

Atmos. Meas. Tech. Discuss., referee comment RC1
<https://doi.org/10.5194/amt-2022-130-RC1>, 2022
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Comment on amt-2022-130

Anonymous Referee #1

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-RC1>, 2022

Furlani et al. describe a new instrument for quantification of "total gaseous chlorine" in air. The instrument uses an inlet furnace to which propane and a Platinum catalyst are added to quantify the generated hydrochloric acid by a commercial cavity ring-down spectrometer. The instrument is conceptually similar to existing "total element" measurement techniques such as C_{γ} (Roberts et al., 1998) and N_{γ} (Stockwell et al., 2018). Its performance was evaluated using diffusion sources containing dichloromethane, 1-chlorobutane or cis-1,3-dichloropropene. Sample data of outdoor air and indoor air measurements are presented. The indoor air data were supplemented by HOCl measurements.

I have major concerns with this manuscript which, in my opinion, requires more data to verify the instrument's performance.

Major comments

(1) The list of Cl containing compounds (Table S1) is incomplete and omits, amongst others, cyanogen and acid halides and chlorinated aromatic compounds such as chlorinated dioxins and other legacy organochlorine pesticides. The list of compounds should be as complete as possible for this to be a "total" measurement. I would also suggest not burying this list in the SI but to move it in to the main manuscript.

(2) Cl_y is defined on line 86 but a clear definition (with stoichiometric factors) of the various compounds that make up total gaseous chlorine TCl_g was absent (something like $TCl_g = HCl + CH_3Cl + 2CH_2Cl_2 + 3CHCl_3 + 4CCl_4 \dots$). This omission is odd considering TCl_g is the new quantity supposedly being measured.

Further along the same vein, the concept of total chlorine exists since stratospheric times (Cl_y), and many in the community use terms such as "active chlorine" or "reactive chlorine" (Zhai et al., 2021). The manuscript needs more discussion on where this new measurement of TCl_g fits in the broader picture.

(3) The authors argue that, because the bond dissociation energy is higher in HCl than all other compounds listed in Table S1, it suffices to only evaluate the conversion efficiency of 3 compounds and assume that the remainder will fall in line and fully convert to HCl when sampled. While this may be true from a thermodynamic point of view, kinetic barriers to dissociation may come into play because the instrument is operated with a relatively short residence time of ~ 1.5 s. More experiments should be conducted to verify the instrument's response to others chlorine containing gases (for example, carbon tetrachloride, hexachlorobenzene, and perhaps a chlorinated dioxin).

(4) The instrument was "validated" using diffusion sources that are calibrated only gravimetrically and are thus not necessarily accurate. Many of the compounds listed in Table S1 can be quantified by established instrumental methods such as GCMS. The output of the diffusion sources could (and probably should) have been calibrated by another instrumental method such as GCMS, and the response compared to that of the new instrument described here.

(5) Interferences need to be evaluated - for example, would the instrument respond to sea salt aerosol or aerosol containing non-volatile Cl-containing compounds or ammonium chloride by evaporating HCl in the oven? Is the conversion efficiency reduced when flame retardants such as PDBEs (present in indoor air) are sampled? Spectral interference from propane was mentioned - are there other spectral interferences?

Was the instrument's response ever evaluated by adding a known amount of DCM, CB and DCP while sampling ambient air to verify the absence of matrix effects?

(6) Was the transmission efficiency of HCl through the oven at normal operating conditions (and in the absence and presence of Pt and propane ever evaluated)? If so, these data should be included in this manuscript.

(7) The major components of TCI_g , according to Table S1, are HCl and ClNO_2 . Have the authors considered implementing a switch to alternate between HCl and TCI_g ? What happens when the oven temperature is scanned while sampling air? Are plateaus observed as in the method developed by the Cohen group for NO_y ?

(8) More instrumental figures of merit should be provided. For example, an LOD is provided for the CRDS, but not for TCI_g (which is likely worse). What is the rise time of this instrument to sudden concentration changes (how quickly does the instrument response return to zero when chlorine-free air is added to the inlet)? What is the instrument's linear dynamic range? Does the catalyst age or need to be changed over time?

(9) More explanation as to role of propane and inlet chemistry is needed. Propane auto-

ignites at a temperature 470 °C. Here, it is being heated to >800 °C. What does this mean for the proposed mechanism in which HCl is formed from reaction of Cl atoms with propane (R1)? It is certainly not as simple as suggested here. More likely, HCl is formed as a result of a series of combustion reactions involving propane oxidation products. There is a lot of literature on the combustion of propane over platinum catalysts that should be incorporated in the discussion (e.g., Titova, N.S., Kuleshov, P.S. & Starik, A.M. Kinetic mechanism of propane ignition and combustion in air. *Combust Explos Shock Waves* 47, 249–264 (2011). <https://doi.org/10.1134/S0010508211030014>) . In particular, section 3.2 should be rewritten.

Specific comments

Title / line 2: "In ambient air". One of the applications described is indoor air measurement. Consider broadening the scope of the title - for example, replace "in ambient air" with "in air".

line 15. "combusting ambient air". Most people would define combustion as the rapid chemical combination of a substance with oxygen, which is not the case here (at least not for the monitored HCl). 'Combusting' is a poor choice of words in this context. Please rephrase.

Is there an inlet aerosol filter before air enters the furnace? If not, HCl could be driven off atmospheric particles.

line 18. "HCl, for which detection by CRDS has been shown to be fast and reliable" This statement is not appropriate to appear in this section (which is the abstract to this paper) because reliable and fast detection of HCl by CRDS was not demonstrated in this manuscript (it was published in an earlier manuscript instead).

line 19. Consider stating the criteria guiding the selection of this compounds (high BDE).

line 22-24. Please state what quantities are plotted against each other - what is the reference measurement or benchmark against which the new instrument was evaluated?

What is the meaning of the errors stated? Clearly, it is precision (since values > 1 are physically not feasible) - but at what level of confidence?

line 24 "Breaking these strong C-Cl bonds represents a proof of concept for complete conversion" replace with "The quantitative conversion of these test compounds that contain relatively strong C-Cl bonds suggests complete conversion"

line 26-27 "reasonable comparisons" - one can compare apples and oranges. Suggest rephrasing to "reasonable agreement"

line 27 "sum of expected HCl from known Cl species" - expected how? known how? Be explicit.

This sum is expected to be highly variable in reality - while it's good to be in the right "ballpark", this comparison is not exactly a rigorous one.

line 61 - "unreactive chloride" - consider mentioning sea salt aerosol in this context.

line 89 "Understanding TCl_g source and sink chemistry". The sources and sinks will differ for each component of TCl_g and are known in many cases. How does the measurement TCl_g fit in and help elucidate sources and sinks?

line 118 - consider adding a table summarizing the various elemental measurements. Are they all using Pt catalyst?

line 137 "Clean" - replace with "Chlorine-free"

line 139 The (typical) CRDS sample flow rate should be stated [it is stated on line 203 but should be stated earlier].

line 148 "Spectral interference" What does this mean? Please explain and show the

interfering spectra.

line 149 "[propane] should only be added when temperatures exceed 650 °C [Furlani et al., 2021]" Furlani et al., 2021 do not mention propane or inlet furnaces, so more explanation as to this constraint is needed. Could it be that at temperatures above 650 °C most of the interfering propane is oxidized?

line 153. "CRDS can capture transient fast HCl formation processes on the time scale of a few minutes" Please show sample data to support this statement. What is the rise time?

line 154. "limited by inlet effects" Would inlet effects? Please explain or rephrase.

line 158 How is LOD defined (1σ , 2σ or 3σ)?

line 160 Figure 1. Is there an overflow or tee between the furnace and the CRDS, or are both operated at the same flow rate?

Are there any pressure drops at higher flow rates?

lines 179-181 - does the 4-week period encompass the time period over which the work in the remaining manuscript was conducted, or was there extrapolation?

Some of these standard deviation are quite large, whereas others are very small. Please explain.

line 190-191 "The conversion temperature was determined when the measured HCl plateaued at 100% conversion." Please rephrase for clarity.

line 192 "flows of 0.6-5.5 L min⁻¹" - how was the furnace coupled to the CRDS or could the CRDS be operated at any of these flow rates if the CRDS flow rate was 2 L min⁻¹ (line 203 - see also line 160). If the CRDS flow rate was variable, is the line shape/pressure of HCl affected?

line 208. It sounds as if ambient air was sampled without an aerosol filter. Please comment on the conversion of aerosol chloride to HCl (e.g., evaporation of ammonium chloride).

line 225-227 Strike "Instances ... (Furlani et al., 2021)" as this is standard practice and certainly isn't unique to this group.

line 229-236 Has the H₂O₂ CRDS been validated to quantify HOCl? More detail is needed to describe the HOCl measurement here (rather than refer to an unwritten/unpublished manuscript draft).

line 246 "Test all TCl_g species is not feasible" - probably not, but surely more than 3 (and especially HCl) should have.

line 259 "six residence times" does the pressure inside the furnace change when the residence time (flow rate) are altered?

line 263 "Expected TCl_g" - Clearly state what you mean by "Expected" - Is it what is summarized Table S1 under expected or based on the leak rates in section 2.3? Note my major concern #4 about using gravimetrically calibrated diffusion sources.

line 264 "optimal" - please state the criteria that were considered optimal (highest conversion efficiency at fastest flow rate?). Based on Fig 2., I would have not thought 1.5 s would be optimal as the conversion efficiency was greater at 4.5 s.

line 273 "slower response time due to increased surface effects of HCl" Please show the data and state how slow the response was.

Figure 2. Please change the axis caption to SI units (seconds should be s).

The figure caption should state relevant details such as oven temperature, flow rate, propane concentration, pressure, etc.

Is the scatter shown in Figure 2 what one would expect (i.e., are the dips at 0.9 s and 2.6 s reproducible or indicative of some sort of random error?). Could you draw a smooth line through all the data?

Rather than showing the run-time precision as error bars, consider repeating the experiment several times over several days and showing the day-to-day precision (which is likely larger).

line 283-285 - "The mixing ratios tested for DCM were 41, 54, 80, 111, 284 and 165 ppbv. The mixing ratios tested for CB were 3.5, 4.6, 6.8, 9.5, and 14 ppbv. The mixing ratios tested for DCP were 121, 259, 468, 651, and 967 ppbv." Please rectify the poor sentence flow and clearly state how these mixing ratios were determined or calculated. If they are based on the mass emission rates from line 180-181, uncertainties/error should be added.

Figure 3 - Axis title: "Expected normalized HCl from PD output": What does this mean?

Please use different symbols (squares, circles and triangles) for DCM, CB and DCP.

Please do not dash the 1:1 line (it's a line, not a dash) and remove the straight fit lines for each of the standards as they obscure the data points.

What is meant by "normalized" here? Why not plot concentration of HCl observed vs concentration of TCI_g emitted?

Table 1 - Fix the formatting of the table (borders) to journal standards. Rather than defining conditions, simply state w/ Pt, w/o Pt, w/ C₃H₈, w/o C₃H₈ etc. in the table heading to improve manuscript clarity and readability.

line 328. "...expected to be between 3.3 and 19 ppbv". That's a huge range.

line 334 "chloride ... is assumed to not be converted". That's an easy experiment to verify. I wouldn't be surprised if ammonium chloride aerosol is quantitatively converted.

line 338 "Measurements of HCl alone were not made" - one could have alternated between furnace and ambient air using a simple switching valve.

Figure 4. Interesting trend and variability in concentration. Can you prove that the signal does not change because of a variable conversion efficiency? I am suggesting a simple experiment adding a known amount (e.g., from one of your diffusion sources) hourly while sampling ambient air to verify that the conversion efficiency does not change.

Figure 5. SI units in axis caption, please. It is unclear what shade corresponds to which application.

Could you compare the response of the new instrument to HOCl with the CRDS (not sure if a source of pure HOCl(g) could be constructed)?

line 410 "using DCM" Would you expect optimized conditions to be different for other molecules?

line 424 insert "and" between "Foundation" and "Natural" and remove comma

line 433 - References.

The formatting for doi's should be consistent but varies between references.
Please properly subscript CO₂, SO₂ etc. (line 458).
The reference on line 476 has been published in AMT (remove "Discuss.").

Supporting information

Table S1 - the formatting of this table (borders, shading) is not to scientific standards.

"observed" in the Table title is unnecessarily confusing (observed where? when? how?) and should be a range, not a single value. Suggest replacing with "Typical" or "Average" or "Expected".

The table omits a number of chlorine containing compounds, for example, cyanogen and acid halides, and chlorinated aromatic compounds such as polychlorinated biphenyls (see major comments). For example, the CRC handbook lists the BDE of Cl-Na as 412 kJ/mol, Darwent, "Bond Dissociation Energies in Simple Molecules" NSRDS-NB Vol 31 (1970) gives a BDE for ClCN- \rightarrow Cl+CN of 439 kJ/mol, the CRC handbook list Cl-CN at 422.6 kJ/mol Cl-CF=CF₂ at 434.7 kJ/mol, and Cl-C₆H₅ at 406.4 kJ/mol.

Figure S1 caption: "High spectral interference" The figure does not show a spectrum, let alone a spectral interference.

Figure S1 axis - expand the y-axis range from to 0 to ~20 ppbv.

The signal appears to be increase / slope upwards between 11:45 am 12:50 pm. Explain how you concluded that thermolysis is complete.

Figure S2 caption: Please give relevant experimental details such as flow rate, DCM concentration, matrix (ambient air, filtered air, room air, etc.), was propane added and if so, how much, etc.

What happens when the temperature is increased above 800 °C?

Figure S3. It's hard to see what's what here.

Figure S4. Unclear what information this figure is adding to describe the new method. Consider saving this figure for another manuscript.

S1. References. Strike "Receive" from Crisp et al.