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Comment on amt-2020-488

Anonymous Referee #1

Referee comment on "An indirect-calibration method for non-target quantification of trace gases applied to a time series of fourth-generation synthetic halocarbons at the Taunus Observatory (Germany)" by Fides Lefrancois et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2020-488-RC1>, 2021

The manuscript by Lefrancois and coauthors evaluates a method to extract quantitative data from mass chromatograms of trace gases in air samples. The analytical method they study is based on cryo-enrichment gas-chromatography mass spectrometry, using a Time of Flight (TOF) mass spectrometer. In contrast to target compound analysis that is common using quadrupole MS in selected ion mode, the TOF analysis obtains full mass spectra over a given range continuously over the chromatographic analysis time. As demonstrated in this manuscript, this ability allows one to examine past chromatograms for mass spectra of compounds not identified at the time of the analysis. The problem addressed in this manuscript is how to obtain quantitative measurement of those compounds without contemporaneous standards, and to determine the uncertainty with this retrospective approach. The authors do a very good job of laying out the procedure and how it was evaluated through several years of analysis of samples collected in flasks and in-situ at the Taunus Observatory. The work is logically presented, thorough, and appropriate conclusions are drawn.

The method that the authors describe is equivalent to the use of internal standard quantitation that is common in analytical chemistry. In conventional use, a known amount of internal standard (or multiple IS's) is added to each sample and relative response of the standard(s) to the sample components are used to obtain quantitative data. The assumption is that absolute response variations will occur, but relative response between internal standard and sample component will be constant. Since no standards are added to each sample, the technique described by the authors uses previously quantified trace gases as internal references for comparison to a series of hydrochlorofluoro-olefins (H(C)FOs). They carry out a rigorous study of the stability of relative responses of gases contained in their calibration standards to find periods of high reproducibility and low variation, and which gas(es) in the calibration mix demonstrates the best properties. Given the choice of reference standard and identification of periods of stability, the author's then do the retrospective quantitation of several H(C)FOs and compare them to more recent analysis that used a direct calibration. They estimate accuracy of the retrospective analysis at better than 25%. Given the very low mixing ratios that are

found, this level of accuracy seems more than adequate.

The analysis raised a question for me (but that doesn't need to be addressed in the manuscript). The question is why don't all compounds work equally well as internal standards? And if they don't all work well, what is the uncertainty of the non-target compounds for any specified period? They might behave well or might not, it seems to me. Also, given the stated precisions of the calibration standards, it is then surprising that the correlations between standard responses show percent errors in the 10% range. I'm not sure how to interpret that.

Other comments are related to some clarification and minor editorial suggestions.

L 81. Suggest eliminate "preceding" or change to "...(ppt)), sample trace gases are enriched by cryofocussing in a sample loop."

L113. Though I think I know what you mean, could you better describe what a "target" standard is?

L120. It would be helpful to describe some more detail of the method. For example, I couldn't find anywhere how the quantitation was accomplished with the QTOF data. Was a single selected ion used for each compound, or the sum of major fragments, or some integration of a peak that has been deconvolved from the total ion chromatogram? Were different methods of sample integration tried? Perhaps there is also a relationship between mass and total ion current that could be used to quantitate certain classes of compounds (at least within 25%)? Other questions: mass resolution of TOF?

L177. Although HCFC_141b elutes near water, it shows excellent precision. So not sure why this might be excluded. Or it might be interesting to learn how water vapor might influence the results.

L179. Not sure if the plots are artificial data from some "arbitrary substances" or if the actual compounds are just not named here. Could you clarify?

L182. It is not clear how the 10% criterion for rejection is applied. Is this from point to point, or relative to some average?

L197. Not sure if you mean "exemplary", as in "best example of the group", or are these just examples of some of the compounds. (also in Figure caption).

Figure 2. As I understand it, this figure compares the peak areas of compound pairs in the same calibration standard over the time of the study. Could you comment on the very large range of peak areas that were observed? Is this a characteristic of the TOF?

L204. Note that the independence of rRF will also depend on linearity and any zero offset.

L209. The observed shift of 152a relative to 133a deserves some comment. Presumably there was no similar shift in the time series ambient measurements of either gas. So, this behavior, though maybe rare, would seem to be a major red flag in applying the proposed method with confidence.

L213. There are a number of compounds that have drifts or anomalies that prevent them from being used as "reference" compounds. Does this have any implication on how these are used for direct calibration? Do these standards cause the sample mixing ratios to be flagged? The authors also suggest that there are a number of potential factors that will influence the relative responses. In cases of outliers or large shifts (such as 152a), have the authors determined specific causes for the deviations?

L214. Not sure of meaning...change "suited" to "suitable"?

L251. I was interested to see that 152a was selected as a reference standard for the in-situ measurement evaluation, though there was a problem with this compound in the canister analysis. As noted, this is disturbing and deserves comment.