Towards an EC-QCL based Sensor for Monitoring Side Products of Formaldehyde Production

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Introduction

Quantum Cascade Lasers are, since their first demonstration in 1994, a powerful light source for infrared spectroscopy. Compared with a thermal infrared source, they offer a much higher intensity (several magnitudes) and the emitted radiation shows a spectral bandwidth $<50\,cm^{-1}$ (with a Fabry Perot cavity). Adding an optical grating (either external [EC] or monolithic integrated [DFB, DBR]) allows single mode operation and the spectral bandwidth is $<1\,cm^{-1}$. The extremely narrow bandwidth makes DFB and DBR-QCLs perfectly suited for resolving the ro-vibrational absorption bands of small gas molecules. EC-QCLs, however, are not commonly used for quantifying gases, as single mode operation is difficult to achieve. In this work we present the applicability of an EC-QCL for measuring two gaseous analytes which show absorption bands $>50\,cm^{-1}$.

Industrial Process - Production of Formaldehyde

- Formaldehyde is an important compound for the chemical industry (e.g. formaldehyde based resins, disinfectant, ...)
- Partial oxidation of methanol on silver catalyst:

$$CH_3OH + 0.5\,O_2 \xrightarrow[600-720\,^{\circ}C]{Ag} HCHO + H_2O$$

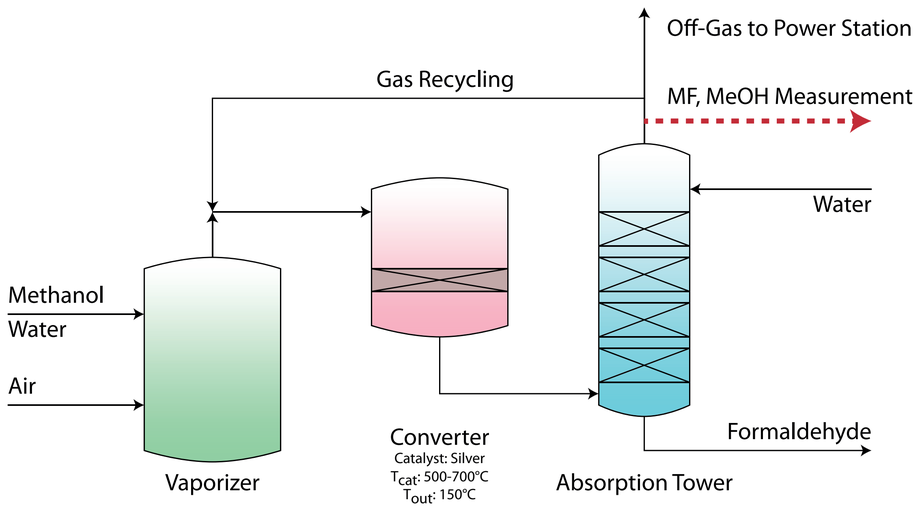

Fig. 1: Basic scheme of a formaldehyde production plant (silver catalyst).

Prototype

- EC-QCL: 890-1240 cm^{-1} (Daylight Solutions)
- Measurement cell: 10 cm pathlength, ZnSe windows, custom built
- Detector: PCI-2-TE-12 (VIGO System)
- Signal acquisition: detector $\rightarrow$ boxcar integrator $\rightarrow$ ADS1115 (16 bit ADC) $\rightarrow$ SAM Cortex M3 $\rightarrow$ PC

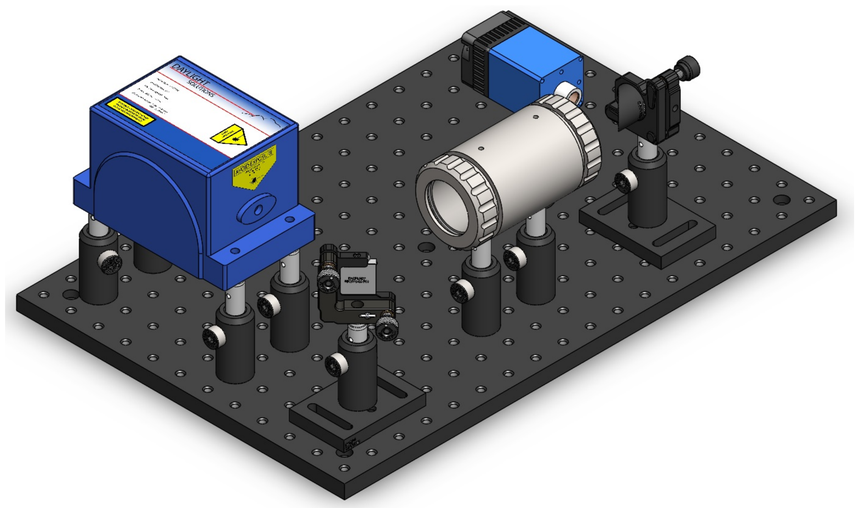

Fig. 2: CAD drawing of the EC-QCL based prototype.

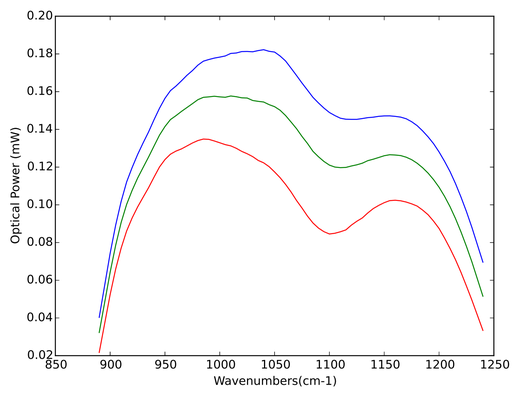

Fig. 3: Optical Power of the EC-QCL at three different gain chip temperatures (13, 18, 23 °C).

Calibrating the Sensor

- Custom built gas mixing rig to mix up to 4 gases
- Saturation module creates a constant vapor stream of the target analytes
- Bruker Matrix and PNNL database for reference measurements (4 cm gas cuvette)

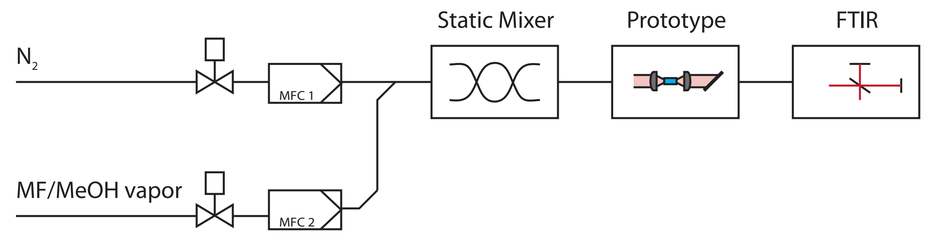

Fig. 4: Gas mixing rig, prototype and Bruker Matrix

Analytes of Interest: Methyl Formate, Methanol

- Side products of formaldehyde production
- Exemplary spectra are shown in Fig. 5 (top)
- Linear regressions are plotted in Fig. 5 (bottom)

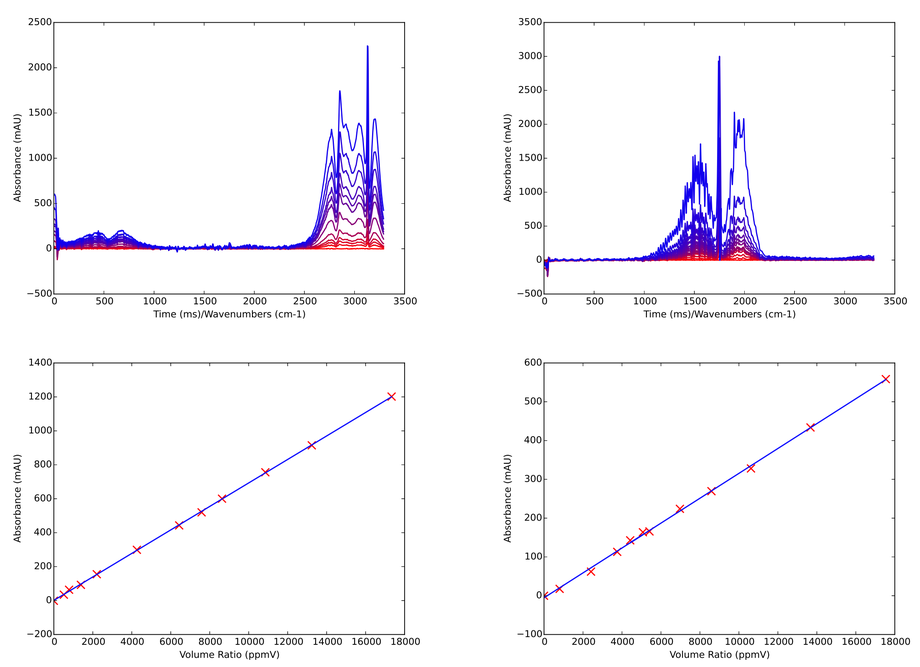

Fig. 5: Examples of recorded spectra and linear regressions for MF (left) and MeOH (right)

LOQ=34.918 ppm/m LOQ=113.752 ppm/m

Outlook

- On-site experiments at Metadynea Austria GmbH
- Additional data processing to improve LOD

Acknowledgments

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