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Atmospheric Measurement Techniques Discussions

Interactive comment on "Gas adsorption and desorption effects on cylinders and their importance for long-term gas records" *by* M. C. Leuenberger et al.

Anonymous Referee #1

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Summary This paper describes the results of laboratory experiments designed to probe the stability of CO2 and other trace gases in high pressure, steel and aluminum gas cylinders. The authors performed two experiments: 1) high-flow decanting, and 2) low-flow measurement of trace gas mole fraction with temperature cycling of the gas cylinders. Their results suggest that surface adsorption of CO2 can be modeled with a Langmuir-type isotherm. The effect of temperature on surface adsorption is significant for steel cylinders, but not for aluminum cylinders. Their results are not inconsistent with what has been previously reported.

General Comments Overall, the experimental design and data quality are only partially

sufficient to support the conclusions. The results for the steel cylinder appear robust and reasonable. However, the results for the aluminum cylinder, although consistent with observations seen in our laboratory, could also have been influenced by analyzer drift. Inclusion of uncertainties would help justify the results. For the aluminium cylinders, the temperature sensitivity study is important to the field. Their results suggest that storing calibration cylinders at temperatures over the range -10 to 40 deg C has no appreciable affect on the CO2 mole fraction. However, the fact that small increases in CO2 were observed during the decanting experiments for aluminum cylinders, and the analyzers used are subject to drift unless calibrated during the experiment, raise questions about conclusions drawn from the data. The fact that the data fit the Langmuir isotherm could be coincidental.

The authors should include information about how the cylinders were filled. For example . . . were the cylinders evacuated prior to filling? Were they conditioned to the same CO2 mole fraction prior to filling? These issues could be important with respect to adsorption. Please describe how the cylinders were filled and any corresponding pretreatment or conditioning. Since analyzer drift may impact experiment 1, it calls into question the results of experiment 2 as well. The authors need to provide evidence that their results are robust and not an artefact of analyzer drift.

Prior to publication, some text and figures could be improved.

Specific Comments

Tables and Figures

Figure 4: You mention that the analyzers were calibrated at the beginning and end of the decanting experiment. This leaves room for analyzer drift. According to the manufacturer's website, the Picarro 2401 is subject to drift of up to 0.1 ppm CO2 in 24 hours, and the drift specification for the 2311f is up tp 0.25 ppm CO2 in 24 hrs. These drift rates are comparable to the changes in CO2 you observed in the high-pressure region. It seems likely that the change in CO2 at low pressure is related to adsorption,

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but are you sure the downward trend in the lower panel, before the cylinder reaches ~5 bar, is not related to analyzer drift?

Fig 4 caption: “cannot determined” change to “could not be determined”

Table 1: In the caption you say that no steam cleaning was applied. Are you sure? Do you know what was done by the manufacturer or supplier? What about cylinder conditioning? Were the cylinders conditioned to similar mole fractions of CO2 and H2O for some time before being filled the final time?

Table 2: Since the temperature dependencies of CO and CH4 could not be detected, I suggest removing these columns from the Table and including a note in the caption: such as “temperature dependencies for CO and CH4 could not be detected within experimental uncertainties”.

Figure 6: This figure is not very helpful. I assume that you are showing the best fit lines rather than individual data because there is a lot of scatter in the data. This information would be better presented in a table, with slope, uncertainty, and r2 values for each cylinder.

Figures 7, 8: Displaying the fit equations leads to confusion. It is not clear that the middle equation is the average of the two (I think). I suggest you report desorption energies in the caption, in units of kJ/mol, and limit to a few significant figures, such that 15096 J/mol becomes 15.1 kJ/mol, unless you really believe the additional digits. In the caption, I suggest replacing “temperature gradient” with “increasing/decreasing temperature”.

Also, the y-axis labels in Figures 7 and 8 have different numbers of parenthesis. Which one is correct?

Introduction

P8085, L10: replace “addressed” with “attributed to”

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Since you focus only on the Langmuir isotherm, much of the theory is unnecessary. You could shorten this section by eliminating the BET discussion. Further, the IUPAC definition, P8086 lines 21-24 are not helpful in this context.

Methods

Please describe how the cylinders were filled and any corresponding pre-treatment or conditioning.

P8086, L13 replace “from either a steel or aluminum” with “both steel and aluminum”

P8089, L3: It is not clear from the text that experiment 2 involved lower flow rates. This should be clearly stated at the beginning of this section. i.e. “The purpose of this experiment was to determine the temperature dependence of the adsorb/desorb process. Gas usage in experiment 2 was designed to be far less than that in experiment 1”.

P8089, L8: “six horizontally” . . . this is the first mention of six cylinders. The number of cylinders studied should be mentioned earlier: ie. “Eight cylinders (5 steel, 3 aluminum) were tested over a temperature range of -10 to 50 deg C . . .”

P8089, L23: Are the calibration coefficients actually relevant here? I would think that to resolve very small CO2 differences, analyzer repeatability and drift rate are the relevant terms.

P8090, L23-24: Do you mean “can be determined experimentally from a fit to the measured mole fraction”?

P8091, L20: I would simply use this information to justify using the Langmuir model. I think it is well known that the actual surface area is likely greater than the geometric area.

P8092, L16: Could this be due to analyzer drift?

P8093, L19: This is a creative way to determine the desorption energy. However, I think

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more explanation is needed. I can see that you plotted the LHS of eq 6 vs (1/T-1/T0), and found the energy E from the slope. And the method is outlined in the Appendix. However, I think a clear explanation should also be included in the main document. Were values for CO2,ads, K(To), and E determined simultaneously, or iteratively? Also in figure 7, the y-axis label is R*ln(1-dCO2/CO2,ads) + b. What is "b", and how was it determined?

P8094, L2: Are these values really known to 1 J/mol? I suggest using kJ/mol and limiting to 1 or 2 decimal places, consistent with actual uncertainties.

Appendix:

P8095, L23: Do you mean "Derivation of equations 5 and 6"?

Equation (A2): what is "a", area?, number of surface sites? Please define.

P8096, L6: "change in the adsorbed amount" . . . Is this the correct term? Or do you mean the "amount adsorbed at pressure, P"

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 8083, 2015.