

Direct Determination of Carbon Dioxide in Aqueous Solution Using Mid-Infrared Quantum Cascade Lasers

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A method for the direct determination of carbon dioxide in aqueous solutions using a room-temperature mid-infrared (MIR) quantum cascade laser at 2330 cm^{-1} is reported. The absorption values of different carbon dioxide concentrations were measured in a $119\text{ }\mu\text{m}$ CaF_2 flow-through cell. An optical system made of parabolic mirrors was used to probe the flow cell and to focus the laser beam on the mercury cadmium telluride (MCT) detector. Aqueous carbon dioxide standards were prepared by feeding different mixtures of gaseous N_2 and CO_2 through wash bottles at controlled temperature. The concentration of the dissolved CO_2 was calculated according to Henry's law, taking into account the temperature and the partial pressure of CO_2 . The carbon dioxide standards were connected via a selection valve to a peristaltic pump for subsequent, automated measurement in the flow-through cell. A calibration curve was obtained in the range of 0.338 to 1.350 g/L CO_2 with a standard deviation of the method s_{no} equal to 19.4 mg/L CO_2 . The limit of detection was calculated as three times the baseline noise over time and was determined to be 39 mg/L .

Index Headings: Quantum cascade laser; Carbon dioxide determination; Carbon dioxide standards; Aqueous carbon dioxide; Mid-infrared.

INTRODUCTION

Rapid and accurate determination of carbon dioxide in aqueous samples is of industrial importance, especially in the beverage industry. As the CO_2 content in water and soft drinks, as well as in alcoholic beverages, is an important parameter for process and quality control it is frequently measured. The measuring principle of the currently most popular CO_2 process analyzer is based on Henry's law, which states that the volume of gas dissolved in a liquid is proportional to its partial pressure at a given temperature. During a measuring cycle a sample is drawn from the process stream and its volume is expanded in a measuring chamber. Due to the volume expansion a gas phase is generated in the measuring chamber. To accelerate equilibration of pressure and temperature between the liquid and gas phase, the sample is stirred with an impeller. In some measuring systems the equilibrium pressure is not reached within an acceptable time and must therefore be extrapolated. The CO_2 content is then calculated from the measured equilibrium pressure and temperature. This measuring principle is inherently not selective for CO_2 as all other gases dissolved in the sample will also influence the gas pressure and thus cause interferences. A selective method for CO_2 determination would be of special interest in situations where in addition to CO_2 other gases are also contained in the liquid. This is the case in beer brands, which in addition to car-

bon dioxide also contain nitrogen. Apart from the lack of selectivity, there are other deficits of the currently used technology. Because the process analyzer performs several operational steps including sampling, stirring, and expansion of the measurement chamber, the result is only available with a delay of about 10 seconds with respect to sampling. Despite this short time, a faster analyzer would be advantageous for many process applications. Also, due to the use of moving parts the robustness of the current technology is limited, which in turn causes increased maintenance costs. A literature survey for alternative methods for carbon dioxide determination reveals other approaches as well. These are capillary-type isotachopheresis,¹ the use of a modified gas analyzer,² flow injection analysis systems,^{3,4} the use of a gas electrode with an air gap, and a pH meter.⁵ While being interesting from a scientific point of view, these methods are lacking robustness and simplicity, which hinders their application in process analytical chemistry.

A selective, direct spectroscopic method that does not require any moving parts is therefore of considerable practical interest. Carbon dioxide dissolved in water gives rise to a strong and characteristic absorption band at 2342 cm^{-1} (Fig. 1). Apart from water practically no other substances that are usually present in carbon-dioxide-containing liquids exhibit absorption bands in this spectral region. This offers the opportunity to develop a simple and selective analytical method for CO_2 determination in aqueous solutions based on mid-infrared (MIR) absorption spectroscopy. Because of the low frequency of this fundamental vibration, its overtone bands cannot, at present, be measured with the required sensitivity in the near-infrared spectral region. A difficulty in measuring the fundamental CO_2 vibration for process analytical applications is the strong absorption of water at 2342 cm^{-1} , which restricts the optical path for transmission measurements to a few micrometers when using conventional thermal light sources. The necessity of using a short optical path is a serious problem in process analytical applications due to the probability of clogging of the flow cell. A possible solution to this problem would be to perform attenuated total reflection (ATR) measurements instead. This measurement principle does not impose restrictions to the inner diameter of the measurement cell. However, the sensitivity of the ATR technique towards pollution of the ATR surface poses practical problems and is thus of concern in process analytical applications. A way out of these problems would be the use of a dedicated, powerful light source that allows transmission measurements at extended optical paths ($>100\text{ }\mu\text{m}$). Only recently, room-temperature quantum cascade lasers (QCL) have become available that provide an average

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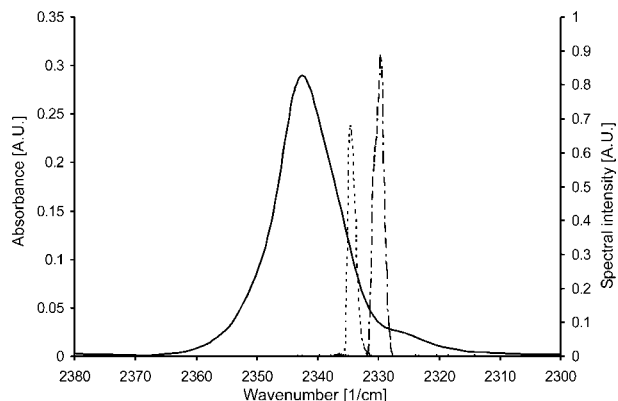


FIG. 1. Comparison of the absorption spectra of aqueous carbon dioxide (1.35 g/L) measured in a 41 μm flow cell referenced against the water filled cell (left scale) and the emission spectra (right scale) of the available QCL. QCL operation temperature: $-30\text{ }^\circ\text{C}$; driving voltage 20 (laser line at 2330 cm^{-1}) and 16 V, respectively (laser line at 2334 cm^{-1}). The width of the laser emission lines are in agreement with the values given in the product information provided by Alpes Lasers.

power of typically 1 mW at a duty cycle of 1.4% within a few wavenumbers in the region of interest for CO_2 analysis (Fig. 1). QCLs are unipolar semiconductor lasers consisting of well-defined thin layers of different chemical compositions, where the light generation is based on an intersubband transition within the conduction band. The use of QCL for MIR spectroscopy has mainly been reported in gas-phase measurements.⁶⁻⁸ However, the advantages of QCLs over diode lasers are also significant when performing measurements in the liquid phase,⁹ as in flow-injection analysis¹⁰ or high-performance liquid chromatography.¹¹ QCLs operate at room temperature or near room temperature. This is a main requirement for systems used in process analytical chemistry. QCLs can be manufactured to emit from 3.4 to 17 μm with the same semiconductor material system. It is a unique feature of this technology that their emission wavelength is fully determined only by the thicknesses of the semiconductor wells and barriers deposited by the MBE process.

EXPERIMENTAL

Standard Preparation. The CO_2 standard solutions were prepared by saturating distilled water with different gas mixtures of N_2/CO_2 (Fig. 2). The used gas mixtures had a ratio of $\text{N}_2:\text{CO}_2$ of 80:20, 60:40, 40:60, and 20:80 (accuracy 2 rel.% of lower component; Messer). The CO_2 free standard was prepared by saturating distilled water with N_2 (tech.; Messer). The different gas mixtures were fed into wash bottles containing 500 mL distilled water. The wash bottles were placed in a temperature controlled water bath at $20\text{ }^\circ\text{C}$ (specified accuracy of the water bath: $\pm 0.05\text{ }^\circ\text{C}$). The standards were saturated with gas for 60 min before they were analyzed. The concentration of the CO_2 solutions was calculated according to the temperature and the partial pressure of CO_2 using the literature value of 0.1688 g/100 g water at $20\text{ }^\circ\text{C}$ and normal pressure.¹²

Liquid-Handling System and Measuring Procedure. The liquid-handling system (Fig. 2) consisted of a Valco selection valve (Houston, TX), a Gilson peristaltic pump (Villiers, France), and a Perkin Elmer flow-through cell

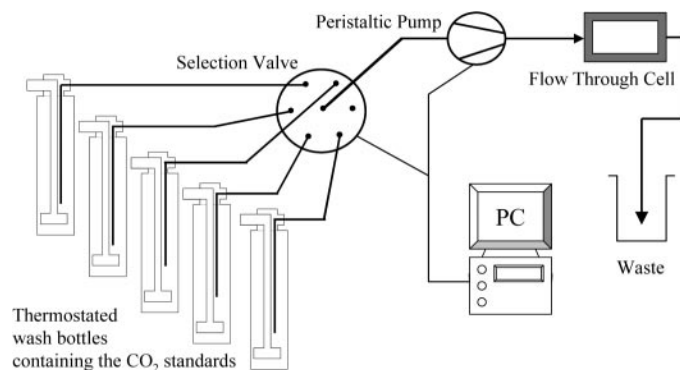


FIG. 2. Schematic drawing of the liquid handling system.

with CaF_2 windows and an optical path of 119 μm (Wellesley, MA). All tubing for feeding the solutions from the wash bottles to the flow-through cell was made of poly(tetrafluoroethane) (PTFE) and had an inner diameter of 1 mm, except for the last 20 cm directly before the cell. This tubing, as well as the tubing after the cell, had an inner diameter of 0.25 mm in order to create a backpressure that prevents degassing of the solutions.

The selection valve and the peristaltic pump were controlled via a home-written software program (Sagittarius 2.0). Starting with the solution saturated with pure N_2 , the valve was switched every 8 minutes to measure the next higher CO_2 concentration. During switching the pump was stopped to avoid a pressure drop. The pump speed was set to 685 μL per minute.

Fourier Transform Infrared Spectrometers and Quantum Cascade Laser Setup. For complementary measurements the Bruker FTIR spectrometers IFS 88 and Equinox 55 have been used. The laser setup (Fig. 3) consisted of the QCL, all driving units from the “starter kit” from Alpes Lasers (Neuchâtel, Switzerland), and a power supply (Velleman, Fort Worth, TX). The “starter kit” contains the Pulse Generator TPG128, the Laser Diode Driver LDD100, the Temperature Controller TC51, the Laboratory Laser Housing LLH, and all necessary connection cables. The original low impedance cable connecting the LLH with the LDD100 was replaced by a shorter and specially shielded version from Alpes Lasers.

A Distributed Feedback Laser from Alpes Lasers (Neuchâtel, Switzerland) emitting at 2330 cm^{-1} was used

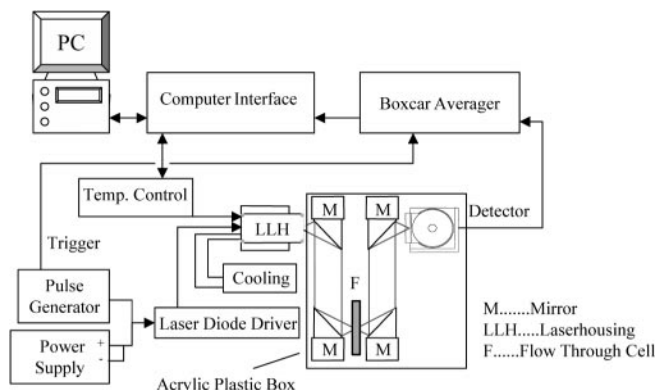


FIG. 3. Schematic drawing of the entire optical and electrical setup for CO_2 determination using a quantum cascade laser.

(N63c21). The laser was mounted in the laser housing, which was filled with nitrogen and closed. The housing was also provided with silica gel pads, a Peltier element, and a compartment allowing water-cooling. The laser was operated in pulsed mode with a pulse duration of 35 ns and a repetition rate of 20 kHz. The laser was driven with 20 V fed to the LDD100, which is 97.5% of the specified maximum. The temperature was set to $-30\text{ }^{\circ}\text{C}$. The TC51 was driven externally by using the external control function and home-made software for controlling and monitoring purposes. The Peltier element was water-cooled. For shielding against electromagnetic radiation a Faradays box made of soft iron with a thickness of 1 mm was built to cover the LLH, the LDD100, the TPG128, and the power supply. The laser beam was collimated and focused on the flow-through cell as well as on the detector element using an optical setup consisting of gold-coated parabolic mirrors made of aluminum with a focal length of 43 mm. The used detector was a mercury cadmium telluride (MCT) detector KMPV12-0,1-J1/100MHZ (Kolmar Technologies, Newburyport, MA). The optical part of the setup was covered with an acrylic plastic box, which was purged at 15 L/min with nitrogen so that the optics was free from gaseous CO_2 .

Data Acquisition. The detector signal was processed using a Boxcar Averager Model SR250 (Stanford Research Systems, Sunnyvale, CA) by averaging the value of 10,000 pulses within a 10 ns gate located at 9–19 ns of the 35 ns pulse. The analog output signal of the Boxcar Averager was converted into a digital signal using a Computer Interface Model SR245 (Stanford Research Systems, Sunnyvale, CA). The signal was recorded using the same home-made software that controlled and recorded the temperature of the Peltier element. A new value was recorded and stored every second.

RESULTS AND DISCUSSION

Preliminary Experiments Using a Fourier Transform Infrared Spectrometer. The full spectral information provided by an FT-IR spectrometer was used to characterize the experimental system under investigation. For this purpose the QCL setup was replaced by an FT-IR spectrometer (Bruker IFS 88). Figure 4 shows a recording obtained when analyzing a solution during its saturation with gaseous CO_2 by purging with a gas mixture containing 80% CO_2 and 20% N_2 . For this purpose the solution was circulated through a flow cell with an optical path of $41\text{ }\mu\text{m}$ so that the increase in dissolved carbon dioxide could be directly measured. During the first 5 minutes of the experiment the solution was not yet purged. In this period the observed absorptions are the result of fluctuations in the concentration of gaseous CO_2 (maximum at 2360 cm^{-1}). The reason for these absorptions, which were recorded during the whole experiment, was the dry air purge of the FT-IR spectrometer, which switched between two different gas treatment columns of different efficiency. From minute 5 up to minute 30 a N_2/CO_2 mixture (80:20) was bubbled through the sample. In doing so, a concentration of 1.35 g/L CO_2 was reached. This increase in CO_2 dissolved in water was reflected by the absorption peak at 2342 cm^{-1} . At minute 30 of the experiment the gas flow was changed to pure nitrogen,

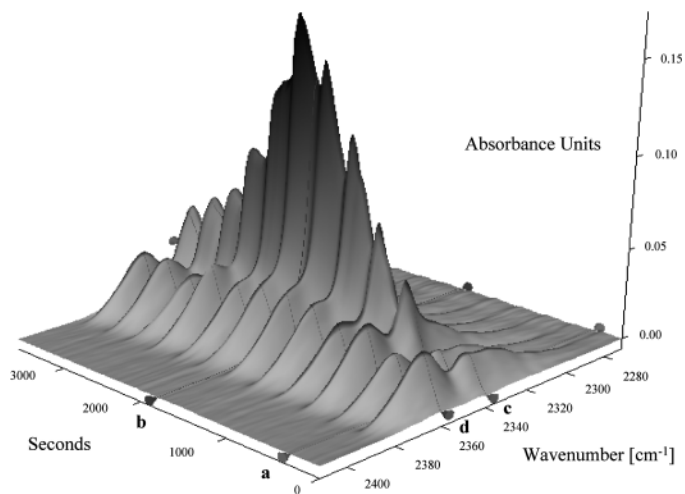


FIG. 4. FT-IR recording when analyzing the saturation process of a 1.35 g/L CO_2 standard. (a) At 300 seconds the saturation with CO_2 was started. (b) At 1800 seconds the solution was purged with pure nitrogen to remove the dissolved CO_2 . In addition to (c) the analyte characteristic absorption band, (d) gaseous CO_2 absorption bands are also visible.

which slowly removed the CO_2 from the solution. From these preliminary experiments it became clear that to obtain reliable analytical results when using the quantum cascade laser the fluctuations in CO_2 gas concentration had to be minimized. This was best achieved by putting the optical system for QCL measurements in a box, which was purged with nitrogen.

The emission wavelength of the available QCL under different operating conditions was experimentally verified as well. For this purpose the globar light source of the Bruker Equinox 55 spectrometer was replaced by the quantum cascade laser. This simple experimental arrangement proved to be sufficient to determine the obtained laser emission wavelengths. In Fig. 1 the absorption band of carbon dioxide in water is compared with the emission lines of the QCL as measured at $-30\text{ }^{\circ}\text{C}$ applying a driving voltage of 20 and 16 V, respectively. From Fig. 1 it became clear that with the available QCL only the tailing edge of the actual CO_2 absorption band could be probed. A further shift of the laser line of the available laser into the absorption band of the analyte would be possible. This, however, would require a more complicated cooling system. For practical reasons this possibility was not investigated.

In preliminary experiments the signal-to-noise level achieved when analyzing a 1.35 g/L CO_2 standard was recorded at different driving voltages and at a temperature of $-30\text{ }^{\circ}\text{C}$. Despite the fact that higher absorptions for the given concentration were achieved at lower driving voltages, the overall signal-to-noise ratio decreased when lowering the driving voltage due to the reduced laser emission powers at these operating conditions.

Calibration with Standard Solution and Quantum Cascade Laser Detection. For the above reasons, the calibration curve was established using the laser line at 2330 cm^{-1} ($-30\text{ }^{\circ}\text{C}$, 20 V). Carbon dioxide standards containing 0.338, 0.675, 1.013, and 1.350 g/L CO_2 were prepared and analyzed twice using the automated flow system. The read-out of each experiment, being the intensities recorded over time, was stored. The intensity

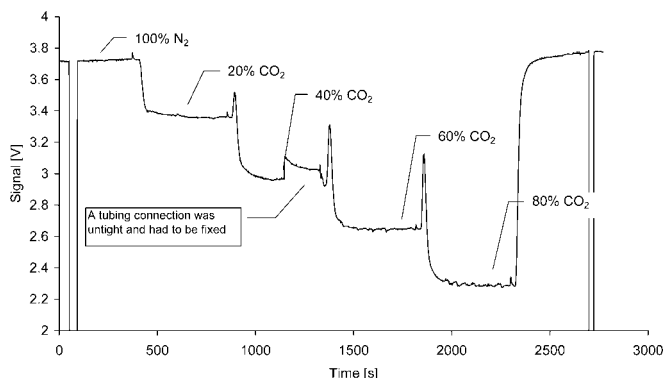


FIG. 5. Recording as obtained during the first measurement cycle. The percentages given correspond to the amount of CO₂ in the gas mixtures used to prepare the CO₂ standards. The peaks appearing directly before the signal drops due to the next higher CO₂ standard are due to volume residing in the tubings connecting the wash bottles with the selection valve. As in these plugs the equilibrium of CO₂ between gas and liquid phase was not reached, higher intensities were recorded as they passed the flow cell.

assigned to each standard was calculated as the mean value from the period where a stable signal had been recorded for the respective standard (Fig. 5). To convert the intensity values in absorbance units the absolute signal for the CO₂ free standard had to be determined. This value was calculated as the difference between the readouts obtained when blocking the laser beam and when measuring the CO₂ free standard. Using the determined absorbance values, a linear regression could be calculated ($y = 0.0603x$). The corresponding regression coefficient R^2 was found to be 0.9983 and the standard deviation of the method s_{x_0} was found to be 0.0194 g/L CO₂ (ISO 8466-1). The limit of detection was furthermore estimated as three times the noise of the baseline over time and was determined to be 39 mg/L CO₂. Again, it should be stressed that the measurements were performed at the edge of the analyte absorption band. Assuming that a QCL of the same quality but with the emission wavelength in the center of the analyte absorption band were available, the sensitivity of the method could be improved by a factor of approximately eight.

This work furthermore showed that the characteristics of the available electronics (Alpes Laser starter kit) were the limiting factor with respect to the achieved analytical figures of merit. Whereas fast and simple operation of the QCL with the electronics provided by Alpes Lasers is feasible, they are, unfortunately, a significant source of noise. The efforts made to improve the shielding of the electronics already significantly reduced the noise level over time. This positive effect of the shielding could also be judged from the flattening of the plateau of a single

laser pulse as recorded with a fast time-gated photovoltaic MCT detector. However, it should be mentioned that full satisfactory operation conditions of the QCL could not be realized with the available means. There is definitely a need for a dedicated, low noise, and compact control unit, which may be placed close to the QCL. Nevertheless, the results achieved clearly show that QCL technology must be considered as a new and very attractive tool for the development of a new generation of chemical process analyzers.

CONCLUSION

This paper has reported on the first QCL based method for the determination of CO₂ in aqueous solution. The proof was made that QCLs can be used for determination of industrially relevant analytes in solution. Despite performing measurements on aqueous samples in the MIR spectral region the optical path length could be extended to a range (>100 μm) already compatible with industrial applications. Compared to standard CO₂ analyzers the new method shows several distinct advantages such as higher selectivity, avoidance of moving parts, and fast response. By using improved electronics and a dedicated QCL whose emission line is matched to the absorption band of carbon dioxide in water, it is very likely that the already achieved LOD of 39 mg/L can be substantially improved upon.

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