Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2022-130

Anonymous Referee #2

Referee comment on "Development and validation of a new in situ technique to measure total gaseous chlorine in air" by Teles C. Furlani et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-130-RC2, 2022

General Comments:

Furlani et al. built a system to measure total gaseous chlorine (TClg) in ambient air. The system converts total chlorinated species to HCl using a heated platinum converter and measures the Cl content using an HCl analyzer. The conversion efficiency was validated using 3 organochlorine molecules. They examined the efficiency of the converter at different conditions, including conversion temperature and flow rates. They tested the system by applying it to measure both outdoor air and indoor air when cleaning with chlorine bleach. Overall, the paper is well written and presents a new method in measuring total chlorine in the atmosphere, which is valuable to the community. However, they should address the following major comments and a few specific comments.

Major comments:

The system was only evaluated for 3 organochlorine molecules, including dichloromethane, 1-chlorobutane, and 1,3-dichloropropene. These three molecules are relatively similar in structure, i.e., they are all chlorinated alkanes/alkenes. However, in the atmosphere, various chlorinated species (both organic and inorganic) are present, and they likely have different conversion efficiency to HCl in the system. They should conduct evaluation for more chlorinated species, e.g., chemicals with more diverse structures and properties. Furthermore, the authors should test the conversion efficiency for major inorganic chlorine species, such as Cl2, inorganic chloramines, HOCl, ClNO2, HCl, etc. These are major chlorinated species from indoor bleach cleaning (Mattila et al., 2020; Wong et al., 2017), and are important reactive chlorines in the ambient air. Another related question: How did the authors evaluate potential loss of reactive chlorine species on the inlet and instrument surfaces?

The introduction: In the current version, the authors focused on discussing the importance

of chlorine in the atmosphere in the Introduction. They should focus more on the measurement techniques of chlorine, especially if there are any total chlorine measurement techniques in the literature, rather than the discussion on the importance of chlorine in the atmosphere. This helps to put the study in the right context, i.e., "development of measurement techniques for chlorine in ambient air". Thus, I suggest the authors to rewrite the introduction of the paper.

Specific comments:

Can the instrument measure particle phase chlorine?

Line 143: what is the size of the platinum mesh? Would the amount of Pt catalyst and the size affect the conversion of Cl species? For example, does finer Pt provide more surface area for the conversion reaction?

Line 149: the authors mention that "all lines and fittings were made of perfluoroalkoxy (PFA)". Were there any issues to use the PFA fittings and lines at high temperatures (~ 650 C-800 C)?

Line 154: Please explain about "inlet effects".

Figure 1: Add flow rates in the diagram. Where is the inlet position? Please add the sampling inlet location.

Line 177: "DryCal Definer" should be "DryCal Defender"

Session 2.4: Was the HCl-TCl optimized for "inorganic chlorine species"?

Line 203: CRDs flowrate of 2 L/min. Is this flow a subflow of the inlet flow? It would be helpful to specify the flows in the diagram in Figure 1.

Line 214-215: If the inlet lines and fittings were maintained at 20-25 C, which is lower than outdoor temperatures (25-28 C), was there water condensation when the humid air from outdoors (at higher T) come indoors (at lower T) into the instrument?

Other than conversion temperature and flow rate, did the authors test the effect of water/humidity on conversion efficiency? And how does RH influence the ambient measurement? This is important for ambient air measurement when RH varies.

Line 218: a URG Teflon coated aluminum cyclone was used to remove particles?

Line 247: please define what is "strong Cl-containing bonds". Is there a threshold for "strong" vs. "weak"?

Line 254: what is "breakthrough temperature"?

Line 256: how about the temperature for inorganic chlorine?

Line 283: these are very high levels. In the real ambient air, their mixing ratios are a lot lower.

Line 289: why are some conversion efficiency >100%?

Line 290-292 are repeating the information on line 289

Line 330: why not test the effect of particle chloride on TCl measurement? The authors could test with chloride containing salt particles.

Line 331-332: "the conditions required to convert chloride to chlorine atoms ..." Do the authors mean organic or inorganic chloride?

Line 343: "in the during the"- delete "in the" or "during the".

Line 359: "productfour" should be "product four"

Line 361 and 362: is it "pptv" or "ppbv"? Mattila and Wong et al. observed 100s ppb level, not ppt.

Line 379: It is unclear what the authors meant - “there was on average 82% of integrated TCl for which we cannot account.”