Room-temperature monitoring of CH$_4$ and CO$_2$ using a metal-organic framework-based QCM sensor showing inherent analyte discrimination

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Abstract

The detection of methane and carbon dioxide is of growing importance due to their negative impact on global warming. This is true both for environmental monitoring, as well as leak detection in industrial processes. Although solid-state sensors are technologically mature, they have limitations that prohibit their use in certain situations, e.g., explosive atmospheres. Thus, there is a need to develop new types of sensor materials. Herein, we demonstrate a simple, low-cost metal-organic framework-based gas leak detection sensor. The system is based on gravimetric sensing using a quartz crystal microbalance. The quartz crystal is functionalized by layer-by-layer growth of a thin metal-organic framework film. This film shows selective uptake of methane or carbon dioxide under atmospheric conditions. The hardware has low cost, simple operation, and theoretically high sensitivity. Overall, the sensor is characterized by simplicity and high robustness. Furthermore, by exploiting the different adsorption kinetics as measured by multiple harmonics analyses, it is possible to discriminate whether the response is due to methane or carbon dioxide. In summary, we demonstrate data relevant towards new applications of metal-organic frameworks and microporous hybrid materials in sensing.
Introduction

Real-time sensing of greenhouse gases is essential in environmental studies, air quality and process monitoring. Fugitive methane and carbon dioxide emissions, e.g., from distribution pipelines, abandoned oil and gas wells and carbon capture sites, have become increasingly concerning due to their effect on global warming. Therefore, real-time monitoring, quantifying and locating emission sources is essential.\textsuperscript{1–3} Commercially available solid-state sensors offer a cost-effective solution but are hampered by poor selectivity, irreversible poisoning at saturation levels and short lifespan under non-ideal conditions. Non-dispersive infrared spectroscopy sensors address some limitations but are sensitive to environmental conditions, especially humidity and rapid temperature changes.\textsuperscript{4} Thus, there is a need to develop sensor technology based on new detection mechanisms and with improved practical applicability.\textsuperscript{5,6}

\begin{figure}[h]
    \centering
    \includegraphics[width=\textwidth]{Fig1.png}
    \caption{Simplified schematic gas detection using functionalized QCM sensors. The drop in frequency corresponds to a change in mass due to the adsorption of guest molecules.}
\end{figure}

Quartz crystal microbalance (QCM) based sensors are technologically simple, cost-effective, and with high theoretical sensitivity.\textsuperscript{7,8} The working principle is based on the piezoelectric property of quartz crystals.\textsuperscript{9} This means that they produce an electrical charge when under mechanical stress. The process is reversible; thus, when an alternating voltage is applied to a quartz crystal, it oscillates at a fundamental frequency. This frequency is dependent on the thickness and mass of the quartz crystal. For use as a sensor, the quartz crystal is typically surface functionalized with a thin film capable of binding target molecules (Figure 1). The sorption of guest molecules changes the mass, yielding a measurable frequency reduction. The relationship between frequency and mass change is linear for rigid films and described by the Sauerbrey equation.\textsuperscript{10} The theoretical mass sensitivity constant of a 10 MHz resonator is 4.4 ng cm\textsuperscript{-2} Hz\textsuperscript{-1}.\textsuperscript{11} For application, the critical challenge is the functionalization of the quartz resonator with a selective analyte-recognizing film. The film is ideally based on a material that binds the target molecule in the presence of other species with high selectivity. Secondly, it can be used for enrichment and sensitivity enhancement, which is especially challenging for low molecular mass analytes.\textsuperscript{12}

Metal-organic frameworks (MOFs) are a class of extended network solids containing potential voids.\textsuperscript{13,14} MOFs are prepared by self-assembling inorganic nodes, typically polyatomic metal clusters, and organic linker molecules (secondary building units or SBUs).\textsuperscript{15} The well-defined
connectivity and topology of the SBUs yield high structural predictability and control.\textsuperscript{16} In simplified terms, this allows us to create materials with specific properties ‘on-demand’ by the purposeful choice of the building blocks. This, combined with high porosity and internal surface area, makes MOFs attractive as analyte-recognizing sensor materials. For QCM sensing specifically, MOFs can be deposited as thin films on the electrode surface, e.g., via liquid-phase layer-by-layer, electrochemical or chemical vapour deposition.\textsuperscript{17,18} Metal-organic frameworks have successfully been demonstrated for detecting humidity, volatile organic compounds and other toxic gases.\textsuperscript{19–23} However, few examples of sensing CH\textsubscript{4} and/or CO\textsubscript{2} have been described.\textsuperscript{24–28} Key challenges that must be addressed, especially significant for CH\textsubscript{4}, include poor response rate and detection limit, directly correlating to the selectivity towards other atmospheric gases (e.g., N\textsubscript{2}, O\textsubscript{2}).

Figure 2. Chemical sketch of the copper paddlewheel building unit and the organic linkers molecule (a). b Space-filling model of [Cu(hfipbb)(H\textsubscript{2}O)] viewed down the crystallographic b (b) and c axis (c). The isosurface calculated using a CH\textsubscript{4} probe is presented in blue. Visualization and surface calculations were done using iRASPA v2.2.5.\textsuperscript{29}

Herein, we demonstrate how quartz crystal resonators functionalized with the microporous MOF [Cu(hfipbb)(H\textsubscript{2}O)] (H\textsubscript{2}hfipbb = 4,4’-(hexafluoroisopropylidene)bis(benzoic acid)) can be used for gravimetric sensing of CH\textsubscript{4} and CO\textsubscript{2} under ambient conditions. This MOF was first described by Jiang et al. in 2009.\textsuperscript{30} Structurally, the MOF is constructed from copper paddlewheel SBUs connected by twisted fluorinated dicarboxylate linkers with a carboxylate-a carboxylate angle of 110 °, giving an interpenetrated helical assembly with tubular channels down the b axis (Figure 2). The channels contain small cavities connected by narrow windows of 2.96 Å (calculated using PoreBlazer 4.0).\textsuperscript{31} This is slightly less than the kinetic diameters of CH\textsubscript{4} and CO\textsubscript{2} (3.80 and 3.30 Å, respectively).\textsuperscript{32} This slight difference yields a measurable difference in diffusion coefficients which may be exploited for analyte discrimination as described later. For device integration, we fabricated thin films on the gold surface of the QCM resonator using a sequential deposition protocol. The sensor shows a rapid response to both CH\textsubscript{4} and CO\textsubscript{2}. Regarding practical applicability, the sensor is fully reversible even at saturation (i.e., 100% gas levels) and shows no performance loss when stored under normal, humid conditions for several months. More interestingly, by the analysis of overtones, it is possible to discriminate whether the response is due to the adsorption of CH\textsubscript{4} or CO\textsubscript{2}, providing a built-in selectivity factor.

**Experimental section**

**Reagents and materials**
All materials and reagents were sourced commercially and used without further purification.

Absolute ethanol, 16-mercaptoundecanoic acid (16-MHDA, >90%), copper (II) acetate monohydrate (>98%) and acetic acid (100%) were purchased from Merck KGaA, Germany. 4,4’-(Hexafluoroisopropylidene)bis(benzoic acid) (>98%) was purchased from TCI Europe NV, Belgium. AT-cut piezoelectric quartz crystal resonators (10 MHz, gold electrodes 6 mm diameter) were purchased from Novaetech S.r.l., Italy. Oxygen (>99.995%), methane (>99.5%) and carbon dioxide (>99.99%) were purchased from Air Liquide A/S, Denmark. Nitrogen (99.999%) was supplied from a Nano GEN2 PSA generator.

Synthesis of [Cu(hfipbb)(H$_2$O)]

A slightly modified literature procedure was used to prepare the MOF in bulk. Cu(CH$_3$COO)$_2$·H$_2$O (73.3 mg, 0.36 mmol) and 4,4’-(hexafluoroisopropylidene)bis(benzoic acid) (144.1 mg, 0.36 mmol) were added to a 20 mL glass pressure vessel containing 15 mL of H$_2$O. The vial was sealed with a crimp cap and sonicated for 15 minutes yielding a suspension of the linker in aqueous copper acetate. The reaction mixture was heated to 125 °C for three days, after which a fine crystalline blue powder precipitated. The powder was isolated by filtration and washed by sonication in acetone (10 mL) followed by ethanol (10 mL) to remove excess linker. The cleaned material was isolated by filtration and air-dried, leaving [Cu(hfipbb)(H$_2$O)] as a light blue powder (132 mg, 0.28 mmol, 78%). The as-synthesized MOF was heated at 140 °C in an oven for 24 hours to remove trapped solvent molecules (hereafter referred to as ‘activated MOF’). IR (FT-ATR diamond anvil, recorded on a Bruker ALPHA II with resolution 2 cm$^{-1}$) v/cm$^{-1}$ IR (cm$^{-1}$): 3674(b), 3419(b), 1609(s), 1559(m), 1402(vs), 1324(w), 1292(m), 1257(s), 1237(s), 1210(s), 1197(m), 1169(vs), 1136(s), 1022(w), 974(m), 962(m), 947(m), 928(m), 860(m), 846(m), 780(s), 749(s), 723(vs), 692(w), 556(w), 532(m), 515(s), 495(s).

Fabrication of sensor films

The quartz crystal resonator was cleaned by ultrasonication in ethanol and dried under a stream of N$_2$. It was then loaded into a custom-built flow cell (Figure S1). A solution of 16-MHDA (0.5 mM) in ethanol containing 10% acetic acid was injected at 10 µL min$^{-1}$ for ten hours using a syringe pump (KD Scientific, Legato 270) to form a carboxylate-terminated self-assembly monolayer (SAM). The monolayer-functionalized resonator was washed with absolute ethanol, dried under a stream of N$_2$ and re-inserted in the flow cell. A 25-cycle program of alternate injections of Cu(CH$_3$COO)$_2$ (1 mM in ethanol, 200 µL min$^{-1}$) followed by washing using absolute ethanol (700 µL min$^{-1}$) was performed to seed the terminal carboxylate of the SAM. The MOF thin films were grown by alternating injections (25 to 120 cycles) of Cu(CH$_3$COO)$_2$ (1 mM, ethanol, 200 µL min$^{-1}$), absolute ethanol (700 µL min$^{-1}$) and H$_2$hfipbb solution (2 mM, ethanol, 200 µL min$^{-1}$) using a multichannel peristaltic pump (Ismatec Reglo ICC). The films were washed with ethanol, dried under a stream of N$_2$ and activated in an oven at 140 °C for 24 hours.

Characterization of sensor films

Scanning electron and atomic force microscopy measurements were performed using an FEI Quanta 650F and Bruker Dimension Icon AFM (tapping mode, TAP150Ai-G probe), respectively. The structural identity of the film was confirmed by powder X-ray diffraction on a Malvern Panalytical Empyrean diffractometer, equipped with a Bragg-Brentano high-
definition incident monochromator and a 1Der detector, using Cu K-α (1.5406 Å) radiation in reflection mode.

Figure 3. Powder XRD diffractograms of the calculated (black), as-synthesized (red), activated (blue) and thin film (green) of [Cu(hfipbb)(H$_2$O)].

Sensor evaluation

QCM data were measured using an openQCM NEXT (Novaetech S.r.l., Italy) with dissipation monitoring and temperature control (T = 23 °C, all measurements). The sensor was connected to a commercial fluidic module with an internal volume of 50 µL (above the sensor). The module's inlet was connected via PTFE tubing (1.02 mm i.d.) to a Y-connector. The Y-connector was fitted with check valves (IDEX CV-3320, one psi cracking pressure) connected to two gas-tight syringes (Figure S2). The primary syringe was filled with N$_2$ and the second with the target gas (CH$_4$, CO$_2$). On-line dilution to create mixtures of target gas in N$_2$ was achieved by flow-rate programming (e.g., 180 µL min$^{-1}$ N$_2$, 20 µL min$^{-1}$ CH$_4$ for 10% CH$_4$ in N$_2$). Each measurement was performed at variable injection rates (200 to 1500 µL min$^{-1}$), typically with a 10-minute flow of N$_2$, 10 minutes of the target gas, and 10 minutes of N$_2$ for sensor regeneration. CO$_2$ and CH$_4$ diluted using synthetic and humid air were injected for sensor evaluation under real-life conditions. Caution! Methane is classified as a GHS Flammable Gas, Category 1, with a flammability limit of 5% in air. Therefore, appropriate precautions should be taken. All manipulations were performed on the smallest practical scale in a ventilated enclosure.
Results and discussion

Sensor fabrication and characterization

The MOF functionalized quartz crystal resonators (hereafter referred to as sensors) were prepared by layer-by-layer epitaxial growth using a custom-designed flow setup. The film deposition cell allowed us to limit exposure of the growth solutions to the gold electrode, avoiding the deposition of crystals on the surrounding quartz surface and the contacts. Before the MOF growth, a SAM of 16-mercaptohexadecanoic acid was deposited on the gold surface. The SAM acts as a binder for an initial layer of copper atoms that are used to sequentially grow the film. Thus, the first layer of the film is covalently bonded to the gold electrode, providing mechanical and chemical strength. The structural identity of the film was confirmed by powder X-ray diffraction (Figure 3). The thin-film powder pattern matches the bulk material and theoretical values calculated from the single crystal structure deposited in the Cambridge Structural Database (CSD reference code VUKHEP). With a carboxylate-terminated SAM, [Cu(hfipbb)(H$_2$O)] has two preferred growth planes; [102] and [010] (Figure S3). SEM imaging shows island growth of tabular/disc-like crystallites with a long edge pointing toward the surface (Figure 4). This is consistent with an [102] oriented film where the 1D channels are perpendicular to the sensor surface. Thus, adsorption of the target analytes is assumed to occur perpendicular to the crystallites, potentially reducing vertical access. The number of deposition cycles was used to control the thickness of the film. For 25 cycles, a thin film with an approximate mass of 29 µg was deposited (calculated using the Sauerbrey equation, assuming that the film is rigid under standard conditions). Increasing the number of cycles to 120 resulted in a film with an approximate mass of 87 µg. SEM of a cross-section of the thin film of 87 µg shows an average thickness of 2.5 µm (Figure S4). Based on the density obtained from single crystal XRD data – 1.707 g/cm$^3$ (disregarding bulk crystal density), the calculated thickness is 1.8 µm, which is in good agreement with the SEM derived thickness. The difference is attributed to voids at the interaggregate grain boundaries, which is also observed in AFM imaging.
imaging. For thicker films, both the 3rd and 5th overtones were dampened to the extent that they could not be measured. The overtones (resonance excited harmonics) provide information on film rigidity as well as increased mass sensitivity (at the cost of signal-to-noise ratio). Thus, the lack of overtones reduces the amount of information about the system that can be determined. Therefore, only thinner films were used for the sensing studies.

Figure 5. Sensor response at various concentrations of CH₄ (v/v% in N₂) showing fundamental frequency f₁, overtones f₃ & f₅ and dissipation d₁ with a) 2-10% CH₄ and b) 20-100% CH₄ at a flow rate of 500 µL min⁻¹. c) Calibration curves for f₁, f₃ and f₅ for sensor response at various concentrations of CH₄ (v/v% in N₂) showing a typical IUPAC Type I adsorption isotherm, fitted with function y = a-b*cˣ.

Sensor performance

Due to the explosive hazard of CH₄ and O₂ mixtures, the primary calibration and adsorption study was carried out with gases diluted in pure N₂. Sensor response at various concentrations was evaluated (Figure 5-6, Table 1) for CH₄ and CO₂. The response (Δfᵣ, defined as change in frequency at equilibrium in analyte gas flow compared to the preceding N₂ flow) follows a typical IUPAC Type I isotherm. The OpenQCM flow module has an internal volume of 50 µL. Thus, at 200 µL min⁻¹, the headspace gas was replaced approximately four times every minute. Here, CH₄ saturation was observed within 150 seconds (t₉₀ ~144 s, t₉₀ defined as the time required to reach 90% of the maximum frequency response), whereas it was slightly faster for CO₂, with t₉₀ ~111 seconds. The effect of increasing flow rate was evaluated by sequential injection of 25% of the test gas in N₂ at 100, 200, 400, 1000 and 1500 µL min⁻¹ (Figure 7). Between 100 and 1000 µL min⁻¹, there is a significant increase for both analytes in sensitivity (47% and 42% for CH₄ and CO₂, respectively, defined as total change in frequency at equilibrium) and the response rate (~3 times and ~7 times faster for CH₄ and CO₂, respectively, defined as change in frequency per unit time). But no significant difference is observed moving to 1500 µL min⁻¹. The adsorption is fully reversible up to 100% for both molecules. Desorption occurs rapidly when the film is exposed to pure N₂ or the atmosphere.

The film shows a noticeable change in dissipation response, indicating a viscoelastic behaviour due to the adsorption process. We attribute this to the swelling of the framework due to the size discrepancy between guest molecules and 1D channels, i.e., the channel windows must expand to accommodate the guest molecules. Although CO₂ has a smaller kinetic diameter, the
dissipation response is higher compared to CH₄. This is assumed to be due to an overall higher molecular uptake due to stronger interactions with the framework.

<table>
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<th>v/v%</th>
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<th>CO₂</th>
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<tr>
<td></td>
<td>Δf₁ (Hz)</td>
<td>Δf₃ (Hz)</td>
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<tr>
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<td>16.7 ± 1.8</td>
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<td>100</td>
<td>58.6 ± 1.9</td>
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Table 1. Frequency and dissipation response for CH₄ and CO₂ respectively when exposed to different concentrations (v/v% in N₂). Δd₁ = Change in dissipation.

Figure 6. Sensor response at various concentrations of CO₂ (v/v% in N₂) showing fundamental frequency f₁, overtones f₃ & f₅ and dissipation d₁ with a) 2-10% CO₂ and b) 20-100% CO₂ at a flow rate of 500 µL min⁻¹. c)
Calibration curves for $f_1$, $f_3$ and $f_5$ for sensor response at various concentrations of CO$_2$ (v/v% in N$_2$) showing an IUPAC Type I adsorption behaviour, fitted with function $y = a - b\cdot c^x$.

The MOF contains binuclear copper nodes with four carboxylate linkers binding to the metal site in bridging mode (i.e., paddlewheel structure). The binding of a water molecule saturates the coordination sphere of each copper atom. The water molecules can be removed by thermal activation, and it is known that open metal sites may increase the binding affinity towards CH$_4$ and CO$_2$.$^{35,36}$ However, the material will, over time, re-adsorb water molecules from the atmosphere (which can be visually corroborated by a change of colour from dark to light blue).

To evaluate the effect of water content, response towards methane was measured for a synthesized sensor pre-activation and again post-activation for the same sensor. Subsequently, the film was saturated by submerging it in water and the response was measured again, followed by reactivation and another measurement. In all cases, a near identical response was observed towards 25% CH$_4$ in N$_2$ (v/v) (Figure S5). Additionally, the effect of relative humidity on the sensor was evaluated by measuring the response towards 25% CH$_4$/CO$_2$ in dry synthetic (80:20 N$_2$:O$_2$), atmospheric (RH38%) and humid air (RH65%, obtained from bubbling compressed air through a saturated aqueous sodium chloride solution).$^{37}$ The relative humidity was verified by a handheld sensor (RS Pro RS-172 datalogger). For CH$_4$, there is a slight decrease in sensitivity when moving to humid air.

**Figure 7.** Sensor response at increasing flow rates showing fundamental frequency $f_1$, overtones $f_3$ & $f_5$ and dissipation $d_1$ with a) 25% CH$_4$ (v/v) in N$_2$ and b) 25% CO$_2$ (v/v) in N$_2$.

**Sensor selectivity**

Cross-sensitivity between CH$_4$, CO$_2$, and O$_2$ in N$_2$ was evaluated. The sensor is responsive to CO$_2$ and CH$_4$ but shows no significant sensitivity towards O$_2$ (Figure S7). The sensitivity is approximately 2.0 and 15.6 Hz per µg of MOF film for CO$_2$ and CH$_4$, respectively. First, we attribute the higher sensitivity towards CO$_2$ to its slightly smaller kinetic diameter, yielding a higher penetration depth of the gas molecules within the film. Secondly, CO$_2$ has a quadrupole moment. This favours electrostatic interaction between the aromatic π system of the linker molecule and the electron-deficient carbon atom. In contrast, CH$_4$ is predominantly expected to interact via weaker, π - HC interaction between the gas molecules and internal MOF surface. This is corroborated by theoretical and experimental adsorption studies on a structurally similar MOF, [Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$], showing that CO$_2$ has a higher heat of adsorption than CH$_4$.$^{38,39}$ Although not identical, both MOFs have a similar internal chemical environment, surface area and porosity. Bao et al. calculated the diffusion coefficient of CO$_2$ and CH$_4$ to be
2.97 $10^{-3}$ s$^{-1}$ and 1.14 $10^{-4}$ s$^{-1}$ respectively, in the same material. However, this is not reflected in the response rate, where the sensor shows relatively similar $t_{00}$ values.

Interestingly, the kinetic and thermodynamic difference results in different penetration depths of both molecules within the film. For a QCM, the penetration depth of the measurement decreases with increasing overtone number as the higher frequencies probe closer to the quartz surface. Thus, analysis of the frequency changes in the fundamental and overtone frequencies allows us to probe adsorption at different vertical regions of the MOF film. This can be exploited to discriminate between CH$_4$ and CO$_2$ (Table 2, Figure 8, Figure S8-S10). The frequency ratio deviations ($f_{\text{ratio},i} = \Delta f_i/\Delta f_1 - i$) were calculated based on the average sensor response of ten consecutive sensing and regeneration cycles. For example, 10% CH$_4$ and 1% CO$_2$ yield an equal response at the fundamental frequency ($\Delta f_1 \approx 14$ Hz). However, at the fifth fundamental, the response is 80 and 73 Hz, yielding a frequency ratio deviation of 0.6 and 0.9 for CH$_4$ and CO$_2$, respectively. It is worth noting that the frequency ratio deviation depends on concentration and should be calibrated equally to frequency reduction before use. Furthermore, the dissipation response for both molecules is slightly different when the fundamental frequency response is the same. This difference can be utilized to distinguish further which molecule is responsible for the sensor response and be used as additional factors/input in more comprehensive data processing methods (e.g., principal component analyses).

<table>
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Table 2. Frequency deviation analysis for different concentrations of CH₄ and CO₂ (v/v% in N₂) that give a similar response for Δf₁

Limit of detection and quantification

The calibration curve for CO₂ and CH₄ corresponds to a type I adsorption isotherm, consisting of a linear Henry region followed by a horizontal plateau at saturation. The partition coefficient (k) describes the distribution of the guest molecules between the gas phase and the porous film. Assuming Henry’s law is valid, and that the frequency change is exclusively a result of guest molecule adsorption, the slope of the linear range in delta f (Hz) versus concentration is the partitioning coefficient. Thus, a steeper calibration curve results from a higher partition coefficient, i.e., sensitivity. The slope of the linear region (Figure S11 - S12) of the calibration curve is -0.69 Hz and -17.25 Hz per vol% for CH₄ (<10%) and CO₂ (<1%), respectively. For CH₄, the experimentally determined LOQ is 1%, with a LOD of 0.4%. For CO₂, the LOQ is 0.2% (all v/v% in N₂).

Stability and robustness

A challenge with MOF-based sensors is stability, especially under humid conditions where water molecules can penetrate the framework and disconnect the relatively labile metal–carboxylate bonds. Therefore, the MOF material was stress-tested in bulk by shaking it in water for three days. Then, samples were taken daily and characterized by powder X-ray diffraction. No crystallinity or material integrity loss was observed during this period (Figure S13). More importantly, the sensors show insignificant performance loss when stored under ambient and uncontrolled conditions for up to 3 months (more extended period not tested), as determined by comparing the response factor of 50% and 100% CH₄ (Figure 9). This indicates that the sensor material is suitable for long-term applicability under standard conditions.
Furthermore, no loss in response factor was observed after multiple adsorptions and desorption cycles (Figure S14). Thus, unlike traditional solid-state sensors, the sensor does not exhibit irreversible poisoning at complete saturation levels. However, compared to CO₂, sensor regeneration after exposure to CH₄ is slightly slower (desorption t₉₀ ~140 versus ~130 s respectively at 100% analyte concentration at a flow rate of 500 µL min⁻¹). This is likely due to the larger kinetic diameter and slower diffusion kinetics. Still, the sensor can be used for repeating measurements and cycling even at saturation levels which is essential for practical applications.

**Conclusions**

We have demonstrated a CH₄/CO₂ sensor based on the principle of QCM with a sensor element composed of a MOF tailored for gas adsorption. The sensor was demonstrated using low-cost and open-source electronics, facilitating system integration with significant customizability. The device is characterized by high sensitivity, selectivity, and robustness under atmospheric conditions over long periods. Most importantly, it is possible to differentiate between a CH₄ or CO₂ response by analyzing multiple harmonics and exploring frequency ratio deviations. In addition to being useful for sensing purposes, this method provides essential information regarding guest molecule transport and adsorption kinetics within porous materials and should be explored further.

Looking forward, we will focus on multivariate calibration and chemometric processing of the sensor response data. First, the goal is to use advanced analyses to not only discriminate between CH₄ and CO₂ but also quantify their ratio in mixtures. Computational methods could also be complemented by adding multiple sensors with different selectivity in an array, i.e., creating an “electronic nose”.28,44 Although the sensor shows excellent metrics for industrial applications where leak detection is the primary goal, the sensor lacks the required sensitivity for environmental monitoring where CH₄ and or CO₂ are present at low ppm levels. QCM is, theoretically, sensitive enough. The limiting factor is the selectivity of CH₄/CO₂ over N₂/O₂. Research and development of new porous materials, or composites, should be invested in to improve this aspect. For MOF materials where channels propagate in one or two dimensions, the development of oriented growth protocols is warranted, as improper alignment of the channels can block the adsorption of guest molecules, reducing response rate and sensitivity.

**Data availability**

Raw data, including sensor characterization and the complete set of QCM measurements, have been deposited to Zenodo with the following doi://10.5281/zenodo.7529501

**Author contributions**


**Acknowledgements**

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