

Interactive
Comment

Interactive comment on “H₂S interference on CO₂ 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

Received and published: 14 September 2015

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



[Interactive
Comment](#)

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,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

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 $0.42 \pm 0.024\%$ 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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

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).

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Response: We reference an apparent decrease in $^{13}\text{CO}_2$ measured by the Picarro instrument with the addition of H_2S which is a result of the spectral overlap of the H_2S with CO_2 in the near-infrared. We know this because we have compared the CRDS measurement of a gas sample containing H_2S to the same sample after it has been scrubbed of H_2S , thereby removing the spectral overlap of CO_2 and H_2S . A real decrease in CO_2 concentration may have resulted due to unanticipated compound reaction, but then it would affect both the sample containing H_2S , and the sample measurement after H_2S was removed. Real concentration changes in CO_2 are known by the large difference between the predicted dilution of CO_2 , and that measured after H_2S had been removed. This is the cause for proposing a reaction which consumes CO_2 .

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.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)