Mid-IR photothermal spectroscopy (PTS) for the detection of caffeine in commercial drinks

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Introduction

01

Mid-infrared (mid-IR) spectroscopy is a versatile analytical technique that allows for qualitative and quantitative analysis. It is based on probing highly selective rotational and vibrational transitions of analyte molecules present in gases, liquids and solids. [1] Classical absorption spectroscopy based on Lambert-Beer´s law relies on detection of minute differences in light intensity. However, as absorbance does not scale with laser power it does not fully benefit from quantum cascade lasers' (QCLs) high power and brilliance. [2] At the contrary, photothermal spectroscopy (PTS) is an indirect detection approach where the generated analytical signal is directly proportional to the applied laser power. [3] In this work, we exploit our technique to detect caffeine in commercial drinks (coffee, black tea and energy drink) and we validate and calibrate our method using gas chromatography (GC) as a reference method. Nowadays, caffeine is the most widely consumed psychoactive drug worldwide and caffeine threshold in commercial drinks is defined by specific laws in each country. For industries is thus important to monitor this quantity to satisfy the applied regulations.

Direct vs. Indirect Spectroscopy

02

DIRECT

Intensity (Absorption) via **Lambert-Beer**'s law:

$$A = \mathbf{L} \cdot c \cdot \varepsilon = \log\left(\frac{I_0}{I}\right)$$

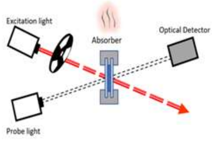
L … Optical pathlength
A …Absorbance
ε … Molar absorption coefficient
c … Concentration
φ … Optical phase
n … Refractive index
l … Wavelength

INDIRECT

Temperature and **refractive index** (Photothermal Spectroscopy (PTS)):

$$\Delta T = \mathbf{P} \cdot \frac{c \cdot \varepsilon}{f_{mod} \cdot A \cdot c_P \cdot \rho}$$

P … Optical power
T_0 … Amplitude of thermal wave
A … *Beam cross section area*
f_{mod} *Modulation Frequency*
c_P … *Heat Capacity*
ρ … *Density*



Sample preparation & Reference Analysis

03

Six standards ([0.1;0.5;1;1.5;2;2.5] mg/mL of caffeine in $CHCl_3$) were measured using GC with a flame ionisation detector. The isolated peak areas were integrated and used as a reference value for calibration and validation. The eluted samples were measured both via the developed PTS and an FTIR spectrometer for qualitative comparison of the obtained IR spectra.

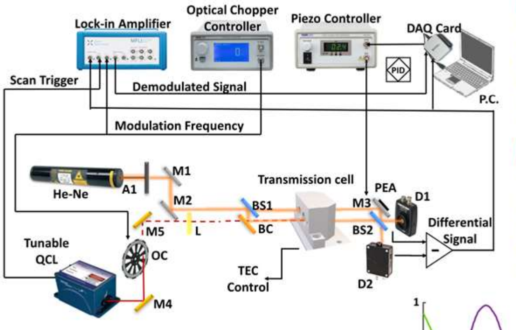
C-18 SPE columns were set up in a manifold and conditioned by passing $CHCl_3$ (5 mL) and H_2O (5 mL). The aqueous samples (coffee, tea and energy drink, 4 mL and 8 mL samples) were loaded onto the sorbent material. After passing through the columns with a flow of 0.2 – 0.5 mL min^{-1}, the sorbent was rinsed with H_2O (1 mL) and dried with a stream of nitrogen. Subsequently, the analyte was eluted with $CHCl_3$ (4 mL).

REFERENCES

[1] Griffiths, P. R.; De Haseth, J. A. Fourier Transform Infrared Spectrometry; John Wiley & Sons, Inc: Hoboken, NJ, 2007.
[2] Schwaighofer, A.; Brandstetter, M.; Lendl, B. Quantum Cas-cade Lasers (QCLs) in Biomedical Spectroscopy. Chem. Soc. Rev. 2017, 46 (19), 5903–5924. https://doi.org/10.1039/C7CS00403F.
[3] Bialkowski, S. E. Photothermal Spectroscopy Methods for Chemical Analysis; John Wiley & Sons, 1996.

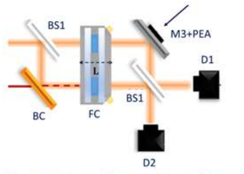
Experimental Setup

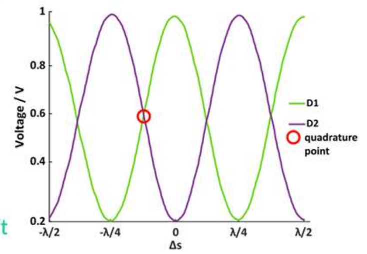
04



Probe laser:
Operation Wavelength ~ 632.8 nm
Power ~ 0.5 mW
Beam Diameter ($1/e^2$) ~ 0.46mm
Linear Polarization

Excitation laser:
Wavenumber range: 1730-1565 cm^{-1}
CW mode modulated by a Chopper at a low modulation frequencies f_{mod} to maxamise the PT signal





Refractive Index Change

$$\Delta n = \left(\frac{n-1}{T_0}\right)\Delta T$$

Phase Shift

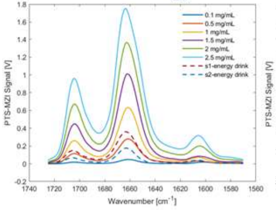
$$\Delta\varphi = \frac{2\pi}{\lambda} \cdot L \cdot \Delta n$$

- **Photothermal Interferometry -** highly sensitive phase sensitive detection technique;
- **Dual-beam collinear configuration –** permits to achieve better absolute sensitivity because a longer interaction length between the beams is provided;
- **Active locking-scheme –** a piezo electric actuator is directly glued on a mirror in one arm of the interferometer to compensate optical-pathlength differences between the two arms via a PID servo-controlled loop;
- **Temperature Stabilization –** allows to reduce thermal drifts and fluctuations;
- **Flushing with dry air –** allows to remove water vapor contribution as a main source of noise;

Results

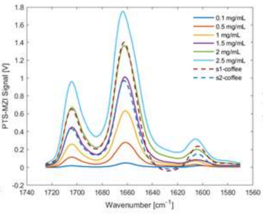
05

Caffeine in energy drink



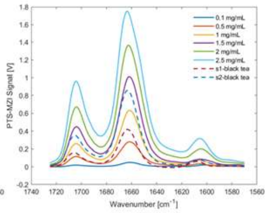
Method	s1 [mg/mL]	s2 [mg/mL]
GC	0.6291	0.3290
PTS	0.5858	0.3283

Caffeine in coffee



Method	s1 [mg/mL]	s2 [mg/mL]
GC	2.0307	1.4402
PTS	2.0379	1.4397

Caffeine in black tea



Method	s1 [mg/mL]	s2 [mg/mL]
GC	0.6722	1.2812
PTS	0.6682	1.2795

Limit of Detection (LOD) and Limit of Quantification (LOQ) – FTIR vs PTS spectrometer

Method	S	σ	LOD [mg/mL]	LOQ [mg/mL]
FTIR (Vertex)	0.3017 [A.U./ mg/ mL]	0.0027 [A.U.·mg/ mL]	0.027	0.089
PTS	0.7165 [V/ mg/ mL]	0.0064 [V·mg/ mL]	0.027	0.089

Conclusions

06

- Photothermal Spectroscopy (PTS) allows for fast, sensitive analysis of liquid samples
- The generated signal in PTS scales direct proportional with the excitation laser power
- Mid-IR PTS allows for direct reagent-free analysis through the measurement of rotational-vibrational transitions in the target analytes
- Quantitative determination of caffeine in coffee/tea/soft drinks has been demonstrated
- Mid-IR PTS allows additionally to retrieve qualitative information. Absorption peaks' positions and band-shape are in very good agreement with records from high-end FTIR spectrometers

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