New approaches and applications for the analysis of liquids using mid-IR quantum cascade lasers

B. Lendl*, M. Brandstetter, A. Genner, G. Ramer, J. Kasberger

*a Inst. Chem Techn. & Analytics, TU Vienna, Getreidemarkt 9/164, Vienna, Austria, 1060
*b RECENDT, Science Park 2 / 2. OG, Altenberger Straße 69, Linz, Austria, 4040

BIOGRAPHY

Bernhard Lendl: He obtained his PhD in chemistry in 1996 at TU Vienna. Since 2001 he is associated professor for Analytical Chemistry at the same university. During a sabbatical leave from 2003-2004 he stayed at the University of Córdoba in Spain. Currently he develops chip based analysis systems for label free investigation of (bio)ligand interaction processes, ultrasound enhanced fiber optic sensors for bioprocess monitoring as well as stand-off Raman systems for the remote detection of explosives. In 2008 he co-founded QuantaRed Technologies GmbH, which concentrates on the development and commercialization of mid-IR laser (QCL) based analyzers with focus on applications in the petrochemical industry. His scientific work is summarized in 160 peer reviewed publications and 8 international patents.

TECHNICAL ABSTRACT

Mid-IR spectroscopy allows direct determination of analytes on basis of their highly characteristic infrared spectrum. Due to the narrow ro-vibrational absorption lines present in small gaseous molecules, single wavelength light source, like distributed feedback QCLs, often provide sufficient selectivity for highly specific analyte determination even in a complex matrix. When analytes in liquids have to measured the situation is different for several reasons. First of all the solvent in which the analyte is present will also contribute to the overall attenuation observed when probing the sample. Secondly, absorption bands in liquids are usually several tens of wavenumbers broad and as a consequence it is most likely that absorption features of several molecules present in the sample will overlap. To account for these particularities either sample pretreatment steps before analysis are needed or measurements at several wavelengths are required. Mid-IR spectroscopic measurements can either be carried out in transmission or using different variants of evanescent wave spectroscopy. A significant advantage of using quantum cascade lasers as compared to conventional thermal mid-IR light sources is their high spectral power density, which allows for increased path lengths in liquid phase analysis. As a consequence more sensitive and more robust analyzers for liquids can be designed.

A good example is the QCL based analyzer “ERACHECK” for measuring total petroleum hydrocarbons (TPH) in water. This analyzer probes the C-H deformation bands of oil extracted from waste water samples into the solvent cyclohexane. Based on this new method an ASTM test method (ASTM 7678-11) for TPH has recently been established, being the first official standard requiring the use of QCLs. Recently, this method has been extended for quantification of oil in soil, where again extraction of the sample with cyclohexane is required prior to measurement. Both applications benefit from the fact that a clean-up step is part of the analysis sequence. This step transfers the analyte into a clean solvent and removes matrix components. Therefore, measurement in a narrow spectral range is sufficient for successful quantification of the target analyte.

For direct determination of single or multiple analytes in liquids measurements have to be carried out at several wavelengths in order to assure selectivity of analysis. Here data analysis requires multivariate (chemometric) methods such as partial least square calibration (PLS), which derive the desired analyte concentration from the recorded absorption values. During chemometric model development and model validation an additional analytical reference method is required that provides independent information on the analyte concentrations of the investigated samples. Once a chemometric model has been established, direct and thus rapid analysis is possible only on basis of the spectroscopic data. A portable, fully automated set-up requiring only thermoelectric cooling of the used laser and detector has been developed for point-of-care analysis of human sera.

*bernhard.lendl@tuwien.ac.at; phone 43 1 58801-15140; www.cta.tuwien.ac.at/cavs
Using a tunable external cavity quantum cascade laser (EC-QCL), a room temperature operated mercury-cadmium-
telluride (MCT) detector and a 150 µm transmission flow cell, a spectral range from 1030-1230 wavenumbers can be
covered. Many molecules present in human serum do show characteristic absorption features in this spectral range and
can thus be quantified. Throughout a 6 week measurement campaign human sera samples from a Viennese hospital
(Allgemeines Krankenhaus, AKH) were obtained and measured using the developed EC-QCL based system. Reference
data for a variety of parameters such as glucose, urea, total protein, albumin, C-reactive protein, total cholesterol and
alike were provided by the hospital. For each parameter a separate chemometric model was established. In figure 1
exemplary results obtained for the parameter total cholesterol as well as glucose are shown.

![Figure 1](image1.png)

**Figure 1:** left: Results obtained for total cholesterol, right: results obtained for glucose.

Whereas the developed set-up based on EC-QCL provided satisfying results, efforts are under way to improve the
current state of the art. A more robust set-up void of any moving parts is desired. In this respect the recent development
of vertically emitting ring-QCLs is of high interest. This new type of QCLs allows for several colors which can be
picked as required and addressed separately using one gain medium. Such a device could target a specific application by
selecting the required wavelengths. Here, we report on first results obtained from characterisation of such packaged
lasers and their use in transmission and evanescent wave spectroscopy.

A further recent development concerns planar slab waveguides consisting either of a 1 mm thick MgF₂ window on
which a 0.85 µm thick Si₃N₄ layer was deposited as the light guiding medium, or a 1 mm thick BaF₂ window carrying a
germanium layer for guiding mid-IR radiation. This improved design for performing evanescent wave spectroscopy is
able to efficiently make use of the high spectral power density of quantum cascade lasers. Using these waveguide
structures an intense interaction between the light and the liquid sample can be achieved in a compact measurement
geometry. In figure 2 a section of the optical set-up is shown along with first spectra recorded of polystyrol using an EC-
QCL covering the spectral range from 1570-1730 cm⁻¹. The light was coupled in and out of the waveguide using grating
couplers. By moving the off-axis parabolic mirror, which was used to focus the light onto the waveguide, it is possible to
select the angle by which the beam hits the waveguide.

![Figure 2](image2.png)

**Figure 2:** left: Optical set-up used. Right: Mid-IR spectra of polystyrol, recorded using an EC-QCL –waveguide (MgF₂ /
Si₃N₄) and a standard FTIR-ATR system.

**Keywords:** quantum cascade laser, analysis of liquids, planar waveguides, human serum, oil in water.