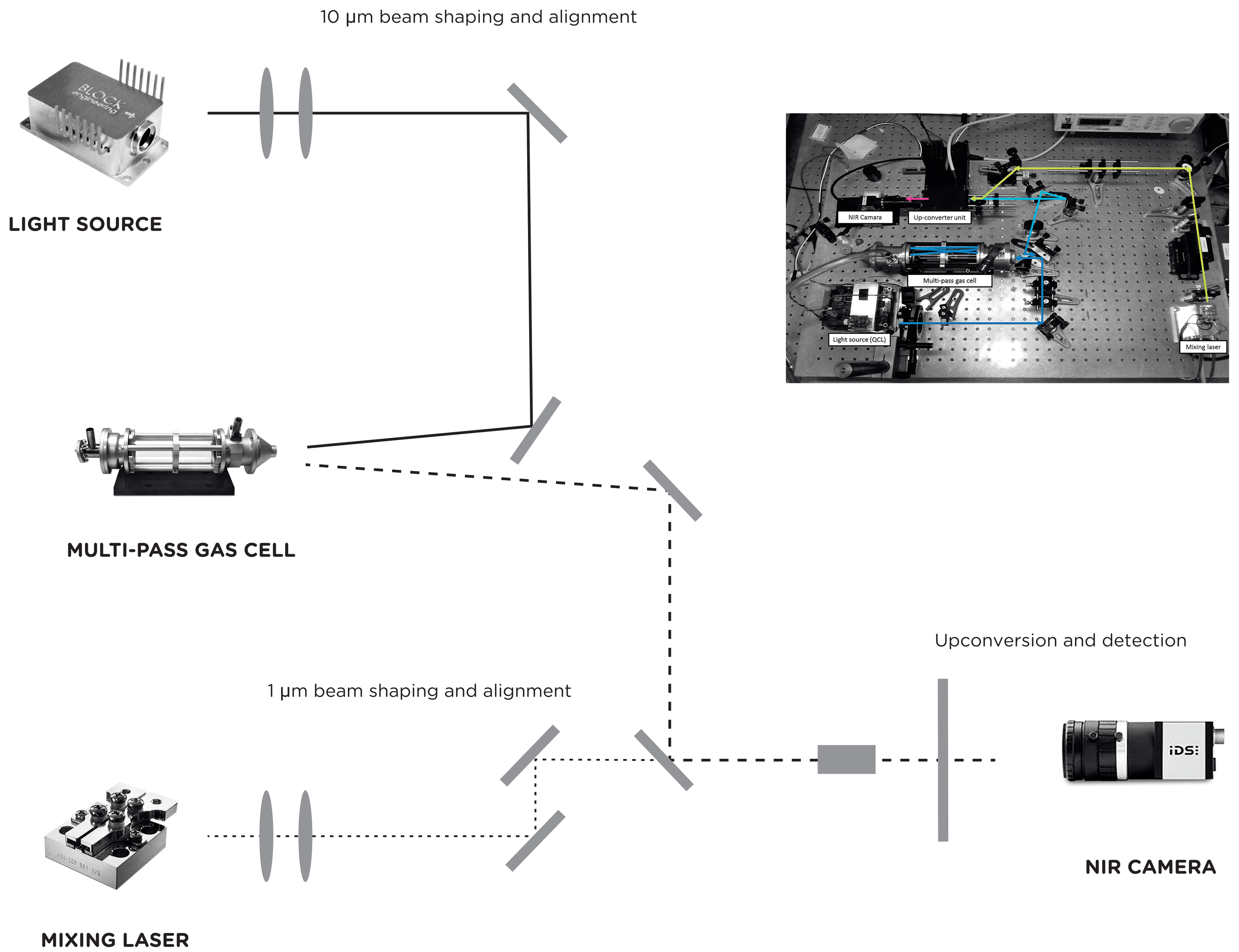
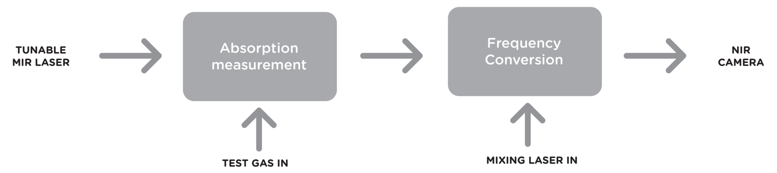
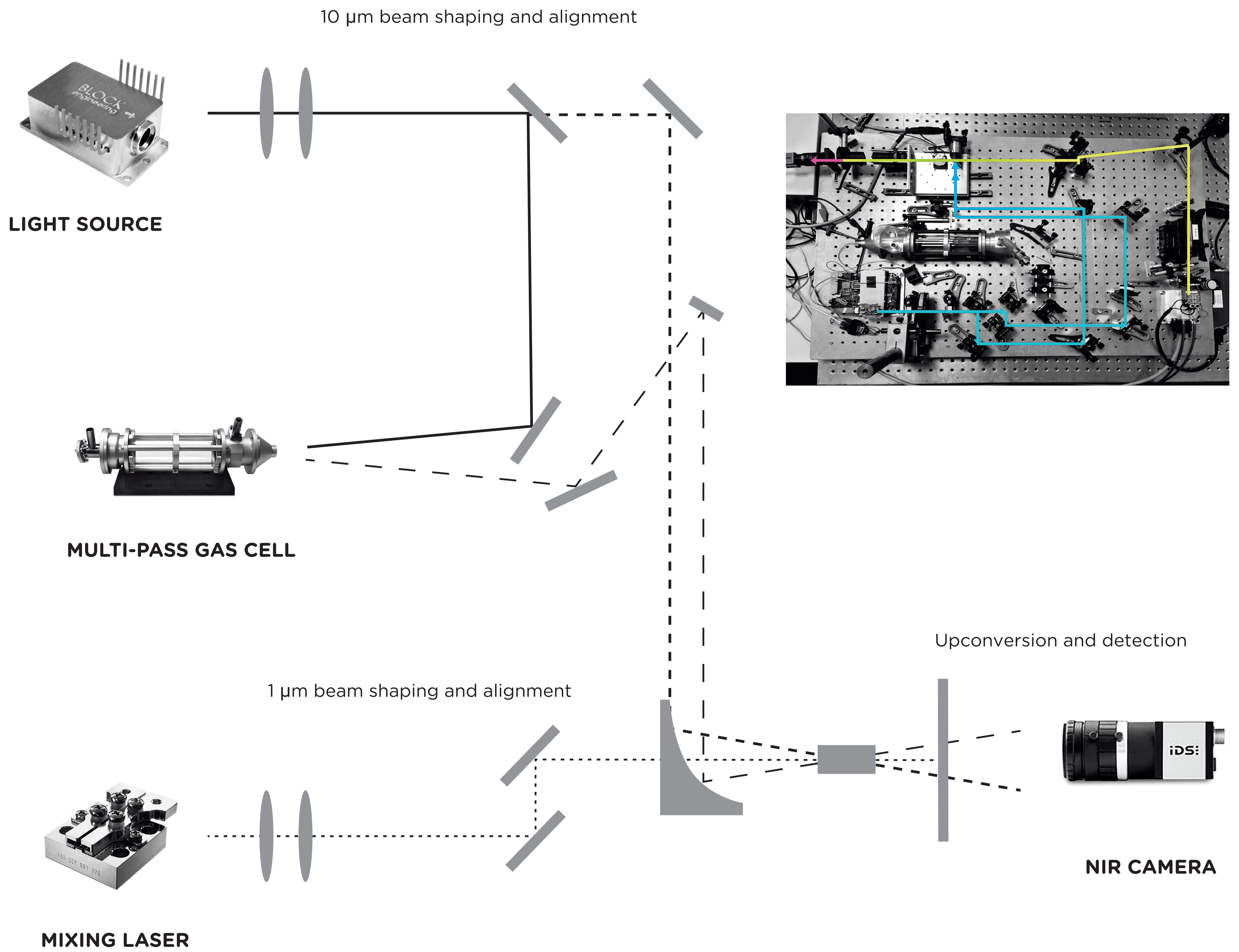
OPTICAL SENSOR FOR REAL TIME MEASUREMENT OF VOLATILE ORGANIC CONTAMINANTS IN AIR

Development and test of a new method for real time measurements of tetrachloroethylene(PCE) and trichloroethylene(TCE) in in soil air and indoor air related investigations of contaminated sites.



1ST GENERATION SETUP





2ND GENERATION SETUP

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BACKGROUND AND OBJECTIVES
Today measurements of volatile organic contaminants (VOC) in indoor air, are performed with sorption tubes or passive samplers over a period of typically 14-21 days. The tubes are analysed at a laboratory and the result obtained corresponds to an average concentration over the sampling period. At present no simple, effective and inexpensive method for direct quantitative measurements of VOCs in air exists.

After more than 5 years of intensive research DTU Fotonik have developed a revolutionary mid-infrared (MIR) detector based on upconversion of the signal which reduces the noise significantly compared to alternative detectors.

The purpose of this project is to build and test a system based on the optical sensor based on MIR spectroscopy to measure PCE and TCE in soil air and indoor air related investigations of contaminated sites. The project focused on the following parameters:

- Seconds-timescale for concentration measurements (high sensitivity using narrow line illumination and long interaction length)
- Minutes-timescale for compound identification (High specificity by turning light source)
- Spatial localization of volatile organic compounds (Confined portable measurement chamber)

1ST GENERATION
The setup of the 1st generation system consists of:

- MIR illumination source (quantum cascaded laser, QCL) with narrow linewidth: 2 cm^{-1} and tunable in the range 9.5 to 12 µm
- Multi-pass Herriot cell with an interaction length of 36 m
- Mixing laser with narrow bandwidth 1064 nm laser
- Frequency upconversion unit transferring the MIR signal to near-infrared (NIR)
- NIR camera for detection of the upconverted signal

First a system based of wavelength scanning of the illumination sources was tested allowing measuring the full spectral shape of the absorption peak associated to TCE and PCE (fig 1 and 2). A second implementation was investigated using one fixed wavelength for each chemical compound. This system showed improved signal to noise ratio, resulting in improved sensitivity (fig 3).

The frequency upconversion scheme is used to convert MIR to NIR (fig 10-13) in which detection is processed via silicon based camera offers:

- High quantum efficiency
- Low noise
- Cost efficient
- Room temperature operation

Scanning of the QCL emission across the absorption spectrum of the compound gives specificity, allows to identify compounds and eliminate cross contamination from other compounds.

The absorption spectrums of TCE and PCE are separated which then allows to measure one gas compound at a time (fig 1 and 2).

Tuning of the wavelength of QCL gives rise amplitude noise in the QCL emission (fig 3).

Power fluctuation / drift in the mixing power will course variations in the upconversion efficiency.
Tuning of the phase-match condition will alter the upconversion efficiency. One test measurement of PCE with the system showed a concentration of 1329 µg/m^3 and reference measurement on sorption tubes showed 1.400 µg/m^3.

2ND GENERATION
To improve the sensitivity, specificity and stability of the system further, to detect concentrations down to few µg/m^3, a self-referencing system was implemented in the 2nd generation setup.

- The correlation between signal and reference presents to what degree the system will be able to compensate noises (fig 5-9).
- The correlation tested by varying power and wavelength of QCL and power of mixing laser shown in fig 5-6 presents the amplitude noise and power fluctuations that can be compensated using common mode rejection.
- The high R-squares shown in fig 7-9 show the potential for common mode noise reduction.

CONCLUSIONS & FUTURE WORK
- It is possible to measure the absorption of VOCs like TCE and PCE using the optical technique
- The self-referencing system (common mode noise reduction) reduced the noise significantly
- It is expected that this detection principle can be further improved to a sensitivity in the µg/m^3 level for TCE and PCE
- The gas measurement is going to be investigated with the noise reduction technology
- The system can be reconfigured to measure other VOCs.
- It is expected that the method will improve investigations of indoor air quality, help identifying intrusion pathways for VOCs to buildings, and help in several other application where fast quantitative measurements of VOCs are needed.
- Transform the system into a robust compact and portable unit for field measurements is considered to be a straight forward engineering task

REFERENCES

1 J. S. Dam et al. "Room temperature mid-IR single photon spectral imaging", Nature Photonics, 6, 788-793 (2012)
2 C. Pedersen et al. "Non-collinear upconversion of infrared light", Optics Express, 22, 28027-28036 (2014)
3 M. Christophersen et al. "Development and test of optical sensor for real time measurement of volatile organic contaminants in air" Oral presentation (ThS 1A.1) AquaConSoil, Denmark, 9–12 June 2015

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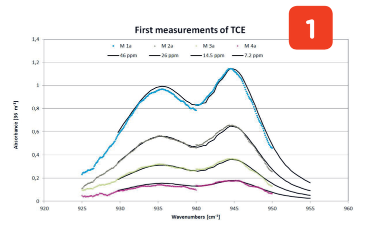
1ST GENERATION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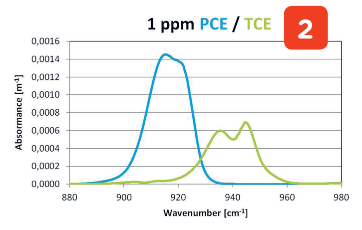

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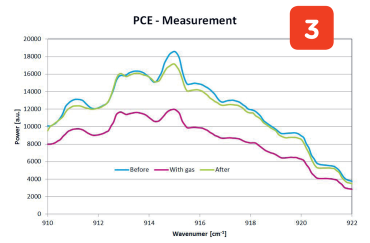

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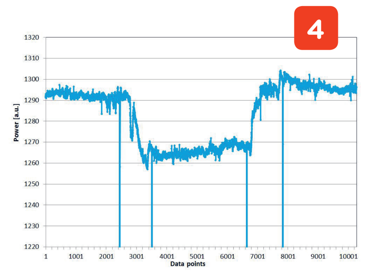
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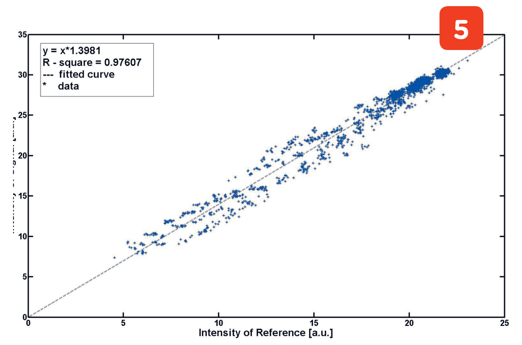
2ND GENERATION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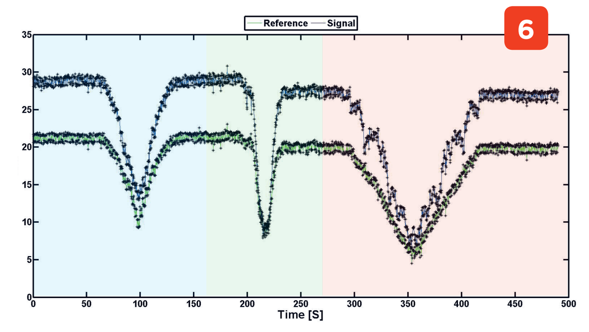
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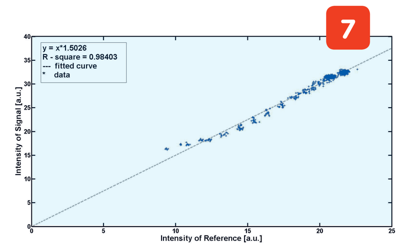
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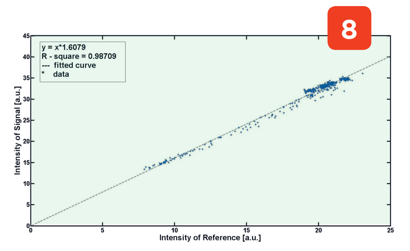
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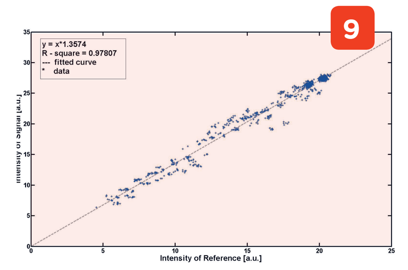
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FREQUENCY UPCONVERSION

Energy Conservation

$$\frac{1}{\lambda_{IR}} + \frac{1}{\lambda_P} = \frac{1}{\lambda_{UP}}$$

Momentum Conservation

$$\boldsymbol{k}_{IR} + \boldsymbol{k}_P = \boldsymbol{k}_{UP}\,;\ |\boldsymbol{k}_j| = \frac{2\pi}{\lambda_j}\, n(\lambda_j, \theta)$$

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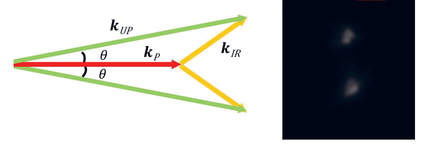
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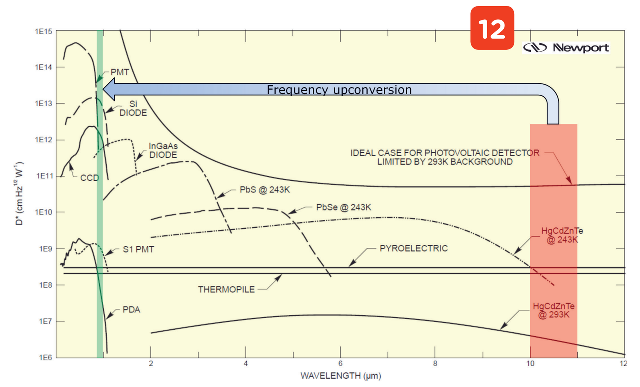

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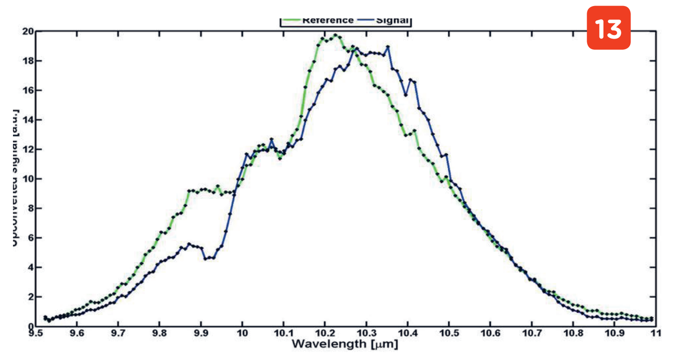

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FIGURES
1. Absorption spectrum of TCE
2. Reference spectrums of TCE and PCE
3. Absorption spectrum of PCE
4. Absorbance of PCE compounds at 915 cm-1 (5 ms each data point / 20 ms sampling time)
5. Correlation of signal and reference by power and wavelength tuning as seen in fig 6.
6. Intensity of signal and reference measured via CCD detector
7. Signal / Reference correlation from power variation of the QCL
8. Correlation originating from power variations of mixing laser
9. Correlation from wavelength tuning of QCL, which also alters the power
10. Energy and momentum conservation
11. Non-collinear phase matching scheme
12. Overview of sensor detectivity
13. Phase-match spectrums of upconverted signal and reference