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[a] Institute of Analytical and Bioanalytical Chemistry University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

[b] University of Natural Resources and Applied Life Sciences, IFA-Tulln, Konrad Lorenz Strasse 20, A-3430 Tulln, Austria

[c] MG Optical Solutions GmbH, Hauptstr.35c, D-86922 Eresing, Germany

Mycospec

Mid-infrared spectroscopy based on GaAs thin-film waveguide and quantum cascade laser technology as a tool for the detection of deoxynivalenol (DON) in maize extracts

Markus Sieger[a], David McMullin[b], Tuba Oener[a], Gregor Kos[b], Matthias Godejohann[c], Rudolf Krska[b], Boris Mizaikoff[a]

Introduction

Mid-Infrared-based (MIR) analytical methods are rapid and non-destructive techniques that require minimal sample preparation. The MIR spectral region (3-20 µm) provides fundamental vibrational and rotational fingerprint absorptions of organic molecules offering inherent molecular selectivity. Quantum cascade lasers (QCLs) are among the most promising light sources for IR sensing applications due to their compact dimensions, long lifetime, and broad tunability when coupled with an external cavity.[1-4] The combination of highly sensitive thin-film GaAs/AlGaAs planar waveguides with broadly tunable QCLs (1925-885 cm^{-1}) was used to increase the sensitivity of conventional IR measurements of *Fusarium graminearum* contaminated maize by attenuated total reflection (ATR) studies[5,6].

FTIR Studies

Maize samples were either naturally contaminated or inoculated with *F. graminearum* and the trichothecene deoxynivalenol (DON) was quantified by high resolution liquid chromatography tandem mass spectrometry (LC-MSMS). Ground maize samples were extracted with methanol and the extracts were subsequently analyzed via IR-ATR using a Fourier transform infrared (FT-IR) spectrometer. A representative IR spectrum of both, an uncontaminated sample (215 µg/kg DON) and a contaminated (22640 µg/kg DON) is shown in figure 1 for solid maize (left) and a maize extract (right).

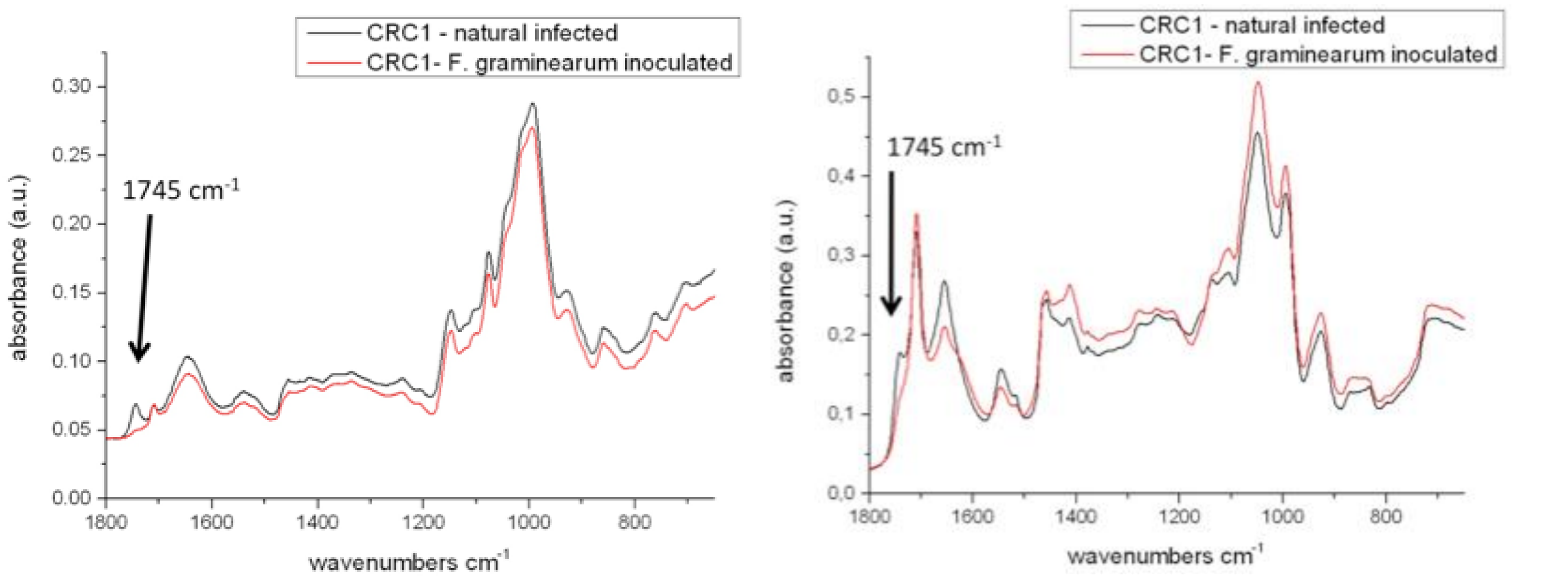


Figure 1: Superimposed IR-ATR spectra of average for solid maize (left) and extracts (right) of naturally infected (black) and *Fusarium graminearum* inoculated maize (red) recorded with a FT-IR spectrometer.

Significant spectral changes in the amide region (1800-1600 cm^{-1}) were observed, and in particular a decreasing spectral feature at 1745 cm^{-1}, which may be indicative of the damage caused by the fungal infection, and can be correlated to the overall mycotoxin concentration in the investigated sample.

PCA Results

The obtained IR spectra were finally evaluated via principle components analysis (PCA) in order to establish a first multivariate calibration/classification model. Therefore, the spectra were averaged, normalized and evaluated by a Matlab-based chemometrics software (Eigenvector PLS Toolbox). PCA was performed for either the pretreated spectra or by using the 1st derivative of the spectra, yet without any data pretreatment.

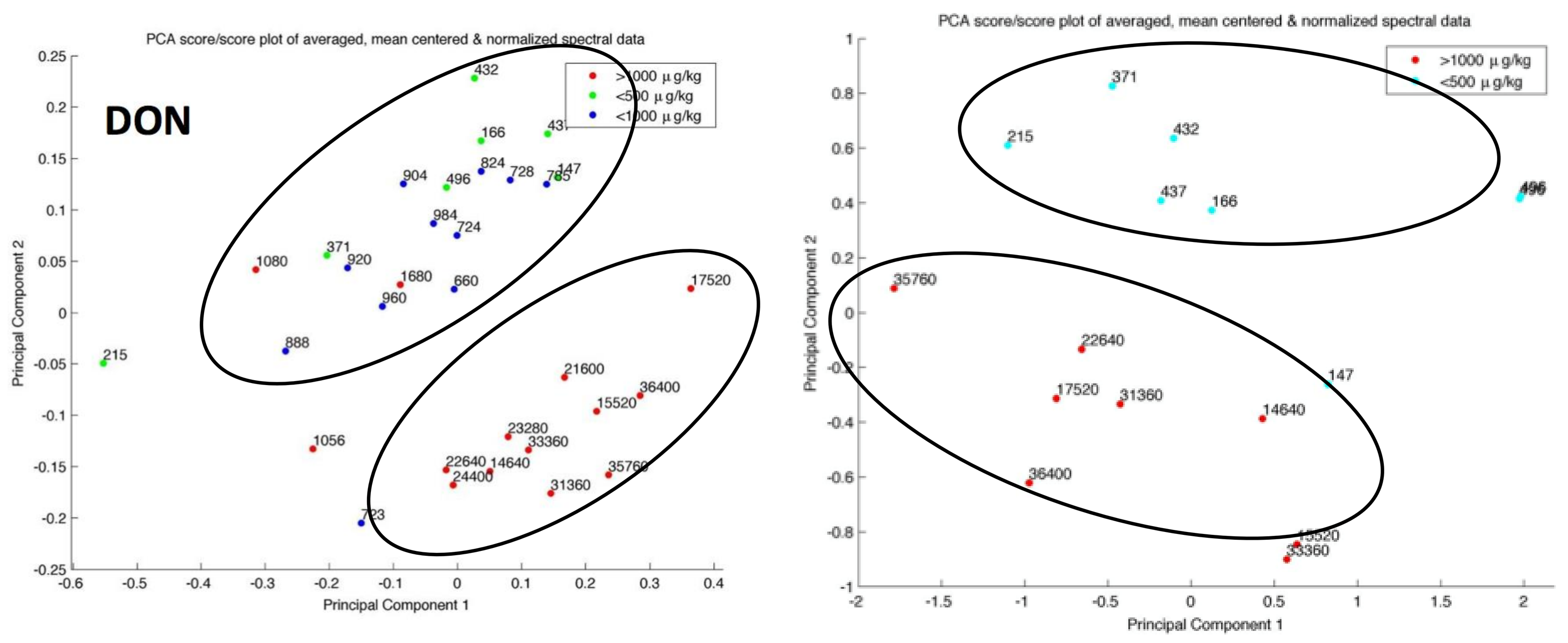
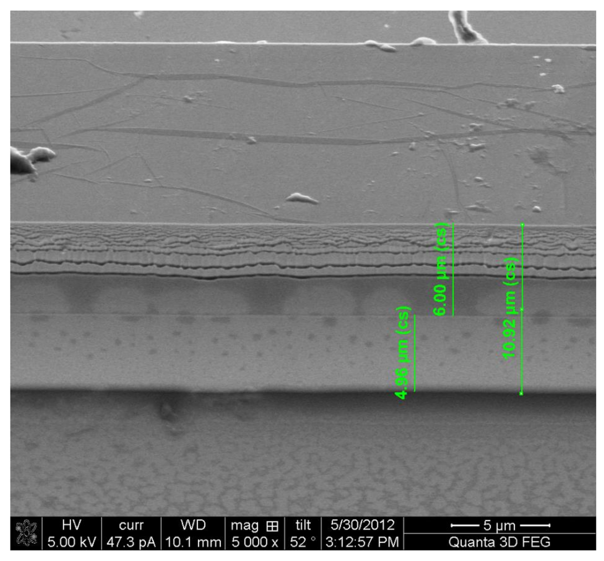
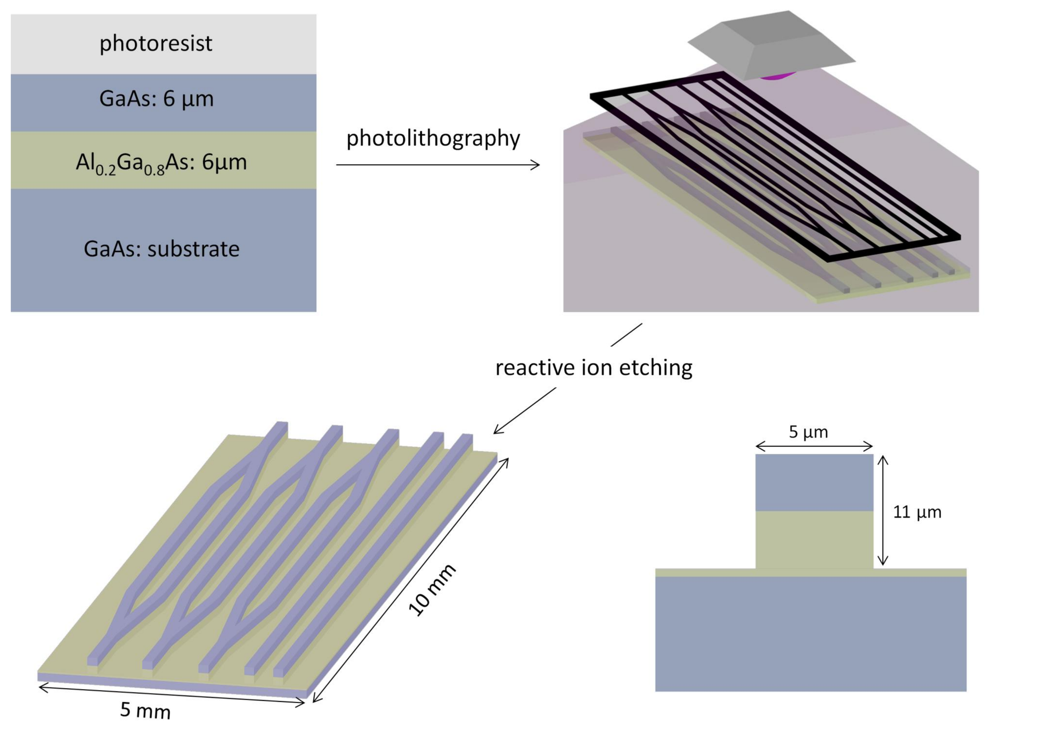


Figure 2: Preliminary PCA results for solid maize (left) and methanol extracts (right).

Waveguide Fabrication

MIR devices were microstructured from waveguide layers deposited at the surface of a 1 mm thick GaAs (n=3.3) wafer with a 6 µm thick optical buffer layer comprising $Al_{0.2}Ga_{0.8}As$ (n=3.2), and the actual GaAs waveguiding layer, again with a thickness of 6 µm. The strip waveguide structures were defined via optical photolithography, and were fabricated using reactive ion etching (RIE).





After spincoating a photoresist onto the surface, the wafer was exposed to UV radiation via a manual mask aligner. The subsequent development process lead to photoresist MZI patterns, which were then transferred to the wafer via RIE.

QCL Measurements

Extracts of uncontaminated maize samples were applied to the GaAs thin-film waveguide via pipetting covering the entire waveguide surface, and were then allowed to evaporate prior to QCL analysis. As expected and clearly evident, some spectral features, which are usually superimposed within broadband FT-IR spectra appear more pronounced in the QCL measurements due to the improved sensitivity attributed to the combination of thin-film waveguides and tunable QCLs.

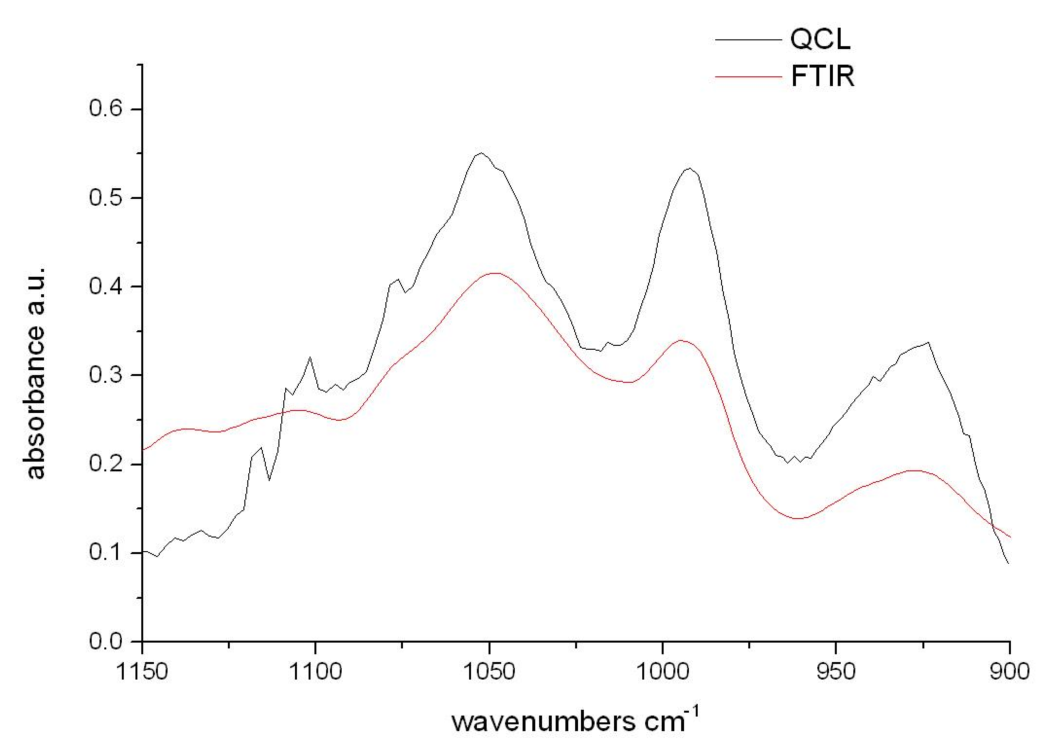


Figure 3: Single-scan QCL spectra of maize extracts for the amide band (black) vs. 100 averaged FT-IR spectra (red).

Conclusions & Outlook

First promising results show the feasibility of QCL-based mid-infrared spectroscopy for the determination of mycotoxins in maize extracts. Further optimization of the chemometric models and in particular the GaAs waveguide design is essential to increase the sensitivity and repeatability. Future work will focus on the chip design (figure 4), as well as the investigation of different contaminated matrices (e.g. peanuts).

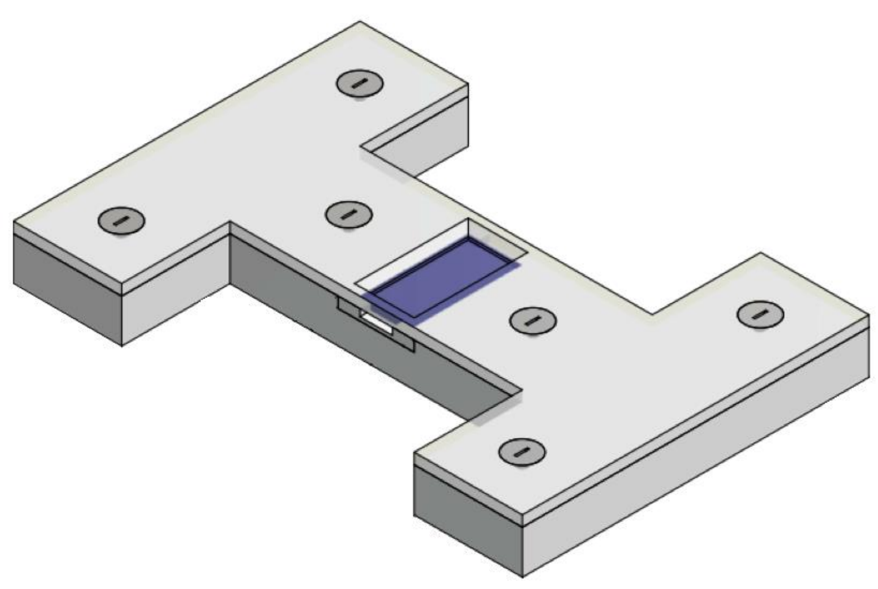


Figure 4: Chip-holder design for GaAs thin film waveguides.

References

[1] C. Charlton, et al., Appl. Phys. Lett., 86, 194102 (2005).
[2] C. Charlton, et al., Anal. Chem., 78, 4224-4227 (2006).
[3] C. Young, et al., Sens. & Act. B, 140(1), 24-28 (2009).
[4] X. Wang, et al., Analyst, 137, 2322-2327(2012).
[5] G. Kos, et al. Anal. Bioanal. Chem., 378, 159-166 (2004).
[6] G. Kos, et al. Vib. Spectros., 29, 115-119, (2002).

CONTACT:
Dr. Boris Mizaikoff
boris.mizaikoff@uni-ulm.de

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