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# Flask sample measurements for CO<sub>2</sub>, CH<sub>4</sub> and CO using cavity ring-down spectrometry

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## Abstract

In recent years, cavity ring-down spectrometry (CRDS) has been demonstrated to be a highly sensitive, stable and fast analytical technique for real-time in situ measurements of greenhouse gases. In this study, we propose the technique (which we call flask-CRDS) of analyzing whole air flask samples for CO<sub>2</sub>, CH<sub>4</sub> and CO using a custom gas manifold designed to connect to a CRDS analyzer. Extremely stable measurements of these gases can be achieved over a large pressure range in the flask, from 175 to 760 Torr. The wide pressure range is conducive to flask sample measurement in three ways: (1) flask samples can be collected in low-pressure environments
 (e.g. high-altitude locations); (2) flask samples can be first analyzed for other trace gases with the remaining low-pressure sample for CRDS analysis of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>3</sub>, for the remaining low-pressure sample for CRDS analysis of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>3</sub>, CO<sub>4</sub> and CO<sub>3</sub>, flask samples can be arehived and re analyzed for validation. The remaining low-pressure sample for CRDS analysis of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>3</sub>, and (2) flask samples can be arehived and re analyzed for validation. The remaining low-pressure sample for CRDS analysis of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>3</sub> and CO<sub>3</sub> flask samples can be arehived and re analyzed for validation.

- CO; and (3) flask samples can be archived and re-analyzed for validation. The repeatability of this method (1 $\sigma$  of 0.07 ppm for CO<sub>2</sub>, 0.4 ppb for CH<sub>4</sub>, and 0.5 ppb for CO) was assessed by analyzing five canisters filled with the same air sample to a
- <sup>15</sup> pressure of 200 Torr. An inter-comparison of the flask-CRDS data with in-situ CRDS measurements at a high-altitude mountain baseline station revealed excellent agreement, with differences of  $0.10 \pm 0.09$  ppm (1 $\sigma$ ) for CO<sub>2</sub> and  $0.9 \pm 1.0$  ppb for CH<sub>4</sub>. This study demonstrated that the flask-CRDS method was not only simple to build and operate but could also perform highly accurate and precise measurements of atmospheric <sup>20</sup> CO<sub>2</sub>, CH<sub>4</sub> and CO in flask samples.

#### 1 Introduction

Trace components in the atmosphere can influence the chemistry and/or physics of the atmosphere, which, in turn, can have significant effects on the climate. The greenhouse gases carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  are major contributors to the green-

<sup>25</sup> house effect and anthropogenic climate change (IPCC, 2007). The leading cause of climate change is the increase in atmospheric CO<sub>2</sub> by 120 ppmv since the pre-industrial



era (IPCC, 2007).  $CH_4$  is also a potent greenhouse gas that has experienced an increase in global average mixing ratio (from 700 ppbv in 1750 to 1800 ppbv in 2011). The global warming potential of  $CH_4$  on a timescale of 100 yr is 25 times greater than that of  $CO_2$  (IPCC, 2007). Carbon monoxide (CO) is another important atmospheric trace gas, produced mainly from fossil fuel combustion, biomass burning and the oxidation of carbon-containing compounds. Changes in CO could indirectly alter the atmospheric oxidizing capacity by reacting with the hydroxyl radical (OH) (Logan et al., 1981; Thompson, 1992). Although CO is not a greenhouse gas (its radiative properties are significantly weaker than  $CO_2$  and  $CH_4$ ), an increased CO level may depress the OH concentration in the atmosphere on the global scale, causing a lower removal rate

- <sup>10</sup> OH concentration in the atmosphere on the global scale, causing a lower removal rate of  $CH_4$  (Thompson and Cicerone, 1986). Due to the possible significant impacts from these three atmospheric gases, an accurate determination of their presence with sufficient spatial and temporal resolution is crucial for diagnosing the conditions of ecosystems and the climate.
- <sup>15</sup> Two types of approaches are commonly adopted for investigating atmospheric gaseous components and their concentrations: (1) on-line measurements by in-situ instruments and (2) flask sampling coupled with in-lab analysis (the off-line approach). The on-line approach is performed by deploying instruments at sites of interest (ground-based stations) or on mobile platforms (ships, aircraft, balloons and satellites)
- <sup>20</sup> (WMO, 2009a, 2011). The main advantage of on-line measurements is the ability to obtain variations of atmospheric components at fixed sites or along paths that the mobile platforms have traversed (Tadić et al., 2012).

In contrast, the off-line approach is well suited for grid or multi-site studies attempting to obtain spatial gradients (Blake and Rowland, 1995; Chen et al., 1999; Blake

et al., 2001; Wang et al., 2000; Simpson et al., 2004). Competent laboratory analysis following field sampling is the key to data quality and the success of the off-line approach. The air samples in flasks can be archived for future validation, re-calibration or the advent of new analytical technologies. A well-maintained and well-calibrated in-lab system can minimize the bias among flasks collected over time, which is important



when subtle differences in time and space become critical. Considering these points, the off-line approach offers an efficient and effective means for examining changes in atmospheric composition, with the greenhouse gases being of primary interest.

- Previously, highly accurate baseline measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO were mainly made using conventional infrared absorption or gas chromatographic (GC) techniques. Although these two methods are well-established and robust, both methods have fundamental weaknesses. For instance, the drift and nonlinearity associated with the infrared technique requires frequent calibration at multiple concentrations. In addition, the GC method has a relatively long turnover time in analysis. Furthermore, both methods require water removal from the samples to report dry base data, adding com-
- <sup>10</sup> methods require water removal from the samples to report dry base data, adding complexity in the instrumentation. Recently, highly accurate continuous measurements of greenhouse gases have been made using a newly available analyzer that is based on cavity ring-down spectrometry (CRDS). CRDS has made the in-situ measurements of CO<sub>2</sub> and CH<sub>4</sub> relatively easy compared to the two aforementioned conventional meth-
- ods (Chen et al., 2010; Winderlich et al., 2010; Richardson et al., 2012). The major advantages associated with the CRDS method are listed as follows: (1) drying prior to analysis may not be necessary because water can be measured simultaneously with the greenhouse gases; (2) its response to concentrations is highly linear, which in theory could require fewer calibration standards, leading to lower costs and easier
- <sup>20</sup> operation; and (3) it is highly stable, requires fewer calibration checks and is less prone to systematic errors in long-term datasets. The CRDS technique has been tested for possible sources of uncertainty (e.g. water dilution, line broadening, drift, water vapor nonlinearity, absolute water vapor calibration) by validating its linearity, precision and accuracy under various environmental conditions (Chen et al., 2010; Crosson et al.,
- <sup>25</sup> 2008; Winderlich et al., 2010; Zellweger et al., 2012). The test criteria for the proposed method must meet the Data Quality Objectives of the Global Atmosphere Watch (GAW) Program of the World Meteorological Organization (WMO) ( $\pm$  0.1 ppm for CO<sub>2</sub>,  $\pm$  2 ppb for CH<sub>4</sub>, and  $\pm$  2 ppb for CO, 95 % coverage factor) (WMO, 2009b, 2010).



CRDS analyzers are often used in real-time applications (e.g. Chen et al., 2010; Winderlich et al., 2010; Richardson et al., 2012; Zellweger et al., 2012). Because flask sampling allows one to measure CO<sub>2</sub>, CH<sub>4</sub> and CO concentrations at many geospatial locations with a single analyzer, the aim of this study is to design and validate a sample manifold that connects with a CRDS analyzer to allow for easy flask measurements. This apparatus and measurement procedure will be called the flask-CRDS method in this study. The sample pressure in the CRDS analyzer cell is 140 Torr, and the volume of the cell is rather small (e.g. about 35 mL). Thus, CRDS is suitable for flask analysis in three ways: (1) flask samples can be collected in low-pressure environments (e.g. high-altitude locations); (2) flask samples can be first analyzed for other trace gases with the remaining low-pressure sample used for CRDS analysis of CO<sub>2</sub>, CH<sub>4</sub> and CO; and (3) flask samples can be archived and re-analyzed for validation. In this

study, the technical details of the construction and operation of the manifold will be presented. The assessment of the proposed flask-CRDS method and the data quality of the CO<sub>2</sub>, CH<sub>4</sub> and CO flask measurements will be discussed. Furthermore, a comparison of flask-CRDS measurements with in-situ CRDS measurements at a high-altitude mountain baseline station will be presented to support the robustness of the method.

## 2 Instrumentation

We designed a sample manifold to connect with the CRDS analyzer to measure  $CO_2$ ,

<sup>20</sup> CH<sub>4</sub> and CO in flask samples. Four experiments were conducted to assess the stability and accuracy of the flask-CRDS method: (1) the stability test of continuously measuring CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O at various pressures (from 750 to 140 Torr) in flasks; (2) the wall-effect test for the manifold; (3) evaluation of repeatability and reproducibility by replicating analyses from the same sample (intra-flask precision) and replicating analyses from multiple flasks (inter-flask precision); (4) test of the degree to which one sample carries over to the measurement of the next sample; and (5) inter-comparison of the flask samples with the in-situ CRDS measurements at the high-altitude moun-





tain baseline station. The results of these experiments are summarized in the following sections.

#### 2.1 Configuration of the flask-CRDS system

Figure 1 shows a schematic diagram of the flask-CRDS system, which consists of a manifold with a pressure gauge, a vacuum pump and a CRDS analyzer (G2401, Picarro Inc., CA, USA). The manifold was designed to introduce flask samples to the CRDS analyzer to measure CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O simultaneously.

A vacuum pump (Varian, SH-110 Dry Scroll Vacuum Pump) with a shut-off valve (SS-41GS2, Swagelok) was used to evacuate the residual air in the manifold prior to introducing the sample. A pressure gauge (Model 600ab trans 1000 tr, Edwards, USA) with a range from 0 to 1000 Torr was employed to monitor the sample pressure. A 3-way valve (SS-41GXS2, Swagelok) was used to switch between the flask sample and the reference cylinder (or standard gases).

A flow-restricting orifice (A-9-NY, Picarro) was used to reduce the sample flow to decrease consumption of the sample. A transfer tubing (stainless-steel tubing coated with fused silica, 1/8 inch × 40 cm, Restek) was used to connect the manifold to the CRDS analyzer.

#### 2.2 Measurement procedure

Flask measurements are performed using the following procedure. A 2-L electropolished stainless-steel canister flask with an air sample (or standard gases) is connected to the flask-CRDS system. Next, the shut-off valve (#1) is opened to the vacuum pump to pump down the manifold to 0.1 Torr in 1 min before closing. The bellows valve is then opened to allow the sample from the canister to expand into the manifold. After 30 s to allow the pressure to balance, the 3-way valve (#2) is switched to direct the sample gas from the manifold into the CRDS analyzer for measurement. Once the measure-

ment ends, the 3-way valve (#2) is switched to the reference cylinder. The reference

cylinder was an ambient air sample pressurized to approximately 68 bar (~ 1000 psi) to maintain an uninterrupted flow to the CRDS analyzer before and after the flask measurements occurred. Furthermore, fixed concentrations of  $CO_2$ ,  $CH_4$  and CO in the reference cylinder can be used to check the stability of the CRDS method. However, water vapor in the reference cylinder was mostly removed during the pressurization process.

# 2.3 Calibration and standard mixtures

 $CO_{2}$ ,  $CH_4$  and CO were calibrated with a series of certified standards ranging from 369.9 to 516.3 ppm for  $CO_2$ , from 1599.74 to 2024.64 ppb for  $CH_4$  and from 62.4 to 291.8 ppb for CO. These standards were purchased from NOAA/ESRL/GMD, which provides calibration services in support of the WMO/GAW network (NOAA/ESRL/GMD, 2013).

#### 3 Results and discussion

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#### 3.1 Stability at various pressures

<sup>15</sup> To test the system's stability at sub-ambient pressures, a 2-L stainless-steel canister filled with ambient air (755 Torr, relative humidity (RH) of 62%, and temperature of 25°C) and was fed to the system. The experiments were conducted at a laboratory temperature of  $26 \pm 1$ °C to prevent water vapor from condensing on the walls of the flasks and manifold before flowing into the analyzer. The temporal resolution of the 20 CRDS analyzer is 5 s.

The CRDS analyzer in this study was operated without a drying device. Many users have taken the approach of concurrently measuring  $H_2O$  in the sample and using experimentally derived algorithms to correct for the dilution and broadening effects  $H_2O$  has on the CO<sub>2</sub> and CH<sub>4</sub> mixing ratios in the sample (Rella, 2012). The  $H_2O$  correction functions have been shown to be adequate for high-accuracy measurements of CO<sub>2</sub>



and CH<sub>4</sub> that satisfy the WMO compatibility goals (e.g. Chen et al., 2010; Winderlich et al., 2010; Rella et al., 2012; Richardson et al., 2012). Figure 2 shows the time series data of CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>O, flask pressure and cavity pressure (the cell pressure of the CRDS analyzer). Time = 0 corresponds to the time at which the 3-way valve was switched to direct the sample gas from the flask through the manifold into the CRDS analyzer for measurement. There was an unstable transition period when the 3-way valve was valve was switched. The measurements of the four gases changed abruptly from the measurements of the reference air to those of the sample in the canister.

A closer look at Fig. 3a with the enlarged plots will find that CO<sub>2</sub>, CH<sub>4</sub> and the cavity pressure also show a slight increasing trend. The data of CO is too noisy to reveal such a trend. It is suspected that the slightly upward trend for CO<sub>2</sub> and CH<sub>4</sub> was mainly caused by the slightly increased cavity pressure over time. Whenever 3-way valve was switched, the pressure in the transfer tubing changed abruptly. Because the cavity needed to maintain a constant pressure of 140 Torr, this could impose a challenging demand on the accuracy of the cavity outlet valve for stabilizing cavity pressure, resulting in a small bias in the actual pressure, which slightly affected the molecules in the optical cavity and the width of the absorption lines of target gases. A known cavity pressure dependence of the reported concentration and correction coefficients for CO<sub>2</sub>

and  $CH_{4}$  are as follows:

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<sup>20</sup> [CONC] = 
$$a \times$$
 [CONC]  $\times P$  (in Torr)

where correction coefficient  $a = +1.26 \times 10^{-3}$  for CO<sub>2</sub> and  $+3.5 \times 10^{-3}$  for CH<sub>4</sub>. [CONC] represents the reported concentration of target gases. *P* is the difference between the standard cavity pressure (140 Torr) and the measured pressure. Shown in Fig. 3b, improvement in CO<sub>2</sub> and CH<sub>4</sub> can be seen after correction for cavity pressure. Although the slightly increasing trend of CH<sub>4</sub> after correction is still noted, the error in accuracy is guite trivial compared with its ambient levels and can meet the WMO/GAW standards.

Table 1 shows the means and standard deviations of the measurements of  $CO_2$ ,  $CH_4$ , CO and  $H_2O$  in the different time intervals since the 3-way valve was switched.



(1)

The measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO became stable after 60 s. In this case, the difference in CO<sub>2</sub> concentrations between the reference cylinder (395.95 ppm) and the air sample in the canister (450.53 ppm) was approximately 55 ppm, and 60 s was needed to stabilize the measurement. In other cases, more or less time may be needed for stabilization, depending on the concentration gradients. The data in the transition period with the larger variations were discarded from the analysis, and the more stable data for CO<sub>2</sub>, CH<sub>4</sub> and CO after the transition period were used to represent the measured data for the three gases.

As shown in Fig. 2 and Table 1, the measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO after the transition period were stable when the remaining pressure in the flask was above 175 Torr. However, unstable CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O measurements occurred when the pressure in the flask decreased below 175 Torr, which resulted in the cavity pressure decreasing to below 140 Torr (the standard cavity pressure of the G2401 analyzer). Due to the restriction caused by the flow restrictor (orifice) and filters that were intis stalled between the manifold and the CRDS cavity, 35 Torr was the minimum pressure gradient needed to maintain the cavity pressure at 140 Torr.

Although water vapor can be measured by CRDS, the water vapor in the flasks does not represent the actual ambient level at the moment of collection. The water vapor concentration in the flasks is lower than the actual value, due to wall adsorption in-

- side the canisters. Figure 3 shows that while the other three gases had rather constant values after the initial transition period, the water vapor displayed a slight increasing trend. This increasing trend of water can be also clearly seen in Table 1 during the measurement period from 60 to 1012s when the other three gases showed rather stable readings. A possible cause for the slight increase could be that the equilibrium
- <sup>25</sup> between the water vapor and the surface of the pathway the sample took to the CRDS analyzer was not reached during the measurement period. However, such a slight increase in the water vapor concentration did not affect the accuracy of the CO<sub>2</sub> or CH<sub>4</sub> measurements; the measurements of dry CO<sub>2</sub> and dry CH<sub>4</sub> were corrected using the manufacturer-supplied water correction factors and were notably stable. This experi-



ment suggests that stable measurements can be easily obtained for  $CO_2$ ,  $CH_4$  and CO over a wide flask pressure range, as long as the flask pressure was above 175 Torr, which can sustain the cavity pressure at 140 Torr.

# 3.2 Manifold adsorption test

- The wall-effect is a common bias associated with any surface to which the air sample is exposed. Because the manifold contains most of the exposed surface of the system, it is important that it be examined for the wall-effect. A pressurized sample of reference air containing CO<sub>2</sub>, CH<sub>4</sub> and CO was analyzed using two procedures. In one procedure, the reference air was directly connected to the 3-way valve in Fig. 1 for analysis, thus bypassing the manifold to minimize the exposed surface area. In the other procedure, the reference air was directed through the manifold to CRDS. Only the stabilized measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO after the transition period were used for the comparison. As shown in Table 2, the three gases showed slight differences between the two approaches with 0.05 ppm for CO<sub>2</sub>, 0.5 ppb for CH<sub>4</sub>, and 0.5 ppb for CO, which
- <sup>15</sup> meet the WMO/GAW objectives for these gases.

# 3.3 Reproducibility

The evaluation of reproducibility was assessed as intra-flask and inter-flask precision. Intra-flask precision was evaluated by repeatedly analyzing the same sample in accordance with the procedure described in Sect. 2.2. An ambient 2-L sample (ambient pressure of 755 Torr, RH of 62%, and temperature of 25°C) was analyzed for nine replicates. Once again, only the readings of CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O taken after the transition period were used as the measured data for the four gases. The repeatability (1 $\sigma$ ) of the flask-CRDS measurements (*N* = 9) was 0.03 ppm, 0.9 ppb, 1.3 ppb and 0.001% for CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O, respectively. The water vapor measurements were fairly stable for the nine analyses. Although water vapor was thought to be partially ad-



sorbed along the pathway as the air was continuously drawn to the CRDS analyzer.

repeated analyses obtained similar results for  $H_2O$  mixing ratios derived from the time interval from 60 to 120 s, despite the fact the equilibrium within the manifold was possibly never reached.

The inter-flask precision was assessed using the same analysis procedure on five different flask samples filled with air from the same larger ambient sample. A 15-L canister (29-11521G, SILONITE Coated, Entech) filled with ambient air was transferred into five 2-L evacuated canisters. The five flasks were only filled to 200 Torr to test the reproducibility of the measurements in conditions close to the low-pressure limit (175 Torr) of the CRDS analyzer. Table 3 summarizes the means and standard deviations of the measurements of the four gases in the five canisters. The inter-flask precision test indicated remarkably high reproducibility with overall relative precisions (1 $\sigma$ ) of 0.07 ppm, 0.4 ppb, 0.5 ppb and 0.003 % for CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O, respectively.

#### 3.4 Sample carry-over

- <sup>15</sup> There is always a legitimate concern of carry-over when analyzing flask samples that could vary widely in concentration. The carry-over test was performed by measuring a group of flasks for the target gases at lower concentration levels by filling with a common sample source, followed by analyzing another group of flasks at much higher levels by filling with another sample source. In this experiment, the three low level sam-
- <sup>20</sup> ples were collected at the coast, whereas the high level samples were collected by a traffic congested road and then transferred into four 2-L evacuated canisters. Had carry-over occurred, the first higher level flask would have been affected more than the rest in the group. Table 4 shows the readings of CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O for the seven consecutive flasks (three for the lower concentrations and four for the higher). Appar-
- ently, the readings for the first high level sample were not significantly lower than those of the rest high-level samples, indicating negligible carry-over. Likewise, the sequence was reversed by first analyzing high-level samples followed by the low-level samples and no noticeable difference was found either.



Prior to the measurement of the canister air, the residual air in the manifold (17 mL) is evacuated down to a pressure of 0.1 Torr. In theory, the residual air left in the manifold would be no more than 0.0005% of the original air in the canister, even when the analysis occurs in a 2-L canister that has a low pressure of 200 Torr. The bias caused by the residual air could contribute to an error of only approximately 0.0005 ppm under the assumption that the difference in CO<sub>2</sub> concentrations between the sample and the residual air was as large as 100 ppm.

## 3.5 Inter-comparison of flask and in-situ measurements

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To test the accuracy of the flask-CRDS method for flask measurements, an intercomparison experiment between the in-situ CRDS method and the flask-CRDS method for canister samples was performed at a high-altitude baseline station (Lulin Atmospheric Background Station) with an elevation of nearly 3000 m. Mixing ratios of several trace gases including the four target gases have been continuously monitored since 2006 to obtain the long-term baseline conditions of the East Asia region (Ou-Yang et al., 2012).

Twelve 2-L evacuated stainless-steel canisters were used to sample air from the air sampling glass manifold (shown in Fig. 4) of the in-situ CRDS (G1301, Picarro Inc., CA, USA) inside the station while the in-situ CRDS measurements of the ambient air continued. The canisters were filled with sample air every two hours during 26–27 Septem-

- <sup>20</sup> ber 2011. A sampling line with a shut-off valve (#1) was connected to one of the ports of the glass manifold in the station for filling canisters with the atmosphere (Fig. 4). Before sampling, the shut-off valve (#1) was opened to allow fresh air from the glass manifold to flush any room air left in the sampling line when connecting a canister. After approximately 10 min, the bellows valve of the pre-evacuated canister was opened for
- one minute to fill the canister and to equilibrate the pressure with the outside ambient pressure, which is approximately 540 Torr at the altitude of 3000 m. When all 12 samples were collected, the canisters were placed in the station and were later analyzed by the same flask-CRDS method at the station during a one-day maintenance period



occurred approximately one month after sampling. The systematic bias was minimized because the same CRDS and calibration scale were used for the measurements. Figure 5 shows the canister results superimposed on the in-situ data measured by the CRDS analyzer at the baseline station. Excellent agreement can be seen between the

<sup>5</sup> high-resolution in-situ data and the 12 canister data points from the off-line method, even though the canisters were stored for one month in the station. The differences between the two methods were approximately 0.10 ± 0.09 ppm for CO<sub>2</sub> and 0.9 ± 1.0 ppb for CH<sub>4</sub>. Several outliers in the in-situ data can be seen in Fig. 5. These outliers were caused when connecting canisters and the flushing step, but the measurements were soon to return to the baseline level when the fresh atmosphere continue to flow into the CRDS analyzer.

## 4 Conclusions

This study demonstrated a CRDS method to analyze atmospheric CO<sub>2</sub>, CH<sub>4</sub> and CO in flask samples. A manifold connected to the CRDS analyzer was configured to ac-<sup>15</sup> commodate flask measurements. The low-pressure requirement of 175 Torr with the flask-CRDS method allowed prolonged stable measurements of the three gases. Our test results showed that the measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO after the transition period were stable over a wide flask pressure range, as long as the cavity pressure can be sustained at 140 Torr.

<sup>20</sup> The flask-CRDS method showed excellent reproducibility for both the intra- and interflask analyses. The potential bias due to the wall-effect in the manifold was found to be either negligible or minimal. The baseline station field test of inter-comparing the flask samples with the in-situ CRDS measurements revealed excellent agreement.

This study demonstrates that the flask-CRDS method can easily perform accurate and precise measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO in flasks. In the future, the method may provide a simple solution to fortify the existing global in-situ network by providing



the needed spatial resolution and improving our knowledge of global distributions and budgets of these three gases.

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**Table 1.** Mean and standard deviation  $(\pm 1\sigma)$  of the readings of CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>O and cavity pressure in different time intervals.

Time (s)	0~60	60~120	120~1012	1012 ~ 1305
Flask pressure range (Torr)	750~676	676~610	610~175	175~140
CO <sub>2</sub> (ppmv)	$444.66 \pm 15.93$	$450.56 \pm 0.03$	$450.55 \pm 0.04$	$448.97 \pm 1.67$
CH <sub>4</sub> (ppbv)	$2109.3 \pm 42.6$	$2117.3 \pm 0.5$	$2117.5 \pm 0.5$	2079.1 ± 32.0
CO (ppbv)	552.5 ± 171.8	$614.3 \pm 6.5$	$615.0 \pm 6.7$	734.8 ± 83.1
H <sub>2</sub> O (%)	$1.736 \pm 0.554$	$1.963 \pm 0.002$	$1.978 \pm 0.007$	$1.905 \pm 0.112$
Cavity pressure (Torr)	$139.94 \pm 0.05$	$139.95 \pm 0.01$	$139.97 \pm 0.02$	$126.36 \pm 9.11$

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Table 2. Differences between the two procedures with one passing through the manifold and the other by-passing the manifold for  $CO_2$ ,  $CH_4$ , CO and  $H_2O$ .

	CO <sub>2</sub> (ppmv)	CH <sub>4</sub> (ppbv)	CO (ppbv)	H <sub>2</sub> O (%)
Through the manifold	$475.91 \pm 0.04$	$1779.7 \pm 0.5$	$275.4 \pm 6.6$	$0.642 \pm 0.00^{-2}$
By-passing the manifold	$475.86 \pm 0.03$	$1779.2 \pm 0.4$	$275.9 \pm 4.6$	$0.644 \pm 0.00^{-1}$
Difference (absolute) <sup>a</sup>	0.05	0.5	-0.5	-0.002
Difference (%) <sup>b</sup>	0.011	0.027	0.185	0.311

<sup>a</sup> Difference (absolute) = passing through the manifold – bypassing the manifold. <sup>b</sup> Difference (%) = (through the manifold – bypassing the manifold)/bypassing the manifold × 100 %.

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Table 3. Means and standard deviations of the readings of  $CO_2$ ,  $CH_4$ , CO and  $H_2O$  in the five flasks.

	CO <sub>2</sub> (ppmv)	CH <sub>4</sub> (ppbv)	CO (ppbv)	H <sub>2</sub> O (%)
Flask#1	$458.66 \pm 0.04$	$1941.9 \pm 0.5$	$280.9 \pm 6.8$	$1.483 \pm 0.002$
Flask#2	$458.77 \pm 0.03$	$1941.5 \pm 0.5$	$281.3 \pm 7.2$	$1.482 \pm 0.002$
Flask#3	$458.78 \pm 0.03$	$1941.5 \pm 0.6$	$281.0 \pm 6.1$	$1.482 \pm 0.002$
Flask#4	$458.71 \pm 0.04$	$1942.3 \pm 0.6$	$280.4 \pm 7.9$	$1.484 \pm 0.002$
Flask#5	$458.84 \pm 0.04$	$1941.6 \pm 0.5$	$281.5 \pm 7.0$	$1.476 \pm 0.002$
Average of 5 flasks	458.75 0.07	1941.8 0.4	281.0	1.481
OD OF O HUGHS	0.07	0.4	0.0	0.000

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Table 4. Means and standard deviations of the readings of  $CO_2$ ,  $CH_4$ , CO and  $H_2O$  in the sample carrier-over test.

Runs		CO <sub>2</sub> (ppmv)	CH <sub>4</sub> (ppbv)	CO (ppbv)	H <sub>2</sub> O (%)
1	Low conc. sample #1	$420.70 \pm 0.03$	$1891.4 \pm 0.6$	$192.7 \pm 6.6$	$2.547 \pm 0.002$
2	Low conc. sample #2	$420.76 \pm 0.03$	$1892.7 \pm 0.6$	$192.8 \pm 5.8$	$2.549 \pm 0.001$
3	Low conc. sample #3	$420.79 \pm 0.03$	$1892.7 \pm 0.5$	$190.0 \pm 7.8$	$2.552 \pm 0.002$
4	High conc. sample #1	$558.01 \pm 0.04$	$2024.6 \pm 0.7$	$674.2 \pm 9.0$	$2.440 \pm 0.002$
5	High conc. sample #2	$558.16 \pm 0.04$	$2025.2 \pm 0.6$	$673.4 \pm 9.7$	$2.443 \pm 0.002$
6	High conc. sample #3	$558.19 \pm 0.05$	$2024.8 \pm 0.6$	$674.2 \pm 6.8$	$2.454 \pm 0.002$
7	High conc. sample #4	$558.00\pm0.04$	$2025.6\pm0.8$	$672.2\pm5.7$	$2.455 \pm 0.002$



Fig. 1. Schematic diagram of the flask-CRDS system.

















Interactive Discussion





Fig. 5. Inter-comparison between flask and in-situ measurements for (a)  $CO_2$  and (b)  $CH_4$ .

