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Interactive comment on “H₂S interference on CO₂ isotopic measurements using a Picarro G1101-i cavity ring-down spectrometer” by K. Malowany et al.

Anonymous Referee #1

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Review of Malowany et al. 2015 – AMT(D) Summary: The manuscript: "H₂S interference on CO₂ isotopic measurements using a Picarro G1101-I cavity ring-down spectrometer" is a well-presented and fluent description of laboratory tests to characterise the impact of H₂S concentrations on the continuous monitoring of d13C in CO₂. The authors nicely describe the scientific background and the need for this type of measurement. Afterwards different, well-designed laboratory tests are performed and the results are presented in a clear manner. The experiments include, among others, cross-sensitivity tests for a large range of H₂S concentrations as well as studies on the dependency of this effect on the measured CO₂ levels. This study furthermore sug-

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Interactive Discussion

Discussion Paper



Interactive
Comment

gests chemical reactions to explain their finding of reduced CO₂ concentrations when adding H₂S to their CO₂ standard. They interpret their results and make suggestions for the future use of the technology in field measurements.

General comments: The findings of this study are undoubtedly crucial for the field of monitoring volcanic CO₂ using G1101 instruments. The tests performed seem well-suited to derive cross-sensitivities and the effect of H₂S is very apparent. This study could be highly valuable for the community, but the description of the work done here unfortunately lacks crucial information to be the basis for this. A major point to clarify is how are the H₂S concentrations measured in these experiments? Is the H₂S value in the Tedlar bags measured or is this based on a calculation? If so, how was the H₂S concentration calculated and what are the typical uncertainties of the measured/calculated H₂S concentrations. Overall the study lacks a critical assessment of uncertainties, both instrumental and procedural. For a key paper in the field (as this one should be) it also lacks important experimental information. What quality and quantity of copper was used in the scrubber - what type (mesh, packed beads, etc.) was in the 10cm tube and what was its diameter, etc. ? According to the suggested reactions of H₂S with CO₂ and H₂S with Co the experiments did produce water vapour – thus the water vapour correction of the G1101i becomes relevant. Please clarify if you are using the factory built-in water vapour correction or if you have determined your own instrument specific correction factors as suggested in previous studies; see e.g. <http://www.atmos-meas-tech-discuss.net/8/4219/2015/amtd-8-4219-2015.html> Another major point is that the known cross-sensitivity of d¹³C in the G1101i to CH₄ levels is not addressed – if this is not a factor (i.e. CH₄ levels are the same during all experiments) this still needs to be considered/ruled out (see e.g. <http://www.atmos-meas-tech.net/6/301/2013/amt-6-301-2013.html>) The abstract furthermore states that OCS and/or CS₂ is produced – however, no proof of this is given. Was the sample gas ever measured for its OCS or CS₂ content? The given reactions could explain the formation of those gases stoichiometrically, but no additional information e.g. reaction rates are given.

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Interactive Discussion

Discussion Paper



Those shortcomings need to be addressed prior to a publication in AMT. However, the importance and impact of these findings for the field of volcanic monitoring are significant and the scope of this study is an excellent fit for AMT. So I would suggest considering the publication after the aforementioned corrections are made. Best regards, Felix Vogel

Specific comments: 5652 Line 14 following: You state that the experiments reveal that OCS and CS2 is formed in the reaction of H₂S and CO₂. This is well possible but no proof of this is given in this paper. Please add information if you conducted an analysis that confirmed the presence of those gases or make a model calculation using the known reaction rates and given concentrations to show that this is feasible. 5654 Line 12 following: You correctly identified the problem that using teflar bags is not ideal and you mitigated this problem by “immediately” processing. Adding the information about the typical delay time between filling and analysis is potentially useful here. 5655 Line 1 following: How where those gas mixtures prepared? As the authors identify the potential impact of sample dilution and chemical reaction in this study it is indispensable to be clear how the mixture was prepared. How where the concentrations (H₂S, OCS, CS₂) measured and what are the uncertainties in the mixture compositions. 5655 Line 1: It would be important to also know the uncertainty of the concentration of the air standard used and who provided it. As it is labelled as a standard, can we assume it is calibrated against the NOAA X2007 scale or a national metrology laboratory recognised by BIPM? 5655 line 20: 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. Could this be room air rather than background air? 5656 Line 14 It would be crucial to be precise on the copper scrubber here. How much copper was used? (10cm length is not sufficient if other information e.g. diameter is not given. What quality of copper was used (presumable pure) ? What was the geometry of this copper? (Mesh, packed beads, etc). If the community should adopt this technique it is key to give clear advice here. 5657 line 13 Please clarify: is there really a decrease of 50% for 13CO₂ in the gas or

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Comment

is this indeed an apparent decreased (i.e. a decreased in the $^{13}\text{CO}_2$ value reported by the Picarro measurement). As chemical reactions that decrease the amount of CO_2 are mentioned later it would be helpful to clearly distinguish apparent concentration changes and real (chemical) concentration alterations.

5657 line 21 and 5658 1: See general comments, how were the gas quantities (3ml and 1000ml) measured (syringe, flow meter, calibrated volumes, etc) and what are the uncertainties of those quantities? 5658 line 6: What is the basis for suggesting these reactions? 5658 line 15 following: The authors mention that the dilution is bigger for the smaller concentration range. Please consider quantifying how much more dilute was used and how this impacted the uncertainty of the mixture composition. 5659 line 14: The authors state that the G1101 lines do not overlap with H_2O and CH_4 . In the following sentence, however, they state that CO_2 measurements are not possible without overlap of H_2O lines -> inconsistent. Concerning the spectral overlap of CH_4 : a cross-sensitivity of $0.42\text{+-}0.024\text{permil/ppmCH}_4$ was reported in previous studies for G1101i instruments (doi:10.5194/amt-6-301-2013) 5661 line 4 See comment 5659 line 14

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