SIMULTANEOUS USE OF TWO QCLs FOR ON-LINE MID-IR DETECTION WITH HPLC FOR WINE ANALYSIS

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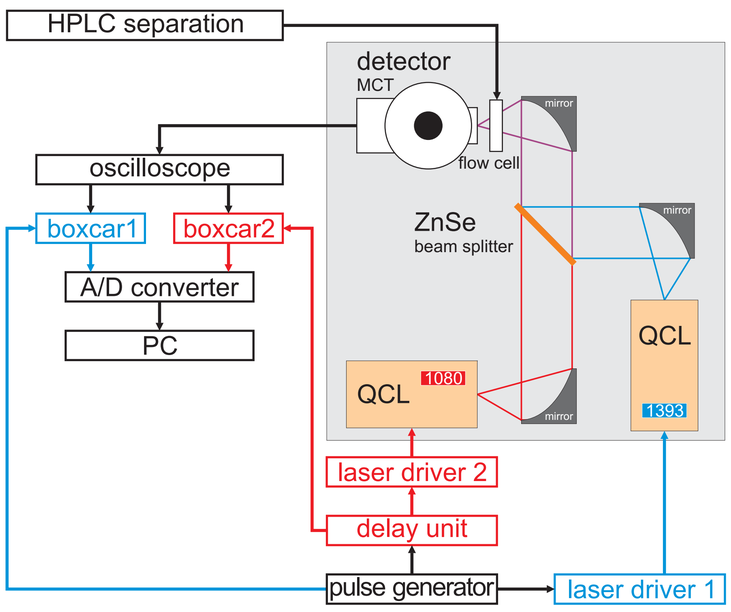
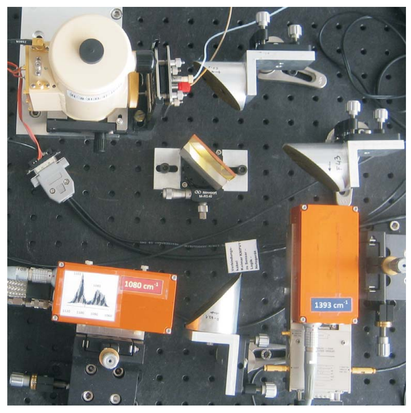
ABSTRACT

In the present study the simultaneous use of two Quantum Cascade Lasers (QCLs) was investigated for the on-line detection in High Performance Liquid Chromatography (HPLC). An optical set-up based on three gold mirrors and a ZnSe beam splitter was used to direct the emitted laser light trough a calcium fluoride flow cell with an optical path length of 52 µm onto a Mercury-Cadmium-Telluride (MCT) detector. Using the separation of eight components of wine and grape juice, on-line dual QCL detection in HPLC could be shown successfully for the first time.

EXPERIMENTAL SETUP

MANIFOLD SKETCH AND PICTURE

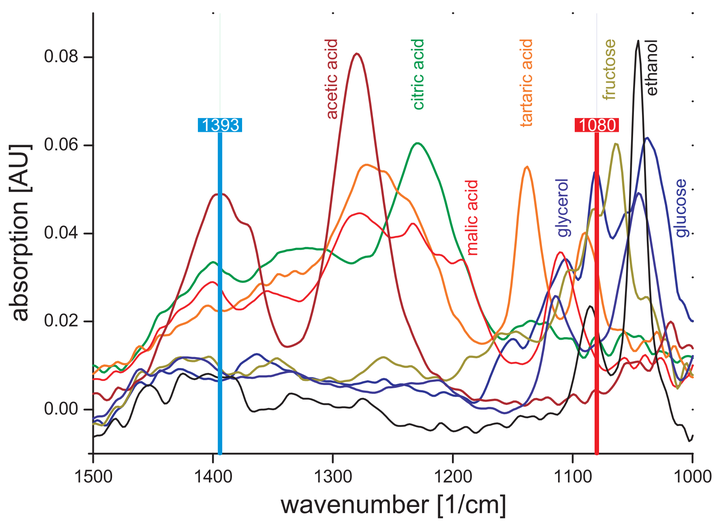




Separation of aqueous solutions of organic acids and sugars is done via High Pressure Liquid Chromatography.
The separated components are pumped through a CaF_2 flow cell with an inner diameter of 52 µm.
The measurement principal is mid- infrared absorption spectroscopy.
Two alternetly pulsed Quantum Cascade Lasers of different wavelength are focused on a MCT detector. The beam intensities are reduced while passing the flow cell, depending on the analyte concentration.
The detector signal is separated electronically using boxcar averagers, processed via A/D converter and stored on a PC.

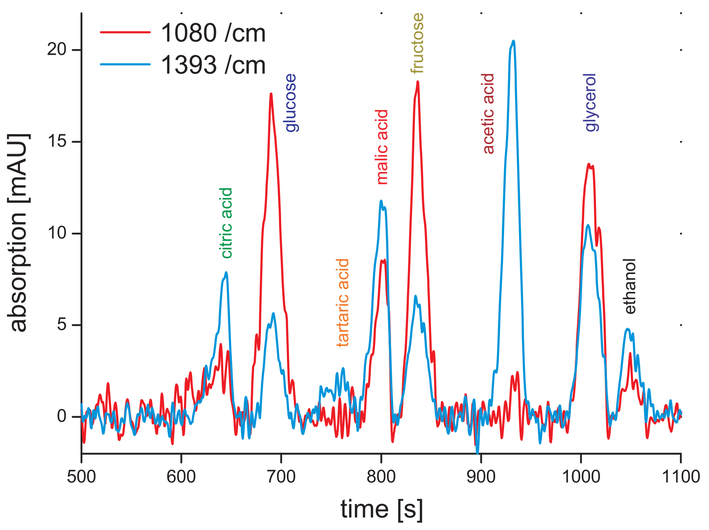
QC - LASERS

Two Quantum Cascade Lasers (QCLs) are used to quantify sugars and organic acids. Substance spectra of 3 g/l solutions in water were analysed on a FTIR spectrometer. At 1393 cm^{-1} the C-O-H in-plane bending vibration of the COOH group is located, allowing the measurement of organic acids. Whereas the C-C-O stretching vibration of the C-O group, between 1210 and 1000 cm^{-1} allows sugar analysis [1].



HPLC - SEPARATION

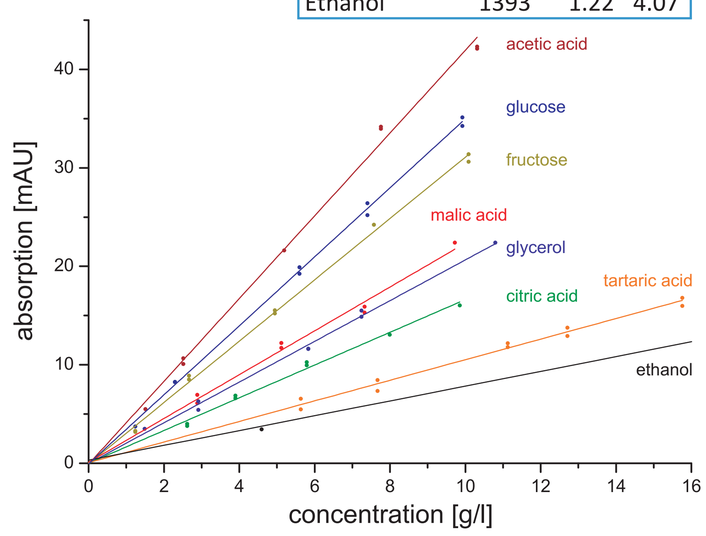
Separation via HPLC using a 50 µl injection loop.
Column: Rezex Monosaccharide Ca^{2+}, 300x7.8 mm
Temperature: 85°C
Flow rate: 0.6 ml/min
Mobile phase: de-ionised water
The graph below shows the chromatograms at both laser wavenumbers (1080 and 1393 cm^{-1}) for substance mixtures of 5 g/l .



CALIBRATION

Calibration using aqueous solutions of eight substances ranging from 1-10 g/l (1-100 g/l for EtOH)

ANALYTE	QCL [1/cm]	LOD [g/l]	LOQ [g/l]
Citric Acid	1393	0.46	1.53
Glucose	1080	0.24	0.72
Tartaric Acid	1393	1.29	4.53
Malic Acid	1393	0.38	1.39
Fructose	1080	0.23	0.69
Acetic Acid	1393	0.19	0.56
Glycerol	1080	0.28	0.92
Ethanol	1393	1.22	4.07



EVALUATION

WINE SAMPLES

The performance of the developed method was tested on real samples with a complex matrix such as wine and grape juice.

The Relative Standard Deviation (RSD) lies between 0.1 and 10% in all measured samples and for all detected analytes.

RECOVERY

Recovery experiments were carried out to assess the accuracy of the proposed method. Previously analysed wine and grape juice samples were spiked with known amounts of the found analytes at two different concentration levels and analysed twice.

The recovery values of all compounds were satisfactory and ranged between 95 and 109%.

CONCENTATION FOUND [g/l] ± s (RSD [%])

ANALYTE	White wine Traminer	White wine Welschriesling	White grape juice	White wine Neuburger	White wine Weissburgunder	Red grape juice	Red wine Zweigelt
Citric Acid	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Glucose	4.5±0.1 (2.20)	< LOD	63.3±0.2 (0.35)	1.5±0.1 (8.64)	1.1±0.1 (9.99)	90.31±0.09 (0.10)	< LOD
Tartaric Acid	4.7±0.4 (8.65)	<LOQ	6.0±0.2 (3.49)	6.1±0.3 (4.48)	5.0±0.4 (8.15)	14.1±0.9 (6.21)	< LOD
Malic Acid	< LOD	<LOQ	4.2±0.1 (2.74)	< LOD	< LOD	< LOD	< LOD
Fructose	24.1±.0.4 (1.55)	2.70±0.03 (1.26)	59.4±0.5 (0.87)	< LOD	1.1±0.1 (9.64)	85.7±0.9 (0.99)	< LOD
Acetic Acid	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Glycerol	5.7±0.3 (5.92)	3.6±0.3 (8.72)	< LOD	5.9±0.5 (8.38)	6.3±0.5 (8.55)	< LOD	7.4±0.3 (3.83)
Ethanol	109.2±3.3 (2.98)	92±2 (2.20)	< LOD	108.1±2.6 (2.37)	113.5±0.4 (0.37)	< LOD	108.5±0.8 (0.70)

CONCLUSION

This study demonstrated, for the first time, the feasibility of the introduced on-line coupling of a HPLC separation to a dual QCL detection system.

All investigated species could be chromatographically separated, detected and quantified in complex matrices, as the analysis of seven different wine and grape juice samples showed.

The use of a dual QCL system leads to more selective and robust measurement systems as more structural information on the investigated system is obtained.

REFERENCES

[1] Lin-Vien, D.; Colthup, N.B.; Fateley, W.G.; Grasselli, J.G.; Infrared and Raman Characteristic Frequencies of Organic Molecules. Academic Press: London (1991) 296.

This project was founded by the ___