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Fiberoptic Gas Monitoring of Flexible Risers

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Abstract

This paper presents a new advancement within the field of optical gas measurement with applications to the monitoring of gases inside the annulus of flexible risers used in the offshore industry. This advancement is based on the novel Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) technology. Specifically, we report on the first demonstation of such a gas sensor system using a spectraphone (a module for detecting laser-induced sound) consisting of a quartz tuning fork (QTF)/microresonator assembly and two commercial single frequency diode lasers operating at λ =1.58 μm for detecting H_2S as well as CO_2 and at 1.65 μm for detecting CH_4. A minimum detectable H_2S concentration of 10 ppmv (parts per million by volume) at the 1σ level was obtained for t=1 s averaging time, scaling down as $1/t^{1/2}$ up to 1000 s (verified) This implies that a 100 s sampling time will result in a minimum detectable concentration of 1 ppm. For CO_2 and CH_4, the minimum detectable concentrations were 270 and 1.5 ppm, respectively. The measurement technique will be described and test results will be presented along with implications for the field of riser condition monitoring.

This system will allow continuous monitoring of the annulus chemical environment in flexible risers. Current gas monitoring solutions are either offline with a low sampling frequency or require cumbersome EX protection near the pipe (gas chromatography). By contrast, the proposed technique will allow a compact sensing unit connected only with fiberoptics that can monitor annulus gas levels continuously and with high accuracy.

Laboratory test results show a high level of measurement accuracy even over short timescales. These results show a clear advantage over conventional systems due to the real-time sampling, and the compact final design being free of electrical leads allows for a compact bolt-on solution which can be installed almost anywhere without compromising working space. This also minimises the number of work-hours necessary near the pipe to maintain the monitoring system.

Wells may change fluid composition in a way which brings the problem of corrosion fatigue to a riser never intended for these conditions. For example, wells which initially were sweet may become sour over time. Having a gas monitoring solution in place will allow for real-time risk assessment as well as a warning system for changes in riser annulus conditions. For sour service pipes, a gas monitoring solution will allow up-to-date and highly precise corrosion fatigue calculations. Combining the input from gas monitoring with the data from other sources, such as strain and temperature monitoring, will give unprecedented insight into the field service conditions of a riser, yielding a far greater level of operating safety than previously feasible.

Introduction

The need for monitoring of flexible risers is becoming ever more apparant as oil exploration moves to greater depths and wells can be hotter and more sour than seen so far. In this situation where the limits of pipe design need to be reliably expanded, continuous monitoring of pipe health becomes a priority.

Internal and external monitoring of pipe strain and temperature are on their way to becoming established technologies (Weppenaar and Kristiansen 2008) with all the operational safety and lifetime extension these technologies enable. However, the field of annulus gas monitoring has so far been lagging, in that no accurate sensing technology which is continuous, accurate and free of electrical leads has existed. Monitoring of annulus gas levels can be vital to a reliable estimate of pipe health, since the presence of gases such as H_2S and CO_2 can dramatically influence corrosion fatigue levels. In fact, knowledge of strain and temperature conditions in a pipe can be insufficient for a pipe operating under sour conditions when it comes to accurately calculating remaining pipe lifetime.

This paper will introduce the QEPAS gas sensing technology and compare it to existing gas monitoring and inspection options. QEPAS [Kosterev, Bakhirkin, Curl and Tittel, 2002, Kosterev, A.A. 2001] satisfies the requirements for the detection, quantification and monitoring of gas mixtures containing H_2S with a precision and accuracy of < 10 ppm, as well as CO_2 and CH_4 of< 1000ppm in flexible risers. The performance of a first prototype sensor consisting of one spectraphone, two near-infrared telecommunication diode lasers and the associated control electronics will be reported. The sensor is capable of monitoring the three target gases simultaneously. Furthermore, the next steps towards a commercially available sensor will be discussed.

Existing gas sensing methods
Due to the demands for EX proofing, transmission lengths and operational robustness, fiberoptical sensing methods are an ideal way of monitoring flexible risers, as explained in more detail by [Weppenaar and Kristiansen, 2008]. However, while the methods of Fiber Bragg Gratings and Brillouin Scattering are relatively easy to adapt for use in the annulus environment, no optical gas sensing method has been feasible for use in flexible pipes due to a number of problems, such as insufficient sensitivity and large optics. Therefore, gas monitoring has been carried out in two ways. One is to install a traditional electrically-based gas sensor such as a gas chromatograph close to the pipe and enclose it in EX protection, which is an expensive and bulky option. The other way has been to manually sample the annulus gas in bags and have these sent to a laboratory for analysis. This approach has the downside that it requires manual work near the pipe, sampling is infrequent, the accuracy is low and the results can be several days in coming. Therefore, a real-time, autonomous optical gas sensing method which can replace existing inspection methods would be highly desirable.

The simplest method of optical gas sensing is absorption spectroscopy (AS) in which broadband light is transmitted through the gas sample to be measured and collected by an analyser afterwards. Since each gas absorbs light at specific wavelengths, the collected light will have a reduced intensity at different wavelengths dependent on the gas types present, their concentration and the length the light has traveled through the sample. Analysing the collected spectrum will allow a determination of which gases are present in which concentrations, but the method suffers from poor sensitivity and selectivity. The light has to pass through several kilometers of sample in order to get a good signal above background noise sources, and even then the detection sensitivity cannot be better than ~ 100 ppmv (parts per million by volume) for a target gas such as H_2S. This sensitivity is not sufficient for a gas such as H_2S, which can have a measurable effect on corrosion fatigue at levels as low as 5 ppmv. Furthermore, the optics needed to provide several km of optical path are sensitive to mechanical disruptions and can easily lose alignment which will make the sensor inoperable. A more advanced version of AS, laser absorption spectroscopy (LAS) can achieve the required sensitivity, but at the expense of complexity, cost and physical size.

Another optical gas sensing method is photoacoustic absorption spectroscopy (PAS), in which laser light is sent through the sample as before, but in this case the laser light is modulated so that the laser sends out short pulses of light, where the pulsing is in the kHz region. In other words, the laser light resembles the output of a stroboscope and in effect 'blinks' very rapidly (Fig. 1). The wavelength of the laser is in this case chosen to match a known absorption wavelength of one of the gases in the sample. When the light is absorbed, the gas is heated locally and expands. Between pulses, the gas contracts again. When this occurs several thousand times per second, the expansion and contraction of the gas makes it act like a loudspeaker and emit sound at the frequency of the laser pulsing. This sound can be picked up by a nearby microphone, and the sound intensity is directly proportional to the gas concentration. To enhance the amplitude of the PAS sound, it is common to surround the gas sample with an acoustic resonator [Miklos,Hess and Bozoki 2001]. In such a configuration the amplitude of the sound wave builds up during Q laser modulation periods, where Q is the quality factor of the acoustic resonator (typically ~ 20-200). Usually PAS resonators are designed for frequency values in the 500 to 4,000 Hz range. A PAS based sensor does not require warm-up, daily calibration, any consumable materials or gases, and is easy to operate. Other important advantages of this method are that the detection sensitivity can be increased by increasing laser power and that it requires no delicate optical components. It is possible to achieve minimum detectable concentrations at ppbv levels using mid-infrared laser sources.
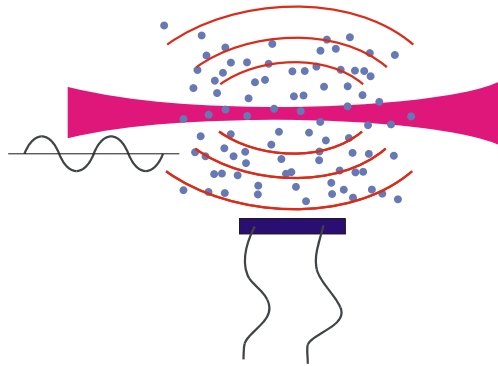
Fig 1: Principle of photoacoustic absorption spectroscopy

However, for monitoring H_2S with a precision and accuracy of < 100 ppm, as well as CO_2 and CH_4 of< 1000ppm, reliable, single-frequency fiber-coupled diode lasers operating in the near-IR region are better suited because of their commercial availability and low cost. The industrial-grade packaging of near infrared diode lasers allows direct integration of such semiconductor sources into compact gas sensors. If necessary due to detection sensitivity requirements, fiber amplifiers can boost the optical power of diode lasers to the several watts level. However, a disadvantage of conventional PAS technology is that it is sensitive to environmental acoustic noise, which is a major drawback in the noisy environment of an operational riser. Compact packaging of PAS can also be challenging

QEPAS based gas sensing technology

In order to address the issues described above of existing gas sensing techniques, a new approach to photoacoustic signal detection was developed by Kosterev and co-workers, which they called Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) [Kosterev, Bakhirkin, Curl and Tittel, 2002; Kosterev 2007]. As the name implies, it builds on the strengths of PAS while achieving comparable sensitivity and not only successfully avoids the shortcomings of PAS but can offer other sensor performance advantages.
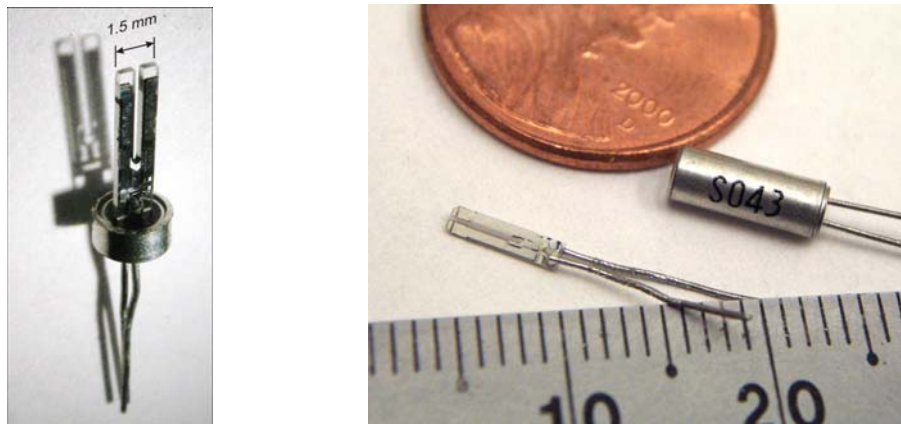

Fig. 2. Quartz tuning fork, exposed (left) and factory sealed.

In QEPAS the acoustic energy is accumulated in a sharply resonant acoustic transducer rather than in a gas filled cell [Kosterev , Tittel, Serebryakov, Malinovsky, and Morozov 2005; Kosterev, Bakhirkin, Tittel, McWhorter and Ashcraft 2008; and Kosterev,Tittel and Bearman 2008]. A readily available resonant transducer is a quartz tuning fork (QTF), mass produced as a frequency reference for digital clock circuits. It has an extremely high Q-factor of >10,000 and a natural vibration frequency $f_0 \approx 32.8$ kHz (Fig. 2). In the QEPAS spectraphone design (Fig. 3), the modulated laser beam is directed through the gap between the TF prongs. The optical energy absorbed by the gas results in its periodic thermal expansion, which gives rise to an acoustic wave. This pressure wave excites a resonant vibration of the QTF, which generates an electrical signal via the piezoelectric effect, and this signal is proportional to the concentration of the target gas. Two small pieces of tubing (usually made of stainless steel) are used to confine and enhance the photoacoustic pressure. Thus, they form a <u>microresonator.</u> Experimentally, it was found that the microresonator improves detection sensitivity 8 to 20 times. A gas enclosure is optional and serves only to separate the gas sample from the environment and control its pressure. Only the symmetric vibration of a

QTF, i.e. when the two TF prongs bend in opposite directions is piezoelectrically active. Since sound waves from distant acoustic sources displace the QTF prongs in the same direction, they do not induce an electrical response.
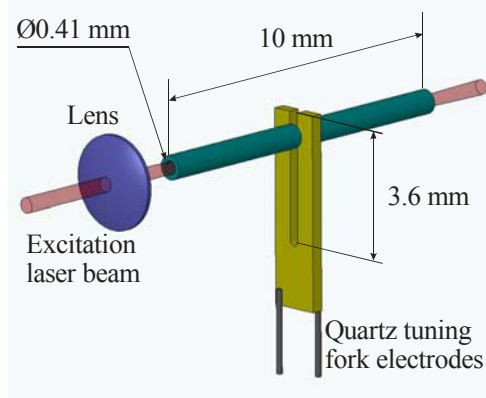

Fig 3. QEPAS spectraphone. The laser beam is directed between the prongs of the QTF and
through the microresonator formed by two pieces of tubing close to but not touching the QTF.
Gaps between each of the tubes and the QTF are typically ~30 μm.

The fundamental limitation of the TF sensitivity arises from thermal excitation of its symmetric mode, i.e., the energy kT stored in its vibration. The most important features of QEPAS are a gas detection sensitivity comparable to traditional laser based PAS, high immunity to environmental acoustic noise, the feasibility to analyze ultra-small gas samples, a compact trace gas sensor platform, and low drift, which allows data averaging over long time periods for increased accuracy. The electrical response to optical absorption is given by:

$$S_{QEPAS} = k\alpha CWQ$$

where α and C are the absorption coefficient per unit concentration and concentration of the target species, respectively; W is the applied diode laser power; Q is the quality factor of the QTF and typically ranges from 10^3 to 10^5 depending on the surrounding gas pressure and the microresonator design.

Application of commercially available QTFs makes the overall sensor platform both cost effective and allows miniaturization. For many target gases the 32.8 kHz frequency represents an optimum choice in terms of providing a time scale of the energy transfer processes in gases and as electric noise decreases at higher frequencies. Furthermore the high operational modulation frequency introduces an additional useful functionality to QEPAS based sensors. In contrast to PAS-based sensors, where in order to maximize the photoacoustic signal the resonant photoacoustic cell operates at a modulation frequency much smaller than molecular relaxation time of the target species (typically ~ 1 to 4 kHz), the QEPAS based sensor detecting the photoacoustic signal at ~ 32 kHz preserves the capability to distinguish between different molecular relaxation times of gases. This functionality can be used as an additional spectroscopic parameter for discrimination between QEPAS signals originating from molecular species with overlapping absorption spectra [Kosterev, Bakhirkin, Tittel, Blaser, Bonetti, Hvozdara 2004]].

In the sensor reported here we used a distributed feedback (DFB) diode laser (DL) operating in near-infrared (NIR) range as an excitation source. There can be several ways to excite an acoustic wave in the gas at the QTF resonant frequency f_0, including amplitude modulation (AM) at f_0, wavelength modulation (WM) at f_0, and WM at $f_0/2$ while the QTF signal is detected at f_0 by means of a lock-in amplifier (2f WM spectroscopy). We used the 2f WM approach as illustrated in Fig. 4. This technique practically eliminates acoustic background from windows and stray radiation absorbed in the gas cell, because the residual AM occurs at f0/2 and thus its signal is not detected buy the QTF [Kosterev, Bakhirkin, Curl and Tittel, 2002]. Another advantage is that WM laser can be easily locked to the absorption line peak as shown in Fig. 4; such locking requires an additional reference gas cell with high concentration of the analyte.

The basic QEPAS concept has now been validated in many laboratory tests and the detection sensitivity has been shown to be comparable to the best reported results for PAS by several research groups [Kosterev, Wysocki, Bakhirkin,So, Lewicki, Tittel Curl, 2008]. QEPAS-based trace gas sensors retain all of the characteristic features of conventional PAS (e.g. intrinsically zero baseline and wavelength independence) in a much simpler and more robust system. QEPAS absorption detection modules or spectrophones (QTF with micro-resonator and low noise preamplifier) are therefore compact, inexpensive, and immune to environmental acoustic noise. QEPAS can be used in multipoint gas-sensing applications by delivering the laser power to each QEPAS spectophone via an optical fiber from a central control unit containing the diode laser(s) and all the associated electronics. QEPAS also permits the spectroscopic analysis of extremely small gas samples (the volume of analyzed gas sample is only limited by the dimensions of the quartz TF, which is < 1mm^3).
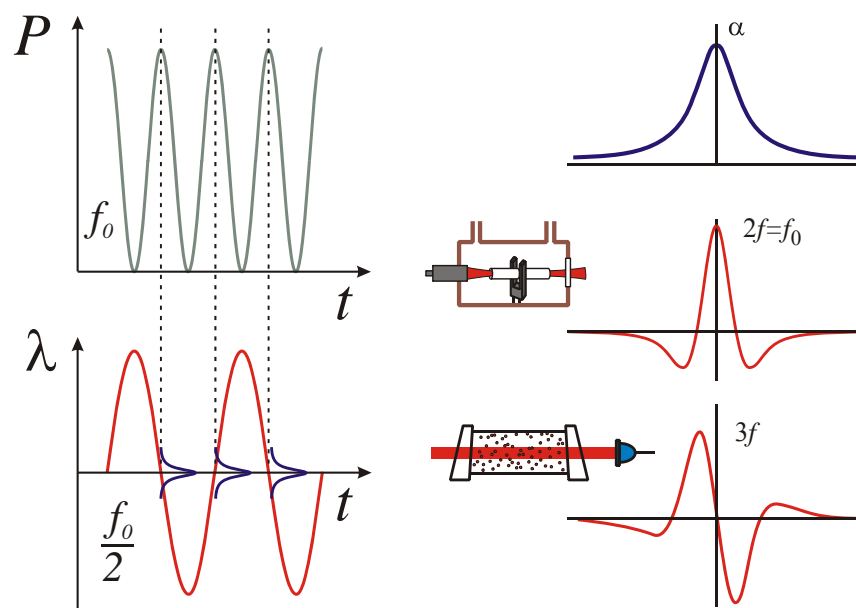
Fig. 4. 2f WM spectroscopy., Pressure bursts are generated at twice the laser modulation frequency when the center wavelength of the modulated laser radiation is on the absorption line (left). At the same time, the 3f component of the photodiode signal after the reference cell is crossing zero at the line peak and therefore can be used as an error signal in the line-locking feedback loop (right).

Selection of the absorption lines and wavelength modulation parameters

Generally for optical detection the greatest detection sensitivities are obtained by utilizing strong absorption features in a suitable spectral region that is free from interfering species. Vibrational overtone bands in the near infrared region are typically two orders of magnitude weaker than the rotational-vibrational transitions located in the mid-infrared. However, the commercial availability and low cost of near-infrared cw telecommunications diode lasers with narrow spectral linewidth, fast tunability and the ability to fiber couple them to a QEPAS spectrophone makes these lasers highly attractive in gas sensing applications in flexible pipes.

H2S has an absorption band in the near infrared centered at ~ 1.6 μm and comprising the overlap of the $v_1 + v_2 + v_3$, 2 $v_1 + v_2$ and $v_2 + 2 v_3$ combination bands. Absorption lines of H_2S in the near infrared are listed on a web site supported by the Institute of Atmospheric Optics, Siberian Branch of Russian Academy of Sciences (http://spectra.iao.ru). We used line parameters from this list in our simulations. The NIR absorption band of H_2S overlaps with an absorption band of CO_2 (Fig. 5), but it is feasible to find individual non-overlapping lines within the bands. On the other hand, such an overlap makes it possible to detect both H2S and CO2 using only one laser. Hence, selection of the best absorption line for H_2S concentration measurements was based on the following criteria:

(1)   6206 to 6538 cm^{-1} spectral range where inexpensive, high power commercial DFB diode lasers are available;
(2)   The least spectral overlap of absorption lines of different species (in this case, H_2S and CO_2, H_2O, CH_4) at atmospheric pressure.

As described in the previous section, we employ 2f WM laser spectroscopy. This approach eliminates most of the acoustic background caused by absorption of stray optical radiation in the sensor. Peak value of the 2f WM spectra of a spectral line depends on the WM amplitude A. For example, for a Lorenzian line optimum A=1.1 of FWHM of the absorption line. Peaks in the absorption spectrum of H_2S at atmospheric pressure are composed of many merged, pressure broadened individual optical transitions. Therefore, we performed numerical simulations of 2f WM spectra to determine the optimum amplitude of WM, which is 0.21 cm^{-1} (Fig. 6a). Next the spectral interference was evaluated for these particular WM conditions (Fig.6b).
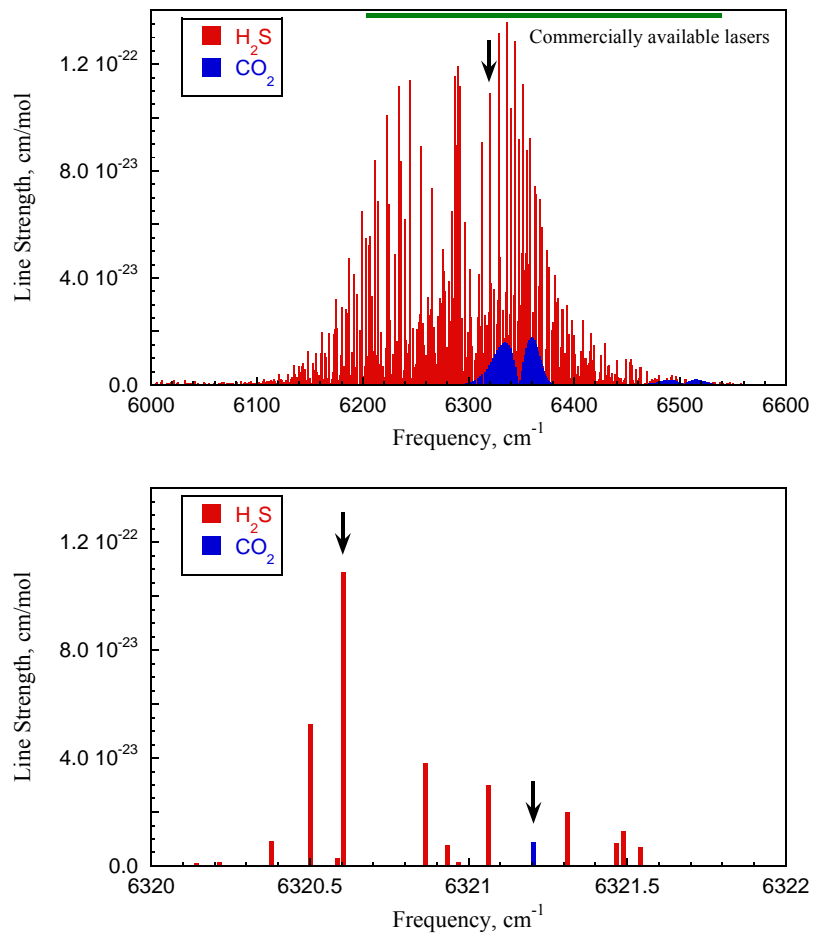
Fig. 5. Stick NIR absorption spectra of H_2S and CO_2 (line positions and integrated intensities are shown, but not line shapes). The selected H_2S and CO_2 lines are marked by arrows.
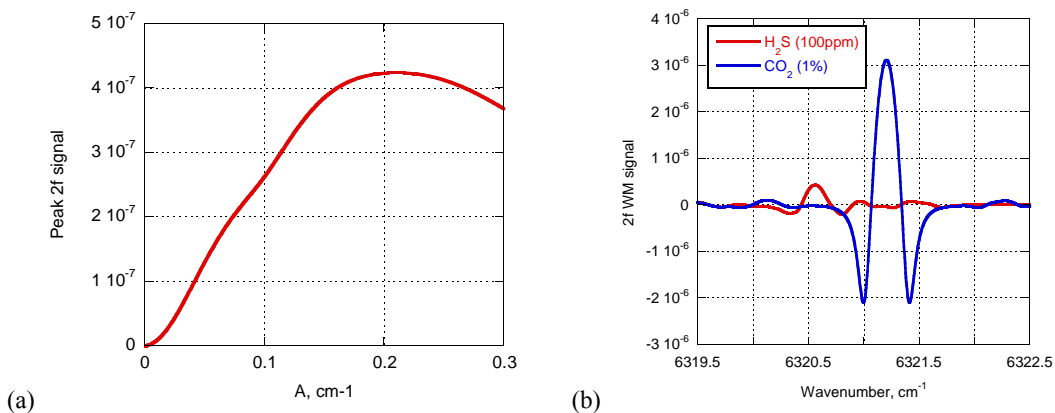

Fig. 6. Numerical simulations of 2f WM spectra. Amplitude of the 2f WM signal from the selected H_2S line as a function of the WM amplitude (a); 2f WM spectra of the selected H_2S and CO_2 lines at atmospheric pressure and A=0.21 cm^{-1} showing negligible spectral interference (b).

It is not necessary to select the strongest CO_2 absorption line to meet the requirements of 0.1% concentration accuracy. Therefore, a weak CO_2 absorption line at 6361.25 cm^{-1} accessible with the same diode laser used for H_2S detection is selected

for CO_2 monitoring. The third target gas, CH_4, is detected with a second diode laser at 6057.1 cm^{-1}.

Autonomous QEPAS based chemical sensor architecture

The response speed of the QEPAS technique is intrinsically limited. The oscillator relaxation time constant is $\tau_r=Q/\pi f_0$. For a Q~3000 (for the presently used spectraphone at atmospheric pressure) and f_0=32.76 kHz, $\tau_r\approx$0.03 s. Therefore, rapid scans common to the laser absorption spectroscopy are not feasible. Besides, obtaining sufficient SNR usually requires longer signal averaging, typically ~1s. Furthermore, QEPAS is a baseline-free technique, which implies that, there is no signal (except for the thermal noise) in the absence of optical absorption. Therefore, it is not practical to configure a QEPAS based chemical sensor for spectral scans of an absorption line. Instead, the laser wavelength must be locked to the line center of target absorption. Such a locking is performed using reference gas cells and photodiodes, as described above and depicted in Fig. 4.

A schematic of a laboratory version of the QEPAS-based autonomous chemical sensor for gas monitoring in flexible risers is shown in Fig. 7. The sensor consists of the following subsystems: an ultracompact spectraphone (incorporating QTF, acoustic microresonator, and pre-aligned, fixed fiber focuser based on a GRIN lens, Fig. 8), transimpedance pre-amplifier, two near-infrared telecommunication diode lasers with a lifetime of > 10 years and an associated control and data processing electronics unit (CEU). The sensor utilizes a 2f wavelength-modulation spectroscopy approach, where 2f=f_0 in the case of QEPAS. Optical excitation is provided by two single frequency, distributed-feedback (DFB) fiber coupled thermoelectrically cooled (TEC) commercial diode lasers. In the current design, the laser for H_2S detection is mounted inside the CEU and provides ~40 mW optical power. The laser for CH_4 monitoring at ~20mW was installed on a separate mount with an independent temperature controller and a current driver. Its current was externally controlled by a voltage level from the CEU. The piezoelectric response of QTF to a photoacoustic signal is picked by a low-noise transimpedance preamplifier located close to the spectraphone, and its output is transferred to the CEU where the data is processed. The result is subsequently displayed on a CEU LCD and can be sent to an interfaced, external PC. The CEU has two primary modes of operation: the measurement mode and the QTF calibration mode. The measurement and digitization accuracy is sufficient for QTF thermal noise detection. The calibration mode is automatically initiated with periodic time intervals programmed by the user, or when the environment temperature changes more than 3°C. The calibration mode can also be initialized manually or via a RS232 interface. The calibration lasts ~ 20 seconds if the zero signal levels are not adjusted, or ~3 minutes if such an adjustment is performed. Coarse adjustment of the diode laser wavelength is obtained by varying the diode operating temperature. Fine adjustment (including locking to the absorption line) is performed by controlling a DC component of the diode laser injection current.
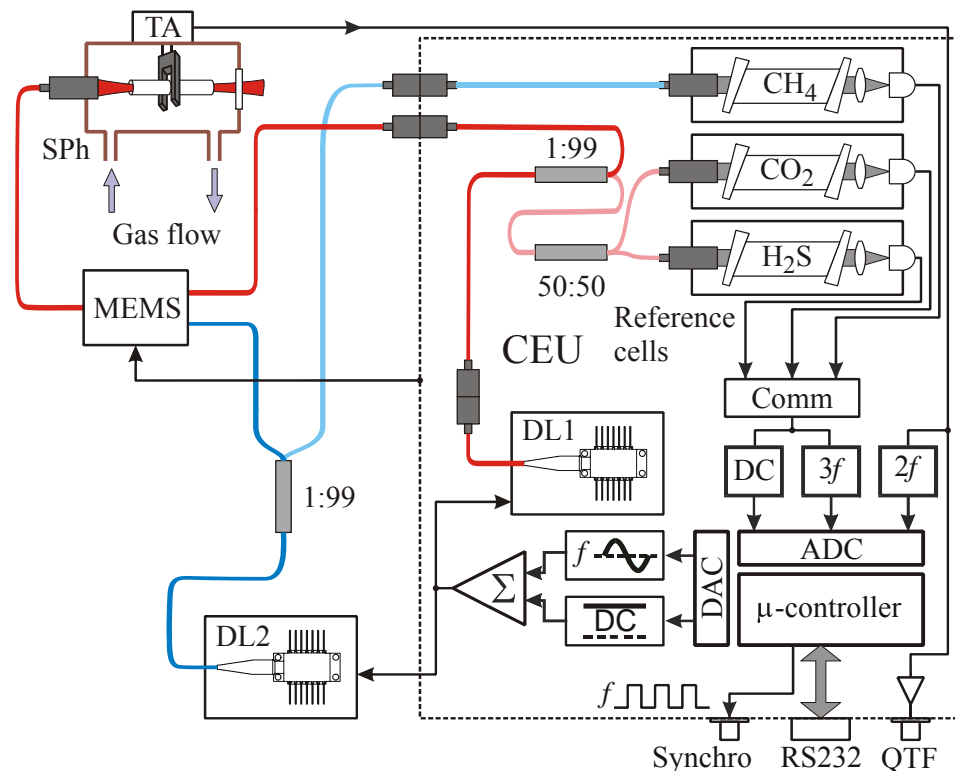

Fig. 7. Multi-species QEPAS trace gas sensor. SPh – spectraphone, TA – transimpedance

pre-amplifier, MEMS – digitally controlled optical switch based on MEMS technology, DL1, 2 – diode lasers for CH_4 and H_2S detection, respectively, and a CEU – control electronics unit.
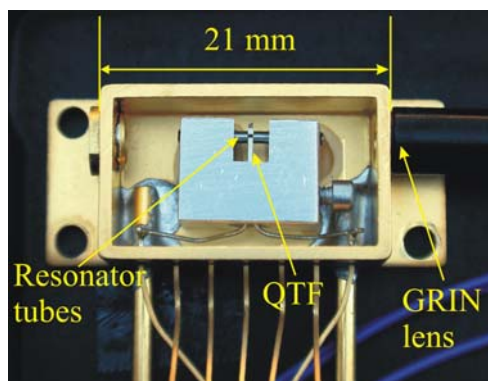

Fig. 8. QEPAS based spectraphone for the NIR spectral region.

Comprehensive Laboratory tests

1. *Individual species in dry nitrogen*

We used gas cylinders with factory-certified concentrations of H_2S, CH_4, and CO_2 in dry N_2 to calibrate the sensor response and derive the detection sensitivity. Specifically, we used 197 ppmv $H_2S:N_2$, 9.9 ppmv $CH_4:N_2$, and 5% $CO_2:N_2$, using an additional dilution with N_2 if needed. Although the normal mode of the sensor operation is when the laser wavelength is locked to the absorption line center, we perform spectral scans for the initial sensor characterization. Such scans helps us verify the results of numerical simulations, zero baseline stability, and the overall sensor performance. Examples of QEPAS spectra for the three mixtures listed above are shown in Fig. 9. In general, the photoacoustic signal is phase-shifted with respect to the laser modulation and has both in-phase (X) and quadrature (Y) components. The spectra shown in Fig. 1 are phase-corrected so that the signal is in the X component; such a correction is also programmed into the CEU for the normal, locked-to-line operation. The Y component is also displayed to give the feeling of the baseline and noise.
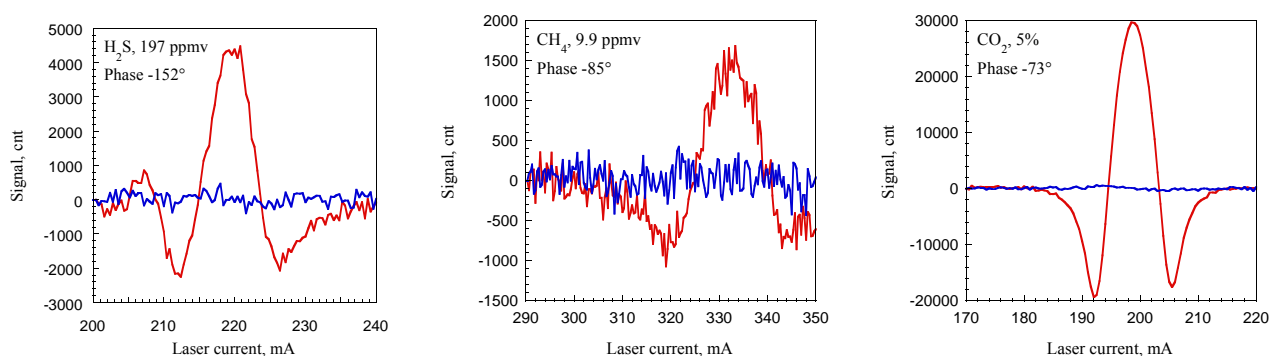

Fig. 9. QEPAS spectral scans for calibrated gas mixtures. Data acquisition time for each point is 2s. Difference in phase reflects different V-T relaxation time.

The signal value on Fig. 9 plots is expressed in counts (cnt) of the CEU internal ADC. Physically, 1 cnt=5.2×10^{-16} A rms current generated by the QTF. The noise observed on the data is the same for all the measurements and equal to the theoretically calculated thermal noise of the QTF, based on its measured dynamic resistance. The sensor calibration results and minimum detectable concentrations are summarized in Table 1.

Table 1. QEPAS sensor calibration for dry gases showing minimum detectable concentrations.

Gas	H$_2$S	CH$_4$	CO$_2$
Absorption line frequency, cm^{-1}	6320.6	6057.09	6321.2046
Laser Power (mW)	38.3	16.0	37.9
Responsivity, cnt/ppm	22.8	152	0.80
Minimum detectable concentration (ppm) in 1 s	**10**	**1.5**	**270**

2. *Individual species in nitrogen containing H$_2$O vapor*

PAS relies on the energy transfer from the optically excited vibrational state of a molecule to the average translational motion of gas molecules. This process called V-T relaxation occurs during molecular collisions in a gas (Fig. 10). It involves a time delay τ, which depends on the initially excited state, structure of energy levels in the two colliding molecules and so on. If the time delay is longer than the modulation period of the optical excitation, the photoacoustic signal amplitude will decrease. Hence, bulk chemical composition of the gas mixture can affect the photoacoustic response by influencing the τ value. In particular, H$_2$O is known to promote fast V-T relaxation in many cases, thus increasing the signal. The phase of the photoacoustic signal also depends on τ, allowing in some cases indirect quantification of the H$_2$O content.
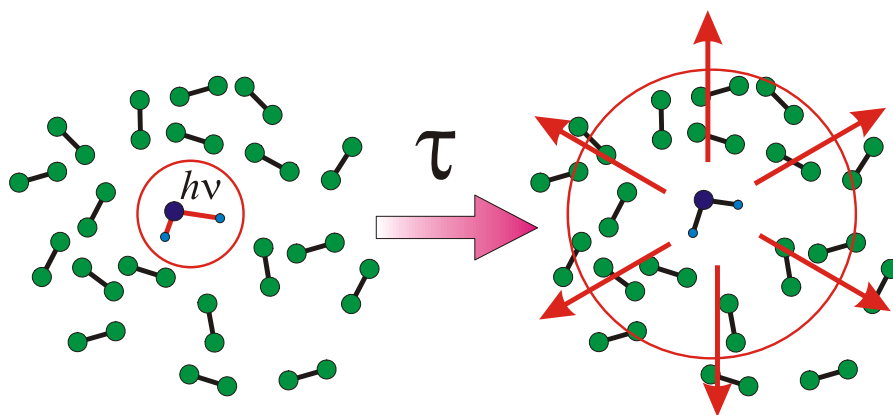

Fig. 10. Physical processes involved in formation of the photoacoustic signal. An optically excited molecule (left side, circled) releases its vibrational energy to the translational motion of the surrounding molecules. This equilibration process involves many molecular collisions and an associated time constant τ.

In order to study the effect of water vapor on the QEPAS sensor response, we used an experimental setup shown in Fig. 11. H$_2$O vapor diffused into a dry N$_2$ flow via semi-permeable tube. Then a dry calibrated gas was mixed with a humid N$_2$. The mixing ratio was controlled by two flow meters. A 50 cm long optical gas cell was used for precise H$_2$O quantification using an auxiliary laser and a photodiode.
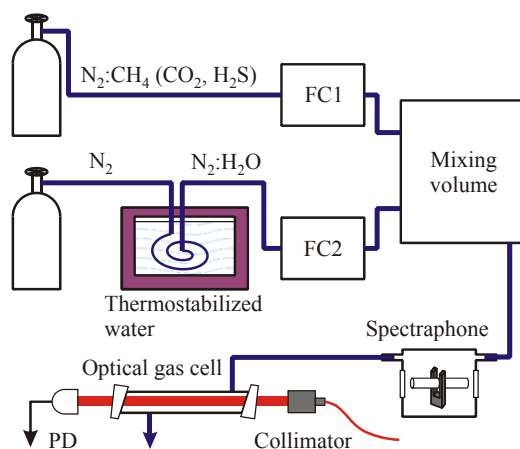
Fig. 11. Experimental setup for studying H_2O vapor influence on the sensor performance. FC1, 2 – flow controllers; PD – photodiode. The optical cell and an auxiliary laser at 1.3 μm delivering radiation to the fiber collimator are used for precise quantification of the H_2O concentration in the gas.

The results are presented in Fig. 12. It can be seen that H_2O enhances the QEPAS signal for all three molecules. However, the H_2S signal changes <20% when comparing gases with and without H_2O presence. It can also be seen that H_2O only has an effect on measurements from 0 to 1% H_2O concentration, and above 1% concentration there is no additional effect. For CO_2, the difference is ~2 times, but the signal is saturated at ~0.2% H_2O concentration. For reference, this corresponds to a 6.4% relative humidity at +25°C. Similarly, a QEPAS response of CH_4 saturates at ~0.6% H_2O concentration. Furthermore, if the concentration of either CO_2 or CH_4 is sufficiently high, phase information can be used to derive the H_2O concentration and use this information to properly normalize the sensor response. Assuming that phase can be accurately measured when SNR=10 and 100s are allowed for the measurement, the mentioned procedure is feasible if CH_4 concentration exceeds 1.5 ppm or CO2 concentration exceeds 270 ppm. These numbers are still lower than the required detection limits. Therefore, accurate measurements and corrections for humidity levels can be performed without installation of the separate humidity sensor. The table at the end of the current section summarizes the sensor performance for a humid gas (H_2O concentration >0.6%).
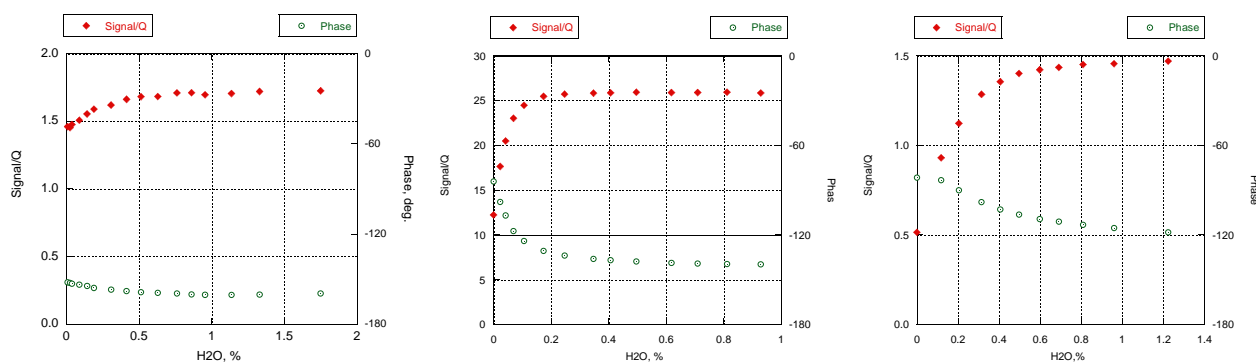

Fig. 12. Water vapor impact on the QEPAS signal. Left to right: H_2S, CO_2, and CH_4 signals normalized to the quality factor Q of the QTF.

Table 2. QEPAS sensor calibration for wet gases showing minimum detectable concentrations.

Gas	H_2S	CH_4	CO_2
Absorption line frequency, cm^{-1}	6320.6	6057.09	6321.2046
Laser Power (mW)	38.3	16.0	37.9
Responsivity, cnt/ppm	25.7	433	1.9
Minimum detectable concentration (ppm) in 1 s	**9**	**0.5**	**120**

3.   Averaging limits (Allan variance analysis)

Chemical analysis of gas in flexible risers does not require a rapid sensor response. It is known that a measurement precision can be improved by longer signal averaging. If the detector noise is white (that is, its spectral power density is constant), then the detection limit decreases as $\sqrt{t}$, where t is the data acquisition time. However, there is usually flicker noise that appears at low frequencies with $1/f$ spectral dependence. As a result, there is a limit for useful averaging time. A common approach to find that limit and hence the ultimate sensor precision is through collecting long records of the sensor readings with the subsequent Allan variance analysis.

The noise in the presented QEPAS sensor is primarily due thermal noise of QTF. This kind of noise can be theoretically calculated and has a white power spectrum. However, there are other noise sources such as resulting from the stray laser radiation, thermal alignment drifts, drifts in the electronics and electromagnetic pick-up. For the sensor noise analysis, we recorded the sensor readings (in-phase and quadratire QEPAS signal components) during a >3 hours time period while 197 ppm H_2S:N_2 gas was supplied to the spectraphone (Fig. 13).
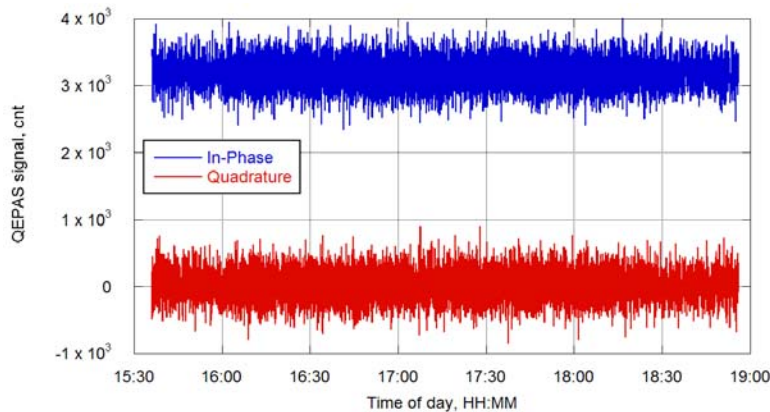

Fig. 13. The sensor response to 197 ppm H_2S:N_2 gas recorded every 2 seconds (with 1s averaging time) during >3 hours. IN-phase component carries the H_2S concentration information while the orthogonal component gives information about the zero level and phase stability.

Then the Allan variance was calculated, and a square root of it (deviation) expressed in H_2S concentration units plotted as a function of averaging time (Fig. 12). This analysis revealed no averaging limit up to 1000 s for laboratory environment.
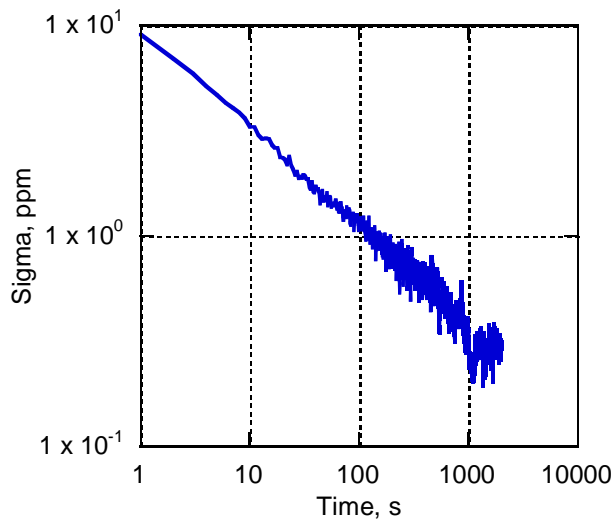

Fig. 14. The QEPAS sensor precision in terms of H_2S concentration as a function of the data averaging time. No averaging limit is observed up to at least 1000 s.

4. Additional laboratory tests to be performed

We plan to perform a number of additional laboratory tests before the sensor can be tested in the field. The principal tests will be:

1) Cross-influence of H_2S, CH_4 and CO_2 at high concentrations. As explained previously, the gas composition can affect the kinetics of V-T relaxation and hence the QEPAS response to a particular species. We shall experimentally study these effects and if necessary introduce mathematical algorithms into the data processing to derive accurate concentrations.

2) The spectraphone and CEU will be tested in a climate chamber at various temperature and humidity conditions. This is to test the accuracy of the readings as a function of external conditions which might be found on platforms from the Barents Sea to the Pacific Ocean.

Outlook

The current laboratory model has primarily been built to demonstrate the usefulness of the QEPAS method, and therefore it has not been tested under the full range of conditions which can be found in the annulus environment of a riser in operation. The additional tests outlined above will demonstrate the suitability of the QEPAS method for offshore field use. Once laboratory testing has been completed, the next step is to design and build a commercial prototype able to address the full environmental range of a riser in operation for a lifetime of ~ 25 years. This prototype will be tested in operation on a platform, and it will also be subjected to simulated lifetime testing to confirm long-term sensor accuracy and corrosion resistance. This prototype will be designed for external retrofitting on the piping from the riser's overpressure valves to the flare, see figure below.
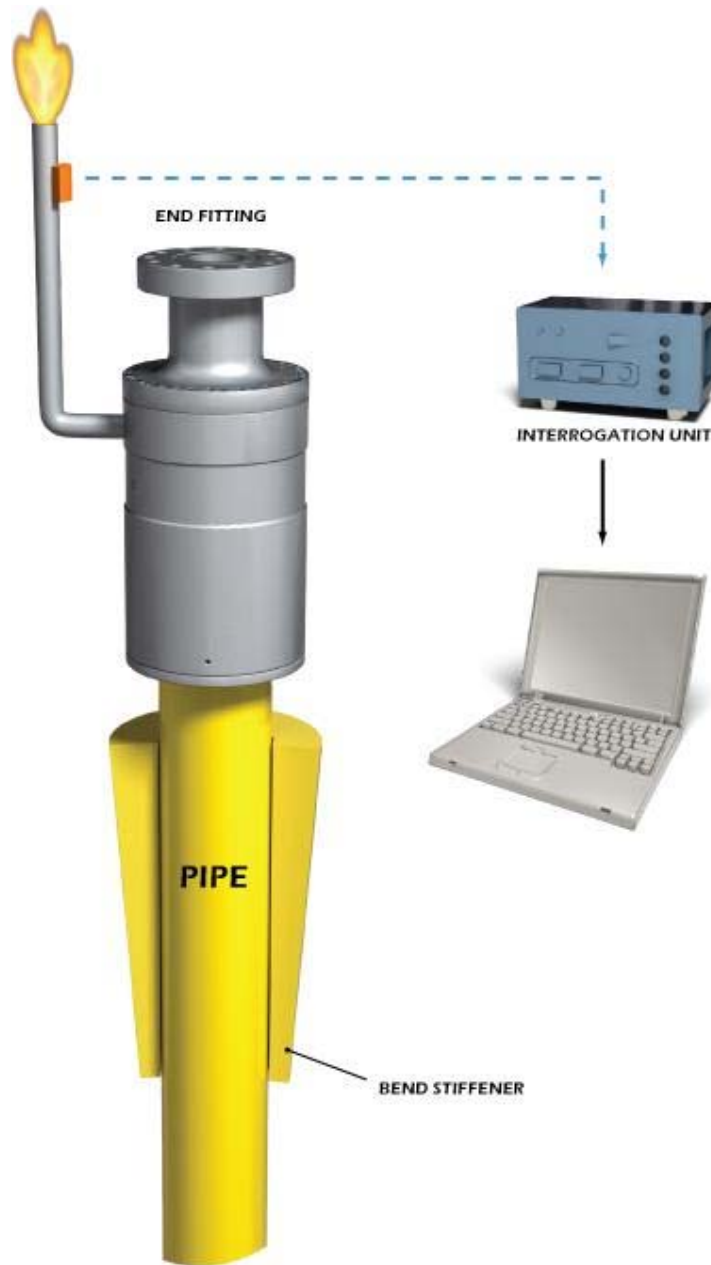
Fig. 15: Schematic of external QEPAS sensor installation

As shown in Fig. 7, the current laboratory model requires the transimpedance amplifier to be very close to the QTF. This amplifier requires electrical power to function and to send a current as output. This output will degrade over the distances of several hundred meters which can be found on a platform. This means that a small amount of electrical power is required near the sensors and that the sensor signal cannot travel very far in its current form. However, the required power for the amplifier is very small (~200 mW), which opens up the option of simply supplying this power to the sensor locally with a suitably shielded electrical lead. A similar small amount of power can be used to power an analog-to-digital converter (ADC) and LED coupled to the amplifier to give a low-power system which converts the electrical signal to a digital optical signal which can be transmitted several kilometers without notable loss. The total power consumption of this system will not exceed 0.5 W.

EX protection

Tuning fork   Sound waves

Laser light in

Electrical
Power in

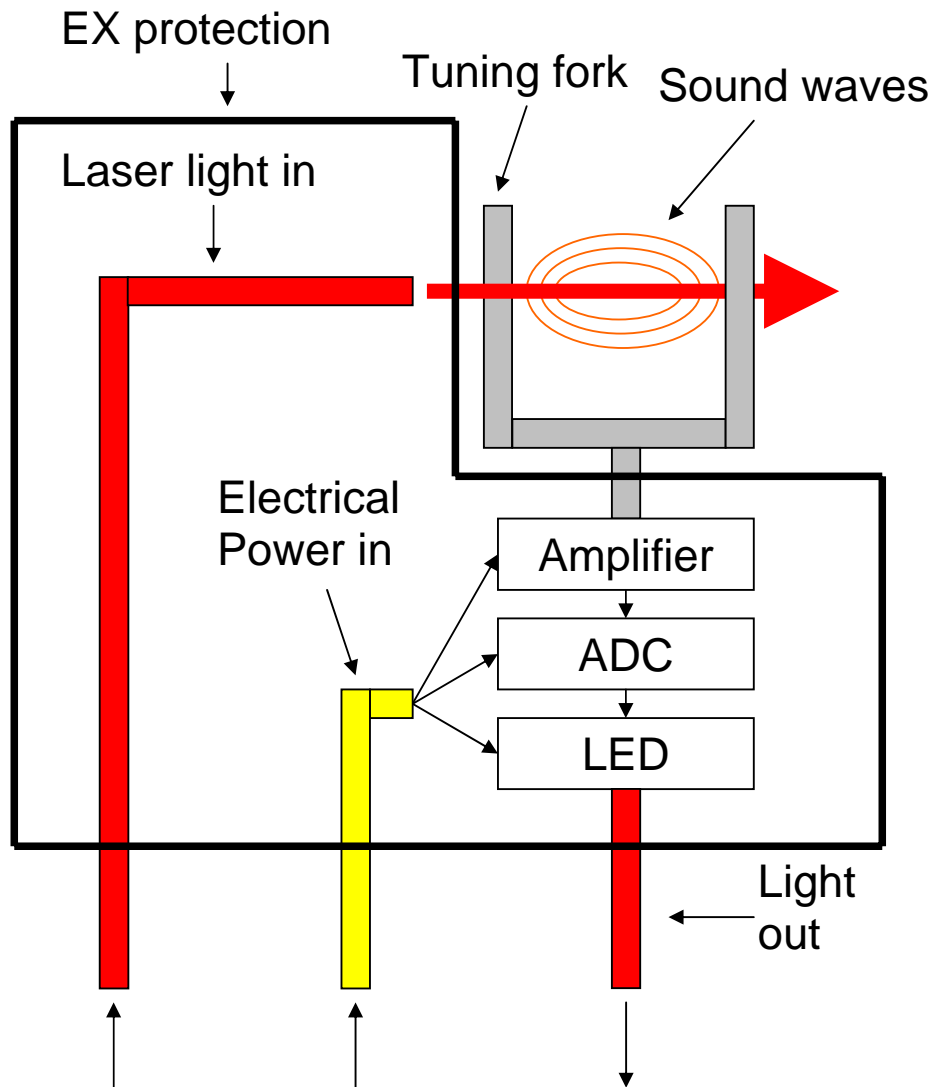Amplifier

ADC

LED

Light
out

Figure 16: Schematic of QEPAS implementation on platform

Alternative approaches exist to make the QEPAS sensing unit completely free of electrical leads, but unfortunately can not be shown at this time due to patent considerations.

Furthermore, the gas sensor architecture is modular which will allow it to be used in other applications of the oil and gas industry, in such diverse areas as air quality monitoring on offshore platforms and downhole exploration.

Conclusions
During the previous 10 years, optical monitoring of flexible pipes has moved from proof-of-concept to field installations, and the trend looks to continue. Advances in technology and manufacturer experience make the use of flexible pipe monitoring easier and more reliable, offering tangible benefits in production reliability and safety.
New optical-based monitoring technologies such as QEPAS promise even greater insight into flexible riser operating conditions, with all the benefits that entails. However, some further development work still remains to be carried out before these new technologies are ready for field use. To date, we have demonstrated the potential of trace detecting H_2S by QEPAS using a DFB laser operating at 1571.6 nm with a minimum detectable H_2S concentration of 10ppm for t=1 s averaging time.

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