An analytical system for studying the stable isotopes of carbon monoxide using continuous flow-isotope ratio mass spectrometry (CF-IRMS)

S. L. Pathirana, C. van der Veen, M. E. Popa and T. Röckmann

Institute for Marine and Atmospheric research Utrecht, Utrecht University, Princetonplein 5, 3584 CC Utrecht, Netherlands

Correspondence to: S.L. Pathirana (supun22@gmail.com)

Abstract

A fully automated system for the determination of $\delta^{13}C$ and $\delta^{18}O$ in atmospheric CO has been developed. CO is extracted from an air sample and converted into carbon dioxide (CO_2) using the Schütze reagent. The isotopic composition is determined in an isotope ratio mass spectrometer (IRMS). The entire system is continuously flushed with high-purity helium (He), the carrier gas. The blank signal of the Schütze reagent is ~4 nmol mol^{-1}, or 1-3 % of the typical sample size. The repeatability is 0.1 ‰ for $\delta^{13}C$ and 0.2 ‰ for $\delta^{18}O$. The peak area allows simultaneous determination of the mole fraction with an analytical repeatability of ~0.7 nmol mol^{-1} for 100 mL of ambient air (185.4 nmol mol^{-1} of CO). An automated single measurement is performed in only 18 min, and the achieved time efficiency (and small volume of sample air) allows repetitive measurements practically

1 Introduction

Carbon monoxide (CO) has an average mole fraction of only ~100 nmol mol^{-1} (parts per billion or ppb) in the atmosphere, but it has a large yearly turnover of about 2700 Tg (Brenninkmeijer et al., 1999), because of its fast reaction rate with the hydroxyl radical (OH·). It is produced by numerous sources at the earth's surface and in the atmosphere. About 1/3 of the atmospheric CO originates from methane oxidation while fossil fuel combustion, biomass burning and oxidation of non-methane hydrocarbons (NMHC) are other important sources (Brenninkmeijer et al., 1999). The strong latitudinal gradient is a result of the main sources being in the northern hemisphere, and the seasonal cycle of CO is largely driven by the seasonality of the OH· (Röckmann et al., 2002). The reaction CO+OH· is not only the main sink for CO but also for OH·, with CO occupying approximately 60% of the atmosphere's OH· based oxidative capacity (Crutzen and Zimmermann, 1991). An increase in the CO mole fraction will therefore cause a decrease in the oxidation efficiency of the atmosphere, resulting in a buildup of other gases, such as the long-lived greenhouse gas methane, which are primarily removed by OH·. Consequently, CO is established as an important indirect greenhouse gas in the recent IPCC assessment report (Hartmann et al., 2014). In addition, under high NO_x (mono-nitrogen oxides) conditions the oxidation of CO leads to the production of ozone, contributing to the buildup of photochemical smog (Westberg et al., 1971).

The stable isotopes of carbon and oxygen in CO, ^{12}C, ^{13}C, ^{16}O, ^{17}O and ^{18}O, are naturally abundant at levels of 98.89%, 1.11% (for carbon) and 99.76%, 0.04%, and 0.20% (for oxygen) (Röckmann and Brenninkmeijer, 1998) respectively. Delta (δ) values are defined as relative isotopic enrichments of a sample to a reference.

$$\delta = \left(\frac{R_{Sample}}{R_{Reference}} - 1\right) \qquad (1)$$

The isotope ratio, R, is $^{13}C/^{12}C$ in the case of carbon ($\delta^{13}C$) and $^{18}O/^{16}O$ for oxygen ($\delta^{18}O$). For CO, δ values for ^{13}C and ^{18}O are usually reported against the international reference materials V-PDB (Vienna Pee Dee Belemnite) and V-SMOW (Vienna Standard Mean Ocean Water) respectively. Since stable isotope variations in nature are small, these δ values are expressed in per mill (‰).

Precise measurements of CO mole fraction and isotopic composition are useful in constraining individual source and sink processes. The combination of the $\delta^{13}C$ and $\delta^{18}O$ values gives a distinct isotopic signature for each individual CO source. CO from methane (CH_4) oxidation is the most

^{13}C-depleted source, with $\delta^{13}C$ values around -50 ‰ (Brenninkmeijer and Röckmann, 1997). $\delta^{13}C$ values for CO from fossil fuel combustion, biomass burning and non-methane hydrocarbon (NMHC) oxidation range between -27 ‰ and -32 ‰ (Manning et al., 1997; Stevens and Wagner, 1989). For CO sources that have a range overlap in $\delta^{13}C$ values (vehicle emissions range ~ -36 to -20 ‰, biomass burning range ~-25 to -21 ‰ and NMHC oxidation range ~-37 to -27 ‰), $\delta^{18}O$ proves to be a better tracer. Carbon monoxide from vehicle emissions has the highest $\delta^{18}O$ values, 24 ‰ (Popa et al., 2014; Tsunogai et al., 2003) compared to 7-10 ‰ for biomass burning (Röckmann et al., 1998; Tarasova et al., 2007). For NMHC oxidation no direct measurements are available and a $\delta^{18}O$ value of 0 ‰ was indirectly derived from isotope budget considerations (Brenninkmeijer and Röckmann, 1997).

Originally, CO isotope analysis was carried out with offline extraction systems, which require large amounts of air (Brenninkmeijer, 1993; Stevens and Krout, 1972), but in recent years, continuous flow techniques have been developed to accommodate smaller sample volumes (Tsunogai et al., 2002; Wang and Mak, 2010). Brenninkmeijer's (1993) method required sample sizes of the order of 100 L, whereas Wang and Mak's (2010) method is optimized for a volume of 0.1 L. There are two conceptually different techniques allowing isotopic analysis of $\delta^{13}C$ and $\delta^{18}O$ of carbon monoxide. One uses the principle of conversion to carbon dioxide (CO_2) and subsequent isotope analysis of CO_2 (Brenninkmeijer, 1993; Stevens and Krout, 1972; Wang and Mak, 2010), and the other uses isotope measurement on CO directly (Tsunogai et al., 2002). The technique of converting CO into CO_2 has the advantage as high precision mass spectrometry is often based on CO_2, which allows the possibility of using standardized techniques and isotope calibration scales (Brenninkmeijer et al., 1999). CO is converted to CO_2 using an oxidizing agent, and if the isotopic composition of this oxidizing agent is constant, its effect on the isotopic composition of the CO_2 product can be taken into account. The need to correct for the additional O atom is the weakness of this method.

In the direct method, CO^+ ion currents at masses 28, 29 and 30 are monitored simultaneously (Tsunogai et al., 2002). Since CO is not converted to CO_2, there is no introduction of an additional oxygen atom that needs to be calibrated.

Current continuous flow-isotope ratio mass spectrometry (CF-IRMS) techniques move towards faster methods, smaller sample sizes and most importantly more precise and reproducible results. Rapid methods allow multiple measurements that can be combined to improve the error of the mean of measurements for one sample. A method that requires a smaller sample volume for a single run, not only gives the opportunity to measure samples multiple times, but also to measure small air samples e.g. from ice cores (Wang and Mak, 2010) or firn air (Petrenko et al., 2013; Wang et al., 2012), expanding the range of possible applications.

This paper presents a method to measure the mole fractions, $\delta^{13}C$ and $\delta^{18}O$ of CO in an air sample in less than 20 minutes. The method uses 100mL of air and the sample flask should have a minimum pressure of ~1550 mbar abs. The blank from the oxidant (Schütze reagent) that is used to convert CO to CO_2 is strongly reduced by continuously flushing the reagent with high purity He, which leads to highly reproducible results.

Conceptually, the key difference to the system by Wang et al., 2010 is that our extraction system operates always under a flow of He; it is thus a conceptually different realization of the same idea of extraction and preparation of CO. The system is particularly well suited for routine operation and automated analysis of many samples. In terms of precision, the overall results are similar to the system described by Wang et al., and the main improvement is the strong reduction of the system blank.

2 Experimental

2.1 Method and Instrumentation

A diagram of the analytical system is shown in Fig. 1. The system consists of an automated multiple sample inlet system, the CO extraction and conversion setup, a gas chromatograph (GC) for purification of the CO_2, an open split system and an IRMS. The system is at all times flushed with ultra-high purity helium (He) with BIP® technology (BIP is Built In Purification, Specification number: He-26507, Assay: 99.997 %), provided by Air Products. Fused silica capillaries are used for connecting components unless specified differently. There are two membrane vacuum pumps (P_1 and P_2) attached to the setup; one to evacuate the multi-sample inlet line (P_1) and the other one at the exhaust of the extraction (P_2), conversion and collection unit. A single, automated, measurement is performed in 18 minutes.

2.1.1 Multi-Sample Inlet System

Samples are connected to the automated multi-sampling unit for analysis. This unit allows automated measurements of the reference gas and up to 8 sample flasks. Samples are connected to a 16-position 8-port Dead-end Flowpath Selector (V_1: VICI, Product number: SD8MWE). The 3-port Switching Valve (V_2: VICI, Product number: 3UWE) after the sample multiport, provides the option to select either the reference gas cylinder or one of the samples. The air to be analyzed is then directed via a mass flow controller (MKS, model 1179, 100 sccm) to a 6-port 2-position valve (V_3: VICI, Product number: 6UWM) from where the gas can be either injected to the extraction system (position "1") or evacuated (position "2"). 1/16 inch Restek Silcosteel® coated stainless steel tubing is used for connecting the individual components (Tsunogai et al., 2000). This multi-sampling unit is controlled by LabView software, which specifically controls V_1, V_2, the flow rate of the mass flow controller, the sample injection time, the sample flush time and the number of times each sample is measured. The Sample is injected into the system at a flow rate of 20mL/min for 5 minutes. A higher flow rate and longer injection time can be used for measuring samples with lower mixing ratios. The LabView program also records the values from the pressure sensor before the mass flow controller and gives a start signal to the ISODAT program to start its acquisition. The interface that is essential for the communication between the valves and the PC is National Instruments USB NI-6008 unit.

When starting an automated measurement sequence, first the 8 samples are connected to V_1 and V_2 is set in the direction of the samples. Then V_3 is set to "evacuation" position and the membrane pump valve is opened, allowing the air from the point of the sample connection to V_3 to be evacuated. Following this procedure each sample position of V_1 is evacuated and tested for leaks. After this leak test the sample bottle/can/cylinder valves are opened. From this point onwards the method is fully automated. The final pressure in the sample admission part of the system prior to the introduction of the sample is ~1 mbar.

To avoid contamination with remaining air when switching between samples via the multi-sample inlet system, V_1 is first set to a "close" position between two sample ports and the system is evacuated for 60 sec. Afterwards the multi-sample inlet system is flushed with the new sample air for 55 seconds at a flow rate of 20 mL/min before it is injected via V_3.

The minimum pressure required in a 1L glass flask, to perform a single run with a stable flow rate of 20 mL/min, is 1550 mbar abs.

2.1.2 Extraction and Conversion Setup

By switching the injection valve (V_3), the sample is injected into the extraction system and directed through a chemical trap containing Ascarite^{TM} (CO_2 absorbent, 8-20 mesh, Aldrich) and Magnesium Perchlorate (Sigma-Aldrich), removing CO_2 and H_2O respectively. The subsequent cryogenic trap (T_1-3 mm ID, 6 mm OD, 62 cm length, glass), containing glass beads (U.S. mesh 40-60), removes CO_2, N_2O and other condensable gases at liquid Nitrogen temperature (-196^o C).

CO is then selectively oxidized to CO_2 using the Schütze reagent (Schütze, 1949; Smiley, 1965) in T_2. The oxidation reactor (T_2) consists of a 10 cm length 6 mm OD glass tube and it is filled with 3g of Schütze reagent. In order to reduce the "Schütze blank", the oxidation tube is located in the loop position of a 6-port 2-position valve (V_4: VICI, Product number: C6UWM) and it is continuously flushed with He (flow rate ~8 mL min^{-1}) when not in use. The flow is directed through the Schütze oxidant only during the sample injection and flushing period.

2.1.3 Synthesis of Schütze Reagent

2.5 g of diiodine pentoxide (I_2O_5, 99.9%, Aldrich) was dissolved in 12.5 mL of water (Sigma-Aldrich, Product Number 270733: CHROMASOLV® for HPLC graded water, filtered through a 0.2 μm filter) to obtain a solution of iodic acid (colorless). 20 g of Silica gel (Grade 40, 6-12 mesh, Sigma-Aldrich) was added to this solution. The mixture, covered with a watch glass, was dried in the oven for 1.5 hours at 145^o C. Immediately out of the oven, 5 mL of concentrated sulfuric acid (H_2SO_4) was added to the mixture and the covered beaker was left overnight in the laboratory hood. This allows the H_2SO_4 to coat the mixture well, dehydrating it. The mixture was then placed in the Schütze reagent reactor (Fig. 2). The Schütze reagent reactor was continuously flushed by a slow nitrogen gas stream and heated at 220^o C for 6 hours or until the mixture was "dry". The air exiting the reactor was passed through a molecular sieve and a large beaker of water. This was done to ensure that the H_2SO_4 vapor carried out with the N_2 was removed before the N_2 was released to the laboratory. The N_2 flow rate was adjusted so that there was a slow release of bubbles visible in the beaker. The active chemical (I_2O_5) was formed only when all the water was removed. The Schütze reagent is white, but sometimes it may have a bright yellow tint when iodosyl salts are formed (Schmeisser and Brändle, 1963).When the reagent turns brown (Formation of iodine: $5CO + I_2O_5 \rightarrow 5CO_2 + I_2$) with use, it must be replaced with a new batch. When the Schütze reagent is replaced, not only the capillaries but also the reagent is exposed to the atmosphere causing a buildup of CO_2. Once the connections are properly tested for leaks, the reagent needs to be flushed well with helium, for 3 days to a week, until the CO_2 blank is back to normal low levels (See Section 3.1).

2.1.4 Collection, Focus and Separation

The CO-derived CO_2 is trapped in the collection trap, T_3 (1/16 inch stainless steel tubing), using liquid nitrogen while the other gases are removed via the vacuum pump. The CO_2 sample is then transferred to a focus trap (T_4), when the 6-port 2-position valve (V_5: VICI, Product number: 6UWM) is switched to "inject" position. In T_4, the 320/430 µm fused silica capillary, used throughout the system, continues through 1/16 inch stainless steel tubing (tubing is used only to protect the capillary). The liquid nitrogen level of the cold traps is controlled by a liquid nitrogen re-filler (NORHOF 900 series LN2 microdosing system) to improve the reproducibility of the peak areas. When T1, T3 and T4 in "down" position the traps acquire the temperature of liquid nitrogen (~-196 ^{O}C) and when the traps are in "up" position they warm up to room temperature (~25 ^{O}C).

The sample is separated from other residual components, on a Poraplot-Q (25 m x 0.25 mm) gas chromatography column (at 50^{o} C). It is then dried via a Nafion dryer. Finally the sample is transferred into a Thermo-Finnigan Delta V Plus IRMS through a custom-made (Röckmann et al., 2003) open-split interface. The ISODAT program controls the components from the cryogenic trap to the open split. All the valves and the traps are air actuated and controlled by solenoids linked to the interface with IRMS.

In routine operation, the entire system is flushed for 425 seconds between runs, the Schütze regent is introduced into the main gas stream 425 seconds before injection of sample air, the sample processing takes 300 seconds, followed by another 300 seconds of flushing before the sample is transferred from trap T_3 to T_4. The cryogenic trap that removes the remaining traces of CO_2 and N_2O is warmed to room temperature for 302 seconds in between runs to remove the eluted gases and is cooled again for 123 seconds before the next sample is admitted.

2.2 Data Processing and Calibration

In order to monitor the performance of the CO isotope system, a reference air sample (Ref) with a known mole fraction and isotopic composition (See Section 2.2.2) is run multiple times. An evaluation of these runs helps determine the reproducibility and accuracy of the system. Ref is also run before and after every sample run to enable calibration and to detect variations in system sensitivity.

CO_2 derived from CO in a sample is analyzed by the mass spectrometer. CO is quantitatively converted to CO_2 using Schütze reagent (Brenninkmeijer, 1993). Therefore the quantity (in moles) of CO is equal to the quantity of CO_2 derived from the CO in the air sample.

Carbon monoxide mole fractions are calculated using a one-point calibration, according to,

$$c_S = \frac{Area\ All_S}{Area\ All_R} \cdot \frac{f_R}{f_S} \cdot \frac{t_R}{t_S} \cdot c_R \qquad (2)$$

where c_S is the mole fraction of the sample, $Area\ All_S$ is the area of the sample peak, $Area\ All_R$ is the area of the Ref peak, $\frac{f_R}{f_S}$ is the ratio of the reference flow rate and sample flow rate, $\frac{t_R}{t_S}$ is the ratio of the reference injection time and sample injection time and c_R is the mole fraction of the reference air cylinder. For typical ambient air samples $\frac{f_R}{f_S} = \frac{t_R}{t_S} = 1$.

The ISODAT software reports the δ values of each peak in the chromatogram (both sample and reference air) versus the laboratory working gas, $\delta_{S\ vs\ WG}$ and $\delta_{R\ vs\ WG}$ respectively. In our data reduction procedure, we first use these values to calculate the isotopic composition of the sample versus the reference, $\delta_{S\ vs\ R}$ according to

$$\delta_{S\ vs\ R} = \frac{\delta_{S\ vs\ WG} - \delta_{R\ vs\ WG}}{1+\delta_{R\ vs\ WG}} \qquad (3)$$

For $\delta_{R\ vs\ WG}$ we use the average of the reference δ values before and after the sample run. Then, the δ value of the sample is converted to the international reference scales via

$$\delta_{S\ vs\ V} = \delta_{S\ vs\ R} + \delta_{R\ vs\ V} + \delta_{S\ vs\ R} \cdot \delta_{R\ vs\ V} \qquad (4)$$

$\delta_{R\ vs\ V}$ is the δ value of the reference air cylinder versus the international standard, V-PDB or V-SMOW.

In $\delta^{18}O$ data evaluation, $\delta_{S\ vs\ V}$ is the δ value of the sample versus the international standard, V-SMOW for CO_2. CO_2 is generated when the CO from the sample is oxidized by the Schütze reagent.

$$CO + I_2O_5 \rightarrow CO_2 \qquad (R1)$$

Therefore a correction has to be made to get the, $\delta_{S\ vs\ V}$ for CO (Brenninkmeijer, 1993).

$$\delta^{18}O_{S\ vs\ V:\ \mathrm{CO}} = 2\delta^{18}O_{S\ vs\ V:\ \mathrm{CO_2}} - \delta^{18}O_{\text{Schütze Reagent}}$$

$$= 2\delta^{18}O_{S\ vs\ V:\ \mathrm{CO_2}} - (2\delta^{18}O_{R\ vs\ V:\ \mathrm{CO_2}} - \delta^{18}O_{R\ vs\ V:\ \mathrm{CO}}) \qquad (5)$$

In Eq. (5), $\delta^{18}O_{S\ vs\ V:\ \mathrm{CO}}$ is the δ value of the sample versus the international standard for CO, $\delta^{18}O_{S\ vs\ V:\ \mathrm{CO_2}}$ is the δ value of the sample versus the international standard for CO_2 and $\delta^{18}O_{\text{Schütze Reagent}}$ is the O from the Schütze reagent which is derived using the δ value of the reference versus the international standard for CO_2 ($\delta^{18}O_{R\ vs\ V:\ \mathrm{CO_2}}$) and the δ value of the reference versus the international standard for CO ($\delta^{18}O_{R\ vs\ V:\ \mathrm{CO}}$).

2.2.1 Mole fraction calibration

The reference air cylinder (Ref) is a Luxfer 30-L Aluminum cylinder with Rotarex- Ceodeux brass valve, used with a Scott Specialty Gases type 51-14C pressure regulator.

The Ref cylinder was filled with dry atmospheric air at Max Plank Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, in 2009. The initial filing pressure was 130 bar. A mole fraction of 185.4 nmol mol^{-1} was assigned by MPI-BGC, and is linked to the WMO X2004 calibration scale.

The Ref cylinder is regularly measured against other gas cylinders, for isotope calibration (see Sect. 2.2.2) and for checking the system stability. No significant drift in CO mole fraction relative to other gases has been observed since the measurements described here were started

2.2.2 Isotope calibration

The CO isotope values of the IMAU reference air cylinder (Ref) were calibrated versus DiCal, which is a gas cylinder made from the calibration gas cylinder (Cal) obtained from Carl Brenninkmeijer, Max Plank Institute for Chemistry, Mainz with values of

$\delta^{13}C_{\mathrm{Cal\ vs\ VPDB}}$ = -44.3 ‰ (Brenninkmeijer 1993) and

$\delta^{18}O_{\mathrm{Cal\ vs\ VPDB-CO_2}} = \delta^{18}O_{\mathrm{DiCal}CO\ \mathrm{vs\ VPDB-CO_2}}$ = 11.43 ‰ (Brenninkmeijer, 1993).

$$\delta^{18}O_{\mathrm{DiCal}CO\ \mathrm{vs\ V-SMOW}} = 53.45\ ‰$$

An independent calibration of the Cal cylinder was published in 1997 (Brenninkmeijer and Röckmann, 1997), which confirmed the originally assigned values after a long period of storage. The gas is CO in nitrogen. The cylinder was labelled as AP57. The uncertainty for $^{18}O_{\mathrm{Cal\ vs.\ VPDB\text{-}CO2}}$ has been given: 11.43 ± 0.3 ‰. The Cal cylinder has a high CO mixing ratio (269×10^3 nmol/mol) and was diluted in a new cylinder, to a suitable mixing ratio (130 nmol/mol) with CO-free zero air (checked with a Peak Performer 1 reduction gas analyzer), labeled DiCal. It is assumed that the diluted gas DiCal has the same isotopic composition as Cal. Then, Ref and DiCal were measured 10 times versus the lab CO_2 working gas using the present measurement system and the averages were used for calibration of the isotopic composition of CO in Ref relative to the isotopic composition of CO in DiCal.

For $\delta^{18}O$, the correction regarding the oxygen atom from the Schütze reagent is done in the same manner as Eq. (5).

$$\delta^{18}O_{R\,vs\,V:\,\mathrm{CO}} = 2\delta^{18}O_{R\,vs\,V:\,\mathrm{CO_2}} - \delta^{18}O_{\text{Schütze Reagent}} \qquad (6)$$

In Eq. (6), the $\delta^{18}O$ of the Ref ($\delta^{18}O_{R\,vs\,V:\,\mathrm{CO}}$) is calculated by deducting the Schütze reagent oxygen ($\delta^{18}O_{\text{Schütze Reagent}}$) from the CO derived CO_2 oxygen ($\delta^{18}O_{R\,vs\,V:\,\mathrm{CO_2}}$). The Schütze reagent oxygen is derived by $\delta^{18}O_{\text{Schütze Reagent}} = 2\delta^{18}O_{DiCal\,vs\,V:\,\mathrm{CO_2}} - \delta^{18}O_{Cal\,vs\,V:\,\mathrm{CO}}$, where $\delta^{18}O_{DiCal\,vs\,V:\,\mathrm{CO_2}}$ is the measured $\delta^{18}O$ of CO_2 from DiCal CO and $\delta^{18}O_{Cal\,vs\,V:\,\mathrm{CO}}$ is the known $\delta^{18}O$ of Cal CO.

Following this calibration, the values of the reference gas (Ref) against the international standards were determined as $\delta^{13}C$(Ref, V-PDB) = -29.61±0.1 ‰ and $\delta^{13}C$(Ref, V-SMOW) = 8.45±0.2 ‰. In the absence of international standards for the isotopic composition of CO, we note that there may be additional systematic errors (e.g. temporal changes of the primary calibration cylinder or dilution artifacts), which may introduce an additional unspecified uncertainty to these values.

The ISODAT software assumes mass dependent fractionation (MDF) when calculating the δ values. However, atmospheric CO possesses mass independent oxygen isotope anomaly with $\Delta^{17}O$ values ($\Delta^{17}O \equiv \delta^{17}O - 0.52 \cdot \delta^{18}O$) between 2.5 ‰ and 7.5 ‰ (Röckmann and Brenninkmeijer, 1998; Röckmann, 1998). Both $^{13}C^{16}O^{16}O$ and $^{12}C^{17}O^{16}O$ contribute to the ion signal at m/z = 45. This means that, when assuming MDF, the contribution of ^{17}O to the ion beam at mass 45 is underestimated, leading to an overestimation in the $\delta^{13}C$. Röckmann and Brenninkmeijer (1998) calculated this overestimation (error) of $\delta^{13}C$ to be 0.08 - 0.25 ‰ for a $\Delta^{17}O$ range of 2.5 - 7.5 ‰. Since the current method does not resolve the contribution from ^{17}O, we report the $\delta\,^{13}C$ and $\delta\,^{18}O$ values calculated assuming MDF.

3 Results and Discussion

3.1 Blanks

A blank run is performed using the same method as a sample run but without the injection of reference or sample gas. The continuous He flow collects the background of the system for the usual injection time of 5 minutes. The peak area of this system blank is ~ 0.1 Vs which is 2.2 % of the average reference gas (Ref) peak area (The system blank ranges between 8-23 pmol in a 0.7 nmol Ref sample). The majority of the blank signal originates from CO_2 that is released by the Schütze reagent. It is an accumulation of CO_2 formed by the system CO blank or CO_2 from the reagent itself, which are released in later measurements.

When a blank run is done excluding the Schütze reagent trap, the peak has an area of ~0.019 Vs. The blank including the background CO_2 released from the Schütze reagent is used as the system blank.

When the system was first built, the system blank was 10 % of the sample peak. The simple modification of adding a 6-port Valco valve to continuously flush the Schütze reagent with He at a flow rate of 8 ml/min reduced the blank to 1-3%. This blank affects both the sample and the reference air in a typical measurement sequence and is not considered when calculating the mole fractions and δ values of a sample.

3.2 Removal Efficiency of CO_2 and N_2O

When the air sample is injected into the extraction system, CO_2 and nitrous oxide (N_2O) must be completely removed. CO_2 in the sample must be removed as CO is converted to CO_2 for isotope analysis. N_2O shares the same molecular mass as CO_2 and interferes with the CO_2 peak derived from CO on the chromatogram. CO_2 is largely and efficiently removed by the Ascarite trap and remaining traces are together with N_2O condensed in the cryogenic trap (T_1) with glass beads. The glass beads increase the surface area for condensation. T_1 is warmed and evacuated at the end of each run.

Periodically checks are done to confirm that CO_2 and N_2O traps (Ascarite trap and T_1 trap respectively) work efficiently. This is done by bypassing the Schütze reagent so the CO is not converted to CO_2. The result of such runs should be the same as a blank run without the Schütze reagent trap. Like a blank run that does not show a CO_2 peak in the chromatogram. If the result shows a CO_2 peak on the chromatogram then the Ascarite trap needs to be changed.

N_2O has the same nominal isotopocule masses as CO_2, but with much smaller molecular isotope ratios ^{45}R and ^{46}R. Therefore a small amount of N_2O seeping through the cryogenic trap can be detected in the resulting δ values. Table 1 shows a comparison of average values of ten runs from the reference gas (Ref) and ten runs from a can with approximately 2000 nmol mol^{-1} N_2O (15 µL of N_2O was added to a 2.5 L steel can and was filled with reference gas, which already contained atmospheric levels of N_2O). The results show that there is no evidence of N_2O leaking from the cryogenic trap (T_1) even at a high mole fraction. Figure 3 shows a case where the N_2O peak appears on a chromatograph because trap T_1 is not used to remove N_2O. The retention time of N_2O is ~355 s, about 25 s longer than for CO_2 at ~330 seconds. Due to the different isotope ratios of N_2O (see above) the isotope ratios show an inverted peak, thus an N_2O interference is easy to recognize.

3.3 Repeatability

The peak area of 100 mL aliquots of Ref is ~ 4.6 Vs with a standard deviation of ~0.03 Vs, which corresponds to a relative repeatability of 0.7 % for the mole fraction on a single sample. $\delta^{13}C$ has a repeatability of 0.1 ‰. $\delta^{18}O$ has a repeatability of 0.2 ‰. System reproducibility is tested on a daily basis and often with overnight runs. When the system stays idle, at least five runs should be performed to regain its normal repeatability. Ref gas is measured often (several times per day) and all the samples are measured relative to the Ref, it is the repeatability on short term (hours to days) that is the most important.

3.4 Linearity

Ideally, the δ value of a sample measured on an isotope instrument versus a certain reference should be independent of the amount of sample that was injected into the instrument. In reality, isotope systems often show a dependence of the isotope results on the total amount of sample injected, which is commonly called a “non-linearity”. The non-linearity of our system was calibrated by injecting varying amounts of sample (for sample linearity) and He (for blank linearity) into the system.

3.4.1 Blank Linearity

A blank linearity test was performed to characterize the effect of the CO_2 released by the Schütze reagent. No sample was injected in these blank experiments. “Injection time” on the x axis of Fig. 4 depicts the period in seconds that the He flow was directed through the complete system (including the Schütze reagent). These injection times are 100 s, 300 s, 600 s, 900 s, 1200 s. Each injection time test was repeated four times. The peak area (area all) as a function of the injection times is shown in Fig. 4 (a). The injection time for a usual measurement is 300 s. The peak area for the blank for this injection time is ~0.1 Vs corresponding to about ~4 nmol mol^{-1}. Figure 4 (b) shows the dependence of $\delta^{13}C$ and $\delta^{18}O$ of the blank peak on the injection time. Since the various injection times lead to different peak areas, Figure 4b implicitly shows the dependence of $\delta^{13}C$ and $\delta^{18}O$ on peak areas from Fig. 4 (a). The blank areas increase roughly linearly in size with injection time, indicating constant accumulation of a trace contamination of CO_2. The δ values do not show a significant trend. The uncertainties of the average δ values for all the runs are ±1.3 ‰ and ±5.1 ‰ for $\delta^{13}C_{V\text{-}PDB}$ (-23.2 ‰) and $\delta^{18}O_{V\text{-}SMOW}$ (55.2 ‰) for these low peak areas.

3.4.2 Sample Linearity

The amount of sample was varied by changing the mole fraction of a sample with initial high mole fraction, by dilution with CO-free air. For the dilution test, 8 mL of high mole fraction (~269 µmol mol^{-1}) CO sample was injected into a 1 L glass flask, which was then filled with zero-air to 1.8 bars. A sequence of 59 measurements was made while the flask air pressure kept constant at 1.8 bar by refilling with zero-air after every run, which results in an extended dilution series. Figure 5 shows the $\delta^{13}C$ and $\delta^{18}O$ values as a function of area all (Vs). The $\delta^{13}C$ values are constant down to about 4 Vs and then start deviating systematically for the low peak areas (i.e. they become non-linear). The $\delta^{18}O$ values are relatively constant (with a small trend) for areas above 1.5 Vs (60 nmol mol^{-1}). The average $\delta^{13}C$ and $\delta^{18}O$ values in the peak area range between 4 and 15 Vs where samples are usually measured are -44.2±0.1 ‰ and 54.1±0.2 ‰ respectively. The small trend at higher peak areas visible in figure 5 in particular for $\delta^{18}O$ is not further investigated. Measurements over many months indicate that the area below which non-linearity is observed depends on the state of the filament in the IRMS. Therefore, the non-linearity is checked regularly.

3.5 Application Example: CO Emissions from Vehicles

As an application example, Fig 6 shows $\delta^{13}C$ and $\delta^{18}O$ values of air samples collected at the Islisberg highway tunnel in Switzerland that were presented and discussed in detail in (Popa et al., 2014). Air samples from the entrance and the exit of the tunnel were collected in 1 L glass flasks under ~1.8 bar pressure and analyzed on the analytical system described here for $\delta^{13}C$ and $\delta^{18}O$. The different color markers in Fig. 6 represent the samples from the entrance and the exit of the tunnel. The exit samples contain air that has accumulated emissions of vehicles passing through the tunnel; these samples have very high (2 – 10 ppm) CO mole fractions, and their isotopic values represent the isotopic signature for CO emitted by vehicles. The isotopic composition of the vehicle emissions based on these samples was $\delta^{13}C = -25.6\pm0.2$ ‰ and $\delta^{18}O = 24.1\pm0.2$ ‰ respectively (Popa et al., 2014). The air collected near the entrance is much closer to background air, but since the collection was actually in the tunnel, it is also influenced in varying proportions by the emissions of vehicles on the highway. These entrance data thus fall in between the CO isotopic signature of fossil fuel combustion and the isotopic composition of background atmospheric CO.

4 Conclusions

A new continuous flow-isotope ratio mass spectrometry system was presented allowing quick and precise measurement of CO mole fractions, $\delta^{13}C$ and $\delta^{18}O$. The technique is based on the conversion of CO in the sample to CO_2 using the Schütze reagent. Prior to the conversion of CO, CO_2 and N_2O are quantitatively removed from the sample by chemical and cryogenic traps. Helium is not only used as a carrier gas to transfer the sample from one component to another but also used for flushing the system. The repeatability for the mole fraction measurement is 0.7 nmol mol^{-1} for a reference air cylinder with a CO mole fraction of 185.4 nmol mol^{-1}. This corresponds to a relative error of 0.4 %. The CO_2 blank that originates from the Schütze reagent is minimized by continuously flushing the reagent with helium. The peak area of the system blank is ~4 nmol mol^{-1}, which is 2.2% of the peak area obtained with the reference air. The $\delta^{13}C$ and $\delta^{18}O$ repeatability are 0.1 ‰ and 0.2 ‰ respectively. The amount of air that is used for a single analysis is only 100 mL, but in the present configuration this has to be supplied from a sample container at a minimum pressure of 1550 mbar abs, so that the actual amount of sample air required is larger. A single measurement is completed in 18 minutes and the system is fully automated and well suited for measurements on air samples from flasks that are routinely employed in atmospheric monitoring networks. .

Acknowledgements

We acknowledge the assistance and the support of Michel Bolder, Henk Snellen, Marcel Portanger, Ulrike Dusek, John Mak, Ruwan A. Pathirana and C. A. M. Brenninkmeijer. This research was funded by the Marie Curie Initial training Network INTRAMIF (Initial Training Network in Mass Independent Fractionation) as part of the European Community's Seventh Framework Program (FP7/2007–2013), Grant 237890.

References

Brenninkmeijer, C. A. M.: Measurement of the abundance of ^{14}CO in the atmosphere and the ^{13}C/^{12}C and ^{18}O/^{16}O ratio of atmospheric CO with applications in New Zealand and Antarctica, J. Geophys. Res., 98(D6), 614,10510–10595, 1993.

Brenninkmeijer, C. A. M. and Röckmann, T.: Principal factors determining ratio of atmospheric CO as derived from observations in the southern hemispheric troposphere and lower statosphere, J. Geophys. Res., 102, 477–485, 1997.

Brenninkmeijer, C. A. M., Röckmann, T., Bräunlich, M., Jöckel, P. and Bergamaschi, P.: Review of progress in isotope studies of atmospheric carbon monoxide, Chemosphere-Global Chang. Sci., 1(1-3), 33–52, 1999.

Crutzen, P. and Zimmermann, P.: The changing photochemistry of the troposphere, Tellus B, 43 AB, 136–151, 1991.

Hartmann, D. L., Tank, A. M. G. K., Rusticucci, M., Alexander, L. V., Brönnimann, S., Charabi, Y., Dentener, F. J., Dlugokencky, E. J., Easterling, D. R., Kaplan, A., Soden, B. J., Thorne, P. W., Wild, M. and Zhai, P. M.: 2013: Observations: Atmosphere and Surface., in Climate Change 2013 - The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley, pp. 159–254, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, Cambridge., 2014.

Manning, M. R., Brenninkmeijer, C. A. M. and Allan, W.: Atmospheric carbon monoxide budget of the southern hemisphere: Implications of $^{13}C/^{12}C$ measurements, Geophys. Res., 102, 10673–10682, 1997.

Petrenko, V. V., Martinerie, P., Novelli, P., Etheridge, D. M., Levin, I., Wang, Z., Blunier, T., Chappellaz, J., Kaiser, J., Lang, P., Steele, L. P., Hammer, S., Mak, J., Langenfelds, R. L., Schwander, J., Severinghaus, J. P., Witrant, E., Petron, G., Battle, M. O., Forster, G., Sturges, W. T., Lamarque, J.-F., Steffen, K. and White, J. W. C.: A 60 yr record of atmospheric carbon monoxide reconstructed from Greenland firn air, Atmos. Chem. Phys., 13(15), 7567–7585, doi:10.5194/acp-13-7567-2013, 2013.

Popa, M. E., Vollmer, M. K., Jordan, A., Brand, W. A., Pathirana, S. L., Rothe, M. and Röckmann, T.: Vehicle emissions of greenhouse gases and related tracers from a tunnel study: CO : CO_2, N_2O : CO_2, CH_4 : CO_2, O_2 : CO_2 ratios, and the stable isotopes ^{13}C and ^{18}O in CO_2 and CO, Atmos. Chem. Phys., 14(4), 2105–2123, doi:10.5194/acp-14-2105-2014, 2014.

Röckmann, T.: Mass-Independent Oxygen Isotope Fractionation in Atmospheric CO as a Result of the Reaction CO + OH, Science (80-.)., 281(5376), 544–546, doi:10.1126/science.281.5376.544, 1998.

Röckmann, T. and Brenninkmeijer, C. A. M.: The error in conventionally reported $^{13}C/^{12}C$ ratio of atmospheric CO due to the presence of mass independent oxygen isotope enrichment, Geophys. Res. Lett., 25(16), 3163–3166, 1998.

Röckmann, T., Brenninkmeijer, C. A. M., Hahn, M. and Elansky, N. F.: CO mixing and isotope ratios across Russia; trans-Siberian railroad expedition TROICA 3, April 1997, Chemosph. - Glob. Chang. Sci., 1(1-3), 219–231, doi:10.1016/S1465-9972(99)00026-4, 1998.

Röckmann, T., Jöckel, P., Gros, V., Bräunlich, M., Possnert, G. and Brenninkmeijer, C.: Using ^{14}C, ^{13}C, ^{18}O and ^{17}O isotopic variations to provide insights into the high northern latitude surface CO inventory, Atmos. Chem. Phys, 2, 147–159, 2002.

Röckmann, T., Kaiser, J., Brenninkmeijer, C. A. M. and Brand, W. A.: Gas chromatography/isotope-ratio mass spectrometry method for high-precision position-dependent ^{15}N and ^{18}O measurements of atmospheric nitrous oxide., Rapid Commun. Mass Spectrom., 17(16), 1897–908, doi:10.1002/rcm.1132, 2003.

Schmeisser, M. and Brändle, K.: Oxides and Oxyfluorides of the Halogens, Adv. Inorg. Chem. Radiochem., 5, 41–89, doi:10.1016/S0065-2792(08)60152-1, 1963.

Schütze, M.: Ein neues Oxidationsmittel für die quantitative Überführung von Kohlenmonoxyd in Kohlendioxyd, Ein Beitrag zur Chemie des Jodpentoxids, Ber. Dtsch. Chem. Ges, 77b, 484–487, 1949.

Smiley, W. G.: Note on a reagent for oxidation of carbon monoxide, Nucl. Sci. Abstr, 3, 391, 1965.

Stevens, C. and Krout, L.: Method for the determination of the concentration and of the carbon and oxygen isotopic composition of atmosspheric carbon monoxide, Int. J. Mass Spectrom. Ion …, 60453(1972), 265–275, 1972.

Stevens, C. and Wagner, A.: The role of isotope fractionation effects in atmospheric chemistry, Zeitschrift für Naturforsch., 44a, 376–384, 1989.

Tarasova, O. A., Brenninkmeijer, C. A. M., Assonov, S. S., Elansky, N. F., Röckmann, T. and Sofiev, M. A.: Atmospheric CO along the Trans-Siberian Railroad and River Ob: Source identification using isotope analysis, J. Atmos. Chem., 57(2), 135–152, 2007.

Tsunogai, U., Hachisu, Y., Komatsu, D. D., Nakagawa, F., Gamo, T. and Akiyama, K.: An updated estimation of the stable carbon and oxygen isotopic compositions of automobile CO emissions, Atmos. Environ., 37(35), 4901–4910, doi:10.1016/j.atmosenv.2003.08.008, 2003.

Tsunogai, U., Nakagawa, F., Hachisu, Y. and Yoshida, N.: Stable carbon and oxygen isotopic analysis of carbon monoxide in natural waters, Rapid Commun. Mass Spectrom., 14(16), 1507–1512, doi:10.1002/1097-0231(20000830)14:16<1507::AID-RCM56>3.0.CO;2-E, 2000.

Tsunogai, U., Nakagawa, F., Komatsu, D. D. and Gamo, T.: Stable carbon and oxygen isotopic analysis of atmospheric carbon monoxide using continuous-flow isotope ratio MS by isotope ratio monitoring of CO, Anal. Chem., 74(22), 5695–5700, 2002.

Wang, Z., Chappellaz, J., Martinerie, P., Park, K., Petrenko, V., Witrant, E., Emmons, L. K., Blunier, T., Brenninkmeijer, C. a. M. and Mak, J. E.: The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950: implications for the CO budget, Atmos. Chem. Phys., 12(10), 4365–4377, doi:10.5194/acp-12-4365-2012, 2012.

Wang, Z. and Mak, J. E.: A new CF-IRMS system for quantifying stable isotopes of carbon monoxide from ice cores and small air samples, Atmos. Meas. Tech, 3, 1307, 2010.

Westberg, K., Cohen, N. and Wilson, K. W.: Carbon Monoxide: Its Role in Photochemical Smog Formation, Sci. , 171 (3975), 1013–1015, doi:10.1126/science.171.3975.1013, 1971.

Table 1: Peak area and isotopic composition of the reference gas, and an aliquot of the reference gas that was spiked with 2000 nmol mol^{-1} N_2O.

	Area All (Vs)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
Ref	4.43±0.03	6.6±0.1	-4.7±0.2
Ref + 2000 nmol mol^{-1} N_2O	4.45±0.03	6.6±0.1	-4.6±0.1

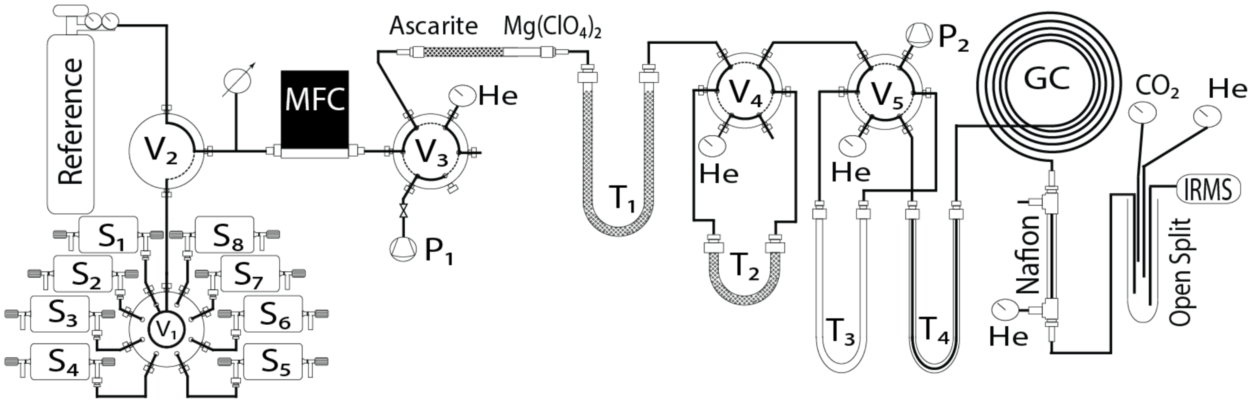

Figure 1: A diagram of the continuous flow-isotope ratio mass spectrometry system for measuring ^{13}C and ^{18}O of CO. S_1 to S_8 represent the sample flasks; the connections to the flask can be changed to accommodate other types of cylinders or cans. The multi-sample inlet system can be evacuated by a pump (P_1). V_1, V_2, V_3, V_4 and V_5 are Valco valves. The sample is admitted to the analytical system via a mass flow controller (MFC) and a six-port valve (V_3) and either sample gas or He carrier gas are processed through the system by a vacuum pump (P_2) at the outlet of the extraction system. T_1, T_2, T_3 and T_4 are the cryogenic trap filled with glass beads, the glass tube with Schütze regent, the collection trap to extract the CO_2 from CO, and the focus trap, respectively. Final separation of the CO-derived CO_2 is achieved on a gas chromatographic column (GC: Poraplot-Q, 25 m x 0.25)

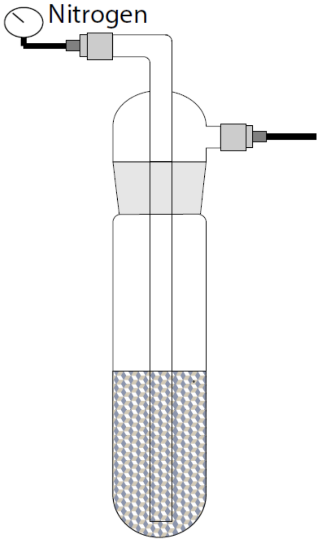

Figure 2: A diagram of the apparatus used for preparing the Schütze reagent. It is mounted in an oven and flushed with a slow continuous flow of nitrogen gas in order to dehydrate the iodine pentoxide coated silica-gel efficiently, while the temperature distribution is homogeneous.

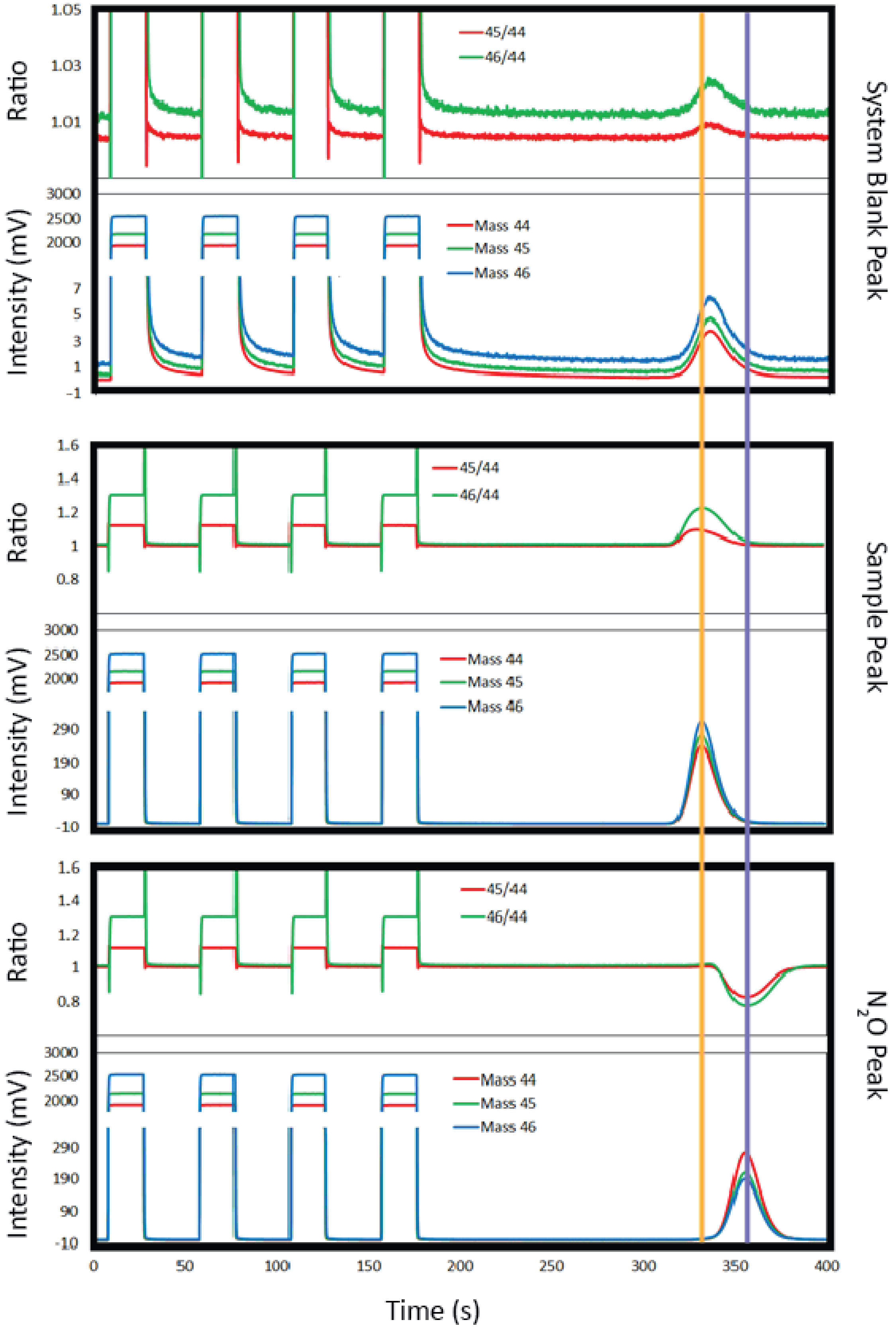
System Blank Peak
Ratio
1.05
1.03
1.01
45/44
46/44
Intensity (mV)
3000
2500
2000
7
5
3
1
-1
Mass 44
Mass 45
Mass 46
Sample Peak
Ratio
1.6
1.4
1.2
1
0.8
45/44
46/44
Intensity (mV)
3000
2500
2000
290
190
90
-10
Mass 44
Mass 45
Mass 46
N_2O Peak
Ratio
1.6
1.4
1.2
1
0.8
45/44
46/44
Intensity (mV)
3000
2500
2000
290
190
90
-10
Mass 44
Mass 45
Mass 46
0
50
100
150
200
250
300
350
400
Time (s)

Figure 3: A visual comparison of the system blank peak (top), the sample peak (middle) and the N_2O peak (bottom). During a normal measurement, N_2O is removed from the sample to avoid isobaric interference with the CO-derived CO_2 masses. As a further precaution N_2O and CO_2 are separated on the gas chromatograph where N_2O peaks at ~355 seconds compared to CO_2 peaking at ~330 seconds. The mass ratio 45/44 and 46/44 traces show inverted compared to the CO_2 and are easily recognizable. The absence of a N_2O signal shows that N_2O is quantitatively trapped in the cryogenic trap and does not reach the IRMS. The mass traces (44, 45 & 46) shown are direct output from the ISODAT software. For the ratios 45/44 & 46/44, a value of 100mV was arbitrarily added to the signals in order to avoid artificial noise arising from the ratio of two small numbers.

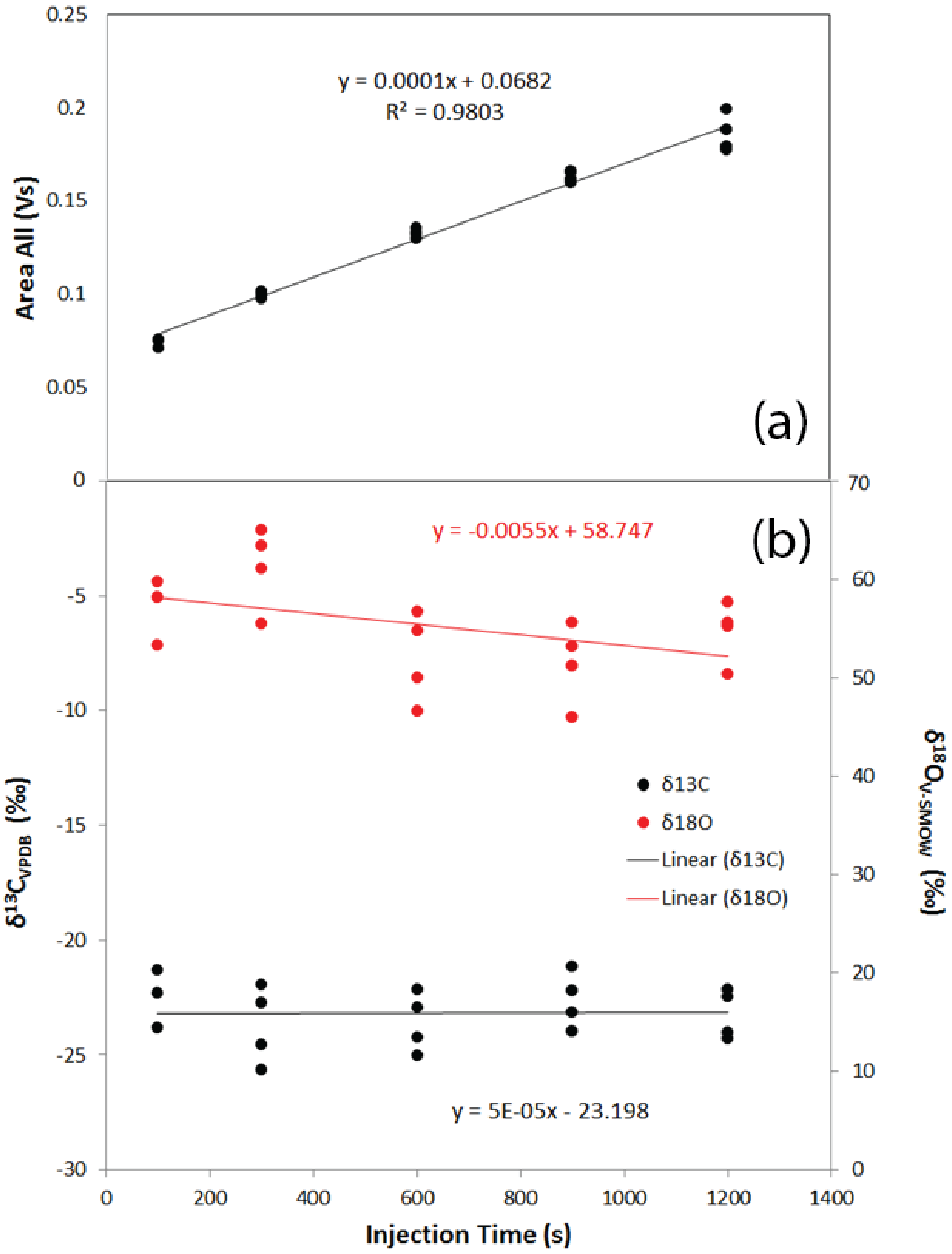

Figure 4: Dependence of the peak area all (a) and δ^{13}C and δ^{18}O (b) on the "injection time" for blank runs, i.e. when the sample inlet valve was actually not opened. The peak area of the blank increases approximately linearly with injection time, and the dependence of the isotope values on injection time is relatively small. Note that the scatter in the isotopic composition measurements is so large because of the very small peak areas of these blank experiments.

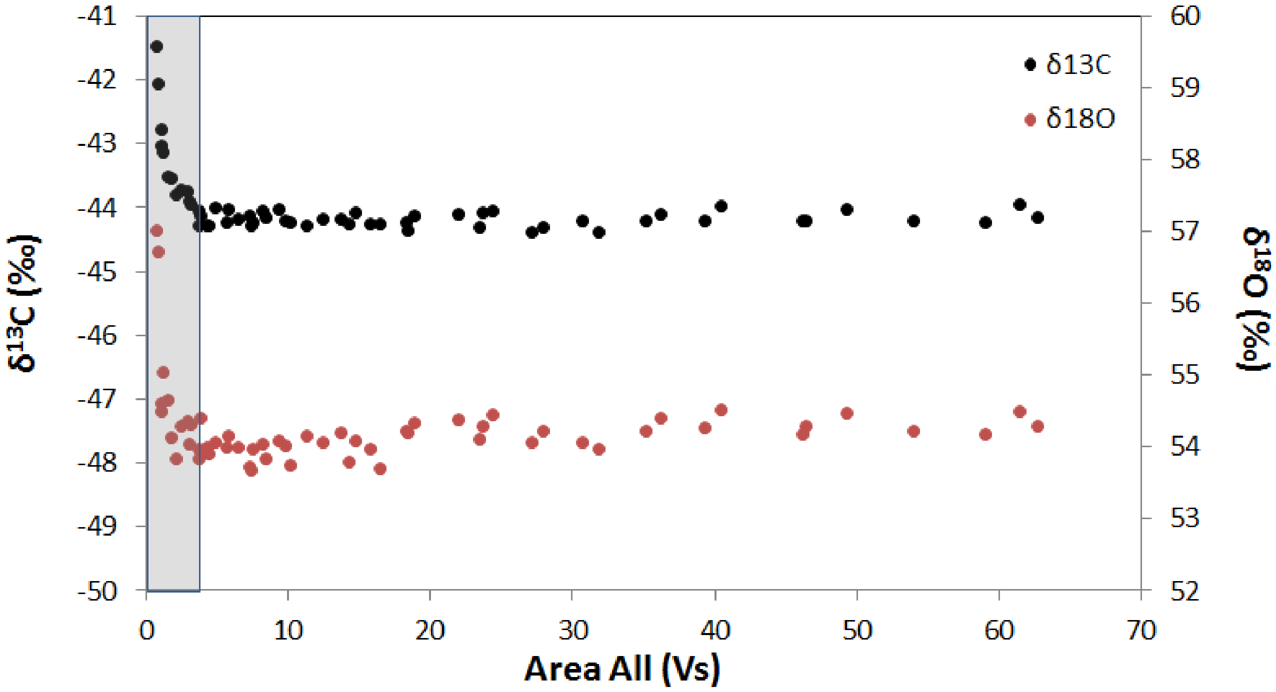

Figure 5: Dilution test: $\delta^{13}C_{V\text{-}PDB}$ (black) and $\delta^{18}O_{V\text{-}SMOW}$ (red) plotted against peak area (area all in Vs). The δ values show a strong non-linearity at peak areas below 4 Vs (shaded region). Values between 4 and 15 Vs are used to calculate the repeatability of the system.

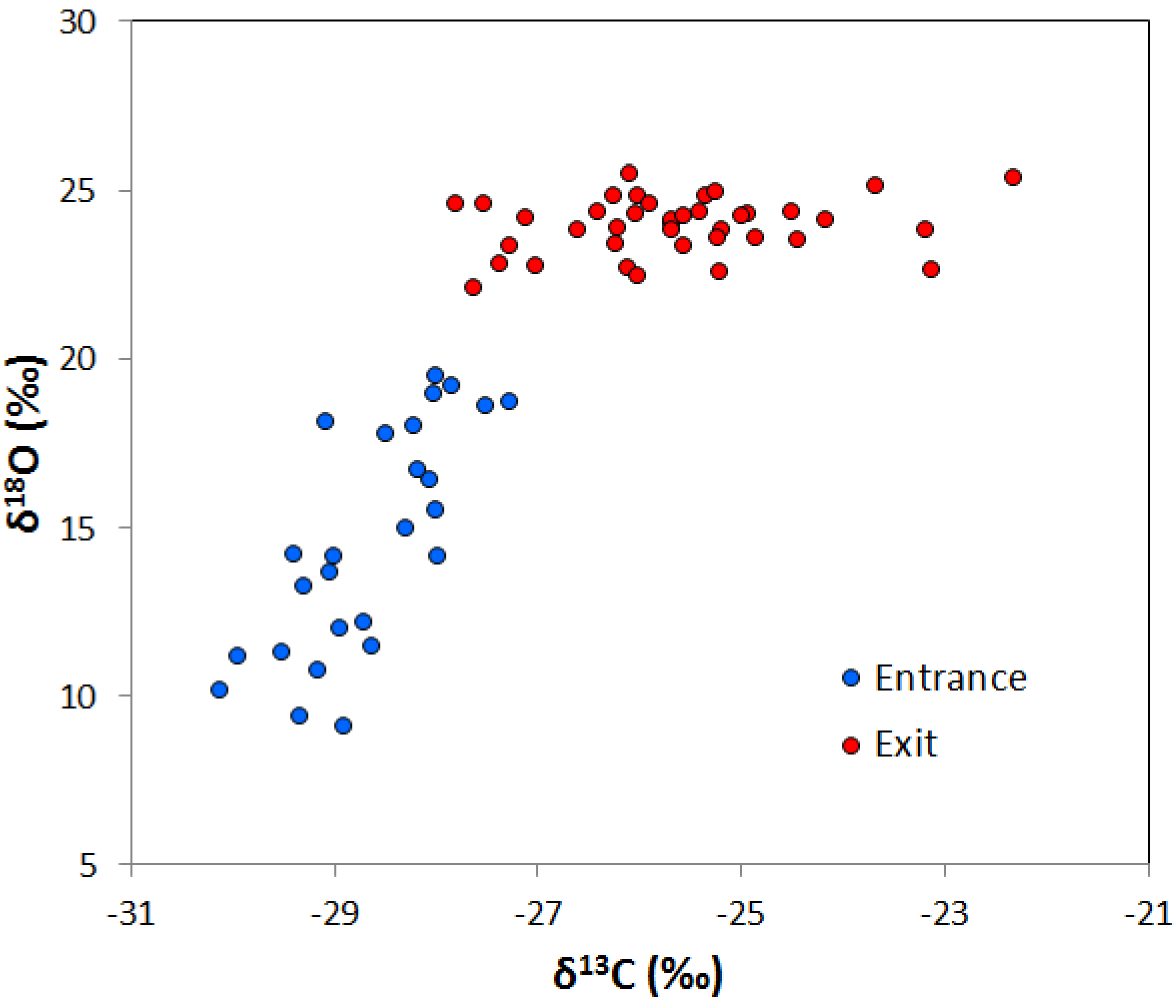

Figure 6: $\delta^{13}C_{V\text{-}PDB}$ (‰) versus $\delta^{18}O_{V\text{-}SMOW}$ (‰) plot of Islisberg highway tunnel samples. Data from Popa et al., (2014). The δ values of the samples collected at the entrance and exit are depicted by blue and red markers respectively.