually %). C1–C2 and C2–C3 mixtures were also tested in the previous studies to demonstrate the capability of detecting multiple hydrocarbons by QEPAS.

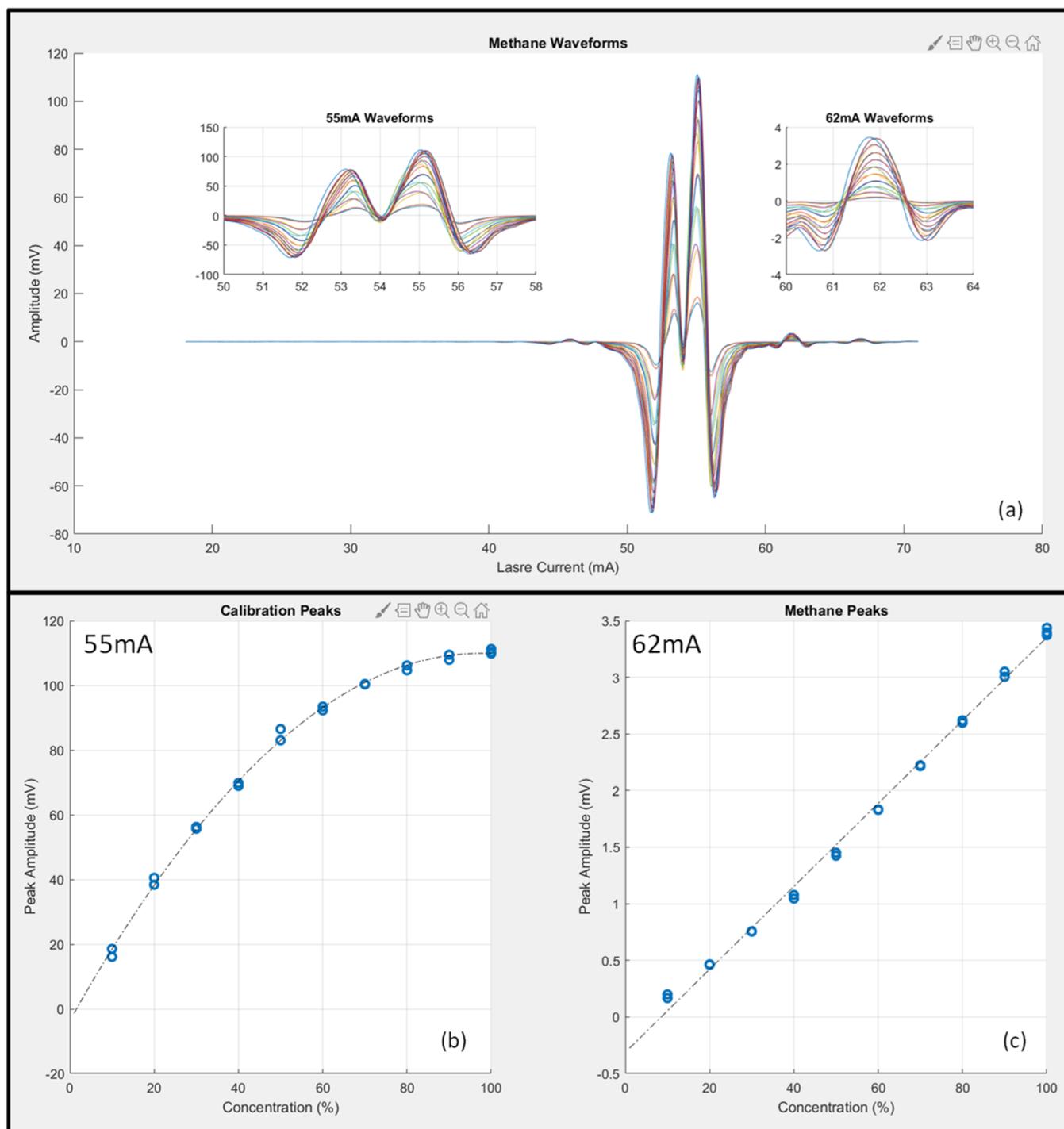
In this study, the QEPAS gas analyzer system including the sensor box and new components of sampling preparation (Figure 3) with enlarged concentration ranges for individual C1, C2, and C3 that are typically encountered in natural gas samples from oil and gas fields (Table 1, Figures 4–6) for linearity assessment is presented. A series of C1–C2 and C1–C2–C3 mixtures were tested, confirming that QEPAS can measure C1, C2, and C3 in the three-hydrocarbon-components gas mixture and extending this capability also at concentrations in the percentage scale.

Table 1. Performance Comparison of QEPAS with Representative Optical Sensors for Hydrocarbon Gas Detection

	CRDS			TILDAS			QEPAS		
	C1	C2	C1	C1	C2	C1	C2	C3	
precision	30 ppb	10 ppb	300 ppt	90 ppb	50 ppb	90 ppb	7 ppb	3 ppm	
response time	<1 s	<1 s	<1 s	<1 s	<1 s	<1 s	<1 s	<1 s	
linearity range	1–5000 ppm	0–500 ppm	0–100 ppm	0–1000 ppm	0–50 ppm	0–1000 ppm	0–1000 ppm	10–1000 ppm	
linearity range				4–1000 ppm		2–100 ppm	2–100 ppm	200–1000 ppm	
linearity range				100 000–1000 000 ppm (10–100%)		10 000–100 000 ppm (1–10%)	10 000–100 000 ppm (0.2–2%)	2000–20 000 ppm	

Sampaolo et al., (2020)<sup>13</sup>

Sampaolo et al., (2019)<sup>12</sup>  
this study



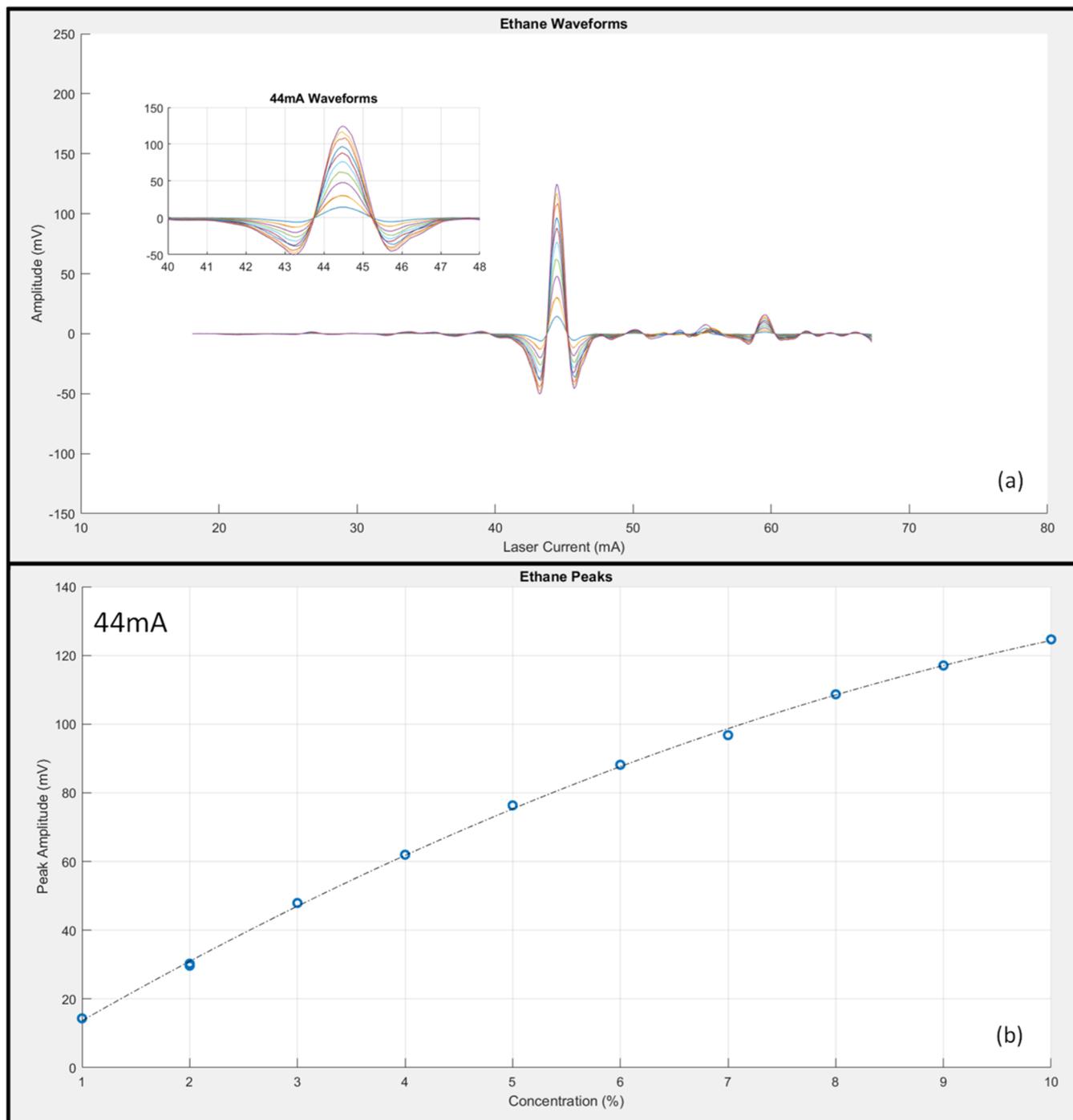
**Figure 4.** (a) QEPAS spectra for methane testing, (b) relation between peak amplitude and concentration for calibration peaks at 55 mA, and (c) relation between peak amplitude and concentration for methane peaks at 62 mA.

#### 4.1. Single Component (C1, C2, and C3) Testing.

Standard C1, C2, and C3 gases with certified concentrations and high purity (99.9999%)  $N_2$  were used to prepare artificial gas samples. Each gas was diluted using the  $N_2$  into different concentrations to generate a hydrocarbon mixture that may be encountered in natural gas samples from oil and gas fields. C1 samples were diluted in a very large concentration range from 10% to 100% for the variation of C1 concentration in oil-associated gas (least C1), condensate, wet gas, dry gas,<sup>3</sup> or

biogenic gas (predominated C1).<sup>2</sup> C2 and C3 samples were diluted in the range of 1 to 10% and 0.2 to 2%, respectively.

Measurements were performed across the range of concentrations for each single gas component. Two samples taken at each target concentration were analyzed to check the reproducibility. QEPAS spectra and calibration for the C1, C2, and C3 QEPAS spectra, respectively, are shown in Figures 4–6. The higher concentration scales considered in this work required the detection strategy to consider the sensible variations of the gas matrix and the non-linearity arising



**Figure 5.** (a) QEPAS spectra and for ethane testing and (b) relation between peak amplitude and concentration for ethane peaks at 44 mA.

from the high absorption coefficients. Indeed, the photoacoustic generation is sensitive to the target molecule relaxation dynamics, which depends on the energy transfer efficiency through collisions with other molecules in the gas mixture. Furthermore, the percentage concentrations reached in this investigation, combined with the intense line-strengths characterizing the C1, C2 absorption features exploited by Sampaolo et al. (2019, 2020),<sup>12,13</sup> determined a non-linear relation between the QEPAS signal recorded at those wavelengths and the concentration of the target molecule. This is due to the Lambert–Beer law, which rules the light absorption through a gas sample as:

$$I_{\text{abs}} = I_0(1 - e^{-\alpha \cdot l})$$

where  $I_0$  is the incident light,  $l$  is the interaction pathlength, and  $\alpha$  is the absorption coefficient.

This relation can be linearized as

$$I_{\text{abs}} = I_0 \cdot \alpha \cdot l$$

for small absorptions, which is the case trace gas detection via QEPAS. This is not the case for the C1 two-fold structure with the strongest peak at 55 mA, C2, C3 calibrations.

In Figure 4, it can be easily noticed that the C1 QEPAS peak signal at 55 mA is saturating while approaching the 100%

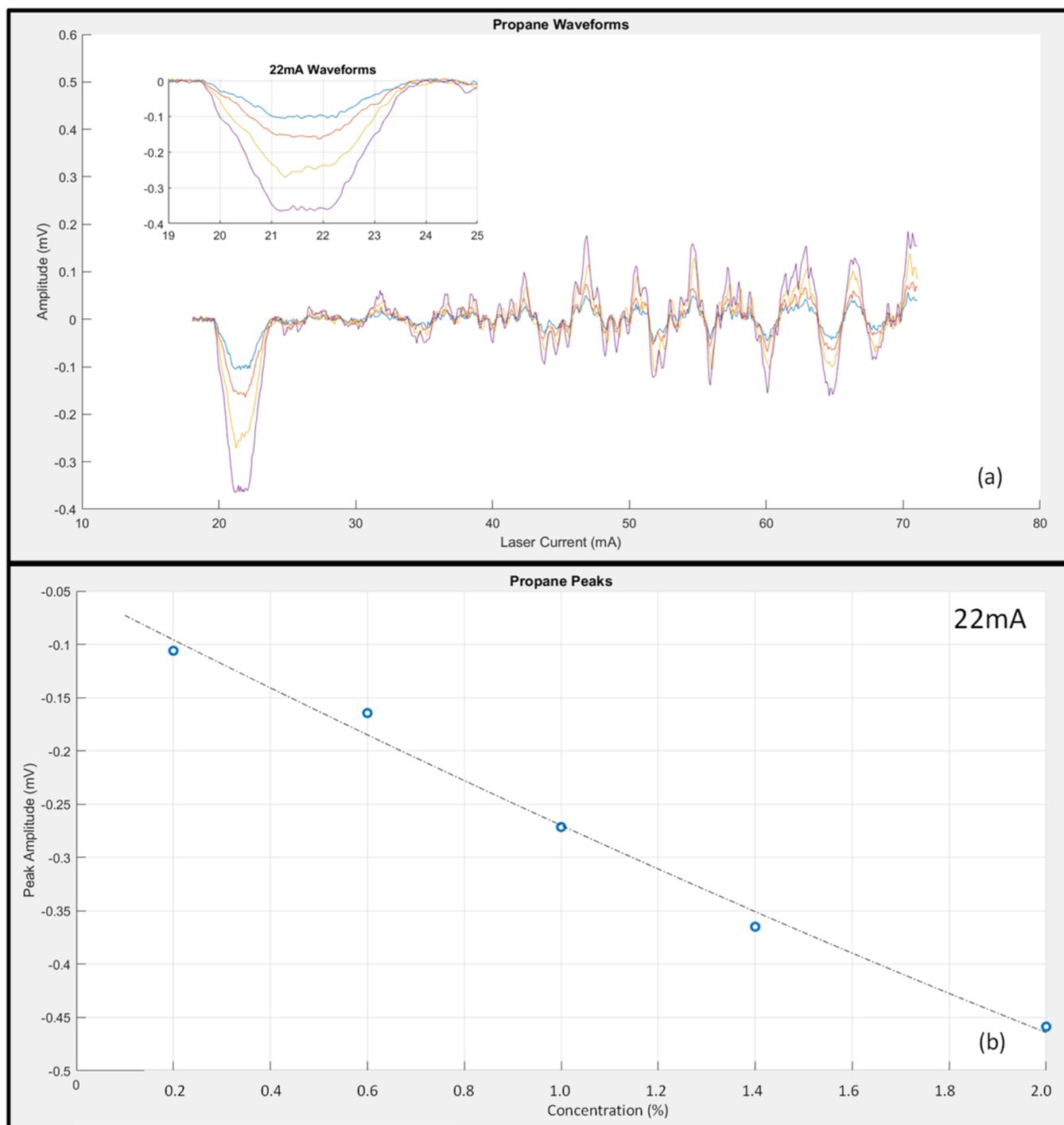


Figure 6. (a) QEPAS spectra for propane testing and (b) relation between peak amplitude and concentration for propane peaks at 22 mA.

concentration (10% after dilution in pure  $N_2$ ) and the shape of the QEPAS spectrum also suffers from a progressive distortion due to the increased absorption. On the contrary, the QEPAS signal at 62 mA shows a good linearity as a function of the concentration because of the much lower line-strength associated with the excited optical transition.

In Figure 5, the calibration of the 44 mA C2 peak signal is plotted. The QEPAS signal amplitude shows a sub-linear trend versus concentration, demonstrating how direct absorption impacts on a C2 calibration curve even in a concentration range one order of magnitude lower with respect to C1. This is due to an overall C2 cross-section at 44 mA approximately

twice as large as C1 at atmospheric pressure. However, this calibration curve is a monotonically strictly increasing function of the concentration, and it can be fitted by a polynomial.

The portion of the QEPAS spectrum used as a diagnostic feature for evaluating the broadband absorption of C3 was identified in the 20–23 mA window, in which a linear behavior (Figure 6) has been verified as well.

**4.2. C1–C2 and C1–C2–C3 Gas Mixtures Testing.** While C1 and C2 detection is straightforward, thanks to the well-defined absorption peaks in the ICL operating range, C3 detection requires the extraction of its characteristic broadband absorption profiles which merge with C1 and C2 background

signals in the ICL tuning range. Previous studies showed no cross-talk between C1 and C2 in the QEPAS spectra of C1–C2 gas mixtures and developed a fitting procedure with a linear combination of reference spectra to retrieve C2 and C3 concentrations with high accuracy in the C2–C3 mixtures under test.<sup>12,13</sup> Because of the abovementioned reasons, the detection scale extension to per cents presented in this work required the implementation of a multilinear regression, based on the iterative analysis of different windows of the QEPAS spectra. The algorithm exploits the saturated absorption of C1 to evaluate the effect of the gas sample matrix on methane and the calibration curves related to each diagnostic peak to extract C1, C2, C3 concentrations. In terms of energy relaxation dynamics within gas samples with fluctuating backgrounds, the cross-correlation among the first three alkanes will be illustrated in detail in a further article, together with a systematic description of the multivariate approaches that can be successfully implemented.

Two- (C1–C2) and three-components (C1–C2–C3) gas mixtures were used in the tests to evaluate the performances of the QEPAS systems, in terms of accuracy, precision, and linearity between actual and measured concentration in multicomponent gas mixtures. Certified 10% C1/N<sub>2</sub>, 10% C2/N<sub>2</sub>, and 10% C3/N<sub>2</sub> cylinders were diluted by pure N<sub>2</sub> in the gas mixing enclosure to make gas samples in the representative range as observed in the field (C1: 70–100%, C2: 2–10%, C3: 0.4–2%). Their actual concentrations and QEPAS-measured values are compared and displayed in Table 2 and Figure 7 for C1–C2 mixture, and Table 3 and Figure 8 for C1–C2–C3 mixture.

**Table 2. Gas Concentrations (%) and Ratios of C1–C2 Mixture in the Bench Testing**

mixture#	C1 (%)		C2 (%)		C1/C2	
	actual	measured	actual	measured	actual	measured
1	98.0	98.0	2.0	1.8	49.0	54.4
2	95.0	94.7	5.0	4.6	19.0	20.6
3	90.0	88.2	10.0	10.0	9.0	8.8
4	90.0	90.4	5.0	4.6	18.0	19.7
5	80.0	81.5	10.0	10.0	8.0	8.2
6	80.0	81.9	5.0	5.1	16.0	16.1
7	70.0	70.4	10.0	10.0	7.0	7.0
8	70.0	70.6	5.0	5.2	14.0	13.6

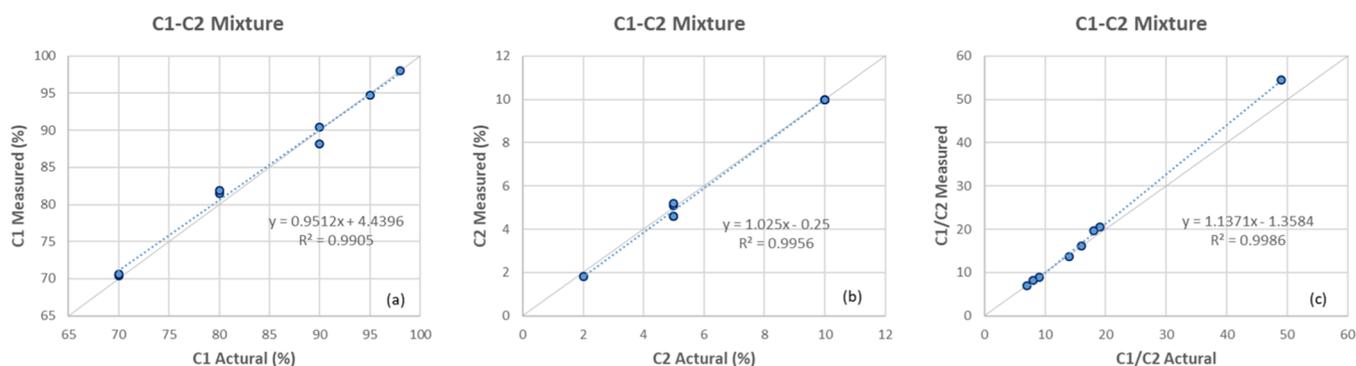
For C1–C2 mixture, the measured C1 and C2 concentrations are very close to their actual values, showing good

linearity with  $R^2 > 0.99$  (Figure 7a,b). The C1/C2 ratio, which is commonly used as a proxy of gas dryness and a geochemical fingerprint,<sup>2</sup> also shows a good linearity ( $R^2 > 0.99$ , Figure 7c), but with a deviation when C1 presented the highest concentration (98%) and C2 presented the lowest concentration (2%) in the samples under test. This is mainly due to the efficiency of the analysis method in discriminating relatively low C2 concentrations from the C1 background absorption signal.

For the first time, the detection of C1, C2, and C3 in a gas mixture at the percentage scale using QEPAS technology is reported. As shown in Figure 8 for the C1–C2–C3 mixture, comparisons between actual and measured data demonstrate a fairly good linearity ( $R^2 > 0.977$ ). C1 concentration values are the most immediate evidence of the margin for improvement that the current analysis method has in quantifying the effect of matrix variations on the detection of individual components. On the other hand, C3 underestimation is an indication that the present spectral range is not the optimum choice for C3 detection in natural gas such as mixtures. Indeed, the identification of a more characterizing fingerprint for C3, clearly distinguishable with respect to the absorption background of the other hydrocarbons and relying on a higher absorption cross-section, would definitely help the analysis method in accurately retrieving propane concentration. Obtaining accurate concentrations for components in a gas mixture consisting of homologous compounds (e.g., hydrocarbons) is much more challenging than dealing with single or two components.<sup>13,26</sup> However, the good correlation and linearity between all measured gas concentrations and ratios and their actual values suggest that QEPAS sensors are capable of detecting C1, C2, and C3 in oil and gas applications and improved algorithms may generate more accurate results. Several aspects will be pursued to enhance the performance of the QEPAS system:

- 1) quantitative control in the gas mixing enclosure;
- 2) selective features for better defining C3 in the background with C1 and C2;
- 3) testing in a larger concentration range for C2 and C3 to have a more dynamic calibration curve;
- 4) trying a partial least square multivariate analysis and machine learning method to optimize the procedure to calculate gas concentrations in the mixture.

Currently, we suggest using the ratios of C1/(C1 + C2 + C3) as a dryness parameter/geochemical fingerprint in the application of the QEPAS system; because the gas ratio as a procedure of normalization eliminates the error and demon-



**Figure 7.** Comparison of actual and measured gas concentrations and ratios in the bench testing on C1–C2 mixture.

Table 3. Gas Concentrations (%) and Ratios of C1–C2–C3 in the Bench Testing

mixture#	C1 (%)		C2 (%)		C3 (%)		C1/C2		C1/(C2+C3)		C1/(C1+C2+C3)	
	actual	measured	actual	measured	actual	measured	actual	Measured	actual	measured	actual	measured
1	93.0	96.0	2.0	2.0	1.0	0.7	46.5	48.0	31.0	35.6	0.97	0.97
2	90.0	91.6	8.0	8.1	0.4	0.2	11.3	11.3	10.7	11.0	0.91	0.92
3	90.0	92.5	5.0	4.5	1.0	0.6	18.0	20.6	15.0	18.1	0.94	0.95
4	85.0	84.3	10.0	10.0	1.0	0.7	8.5	8.4	7.7	7.9	0.89	0.89
5	80.0	80.6	10.0	10.0	2.0	1.6	8.0	8.1	6.7	6.9	0.87	0.87

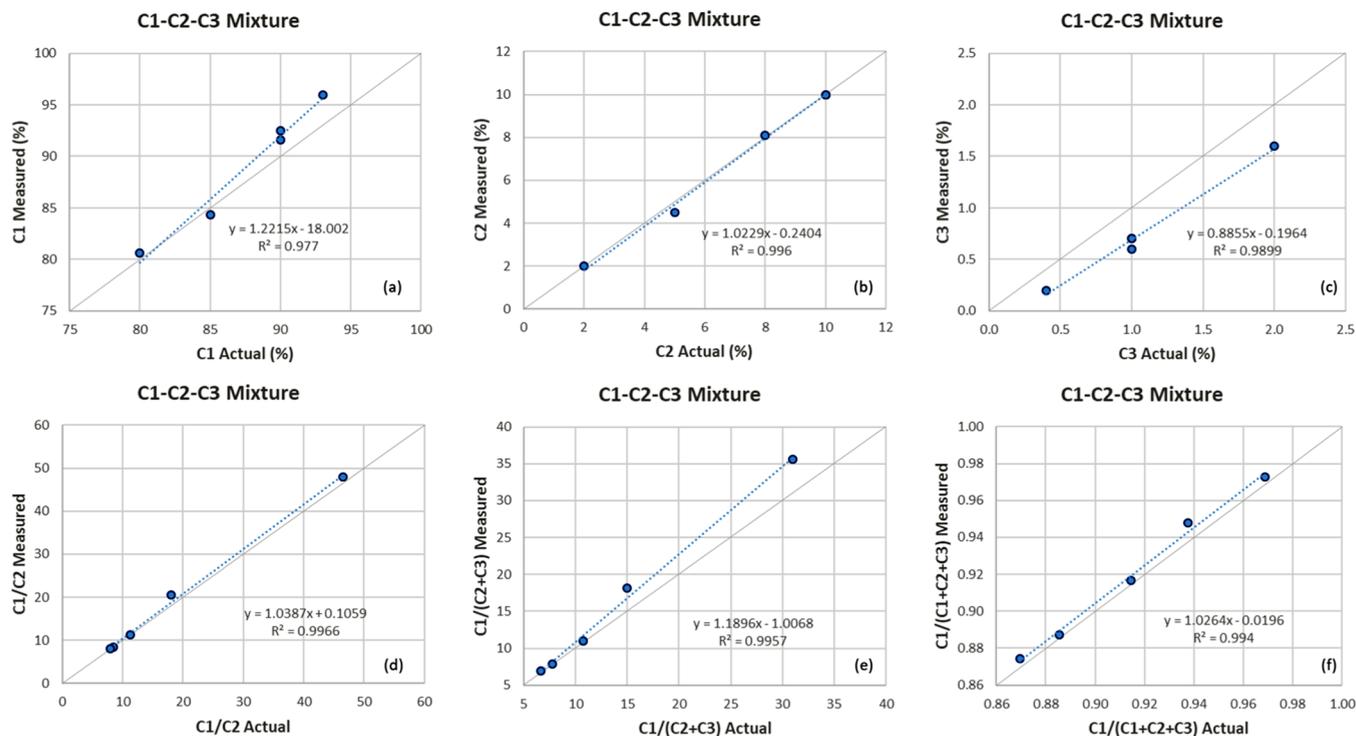


Figure 8. Comparison of actual and measured gas concentrations and ratios in the bench testing on C1–C2–C3 mixture.

strates better results than direct use of the concentrations (Figure 8d,f).

## 5. DISCUSSION

**5.1. Gas Species, Multicomponent Mixtures, and Natural Gas Samples.** The QEPAS system reported in this study represents an advancement of QEPAS sensor prototypes demonstrated by Sampaolo et al. (2019; 2020)<sup>12,13</sup> by expanding the detection range to per cents scale and setting the basis for C3 detection in multicomponent mixtures mainly based on hydrocarbons. More than 25 gas species now can be detected and quantified by QEPAS,<sup>9,11,14,23,24,28–30</sup> including the most common and business-impacted gas species (C1, C2, C3, CO<sub>2</sub>, and H<sub>2</sub>S) in the upstream of oil industry (Figure 9). The best noise equivalent concentration, as a parameter of minimum detection limit, were reported as a function of the employed laser wavelength.<sup>9,29</sup> Although GC-FID/TCD and QMS used in laboratory and mud gas unit can measure the full range of hydrocarbon gas species (C1–C10) and more inorganic gas components, QEPAS demonstrates extremely high sensitivity as ppb level of some gases can be detected (Figure 9) over GC-FID/TCD and QMS (usually ppm level).<sup>16,17</sup>

QEPAS can reach high detection sensitivity at the short optical pathlength and have immunity to environmental noise,

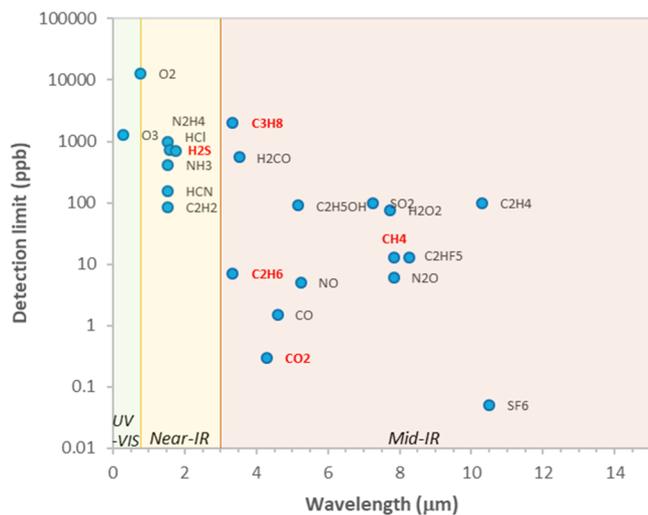


Figure 9. Minimum detection limits and operating spectral region for QEPAS-based gas sensors. The gas species with interest from the oil industry are marked with red labels.

representing the main distinct advantages among optical absorption spectroscopies.<sup>9,29</sup> In contrast to those well-developed optical absorption techniques (e.g., CRDS and

TILDAS), QEPAS detection displays some cons and pros (Table 1). The three sensors listed in the table are portable devices sharing the advantage of a fairly low response time and high precision and sensitivity, thus allowing for measurements in real-time and/or in a continuous monitoring mode. As discussed by Sampaolo et al., (2020),<sup>13</sup> the outstanding precision in the ppt range provided by the TILDAS sensor limits on the other hand the detection range, leading to the deployment of this device mainly in environmental monitoring of C1 and C2 (as stray gas) and scientific studies (e.g., space exploration). Another distinct advantage of QEPAS over TDLAS and other absorption spectroscopy is that its performance can be improved when the output of the excitation laser source is increased.<sup>23</sup> The QEPAS sensor tested shows comparable performances in terms of precision compared to the CRDS sensor, and additionally offers C3 concentration with a precision in the ppm range. In the study by quantitative dilution performed in the gas mixing enclosure of our QEPAS system, the detection ranges have been significantly enlarged for natural gas samples from oil and gas fields (Table 1).

QEPAS has demonstrated the capability of detecting multiple gas species,<sup>9,22,26,29</sup> which is a main advantage over “unconventional” semiconductor and electrochemical gas sensors. Individual H<sub>2</sub>S, CO<sub>2</sub>, and C1 gas (diluted in N<sub>2</sub>) were successfully tested in laboratory with QEPAS, and the technology was introduced to oil industry for continuous monitoring the chemical environment inside flexible risers by Weppenaar et al., (2009).<sup>7</sup> However, application of QEPAS to chemical composition analysis on multicomponent gas mixtures is difficult because of complex processes linked to the speed of sound, molecular relaxation dynamics, and overlapping of absorption lines. A QEPAS using near-infrared, fiber-coupled diode lasers as an excitation source and data analysis algorithm were developed to determine chemical composition of gas mixtures with H<sub>2</sub>S, CO<sub>2</sub>, and C1 at concentrations 0–100%.<sup>26</sup> The pilot study provided a guideline and suggested that it was possible to utilize multivariate regression, nonlinear least square fitting, or machine learning for deriving gas concentrations regardless of the complexity of the involved phenomena.

Simultaneous multicomponent gas detection using a standard QEPAS approach is not feasible because the standard configuration is based on a sequential excitation of separated absorption features, or a continuous wavelength scan over a broad absorption to discriminate the different contributions to the spectrum. The force sensing-based QTF cannot recognize the gas component inducing the acoustic wave. In both cases, there is a time delay in measuring two or multiple gas target concentrations.<sup>29</sup> The fundamental resonance frequency was recently reduced via custom QTFs, allowing the simultaneous excitation of the QTF on both the fundamental and first overtone modes employing the same or different laser sources. A QTF frequency division multiplexing technique was developed for the first demonstration of simultaneous dual-gas (C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub>O) sensing by QEPAS.<sup>31</sup> A number of dual-gas (two components) can be simultaneously detected by QEPAS, however, the triple-gas (three components) still require a wavelength scan. We demonstrate in the paper a QEPAS gas analyzer that is capable of a fast response detection of C1, C2, and C3 using a single ICL source operating around 3.3 μm, representing a breakthrough of QEPAS technology for hydrocarbon sensing applications.

Expanding the detection for C3+ gas species and including H<sub>2</sub>S and CO<sub>2</sub> in a QEPAS sensor is a very challenging task, but very important for applying the QEPAS sensor in analyzing natural gas samples from drilling, downhole sampling, well testing, and production. In the natural gas sample, the background absorption will rise up from C2, C3 and the heavier molecules (C4, C5, etc.),<sup>13</sup> and there might be cross-talk between the partial overlapping lines of CO<sub>2</sub> and H<sub>2</sub>S.<sup>26</sup> In this case, each molecule must be spectrally characterized to generate a reference spectrum as a function of the laser wavenumber  $\lambda$  at a fixed concentration. Then, a fitting procedure based on linear combination of reference spectra can be constructed for correlating the QEPAS response with gas concentration.<sup>13,29</sup>

**5.2. Isotope Analysis.** Gas isotopes, in particular the isotopic composition or isotope ratio of a gas component (e.g.,  $\delta^{13}\text{C}$  of CH<sub>4</sub>), are very useful in determining the origin of gas, estimating thermal maturity, and representing a fingerprint of reservoir compartmentalization study and production allocation.<sup>2,18</sup>

An early study using the modulation cancellation method separated H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>16</sup>O in water vapor from QEPAS signal. The sensitivity in measuring the deviation from a standard sample was 1.4‰ for  $\delta^{18}\text{O}$ , in 200 s of integration time.<sup>32</sup> A QEPAS sensor with a continuous-wave ICL, emitting at 4.35 μm, was capable of distinguishing <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> and measuring  $\delta^{13}\text{C}$  of CO<sub>2</sub> with an average precision <1‰, which fulfills the precision requirement of most medical and field applications.<sup>33</sup> A mid-IR QCL emitting at 7.73 μm, was used in a QEPAS sensor to selectively detect <sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> isotopologues at ppb sensitivity level.<sup>13</sup> A standard methane sample was tested, and the standard abundances of ~98.82% <sup>12</sup>CH<sub>4</sub> and 1.11% <sup>13</sup>CH<sub>4</sub> were verified. The QEPAS sensor is expected to detect the variation of  $\delta^{13}\text{C}$  below 1‰ with an integration time in the order of magnitude of tens of seconds for methane with percents concentration in a gas mixture, typical of natural gas samples. The two prototypes for C1 isotope and hydrocarbon gas (C1–C3) concentrations determination can be potentially integrated into a QEPAS sensor box.<sup>13</sup>

Isotope ratios are critical geochemical parameters or fingerprints for petroleum system analysis, fluid characterization, and injection and production surveillance. The advances in isotope analysis with QEPAS sensors add a strength of the optical sensing technology in geochemical analysis, which would promote the application of QEPAS gas sensing in on-site fluid characterization and real-time/time-lapse monitoring.

## 6. CONCLUSIONS AND THE WAY FORWARD

QEPAS is a novel laser-based optical absorption technology for gas sensing and chemical analysis. The technology is versatile in detecting trace gas and measuring concentrations and isotopic compositions of multiple gas components. Recent advances have demonstrated the features of QEPAS sensor, including extremely high sensitivity (down to ppb/ppt), high level of compactness, immunity to environmental noise, insensitivity of resonator to the excitation wavelength, potential for continuous monitoring, reliability, and robustness for in-situ operation.

QEPAS takes the main advantages in multicomponent gas detection and quantitative analysis over semiconductors and electrochemical sensors. QEPAS currently cannot measure the

extensive gas species for their concentrations and isotopic compositions in natural gas samples as the laboratory-based analytic instruments (e.g., GC-FID/TCD, QMS, IRMS). However, the optical sensor is much smaller and relatively cheaper, requiring less maintenance and offering quicker analysis with higher sensitivity than the laboratory-based instruments. As discussed, the two advantages of the QEPAS over other optical sensing techniques (e.g., CRDS, ICOS, TILDAS) are (1) the capability to measure C3 concentration and (2) extremely high sensitivity in short optical pathlengths. Comparing technical specifications and performances is beyond the scope of the paper.

Being beneficial from the features and advantages, QEPAS has been proposed for field applications in monitoring sour gas (H<sub>2</sub>S, CO<sub>2</sub>) in an offshore riser,<sup>7</sup> downhole gas analysis,<sup>10</sup> early fire,<sup>6</sup> leak detection, and health-safety-environment monitoring.<sup>29</sup> A typical QEPAS sensor system can be compacted in a small size with light weight, supporting the deployment of the sensor in a portable analyzer, a downhole tool, and an unmanned aerial vehicle.<sup>23,34</sup> Several real-world applications of QEPAS have already been reported,<sup>35,36</sup> including carbon monoxide (CO) detection in urban area, monitoring of methane (CH<sub>4</sub>) in landfills, and leak detection of sulfur hexafluoride (SF<sub>6</sub>) in a vacuum-seal test station for diesel engine injector.

In this study, a QEPAS-based hydrocarbon gas analysis system was developed and tested. The QEPAS sensor is highly sensitive for hydrocarbon gas detection (ppb to 10 ppm level). The sensor is not suitable for direct analyzing natural gas samples with hydrocarbon components in ppm to % level. We integrated multiple enclosures for gas introducing, mixing, and drying with a QEPAS sensor box in a rack and developed the associated software to monitor sample preparation and retrieve the hydrocarbon concentrations. We realized a new QEPAS prototype for detecting hydrocarbon gas (C1, C2, and C3) and measuring their concentrations for the oil industry sample by quantitative dilution and optical sensing. The implementation of quantitative dilution in our system expands the linearity range of the QEPAS detection from ppm to % range.

The prototype system was tested with C1, C2, and C3 single components and C1–C2 and C1–C2–C3 mixtures, with a series of concentration gradients that are typically encountered in natural gas samples from oil and gas fields. Good linearity relations between QEPAS response and concentration at % level are shown for the single, binary and ternary components, confirming that measuring concentrations in % level and multicomponent gas detection can be achieved by the system. Especially, it is the first time to report the ternary C1–C2–C3 mixtures at % level.

Although there are some deviations of measured C1%, C3%, and C1/(C2 + C3) ratio compared to actual values, all measured concentrations and gas ratios illustrate good linear correlation with actual values (Figure 8), suggesting that it is highly possible to generate more accurate results by improving calibration curves and the multivariate approach implemented.

Future developments and applications of QEPAS technology in the oil industry include (1) testing natural gas samples and developing the detection strategy to determine gas concentrations and isotopic compositions in the real samples (complex mixture); (2) integrating CO<sub>2</sub> and H<sub>2</sub>S sensors with the hydrocarbon gas sensor in a compact device; (3) reducing the size and increasing robustness for field deployment; and (4) developing the applications of on-site gas

analysis while drilling, testing, and production, by the advanced sensing, to support real-time decision making and time-lapse operation.

## AUTHOR INFORMATION

### Corresponding Authors

**Pan Luo** – EXPEC Advanced Research Center, Saudi Aramco, Dhahran 31311, Saudi Arabia; [orcid.org/0000-0002-6548-4179](https://orcid.org/0000-0002-6548-4179); Email: [pan.luo@aramco.com](mailto:pan.luo@aramco.com)

**Jonathan Harrist** – Houston Research Center, Aramco Americas, Houston, Texas 77084, United States; Email: [jonathan.harrist@aramcoamericas.com](mailto:jonathan.harrist@aramcoamericas.com)

**Angelo Sampaolo** – Polysense Lab, University and Politecnico of Bari, Bari 70126, Italy; Email: [angelo.sampaolo@poliba.it](mailto:angelo.sampaolo@poliba.it)

### Authors

**Giansergio Menduni** – Polysense Lab, University and Politecnico of Bari, Bari 70126, Italy

**Rabah Mesdour** – Unconventional Reservoir Engineering Department, Saudi Aramco, Dhahran 31311, Saudi Arabia

**Nathan StMichel** – Houston Research Center, Aramco Americas, Houston, Texas 77084, United States

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.1c05645>

### Notes

The authors declare no competing financial interest.

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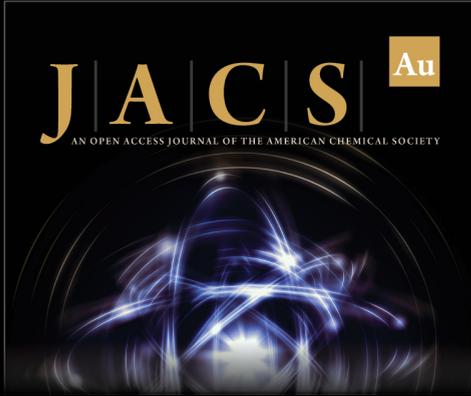
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