

Cocaine detection in liquid using a fibered platform and a mid-infrared quantum cascade laser

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Abstract: A miniaturized, trace level sensor for cocaine is presented. A quantum cascade laser emitting at 1720 cm⁻¹ is coupled to a fibered absorption flow-cell. A detection limit lower than 250 ng/mL (84 ppb) is reported.

OCIS codes: (300.6340) Spectroscopy, infrared; (300.6360) Spectroscopy, laser

1. Introduction

An increasing demand for compact, selective and sensitive systems for trace analyses of various chemical species emerges in many areas of human activities, medical care being among the most important ones. The mid-infrared band is well suited for building spectroscopic sensors, due to the multitude of chemical species having fundamental ro-vibrational modes in resonance with the mid-infrared radiation frequencies (tens of THz). Compared to the light sources used in FTIR, Quantum cascade lasers (QCLs) provide significantly higher spectral densities (10⁶ times higher) and very narrow emission lines (few MHz). The high spectral density of the light allows for transmission over much longer optical paths compared to broadband sources. This inherently provides a high sensitivity. The narrow emission spectrum eliminates the need of an analyzer element in the sensor's scheme, making it potentially compact as compared to a spectrometer. Previous developments in mid-infrared liquid spectroscopy using QCLs have demonstrated detection limits to the order of 0.5 ppm [1–3].

2. Experiment

A quantum cascade laser emitting at 1720 cm⁻¹, targeting the C=O bond of cocaine has been used in conjunction with a fibered absorption cell of 3 µL volume. The carboxyl-group resonance of cocaine around 5.8 µm (1720 cm⁻¹) provides a small cross-talk with other potentially interfering species [4]. Trace quantities of cocaine solution in tetrachloroethylene (PCE) at varying concentrations have been pumped continuously through the cell, while recording the response using lock-in technique. The QCL was specifically designed and fabricated for this experiment and its emission wavelength was finely tuned, adjusting the operating point of the device to match the maximum of the analyte's absorption.

A schematic of the setup is shown in Fig. 1. The laser beam was collimated using a positive meniscus ZnSe lens. An optical chopper set at a frequency of 370 Hz provided amplitude modulation of the beam for synchronous detection. The beam was focused into a single mode fiber using a gold coated 15X/0.28NA reflective microscope objective. The light was then coupled into a multi-mode stainless steel flow cell with a 0.5 mm internal diameter. The path length inside the cell was 15 mm (± 1 mm). The output of the cell was butt-coupled into a mercury cadmium telluride (MCT) room temperature photovoltaic detector via a multimode fiber. The signal from the MCT was converted in a transimpedance amplifier and sent into a lock-in amplifier referenced by the chopper. The analog output of the signal from the lock-in amplifier was digitalized and recorded in time.

The liquid dosing setup consisted of two recipients containing the sample and pure matrix (PCE), each connected to a 3-way valve via a 15 cm long PTFE hose with a 0.8 mm internal diameter. The output of the valve was connected to the flow cell via an 80 cm long PTFE hose. The first solution was prepared taking 1 mg of cocaine dissolved in 20 mL of PCE (50 µg/mL) and lower concentrations were prepared by subsequent dilution of this standard. The system was verified with a solution independently prepared at the Laser Spectroscopy and Sensing Lab at ETH Zürich, following a procedure previously reported [5]. A pressure of 150 kPa has been applied in the head volume of the recipients to propel the liquids through the system.

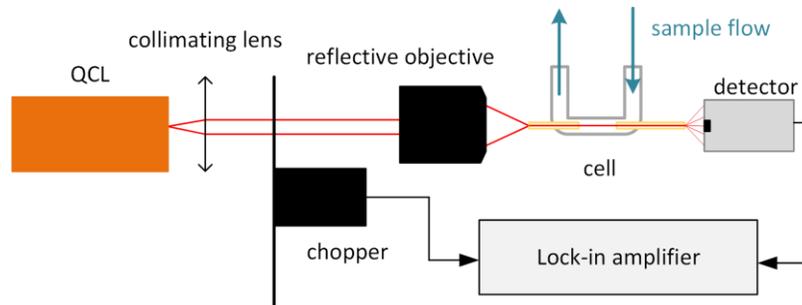


Fig. 1. Schematic of the setup. The collimated laser beam is focused into a fibered flow cell. The absorption level is measured via a mid-infrared photovoltaic detector butt-coupled to the output fiber of the cell.

The transmission level was benchmarked and stabilized while the pure PCE flowed through the cell. The valve was then switched to allow the sample with cocaine from the second recipient to enter the cell. The valve was left in that state for 2 minutes and then switched back to the pure PCE. As the cocaine solution replaced the pure PCE inside the flow cell, the signal from the lock-in amplifier dropped to the level corresponding to the absorption of the cocaine in the sample. From the moment it started falling, the signal took about 4 minutes to recover its base level. Multiple measurements were made in a row, alternating between the reference and the sample. Once a series of measurements for one concentration was terminated, the test sample bottle was exchanged with a pure PCE bottle and its contents pumped through the capillaries in order to clean them. The samples were measured starting from the smallest concentration to the highest one, in order to minimize any parasitic signal that could occur from a potential residual contamination of the capillaries by the previous sample.

The absorption inside the cell was evaluated by taking an average value of the signal while at its lowest point and dividing it by the average of the signal corresponding to the pure PCE.

3. Results

Figure 2 shows the absorption ratio for different concentrations, using the same cell and applying the same flow rate. The lowest concentration that we were able to repeatedly detect without any data treatment was 250 ng/mL (84ppb). It was noticed that, for small concentrations, the flow rate of the solvent inside the cell had an impact on the measurements. Figure 3 shows the absorption ratio of the same sample of cocaine through the cell under the effect of different flow rates. On this figure, low rates coincide with a lower absorption than the high ones. This could be explained by penetration of the cocaine into the PTFE walls of the tubing. There is also a possibility of diffusion of the cocaine into the neighboring pure solvent sections. This effect was much less pronounced in the case of the maximum concentrations we measured and tends to diminish with the increase of the flow rate. The flow rate was therefore kept to the highest possible value and controlled to be the same through all the measurements, around 0.015 mL/s. Figure 4 shows the signal from the detector, when a 25ug/mL concentration of cocaine in PCE flows through the cell.

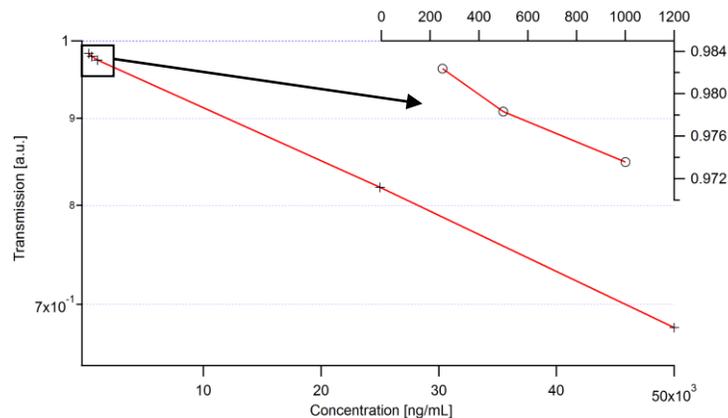


Fig. 2. Relative transmission of the cell as a function of the concentration of cocaine in PCE, the vertical scale is logarithmic. As expected, the absorption inside the cell increases with increased cocaine concentration. The lowest detectable concentration is 250 ng/mL.

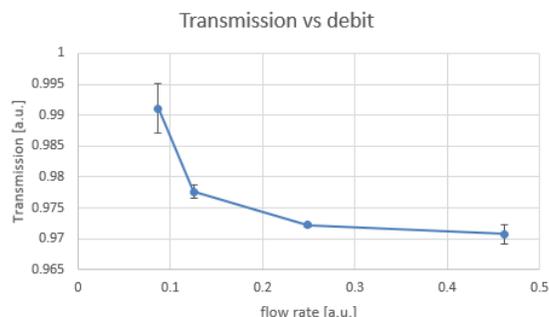


Fig. 3. Minimum transmission of the cell as a function of various flow rates for a concentration of $1\mu\text{g/mL}$. This effect is to be assigned to the influence of the signal arising from diffusion of the analyte into the PTFE tubing walls.

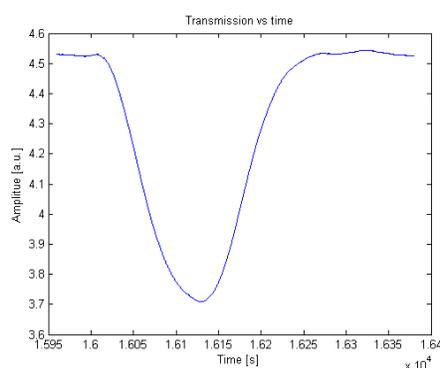


Fig. 4. Drop of transmission of the cell for a sample at $25\mu\text{g/mL}$ of cocaine. This graph represents the raw data from the system without any signal post-processing applied

The system can be improved in many aspects in order to achieve a better stability and sensitivity. A differential measurement can eliminate the fluctuations of the signal caused by instability of the laser. Direct fiber coupling without the use of macroscopic optical elements will further contribute to the system's stabilization and miniaturization. In its current state, the setup is limited to the detection of cocaine and is subject to interferences if other compounds with a close absorption line are present. Using a tunable laser or multiple laser sources will increase the selectivity of the setup, and also make it more versatile.

4. Conclusion

We have realized a device capable of sensing trace amounts of cocaine in liquid based on a quantum cascade laser and a fibered absorption cell. A concentration as low as 250 ng/mL could be detected, which corresponds to about 84 ppb . The entire detection process takes less than 10 minutes. This device could easily be adapted to the detection of other substances in liquid by adapting the wavelength of the laser source.

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5. References

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