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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 #1

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This is an important paper that reports analytical system for both concentration and stable isotopic compositions (d13C and d18O) of CO. The system is mostly fair and reliable except for some problems shown later. Although similar analytical systems that convert CO to CO2 using Schütze reagent and introduce CO2 to CF-IRMS had already been developed more than 10 years ago (Mak and Yang, Anal. Chem., 1998; Tsunogai et al., RCM, 2000; Wang and Mak, 2010), this new system is much better than the old ones. While performances of the old systems were limited by blank CO2 eluted from Schütze reagent (Tsunogai et al., 2000), the authors succeeded to reduce the blank size less than a few percent during the measurement of background northern

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hemispheric air samples. Besides, they also reduced the time needed for analyses as well. I think the paper is worth publication in AMT if the authors can properly address the issues shown bellow.

The sample injection and purification processes shown in Sections 2.1.1 and 2.1.2 are important points to determine the performance of this system. Following important descriptions, however, were missing in the manuscript and should be added:

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 contaminationïijÑsuch as flushing 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).

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.

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,

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and the time needed for each injection.

The other points are listed bellow:

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

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.

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.

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.

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

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and T4 automatically.

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.

8. (P11/ L14-11) The blank levels determined by the authors might correspond to CO2 quantities eluted from the reagent under vacuum condition. They could be different from CO2 quantities eluted under the flow of air. As for the blank levels of the system, those during zero air analyses should be used.

9. (P14/L7, Figures 4 and 5) While the authors presented each data as a function of 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 (CO2) quantity (e.g. XXX pmol).

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.

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