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Comment on amt-2020-488

Anja Claude (Referee)

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-RC4>, 2021

The paper by Lefrancois et al. addresses a relevant question in the field of atmospheric background observations and scanning using GC/MS. Basis for every high-quality measurement is a good calibration of the instrument. While for GC FID systems, applying C-response factors, a calibration is achieved also for substances not available in the reference gas mixture, for GC/MS systems, the existence of a compound in a reference gas mixture is usually mandatory.

The here presented method to derive calibration factors from known and well calibrated substances provides a solution for new gases which are not or have not been available in calibration gases at the time of sampling. The relative response factors usually applied for the Internal Standard concept is here extended to an external standard. Similar methods are certainly used in labs as a work around for compounds not available in working standards gases, but Lefrancois et al. provide a description of the concept and present the results of elaborated testing of this method. Application of this concept leads to a new data set of recent HFO data observed at the Taunus Observatory. HFOs were quantified until back 2014 and the quality of the data was assessed proving the applicability of the here presented method.

The overall presentation is well done, presented results support sufficiently the interpretations and conclusions. The authors have clearly indicated their work and contributions from Co-Authors and as far as my understanding goes the presented results are traceable. Some (minor) issues that require some discussion though.

The title seems quite long. The relative response concept used for the indirect calibration and its validation is not mentioned even though it the major aspect of this paper as it is written. Therefore, the authors might think of a revised title.

The language is basically good. I am not a native speaker myself – as you can easily read here – but in some parts the use or non-use of the definite and indefinite article seem a bit arbitrary and some sentences should be re-formulated for clarification.

Close work with European metric institutions has brought up a discussion on “correct vocabulary”. Among this the terminus “mole fraction”. As “mole” is a unit, NMIs requested the use of “amount fraction” instead and the correct unit would be “nmol/mol” (instead of ppt) - just a remark, as I came across this discussion often recently.

As already stated, the overall presentation is good, however, some parts suffer slightly from not always clear structure leading to some open question (especially Section 3). Examples are listed below.

Introduction:

I. 47, “These hydro(chloro-)fluoroolefines are the so-called fourth generation of synthetic halocarbons...” - there are no other fourth generation synthetic halocarbons?

I.51: “However, some HFO, as some HFC and HCFC, can form the very persistent and toxic trifluoroacetic acid (TFA) as...” check commas and the use of “some”

Are the three substances of this paper among the TFA forming HFOs?

I. 63 & 64: I think it has to be “Section” with “S” à please check!

I.70: “locations of industry” à maybe better “industrial areas” ?

Section 2:

I. 77: What does “approximately weekly” mean?

I. 86: “ ...the sample loop is heated to approx. 200 °C...” - approximately?

l. 99 "mud dauber" ...an insect screen, I guess?

l. 107ff: Are the sample inlets mounted in a separate heated box or are all parts in one single box? The description for the continuous instrument jumps a bit. Starting with the sampling procedure (flows, sample volume, desorption temperature) you continue with the unit set up (heated box, materials) and then return to the flushing procedure. The adsorption temperature is the same as in 2.2. (-80°C)? Streamlining this paragraph might improve the reading.

l. 133 : You neglect data for calibration intervals which deviate more than the weekly 1s-precision, ok – I am just interested: Did you ever take in account/discuss to add the additional error to the uncertainty?

Section 3:

Figure 1: as I understand this figure is explanatory only, in order to describe the method how stable periods were defined. Therefore the plotted compounds are not mentioned. Nevertheless, the question bothered me while looking at the plot, what substances are plotted. Later on, in Figures 5 and 7 you show the similar plots again. I wonder, if you could combine those?

l. 181: Why did you choose the stability criterion to be 10%?

l. 195 ff. I had to read this sentence several time. Just to be sure: MAPE is the difference " $A_{\text{measured}} - A_{\text{odr}}$ ", with " A_{odr} " being the ODR fit of peak areas forced through the origin

l. 210: "Using HFC-227ea and..." You already present a single result of the analysis that follows in the next paragraph. I found this is confusing. From my point of view you can delete this sentence.

Figure 5 (&7): I understood that you derived stable periods from calibration measurements as well. However, in the caption of Figure 5 you mention "data of the weekly flask sampling measurements". Please clarify.

l. 221ff: "To quantify the differences..." I do not understand this sentence, please explain. As a consequence please also explain panels d and h in Figures 5 and 7. Not clear to me.

I. 229ff: "In summary..." These are the characteristics you expect from your relative Response factor to achieve a good calibration and which set the frame for your checks you presented in the preceding lines. Might be good to have it earlier in the text?

I. 237: "Using HFC-125 as evaluation substance with HFC-143a, the difference standard deviations of the mean rRF selected via the test substances and selected via itself ranges between 1 and 10 %." Do you mean "different"?

I. 243: "In this test case, mole fractions of HFC-227ea shows the best correlation ..." "show" instead of "shows".

I. 249: You end this paragraph with a statement about the importance of having a constant sensitivity. You take up this point but then do not really discuss it. It would be nice to have all the presented results of 3.2.2 "wrapped up" at this point in final short summery

Table 2: With standard deviation you mean the standard deviation of the average relative difference? Is it this really necessary to have this table or could you add this information into Fig.6. ?

Figures 8 and 6: When you calculated the amount fractions via the indirect way you applied the method for data in the stable periods (as derived in Figure 5 and 7 respectively). The constant rRFs you used to "attach" the test substances to the reference substance are determined using the average rRF in the calibration measurements also during the stable times? This is not clear to me?

Why did you use the measurement precision as error bars? How does this reflect the uncertainty factors of the different calibration methods?

Figure 6: What happens if you omit the two single data points in January 2018 for HFC-32? Any idea what happened here?

Figure 8: What happens to the regression lines when you omit the high amount fractions?

Tables 2+3: Do you use this deviation to derive the uncertainty of the method?

I. 262: "This is caused by long-term drifts..." What does this tell you about the possible errors arising from differences between the evaluation and test substances, even though you have filtered out periods with a larger variability?

Section 4:

Figures 9 and 10: maybe you keep the zoomed in plot, only? What do the error bars represent?

I. 291: "These larger amounts could be..." So, this is the effect of non-linearity or a larger integration error for the small calibration peak?

Conclusion:

You have presented methods to derive the best possible reference substances for your indirect calibration and you evaluate this indirect calibration procedure regarding its performance.

It would have been nice to see an assessment of how uncertainties arising from the determination of the rRF and evaluation of stable periods (by the evaluation) are reflected in the results of the test compound analysis. E.g. do expected errors match with observed differences between indirect and direct calibration?