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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.
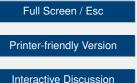
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Received and published: 29 June 2015

We thank the referee for the thorough and positive review of our manuscript and reply to the comments in detail below. Revised Manuscript is attached as a supplement.

1. Prior to introduce sample air into the line shown in Fig. 1, I think the authors should evacuate inside of the line, including the 8-port value, the 3-port valve, MFC, the 6-port valves, T1, T2, and T3, otherwise samples were contaminated by ambient air and/or residual previous sample in the line. The authors should describe the evacuation procedures (or the other procedures to avoid such contamination such as flushing

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by sample) prior to sample introduction, including the time needed for evacuation (or flushing), the final inner pressure prior to sample introduction (in case of evacuation), and sample volume needed for flushing (in case of flushing).

We do indeed evacuate and flush the system between different samples and have added the required information. We also include a description of the process of connecting samples and evacuating the connecting lines. The following paragraphs were added (page 6, from line 18 in the revised manuscript): When starting an automated measurement sequence, first the 8 samples are connected to V1 and V2 is set in the direction of the samples. Then V3 is set to "evacuation" position and the membrane pump valve is opened, allowing the air from the point of the sample connection to the V3 to be evacuated. Following this procedure each sample position of V1 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, V1 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 V3.

2. While the authors used the Valco valves (VICI products) under the vacuum condition, usual Valco valves are not so tight to air leakage under vacuum condition. The authors should present leak velocity of the line under the vacuum condition to justify the performance of their system.

We are aware that the Valco valves are not perfectly leak tight, but the combination of evacuation and flushing as described above assures that no mixing between samples takes place (also tested with very different samples). As soon as a sample is injected none of the Valco valves are under extreme vacuum conditions as there is a continuous He flow. The continuous He flow through the analytical system not only transports the

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sample air, but also flushes the system clean in between samples.

3. The authors used uniform flow rate for each sample as shown in equation (2). To maintain uniform flow rate from the beginning until the end of each sample injection, however, the authors should keep the inner pressure of sample bottle higher than the lowest limit needed to maintain the flow rate. Thus, sufficiently large volume may be needed for each sample bottle to be analyzed using this system. Besides, I guess it could be difficult to inject full volume in each sample bottle. This information is very important for field studies, such as to decide volume of bottles for sampling. The authors should present the details, including the flow rate setting of the mass flow controller, inner volume of sample bottle they used, initial and final inner pressure of sample bottle, and the time needed for each injection.

This is correct, and 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. This information was added to page 6 line 29 in the revised manuscript.

The other points:

1. (P2/L2-5) I don't think these general descriptions are essential in abstract. Should be deleted.

Deleted.

2. (P2/L10-13) "Typical sample size" and "typical ambient air" may be those of northern hemisphere. The CO-depleted southern hemispheric air is preferable to present the performance of new system.

We have specified that this relates to typical NH air (which we have focussed on in previous measurements). We note in the revised version that a higher flow rate or a longer injection time or a combination of a higher flow rate and longer injection time could be used for measuring samples with lower mixing ratios. At 50 ppb CO mixing ratio this will require about 300mL of sample to reach a comparable peak area.

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3. (P3/ L10) The relative blank level (1-3%) is a function of sample size. The absolute blank level is better to be presented, such as XXX pmol in YYY nmol sample size.

The system blank ranges between 8-23 pmol in a 0.7 nmol sample. This has been added to the manuscript (page 12 line 11).

4. (P3/ L25-P4/L1) Both d13C and d18O values of CO from modern vehicles including their 18O-enrichment relative to old ones were first reported by Japanese group (Tsunogai et al., Atm. Environ., 37, 4901-4910, 2003). The paper should be cited. Besides, as presented in their paper, 13C values of CO from modern fossil fuel combustion is higher than those in old reports (such as Stevens and Wagner, 1989), due to catalyst to remove CO from exhaust.

This has been added to the revised manuscript.

5. (P4/ L22-24) Preparing CO standard gas with a known isotopic composition is the issue not only for the direct method but also for those using Schütze reagent. Should be deleted.

Deleted.

6. (P5/ L18-P6/L19) While the authors presented that they developed "a fully automated system", they just mentioned "this multi-sampling unit is controlled by LabView software" for the automation and the other details of the automation were not presented. First of all, please clarify whether the other valves were automatic or not, including the valves of sample bottles. Besides, please specify the type the automatic valves used (air actuated? solenoid? or motor driven?). Furthermore, please specify the interface that must be essential to connect PC (installed with LabView software) and the valves. Finally, please clarify how to change the temperature of the traps T3 and T4 automatically.

As described in the additional information above, the sample connection and leak check is performed manually, but after that step the system is fully automated. The 16-

postion 8-port Dead-end Flowpath Selector, 3-port Switching Valve, 6-port 2-position Valve, flow rate of the mass flow controller and the 6-port 2-position Valve of the multi-sample unit are controlled by the LabView program. 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 (Page 6 Line 10). T1, T3, T4, the two 6-port 2-position Valves and the capillaries of the open-split are controlled by the ISODAT software (Page 8, Line 16). All the valves and the traps are air actuated and controlled by solenoids linked to the interface with IRMS (Page 8 Line 17). The interface that is essential for the communication between the valves and the PC is National Instruments USB NI-6008 unit (Page 6 Line 16). When T1, T3 and T4 in "down" position the traps acquire the temperature of liquid nitrogen ($\sim$-196 OC) and when the traps are in "up" position they warm up to room temperature ($\sim$25 OC) (added to Page 8, Line 11).

7. (P6/ L4) Better to use Restek Silicosteel for analyzing CO isotopes, instead of usual stainless steel, might be first proposed by Tsunogai et al. (2000). The authors should acknowledge the original here.

Acknowledged the original.

8. (P11/ L14-11) The blank levels determined by the authors might correspond to CO_2 quantities eluted from the reagent under vacuum condition. They could be different from CO_2 quantities eluted under the flow of air. As for the blank levels of the system, those during zero air analyses should be used.

Blank levels are not measured under vacuum conditions but under a normal He flow though the system (but without adding sample air through it). It is true that therefore the pressure may be slightly lower than during a sample run, but it is definitely not under vacuum conditions. It is one of the important characteristics of our system that it is always under a gas flow.

9. (P14/L7, Figures 4 and 5) While the authors presented each data as a function of

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output (area) in MS, the area will change depending on the condition and performance of MS and its open split interface. To present performance of the injection system comparable to the other systems, the authors should present each data as a function of CO (CO_2) quantity (e.g. XXX pmol).

For the reasons mentioned by the referee, we actually prefer showing the data as a function of the peak area. The same peak area may be achieved with different quantities of CO, by changing the split ratio or the sensitivity of the IRMS, as the referee mentions. If the non-linearity is due to effects in the IRMS, the relevant quantity is the peak area, not the total amount of sample CO. If the non-linearity comes from a blank, its contribution will depend on the total amount of sample. And there are other factors (incomplete trapping, etc) that will affect both parameters differently. We prefer to show the non-linearity as function of peak area, and this is also used in other publications.

10. (P14/L14- P15/L2 and Fig. 6) To support the entrance data really represented background air that has been influenced in varying proportions by the emissions of vehicles on the highway, please plot the isotopic compositions as a function of CO concentration. Besides, please estimate the end member d13C and d18O values.

We show these data mainly as an evaluation of the system. The scientific interpretation of the data as suggested by the referee is performed in Popa et al. 2014, where the suggested figure (isotopic composition as a function of mole fraction) is actually presented and discussed.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/8/C1733/2015/amtd-8-C1733-2015-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 2067, 2015.

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