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Munksgaard, Niels C., and Nelson, Paul N. (2021) *Coupled polymer-membrane equilibration and cavity ring-down spectrometry for the highly sensitive determination of dissolved methane in environmental waters*. *Analytical Letters*, 54 (3) pp. 430-441.

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<https://doi.org/10.1080/00032719.2020.1767122>

Coupled polymer-membrane equilibration and cavity ring-down spectrometry provides highly sensitive measurement of dissolved methane in environmental waters

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Abstract:

High sensitivity field-based analysis of dissolved methane in surface water and groundwater is needed to monitor environmental impacts of natural gas field developments and understand microbial carbon cycling in water bodies.

A new analytical technique using a polymer membrane contactor coupled to a laser-based cavity ring-down spectrometer was developed and tested. By recirculating a water sample for ≈ 10 min, equilibrium was established between dissolved methane in the sample and methane in the measured gas phase, according to Henry's Law. The performance of the system was investigated by replicate analyses of several different water samples, spike recovery tests, comparison to analysis by headspace gas chromatography, and consideration of memory effects.

The technique provided an adequate detection limit for analysis of natural background concentrations of methane in environmental waters and was ≈ 28 times more sensitive than analysis by gas chromatography. The system is field-capable, simple to operate and calibrate and takes advantage of the low-drift characteristics of the cavity ring-down spectrometer.

Keywords: laser spectroscopy; membrane contactor; Henry's Law; methane; carbon dioxide

Introduction:

Laser-based cavity output spectrometers are robust and highly sensitive gas analysers that are increasingly used for field surveys of greenhouse gas concentrations to determine emissions from natural gas fields, agricultural and urban sources (Maher, Santos, and Tait 2014; Zellweger et al. 2016; Wilkinson et al. 2018). Being able to use the same instruments for field analysis of dissolved methane (CH₄) and other gases in surface water and groundwater would provide valuable additional data on the environmental impacts of gas field developments. It would also provide a valuable tool for understanding microbial carbon cycling in water bodies (Maher et al. 2013; Owen et al. 2016; Gruca-Rokosz and Koszelnik 2017).

Analysis of dissolved gas concentrations requires transfer of the analyte from the water sample to the gas phase. Gas-liquid equilibration devices, underpinned by Henry's Law, have been used for this purpose in several analyser designs. These include equilibrator inlet mass spectrometers (e.g. Cassar et al. 2009) and membrane inlet mass spectrometers (e.g. Mächler, Brennwald and Kipfer 2012). In their study of carbon cycling in estuarine waters, Maher et al. (2013) used a field-deployable cavity ring-down spectrometer (CRDS) and a shower-head equilibration device to measure dissolved CO₂ and CH₄ concentrations and their carbon isotope compositions. Subsequently, Gonzalez-Valencia et al. (2014) described an analytical system that coupled a non-porous polydimethylsiloxane (PDMS) membrane contactor to an off-axis integrated cavity output spectrometer (OA-ICOS) for the determination of the concentrations of CH₄ and CO₂ dissolved in water. The use of a membrane contactor for achieving gas-liquid equilibration safeguards the analysing instrument by preventing entry of liquid and enables a compact and robust design.

Although the instrument designed by Gonzalez-Valencia et al. (2014) employed a membrane contactor, it used continuous sample flow, which required a relatively complicated calibration procedure to account for the unknown transfer efficiency of analytes from the water sample to the measured gas phase. Achieving low drift and reliable calibration of

complex instruments can be challenging when operating in the field. An instrument based on the Gonzalez-Valencia et al. (2014) design is commercially available although it uses a hydrophobic micro-porous membrane comprised of polypropylene hollow fibres instead of a PDMS membrane (LGR 2019).

The aim of this work was to construct a field-operable instrument capable of measuring dissolved CH₄ in environmental water samples at natural background levels. This requires a system with detection limit <1 µg L⁻¹. Based on the design of Gonzalez-Valencia et al. (2014), a PDMS membrane contactor was coupled to a CRDS instrument. However, equilibrium between dissolved CH₄ and CH₄ in the measured gas phase was established using a recirculating water sample rather than continuous flow. This enabled a simple calibration procedure and takes advantage of the ease of operation and robust, low-drift characteristics of the CRDS.

Materials and methods:

Instrument design

The gas-liquid equilibrators involve the transfer of gas molecules from a water sample to the gas phase across a non-porous PDMS hollow-fibre membrane contactor (PermSelect PDMSXA-2500). This contactor contains 3200 fibres and has a surface area of 2500 cm², which enables fast gas transfer by a dissolution-diffusion process (Bazhenov, Bildyukevich, and Volkov 2018; PermSelect 2019). The equilibrators consist of two loops: a water (sample) loop and a gas loop (Figs. 1 and 2). The design criteria were a small footprint for ease of field use, a small gas loop volume for fast equilibration, and a relatively large water loop volume for high sensitivity. The shell side (outside) of the tubular PDMS membrane is connected to the gas loop, while the tube side (inside) is integrated with the water loop.

The water loop includes a 30-m long, 4-mm internal diameter coil of polytetrafluoroethylene (PTFE) tubing, a diaphragm pump with pulsation damper (NF1.300-DCB, KNF Neuberger GmbH, 3 L min^{-1} at atmospheric pressure) and solenoid-actuated valves (R-mini 2-way, Beta Valve Systems Ltd) to enable water samples to be either loaded into, or recirculated through, the loop. A needle valve (Omega FVLT101) enables adjustment of the water pressure (Omega DPG 1000B gauge) within the contactor. It is usually set at $\approx 1.7 \text{ atm}$ absolute, in accordance with the membrane manufacturer's recommendation. The volume of the water loop (0.575 L) was measured by the volume of discharged sample at the end of each analytical cycle. It can be varied by changing the length of the coil. Increasing the length of the coil lowers the detection limit and increases the required sample size, and vice versa (see below).

The main gas loop incorporates a diaphragm pump (NFP-015B, KNF Neuberger GmbH, 1.3 L min^{-1} at atmospheric pressure) and two 3-way solenoid-actuated valves (Clippard NR2-3-12) used to select either purging or measurement mode. A needle valve (Omega FVLT101) enables adjustment of the PDMS shell-side pressure (Omega DPG 1000B gauge), which is usually set at $\approx 0.75 \text{ atm}$ absolute, in accordance with the membrane manufacturer's recommendation. A small-volume secondary gas loop connects the CRDS (details below) to the main gas loop, a necessary configuration to ensure rapid mixing of the total gas loop volume, which would otherwise be limited by the low pump rate of the CRDS system ($\approx 0.03 \text{ L min}^{-1}$). The total volume of the gas loop is $\approx 0.131 \text{ L}$ based on volumetric measurements of components and the internal volumes of the CRDS system (data provided by Picarro Inc). A cylinder of high purity nitrogen (N_2) provides purge gas at a slight overpressure ($\approx 1.05 \text{ atm}$). The PDMS shell- and tube-side pressures must be maintained within the limits specified by the manufacturer to avoid membrane rupture. Furthermore, an

in-line water filter should be fitted to the intake line if analysing turbid water. The cost of components to build the equilibrator system (excluding the CRDS analyser) is \approx US\$ 5,000.

Fig. 1.

Fig. 2.

Cavity ring-down spectrometer (CRDS)

A field-deployable CRDS (G2131-I, Picarro Inc.), which simultaneously measures H₂O, CO₂ and CH₄ molar fractions in the gas phase, was connected to a vacuum pump designed for leak-free recirculation experiments (A0702, Picarro Inc.). While this study focussed on CH₄, CO₂ data was also assessed to further characterise analytical performance. A range of gas species and isotopologues could conceivably be measured using alternative gas analysers.

In CRDS a gas stream flows through a precise optical cavity within which its optical absorbance is measured by a ‘ringdown’ time measurement as light intensity decays after the laser light source is rapidly turned off. An effective path length through the sample gas of several kilometres gives CRDS high sensitivity, while wavelength monitoring of the absorption features and tight control of gas temperature and pressure provides high precision and low drift (Crosson 2008; Picarro 2019a). The G2131-I records data at \approx 1 Hz.

The CRDS has no user selectable settings and was operated with factory calibration. The analytical results were post-processed using a linear calibration equation established by daily analysis of certified gas standards. They had concentrations of 0, 10 and 50 ppm vol. CH₄ in air (Gastech Australia) and 0 and 1010 ppm vol. CO₂ in air (Scotty Speciality Gases).

Five-layer gas bags (Supel-Inert, Sigma Aldrich) were loaded with the standard gases and immediately connected directly to the CRDS inlet.

Instrument operation

The equilibrator-CRDS system was tested by manual switching of the valves. However, the system could readily be automated using the CRDS valve sequencer software.

The analytical sequence (Table 1) commences by loading a water sample through the inlet tube and letting it flow through the water loop to the outlet. Simultaneously, purge gas (N_2) flows through the gas loop to the outlet (3-way valves '1' and '2' open to gas inlet and outlet, Fig. 1). When the water loop is full (air bubbles disappear from the PDMS shell) both water and gas valves are switched to the measurement mode, in which the contents of the water and gas loops are recirculated, isolated from each other, but in contact across the PDMS membrane. From initial experiments using a range of measurement times, a 10-minute duration was found sufficient to closely approach equilibrium partitioning of CH_4 between gas and liquid (Fig. 3). Following completion of the measurement step, the water sample is discharged, with the sample inlet tube in air, and the gas loop purged by switching back to N_2 input. Upon reaching background CH_4 and CO_2 concentrations (typically <0.05 and <30 ppm vol, respectively after 3 minutes), the sample inlet tube is inserted in the next sample and the analytical sequence is repeated.

During extended use, small amounts of condensation can accumulate in the gas loop, principally in the water trap (a small 20-mm diameter tube to prevent ingress of condensation to the CRDS), so it should be drained daily. The water loop should be flushed with deionised water and the gas loop flushed with dry air prior to switching off the system, to prevent any algal growth during storage.

Table 1

Data processing

The CRDS data file was imported to a spreadsheet (Excel™) for processing (available from the corresponding author upon request). The mean CH₄ and CO₂ ‘dry’ (H₂O compensated) concentrations (volume fractions) of the last 60 readings during the measurement step (≈ 60 secs) were used to derive the concentrations in the original water sample in the following steps.

Firstly, the quantity of analyte (i) in the gas loop (n_{i-g} , moles) was calculated as:

$$n_{i-g} = P_i \cdot V_{\text{gas}} \cdot R^{-1} \cdot T_{\text{gas}}^{-1} \quad (1)$$

where P_i is the partial pressure of the analyte (Pa), which is derived by multiplying the mean total gas loop pressure (P_T , Pa) by the CRDS volume fraction (VF_i).

$$P_i = P_T \cdot VF_i \quad (2)$$

During recirculation the gas loop pressure varies between different sections due to the flow constrictions imposed by the needle valve and the CRDS flow controller. While it is not feasible to measure this variation accurately, the mean total pressure in the gas loop is assumed to be approximately equal to the ambient pressure, as the loop outlet is open during the purging step immediately before the valves switch to close the loop. The gas loop volume (V_{gas} , m³) was measured by adding the volume of all components including the internal volume of the CRDS. R is the gas constant (m³ Pa mol⁻¹ K⁻¹). Temperature, like pressure, varies between different parts of the gas loop. However, the mean temperature (T_{gas} , K) was

2-3 K above ambient temperature, which was measured by inserting a temperature probe via temporary ports and allowing for the internal CRDS temperature.

Secondly, the quantity of analyte (i) in the water loop (n_{i-w} , moles) was calculated as follows:

$$n_{i-w} = C_{i-w} \cdot V_{\text{water}} \quad (3)$$

where V_{water} (m^3) is the water loop volume and C_{i-w} (mol m^{-3}) is the concentration of analyte in the water, calculated as

$$C_{i-w} = P_{\text{shell}} \cdot V F_i \cdot H^{\text{cp}}_i \quad (4)$$

Where P_{shell} (Pa) is the gauge pressure in the contactor shell side and H^{cp}_i ($\text{mol m}^{-3} \text{ Pa}^{-1}$) is the temperature-dependent Henry constant (Sander, 2015 section 2.4.1). The values used for Henry constants and the temperature dependence equations were the ‘Sander 2011’ values in Sander (2015). Note that Henry’s law constants differ in saline solutions (Sander 2015).

Finally, the analyte concentration in the original sample ($C_{i\text{-sample}}$, mol m^{-3} or converted to $\mu\text{g L}^{-1}$) was calculated by summing the molar quantities from equations 1 and 3 and dividing by the water loop volume (V_{water} , m^3).

$$C_{i\text{-sample}} = (n_{i-g} + n_{i-w})/V_{\text{water}} \quad (5)$$

Performance assessment

Performance of the equilibrator-CRDS was assessed in several ways. Applicability, precision and detection limits were assessed by replicate analyses of tap water, bottled water, deionised laboratory water and natural river water from diverse sources. Method accuracy was assessed by analysis of CH_4 -spiked water samples. The spiked samples were prepared by equilibrating

tap water with 10 and 50 ppm (vol) CH₄ standard gases. Sample-to-sample memory effects were investigated by alternating analysis of samples with low and high CH₄ concentrations.

The equilibrator-CRDS results were also validated by comparison to analysis by gas chromatography (GC) of CH₄ concentration (volume fraction) in equilibrated head space gas. Water samples (6 mL) from diverse sources were equilibrated with N₂ gas (9 mL) in pre-evacuated Exetainer® vials and concentration of CH₄ in the headspace was measured using a Shimadzu GC-2010. Gas separation was effected using a Shincarbon packed column (Serial number C39711-01, length 2.0 m, internal diameter 2.1 mm) at 280 °C. The carrier gas was helium, at a flow rate of 30 mL min⁻¹. CH₄ was detected using a flame ionisation detector at 300 °C supplied with air (450 mL min⁻¹) and H₂ (10 mL min⁻¹). The methaniser was set at 390 °C, using H₂ as makeup gas (35 mL min⁻¹). Peak areas were measured using Shimadzu LabSolutions software and converted to concentrations by calibration against high purity N₂ (zero standard) and two certified standards (4.1 and 41.6 ppm vol. CH₄, BOC Australia).

Results and Discussion:

A typical 10-min time series of CH₄ and CO₂ concentrations in the gas loop during analysis of a CH₄-spiked tap water sample is shown in Figure 3. Concentration rose rapidly during the initial \approx 1.5 mins of the measurement step and then fluctuated slightly for \approx 3 mins. This fluctuation is caused by the interaction of the main and secondary gas loops, which circulate at different rates. For the remainder of the measurement period, CH₄ concentration stabilises while CO₂ concentration continues to slowly rise. An analysis time shorter than 10 min would be insufficient to ensure equilibrium has been reached and a longer analysis time would be of no additional benefit. At the switch to purging mode, concentrations fall rapidly

and reach background levels within 3 minutes, again subject to slight fluctuations, until both gas loops have been purged.

Fig. 3.

The stable CH₄ concentration recorded after \approx 5 mins indicates equilibrium between CH₄ concentrations in the water and gas loops. Furthermore, if CH₄ concentration in the gas loop differs substantially from that in the ambient atmosphere (e.g. \approx 7 ppm vol. in example shown in Figure 3, cf. \approx 1.8 ppm vol in the atmosphere), a stable concentration during the measurement step proves the integrity of the gas loop, as a leak to the atmosphere would result in a gradual decrease in CH₄ concentration. A faster equilibrium time would be expected for CO₂ than CH₄ because the CDMS permeability coefficient of CO₂ is \approx 3 times that of CH₄ (PermSelect 2019). However, this was not observed; it is likely that the continued increase in CO₂ concentration occurs due to deprotonation of dissolved HCO₃⁻ and transfer of dissolved CO₂ across the equilibrator membrane to the gas loop.

The dissolved concentrations of CH₄ measured in several water samples (Table 2) demonstrate that a precision of \pm 6 % (1σ) or better can be expected in typical water bodies. Samples from a rainforest stream (Atika Creek) analysed immediately after sampling had a dissolved CH₄ concentration of 0.175 $\mu\text{g L}^{-1}$ whereas bottled spring water (various brands and bottling dates) ranged from 0.048 to 2.08 $\mu\text{g L}^{-1}$. The concentration of dissolved CH₄ in freshwater bodies in equilibrium with atmospheric CH₄ has been estimated at 0.041 to 0.064 $\mu\text{g L}^{-1}$ (Gonzalez-Valencia et al. 2014) but concentrations can be orders of magnitude higher in ecosystems with strong methanogenesis (Gonzalez-Valencia et al. 2014; Magan et al. 2014).

Close correspondence between measured CH₄ concentrations and those in spiked samples or measured by headspace-GC analysis (Fig. 4) indicate that the accuracy of the equilibrator-CRDS system is better than $\pm 5\%$ (1σ) for CH₄. However, equilibrator-CRDS analysis of samples with high concentrations of HCO₃⁻, can yield too high concentrations of dissolved CO₂ due to generation of CO₂ from dissolved HCO₃⁻ during the measurement period. CO₂-spiking tests were not carried out due to the potential for speciation changes. The close correspondence between measured CH₄ concentrations and those in spiked samples or measured by headspace-GC analysis also indicated that the assumption of mean atmospheric gas pressure in the gas loop was correct.

Table 2.

Fig. 4.

The detection limit for equilibrator-CRDS analysis of CH₄ depends on the sample volume in the water loop (Figure 5). In the test configuration of the equilibrator-CRDS (water loop volume = 0.575 L) the detection limit for dissolved CH₄ is $\approx 0.005 \mu\text{g L}^{-1}$ based on a CRDS detection limit of 0.03 ppm vol. CH₄ (3 x standard deviation of the concentration measured in gas with zero CH₄). The OA-ICOS system described by Gonzalez-Valencia et al. (2014) achieved a similar CH₄ detection limit ($2.76 \cdot 10^{-10} \text{ mol L}^{-1} = 0.004 \mu\text{g L}^{-1}$). In comparison, the detection limit for headspace-GC analysis in this study was $\approx 0.14 \mu\text{g L}^{-1}$.

Fig. 5.

The equilibrator-CRDS system was affected by some sample-to-sample memory when analysing samples with a markedly lower CH₄ concentration than the previous sample. Using a purge time of 3 mins, the measured concentration of a sample containing 0.18 µg L⁻¹ CH₄ was 7 % too high when it followed a sample containing 2.08 µg L⁻¹ CH₄. This memory effect can be reduced by longer purging time or by replicate analysis, both of which are recommended when analysing samples with highly variable CH₄ concentrations.

Unlike continuous flow systems, the equilibrator-CRDS system can be simply calibrated using certified gas standards, due to its recirculating design. This is because results are not subject to the transfer efficiency of analytes across the polymer membrane as is the case in a continuous flow system where there is insufficient time for water/gas equilibrium to be established (Gonzalez-Valencia et al. 2014). In the equilibrator-CRDS system gas measurement occurs only after water/gas equilibrium has been established. This simplifies field operation by avoiding the need to measure the transfer efficiency and control the water and gas flows. Furthermore, CRDS is characterised by very low drift (<1 ppb CH₄ over 24 hours (Crosson 2008; Picarro 2019b) so the equilibrator-CRDS system provides accurate and precise analyses with only infrequent (daily) calibration checks required.

The system can be readily modified to meet diverse analytical needs. For example, automating the valve switching sequence would enable unattended analyses at ≈14 min intervals, facilitating monitoring of water bodies subject to rapid changes in CH₄ concentrations, such as tidally influenced estuaries and wetlands subject to strong diel changes. An additional advantage of employing sample recirculation, as compared to a continuous flow design, is that extended analysis time is possible without requiring a large sample volume. For example, a longer analysis time is required for precise isotopic analysis

of trace gases by CRDS (Picarro 2019c). The PDMS equilibrator could be coupled to other gas analysers and used to analyse other gases with high silicone permeability coefficients, e.g. NH₃, C₂H₆, H₂S, N₂O, SO₂ (PermSelect 2019).

Conclusions:

The equilibrator-CRDS system provides accurate and precise analysis of dissolved CH₄ concentration in water. It provides a sufficiently low detection limit to enable analysis of natural background concentrations of CH₄ in environmental waters and is more sensitive than headspace-GC analysis. The system is suitably robust for field deployment, and operation, calibration and data processing are simple. Analysis of CO₂ is also possible, but tends to overestimate concentrations in bicarbonate-rich waters due to HCO₃⁻ conversion to CO₂. The PDMS equilibrator component could be coupled to other gas analysers and used to analyse other gases with high silicone permeability coefficients.

Disclosure statement:

The authors declare no financial interest or benefit.

Funding details:

No specific grant was received for this project.

Credit author statement:

N.C. Munksgaard: Conceptualization; Methodology; Investigation; Formal Analysis; Writing - original draft; Writing - review & editing.

P.N. Nelson: Investigation; Formal Analysis; Writing - review & editing.

Acknowledgements:

The Research Institute for the Environment and Livelihoods, Charles Darwin University supported this project.

References:

Bazhenov, S. D., A. V. Bilyukevich, and A. V. Volkov. 2018. Gas-Liquid Hollow Fiber Membrane Contactors for Different Applications. *Fibers* 6: 76-116. doi: 10.3390/fib6040076.

Cassar, N., B. A. Barnett, M. L. Bender, J. Kaiser, R. C. Hamme, and B. Tilbrook. 2009. Continuous High-Frequency Dissolved O₂/Ar Measurements by Equilibrator Inlet Mass Spectrometry. *Analytical Chemistry* 91: 1955-1964. doi: 10.1021/ac802300u.

Crosson, E. R. 2008. A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor. *Applied Physics B* 92: 403-408. doi: 10.1007/s00340-008-3135-y.

Gonzalez-Valencia, R., F. Magana-Rodriquez, O. Gerado-Nieto, A. Sepulveda-Jauregui, K. Martinez-Cruz, K. Walter-Anthony, D. Baer, and F. Thalasso. 2014. In Situ Measurement of Dissolved Methane and Carbon Dioxide in Freshwater Ecosystems by Off-Axis Integrated Cavity Output Spectroscopy. *Environmental Science and Technology* 48(19): 11421-11428. doi: 10.1021/es500987j.

Gruca-Rokosz, R., and P. Koszelnik. 2017. Production pathways for CH₄ and CO₂ in sediments of two freshwater ecosystems in south-eastern Poland. *PLoS ONE* 13 (6): e0199755. doi: 10.1371/journal.pone.0199755.

LGR. 2019. Dissolved gas extraction system.

<http://www.lgrinc.com/analyzers/isotope/dissolved-gas-extraction-unit> (accessed 8/11/2019).

Magen, C., L. L. Lapham, J. W. Pohlman, K. Marshall, S. Bosman, M. Casso, and J.P.

Chanton. 2014. A simple headspace equilibration method for measuring dissolved methane.

Limnology and Oceanography: Methods 12: 637–650. doi: 10.4319/lom.2014.12.637.

Maher, D. T., I. R. Santos, J. R. F. W. Leuven, J. M. Oakes, D. V. Erler, M. C. Carvalho, and

B. D. Eyre. 2013. Novel Use of Cavity Ring-down Spectroscopy to Investigate Aquatic

Carbon Cycling from Microbial to Ecosystem Scales. *Environmental Science and*

Technology 47: 12938–12945. doi: 10.1021/es4027776.

Maher, D. T., I. R. Santos, and D. R. Tait. 2014. Mapping methane and carbon dioxide

concentrations and $\delta^{13}\text{C}$ values in the atmosphere of two Australian coal seam gas fields.

Water Air and Soil Pollution 225: 2216-2224. doi: 10.1007/s11270-014-2216-2.

Mächler, L., M. S. Brennwald, and R. Kipfer. 2012. Membrane Inlet Mass Spectrometer for

the Quasi-Continuous On-Site Analysis of Dissolved Gases in Groundwater. *Environmental*

Science and Technology 46: 8288-8296. doi: 10.1021/es3004409.

Owen, D. D., O. Shouakar-Stash, U. Morgenstein, and R. Aravena. 2016. Thermodynamic

and hydrochemical controls on CH₄ in a coal seam gas and overlying alluvial aquifer: new

insights into CH₄ origins. *Scientific Reports* 6: 32407-32426. doi: 10.1038/srep32407.

PermSelect. 2019. Membrane Basics. <https://www.permselect.com/membranes> (accessed

26/11/19).

Picarro. 2019a. Cavity Ring-Down Spectroscopy (CRDS).

<https://www.picarro.com/company/technology/crds> (accessed 26/11/2019).

Picarro. 2019b. G2301 Gas concentration analyser.

https://www.picarro.com/g2301_gas_concentration_analyzer (accessed 26/11/2019).

Picarro. 2019c. G2201-i Isotopic Analyzer.

https://www.picarro.com/products/g2201_i_isotopic_analyzer (accessed 26/11/2019).

Sander R. 2015. Compilation of Henry's law constants (version 4.0) for water as solvent.

Atmospheric Chemistry and Physics 15: 4399–4981. doi: 10.5194/acp-15-4399-2015.

Wilkinson, J., C. Bors, F. Burgis, A. Lorke, and P. Bodmer. 2018. Measuring CO₂ and CH₄

with a portable gas analyzer: Closed-loop operation, optimization and assessment. PLoS

ONE 13(4): e0193973. doi: 10.1371/journal.pone.0193973.

Zellweger, C., L. Emmenegger, M. Firdaus, J. Hatakka, M. Heimann, E. Kozlova, T. G.

Spain, M. Steinbacher, M. V. van der Schoot, and B. Buchmann. 2016. Assessment of recent

advances in measurement techniques for atmospheric carbon dioxide and methane

observations. Atmospheric Measurement Techniques 9: 4737-4757. doi: 10.5194/amt-9-

4737-2016.

Table 1: Operational sequence, refer to Fig. 1 for labelling of valves.

Step	Duration (min)	Air and water pumps	Inlet tube	Water loop valves A,B,C	Gas loop valves 1, 2
Sample uptake and gas loop purge	1	On	In water sample	On (load)	On (purge)
Measurement	10	On	-	Off (circulate)	Off (circulate)
Sample discharge, gas loop purge	3	On	In air	On (load)	On (purge)

Table 2: Dissolved CH₄ concentrations in water samples.

Sample	Analysis date	N (bottles and bottling date)	CH₄ (µg L⁻¹) Mean ± 1 st.dev.
Bottled water A	19 May 2019	2 (same bottle)	0.059 ± 0.004
Bottled water B	19 May 2019	2 (2 bottles, same date)	2.08 ± 0.01
Atika Creek water	19 May 2019	2 (same bottle)	0.175 ± 0.001
Bottled water B	17 September 2020	4 (4 bottles, different dates)	0.483 ± 0.180
Bottled water C	17 September 2020	3 (same bottle)	0.079 ± 0.002
Bottled water D	17 September 2020	3 (3 bottles, same date)	0.048 ± 0.001
Cairns tap water	17 September 2020	3 (same bottle)	0.072 ± 0.002
De-ionised water	17 September 2020	3 (same bottle)	0.053 ± 0.002

Figure legends:






Fig. 1. Schematic of the equilibrator-CRDS system with water loop in green and gas loop in blue.

Fig. 2. Equilibrator-CRDS system. (A) front view, (B) rear view. 1: Switch box; 2: Water loop pressure gauge; 3: Pulse dampener; 4: Water inlet tube; 5: Water loop pump; 6: Water loop needle valve; 7: Gas loop 3-way valves with N₂ inlet / outlet; 8: Gas loop needle valve; 9: Gas loop pressure gauge; 10: Gas loop pump; 11: Water outlet tube; 12: Condensed water trap; 13: PDMS contactor; 14: Water loop 2-way valves; 15: Inlet / outlet connections to CRDS; 16: Water loop coil.

Fig. 3. CH₄ and CO₂ concentrations in CH₄-spiked tap water (CH₄ = 1.15 μg L⁻¹) during a purge-measurement-purge cycle of an equilibrator-CRDS analysis. The sample was not spiked with CO₂.

Fig. 4. (A) Comparison of CH₄ concentrations determined by equilibrator-CRDS and known concentrations of CH₄ in spiked water samples (n=15). (B) Comparison of CH₄ concentrations in water samples determined by headspace-GC and equilibrator-CRDS (n=8). Error bars indicate analytical precision (± 6%, 1σ).

Fig. 5. Calculated detection limits for dissolved CH₄ as a function of water loop volume of the equilibrator-CRDS system.

-  PUMP
-  PRESSURE GAUGE
-  NEEDLE VALVE
-  3-WAY VALVE
-  2-WAY VALVE

