Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2019-197-RC2, 2019


Atmospheric Measurement Techniques Discussions

# *Interactive comment on* "Investigation of adsorption/desorption behavior of small volume cylinders and its relevance for atmospheric trace gas analysis" *by* Ece Satar et al.

**Anonymous Referee #2**

Received and published: 26 July 2019

General comments:

This paper investigates the trace gas stability of air stored in high pressure steel and aluminum cylinders with respect to adsorption/desorption surface processes. Experiments were designed to look at gas phase changes in CO2, CH4, CO and H2O as functions of gas pressure and temperature.

The matter of trace gas stability in air standards is critical to atmospheric measurement programs. A better understanding of how surface processes affect trace gas concentrations could lead to better selection of cylinder materials and operating procedures.

This paper addresses these matters. It gives detailed descriptions of the experiments



performed, which are new and informative, but the conclusions are somewhat vague. I am left with some unanswered questions. To what extent are the results consistent with the Langmuir adsorption model? The QCLAS measurements at sub-ambient pressures were presumably done to test the adsorption model under extreme pressure conditions. Did the experimental results support the model? Was the observed temperature dependency consistent with the model?

Four different gases were measured but analysis of the results focuses on CO2. This may be because CO2 showed the strongest signals, but the authors should comment on why this is the case, and provide some more discussion of what the results say about the other gases. For example, do the gases differ in their sensitivity to adsorption on account of their molecular properties? Can this explain the different pressure and temperature dependencies observed for the different gases? What conclusions can be drawn for how air standards should be prepared and used?

I think the paper could be suitable for publication in AMT if these questions are addressed.

Specific comments:

It is unclear in some parts of the text if quoted gas pressures are absolute or relative to ambient atmospheric pressure. There is potential for more confusion when referring to cylinder and cell pressures.

Page 8, line 4 – It should be noted here that CH4 decreased while the other three gases increased in concentration. What does this say about the favored explanation of outgassing?

Page 12, line 2 – It is claimed that CO and CH4 dependency on pressure was not significant, but in Figure 6 for CH4 at least, the "Steel before heating" and "Aluminum after heating" plots show elevated CH4 at low pressures. Is this an analytical artefact or a real bias? If real, it requires some comment. The authors should also comment

on why there is a clear effect for CO2 and H2O but not for CO and CH4.

Page 15, Section 3.3.2 – It appears that all four gases are correlated in their response to temperature changes. If so this should be made clear. Is there a reason why the figures and the table consider only correlations between the pairs CO2 – CH4 and CO – H2O?

The readability of the paper is fairly good, but could be improved in places with a little attention from a proficient English speaker. Maybe the editor could help with this. Some specific suggestions are included below.

Technical comments:

Page 1, line 9 – replace “until pressures as low as 150 mbar” with “for pressures down to 150 mbar”

Page 1, line 17 – reword to “measurements of CO2 were made at Mauna Loa, Hawaii in the late 1950s. . .”

Page 1, line 19 – “with an increasing number”

Page 1, line 21 – Global Atmosphere Watch

Page 2, line 13 – has received attention

Page 2, line 18 – amount fractions

Page 2, line 25 – gas cylinder usage

Page 3, line 3 – reword to “enables placement of test materials. . .”

Page 3, line 31 – interpret

Page 4, lines 1-2 – Provide some more detail about the flow rate used and the length of time required to obtain reliable measurements. Was there significant change in cylinder pressure?



Page 5, line 7 – I’m not sure that “contamination” is the right word to use here, but that may depend on what caused the stains. Can the authors comment on this?

Page 5, line 10 – replace “until 0.05 mbar” with “to 0.05 mbar”

Page 20, line 10 – beginning

Page 20, line 14 – “Above temperatures of”; again, consider if “contaminations” is the best word to use

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-197, 2019.