

Review of Shuck et al.; Stability of halocarbons in whole air samples from the upper troposphere and lowermost stratosphere

Shuck et al., present the results of short and long-term storage tests conducted on stainless steel whole air samples that together form the HIRES sampling system. HIRES is part of the CARIBIC instrument package. The paper focuses on the stability of a range of halocarbons, many of which are important both from a climate and stratospheric ozone perspective. Given the significance of a number of these compounds, and the importance of whole air sampling as a means of complimenting the existing measurement framework, this work fits within the scope of AMT. The paper is, in general, well written and should be published after some revision.

Main comments:

Figure 3. There seems to be some confusion regarding which species are presented. Panel B shows results for dichloromethane, whereas the text talks about tetrachloroethene (P6 L30, P7 L3). I'm assuming this is simply a mix-up, but it makes the entire section rather difficult to understand. With regards to Figure 3, it is also not clear to me as to why the dichloromethane/CFC-12 ratio of the 'orange' sample is higher than the other two samples filled with the exact same ratio of standard/synthetic gas. I suspect that all three are within the measurement uncertainty. In which case it might be good to find some way of showing the error bars which are currently omitted.

While there were several very interesting results presented, I did not feel that the authors provided much in the way of reasoning for a number of their findings. For instance, why did bromomethane and chloromethane increase in the cylinders over the length of the short-term (and long-term) storage tests? Presumably due to production as a result of the decomposition of more complex chlorinated compounds? The same can be said of H-1301, which would appear to be a strange result. I would not expect to see complex chemical mechanisms in this sort of paper, but it would be useful to have some brief discussion of these points.

Technical corrections:

I think the title needs to be revised. At current, it suggests that the storage tests were conducted on samples collected in the UTLS, while in fact they were conducted using samples prepared in the laboratory.

P1 L1. 'Halogenated halocarbons of' should be changed to 'halocarbons in'.

P1 L17. The sentence needs extending. Suggest 'growth was observed during storage for some compounds,...'

P1 L21. Delete 'the' before stratospheric.

P2 L7. Remove comma after 'both'.

P2 L24. Remove comma after 'both'.

P2 L26. 'Flask' should be plural.

P2 L33. Start of sentence does not read correctly. Suggest replacing 'got' with 'has been'.

P4 L26. 'Details' should be singular.

P5 L4. There should be a space between 'Figure' and '2'.

P5 L6. This sentence doesn't quite make sense. I think it's supposed to read 'bellows pumps, in this set-up *the samples* are pressurized...'

P5 L15. Purely out of curiosity – how many samples can be obtained from a single whole air sample at a flow rate of 100/150 ml/min? It might be good to include this figure at some point in the text.

P6 L16. The mention of the presence of an air-conditioning unit in the laboratory is fitting given the nature of the gases studied. However, it would be more useful to quote the refrigerant blend used, e.g. R-410A. Very high levels of these gases in the laboratory environment might affect the analysis, if there are small leaks in the system.

P7 Figure 3 caption. I'm confused by what the solid black line represents. From the caption 'The solid black line represents the value expected from direct measurements of the standard gas and the synthetic air.' Why is the black line a mix of the two gases? I would have thought it would be better if the black line was a direct measurement of the undiluted standard gas? Or is this to account for contamination in the synthetic air. Some additional description would be useful here.

P7 L9. Throughout the previous paragraph tetrachloroethene is referred to as 'C₂Cl₄', but here it is referred to be its full name. Suggest using C₂Cl₄ throughout.

P8 L2. Suggest replacing 'right' with 'immediately'.

P8 L19. 'Is' should be 'are'.

P9 Figure 4. Some more explanation of the light blue trend in panel b) is required.

P9 Figure 4. There is no mention of HFC-152a (panel c) in the caption.

P9 L1. Why did HFC-152a increase over time?

P9 L3. Why did H-1301 increase over time?

P11 Figure 5. Are the ozone measurements from multiple instruments? What is the difference between the diamonds and the red line? It looks like one is an in-situ instrument and the other based on the flasks – either way, it would be good to include this information in the Figure caption.

P13 Figure 6. It would be useful to include the R value somewhere on each individual plot.

P13 Figure 6. There is some overlap of the colour bar with the underlying scatter plot.