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

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## Abstract

In the atmosphere, carbon monoxide (CO) is the major sink for the hydroxyl radical (OH $\cdot$ ), has multiple anthropogenic and natural sources and considerable spatial and seasonal variability. Measurements of CO isotopic composition are useful in constraining the strengths of its individual source and sink processes and thus its global cycle. A fully automated system for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  analysis has been developed to extract CO from an air sample, convert CO into carbon dioxide (CO $_2$ ) using the Schütze reagent, and then determine the isotopic composition 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 only 1–3 % of the typical sample size. The repeatability is 0.1‰ for  $\delta^{13}\text{C}$  and 0.2‰ for  $\delta^{18}\text{O}$ . The peak area allows simultaneous determination of the mole fraction with an analytical repeatability of  $\sim 0.7 \text{ nmol mol}^{-1}$  for 100 mL of typical ambient air (185.4 nmol mol $^{-1}$  of CO). A single, automated, measurement is performed in 18 min, so multiple measurements can be combined conveniently to improve precision.

## 1 Introduction

Carbon monoxide (CO) has an average mole fraction of only  $\sim 100 \text{ nmol mol}^{-1}$  (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 $\cdot$ ). 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 $\cdot$  (Röckmann et al., 2002). The reaction CO + OH $\cdot$  is not only the main sink for CO but also for OH $\cdot$ , with

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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<sub>x</sub> (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, <sup>12</sup>C, <sup>13</sup>C, <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>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 ( $\delta$ ) values are defined as relative isotopic enrichments of a sample to a reference.

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

The isotope ratio,  $R$ , is <sup>13</sup>C/<sup>12</sup>C in the case of carbon ( $\delta^{13}\text{C}$ ) and <sup>18</sup>O/<sup>16</sup>O for oxygen ( $\delta^{18}\text{O}$ ). For CO,  $\delta$  values for <sup>13</sup>C and <sup>18</sup>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  $\delta$  values are expressed in per mil (‰).

Precise measurements of CO mole fraction and isotopic composition are useful in constraining individual source and sink processes. The two independent quantities  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  represent a distinct isotopic signature for each individual CO source. CO from methane (CH<sub>4</sub>) oxidation is the most <sup>13</sup>C-depleted source, with  $\delta^{13}\text{C}$  values around -50‰ (Brenninkmeijer and Röckmann, 1997).  $\delta^{13}\text{C}$  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 of  $\delta^{13}\text{C}$  values,  $\delta^{18}\text{O}$  proves to be a better tracer. Carbon monoxide from vehicle emissions has the highest  $\delta^{18}\text{O}$  values, 24‰.

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(Popa et al., 2014) compared to 7–10% (Röckmann et al., 1998; Tarasova et al., 2007) for biomass burning and an assumed value of 0% (Brenninkmeijer and Röckmann, 1997) assumed for NMHC oxidation.

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  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of carbon monoxide. One uses the principle of conversion to carbon dioxide ( $\text{CO}_2$ ) and subsequent isotope analysis of  $\text{CO}_2$  (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  $\text{CO}_2$  has the advantage as high precision mass spectroscopy is often based on  $\text{CO}_2$  (Brenninkmeijer et al., 1999), which allows the possibility of using standardized techniques and isotope calibration scales. CO is converted to  $\text{CO}_2$  using an oxidizing agent, and if the isotopic composition of this oxidizing agent is constant, its effect on the isotopic composition of the  $\text{CO}_2$  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,  $\text{CO}^+$  ion currents at masses 28, 29 and 30 are monitored simultaneously (Tsunogai et al., 2002). Since CO is not converted to  $\text{CO}_2$ , there is no introduction of an additional oxygen atom that needs to be calibrated. However, this method presents some challenges when preparing CO standard gas with a known isotopic composition and extracting pure CO (Wang and Mak, 2010), as trace amounts of nitrogen ( $\text{N}_2$ ), possessing the same masses as CO, can interfere.

Current continuous flow-isotope ratio mass spectroscopy (CF-IRMS) techniques move towards faster methods, smaller sample sizes and most importantly precise and reproducible results. Rapid methods allow multiple measurements that can be in principle combined to improve precision. A method that requires a smaller sample volume

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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,  $^{13}\text{C}$  and  $^{18}\text{O}$  of CO in an air sample in less than 20 min. The method uses 100 mL of air and the sampling flask or bottle should have a minimum pressure of  $\sim 800$  mbar. The reproducibility and the precision are improved by significantly reducing the Schütze blank to 1–3 % of the sample size.

## 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  $\text{CO}_2$ , an open split system and an IRMS. The system is at all times flushed with ultra-high purity helium (He) with BIP<sup>®</sup> 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.

#### 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 (VICI, Product number: SD8MWE). The 3-port Switching Valve (VICI, Product number: 3UWE) after the sample multiport, provides the option to select either the reference gas bottle 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 (VICI, Product number: 6UWM) from where the gas can be either injected to the extraction system (position “1”) or evacuated (position “2”). This multi-sampling unit is controlled by LabView software, and 1/16 inch Restek Silcosteel<sup>®</sup> coated stainless steel tubing is used for connecting the individual components.

### 2.1.2 Extraction and conversion setup

By switching the injection valve, the sample is injected into the extraction system and directed through a chemical trap containing Ascarite<sup>™</sup> (CO<sub>2</sub> absorbent, 8–20 mesh, Aldrich) and Magnesium Perchlorate (Sigma-Aldrich), removing CO<sub>2</sub> and H<sub>2</sub>O respectively. The subsequent cryogenic trap (T<sub>1</sub>-3 mm ID, 6 mm OD, 62 cm length, glass), containing glass beads (US mesh 40–60), removes CO<sub>2</sub>, N<sub>2</sub>O and other condensable gases at liquid Nitrogen temperature (–196 °C).

CO is then selectively oxidized to CO<sub>2</sub> using the Schütze reagent (Schütze, 1949; Smiley, 1965) in T<sub>2</sub>. The oxidation reactor (T<sub>2</sub>) consists of a 10 cm length 6 mm OD glass tube and it is filled with 3 g 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 (VICI, Product number: C6UWM) and it is continuously flushed with He (flow rate ~ 8 mL min<sup>-1</sup>) 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<sub>2</sub>O<sub>5</sub>, 99.9%, Aldrich) was dissolved in 12.5 mL of water (Sigma-Aldrich, Product Number 270733) 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 h at 145 °C. Immediately out of the oven, 5 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was added to the mixture and the covered beaker was left overnight in the laboratory hood. This

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allows the  $\text{H}_2\text{SO}_4$  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  $220\text{ }^\circ\text{C}$  for 6 h or until the mixture was “dry”. The active chemical ( $\text{I}_2\text{O}_5$ ) 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:  $5\text{CO} + \text{I}_2\text{O}_5 \rightarrow 5\text{CO}_2 + \text{I}_2$ ) 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  $\text{CO}_2$ . 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  $\text{CO}_2$  blank is back to normal low levels (see Sect. 3.1).

### 2.1.4 Collection, focus and purification

The CO-derived  $\text{CO}_2$  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  $\text{CO}_2$  sample is then transferred to a focus trap ( $T_4$ ). In  $T_4$ , the  $320/430\text{ }\mu\text{m}$  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.

The sample is purified on a Poraplot-Q ( $25\text{ m} \times 0.25\text{ mm}$ ) gas chromatography column (at  $50\text{ }^\circ\text{C}$ ) and dried via a Nafion trap.

There are two membrane vacuum pumps attached to the setup; one to evacuate the multi-sample inlet line and the other one at the exhaust of the extraction, conversion and collection.

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.

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## 2.2 Data reduction 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 Sect. 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<sub>2</sub> derived from CO in a sample is analyzed by the mass spectrometer. The CO:CO<sub>2</sub> ratio is 1:1; in other words, every CO molecule is converted to a CO<sub>2</sub> molecule by adding an O atom from the Schütze reagent. Therefore the quantity (in moles) of CO is equal to the quantity of CO<sub>2</sub> derived from the CO in the air sample.

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

$$c_S = \frac{\text{Area All}_S}{\text{Area All}_R} \cdot \frac{f_R}{f_S} \cdot \frac{t_R}{t_S} \cdot c_R \quad (2)$$

where  $c_S$  is the mole fraction of the sample, Area All<sub>S</sub> is the area of the sample peak, Area All<sub>R</sub> 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  $\delta$  values of each peak in the chromatogram (both sample and reference air) vs. the laboratory working gas,  $\delta_{S \text{ vs. WG}}$  and  $\delta_{R \text{ vs. WG}}$  respectively. In our data reduction procedure, we first use these values to calculate the isotopic composition of the sample vs. the reference,  $\delta_{S \text{ vs. R}}$  according to

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

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

$$\delta_{S \text{ vs. } V} = \delta_{S \text{ vs. } R} + \delta_{R \text{ vs. } V} + \delta_{S \text{ vs. } R} \cdot \delta_{R \text{ vs. } V} \quad (4)$$

$\delta_{R \text{ vs. } V}$  is the  $\delta$  value of the reference air cylinder vs. the international standard.

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



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

$$\begin{aligned} \delta^{18}O_{S \text{ vs. } V:CO} &= 2\delta^{18}O_{S \text{ vs. } V:CO_2} - \delta^{18}O_{\text{Schütze Reagent}} \\ &= 2\delta^{18}O_{S \text{ vs. } V:CO_2} - \left(2\delta^{18}O_{R \text{ vs. } V:CO_2} - \delta^{18}O_{R \text{ vs. } V:CO}\right) \end{aligned} \quad (5)$$

In Eq. (5),  $\delta^{18}O_{S \text{ vs. } V:CO}$  is the  $\delta$  value of the sample vs. the international standard for CO,  $\delta^{18}O_{S \text{ vs. } V:CO_2}$  is the  $\delta$  value of the sample vs. 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  $\delta$  value of the reference vs. the international standard for  $CO_2$  ( $\delta^{18}O_{R \text{ vs. } V:CO_2}$ ) and the  $\delta$  value of the reference vs. the international standard for CO ( $\delta^{18}O_{R \text{ vs. } V:CO}$ ).

### 2.2.1 Mole fraction calibration

The mole fraction of the reference air bottle, Ref, was determined to be  $185.4 \text{ nmol mol}^{-1}$  and was measured at Max Plank Institute for Biochemistry (MPI-BGC) Jena in 2009.

## 2.2.2 Isotope calibration

The IMAU reference air bottle (Ref) was calibrated vs. the calibration gas cylinder (Cal) obtained from Carl Brenninkmeijer, Max Plank Institute for Chemistry, Mainz with a value of

$$\delta^{13}\text{C}_{\text{Cal vs. VPDB}} = -44.3\text{‰} \text{ (Brenninkmeijer, 1993) and}$$

$$\delta^{18}\text{O}_{\text{Cal vs. VPDB-CO}_2} = \delta^{18}\text{O}_{\text{DiCalCO vs. VPDB-CO}_2} = 11.43\text{‰} \text{ (Brenninkmeijer, 1993).}$$

$$\delta^{18}\text{O}_{\text{DiCalCO vs. V-SMOW}} = 53.45\text{‰}$$

The Cal bottle has a very high CO mixing ratio ( $269 \times 10^3 \text{ nmol mol}^{-1}$ ) and was diluted in a new cylinder, to a suitable mixing ratio ( $130 \text{ nmol mol}^{-1}$ ) 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 vs. the lab CO<sub>2</sub> working gas and the averages were used for calibration.

For  $\delta^{18}\text{O}$ , the correction regarding the oxygen atom from the Schütze reagent is done as shown below.

$$\delta^{18}\text{O}_{\text{R vs. V:CO}} = 2\delta^{18}\text{O}_{\text{R vs. V:CO}_2} - \delta^{18}\text{O}_{\text{Schütze Reagent}} \quad (6)$$

In Eq. (6), the  $\delta^{18}\text{O}$  of the sample ( $\delta^{18}\text{O}_{\text{R vs. V:CO}}$ ) is calculated by deducting the Schütze reagent oxygen ( $\delta^{18}\text{O}_{\text{Schütze Reagent}}$ ) from the CO derived CO<sub>2</sub> oxygen ( $\delta^{18}\text{O}_{\text{R vs. V:CO}_2}$ ). The Schütze reagent oxygen is derived by  $\delta^{18}\text{O}_{\text{Schütze Reagent}} = 2\delta^{18}\text{O}_{\text{DiCal vs. V:CO}_2} - \delta^{18}\text{O}_{\text{Cal vs. V:CO}}$ , where  $\delta^{18}\text{O}_{\text{DiCal vs. V:CO}_2}$  is the measured  $\delta^{18}\text{O}$  of CO<sub>2</sub> from DiCal CO and  $\delta^{18}\text{O}_{\text{Cal vs. V:CO}}$  is the known  $\delta^{18}\text{O}$  of Cal CO.

Following this calibration, the values of the reference gas (Ref) against the international standards were determined as  $-29.61 \pm 0.1 \text{‰}$  and  $8.45 \pm 0.2 \text{‰}$  for  $\delta^{13}\text{C}_{\text{V-PDB}}$  and  $\delta^{18}\text{O}_{\text{V-SMOW}}$  respectively. However there may be other systematic errors (e.g. temporal

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changes of the primary calibration cylinder or dilution artifacts), which may introduce an additional unspecified uncertainty to these values.

ISODAT software assumes mass dependent fractionation (MDF) when calculating the values. However, in nature the occurrence of mass independent fractionation (MIF) in atmospheric CO presents a  $\Delta^{17}\text{O}$  cycle with values ranging between 2.5 and 7.5‰ (Röckmann and Brenninkmeijer, 1998; Röckmann, 1998). This means when assuming MDF, the  $\text{CO}_2^+$  ion beam  $e/m = 45$  is underestimated leading to an overestimation in the  $\delta^{13}\text{C}$ . Röckmann and Brenninkmeijer (1998) calculated this overestimation (error) of  $\delta^{13}\text{C}$  to be 0.08–0.25‰ for a  $\Delta^{17}\text{O}$  range of 2.5–7.5‰. Since this method currently does not measure  $\delta^{17}\text{O}$ , we do not know the  $\Delta^{17}\text{O}$  of the samples. Therefore we report the  $\delta$  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 min. The peak area of this system blank is  $\sim 0.08$  Vs which is 1.8% of the average reference gas (Ref) peak area. When a blank run is done excluding the Schütze reagent trap, the peak has to be manually integrated and has an area of  $\sim 0.019$  Vs. The blank including the background  $\text{CO}_2$  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 and continuously flushing the Schütze reagent with helium reduced the blank to 1.8%. This blank affects both the sample and the reference air in a typical measurement sequence and is considered negligible when calculating the mole fractions and  $\delta$  values of a sample.

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## 3.2 Trapping of CO<sub>2</sub> and N<sub>2</sub>O

When the air sample is injected into the extraction system, CO<sub>2</sub> and nitrous oxide (N<sub>2</sub>O) must be completely removed. CO<sub>2</sub> in the sample must be removed as CO is converted to CO<sub>2</sub> for isotope analysis. N<sub>2</sub>O shares the same molecular mass as CO<sub>2</sub> and interferes with the CO<sub>2</sub> peak derived from CO on the chromatogram. CO<sub>2</sub> is largely and efficiently removed by the Ascarite trap and remaining traces are together with N<sub>2</sub>O condensed in the cryogenic trap (T<sub>1</sub>) with glass beads. The glass beads increase the surface area for condensation. T<sub>1</sub> is warmed and evacuated at the end of each run. Periodically checks are done to confirm that CO<sub>2</sub> and N<sub>2</sub>O traps work efficiently. This is done by bypassing the Schütze reagent so the CO is not converted to CO<sub>2</sub>. The result of such runs should be the same as a blank run without the Schütze reagent trap. If the result shows a CO<sub>2</sub> peak on the chromatogram then the Ascarite trap needs to be changed.

When measured vs. CO<sub>2</sub>, atmospheric N<sub>2</sub>O shows characteristic extremely depleted values for both apparent  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . Therefore a small amount of N<sub>2</sub>O seeping through the cryogenic trap could be easily detected. Table 1 shows a comparison of average values of ten runs from the reference gas (Ref) and ten runs from a bottle where 2000 nmol mol<sup>-1</sup> N<sub>2</sub>O was added to the reference gas (which already contained atmospheric levels of N<sub>2</sub>O). The results show that there is no evidence of N<sub>2</sub>O leaking from the cryogenic trap even at a high mole fraction. Figure 3 shows a case where the N<sub>2</sub>O peak appears on a chromatograph because the cryogenic trap is not used. The N<sub>2</sub>O retention time is about 25 s longer than the retention time of CO<sub>2</sub>, and the isotope ratios show an inverted peak, thus a N<sub>2</sub>O incomplete trapping problem is easy to recognize.

## 3.3 Repeatability

The average peak area of a 100 mL air sample with 185.4 nmol mol<sup>-1</sup> CO mole fraction is ~ 4.6 Vs with a SD of ~ 0.03 Vs, which translates to a repeatability of 0.7 % for the

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mole fraction determination on a single sample.  $\delta^{13}\text{C}$  has a repeatability of 0.1 ‰.  $\delta^{18}\text{O}$  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.

### 3.4 Linearity

Ideally, the  $\delta$  value of a sample measured on an isotope instrument vs. 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 understand the effect of the  $\text{CO}_2$  released by the Schütze reagent. No sample was injected in these blank experiments. “Injection time” on the  $x$  axis of Fig. 4 depicts the number of seconds the He flow was directed through the complete system (including the Schütze reagent). These injection times are 100, 300, 600, 900, 1200 s. Each injection time run was repeated four times. The peak area (area all) as a function of the injection times is shown in Fig. 4a. Figure 4b shows the dependence of the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values on the injection time, which is basically the dependence on peak area shown in Fig. 4a for very small areas. The blank increases roughly linearly in size as the injection times are increased, indicating constant accumulation of a trace contamination of  $\text{CO}_2$ . The  $\delta$  values do not show a significant trend. The uncertainties of the average  $\delta$  values for all the runs are  $\pm 1.3$  and  $\pm 5.1$  ‰ for  $\delta^{13}\text{C}_{\text{V-PDB}}$  ( $-23.2$  ‰) and  $\delta^{18}\text{O}_{\text{V-SMOW}}$  ( $55.2$  ‰) for these low peak areas.

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### 3.4.2 Sample linearity

The amount of sample was varied by changing the concentration of a sample with initial high concentration, by dilution with CO-free air. For the dilution test, 8 mL of high mole fraction ( $\sim 269 \mu\text{mol mol}^{-1}$ ) CO sample was injected into a 1 L glass flask and which was then filled with zero-air to 1.8 bar. 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. Figure 5 shows the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values as a function of area all (Vs). The  $\delta^{13}\text{C}$  values are constant down to about 4 Vs and then start deviating systematically in the low peak areas (i.e. they become non-linear). The  $\delta^{18}\text{O}$  values are relatively constant (with a small trend) for areas above 1.5 Vs. The average  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the linear data are  $-44.2 \pm 0.1 \text{‰}$  and  $54.1 \pm 0.2 \text{‰}$  respectively. Measurements 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.

### 3.4.3 Application example: CO emissions from vehicles

Samples collected at the Islisberg highway tunnel in Switzerland were measured for CO stable isotopic composition as a contribution to a larger project to find out the current vehicle emissions of greenhouse gases and related tracers (Popa et al., 2014). Air samples from the entrance and the exit of the tunnel were collected in glass flasks and analyzed at IMAU for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ .  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  results are shown in Fig. 6, with different color markers for the samples from the entrance and the exit of the tunnel. The exit samples contain air that has accumulated emissions of many vehicles passing through the tunnel; these samples have very high CO concentrations, and their isotopic values essentially represent the isotopic signature for CO emitted by vehicles. The reported (Popa et al., 2014) average values for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of vehicle emissions were  $-25.6 \pm 0.2 \text{‰}$  and  $24.1 \pm 0.2 \text{‰}$  respectively. The entrance data represents background air that has been influenced in varying proportions by the emissions of vehicles on the

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highway. These entrance data fall in between the CO isotopic fingerprint of fossil fuel combustion and the isotopic composition of background atmospheric CO.

## 4 Conclusions

A new continuous flow isotope ratio mass spectrometry method was presented allowing quick and precise measurement of CO mole fractions,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . It is based on the route of converting CO in the sample to  $\text{CO}_2$  to mainly avoid isobaric interferences from atmospheric  $\text{N}_2$ . Prior to the conversion of CO,  $\text{CO}_2$  and  $\text{N}_2\text{O}$  are completely removed from the sample injected. The oxidation of CO is done using the Schütze reagent. The  $\text{CO}_2$  blank, that Schütze reagent is known to produce, has been significantly reduced in this method by continuously flushing the reagent with helium. The repeatability is 0.7 % for the mole fraction determination on a single sample and the system blank is 0.08 Vs. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  repeatability values are 0.1 and 0.2 % respectively. A single measurement is completed in 18 min. This method requires only 100 mL of air and can be used for measuring air from the atmosphere, soil, firn air or ice cores.

*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.

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**Table 1.** Trapping Efficiency of N<sub>2</sub>O.

	Area All (Vs)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
Ref	4.43 ± 0.03	6.6 ± 0.1	-4.7 ± 0.2
Ref + 2 nmol mol <sup>-1</sup> N <sub>2</sub> O	4.45 ± 0.03	6.6 ± 0.1	-4.6 ± 0.1

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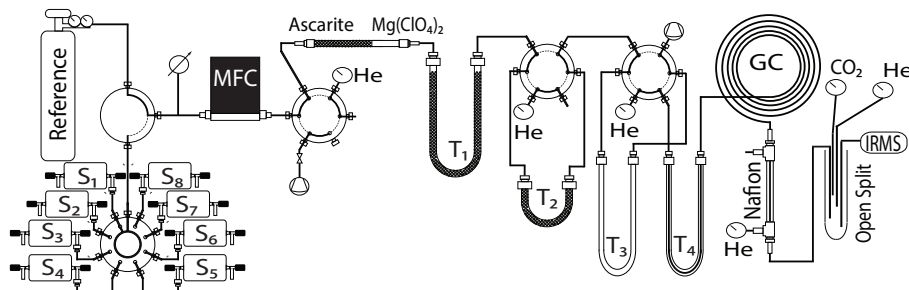
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**Figure 1.** A diagram of the continuous flow-isotope ratio mass spectroscopy method for measuring  $^{13}\text{C}$  and  $^{18}\text{O}$  of CO.  $S_1$  to  $S_8$  represent the sample flasks; the connections to the flask can be changed to accommodate other types of cylinders or cans.  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  are the cryogenic trap filled with glass beads, the glass tube with Schütze reagent, the collection trap, and the focus trap, respectively.

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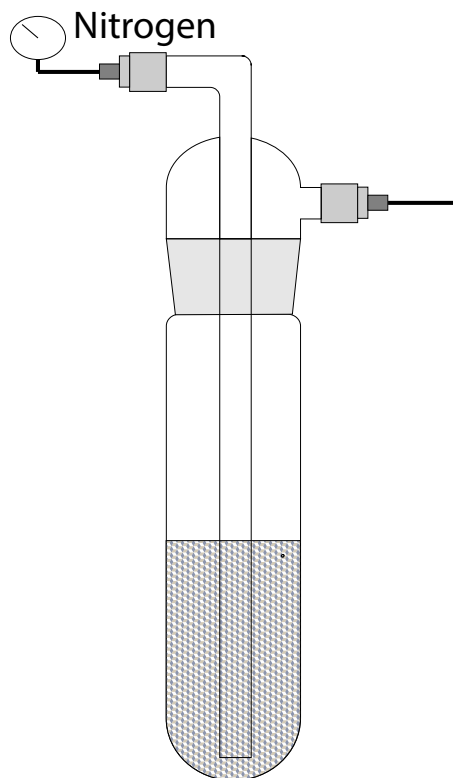
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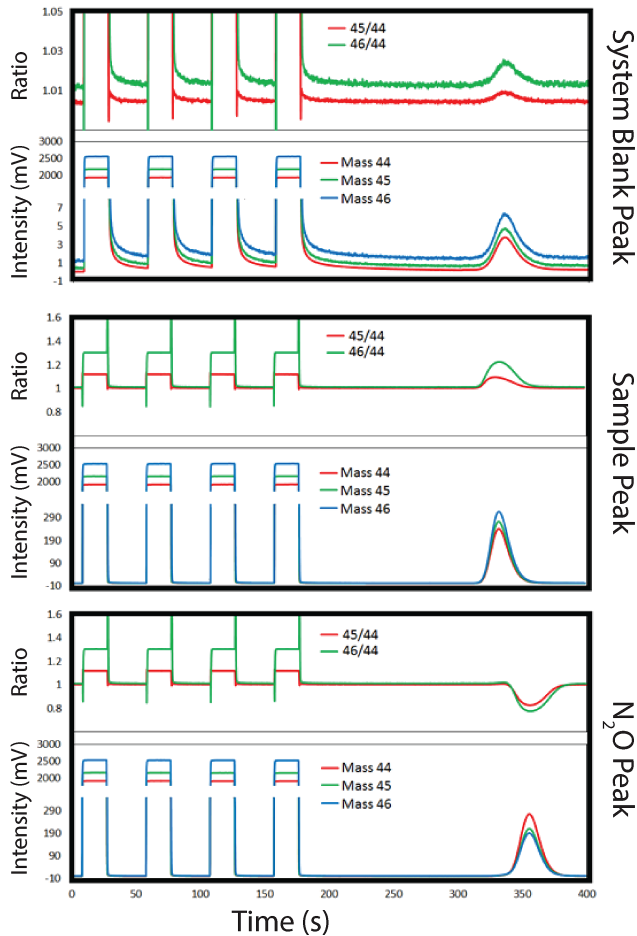


**Figure 2.** A diagram of the apparatus used for preparing the Schütze reagent. This apparatus is set up in the oven. The slow and continuous flow of nitrogen dehydrates the iodine pentoxide coated silica-gel efficiently and keeps the temperature distributed evenly.

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**Figure 3.** A visual comparison of the system blank peak, the sample peak and the N<sub>2</sub>O peak. The first chromatogram is a system blank run, the second is a sample run and the last shows a peak when N<sub>2</sub>O is not trapped during the extraction. During a normal measurement, N<sub>2</sub>O is removed from the sample to avoid its isobaric interference with the CO-derived CO<sub>2</sub> masses. N<sub>2</sub>O peaks at ~ 355 s compared to CO<sub>2</sub> peaking at ~ 330 s and the N<sub>2</sub>O peaks of mass ratios 45/44 and 46/44 are inverse compared to the CO<sub>2</sub> mass ratios. Also, for N<sub>2</sub>O, the 45/44 ratios are higher than the 46/44 ratios, in contrast to the CO<sub>2</sub> reference peaks where the 46/44 ratios are higher than the 45/44. If CO<sub>2</sub> in the sample is not properly trapped by Ascarite, it would be visible in the blank run. This shows that there is no N<sub>2</sub>O in the CO<sub>2</sub> sample (derived from the extracted CO) and that it is well trapped in the cryogenic trap, since its presence can be easily detected. The time and the masses (44, 45 and 46) were outputs from the ISODAT software and 45/44 and 46/44 were obtained by adding 100 to the masses before calculating the ratios.

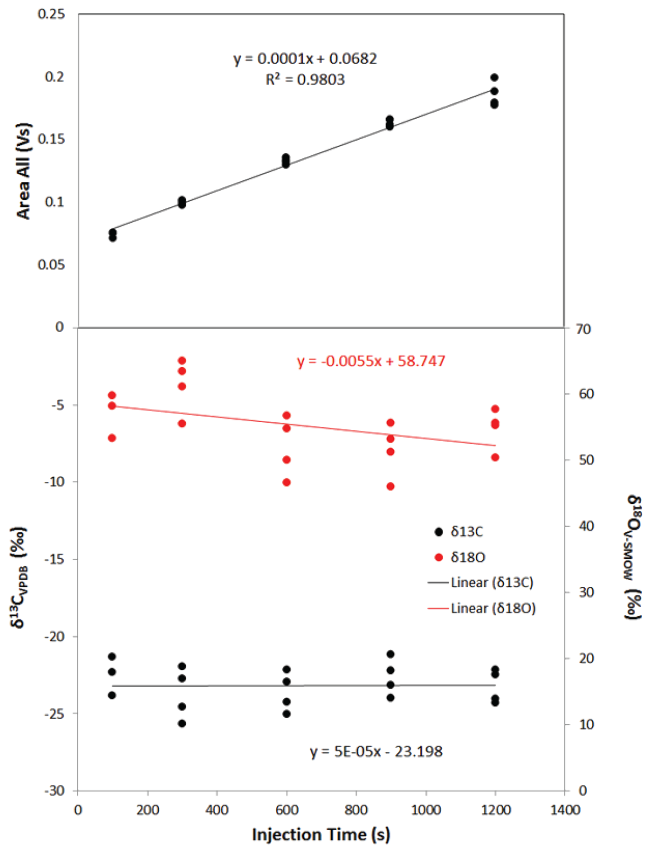
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**Figure 4.** Dependence of the peak area all **(a)** and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  **(b)** on the “injection time” for blank runs, i.e. when the sample inlet valve was actually not opened. The peak area of the blank increases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

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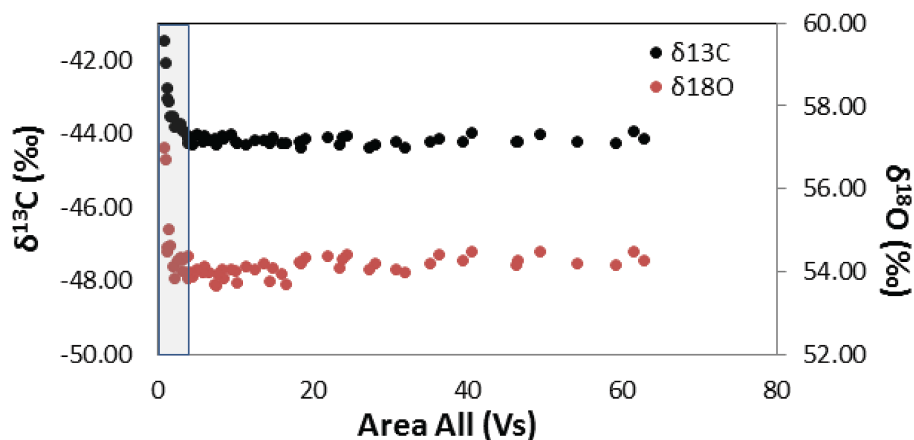
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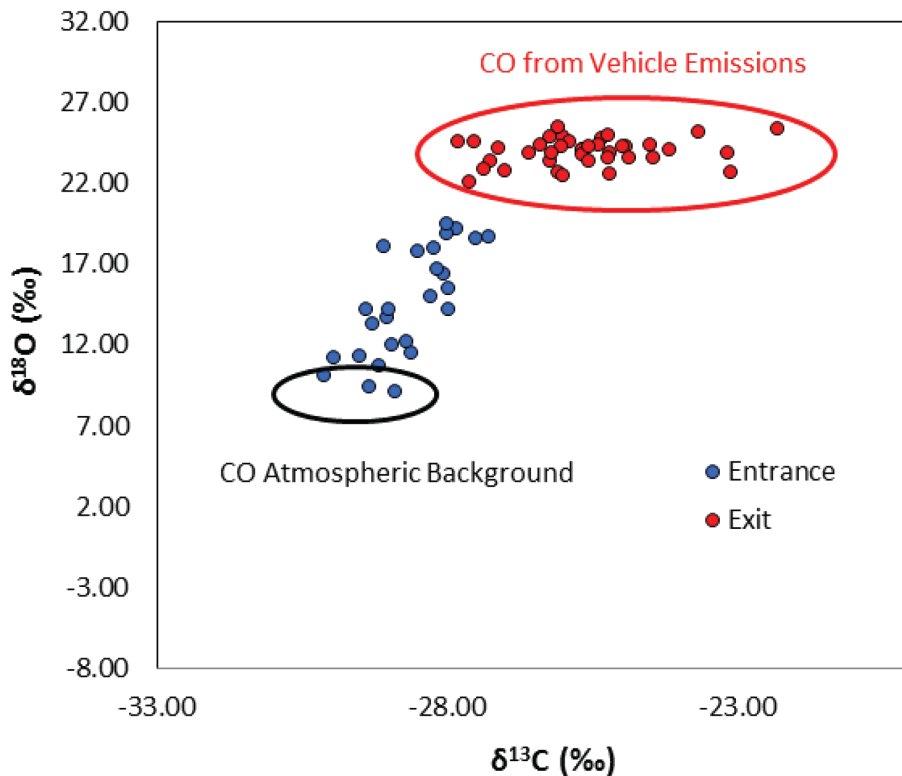
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**Figure 5.** Dilution test:  $\delta^{13}\text{C}_{\text{V-PDB}}$  (‰) and  $\delta^{18}\text{O}_{\text{V-SMOW}}$  (‰) plotted against area all (Vs). The black markers show the variation in  $\delta^{13}\text{C}$ -against peak area. The red markers show the variation in  $\delta^{18}\text{O}$  against peak area. The  $\delta$  values are non-linear at peak areas lower than 4 Vs (shaded region).

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**Figure 6.**  $\delta^{13}\text{C}_{\text{V-PDB}}$  (‰) vs.  $\delta^{18}\text{O}_{\text{V-SMOW}}$  (‰) plot of Islisberg highway tunnel samples. The  $\delta$  values of the samples collected at the entrance and exit are depicted by blue and red markers respectively. The entrance results fall in between the CO atmospheric background (black oval) and the vehicle emission signature (red oval) showing the mixing between the two reservoirs.

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