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Mid-Infrared Quantum Cascade Lasers for Flow Injection Analysis

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A Fabry-Pérot quantum cascade laser (QCL) was used as a powerful light source for mid infrared (MIR) detection in flow injection analysis. The QCL lased at several wavelengths close to each other within a few wavenumbers ($990–1010$ cm^{-1}), hence fitting well to the broad absorption bands of molecules in liquid phase. As compared with that of a state-of-the-art Fourier transform spectrometer, the signal-to-noise ratio could be improved by a factor of 50. Additionally, by using a QCL as the light source, optical path lengths of more than 100 μm could be used even in aqueous matrixes which reduced the danger of cell clogging. In the example shown here phosphate was determined in Diet Coke samples. The flow injection system used allowed the measurement of the sample at two pH values (5 and 13) at which the analyte was present as $H_2PO_4^-$ and PO_4^{3-}, respectively. As the analytical readout the difference in IR absorption of $H_2PO_4^-$ and PO_4^{3-} at the laser wavelengths was taken. The FIA-QCL measurements were corroborated by ion chromatography which was used as a reference method.

We report on the first application of a Quantum Cascade Laser (QCL) as a new, powerful mid infrared (MIR) light source for aqueous flow injection analysis. MIR spectroscopy is of great interest to analytical chemistry as almost all molecules exhibit characteristic absorption bands between 400 and 4000 cm^{-1}. Unfortunately, this advantageous feature of MIR spectroscopy also entails the drawback that matrix components also absorb MIR radiation which results in strong spectral interferences especially in the case of aqueous solutions. Using state-of-the-art FT-IR instrumentation, the optical path must be in the low micrometer range (typically between 10 and 50 μm) to be able to perform measurements in the water window of the fingerprint region between 1600 and 950 cm^{-1}. In addition to a limited sensitivity due to the short optical paths, practical problems such as cell clogging might occur when particle-containing samples are measured. For these reasons, new developments enabling the use of longer optical paths are highly desirable. In this respect, the development of IR lasers holds some promise, especially if sensitivity and not selectivity based on multiwavelength measure-

ments, is asked for. In gas-phase measurements the situation is different. Here selectivity can be maintained when using lasers because substance identification can frequently be achieved by selection of a very narrow wavelength range where only the analyte absorbs. However, in condensed-phase applications, like aqueous flow analysis, broad absorption bands occur which do not allow this approach. To ensure selectivity of the whole analytical system, additional sample modulation must be carried out. In flow analysis, selectivity is achieved by performing reaction (Flow Injection Analysis, FIA) or separation (Liquid Chromatography, LC) steps prior to detection. Here, the much higher light intensity for measurements compensates for the loss of spectral information that occurs when replacing a spectrometer (e.g., diode array UV–vis spectrometers or FT-IR spectrometers) with lasers. This is particularly true for the UV, visible, and near-infrared spectral region where small, portable, and inexpensive lasers covering the whole spectral region were already available. The situation in the MIR range is different as powerful CO or CO$_2$ lasers emit only at selected wavelengths and tunable free electron lasers[2] are neither portable nor cheap. MIR lead-salt diode lasers which cover the whole MIR spectral range have become portable and reasonably priced in the last years but have only microwatt powers. Their usefulness for gas-phase spectroscopy is proven here because the sharp absorption bands of gas-phase MIR spectra are well matched to the sharp laser emission lines, providing both selectivity and sensitivity.[3] However, when measurements in the liquid phase are considered this is not the case. Here, because of the broad absorption bands of condensed-phase MIR spectra together with the low power of MIR diode lasers, no significant gain in sensitivity could be achieved as compared with that achieved through the use of broad band light sources (globar) which are used to probe the whole analyte absorption band.

However, quantum cascade lasers should bring a change in this respect. Quantum cascade lasers are pulsed light sources which can be designed to cover small spectral areas or single wavenumbers over the whole MIR spectral region. QCLs can be operated at room temperature having powers in the tens of

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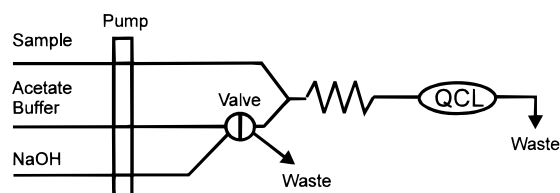[†] Also with Alpes Lasers, CP58, CH-2008, Switzerland, www.AlpesLasers.ch.

(1) van der Meer, A.; van der Weil, M. *Appl. Spectrosc.* **1997**, *51*, 574–575.
(2) Stepanov, E. V.; Kouznetsov, A. I.; Zyrianov, P. V.; Artjushenko, V. G.; Selivanov, Y. G. *SPIE-Int. Soc. Opt. Eng. Proc.* **1995**, *2508*, 224–232.
(3) Faist, J.; Capasso, F.; Sivco, D. L.; Sirtori, C.; Hutchinson, A. L.; Cho, A. Y. *Science (Washington, D.C.)* **1994**, *264*, 553–556.

Figure 1. Flow injection manifold used for phosphate analysis based on pH modulation.
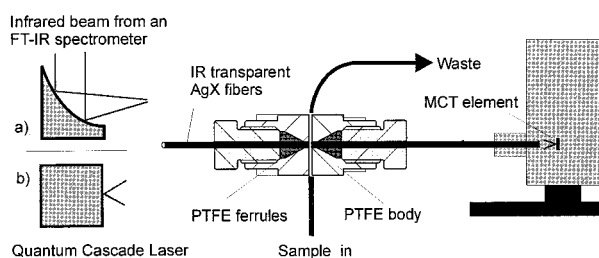

Figure 2. Sketch of the fiber-optic flow-through cell used for MIR transmission measurements. (a) A parallel beam from an FT-IR spectrometer is coupled into the silver halide fiber using an off-axis parabolic mirror. (b) The MIR light emitted by the quantum cascade laser is directly coupled into the silver halide fiber.

milliwatts. As quantum cascade lasers are microstructured, they are small in size and can be mass produced, leading to inexpensive mass production. The fast development of this technology since the first report in 1994[4] indicates that the current state of the art still can be improved so that a further increase in laser power as well as multi-color lasers or arrays of lasers covering several spectral regions in the MIR region can be envisioned.

EXPERIMENTAL SECTION

Reagents. All chemicals used were of analytical grade and obtained from Merck. The phosphate stock solution was prepared by dissolving 16.42 g of sodium dihydrogenphosphate monohydrate ($NH_2PO_4 \cdot H_2O$) in 1 L of distilled water. The acetate buffer solution used was made of 20 mmol/L acetic acid and 60 mmol/L sodium acetate and adjusted to pH 5; the sodium hydroxide solution contained 20 g/L NaOH. Additionally, a 1% (v/v) solution of acetic acid isobutylester in tetrachloroethylene was prepared for evaluation of the optical path length of the fiber-optic flow cell used.

Flow Injection Analysis (FIA) Manifold. The FIA manifold (Figure 1) was set up with a Gilson Minipuls 3 peristaltic pump (Gilson S. A., Villiers Le Bel, France) and a six-port injection valve (Valco Instruments, Houston, TX) equipped with a 125-μL sample loop. Teflon tubings (i.d., 0.02 in.; Global FIA, Gig Harbor, WA) were used throughout. The flow rates were set to 3.4 mL/min for the sample solution and 0.4 mL/min for the acetate buffer stream, respectively; thus, excessive dilution of the sample stream was avoided.

Phosphate reference measurements were performed on a standard ion chromatograph equipped with a conductivity detector.

Quantum Cascade Laser (QCL). The QCL is a semiconductor laser involving only one type of carrier and which is based on two fundamental phenomena of quantum mechanics, namely tunneling and quantum confinement.[3] In conventional semiconductor diode lasers (as used, e.g., in compact disk players), the light originates from the recombination of negative and positive charges (electrons and holes) across the energy gap existing between the conduction and valence bands of the crystal. The energy separation between the two bands thus determines the lasing wavelength. However, in QCLs, electrons are making transitions between bound states created by quantum confinement in ultrathin alternating layers of semiconducting materials. Since these ultrathin layers, called quantum wells, have a size comparable to the electron's deBroglie wavelength, they restrict the electron motion perpendicular to the plane of the layer. Because of this, the electron can only jump from one state to the other by discrete steps, emitting photons of light. The spacing between the steps depends on the width of the layer and increases as the

layer size is decreased. In a pictorial way, this laser is freed from "bandgap slavery", i.e., the emission wavelength depends now on the layer thicknesses and not on the band gap of the constituent materials. This has allowed, using the same base semiconductors (InGaAs and AlInAs grown on InP), the manufacture of lasers with emission wavelengths from 3.5 to 17 μm which corresponds to 2860 to 590 wavenumbers. The QCL used in these experiments had a Fabry-Pérot cavity geometry and was obtained from Alpes lasers (Neuchâtel, CH). In general, QCLs must be operated in a pulsed mode with a maximum pulse width of 200 ns. The operation temperature extends from 4 K to 105 °C. Whereas Fabry-Pérot QCLs have a quasi monomode spectrum at low power, they become multimode at high power. Typical instantaneous pulse powers obtained at room temperature are 75 mW.

IR Detection. Figure 2 shows the fiber-optic flow cell used as well as the different arrangements for performing FT-IR and QCL measurements. For FT-IR measurements (Figure 2a), which were conducted to evaluate the actual optical path of the fiber-optic flow cell, a parallel beam of the IFS 88 FT-IR spectrometer (Bruker Optik GmbH, Karlsruhe, Germany) was focused on the fiber tip ($AgCl_{0.3}Br_{0.7}$ fiber; radius, 1 mm) extending from the fiber-optic flow cell using an off-axis parabolic mirror.[5,6] After passing through the detection volume, the MIR radiation was collected by the second fiber piece, guided through the homemade detector housing, and finally focused onto a 100×100 μm sized MCT element (Belov Technology, USA). The construction of the fiber-optic flow cell allowed adjustment of the optical path by simply adjusting the fiber tips to different positions. For QCL measurements, the laser was placed directly in front of the fiber so that the radiation directly entered the fiber. Even though the light emitted by the QCL was diverging, no additional optics were needed to couple the light into the fiber because of the small size of the lasing element (24×4 μm^2) compared with the fiber diameter (1 mm). For FT-IR detection the signal of the MCT detector was transferred to the FT-IR spectrometer. In the case of QCL measurements, the MCT signal together with the pulse sequence of the laser was fed into a lock-in amplifier (model SR 850 DSP, Stanford Research Instruments) and the resulting voltage signal was used for data evaluation.

(4) Lendl, B.; Schindler, R.; Frank, J.; Kellner, R.; Drott, J.; Laurell, T. *Anal. Chem.* **1997**, *69*, 2877−2881.
(5) Frank, J.; Schindler, R.; Lendl, O.; Lendl, B. submitted to *Appl. Spectrosc.*
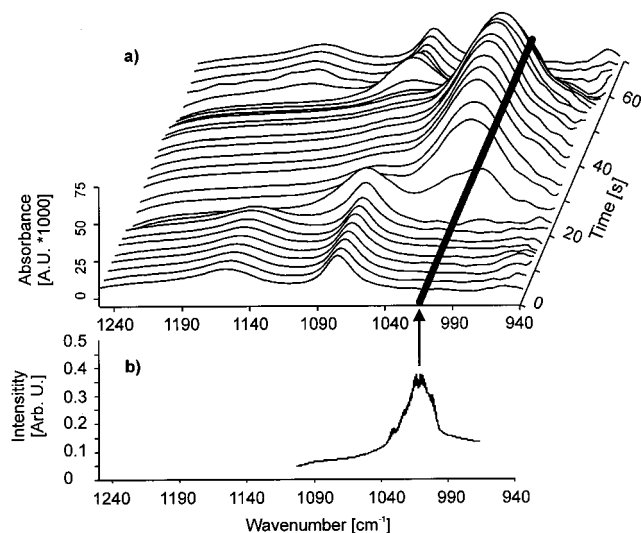(6) Vonach, R.; Lendl, B.; Kellner, R. *Analyst (Cambridge, U.K.)* **1997**, *122*, 525−530.

Figure 3. (a) 3-D plot from the analysis of a 1 g/L phosphate sample. (b) Emission characteristics of the quantum cascade laser used.
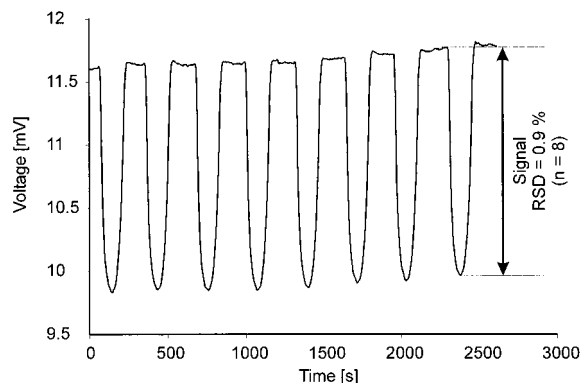

Figure 4. FIA-QCL recording from the analysis of phosphate in Diet Coke performing eight consecutive injections of sodium hydroxide. The negative peaks resulted from an increased analyte absorption (formation of PO_4^{3-} out of $H_2PO_4^-$) due to changing the sample pH from 5 to 13.

The laser output characteristics of the QCL were measured using an Equinox 55 FT-IR (Bruker Optik GmbH, Karlsruhe, Germany) spectrometer (Figure 3b). For this purpose the globar was replaced by the QCL laser. This experimental setup allowed a rapid verification of the laser frequencies which were needed to ensure the proper performance of the device. For verification of the optimal performance of the flow injection system for phosphate analysis, the fiber-optic flow-cell was substituted with a conventional IR flow cell (CaF_2 windows optical path, 45 μm) which was placed in the sample chamber of the IFS 88 FT-IR spectrometer.

RESULTS AND DISCUSSION

Determination of the Optical Paths of the Fiber-Optic Flow Cell. The optical path length (45 μm) of a reference cell was calculated from the interference fringes in the single-beam spectrum recorded of the empty flow cell. The absorbance of the ν-C=O of a 1% (v/v) solution acetic acid isobutylester in tetrachlorethylene (background: tetrachlorethylene) in this cell was then recorded. As tetrachlorethylene is highly transparent in the MIR spectral region, the absorbance of the ν-C=O of acetic acid isobutylester in the fiber-optic flow cell at different path lengths could be measured using the FT-IR spectrometer. Finally, the effective path length of the fiber-optic flow cell was calculated by multiplying the path length of the reference cell by the ratio of the absorbance values.

Estimation of the Signal-to-Noise Ratio Achievable Using QCL vs FT-IR Detection. A cell path length of 106 μm was investigated with respect to the signal-to-noise (S/N) ratio for an injection of a 2 g/L sucrose solution using a single-line flow injection manifold. Because of dispersion, the sample was diluted by a factor of about 10 before being probed in the flow cells. The S/N ratio was calculated from the baseline noise and the flow injection peak height and was found to be about 1100. To compare the approaches, the same amount of sucrose (2 g/L) with the same manifold was measured using a 45-μm flow cell with FT-IR detection (100 scans per spectrum; spectral resolution, 8 cm^{-1}). A wavelength region between 990 and 1010 cm^{-1}—which cor-

responded to the laser wavelengths—was integrated and recorded over time yielding a single trace of the sucrose injection. Again, the signal-to-noise ratio was calculated from baseline noise and flow injection peak height of the trace and determined to be about 22. Thus, limits of detection that are approximately 50 times lower can be achieved using the QCL.

Determination of Phosphate by FIA-QCL. The principle of phosphate determination by FIA-FTIR using a pH modulation was described in detail elsewhere.[7] The principle involves changing the pH of the sample solution from about 5 to 13 by injection of a concentrated base into the buffered sample stream to convert the dihydrogenphosphate anion $H_2PO_4^-$, present at pH 5, into the phosphate anion PO_4^{3-} present at pH 13. Other sample components without pronounced acid/base properties remain unchanged. This technique is implemented with the FIA manifold shown in Figure 1, where the sample stream is mixed in a ratio of 10:1 with a concentrated acetate buffer solution of pH 5. If the injection valve is switched, the buffer stream is replaced by concentrated sodium hydroxide, and the pH of the sample is adjusted to high values after the mixing point. This pH modulation approach is accompanied by strong spectral changes as the $H_2PO_4^-$ anion shows strong IR absorptions in the spectral range from 900 to 1600 cm^{-1} at 1159, 1078, and 941 cm^{-1} in contrast to a single strong absorption band of the PO_4^{3-} anion at 1009 cm^{-1}. Figure 3a shows a 3-D plot recorded from the analysis of a 1 g/L phosphate solution using the FT-IR spectrometer as detector. One clearly sees spectral changes induced by injection of the NaOH solution in the acetate buffer stream. In Figure 3b, the emission characteristics of the QCL used are shown. When using the QCL as the light source, a decrease in detector output voltage upon injection of the NaOH solution was recorded because of the increased IR absorption due to PO_4^{3-} formation (Figure 4). The key advantage of the pH modulation is the effective elimination of long term detector drift and fluctuation in light intensity which occur if the laser position in front of the fiber slightly changes. Using the QCL, a linear calibration was established from 0.01 to 2 g/L of phosphate. The rather large intercept of the calibration curve obtained ($y = 7.08 \times 10^{-5}x + 0.035$, $r^2 = 0.996$) is due to the increase in the background absorption because of the

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(7) Max, J.-J.; Trudel, M.; Chapados, C. *Appl. Spectrosc.* **1998**, *52*, 226−233.

increased OH^- ion concentration.[7] The phosphate contents of two real samples (Diet Coke) were determined to be 470 ± 10 mg/L ($n = 8$, $P = 0.95$) and 530 ± 11 mg/L ($n = 8$, $P = 0.95$), respectively, which are in very good agreement with the values found by ion chromatography (478 ± 21 mg/L and 511 ± 22 mg/L, $P = 0.95$, respectively).

CONCLUSION

The first results using quantum cascade lasers for chemical analysis in the condensed phase were obtained in this study showing that QCLs offer some highly interesting features. First, QCLs are powerful light sources which allow increased sensitivity of MIR measurements in liquids, which is of special interest for aqueous solutions. Second, their small size and room-temperature operation will facilitate their incorporation into different analytical systems. Therefore, quantum cascade lasers should find frequent applications in analytical chemistry. The figures of merit of the results presented here can be improved by optimizing a better match between laser emission and analyte absorption bands. Furthermore, it is supposed that QCLs should also be applicable to liquid chromatography to generate functional-group-specific chromatograms.