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Quantum cascade laser modulation for correction of matrix-induced background changes in aqueous samples

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ABSTRACT A robust method for the determination of carbon dioxide in sugar containing solutions using a single distributed feedback quantum cascade laser (QCL) has been developed. By switching the driving current between two selected values, 1.6 and 1 A, emission wavelengths at 2341.4 and 2341.6 cm^{-1} could be achieved.

The method is based on absorbance measurements in transmission and the calculation of the absorbance differences between both wavenumbers. This allows the elimination of indirect matrix interference produced on carbon dioxide measurements with increasing sugar concentrations. A flow injection setup was employed to produce carbon dioxide standards from a series of bicarbonate solutions (0–3 g/l) by adjusting the pH with a sodium hydroxide/citric acid buffer solution to pH 3.13. Different concentrations (0–90 g/l) of sugar were also mixed on line with the analyte to study their influence on carbon dioxide measurement. As the difference in the two evaluated wavelengths is small compared to the absorption peak of CO_2, the analytical readout of the QCL modulation can be seen as a proportional parameter to the first derivative of FTIR spectra in this spectral region.

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1 Introduction

Mid-infrared laser spectroscopy is a powerful tool for many sensing applications [1, 2]. Most molecules exhibit their fundamental vibrations in the mid-infrared region showing higher absorption coefficients than the overtones in the near infrared. Compared to broadband emitters, laser light sources provide increased spectral power densities enabling one to improve signal to noise ratios and hence reduced detection limits. The demands on the laser source [1] are a compact design, a narrow line width and preferable room temperature or near room temperature operation. Ideally, the wavelength should be tuneable across absorption lines of one or more analytes. Quantum cascade lasers (QCLs) are semiconductor lasers that can easily fulfill these demands in gas sensing applications. The light generation in QCLs is based on intersubband transition within the conduction band [3]. The electron states arise from size quantisation in semiconductor heterostructures. The wavelength can be tailored by bandstructure engineering over a wide spectral region and to the particular need of a given application. The distributed feed back [4] (DFB) design ensures narrow line width. Most application of QCLs aim at the detection of trace gases [5–10] with various techniques. In the gas phase mostly – with some exceptions [11] – it is usually possible to find background free, isolated absorption lines that can be used for sensitive and selective measurements.

However, absorption bands in the condensed phase are much broader than in the gas phase, and spectral overlapping is frequent. For some applications in the liquid phase, it is advisable to apply more than one laser to explore an extended wavelength region. Martin et al. [12] demonstrated this for the monitoring of glucose in serum by performing subsequent measurements at 1036 and 1194 cm^{-1}on the same sample. An improved setup allowing for quasi simultaneous measurements using two Fabry–Pérot QCLs (1393 and 1080 cm^{-1}) has recently been reported by Schaden et al. and applied to the simultaneous measurement of glucose and sodium acetate [13] as well as sulfite/sulfate and peroxide [14]. Separation of the analytes from interfering matrix molecules prior to the detection as well as a chemical modulation to induce analyte characteristic spectral changes are alternative strategies to increase selectivity in liquid phase. This was demonstrated for QCL absorption spectroscopy in combination with high performance liquid chromatography [15], capillary electrophoresis [16] and flow injection analysis [17].

The high spectral power density of QCLs as compared to thermal light sources brings also substantial advantages for liquid phase measurement. In this context the possibility of increasing the employed optical path for transmission measurements from typically 8–30 μm as used in FTIR-spectroscopy to about 120–150 μm [18] must be mentioned.

Beside spectral overlapping of the analytes and strong solvent absorption FTIR spectroscopy in aqueous phase is often made difficult by changes in the water background absorption arising from pH changes [19] or changing concentrations of solutes [20–22]. As a consequence baseline changes are often observed in the analyte spectra. Calculation of first derivative spectra is a common approach to compensate for baseline drifts arising from these effects. To apply this concept to QCL spectroscopy it becomes essential to perform meas-

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urements at least at two neighboring wavelengths. Evaluation of the recordable absorbance differences is thus a promising approach for robust QCL absorption spectroscopy in liquid phase.

In this paper we used the above outlined concept for the first time to compensate for matrix interferences in the determination of CO_2 due to changing sugar concentrations. The possibility of a QCL based measurement of dissolved CO_2 has been demonstrated previously using a single wavelength for analysis [23]. However, further studies showed that for the realization of a robust QCL based process analyzer for CO_2 means to correct changes in the water background absorption due to the presence of other constituents in beverages had to be found.

2 Experimental

2.1 *Chemicals*

All used chemicals were of analytical grade. Fructose, sucrose and sodium hydrogen carbonate ($NaHCO_3$) were purchased from Merck. Glucose and sodium hydroxide (NaOH) were purchased from Fluka and citric acid from Sigma/Aldrich. All solutions were prepared in distilled water. The buffer solution (100 mM) was prepared by dissolving citric acid crystals in distilled water and adjusting the pH value to 3.13 with a 1 M NaOH solution.

2.2 *Flow system setup and procedure*

The manifold (Fig. 1a) consisted of a Gilson Minipuls 3 peristaltic pump (Gilson S.A., Villiers Le Bel, France) and two multi-port selection valves (Valco Instruments, Houston, TX). All tubings were made of polytetrafluoroethane (PTFE) and had an inner diameter of 0.75 mm. The flow rates used were 2.0 mL/min for the buffer, 1.8 mL/min for the $NaHCO_3$ standards and 1.9 mL/min for the sugar solutions.

A series of bicarbonate standards is mixed on line with the buffer solution. In this way, acidic pH shifts the reaction equilibrium ((1), pKa = 3.6) to produce in situ carbonic acid. Carbonic acid is present in equilibrium with its hydrated anhydride (CO_2aq). As this equilibrium ((2), pKa = 2.77), is strongly on the side of CO_2aq, this species needs to be monitored.

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3\,, \qquad (1)$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2aq\,. \qquad (2)$$

$NaHCO_3$ standards (0, 1, 2 and 3 g/l) were used to obtain a defined concentration of aqueous CO_2 (0, 165, 331 and 496 mg/l) in the cell. Common used sugars, sucrose, fructose and glucose as well as mixtures (1 : 1 : 1) showed similar influence on the water background in the region where measurements are made (Fig. 2). Therefore, to study the influence of the sugars in the signal, sucrose was chosen to act as modeling substance. For that, different solutions of sucrose (0, 30, 60 and 90 g/l) were mixed on-line with the $NaHCO_3$ standards previously to the mixing with the buffer resulting in sucrose concentrations of 0, 10, 20 and 30 g/l in the cell. Each sample (combination of hydrogen carbonate standards and sucrose) was pumped for 4 min through the flow cell while measurements are performed.

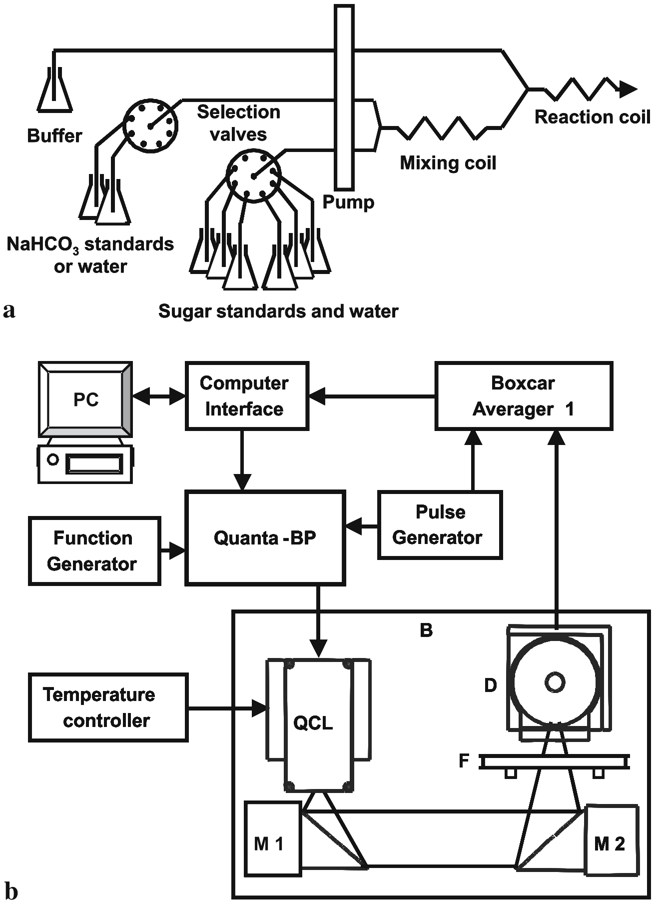

FIGURE 1 Experimental setup. (**a**) Flow system; (**b**) QCL system (M, mirror; F, flow cell; D, detector; B, purged box)

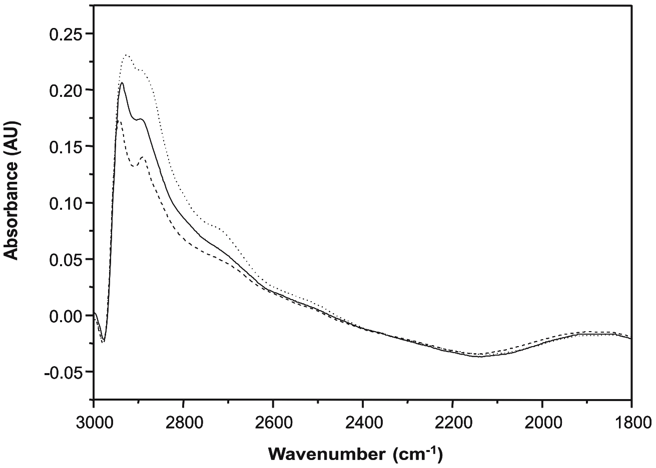

FIGURE 2 FTIR spectra normalized on the target wavenumber of 2341.6 cm^{-1} for sucrose (*solid line*), fructose (*dashed line*) and glucose (*dotted line*). Concentration is in all cases was 30 g/l

2.3 FTIR *system*

A Bruker IFS 88 spectrometer (Bruker Optik GmbH, Karlsruhe, Germany) with a mercury cadmium telluride (MCT) detector was used to record the spectra. For the

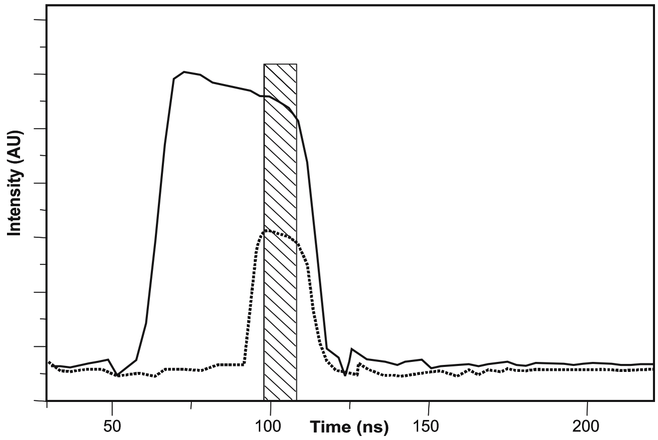

FIGURE 3 Pulse shapes obtained using a pulse amplitude of 1.6 A (*solid line*, 2341.4 cm^{-1}) and 1.0 A (*dotted line*, 2341.6 cm^{-1}). Location of 10 ns gate is also shown

measurements a flow cell with CaF_2 windows (Perkin Elmer, Wellesley, MA, USA) and a spacer generating an optical path of 30 μm were used. Each spectrum was a result of 128 co-added scans, recorded with 2 cm^{-1} resolution, Blackman–Harris three-term apodization and at 100 kHz scanning rate. In order to avoid background absorption of the gaseous CO_2, the spectrometer was purged with technical nitrogen.

2.4 *Quantum cascade laser system*

For all experiments a distributed feed back QCL (sb78, Alpes Lasers, Neuchatel, Switzerland) placed in a laser housing equipped with a Peltier element, a compartment for water-cooling and a silica gel pad was used. Before closing, the laser housing was filled with technical nitrogen. The emission wavelength of the QCL under different operating conditions, especially different pulse amplitudes, operation temperatures and frequencies, was experimentally verified. For this purpose the globar light source of a Bruker Equinox 55 FTIR-spectrometer was replaced by the quantum cascade laser.

The specified maximum pulse power of the QCL was 50 mW. The QCL was operated at a temperature of −30 °C controlled via TC-51 unit (Alpes Lasers, Neuchatel, Switzerland). The pulse frequency has an influence on the emission wavelength [24] and also on the accessible tuning range. Tuning a QCL is more efficient using higher duty cycles as the cavity is effected more by the generated heat. According to the datasheet provided by the producer this QCL shows a maximal tuning range of 1.3 cm^{-1} at −30 °C using 400 kHz and 1 and 1.6 A. In our experiments the operation frequency was limited by the laser driver QUANTA-BP (Laser Components, Olching, Germany) so the QCL was operated at the maximum possible frequency of 247.5 kHz. The control voltage needed by the laser driver for determining the pulse amplitude was delivered by the Function generator 33120A (Agilent Technologies, Palo Alto, California). The function generator was programmed to deliver a square wave function. That way the pulse amplitude of the QCL was modulated with a frequency of 50 mHz. The two alternating pulse amplitudes of 1 and 1.6 A levels were determined by the extreme values possible for the laser and resulted in a maximum of the emission spectra of 2341.6 cm^{-1} and 2341.4 cm^{-1} respectively (see Fig. 4a). Using these operating parameters the wavelength shift in the emission was 0.2 cm^{-1}. Pulse duration was fixed at 50 ns. However, according to the manufacturer of the laser pulser, the pulse amplitude of 1.0 A is already in a range in which the real pulse shape can differ from the adjusted parameters. This can be seen in Fig. 3, where the pulse at 1 A has shorter duration than 50 ns and also starts later than the corresponding to 1.6 A. For data acquisition a gate of 10 ns located at the center of the less intense pulse was set with the boxcar averager.

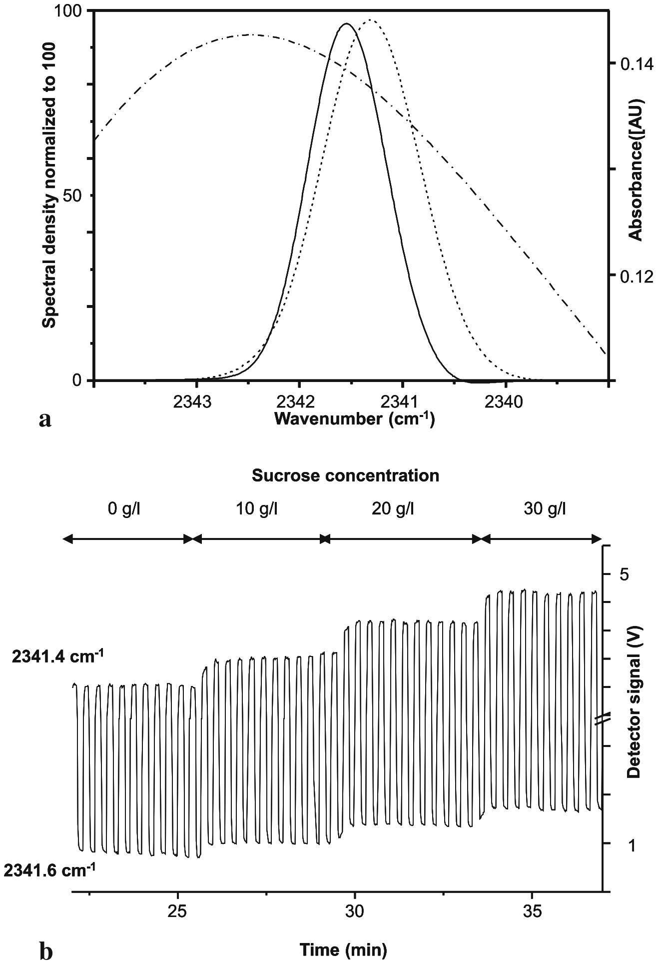

FIGURE 4 (**a**) Normalized QCL emission spectra (*left scale*) for pulse amplitudes of 1.0 A (*solid line*) and 1.6 A (*dashed line*). In the *right scale*, absorption spectra (*dash-dot line*) of aqueous carbon dioxide (spectra of water was taken as background) is shown. (**b**) Recorded signal of a CO_2 standard (165 mg/l) with different amounts of sucrose. The higher intensities correspond to pulse amplitude of 1.6 A (2341.4 cm^{-1}), lower intensities correspond to the emission with 1.0 A (2341.6 cm^{-1}). Increasing sugar concentrations led for both wavelengths to higher detector signals and therefore decreasing absorption values

The used optical setup is given in Fig. 1b. The QCL beam was collected using an off axis parabolic mirror (focal length 43.1 mm) and focused through the flow cell (same as for the FTIR experiments but with a 120 μm spacer) on a photovoltaic MCT detector KMPV12-0,1-J1/100 MHZ (Kolmar Technologies, Newburyport, MA, USA) using a second off axis parabolic mirror (focal length 69 mm). The whole optical part of the set-up was covered with an acrylic plastic box, which was purged at 15 l/min with technical nitrogen to avoid background absorption of the gaseous CO_2. The detector signal was processed using a Boxcar Averagers, Model SR250 (Stanford Research Systems, Sunnyvale, California, USA) by averaging the value of 10 000 pulses.

The maximum working frequency of the boxcar averager was 20 kHz. Hence only 8% of the generated pulses were processed. The analog output signal of the boxcar averager was converted into a digital signal using a computer interface model SR245 (Stanford Research Systems, Sunnyvale, California, USA). The QCL signal was recorded using custom software (Fig. 4b). A new value was recorded and stored every second. The function generator modulated the emission of the QCL automatically while the samples were passing the flow cell.

3 Data analysis

3.1 *FTIR data*

FTIR spectra were treated in Matlab 7.0 (The Math Works Inc., Natick, MA, USA, 1999). A Savitzky–Golay smoothing and differentiation was performed obtaining the first-derivative row vectors resulting from a seven-point first order Savitzky–Golay smoothing of each row of the matrix composed by all the spectra.

3.2 *QCL data*

The recorded data were further evaluated using a spreadsheet software program. From the recorded intensities, absorbance value was calculated using the transmission obtained for distilled water as background. For both wavelengths and each combination of CO_2 with a sugar standard the corresponding absorption values were determined.

4 Results and discussion

4.1 *FTIR spectra*

Figure 5a shows how the spectra of increasing concentrations of sugar mixtures (1 : 1 : 1) measured against distilled water caused an increasing sloping baseline with an isosbestic point at 2450 cm^{-1}. The same baseline shift can be observed in the presence of a constant carbon dioxide concentration (Fig. 5b). If quantification of the CO_2 would be based on the measurement of the absorption at a single wavenumber changing sugar concentration would significantly influence the result. First derivative spectra were calculated from these spectra (blank and CO_2 solutions with different sugar concentrations). From Fig. 5c and d, it can be seen that the influence of the changing sugar concentration is negligible and the first derivative of the absorption band of CO_2 is not influenced by the changing sugar concentration. Calculation of the first derivative is thus, an appropriate means to correct baseline shifts due to the presence of sugars in the matrix.

4.2 *QCL modulation measurements*

The absorption values of CO_2 at 2341.6 cm^{-1}, measured with different concentrations of sucrose were used to determine the influence of sucrose on the measured CO_2 concentration. Evaluating one wavelength, sucrose concentrations above 9.46 g/l led to an underestimation of the CO_2 concentration. An increase of the sucrose concentration of 10 g/l in the sample results in a decrease of the measured CO_2 concentration of 11.9 mg/l.

To avoid this influence, absorption values at both wavenumbers, 2341.6 cm^{-1} and 2341.4 cm^{-1} were calculated for all combinations of CO_2 and sucrose concentrations and subtracted, obtaining absorption differences. These values are proportional to the first derivative spectra and are only hardly

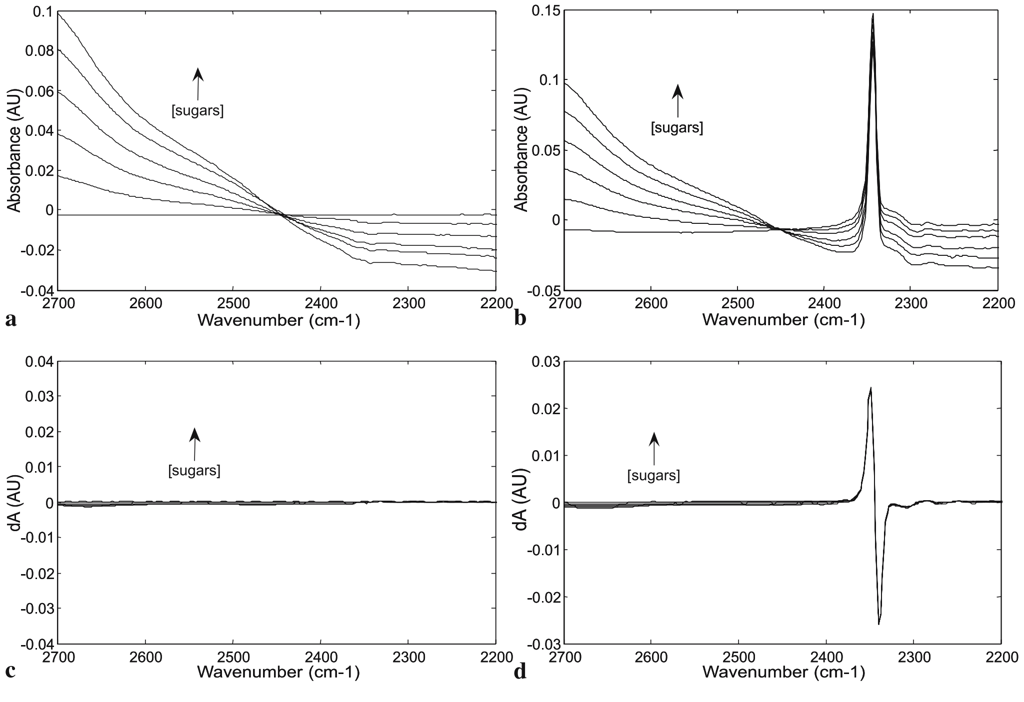

FIGURE 5 Original FTIR spectra of (**a**) water and (**b**) a carbon dioxide solution (331 mg/l) in the presence of increasing concentrations of sugars. First derivative spectra from the same experiments respectively (**c**) and (**d**)

Sucrose [g/l]	*d* [AU]	*k* [AU/(g/l)]
$2341.6\,\mathrm{cm}^{-1}$		
0	–0.0008	0.5945
10	–0.0055	0.5945
20	–0.0123	0.6041
30	–0.0191	0.6172
Absorbance differences		
0	–0.00005	0.1098
10	0.00121	0.1037
20	0.00005	0.1078
30	–0.00085	0.1112

TABLE 1 Calibration parameters of the determination of CO_2 in aqueous sucrose solutions

influenced by changes in the sucrose concentration. Table 1 resumes the results; carbon dioxide calibration (0–496 mg/l) was performed for different sucrose concentrations ranging from 0 to 30 g/l. When analyzing just one wavelength the intercepts of the regression equations when sucrose concentration is increasing were decreasing while they remained almost constant when the modulation method was applied. The absorption values of the modulation method when sucrose was present were within the standard deviation of the values when no sucrose was present. The analytical parameters for the calibration using these values were a regression coefficient R^2 of 0.9964, a standard deviation, according to ISO 8466-1, s_{ox} of 11.3 mg/l CO_2 and a detection limit of 33.9 mg/l CO_2. Standard deviation is smaller than the decrease in the absorption values for CO_2 that occurs when sucrose is present.

The evaluation of only one wavelength (namely at $2341.6\,\mathrm{cm}^{-1}$) shows an approximately 3.2 times lower standard deviation and therefore better limit of detection compared to the evaluation of the absorbance difference. But both methods show a better performance compared to previously reported works, where a standard deviation of 19.4 mg/l CO_2 has been reported. The main reason for the lower standard deviation can be found in the better match between the absorption line of the analyte and the emission line of the used QCL. Nevertheless, for the quasi-first derivative spectra, better results could be achieved with a higher tuning range of the QCL. An enhanced spectral difference between the two evaluated wavenumbers would result in bigger differences of the absorption values of these wavenumbers and therefore also in a higher analytical signal.

5 Conclusions

Wavelength tuning of a QCL was successfully applied in liquid phase spectroscopy as a promising tool for compensating background changes. Even if the tuning range of the used QCL was essentially smaller than the absorption band of the analyte, the gained information of two neighboring wavenumbers was sufficient to compensate changes in the water background arising from variations in the matrix. We demonstrated the feasibility of measuring carbon dioxide dissolved in water independently of the sugar concentration. The evaluation of only one wave number showed a negative correlation with the sucrose concentration that was successfully eliminated by evaluation of the absorbance difference at two wavenumbers. We therefore consider this method highly promising for the development of a robust QCL based CO_2 sensor for different kind of liquid samples.

The proposed method successfully employs a standard room temperature DFB-QCL with only limited wavelength tuning capabilities. For liquid phase applications an extended tuning range would be beneficial. Therefore improvement and extension of this work could be achieved by taking advantage of recent developments in widely tunable QCL based on external cavity [25–27] as well as electrically wavelength tuning [28].

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