Atmospheric
Measurement
Techniques

Design and performance of a Nafion dryer for continuous operation at CO_2 and CH_4 air monitoring sites

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Abstract. In preparation for routine deployment in a network of greenhouse gas monitoring stations, we have designed and tested a simple method for drying ambient air to near or below 0.2 % (2000 ppm) mole fraction H_2O using a Nafion dryer. The inlet system was designed for use with cavity ring-down spectrometer (CRDS) analyzers such as the Picarro model G2301 that measure H_2O in addition to their principal analytes, in this case CO_2 and CH_4. These analyzers report dry-gas mixing ratios without drying the sample by measuring H_2O mixing ratio at the same frequency as the main analytes, and then correcting for the dilution and peak broadening effects of H_2O on the mixing ratios of the other analytes measured in moist air. However, it is difficult to accurately validate the water vapor correction in the field. By substantially lowering the amount of H_2O in the sample, uncertainties in the applied water vapor corrections can be reduced by an order of magnitude or more, thus eliminating the need to determine instrument-specific water vapor correction coefficients and to verify the stability over time. Our Nafion drying inlet system takes advantage of the extra capacity of the analyzer pump to redirect 30 % of the dry gas exiting the Nafion to the outer shell side of the dryer and has no consumables. We tested the Nafion dryer against a cryotrap ($-97\,^\circ$C) method for removing H_2O and found that in wet-air tests, the Nafion reduces the CO_2 dry-gas mixing ratios of the sample gas by as much as 0.1 ± 0.01 ppm due to leakage across the membrane. The effect on CH_4 was smaller and varied within ± 0.2 ppb, with an approximate uncertainty of 0.1 ppb. The Nafion-induced CO_2 bias is partially offset by sending the dry reference gases through the Nafion dryer as well. The residual bias due to the impact of moisture differences between sample and reference gas on the permeation through the Nafion was approximately -0.05 ppm for CO_2 and varied within ± 0.2 ppb for CH_4. The uncertainty of this partial drying method is within the WMO compatibility guidelines for the Northern Hemisphere, 0.1 ppm for CO_2 and 2 ppb for CH_4, and is comparable to experimentally determining water vapor corrections for each instrument but less subject to concerns of possible drift in these corrections.

1 Introduction

There is increasing interest in regional greenhouse gas emissions estimates as stakeholders aim to reduce and verify emissions at international, national, state and city levels (NRC, 2010). Two of the most important greenhouse gases of interest are CO_2 and CH_4. Atmospheric inversion methods provide a means of inferring emission rates based on atmospheric concentration measurements, but their usefulness at the regional level has been hampered by sparse greenhouse gas monitoring locations (Butler et al., 2010; Gurney et al., 2002) and uncertainty in atmospheric transport (Houweling et al., 2010; Lin et al., 2006; Stephens et al., 2007). Recently, Earth Networks, Inc. has proposed to greatly increase the density of atmospheric surface measurements by deploying a network of close to 50 continuous observation stations across the United States (http://www.earthnetworks.com/OurNetworks/GreenhouseGasNetwork.aspx). It is important that the data collected by this network, and others, be of high quality and meet or exceed the WMO compatibility goals of 0.1 ppm CO_2 in the Northern Hemisphere and 0.05 ppm CO_2 in the Southern Hemisphere, and 2 ppb CH_4 (WMO, 2012).

Until recently, most high-accuracy continuous CO_2 measurements were made using non-dispersive infrared (NDIR) spectroscopic analyzers (e.g. Bakwin et al., 1998). These analyzers require frequent calibration and complete drying of the air prior to analysis. A newer approach using wavelength-scanned cavity ring-down spectroscopy (CRDS) has greater stability, reducing the frequency of calibration, and has the potential to eliminate the need for drying (Crosson, 2008). Water vapor interferes with CO_2 and CH_4 concentration measurements by diluting the mixing ratios in air and by broadening the spectroscopic absorption lines of other gases. The approach that is implemented in CRDS is to concurrently measure H_2O of the sample and use experimentally derived water vapor correction algorithms to correct for the dilution and broadening effects on CO_2 and CH_4 (Crosson, 2008; Rella, 2010; Baer et al., 2002).

It is difficult to accurately calibrate the absolute H_2O measurements on any instrument due to a lack of precise reference humidity generation and delivery. The CRDS instruments have an absolute H_2O uncertainty of ∼ 1 % (Chen et al., 2010) and this introduces a source of error into using a single water vapor correction algorithm for all instruments. However, the CRDS instruments can make very precise measurements of relative H_2O differences, so if a set of water vapor correction coefficients is determined for each instrument, the uncertainty in the CO_2 and CH_4 dry mixing ratios can be reduced. There have been a few studies published testing the transferability and stability of the water vapor correction algorithm for Picarro CRDS instruments (Chen et al., 2010; Winderlich et al., 2010; Richardson et al., 2012; Rella et al., 2013). Chen et al. (2010) suggests that applying the same set of coefficients to multiple instruments can yield high-quality data even with small differences in the H_2O calibration from instrument to instrument. They found the residual error after using a single set of water vapor correction coefficients on multiple instruments is below 0.05 ppm for CO_2 and below 0.5 ppb for CH_4. Winderlich et al. (2010) conclude that the water vapor correction for an individual instrument is stable over a year and half and estimates the repeatability of the corrected measurements is within 0.03 ppm for CO_2 and 0.3 ppb for CH_4. Even so, the manufacturer conservatively recommends experimentally determining the water vapor correction coefficients through repeated testing for each individual instrument at the start of operations in order to meet WMO compatibility goals at water levels greater than 1 % (Rella et al., 2013).

These types of water vapor correction experiments are inherently difficult to perform because H_2O and CO_2 can interact with tubing walls in most experimental setups. CO_2 can adsorb to the tubing walls, and increasing H_2O will displace that CO_2, creating an artifact in dry/wet-air comparisons used to calculate correction coefficients, especially in setups where the H_2O level is changing continually. Also, the accuracy of the water vapor corrections are based on CO_2 and CH_4 measurements of and are statistically limited by the

accuracies of the CO_2 and CH_4, in addition to H_2O measurements themselves (Rella et al., 2013). Reducing the H_2O in the sample would reduce the uncertainty in the corrected dry-gas mixing ratios. The simple drying technique we present here does not eliminate the water vapor influence, but reduces the water vapor correction by an order of magnitude or more, thus eliminating the need to characterize the water vapor correction on each instrument before deployment and to monitor that calibration over time.

The Nafion membrane is known to be semi-permeable to water vapor and relatively impermeable to other gases (Leckrone and Hayes, 1997). Nafion dryers are built with a tubing of semi-permeable membrane separating an internal sample gas stream from a counterflow purge gas stream contained within a stainless steel outer shell. If the partial pressure of water vapor is lower in the purge gas stream, then water is removed from the sample gas stream. There are many different ways to supply the purge gas to Nafion dryers. Common methods include those with no consumables, like reusing the sample gas itself after it is partially dried passing through the inner Nafion membrane (as in this study) or supplying purge air from a dry-air generator, and methods with consumables that must be replaced, such as using molecular sieve to remove all the water from the sample after the Nafion and before it is reused as the purge gas (e.g. Stephens et al., 2011) or dry air from a tank. The choice depends largely on what the tolerance is for residual water in the sample gas and how frequently technicians are able to service the dryer.

For the Earth Networks installations, we designed a simple drying inlet system for ambient air monitoring (Fig. 1) using a 72-inch-long Nafion membrane dryer (PermaPure, Inc., model MD-050-72S-1). This inlet drying configuration takes advantage of the extra capacity of the external analyzer pump to redirect 30 % of the dried gas exiting the Nafion to the outer shell side of the dryer, creating both a gradient in the H_2O partial pressure and total gas pressure across the Nafion membrane. This total pressure drop across the membrane enhances the drying capacity of the Nafion and conserves sample and reference gas volumes.

This setup also unavoidably produces partial pressure gradients in CO_2 and CH_4 across the membrane that may allow small amounts of these trace gases and the major components of air to also permeate across the membrane (Ma and Skou, 2007). To reduce the influence of any such permeation on the sample measurements, the network sampling setup uses active pressure stabilization for all ambient air intakes and reference tank gases. This will ensure that the Nafion is exposed to sample and reference gases at identical total pressures, so that any direct effect of pressure-dependent permeation of CO_2 and CH_4 is canceled in the comparison between sample and reference gases.

Even with the pressure stabilization, one important difference still exists between sample air and reference tanks. The sample gas enters the Nafion with much higher moisture levels than the dry reference gases. The permeation of CO_2 and
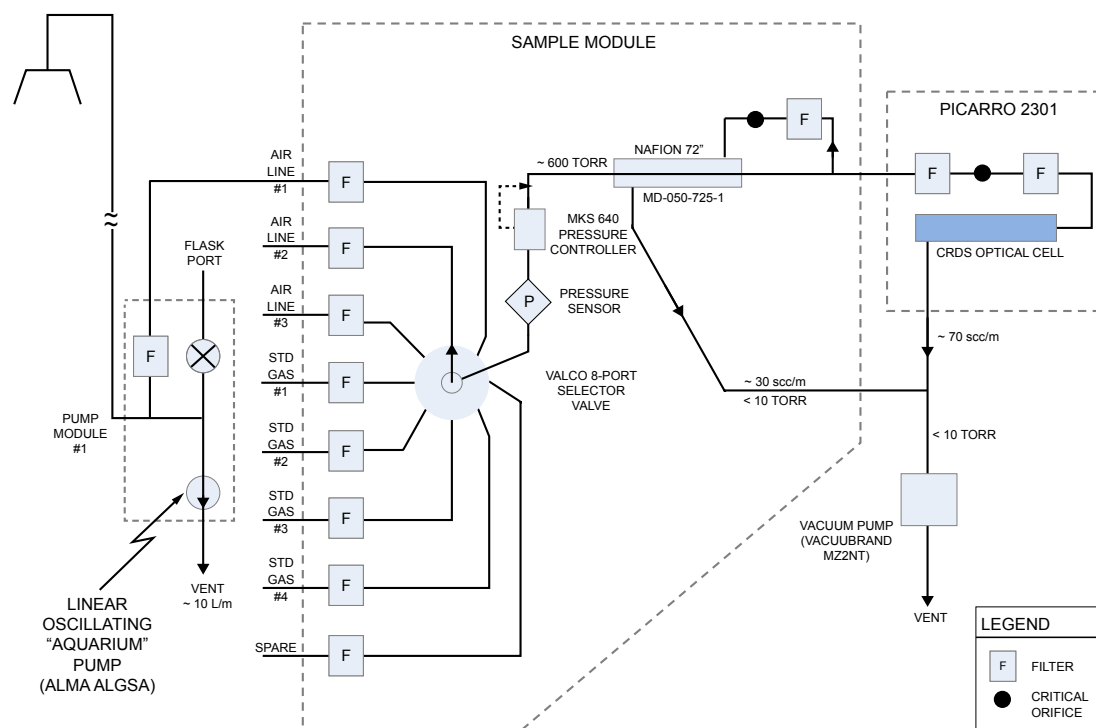
Fig. 1. The gas-handling configuration for the Earth Networks greenhouse gas monitoring stations. The "Sample Module" houses the Nafion dryer system. All sample air and reference gases pass through the Nafion dryer.

CH_4 through the membrane may be moisture-dependent (Ma et al., 2005), and this could lead to differential biases between sample and calibration gases that do not cancel.

The ideal inlet drying system removes water vapor without modifying CO_2 or CH_4. In this study, we test the performance of the inlet drying system by ensuring that any changes to CO_2 or CH_4 are small or correctable. We present results of tests that evaluate the performance of two similar drying systems, a lab-built test setup and an Earth Networks sample module. We show that the dryer is effective in reducing H_2O to between 0.1 to 0.15 % levels, and quantified moisture-dependent changes in the permeation of CO_2 and CH_4 across the Nafion membrane. We evaluated the lab test setup before and after 9 months of continuous operation at room temperature to test for aging effects, and tested the Earth Networks sample module at room temperature and heated. We also quantify the time required for the Earth Networks Nafion dryer sample module to stabilize after dry reference gases are introduced and test for any transient offsets that may occur.

2 Methods

Testing the Nafion dryer requires a humidified air source with known dry-gas mixing ratios of CO_2 and CH_4. It is difficult to humidify air without changing its dry-gas CO_2 mixing ratio slightly because the gasses dissolve in water

via Henry's Law and also the propensity of CO_2 to interact with water adsorbed on tubing walls. For this reason, we compared our Nafion dryer system with a cryotrap at $-97\,°C$ using the experimental design in Fig. 2. Similar cryotraps have been used in this community for decades and any effects on CO_2 and CH_4 are known to be very small, but published studies documenting the cryotrap biases are lacking. We confirmed this in our laboratory comparing dry tank air to the same air that was humidified to 2 % H_2O by a bubbler filled with 15 mL of water acidified with phosphoric acid at $20\,°C$ and then dried by a cryotrap at $-97\,°C$. Initially, when the cryotrap is placed in the chiller, it absorbs CO_2 onto surfaces, but quickly saturates and achieves a steady state. The time that it takes to reach steady state depends on the surface area inside the trap (walls and glass beads). Henry's Law predicts an increase in the CO_2 of the humidified/dried treatment of ~ 0.005 ppm based on the release of dissolved CO_2 from the water that evaporates. We repeated the experiment twice and found differences close to Henry's Law, 0.004 ± 0.002 ppm and 0.006 ± 0.009 ppm. Likewise, the Henry's Law prediction for CH_4 is ~ 0.001 ppb and we found differences within measurement uncertainty of 0.003 ± 0.014 ppb and -0.038 ± 0.06 ppb. Thus, we believe showing that the Nafion system is as good as such a cryotrap is a suitable performance benchmark.

The analyzer used for testing this application was a Picarro G2301 CRDS $CO_2/CH_4/H_2O$ gas analyzer, but this
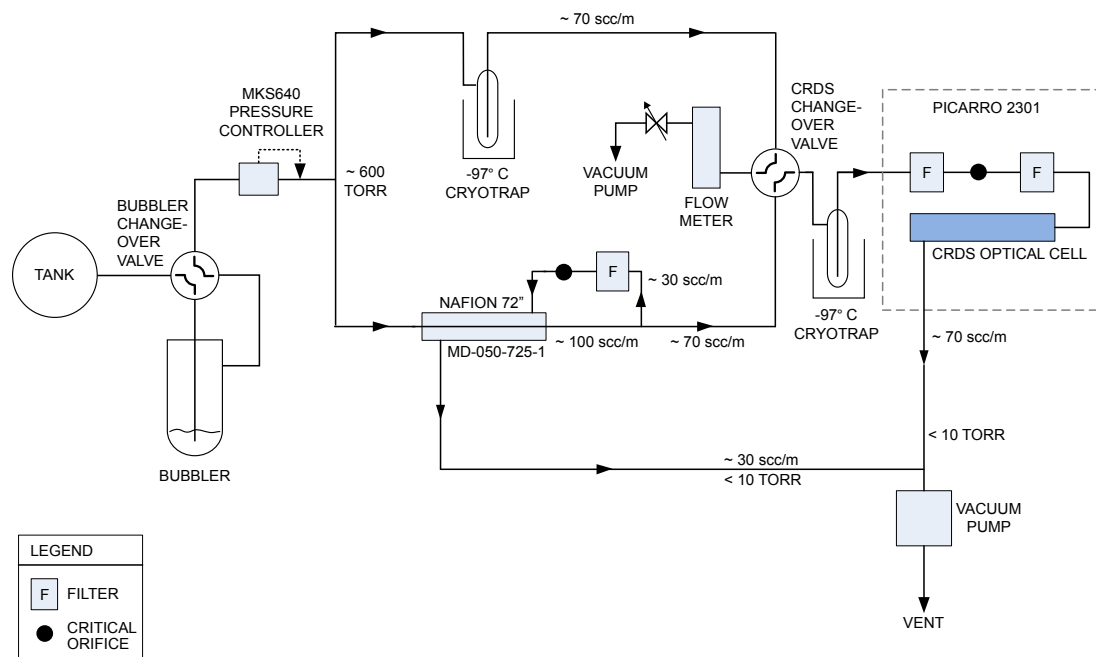
Fig. 2. Experimental test setup for testing the Nafion dryer. Dry tank air is humidified with a bubbler. The Nafion and cryotrap treatments are continuously flowing and the CRDS changeover valve allows the CRDS analyzer to alternately monitor each one. The second cryotrap downstream of the CRDS changeover valve was added after Exp. 1.1 and 1.2 to remove the residual water exiting the Nafion and eliminate the need to apply any water vapor correction. In the dry-air experiments the first cryotrap was either left at room temperature or removed. The downstream cryotrap was used to remove the residual water from the Nafion treatment, thus avoiding any H_2O/CO_2 interaction on surfaces within and immediately upstream of the Picarro.

application may be used with any similar gas analyzer. The external pump used was a KNF pump unit supplied by Picarro, retrofit with tighter leak-free connections in order to ensure that the gas flow exiting the pump was identical to the gas flow through the CRDS analyzer. The same analyzers are used in the Earth Networks greenhouse gas network design but with a different external pump and a few slight changes to set air flow rates. Flow rates in the test system were controlled by manually adjusting needle valves at the CRDS inlet and in the Nafion counterflow loop (Fig. 2). In the deployed network design, the flow rates are set by replacing the Picarro factory default O'Keefe A-18-NY orifice with a smaller A-9-NY, and in the Nafion counterflow by an A-6-NY orifice (Fig. 1). For these orifices to work, the downstream pressure has to be low enough to assure sonic velocity in the orifice. This is needed for the critical flow to be constant regardless of upstream pressure. It is also important to filter the gas upstream of the orifice to avoid clogging.

Dry air from a compressed gas cylinder was passed through a temperature-controlled bubbler-style humidifier in wet-air tests or bypassed in dry-air tests (Fig. 2). The resulting wet air (or dry air) was split between the Nafion dryer and the cryotrap, each constantly flowing at $\sim 70\,\mathrm{cm}^3\,\mathrm{min}^{-1}$, and alternately sampled by the Picarro analyzer, or sent to a waste pump. The primary cryotrap was

stainless steel, with a 1/2 inch outer tube and a 1/8 inch inner dip tube. Air flowed in through the outer tube, and 3 mm glass beads at the bottom reduced the chance of ice crystals entering the inner tube along with the airflow out of the cryotrap. We also added heat tape to the top of the cryotrap, above the chiller, to discourage liquid water build up at the top of the trap. The H_2O mixing ratio of the humidified air could be adjusted by changing the temperature of the water bath surrounding the humidifier and by changing the gas pressure inside the humidifier. Delivery pressure to the Nafion dryer and cryotrap was maintained at 600 Torr by an MKS640 pressure controller in order to simulate conditions for routine sampling of ambient air.

The experiments using this test setup of the Nafion drying system were conducted at ambient laboratory temperature of $\sim 25 \pm 1\,°C$ over the course of each experiment. The drying systems deployed by Earth Networks are in an enclosure warmed approximately 10–20 °C above ambient in order to minimize the chance of condensation forming in the inlet system. This temperature increase makes the Nafion less efficient at removing water (Leckrone and Hayes, 1997), by approximately 0.01 % H_2O, based on side-by-side operation of the test system described here and a heated network system sampling from the same air intake from the Scripps Institution of Oceanography (SIO) pier in La Jolla, California.

Table 1. Mid-point differences between Nafion and cryotrap treatments (Nafion minus the mean of cryotrap measurements before and after).

Date	Exp	Setup	H$_2$O (%)	Temp (°C)	n[a]	CO$_2$ mean (ppm)	CO$_2$ stdev[b] (ppm)	CH$_4$ mean (ppb)	CH$_4$ stdev[b] (ppb)
29-Jul-11	1.1[c]	Test setup	0	25	11	−0.01	0.01	−0.07	0.27
1-Aug-11	1.2[c]	Test setup	2.1	25	4	−0.03	0.01	−0.08	0.05
2-Aug-11	1.3	Test setup	2.1	25	5	−0.05	0.01	−0.02	0.10
18-Aug-11	1.4	Test setup	2.1	25	3	−0.03	0.01	0.10	0.05
24-May-12	2.1[c]	Test setup	0	25	14	0.01	0.01	−0.05	0.10
30-May-12	2.2	Test setup	2.2	25	10	−0.03	0.01	0.08	0.06
23-Feb-13	3.1	Sample module	0	25	22	−0.02	0.01	0.03	0.11
18-Feb-13	3.2	Sample module	2.0	25	7	−0.07	0.01	−0.01	0.15
19-Feb-13	3.3[d]	Sample module	2.0	25	4	−0.06	0.01	0.11	0.08
22-Feb-13	3.4	Sample module	0	35	6	−0.04	0.01	0.08	0.15
20-Feb-13	3.5	Sample module	2.0	35	7	−0.10	0.01	0.22	0.13

[a] number of Nafion intervals measured; [b] standard deviation of the mid-point differences; [c] water vapor correction applied to the Nafion treated data; [d] ethanol and dry ice slush (−72 °C) used in place of the −97 °C chiller.

The permeability of the Nafion to CO$_2$ has also been shown to be temperature-dependent (Ma and Skou, 2007). For these reasons, we repeated the testing using one of the Earth Networks sample modules described in Fig. 1 at room temperature and also heated.

Three types of experiments were completed at the start of the test setup operation: one dry-air run (Exp. 1.1), one wet-air run (2.1 % H$_2$O, Exp. 1.2), and two wet-air runs (2.1 % H$_2$O) with a secondary cryotrap after the Nafion dryer to eliminate the need to apply the water vapor correction (Exp. 1.3 and 1.4). The secondary cryotrap was placed immediately before the CRDS. This secondary cryotrap used a "cold finger" design similar to that of the primary cryotrap, but smaller, 1/4 inch stainless steel outer tube and 1/16 inch inner tube, with no glass beads.

In all these experiments, gas was constantly flowing through the Nafion system at ~ 100 cm^3 STP min^{-1} (with ~ 30 cm^3 STP min^{-1} of that redirected to the counterflow purge) and the cryotrap at ~ 70 cm^3 STP min^{-1}. We used the CRDS changeover valve (Fig. 2) to alternately switch the CRDS intake between the Nafion and cryotrap, quantifying any differences in the CO$_2$ and CH$_4$ mixing ratios between the two treatments.

For the wet-air runs, the H$_2$O values were approximately 2 %, as high as we could achieve with the bubbler humidifier at 20 °C, maintaining an operating pressure greater than 600 Torr, and keeping the test setup at laboratory temperature. This corresponds to a dew point temperature of approximately 17 °C. Since the Nafion-dryer treatment without the secondary cryotrap did not completely remove all of the H$_2$O from the air, and in the case of the dry-air run it added H$_2$O to the air, we applied the water vapor correction from Chen et al. (2010) as recommended by Rella et al. (2013) to the data

from Exps. 1.1 and 1.2. (Appendix A). These corrections are on the order of 1.0 ppm CO$_2$ and 3.7 ppb CH$_4$ for 0.2 % H$_2$O.

For most of these tests, we switched the changeover valve every 60 min. Preliminary tests using 15 min switching intervals showed drifting CO$_2$ values presumably because of different flow resistances between the Nafion system and the cryotrap, causing small pressure changes that in turn caused CO$_2$ to be adsorbed or desorbed on the walls after switching.

After completing a first round of tests as described above, the Nafion dryer test setup inlet system with the CRDS was used continuously for nine months of routine air measurements. We then repeated the dry-gas experiment (Exp. 2.1) and wet-gas experiment (Exp. 2.2) to see if the aging of the Nafion over the nine-month period had any impact on the permeability of CO$_2$ and CH$_4$.

For testing the Earth Networks sample module, we made one modification, splitting the flow of air downstream of the pressure controller to send a portion through a bypass or cryotrap treatment. The secondary cryotrap was used in all of these experiments (Exp. 3.1–3.5).

All data were processed on 1 min running means, discarding the first 30 min of data after switching. There was no evidence of drift in CO$_2$ or CH$_4$ in the last 30 min of data for each treatment. The number of switching intervals varied in each experiment, as the primary cryotrap would plug with ice after several hours of use, thereby blocking the air flow and ending the experiment. Biases between the Nafion and cryotrap treatments were calculated as the differences between Nafion and the mean of the two cryotrap treatments before and after, i.e. the mid-point difference, and then averaged over the total number of sampling pairs. In Table 1, we report the mean and standard deviation of the mid-point differences.
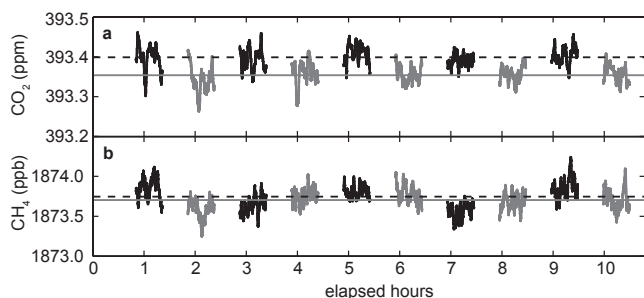
Fig. 3. Wet-air Exp. 1.3 on 2 August 2011. The cryotrap treatment is shown in black and the Nafion treatment is in grey for **(a)** CO_2, **(b)** CH_4. The first 30 min of data were excluded for each treatment. The straight lines are mean values for the cryotrap (black dashed) and Nafion (solid grey) over the entire experiment. The cryotraps plugged up with ice, ending the experiment after approximately 11 h. The secondary cryotrap was used in this experiment to remove the water remaining after the Nafion, so no water vapor correction was applied.

3 Results

3.1 Test setup

In the first dry-air experiment, Exp. 1.1 (Fig. S1 in the Supplement), we ran dry tank air with a CO_2 dry-gas mixing ratio of ~ 506 ppm and CH_4 of ~ 4787 ppb, switching between the Nafion and bypass. In this case, the cryotrap was in-line but not chilled, rather at ambient laboratory temperature since the air was dry already. The mean mid-point difference of the Nafion and bypass treatments was -0.01 ± 0.01 ppm for CO_2 and -0.07 ± 0.27 ppb for CH_4 (summarized in Table 1). Negative values mean that there was slightly less CO_2 and CH_4 after the Nafion treatment compared with the cryotrap treatment.

In the first wet-air experiment, Exp. 1.2 (Fig. S2), we humidified tank air with a CO_2 dry-gas mixing ratio of ~ 393 ppm CO_2 and ~ 1874 ppb CH_4 to 2.1 % H_2O. The Nafion dryer reduced the H_2O in the humidified sample down to 0.12 %, and we applied the water vapor correction to these data to calculate dry-gas mixing ratios for CO_2 and CH_4 using Eqs. (A1) and (A2). We then compared the Nafion dryer treatment with the cryotrap and found a mean mid-point difference over four pairs of Nafion/cryotrap switching of -0.03 ± 0.01 ppm for CO_2 and -0.08 ± 0.05 ppb for CH_4 (Table 1).

The final two wet-air experiments, Exp. 1.3 (Fig. 3) and Exp. 1.4 (Fig. S3), used the additional cryotrap to completely remove the residual water that is not removed by the Nafion. The CRDS confirmed that the air was dry and no water vapor corrections were applied. The largest mean Nafion minus cryotrap differences were -0.05 ± 0.01 ppm of CO_2 and 0.1 ± 0.05 ppb of CH_4 (Table 1). In this set of wet-air experiments, the cold trap plugged with ice after 3 to 5 pairs of Nafion/cryotrap switching.

3.2 Test setup after nine months of operation

After nine months of continuously monitoring ambient air from intakes on the SIO pier, we repeated similar tests to see if age or use affected the permeability of the Nafion to CO_2 and CH_4. We repeated the dry-air experiment, Exp. 2.1, using a different dry-air tank with approximately ~ 394 ppm CO_2 and ~ 1873 ppb of CH_4, again, leaving the cryotraps at room temperature (Fig. S4). We applied the water vapor correction to account for the small amount of water added from the Nafion treatment. The mean of 14 pairs of Nafion minus cryotrap mid-point differences was 0.01 ± 0.01 ppm for CO_2 and -0.05 ± 0.1 ppb for CH_4 (Table 1).

We also repeated the wet-air experiment, Exp. 2.2 (Fig. S5) using the same dry air tank as in Exp. 1.2, but humidified to 2.2 % H_2O. We used the secondary cryotrap, which eliminated the need to apply the water vapor correction. The mean of 10 pairs of Nafion minus cryotrap mid-point differences was -0.03 ± 0.01 ppm of CO_2 and 0.08 ± 0.06 ppb of CH_4 (Table 1). These results are similar to Exp. 1.3 and 1.4, run prior to routine operation, and show no sign of age effects on Nafion after nine months.

3.3 Earth Networks sample module

In early 2013, we tested a typical Earth Networks sample module, inlet dryer system, to compare its performance to the test setup system and further evaluate the Nafion at elevated temperature. Several sets of experiments were done with the sample module, and it became clear in these experiments that CO_2 mixing ratios were influenced by exchange processes on surfaces inside the stainless steel tubing and traps with glass beads. Replacing tubing and cleaning the traps and beads led to differences in the Nafion minus cryotrap offsets. These differences highlighted the challenges of measuring CO_2 in wet air as CO_2 and H_2O adsorb to surfaces and compete for the same surface sites. Representative results are summarized in Table 1. In the dry-air room temperature experiments (~ 25 °C, Exp. 3.1, Fig. S6), the Nafion minus cryotrap offset was -0.02 ± 0.01 ppm for CO_2 and 0.03 ± 0.11 ppb for CH_4. Two experiments were done using wet air (2.0 % H_2O, Exp. 3.2, Fig. S7 and Exp. 3.3, Fig. S8) at room temperature, the largest offsets increased by 0.05 ppm to -0.07 ± 0.01 ppm for CO_2 and only negligibly (0.11 ± 0.08 ppb) for CH_4. The sample module dried the air from 2.0 % to 0.05 % at room temperature.

The drying capacity and the CO_2 permeability were slightly different in the sample module experiments compared with the test setup. This is because the flow rates and pressures inside the Nafion and in the purge counterflow are slightly different using the critical orifices to regulate the flow compared to the needle valves in the test setup. This sets up different gradients in partial pressures across the Nafion membrane resulting in different rates of drying and CO_2 permeation.
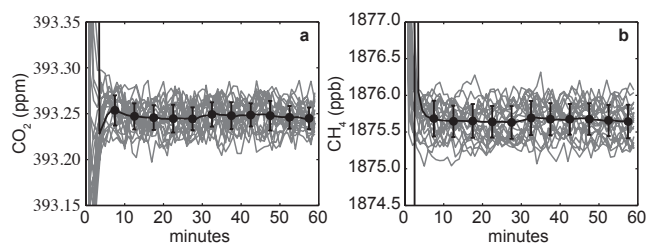
Fig. 4. Stabilization times for CO_2 and CH_4 of dry reference tanks after switching from moist ambient air. These data were collected during the month of January 2013 using the Earth Networks station at SIO with a sample module Nafion dryer inlet. Grey lines are the 1 min averages of the first reference tank switched to after ambient air during the daily reference tank checks for **(a)** CO_2 and **(b)** CH_4. This tank was sampled for 1 h. The 5 min ensemble averages over every daily tank run are shown in black, plotted at the mid-point, along with 1-standard deviation error bars.

The high temperature experiments, approximately 35 °C, dry and wet (Exp. 3.4, Fig. S9 and Exp. 3.5, Fig. S10), showed larger losses of CO_2 across the Nafion membrane as predicted. The dry air Nafion minus cryotrap differences were -0.04 ± 0.01 ppm for CO_2 and 0.08 ± 0.15 ppb for CH_4. The wet air (2.0 %) differences were -0.10 ± 0.01 ppm for CO_2 and 0.22 ± 0.13 ppb for CH_4. The drying efficiency of the Nafion was reduced, yielding 0.10 % H_2O at the higher temperature.

3.4 Transition times

The experiments described above (Sects. 3.1, 3.2 and 3.3) quantified the offsets in CO_2 and CH_4 between Nafion and cryotrap treatments in steady-state wet and dry conditions. We were also interested in addressing how much time is required for the system to stabilize under routine conditions when the intake selector switches from wet ambient air to dry reference tank air. It is possible that switching from moist air to a dry reference tank could cause transient offsets in CO_2 and CH_4 while the Nafion dries. In Fig. 4 we show the ambient air to dry tank transitions from one month of routine operation by the SIO Earth Networks station in January 2013. The water vapor correction in Appendix A was applied to these data. The humidity of the reference gas exiting the Nafion is shown to decrease from about 0.13 % to 0.09 % as the Nafion slowly dries over the course of one hour. After switching to the dry tank air, the Nafion inlet sample module is initially a weak sponge for CO_2, and it takes the CRDS measurements about 10 min to recover and stabilize. The CO_2 5 min mean standard deviations decrease from 0.37 to 0.20 ppm from 10 min to 60 min after tank switching with a 0.005 ppm increase in the mean values. The CH_4 5 min mean standard deviation remains nearly constant at 0.0003 ppb CH_4 over this hour with negligible drift in the mean values.

4 Discussion

We find that the permeation of CO_2 through the Nafion membrane in the wet-air experiments, relative to a -97 °C cryotrap, results in offsets of -0.07 ppm at 25 °C and -0.10 ppm and 35 °C using the Earth Networks sample module configuration. As expected from previous literature (Ma et al., 2005; Ma and Skou, 2007), we found that the CO_2 loss across the Nafion increased with sample air humidity and with temperature. The permeation rates that we found are far less than the maximum permeation rates measured by Ma and Skou (2007). The maximum permeability they found in the fully hydrated Nafion case (soaked in liquid water) at 50 °C translates to a 2.2 ppm drop in CO_2 through the dryer as a result of loss across the membrane. Our results are much closer to their dry Nafion condition, which we estimate would be a 0.02 ppm loss at 25 °C and a 0.031 ppm loss at 45 °C. Their experiments used argon as the gas matrix instead of air. In the tested Earth Networks measurement design, the sample modules were not temperature controlled, but rather heated above ambient to prevent condensation. Partly as a result of this work, Earth Networks is modifying the sample module design to be thermostated in the 35 °C to 40 °C range. This will reduce vulnerability to different CO_2 loss rates through the Nafion at different installations and times of year.

The Nafion effects on CH_4 are much smaller, and mixed, than CO_2 because CH_4 is not a polar molecule. The offsets ranged from a loss of 0.07 ppb to a gain of 0.20 ppb. These values are close to the detection limit of the CRDS analyzer.

Our procedure of delivering both sample air and reference gases through the Nafion at the same pressure makes the drying bias due to permeation through the Nafion smaller in routine operation, i.e. the bias will cancel out after applying the CO_2 and CH_4 calibrations to the sample air based on reference gas analysis. For example, in our tests of the heated sample module, we saw a loss of 0.10 ppm CO_2 through the Nafion with wet air and a loss of 0.04 ppm with dry air. After applying the CO_2 calibration to the sample air, this would result in a 0.05 ppm systematic loss of CO_2 (avoiding rounding errors). This is the value we use in our uncertainty analysis. Also, because the Nafion dryer has a slow response time for H_2O, the Nafion humidifies the reference gases so the uncertainty in the water vapor correction further cancels out (Richardson et al., 2012). This effect could be capitalized on further by running each reference gas separately for a shorter period of time (e.g. 20–30 min, rather than multiple tanks run sequentially) to limit the degree to which the Nafion dries out.

The advantage of partially drying the sample gas can be determined by comparing the estimated measurement uncertainties from multiple sources for three cases: (1) using the manufacturer-supplied water vapor correction coefficients, (2) using instrument-specific correction coefficients experimentally determined at the start of operation

Table 2. Summary of errors for different CRDS application approaches.

Error types	No drying with universal water vapor correction[a] 2 % H_2O		No drying with instrument-specific water vapor correction 2 % H_2O		Nafion drying with universal water vapor correction[a] 0.15 % H_2O	
	CO_2 (ppm)	CH_4 (ppb)	CO_2 (ppm)	CH_4 (ppb)	CO_2 (ppm)	CH_4 (ppb)
Instrument precision[b]	0.025	0.22	0.025	0.22	0.025	0.22
Noise in H_2O[c]	0.015	0.071	0.015	0.071	0.014	0.069
Water vapor correction[d]	0.10	1.6	0.06	0.7	0.015	0.21
Nafion-induced bias[e]	N/A	N/A	N/A	N/A	0.05	0.22
Sum of errors[f]	0.10	1.62	0.07	0.74	0.08	0.53

[a] Universal water vapor correction used was from Chen et al. (2010). [b] 5 min mean from the Picarro G2301 manufacturer specifications sheet downloaded 18 October 2012. [c] Based on Rella et al. (2013). [d] Based on Rella et al. (2013). [e] From this experiment. [f] The quadrature sum of errors for first 3 rows plus the Nafion bias. Error = sqrt($a^2 + b^2 + c^2$) + d. This was used assuming that the first 3 errors are not correlated and do not act in the same direction.

and (3) partial drying with our Nafion dryer system and applying manufacturer-supplied water vapor corrections to the residual water (Table 2). Instrument precision from the manufacturer's specifications for 5 min averages is 0.025 ppm for CO_2 and 0.22 ppb for CH_4, with precision improving with longer integration times. The random noise in the instrument's H_2O measurement contributes uncertainty to CO_2 and CH_4 through the water vapor correction as described in Rella et al. (2013). At 2 % H_2O, it adds uncertainties of 0.015 ppm for CO_2 and 0.071 ppb for CH_4. At 0.15 %, it is reduced only slightly to 0.014 ppm for CO_2 and 0.069 ppb for CH_4. Rella et al. (2013) summarized the uncertainty in the water vapor correction using the results from several different instruments tested in different laboratories. The uncertainty at 2 % H_2O is approximately 0.10 ppm for CO_2 and 1.6 ppb for CH_4 using the coefficients from Chen et al. (2010) and is reduced to 0.06 ppm for CO_2 and 0.7 ppb for CH_4 using experimentally determined instrument-specific coefficients. Drying the sample air to 0.15 % H_2O lowers the water vapor correction uncertainty using the Chen et al. (2010) coefficients to 0.015 ppm for CO_2 and 0.21 ppb for CH_4.

The total estimated uncertainty in the CO_2 and CH_4 measurements at 2 % H_2O is determined by adding the instrument precision, the effect of noise in the H_2O measurements, and the uncertainty in the water vapor correction (first three rows in Table 2) in quadrature because they do not necessarily act in the same direction, and then add the Nafion-induced bias on top of that. The estimated errors for utilizing the Nafion dryer and correcting the residual water using the manufacturer-supplied coefficients based on Chen et al. (2010) are 0.08 ppm for CO_2 and 0.41 ppb for CH_4. This is an improvement over not drying the air and using the Chen et al. (2010) coefficients, and comparable to characterizing an instrument-specific water vapor correction (Table 2). Another study by Nara et al. (2012) also recommends at least

partial drying of the sample air for precise measurements. The statistical advantages of applying smaller water vapor corrections to partially dried air increase as water levels exceed 2 %, however, these advantages may be offset by greater permeation of CO_2 through the Nafion at higher humidity.

The errors discussed in Rella et al. (2013) are limited in two ways. First, they have not attempted to diagnose the residual systematic error from CO_2 and H_2O adsorption on tubing walls. Especially in the case of the water droplet methods where H_2O is continually changing, this can lead to biases in the CO_2. It is hard to prove the absence of a bias at the level of 0.1 ppm at 2 % H_2O. The random errors across the different water vapor correction experiments in Rella et al. (2013) were found to be less than 0.1 ppm up to several percent H_2O, but this does not confirm the absence of systematic errors. Second, at least part of the range in the errors of manufacturer-supplied water vapor correction coefficients reported from the participating laboratories could be the result of experimental artifacts and may not reflect actual response differences among analyzers.

The main systematic error in our case is the cryotrap bias, which the community has accepted as small enough for many years and we confirmed is negligible. It is also possible that individual Nafion dryers have different permeability characteristics, and more Nafion dryers (e.g. beyond the two tested here) may need to be tested.

5 Conclusions

We have tested a design for drying air using a Nafion dryer, both as a test setup and as a field sample module, in conjunction with a CRDS analyzer. These inlet dryer systems are entirely self-sustaining and have required no intervention in over a year of operation. We also find that the performance of

the system is not subject to problems of Nafion degradation, at least over a 9-month time frame. Our experiments show that the bias between the permeability of CO_2 through the Nafion membrane in wet and dry tank air may be as large as 0.05 ppm CO_2 using an Earth Networks sample module configuration. The bias is negligible for CH_4. Combining the Nafion effects with other random errors in the CRDS measurements, we estimate the uncertainty to be approximately 0.08 ppm for CO_2 and 0.53 ppb for CH_4.

The setup eliminates the need to establish the water vapor correction on each analyzer and monitor their stability over time. It also reduces the complexity of post-processing the data if the correction is found to change over time. This method more fully capitalizes on the ability of the CRDS to provide high-quality measurements with reduced calibration activities, thereby saving labor costs for deployments involving an extensive network of analyzers such as that planned by Earth Networks.

Appendix A

Water vapor correction

The water vapor correction from Chen et al. (2010), as recommended by Rella et al. (2013), is summarized in Eqs. (A1) and (A2).

$$\frac{(CO_2)_{wet}}{(CO_2)_{dry}} = 1 + a H_{rep} + b H_{rep}^2 \tag{A1}$$

$$\frac{(CH_4)_{wet}}{(CH_4)_{dry}} = 1 + c H_{rep} + d H_{rep}^2 \tag{A2}$$

where H_{rep} is the reported H_2O mixing ratio by the analyzer, $(CO_2)_{wet}$ and $(CH_4)_{wet}$ are the measured mixing ratios of the wet gas, $(CO_2)_{dry}$ and $(CH_4)_{dry}$ are the true dry-gas mixing ratios, $a = -0.012000$, $b = -0.0002674$, $c = -0.00982$, and $d = -0.000239$.

Supplementary material related to this article is available online at: http://www.atmos-meas-tech.net/6/ 1217/2013/amt-6-1217-2013-supplement.pdf.

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