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Atmospheric Measurement Techniques
Discussions

Interactive comment on "An analytical system for studying the stable isotopes of carbon monoxide using continuous flow-isotope ratio mass spectrometry (CF-IRMS)" *by* S. L. Pathirana et al.

Anonymous Referee #2

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Summary of the manuscript

This paper presents a continuous-flow isotope ratio spectrometry system for measurements of carbon and oxygen isotopic ratios of carbon monoxide. The system requires 100 mL aliquot of air at ambient concentration level and it takes only 18 min for a single analysis. The measurement precision of the system is 0.7% for CO mole fraction, 0.1‰ for δ13C and 0.2‰ for δ18O. Performance of the system including blank and linearity tests is presented and examined using air samples collected at a highway tunnel.

General comments

Measurement of isotopic composition of atmospheric carbon monoxide requires high techniques and the system presented in this paper combines novel laboratory convenience and high precisions. This achievement is a high value to be shared in the research community. However, the manuscript has large room to improve, especially in that some essential and key descriptions are missing. I recommend that, when the text is much more enriched and information lacking is sufficiently fulfilled, publication of this manuscript in AMT should be considered. My major concerns are given below.

1. The best achievement in this study appears to be the short-time analysis and the small volume of air required, although the latter has been already achieved by Wang and Mak (2010). This could be more highlighted in the manuscript and preferably in introduction the authors might give what kind of solutions the achievement can provide in scientific viewpoint.
2. The authors can highlight and discuss what is new and advantages of the system compared to previously reported systems.
3. The authors might describe time procedures of every step exactly. Only the total measurement time (18 min) is given, but almost no information is available for specific processes. I think this is helpful information for readers. For instance, flow rate and time (plus trapping efficiency) determines how much amount of the target gas is processed in a trap.
4. Description of calibrations of both mole fraction and isotopic ratios is not given explicitly. Namely, the manuscript does not guide readers so that they can link the authors' reference gas ultimately to international standards. See specific comments.
5. Description of the measurement result (section 3) is far from complete. The section should be much more enriched. See specific comments.

Specific comments

P2068 L6: for δ13C and δ18O “analyses”

P2068 L13: I would delete “typical”, because 185.4 nmol mol-1 is an CO concentration that can be observed in an urban area (rather than at clean background sites) and, in such an area, it may not be easy to determine a representative value due to high variability. Remind that the authors mention to 100 nmol mol-1 at the beginning of the introduction.

P2068 L13: Here 0.7 nmol mol-1 is given, while 0.7% appears in the other places.

P2068 L13: a suggestion “An automated single measurement is performed only in 18 min, and the achieved time efficiency (and small volume of sample air) allows repetitive measurements practically.” In my opinion, the phrase “to improve precision” is misleading and I would leave it out. The multiple measurements do not improve precision (in a performance sense) of the measurement system, but improve standard error of the mean of measurements for one sample.

P2069 L27: a range of overlap “in” δ13C “signatures” – but the authors stated isotopic signatures are distinct in a few sentence before. It is unclear that which CO sources overlap in δ13C signatures.

P2070 L1: compared to 7–10‰ “for biomass burning (Röckmann et al., 1998; Tarasova et al., 2007)” and “an assumed value of 0‰ for NMHC oxidation (Brennikmeijer and Röckmann, 1997)”.

L2070 L2: What is assumed in assigning δ18O signature of CO from NMHC oxidation?

L2070 L14: “an” advantage “that mass spectrometry is based on CO2, which allows use of better standardized measurement techniques and calibration scales (Brenninkmeijer et al., 1999).” – I am not sure the position of the reference is correct (is the latter part of the sentence written in the paper?).

P2070 L26: “spectroscopy” to “spectrometry”, same for every place

P2070 L29: Same comment as that on P2068 L13.

P2071 L18 : Laboratory air intrudes in the lines when exchanging sample flasks. How is the laboratory air flushed or pumped away from the system?

P2072 L1: How high is the flow rate and how long is it kept at the flow rate?

P2072 L16: The authors might explain “Schütze blank” better – what it is, why it interfere the measurement, and why it is reduced by being flushed with He. How did you determine the He flow rate?

P2072 L20: Schütze reagent is probably commercially available. What is the advantage to produce it in your own laboratory? And is it a standard method in analyzing CO isotopes?

P2072 L21: purified water?

P2073 L3: How high is the N2 flow rate?

P2073 L12: “purification” is not a correct word. The sample is not “purified”, but the CO-derived CO2 is separated from the other residual component.

P2073 L20: Same as the comment on P2073 L12.

P2073 L20: The dehydration of sample air should be given in a separate sentence, because it is totally a different process from GC separation. For what purpose the Nafion dryer (“trap” is not a suitable word) is installed here? Where is the source of water in the upstream part?

P2073 L22: Here readers can understand the system is connected to vacuum pumps. As I commented on P2071 L18, this description could appear earlier, for instance in section 2.1 (before section 2.1.1), and the authors might write how and when the lines are evacuated.

P2073 L26: a custom-made open-split interface “(Röckmann et al., 2003)”. Here the authors might briefly describe how the open-split interface was modified and improved.

P2073 L28: The authors might describe how long does it take to process every step (extraction, conversion, collection of CO-derived CO2 and cryofocus). See general comment.

P2073 L28: Does the 18 min include the all process described from section 2.1.1 to 2.1.4? Then I would bring this sentence in section 2.1 (just before 2.1.1).

P2074 L1: I do not get what “reduction” means.

P2074 L8: It is the case if the conversion efficiency from CO to CO2 is 100P2074 L14: . . . the area of the sample peak “of signal m/z=44 on the mass spectrometer?” P2074 L17: I do not find the reason of this sentence. Does it mean that you set the sample and reference at the same flow for the same flow time when a sample to analyze is expected to be at an ambient mole fraction level? Are there any cases you set differently?

P2075 L5: . . .the international standard “VPDB or VSMOW” –to clarify the reason of the subscript “V”.

P2075 L7: CO2 “is generated” when the CO from sample air “is” oxidized by the Schütze reagent.

P2075 L13: Here readers may wonder how the last term can be obtained, because it is not measureable. The authors might mention to that it is described later.

P2075 L19: Almost no information on the calibration is given. The authors should mention to, for instance, the origin of air (when and where the air is pressurized into the bottle), size and material of the bottle, and the initial inner pressure. Such information might be given at the beginning of the section (where the reference air appears for the first time). Which method is used to analyze air in the cylinder and relative to what types of standards? On which scale is the mole fraction? Also, it is known that CO mole fraction in a cylinder could fluctuate during storage (e,g, Novelli et al. 2003, JGR). Did you make any experiments to examine stability of the reference air in the bottle? Otherwise accuracy of the mole fraction measurement would not be guaranteed, thinking that 5 years has passed already since the time of calibration.

Novelli et al. (2003), Reanalysis of tropospheric CO trends: Effects of the 1997–1998 wildfires,

J. Geophys. Res., 108, D15, 4464, doi:10.1029/2002JD003031.

P2076 L4: “values of”

P2076 L5: What is the gas (e.g. CO in synthetic air or nitrogen)? How is the Cal bottle labeled? The authors might give this information so that readers can match it to one of bottles listed in Brenninkmeijer (1993). At least I cannot find the match. Also, the authors should give at least briefly how the Cal gas was calibrated originally relative to what types of standard in the description so that you can clearly state your reference gas is ultimately referenced to VPDB. Is there any uncertainties given by Brenninkmeijer?

P2076 L8: The Cal bottle had been stored for 20+ years. Is it assumed that the gas stayed identical in CO isotopic ratios?

P2076 L9: How was this mole fraction determined?

P2076 L10: Is there any evidences to support this assumption? As described earlier, CO mole fraction in a cylinder could fluctuate, but isotopic ratios of CO could stay same?

P2076 L12: . . .vs. the lab CO2 working gas “using the present measurement system” and the averages were used for calibration, “by which isotopic ratios of CO in Ref is referenced to those in DiCal.”

P2076 L14: is done “in the same manner as equation (5):”

P2076 L24: “However, . . .” as suggested above, I would discuss possible uncertainties where relevant information is given.

P2077 L3: . . .when calculating “δ13C and δ18O values from measured m/z ratios 45/46 and 46/44.”

P2077 L4: “However, . . .” hard to understand this sentence and the following sentences. Might be better elaborated.

P2077 L7: “e/m” to “m/z”

P2077 L11: . . . “the δ13C and δ18O” values. . .

P2077 L16: The injection time “5 min” should be given earlier in section 2.1.1.

P2077 L16: peak area of m/z=44?

P2077 L18: I would delete “has to be manually integrated and”.

P2077 L22: . . . a 6-port Valco valve “to continuously flush” the Schütze reagent. . .

P2077 L22: What is the origin of CO2 when the Schütze reagent trap was not flushed by He? Does it mean that small amount of CO2 is generated in the trap with a compound contained in laboratory room air that could not be completely removed from the other parts of lines? If so, where is the “leaky” place? Otherwise any other explanations?

P2078 L1: Trapping (or removal) “efficiency” of CO2 and N2O

P2078 L9: the “CO2 and N2O traps” means both the Ascarite and T1 traps? Please clarify.

P2078 L10: What is the actual result? I suggest that this section should be rewritten so that readers can understand the trapping efficiency of the traps clearly. The blank tests show CO2 is not eluted from the traps and perhaps you might present difference between with and without the traps.

P2078 L18: The text tells 2000 nmol mol-1, while Table 1 gives 2 nmol mol-1. Please clarify, although the former is likely. How was this gas produced? “Adding 2000 nmol mol-1 N2O” sounds strange. For instance, “adding 2000 nmol N2O” is understandable. “nmol mol-1” represents mole fraction and the mole fraction of the product gas is determined by relative fractions of the two gases of mixture (namely the gas’s mole fraction should be between 2000 nmol mol-1 and ambient level that Ref has depending on fraction of mixture). Again, the authors should give the origin of the reference gas air, and the N2O mole fraction should be given preferably. If the reference gas was not calibrated for N2O, “approximately” 2000 nmol should be given.

P2078 L20: . . .the cryogenic trap “(T1)”. . . same for the other places

P2078 L20: What gas was analyzed for this experiment? The reference gas?

P2078 L26: The average peak area of a 100 mL “aliquot of Ref” is . . . Presenting the mole fraction is redundancy. The number of measurements (N=?) should be given. And the period of the measurements might be given to indicate longer-term reproducibility.

P2078 L27: . . ., which “is translated” to repeatability of 0.7P2079 L1: How were the repeatabilities of δ13C and δ18O determined? Elaborate clearly.

P2079 L2: This daily-basis test yielded the repeatability given in the previous sentences? Otherwise you might give result of this test (probably with larger number of measurements), which better represents reproducibility of the system?

P2079 L3: “After an idling period (how long is it?), at least 5 measurements are made to stabilize the system.” What is the difference of status of the system between the measurement and idling mode and what causes the worse reproducibility after an idling period?

P2079 L15: “the number of seconds” to “time in seconds”

P2079 L13: The “injection time” for usual measurements is 300s? This should be given somewhere in this paragraph and the peak area observed for this injection time corresponds to what amount (in nmol mol-1) of CO2 (or originally CO)?

P2079 L19: I do not get what the subsentence “which is basically. . .” means.

P2079 L21: Is the origin of the CO2 the Schütze reagent trap?

P2080 L4: Delete “and” after “glass flask”

L2080 L10: Please give how much mole fraction the 1.5 Vs corresponds to.

L2080 L10: The small decreasing trend is visible in Figure 5. Please discuss if it is significant or not.

L2080 L11: What is the “linear data”? I do not think this is a correct term. If there is a significant decreasing trend in δ18O measurements, the average would not make sense.

L2080 L14: It appears that the authors show data that have been already presented in a paper published from their group. This might not be against the journal's policy (please double-check), but it would be even preferable if any other dataset analyzed by the present system could be shown. Otherwise clearly state that the data presented is identical to those in Popa et al. (2014).

L2080 L14: Start a new section (3.5). This section does not give enough description so that readers can judge performance of the measurement system. Rigorous description of the data is lacking, which is, in my opinion, not allowed if the authors would like to convince readers for performance of the system. First, no data of CO mole fraction are presented. Readers cannot find whether the present system yield reasonable measurement result or not. This is also a reason why readers cannot identify which air samples are considered to be background. Second, quantitative discussion on the measured mole fraction and isotopic values is missing. Discuss whether the "background" values indeed represent clean air values by reviewing previously papers. Discuss whether the estimated isotopic signatures of vehicle's exhaust are in agreement with previous reports or whether they are new findings.

P2080 L16: I suggest to leave out words after "as a contribution to…".

P2080 L18: Please give size of the flasks and pressure at the sample collection.

P2080 L19: Were the CO mole fraction not analyzed? Otherwise the results should be given.

P2080 L21: Delete "many" if the authors cannot give anything quantitative (counts, frequency etc.)

P2080 L22: "very high CO concentrations" Please give the CO mole fraction explicitly (be quantitative). Change "concentration" to "mole fraction" to be consistent in the whole text.

P2080 L23: I do not get what "essentially" means. Please be quantitative and discuss in numbers.

P2080 L24: Move (Popa et al., 2014) to the end of the sentence.

P2080 L25: If the entrance air varied in CO mole fraction influenced by vehicles' emission, I would not consider that the air represents "background". And this "background" contradicts the following sentence in which the authors write that the entrance data are between "background" and "fossil fuel combustion" signatures.

P2081 L3: This section should be rewritten after revision of the whole manuscript.

P2081 L4: Insert "-" between "flow" and "isotope" to be consistent with other places. "method" to "system".

P2081 L8: Perhaps these compounds cannot be removed "completely", although the level of elution was lowered so that they negligibly interfere the measurement of the targets.

P2081 L9: "that" to "which"

P2081 L10: Delete "in this method"

P2081 L11: Please give how much nmol mol-1 the 0.7P2081 L11: I do not get what "on a single sample" means.

P2081 L12: Please give relative fraction of the blank with respect to the sample measurement with air at ambient CO mole fraction level.

P2081 L12: delete "values"

Figure 3 caption: Large part of the sentences (after "During a normal measurement, …), should be given in the text (in the second paragraph of section 3.2), not in caption.

Figure 6: How did you determine the position and the size of the ovals? Readers cannot judge the representativeness. Elaborate clearly in the text.

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