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Atmospheric Measurement Techniques Discussions

Interactive comment on "H_2S interference on CO_2 isotopic measurements using a Picarro G1101-i cavity ring-down spectrometer" *by* K. Malowany et al.

K. Malowany et al.

kalina.malowany@mail.mcgill.ca

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We found the comments presented by Refere#1 were very constructive and would like to thank the reviewer for their examination of the manuscript. We have attempted to address the key points raised by the reviewer and to provide adequate solutions to their concerns.

General Comments:

The first general comment indicated the need to clarify how the H2S concentrations were measured. For all the experiments, this was based upon the dilution of an aliquot

of an H2S gas from a prepared cylinder with a concentration of 100 ppm into 1 L of certified 995 ppm (±20 ppm) CO2. The H2S aliquot was taken with a syringe accurate to ±0.05 mL and the CO2 volume was measured by flowmeter at a rate of 500 mL/min (± 10 mL/min). Dilution calculations estimated the amount of H2S present in the samples and are accurate to ±5 ppb, whereas the CO2 concentrations were measured by the CRDS after the removal of H2S using the copper scrub. For H2S concentrations between 1 and 100 ppb, there was an additional dilution step, where the H2S gas was first diluted to 1 ppm before being added to the 995 ppm CO2 gas. This allowed us to add measureable amounts of H2S to the gas bags, however, it also resulted in increased dilution of the CO2 for the samples run with H2S concentrations of 1 – 100 ppb. In the second suite of gas mixtures, the CO2 concentrations were prepared first from a cylinder of certified 100% CO2 by dilution with CO2 –scrubbed air. Then an aliquot of the 100 ppm H2S gas added with the same uncertainties as the previous gas mixtures.

Clarification on the copper grade and type were requested by the reviewer and have now been added to the manuscript. In order to remove the H2S from the gas samples effectively before analysis with the CRDS, we reacted the gas sample with a copper tube filled with copper filings. This tube is a 10 cm long utility grade copper tube with an outer diameter of 9.6 mm and an inner diameter of 7.5 mm filled with CHEM.57B copper filings which contain up to 10% metal impurities. These materials are easily acquired and the copper grade appears to be sufficient for scrubbing of large H2S concentrations. The filings are necessary to provide large surface area for reaction with H2S. Trials with only the copper tube did not remove all H2S.

Concern about the interference resulting from the water produced during the reaction of H2S with Cu was brought up. The reaction of H2S produced water vapour, but the concentrations were not significant to the overall correction factor. We use the built-in water vapour correction to correct for variable water concentrations in each sample (Rella et al.2013). Water concentrations are below 2% volume H2O in all samples, thus the instrument correction factor remains valid at these concentrations such that the dry mol fraction of CO2 is maintained within the Global Atmospheric Watch limits of ±0.1 ppm. This clarification has been added to the manuscript.

The reviewer commented that methane concentrations were not reported for this study and should be considered. Methane concentrations were monitored during each run for concentrations which would cause significant changes to the isotopic value using the sensitivity value of 0.42±0.024‰ ppm-1 of methane (Vogel et al. 2013). CRDS reported CH4 levels were constant at 3.86 ±0.21 ppm for all runs with the 995 ppm CO2 standard, and were much lower for samples run with the 100% CO2 standard (1.65 ± 0.1 ppm CH4). Overall, variability in the methane concentration is negligible during all runs with a given standard allowing for comparison of results; however comparison of the runs using different CO2 standard gases is not advised due to the different methane levels contained therein. This information has been added to the manuscript for future reference.

It was also pointed out that the abstract states that OCS and/or CS2 is produced, however, no proof of this is given. We did not measure the CS2 and OCS directly. The reason for suggesting their reaction is due to the clear consumption of CO2 after reaction with H2S independent of the copper scrub. There is some reaction which consumes CO2 and since both gases are diluted with air, the reaction is likely due to the presence of H2S or another sulfur compound. However, I have now checked the reaction rates to form OCS and CS2, and they require temperatures in the range of 300 - 900°C for the spontaneous formation from CO and S. There are secondary reactions between SO2, C and O2 at high humidity and ambient temperatures which can produce S, H2S and CS2 (Fern, 1957). However, decomposition of CS2 is prevalent at atmospheric conditions in the presence of oxygen and water. This reaction may also produce OCS as CS2 is oxidized. Unfortunately it is difficult to tell if either of these products is produced or if there is another intermediate which is consuming CO2 in the presence of H2S. The production of OCS and CS2 is perhaps a bit overstated in

the previous version of the manuscript, so we will suggest more broadly that there is a reaction which consumes minor amounts of CO2, however, since the products of the mixture were not analyzed we cannot tell what the potential reaction may be.

Specific comments; *Some of the specific comments are addressed in the general comments section above.

Comment: Add information about the typical time delay between filling and analysis of the Tedlar bags.

Response: The gas was prepared in Tedlar bags and then analyzed with the CRDS within 10 minutes of preparation.

Comment: What is the uncertainty of the concentration of the air standard used, and who provided it?

Response: The standard CO2 gas of 995 ppm (±20 ppm) was provided by Praxair and certified according by FTIR with reference to the NOAA X2007 CO2 international standard. It has an isotopic composition of -28.5‰ relative to Vienna Pee Dee Belemnite (VPDB).

Comment: The so called background concentrations are well above typical atmospheric values and also clearly depleted in d13C. The test presented in Figure 2 seems to indicate strong temporal variations of the background air. Could this be room air rather than background air?

Response: The temporal variations observed in the background concentration from Figure 2 reflect the changes in the lab air due to human respiration. The instrument was exposed to lab air in between each analysis, therefore we have changed the term “background air” to “lab air” to eliminate confusion for the reader.

Comment: Is there really a decrease of 50% for 13CO2 in the gas or is this indeed an apparent decrease (i.e. a decreased in the 13CO2 value reported by the Picarro measurement).

Response: We reference an apparent decrease in 13CO2 measured by the Picarro instrument with the addition of H2S which is a result of the spectral overlap of the H2S with CO2 in the near-infrared. We know this because we have compared the CRDS measurement of a gas sample containing H2S to the same sample after it has be scrubbed of H2S, thereby removing the spectral overlap of CO2 and H2S. A real decrease in CO2 concentration may have resulted due to unanticipated compound reaction, but then it would affect both the sample containing H2S, and the sample measurement after H2S was removed. Real concentration changes in CO2 are known by the large difference between the predicted dilution of CO2, and that measured after H2S had been removed. This is the cause for proposing a reaction which consumes CO2.

References: Ferm, Robert J. "The chemistry of carbonyl sulfide." Chemical Reviews 57.4 (1957): 621-640.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 5651, 2015.