

Review of “Technical Note: Inexpensive modification of Exetainers for the reliable storage of trace-level hydrogen and carbon monoxide gas samples” by Nauer et al.

This is a valuable piece of work, well suited for a technical report. The authors produce and test a modified version of commercial Exetainer, that will be useful for many scientists taking gas samples in the field.

H₂ and CO are sometimes difficult to preserve in gas samples stored in common containers. Two main processes can modify the mole fraction of H₂ and CO: emission from materials in contact with gas (e.g. container walls or septa), and diffusion through container wall or seal. This paper presents a modification of commercial Exetainers in which both these processes are minimized, resulting in an improved gas stability performance.

The paper is well written and to the point. I have only few minor comments as listed below.

General comments

- from line 36: The authors compare the convenience of large glass flasks with the small glass vials, but we should be aware that these are used by partly different communities with different requirements. The (1-L and larger) glass flasks are widely used in the atmospheric science community (e.g. NOAA), where often a large air sample is needed. The stability requirements are also much stricter - there, a change in the mole fraction of e.g. CH₄ of 2 ppb (0.1%) over several months is already not acceptable (see for examples the WMO compatibility goals - the sample stability should fit well within these limits) (Table 1 in WMO, 2018). The modified Exetainers are useful in situations where signals are large thus precision requirements are more relaxed. Stating this more clearly would be useful.

- some materials emit CO under light. How were the samples stored, in light or dark? Please specify in the method section.

- a short discussion of possible phenomena, and on why these materials were chosen (SS to minimize diffusion through the cap, silicone to minimize the emissions) may be useful for other scientists trying to make similar experiments for other containers or other gases.

Specific comments

- line 23: compared to many other gases in atmosphere, CO and H₂ are actually not “highly reactive”, as they have lifetimes of several months and 2 years resp. I suggest removing these words.

- lines 36 - 39: glass flask are widely used for atmospheric samples for mole fraction measurements as well, see also general comment

- line 63: the materials were washed and treated, which I assume passivate the surface, but then they were cut into pieces. Does this not counteract the passivation, since it exposes fresh emission surfaces?

- line 80: consider adding the info that the silicone purpose is to keep emissions inside container low

- lines 79-81: consider stating that the silicone and oring were chosen as the best options based on the tests at 2.1? Also, mention the type of oring, and whether it was tested in the previous experiment

- line 92: why did the authors use bolts, and not e.g. a simple round piece of stainless steel?

- lines 182 – 183: unclear, the 0.2 ppm increase in CO cannot be equal to the contamination with a small amount of ambient air as introduced by a needle, since the ambient air is normally around 0.1 to 0.2 ppm.

- lines 188 – 189: the indication of an underlying zero order reaction is interesting, maybe important enough to mention in the abstract? Also, such a zero order (degradation) reaction may be temperature and light dependent – does this suggest that exetainers stored in cold and dark will be more stable?

Technical comments

- line 56: 2.2 should be 2.1
- line 91: reference(s) missing
- “concentration” usually refers to mass/volume. The units “ppm”, “ppb” normally mean mol/mol (or volume/volume), thus refer to mole fractions or mixing ratios.
- Table 1, caption: part of the text missing?
- Fig. 2: I suggest indicating in the figure caption that the y-axes are different
- line 151: “0.18 ppb” should be “0.18 ppm”
- Figure 4, caption: I think the figure does not show the relative differences (rel dif would be (stored – fresh) / fresh), but the absolute values of fresh and stored gas.
- Supplement figure: I think the “fresh” and stored” are reversed, the stored gas is the one changing.

References

NOAA Cooperative Air Sampling Network, <https://www.esrl.noaa.gov/gmd/ccgg/flask.html>

WMO, 2018: https://library.wmo.int/index.php?lvl=notice_display&id=20698