Robust mid-IR spectroscopy using a pulsed external cavity QCL for liquid phase analysis

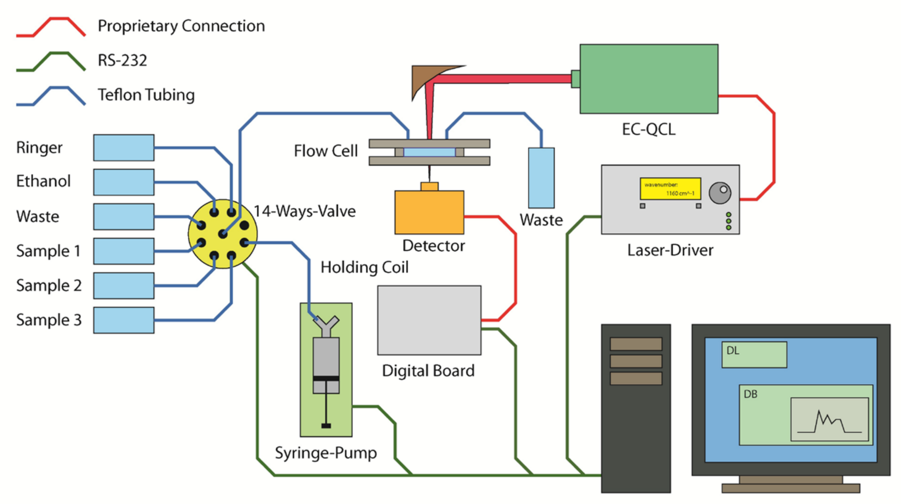
Markus Brandstetter, Georg Ramer, Andreas Genner, Jürgen Kasberger, Bernhard Lendl

Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria
www.cta.tuwien.ac.at/cavs

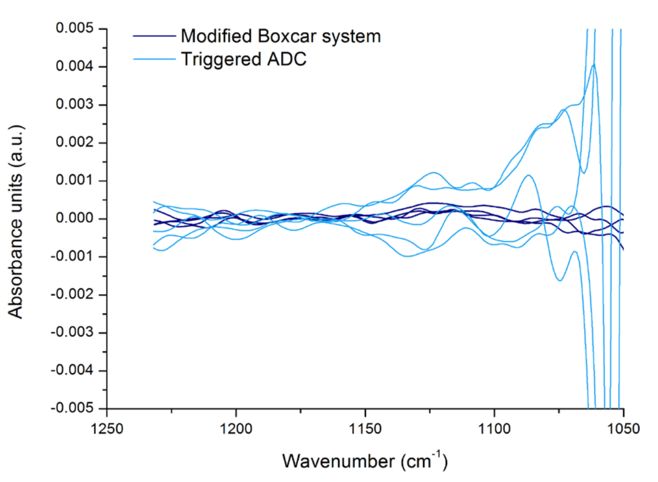
Introduction

Due to their spectral properties and their high emission power, Quantum Cascade Lasers (QCLs) are nowadays robust and powerful sources for mid-infrared radiation. QCLs are available in various modifications concerning the laser type. External Cavity-QCLs (EC-QCLs), e.g., are optimized for a tuning range of several hundred wavenumbers and are therefore well suited for liquid phase spectroscopy (broad absorption bands). For **application to physiological samples** the strong absorption bands of H_2O in the carbohydrate region (around 1000 cm^{-1}) [1] and the protein region (around 1640 cm^{-1}) require high emission power levels, rather than mode-hop free continuous wave operation.
Moreover, signal handling and data processing are both crucial parts for achieving measurement results with sufficient reproducability. One way of improving such an experimental setup is, e.g., to increase the tuning range and/or the laser's intensity which usually means the acquisition of a new laser. A way to circumvent this rather costly undertaking to a certain extent is to optimize the peripheral devices and the software.
Here we report on the development **of two EC-QCL based mid-IR sensor systems comprising a transmission based sensor and a novel slab-waveguide sensor** for robust and sensitive measurements in physiological solutions. The employed EC-QCLs offered a tuning range of 145 cm^{-1} in the protein region and 200 cm^{-1} in the carbohydrate region at an emssion power of 800 mW and 350 mW respectively.

EC-QCL No.1: **Transmission** sensor 8.12 – 9.77 µm

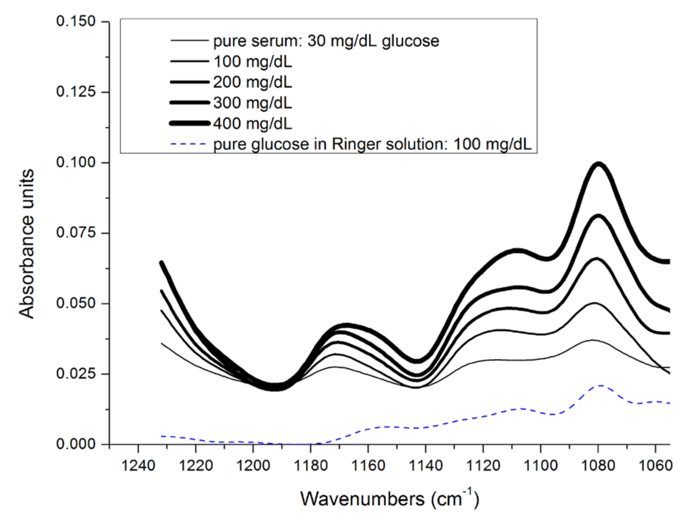


RMS noise < 0.3 mAU at an optical pathlenght of 135 µm



The fully automated sampling system supplied the transmission cell with the blood serum samples; all involved devices, including the tunable QCL were controlled by the user-friendly server/client-based software control ATLAS (Advanced Total Lab Automation System) which was developed in house [2].

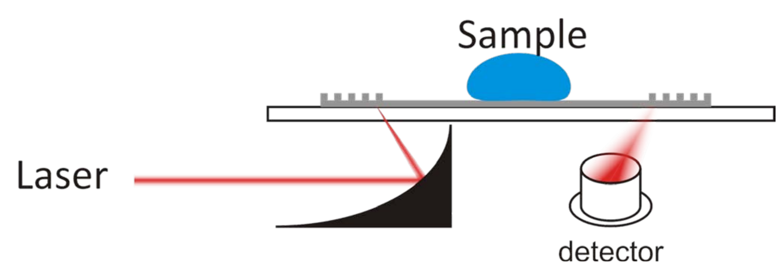
Standard data acquisition is done either by a triggered ADC (single shot detection) or a Boxcar integrator (gated detection).
We chose a new approach with a **modified Boxcar system using a sample/hold element**. A comparison of the 100% lines reveals an improved performance compared to a triggered ADC (16 bit)



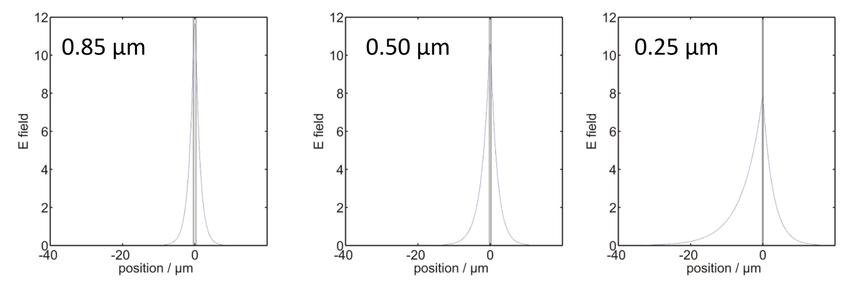
Key advantages	→ **High sensitivity due to high pathlength** → **The whole sample is probed**

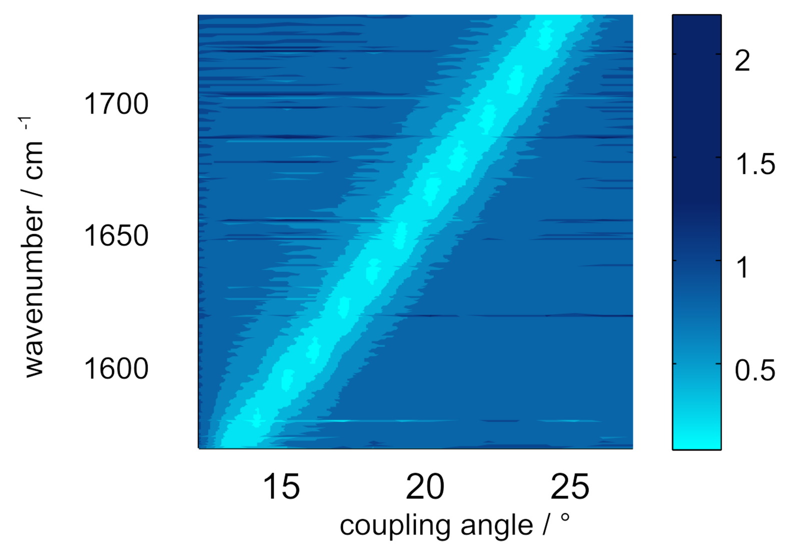
EC-QCL No.2: **Waveguide** sensor 5.78 – 6.3 µm

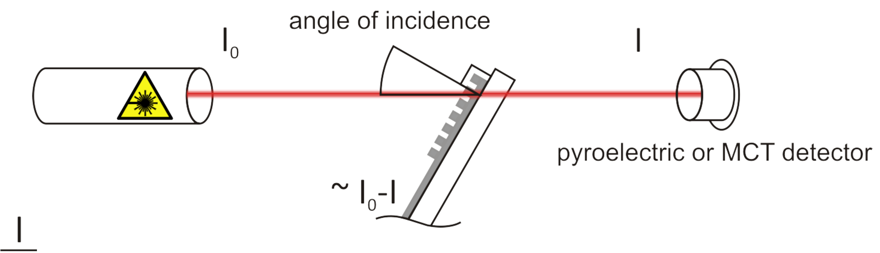
The EC-QCL laser beam was coupled into the slab waveguide by **grating couplers**. This enabled stable and efficient coupling conditions. A thermoelectrically cooled MCT detector (Vigo Systems, Inc.) served as detector.



We used a **single mode waveguide** offering high depths of penetration of the evanescent field into the sample. The actual waveguide material was SiN_3 which was deposited on a MgF_2 substrate.





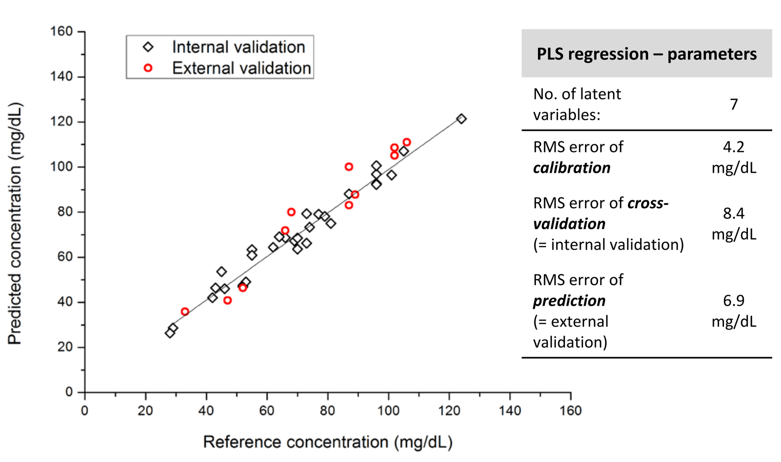


The coupling efficiency of the mid-IR laser depends on the coupling angle and the emission wavenumber. The upper image shows the simple setup for the determination of the coupling efficiency. The results are plotted in the left graph.

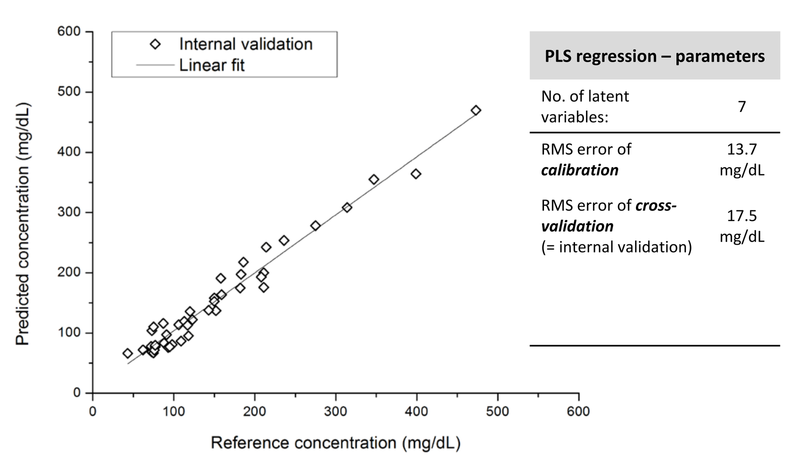
Key advantages	→ **Robustness** → **Fast and easy sampling**

Application: **Quantitative analysis in blood serum**

Glucose

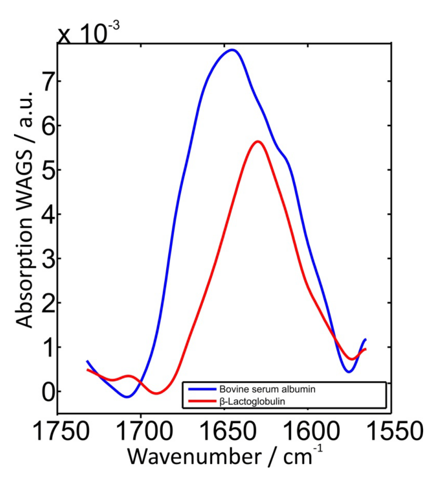


Triglycerides



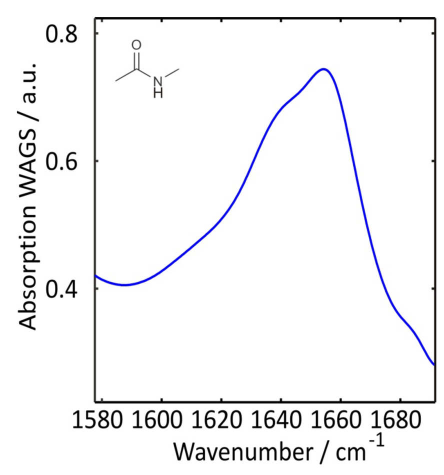
Application: **Measurement of proteins**

Albumin and β-Lactoglobulin



The EC-QCL based waveguide sensor (WAGS) could prove its ability to determine differences in the structure of the amide I band of different proteins.

N-Methylacetamide



References

[1] M. Brandstetter, A. Genner, K. Anic, B. Lendl, "Tunable external cavity quantum cascade laser for the simultaneous determination of glucose and lactate in aqueous phase", *Analyst* **135**, pp. 3260-3265 (2010).
[2] C. Wagner, A. Genner, G. Ramer, B. Lendl, "Advanced Total Lab Automation System (ATLAS), in: *Labview – Modelling, Programming and Simulations*, INTECH (2010).
[3] H.M. Heise, U. Damm, O. Vogt, V. Konderpati, "Towards reagent-free blood glucose monitoring using micro-dialysis and infrared transmission spectrometry", *Vib.Spec.* **42**, pp. 124-129 (2006).

Conclusion

An External-Cavity QCL can be applied for robust and portable sensing applications in the liquid phase, demonstrated by **glucose and triglyceride** measurements in human blood serum using a transmission set-up. The achieved results can compete with those gained with bulky FT-IR spectrometers [3], although the covered spectral range was limited by the maximum tunability of the employed QCL. Moreover a **new slab waveguide sensor** based on a tunable EC-QCL was developed and applied for the measurement of proteins in aqueous solutions.

Financial support was provided by the Austrian research funding association (FFG) under the scope of the RSA (Research Studios Austria) programme and the COMET programme within the research network "Process Analytical Chemistry (PAC)" (contract #825340)