SPIE Photonics West

Interband cascade laser based Quartz Enhanced Photoacoustic sensor for multiple hydrocarbons detection

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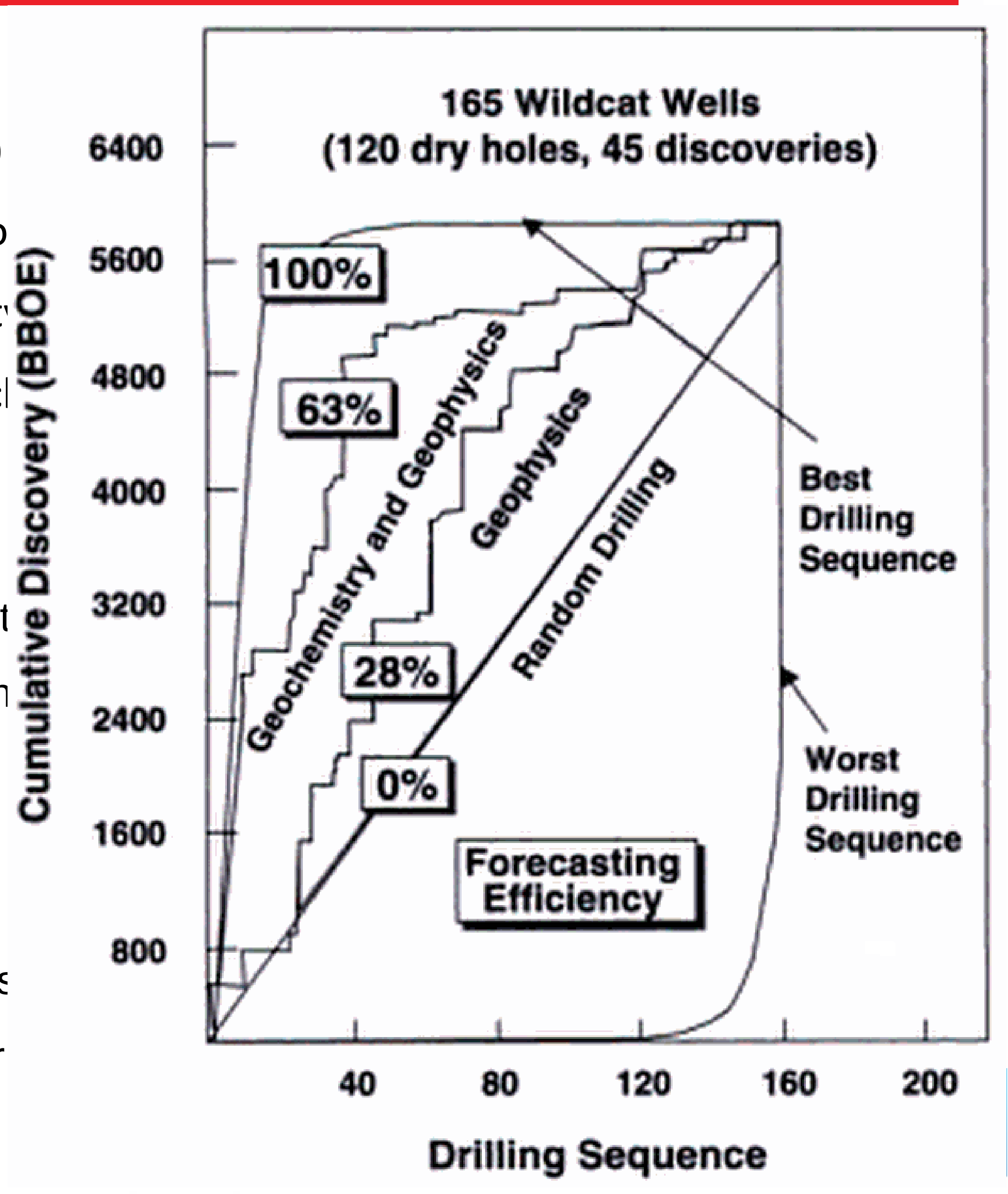
Motivations

- **Oil&Gas industry**: methane propane (C3) and butane (C4) detection to predict productio and assess raw material qualit reservoirs. Isotope ratios sucl rock characterization.

- **Petrolchemical Industry**: Nat distillates from petroleum refin materials for the production polymers and detergents;

- **Safety**: toxic gas emissions refining processes for safe wor



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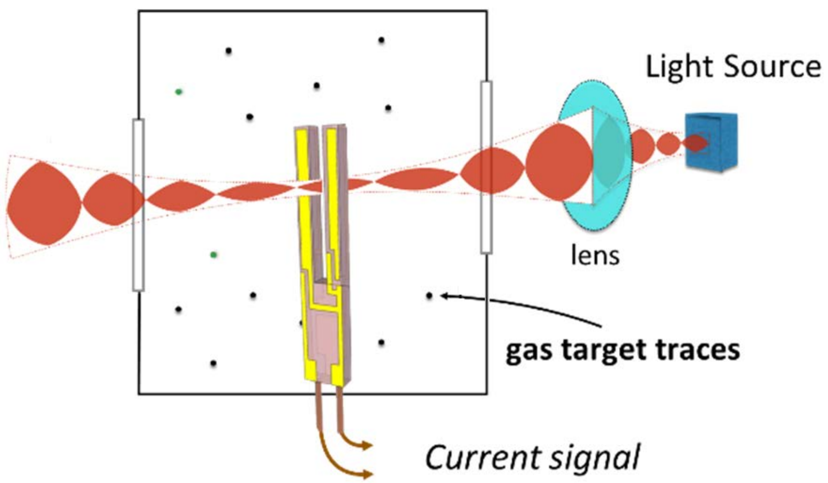
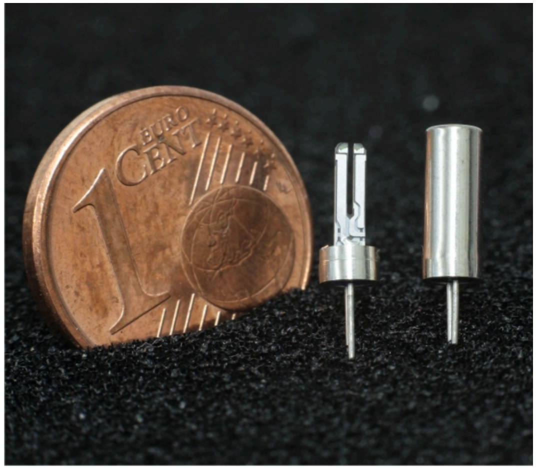
Quartz Enhanced Photoacoustic detection: QEPAS

- **Quartz Tuning Fork** (**QTF**) as a resonant acoustic transducer
- **Optical radiation** is focused between prongs of QTF ($\sim 300\ \mu m$)
- **Modulated absorption** is induced to create an acoustic wave
- **Resonant mechanical vibration** is excited by the acoustic wave
- **Piezo-current** ∝ α×P×Q×ε





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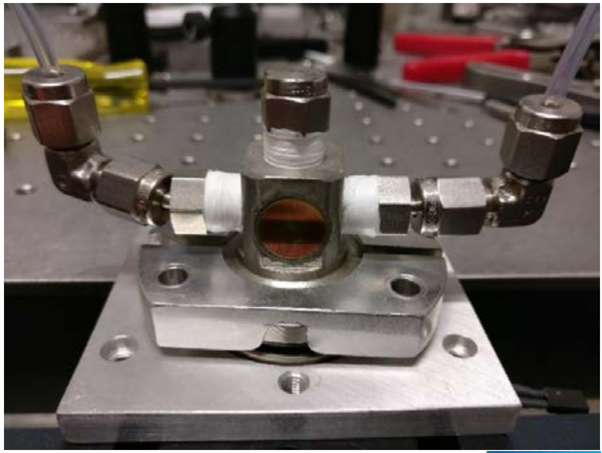
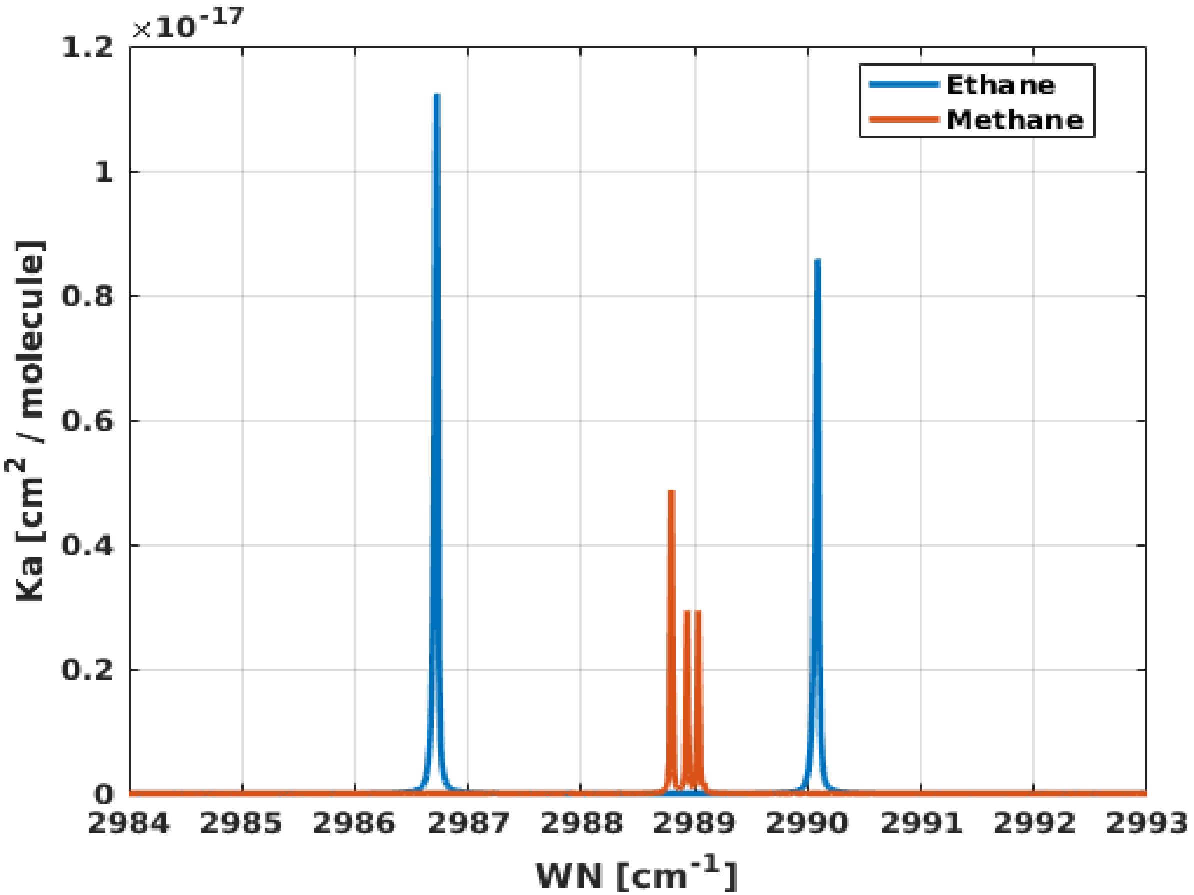
Why QEPAS for downhole hydrocarbon monitoring?

- **Quartz tuning fork (QTF)** : Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
  - Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal QTF noise
  - Frequency and spatial selectivity of acoustic signals
  - Resonant frequency ~32.7 kHz
  - Extremely low dissipative losses: Q~10 000 at 1 atm, Q~100 000 in vacuum
  - Low cost (<$0.30)
  - Record sensitivity: 50 part-per-trillion $\lambda = 10.54\ \mu m$ (SF_6)
- Very small sensing module and sample volume (few mm^3)
- **Optical detector is not required**
- The whole sensor can fit into a 2 inch internal diameter pipe for downhole operations



C1, C2 absorption lines

Absorption cross-sections for methane, ethane simulated from HITRAN database at 50 torr in a spectral region as wide as a typical interband cascade laser tuning range.



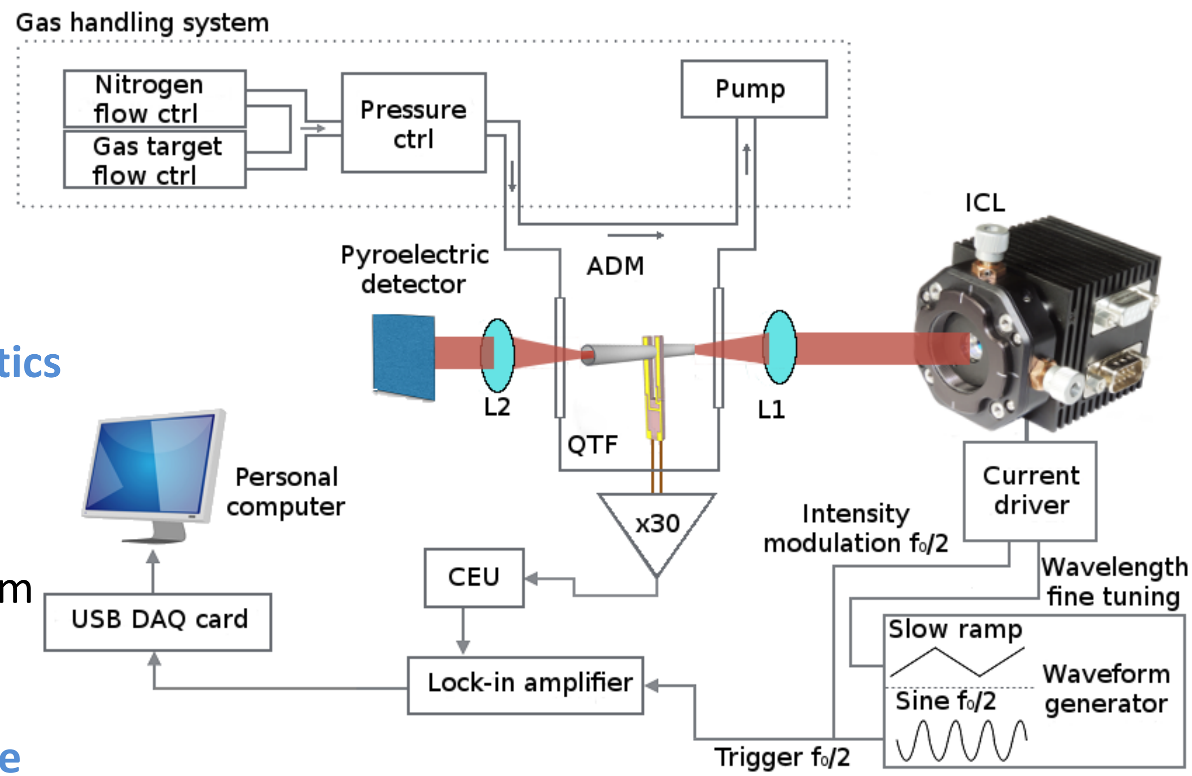
Experimental Apparatus

ILC characteristics

- $\lambda_{emission}$: **3345 nm**
- Tuning range: **12 nm**
- Optical Power: **12 mW**

Spectrophone characteristics

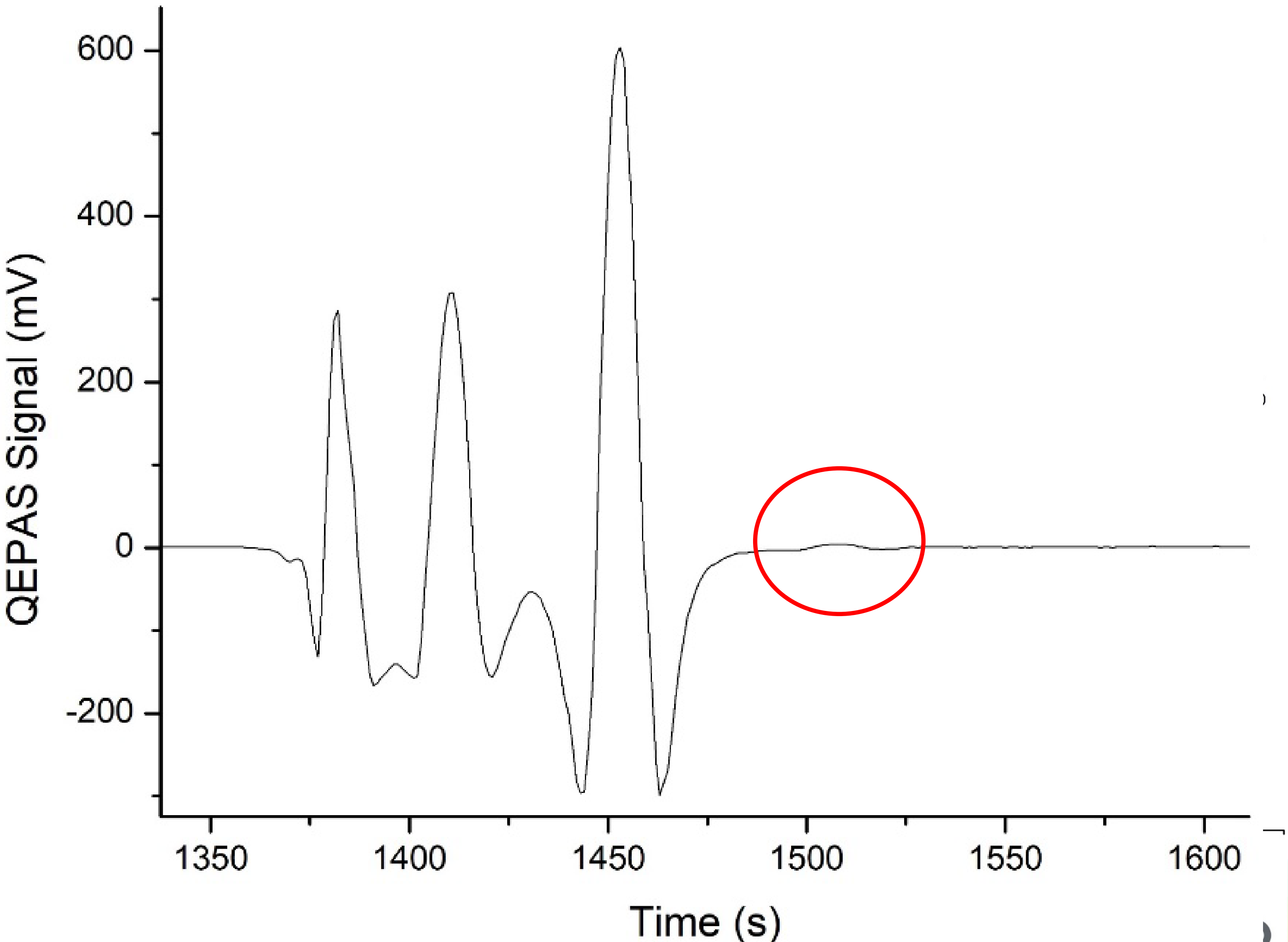
- Standard QTF @ **32kHz**
- Double micro-resonator tube amplification system
- Q at atm pressure: **1200**



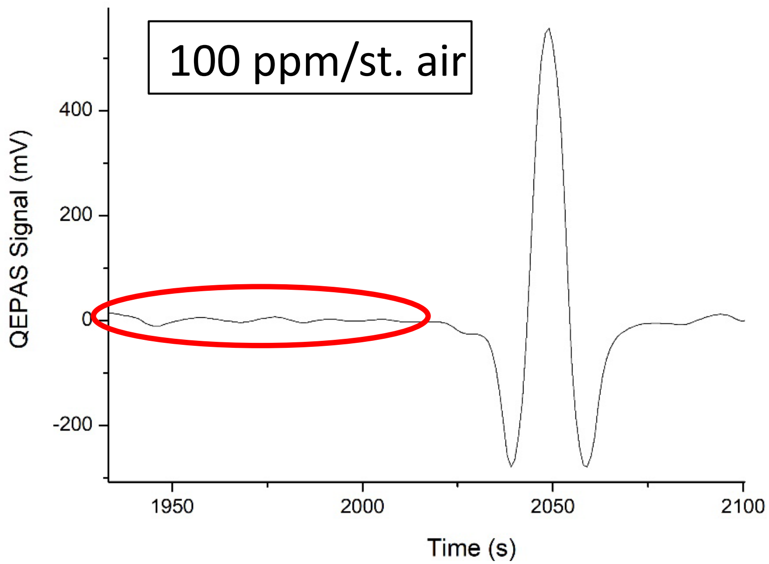
Spectroscopic technique

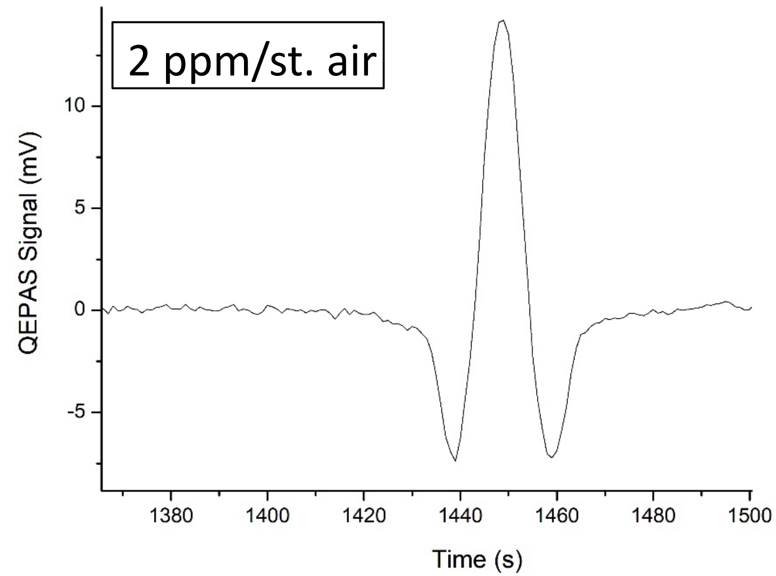
- **2f wavelength modulation**: laser current modulated at the half of the QTF resonance frequency and QEPAS signal demodulated by lock-in amplifier at the QTF resonance frequency → **background free detection**

C1 detection



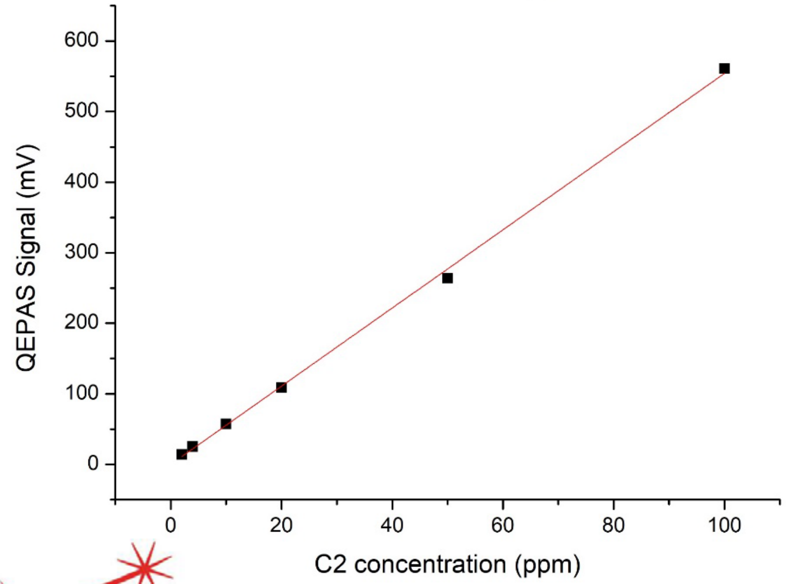
C2 detection





Working conditions

- T_{ICL}= 15°C
- I_{ICL}= 66 mA
- P = 200 torr
- Modulation amplitude = 130 mVp-p
- Phase = 166.15°
- Linearity: $S = 5.54 \frac{mV}{ppm} \cdot conc + 0$
- **Broadband absorption background**



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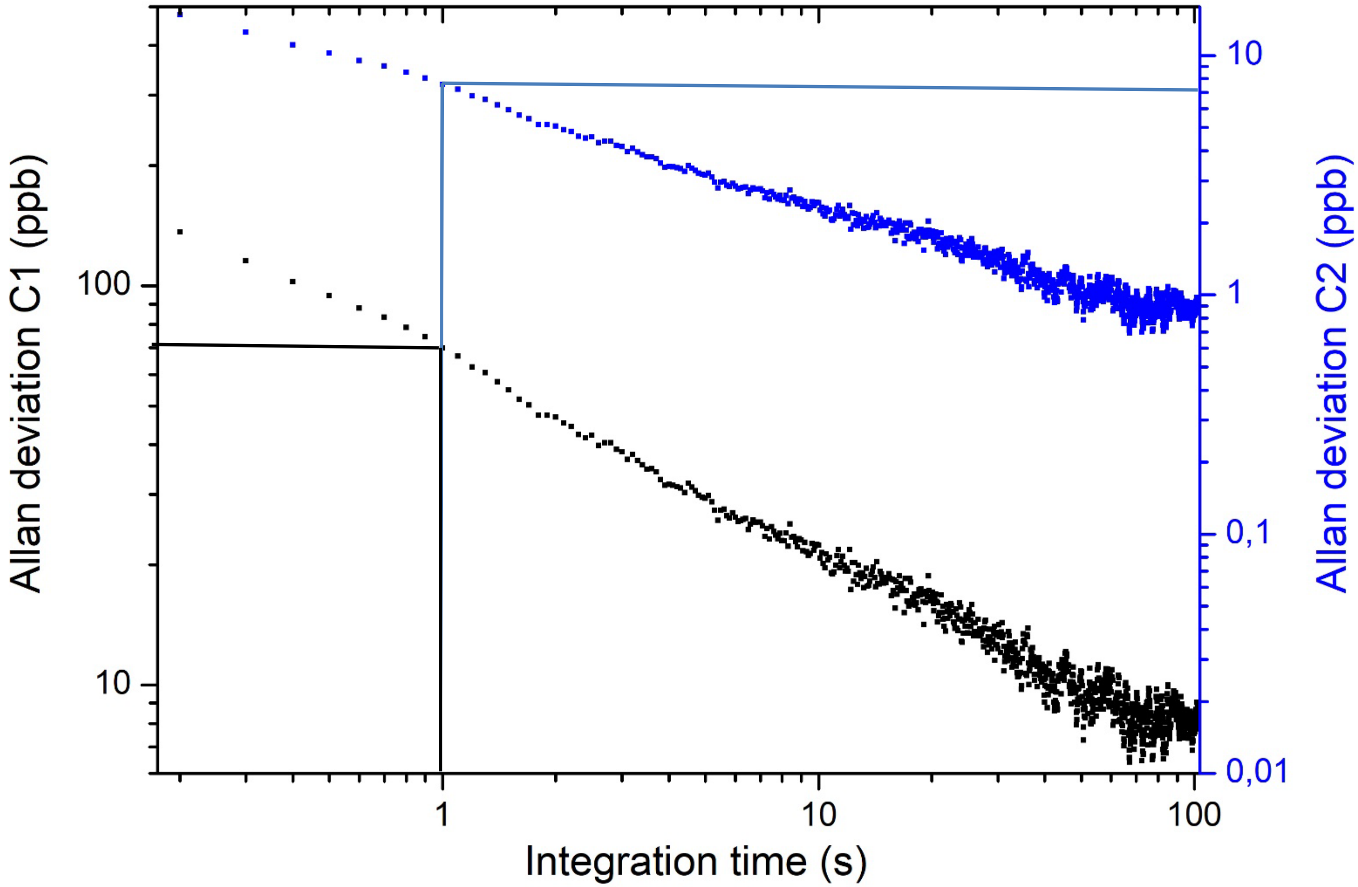
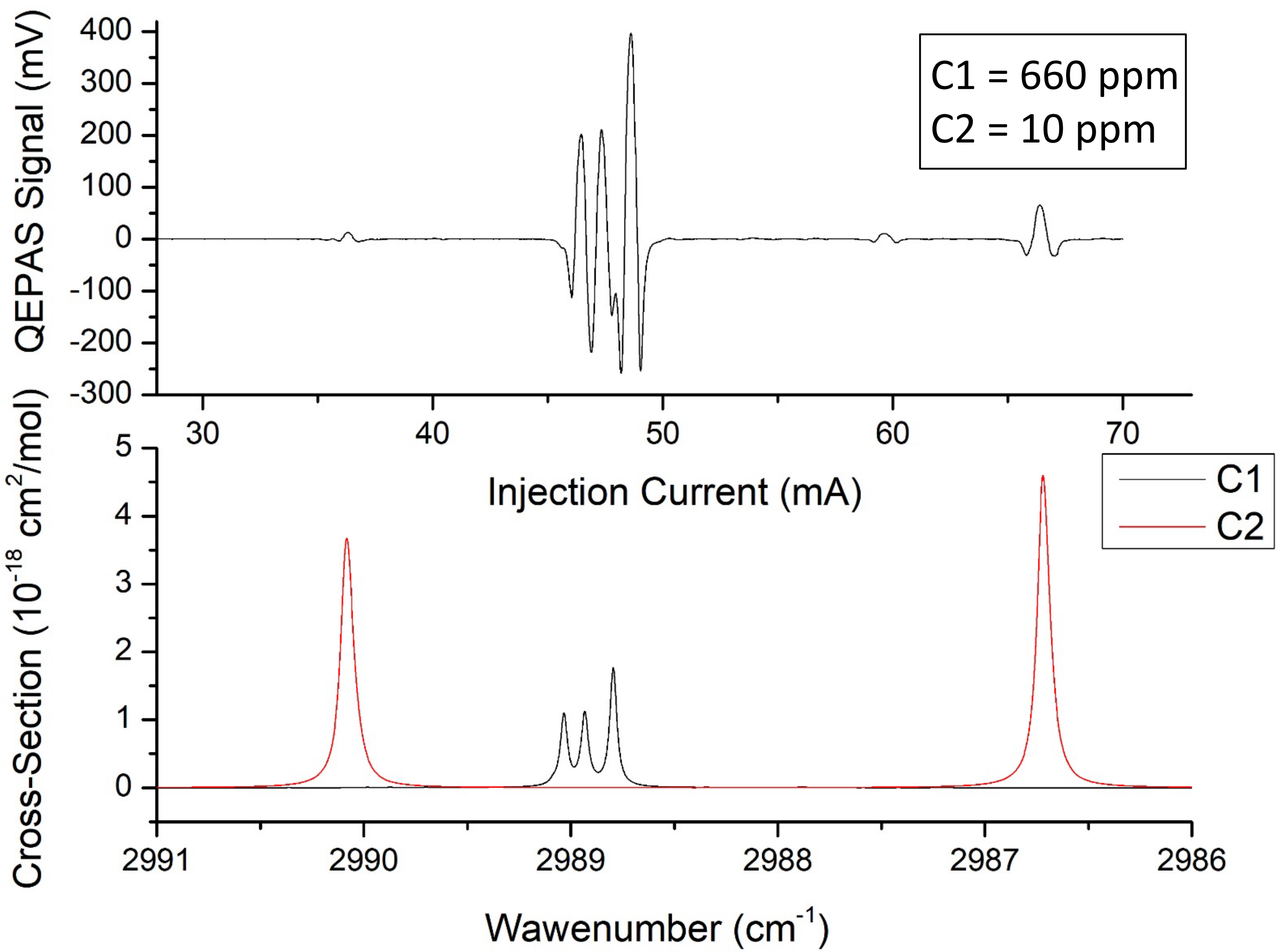
Detection Limits – Allan deviation analysis

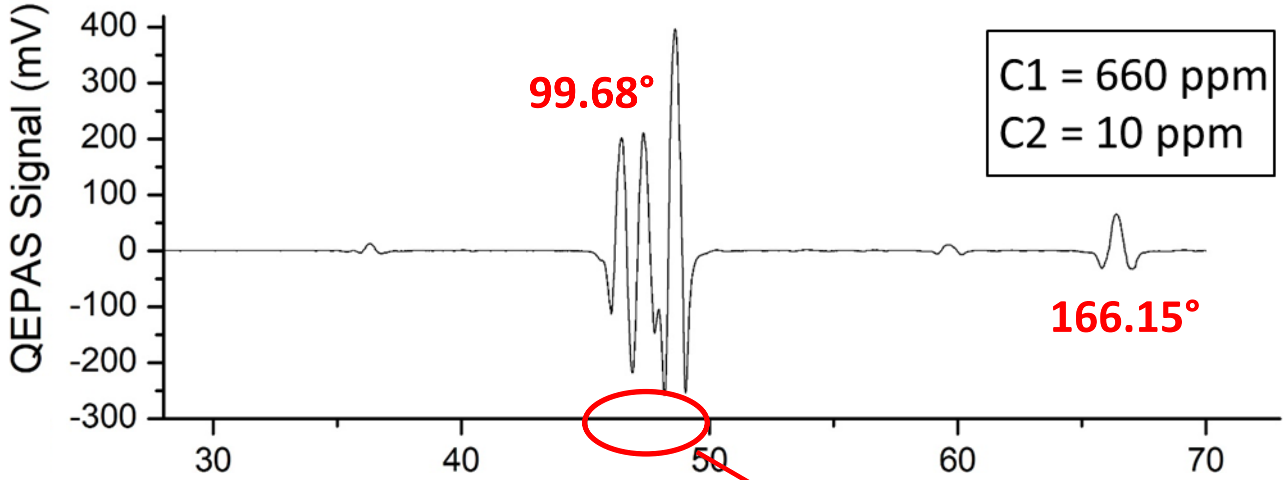


- Detection limit C1: **70 ppb** @ integration time **1 s**
- Detection limit C2: **7 ppb** @ integration time **1 s**, **RECORD for QEPAS technique**

C1/C2 mixture

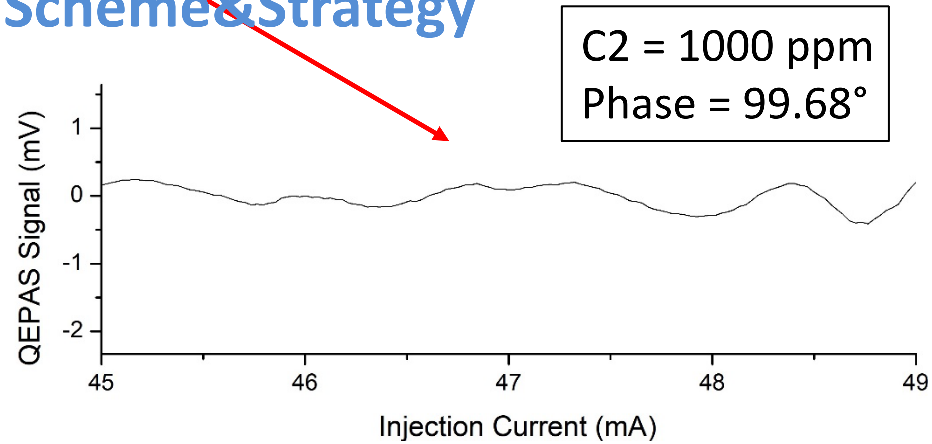


C1/C2 mixture



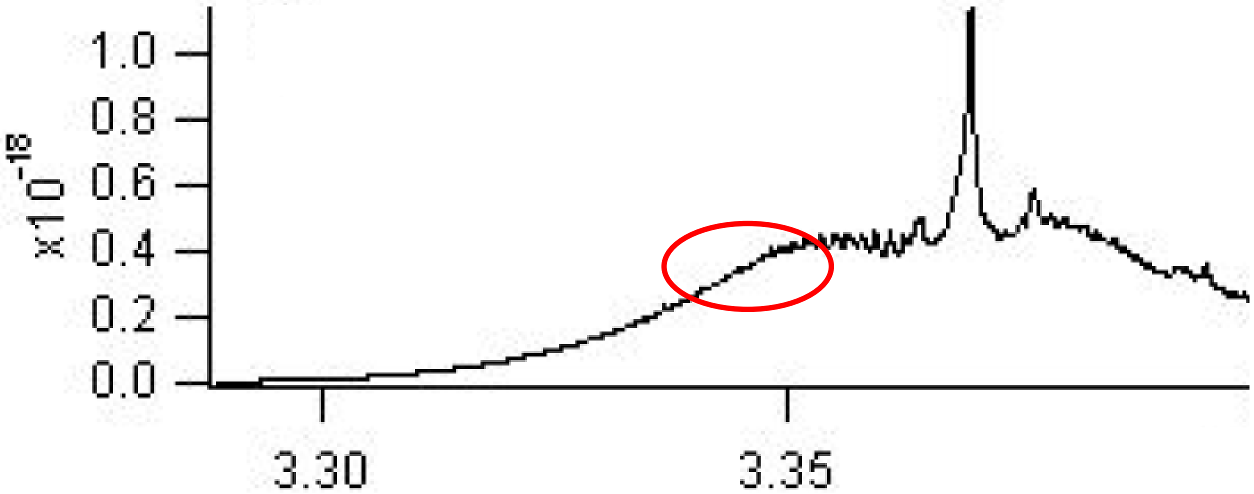
Detection Scheme&Strategy

- P = 200 torr
- T_{ICL}= 15°C
- I_{ICL} span from 30 mA to 70 mA
- Modulation amplitude = 130 mVp-p
- Phase = 99.68° @ C1, 166.15° @ C2
- **C2 absorption background was leveled off!**



What about broadband absorption background from heavier molecules?

Propane C_3H_8 (C3)



Questions

- **Are these absorption features defined enough for wavelength modulation approach? What about amplitude modulation?**
- **Is the QEPAS response over this broad absorption spectrum linear?**

The best chance is…

P = 760 torr, Modulation amplitude = 300 mVp-p, Phase = 142°

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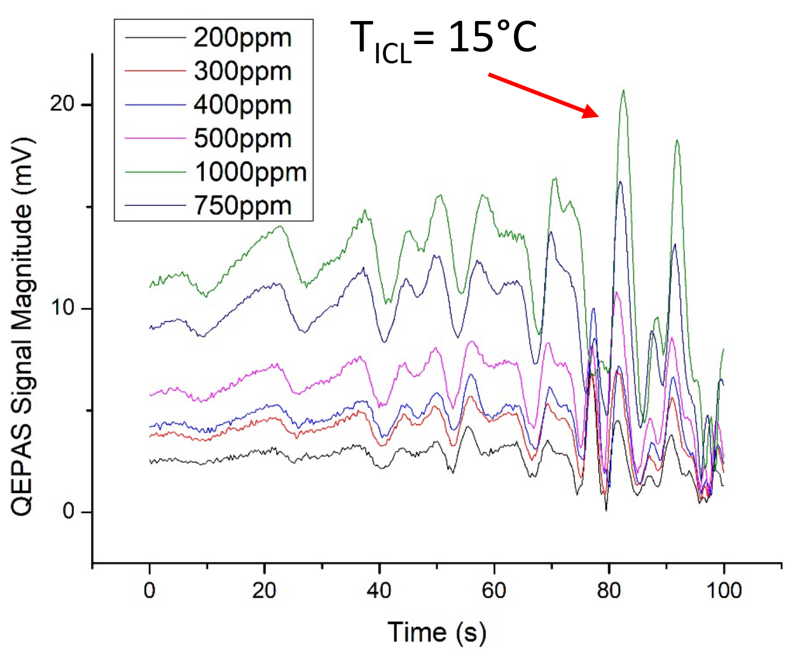
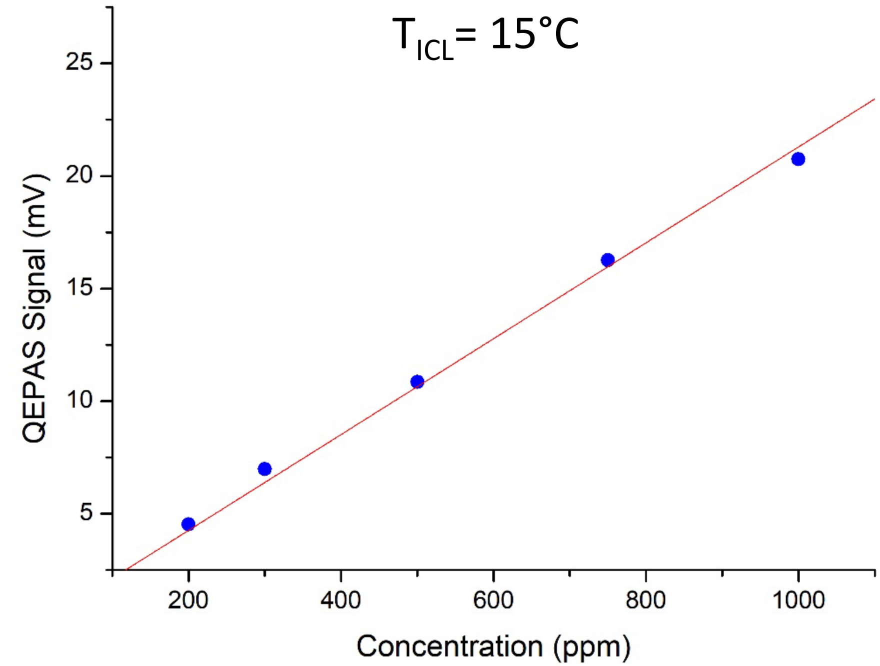
C3 detection – preliminary results

Integration time 0.1 s





- Linearity has been demonstrated for three different peaks also at T_{ICL} = 5°C, 10°C
- Detection limit @ 1s for peak at 5°C is 20 ppm
- **Can C3 absorption background be leveled off?**
- **Can C3 be detected and discriminated by C2 absorption background?**

Conclusions

- Design of a benchtop sensor prototype for unambiguous detection of C1, C2;
- The detection scheme is simple and suitable for rapid scan measurements;
- Broadband absorption from C3 is still detectable by wavelenght modulation;

Future Perspectives

- Investigation of heavier molecules such as C4;
- Study of the broadband absorbers effects on C1, C2 detection;
- Study of the effects of variable gas matrix;
- Training and validation of the sensor by analyzing gas mixtures from the well site;
- Design of a compact and ruggedized sensor to be implemented in pre existing tools devoted to assisted drilling.