

MEMS-based Spectrometric Sensor for the Measurement of Dissolved CO₂

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Abstract — In the last few years several types of MEMS-based spectrometer systems emerged, mainly addressing the NIR spectral range. The presented MEMS-based sensor prototype operates in the mid-IR range between 2200 cm⁻¹ and 2500 cm⁻¹. The main element is a blazed micro-electro-mechanical reflective grating device with an aperture of 3x3 mm². The optical setup of the sensor corresponds to a Czerny-Turner type monochromator with an immense potential for further miniaturization due to its MEMS core. This allows designing and building competitively priced handheld analyzers for a range of applications that up to now has been restricted to large and expensive instruments. This work focuses on the development of an analyzer for dissolved CO₂ showing the methodology and also first implementation steps towards a sensor solution. CO₂(aq) calibration samples were prepared by different NaHCO₃ concentrations in solution. Spectra and calibration data acquired with the prototype are presented.

I. INTRODUCTION

The number one advantage of infrared (IR) spectroscopic sensors is their capability to directly and specifically detect and quantify (most) chemical substances by their inherent vibrational absorption properties [1,2]. An obstacle, however, is the limited availability of suitable, competitively priced sensor instrumentation, in particular in the mid-IR. Currently, most mid-IR sensors use non-dispersive (NDIR) technology, i.e. measure at a small number of wavelengths only. While simpler and hence smaller and cheaper in instrumentation, the reduction of the spectral information to a few pre-determined wavelengths forfeits the inherent capability of spectroscopic devices to selectively detect single substances even in the presence of spectrally interfering sample constituents. Fully spectroscopic sensors capable of scanning a wider spectral range around the target analytes' spectral absorption features would have significant advantages here, including the option of using smart chemometric algorithms for advanced data evaluation.

One such example where a fully spectroscopic sensor would have clear advantages over NDIR devices and other sensors is the detection of dissolved carbon dioxide in aqueous solu-

tions (CO₂(aq)). The concentration of dissolved CO₂, e.g. in carbonised beverages or beer, significantly influences the sensory experience during consumption. CO₂(aq) levels hence are a key parameter in (on-line) quality control. Presently, CO₂(aq) levels are mostly determined using gas extraction methods [3]. The classical technique is to expand the volume over a sample and measure the change in gas pressure due to out-gassing of CO₂. While well proven, this method relies on sampling and thus is limited in its applicability for on-line process monitoring. An alternative is the use of semi-permeable membranes that allow a part of the dissolved CO₂ to diffuse into a measurement chamber, where it is detected directly using an NDIR detector or optically through its influence on a pH-sensitive dye. The chief limitation of these approaches is the limited compatibility with industrial food processing, in particular its stringent clean-in-place (CIP) requirements. Also, equilibrating between solutions and sensing devices may cause a time lag that limits the practical process applicability.

For industrial in-line monitoring, the ultimate solution would be a sensor that directly measures the dissolved carbon dioxide, e.g. in a process line or a storage tank. While well suited for measuring gaseous CO₂, NDIR sensors have a problem with this, since the absorption band of CO₂(aq) at 2343 cm⁻¹ / 4,27 μm overlaps with the short-wavelength tailing of the water combination band at 2130 cm⁻¹ / 4,7 μm (Figure 1). As mid-IR water absorptions are variable with temperature and the nature and concentration of chemically or physically dissolved substances, the shape and intensity of this interfering water band will change with e.g. the levels of sugars, alcohol or dissolved salts present in the beverage. Another complication is the pH-dependent equilibrium presence of spectrally different CO₂-related chemical species, i.e. hydrogen carbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions.

This clearly calls for the application of a sensor system capable of reliably discerning between the CO₂(aq) feature and such interferences.

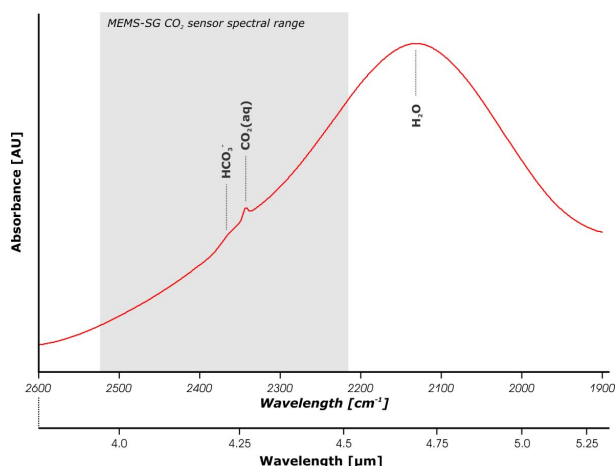


Figure 1. Absorption spectrum of an aqueous solution of 1.5 g/L carbon dioxide in water at 21 °C and pH 6; the shaded area indicates the spectral working range of the MEMS-SG CO₂ sensor prototype

II. MEMS SPECTROMETER HARDWARE

To determine the relevant spectral range, the absorption spectra of various aqueous solutions containing dissolved carbon dioxide together with other typical beverage ingredients, such as sugars, artificial sweeteners, phosphates or alcohols, were measured under controlled laboratory conditions. The subsequent analysis resulted in the identification of a spectral range ($2550\text{ cm}^{-1} - 2200\text{ cm}^{-1}$ / $3.9\text{ }\mu\text{m} - 4.55\text{ }\mu\text{m}$) containing the significant spectral signatures of both the target analyte and relevant interferents. With a width of about $0.6\text{ }\mu\text{m}$ this required spectral range is sufficiently narrow to be covered with a grating spectrometer device using a single refraction grating.

Based on that, a previously developed compact near-IR scanning grating (SG) spectrometer using a micro-electro-mechanical (MEMS) grating mirror [4,5] was redesigned to meet the specific needs of this application, i.e. operation in the mid-IR around $4.2\text{ }\mu\text{m}$. Implementing MEMS technology allows realising compact and reliable spectral analysers with good spectral properties and fast response times. Together with outstanding mechanical stability and a potentially low price due to the mass production of MEMS elements, such a system has the potential for being used as in-line sensor in industrial environments, e.g. directly flanged to a transfer line.

A. Monochromator Layout

The spectral analyser was designed using a modified Czerny-Turner monochromator layout with 15° deviation angle (Figure 2). The incident light from the sample is collimated by an off-axis parabolic mirror with 10 mm focal length. Together with the $3 \times 3\text{ mm}^3$ aperture of the scanning grating micro-element, this yields a good compromise between compact size, high radiation throughput ($f/3.7$) and good spectral resolution. The first order diffractions are directed towards a spherical mirror focussing the beam through

an order-sorting filter (Spectrogon LP-3500) and an exit aperture onto a thermo-electrically cooled single-element MCT detector (Vigo PVI-2TE-5-0,5, BaF₂ window; VIGO S.A., Poland).

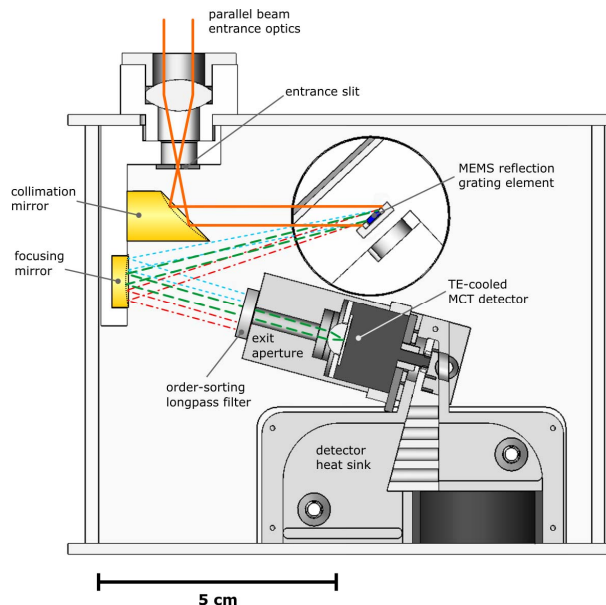


Figure 2. Optical layout of the prototype MEMS grating monochromator for operation in the $4.0 - 4.5\text{ }\mu\text{m}$ range

B. MEMS Component

To scan a grating monochromator through, the diffraction grating needs to be able to rotate or oscillate. On the micro-element scale, this translates favourably into a resonantly driven, electrostatically actuated oscillating micro-mirror device developed by the Fraunhofer Institute for Photonic Microsystems (IPMS) [6]. Using a number of in-plane comb electrodes to actuate an oscillatory movement around a central axis, large mechanical deflection angles can be achieved at low actuation voltages [7]. Depending on the design, oscillating micro-mirror components with deflection angles exceeding 10° can be driven at voltages less than 40 V. In order for such a component to function as a reflection grating element, the top surface of the mirror plate has to be modified by “cutting” a grating structure into it. In MEMS components, this can be achieved through anisotropic wet etching [8], followed by covering the structure with a thin metallic reflection coating, e.g. 100 nm aluminium, to ensure a high reflectivity in the mid-IR.

For the present study, a MEMS device with $3 \times 3\text{ mm}^2$ aperture and a 400 grooves/mm V-shaped grating was used (Figure 3). Using a pulsed driving voltage of 36 V, the micro-mirror was operated at a mechanical deflection angle of $\pm 7^\circ$ at an oscillation frequency of 130 Hz. Designed for the spectral range $1.2 - 2.5\text{ }\mu\text{m}$, operating this grating at a diffraction angle $\beta = 66.5^\circ$ yields a first order centre wavelength of $4.25\text{ }\mu\text{m}$ and allows covering the relevant spectral range from 4.0 to $4.50\text{ }\mu\text{m}$.

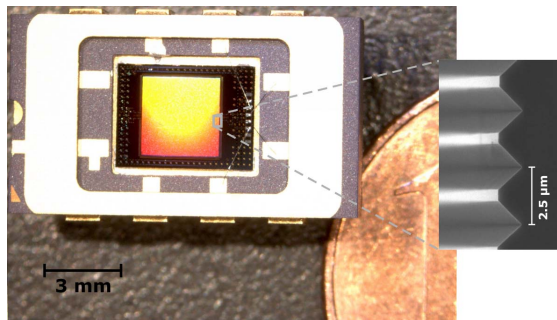


Figure 3. MEMS micro-mirror component with a 2.5 μm spaced V-groove grating mirror, as used for the MEMS-SG CO_2 sensor; on the right a part of one Euro-cent coin for size comparison.

C. System Performance

The resulting spectrometric device covers a spectral range from 3,968 μm to 4.520 μm at a (simulated) spectral resolution of 10 nm; the experimental verification yields a spectral resolution better 15 nm, which is consistent. While not optimal in terms of grating efficiency (simulated average efficiency of 0.4) and effective grating aperture (the high angular inclination against the incident beam reduces the lateral aperture to approx. 1.2 mm), when compared to the effort of designing and producing a new grating the performance was deemed sufficient for proving or disproving the basic feasibility of the concept.

Another interesting feature of this device is its high scanning speed. At an oscillation frequency of 130 Hz the sensor can acquire one spectral scan every 7.7 ms, or one spectrum integrating 1000 scans within less than 8 s. It is thus easily possible to compensate for the inferior signal-to-noise ratio by co-adding a high number of spectral scans within a few seconds.

Encased in a robust standard housing, the MEMS-SG spectral transducer prototype has a typical footprint of 100 x 80 x 75 mm^3 , a weight of 0.6 kg and a typical power consumption of less than 5 W.

III. EXPERIMENTAL

A. Sample Preparation

As the equilibrium solubility of carbon dioxide in water is low, aqueous solutions containing dissolved CO_2 need to be kept under pressure to avoid uncontrolled out-gassing. For this study, aqueous solutions containing controlled amounts of dissolved CO_2 were produced in a closed flow system by mixing sodium hydrogen carbonate (NaHCO_3) solutions in equal parts with a citrate buffer adjusted to pH 3.0. The change in the pH of the solution causes the hydrogen carbonate ($\text{p}K_{\text{a}1}(\text{H}_2\text{CO}_3) = 6.35$) to transform into dissolved carbon dioxide, resulting in well-controlled standard solutions. In addition, a number of real samples (different mineral waters, dry sparkling wine, carbonated and sweetened dark coloured soft drink) were measured by pumping the respective sample through the measurement cell.

The measurement cell, a transmission flow cell with parallel CaF_2 windows spaced 25 μm apart, was directly connected to the flow system. The system proved pressure-stable up to 6 g/L NaHCO_3 in the stock solution, equalling about 1.6 g/L dissolved carbon dioxide in the final standard solution. At higher concentrations the pressure provided by the peristaltic pump was no longer sufficient to reliably prevent the formation of gas bubbles in the flow cell.

B. Data Acquisition & Post-Processing

All samples were measured in an open parallel beam setup consisting of a 20 W ceramic filament IR source, an off-axis parabolic mirror, the 25 μm transmission flow cell and the MEMS-SG spectral analyser. The standard solutions were measured in flow at 1000 scans per spectrum (time resolution approx. 8 s) against a water/buffer background. To prevent water vapour or atmospheric carbon dioxide from interfering, the setup was encased in a glove box continuously flushed with dry nitrogen gas.

The measured absorption spectra were evaluated by integrating the peak area in the range 2327 cm^{-1} to 2353 cm^{-1} (4.30 – 4.25 μm), using a parabolic four-point baseline fit to compensate for baseline distortions due to the underlying water band.

IV. RESULTS

Figure 4 shows some example spectra of $\text{CO}_2(\text{aq})$ standard solutions. The strong variability of the baseline, in this case most likely due to temperature variations during the out-of-sequence measurement of the different standards, is clearly discernible, illustrating the need for a spectrometric analytical device able to identify and correct such baseline artefacts. A baseline-corrected integration of the area under the $\text{CO}_2(\text{aq})$ peak yields a linear calibration curve (Figure 5, $R^2=0,991$) with an estimated level of detection of 0,25 g/L.

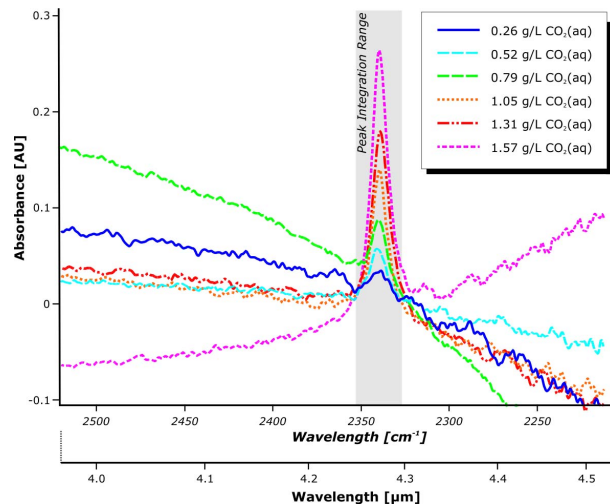


Figure 4. Absorption spectra of $\text{CO}_2(\text{aq})$ solutions at different concentration levels, baseline offset corrected for the peak range. The shaded area indicates the peak integration range used for quantitative data evaluation.

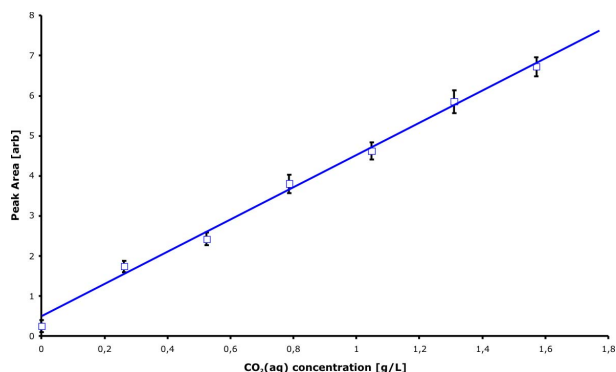


Figure 5. $\text{CO}_2(\text{aq})$ calibration curve measured with the MEMS-SG CO_2 sensor prototype

When attempting to measure strongly carbonated real samples out-gassing occurred, causing bubbles in the measurement cell. This out-gassing manifests itself also in the spectra (Figure 6), namely in a general decrease of intensity and the appearance of the characteristic double feature of gaseous CO_2 .

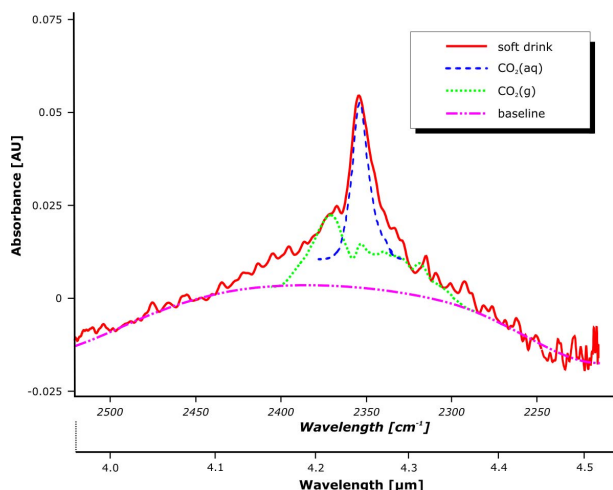


Figure 6. Typical absorption spectra of a strongly carbonated soft drink after partial out-gassing. The component spectra of dissolved CO_2 , gaseous CO_2 and the baseline distortion are shown in overlay.

V. CONCLUSION & OUTLOOK

The findings of this study prove that using micro-electro-mechanical optical elements to build compact, robust spectrometric devices that could be used as the transducer core for dedicated IR sensors is feasible. Using dedicated gratings optimised for the respective wavelength range of interest, such devices can be tuned to specific analytes. Exploiting the fully spectroscopic measurement, multiple analytes absorbing in the same spectral region could be qualitatively and quantitatively detected, while interferences can be corrected

for. Exploiting the rapid scanning capabilities of the MEMS grating element, the limited optical signal throughput could be successfully compensated by co-adding large numbers of spectral scans in very short time. Thus, for the example application “dissolved CO_2 in aqueous solutions” satisfactory results could be obtained even under less than optimal circumstances.

Next steps will include designing a mirror specifically for the spectral range 4 – 5 μm . Besides improving the grating efficiency, this will allow increasing the f-number of the monochromator, thus improving the signal-to-noise characteristics. Combined with a high-pressure sample delivery system, this layout will be used for further measurements, including a wider study of real samples. Parallel to that, efforts will be made to further miniaturise the monochromator, with the aim of fitting it into a cube of about 5x5x5 cm^3 . Produced using standardised components, many of which can be produced cheaply using standard semiconductor processing technology, this could significantly reduce the prices for spectrometric analysers and thus make spectrometric IR competitive against their NDIR brethren.

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