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Atmospheric Measurement Techniques Discussions

Interactive comment on "Towards an understanding of surface effects: Testing of various materials in a small volume measurement chamber and its relevance for atmospheric trace gas analysis" *by* Ece Satar et al.

Anonymous Referee #2

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1 General comments

This manuscript deals with adsorption/desorption of trace gases in air on various metal surfaces. While many existing studies have focused on real cases, testing types of cylinders in use in the atmospheric measurement community, this manuscript on the contrary describes experiments performed using specifically designed test cylinders, filled with an air mixture and various materials, to study potential adsorption phenomenon of gases (CO_2, CO, CH_4, water vapour) on the tested surfaces. The results

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presented in this manuscript represent many hours of preparation and measurement, and are surely of value for the community measuring trace gases in the atmosphere and preparing reference gas mixture for this purpose. In particular, this study reports detectable and quite large effects for the coating Dursan for CO_2, which was unexpected, Dursan being advertised as a passivation treatment. Irreversible alteration of the amount fraction for most species and materials at temperatures equal or above 80°C are also reported. In many other cases, no clear adsorption/desorption effect can be seen, which is at the same time a bit disappointing for process analysis but also good news from the user's point of view. The manuscript is well organised and figures in particular have been prepared with great care and display the results very clearly. Some descriptions in the text may gain in clarity (suggestions hereafter under 'specific comments').

2 Specific comments

What is your method's limit of detection, i.e. the smallest adsorption/desorption effect that could be detected using the chosen measuring instrument? What does the thresholds of 0.2 μmol/mol you mention for CO_2 p. 9 l. 9, 6 nmol/mol for CO and 1 nmol/mol for CH_4 (p. 7 l. 15) represent? If these questions are answered in the companion paper, please cite it.

For the pressure tests in particular, very little adsorption/desorption effect is seen, making likely very hard to actually estimate a number of molecules adsorbed per unit of surface area and/or to compare with theoretical adsorption curves (even if, from the user's point of view, this is actually good news). This stated, it seems also clear that a new design allowing to cause larger adsorption effect would demand a substantial work and is beyond the scope of this manuscript. Still, how would you design a new test chamber / test material or how would you conceptually modify the present equip-

ment to provoke a larger effect that could then be better analysed? I would suggest to add a few lines discussing this in the discussion and/or conclusion.

Distinction container/content: I would suggest making clear reference to a gas mixture when writing of measuring, spiking or being adsorbed (e.g.: working gas, mother mixture), and to a gas container when writing of evacuating, cleaning, connecting, etc. (e.g.: working cylinder, mother cylinder). A few examples:

p. 3 l. 29: The fillings were done using compressed air from high pressure 50 l aluminium cylinders (LUX3586 and LUX 3575).

p. 3 l. 29-30: These two cylinders are called the mother cylinders and their air content the mother mixture from here on.

p.3 l. 31: In addition to the mother mixture, another mixture of comparable content and from a cylinder of comparable material and equipment to the mother cylinder was measured [...].

p. 3 l. 33: This mixture (from cylinder LUX3579) is refereed to as the working gas.

p. 4 l. 2-4: [...], the mother mixtures we spiked [...] using another compressed air mixture as carrier gas.

Please check that this distinction is clear through the manuscript.

p.5 l. 6: 'empty cylinder': it is stilled filled using the mother mixture so it is not empty strictly speaking. Maybe 'blank cylinder' (with the same meaning as 'blank measurement') would be more precise. Please modify through the manuscript (text, Tables, Figures).

p. 7 l. 12: 'end amount fraction': I would suggest replacing by 'final amount fraction'. Please check through the text.

3 Technical corrections, phrasing

Abstract: a direct mention of adsorption right at the beginning would be more clear. Suggestion: A critical issue [...] employed. Both measuring and preparing reference gas mixtures for trace gases are challenging due to e.g. adsorption/desorption of the substances of interest on surfaces; this is particularly critical at low amount fraction and/or for reactive gases. Therefore, to ensure [...]. This study focuses on testing potential adsorption/desorption effects for different materials [...].

Abstract l. 10: [...] to investigate the pressure dependency of adsorption up to 15 bar, and its temperature dependency [...].

p. 1 l. 18, suggestion: In order to achieve a high level of compatibility for data obtained at different sites and/or at different time, the World Meteorological Organisation [...].

p.1 l. 22: [...] but also by limiting any cause of molar fraction alteration.

p. 1 l. 22: maybe mention an order of magnitude for the lifetime of a standard cylinder?

p. 2 l. 8: larger volume

p. 2 l. 18: we aim at distinguishing these effects

p. 2 l. 28: on various surfaces.

p. 2 l. 30: According to the current literature,

p. 2 l. 34: the adsorption loss on the stainless steel surface

p. 3 l. 14: [...] we used the aluminium cylinder only.

p. 3 l. 17: [...] used in the atmospheric measurement community. This custom-made [...]

p. 5, legend of Fig. 2: related to the cleaning procedure

p. 7 l. 2: For the data analysis, for each temperature step the first 10 minutes of the measurements were not included in order to allow time for equilibration; the mean of the remaining 25 minutes was calculated.

p. 9 legend of Fig 5: whereas in the second and third panels

p. 9 l. 10 For example, [...] analyser showed [...] pressure run, whereas the mass flow [...].

p. 10 l. 6: Based on the results of the pressure tests, the temperature experiment were conducted within a pressure range for which no pressure effect should occur, [...].

p. 10, legend of Fig. 6: The x-axes correspond to the temperature cycles (cf. Fig. 3),

p. 10, legend of Fig. 6: does the y-axis show the amount fraction differences relative to the first measurement bloc done at 20°C? (There are three measurement blocs done at 20°C.)

p. 10 l. 7: In order to graphically distinguish [...]

p. 11 l. 9: remove 'Please' (check through the text).

Suggestion: displaying Fig. 6 and 7 on the same page.

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