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The Determination of $ClNO_2$ via Thermal Dissociation-Tunable Infrared Laser Direct Absorption Spectroscopy

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Abstract. Nitryl chloride ($ClNO_2$) is a reservoir species of chlorine atoms and nitrogen oxides, both of which play important roles in atmospheric chemistry. To date, all ambient $ClNO_2$ observations have been obtained by chemical ionization mass spectrometry (CIMS). In this work, Thermal Dissociation Tunable Infrared Laser Differential Absorption Spectrometer (TD-TILDAS) is shown to be a viable method for quantifying $ClNO_2$ in laboratory and field settings. This technique relies on the thermal dissociation of $ClNO_2$ to create chlorine radicals, which undergo fast reactions with hydrocarbons to produce hydrogen chloride (HCl) that is detectable by the TILDAS instrument. Complete quantitative conversion of $ClNO_2$ to HCl was achieved at temperatures > 400°C, achieving 1 Hz measurement precision of 11 ± 1 pptv (3σ limits of detection of 34 ± 2 pptv) during laboratory comparisons with other $ClNO_2$ detection methods. After blank- and line loss-corrections, method accuracy is estimated to be within ± 5%. Performance metrics of TD-TILDAS during ambient sampling were a 1Hz precision of 19 ± 1 pptv and 3σ limits of detection of 57 ± 3 pptv), which is directly comparable to previously reported $ClNO_2$ detection by quadrupole CIMS. Thus, TD-TILDAS can provide an alternative analytical approach for a direct measurement of $ClNO_2$ that can complement existing datasets and future studies. The quantitative nature of TD-TILDAS also makes it a potentially useful tool for the calibration of CIMS instruments. However, interpretation of ambient data may be potentially complicated by interference from unaccounted-for sources of thermolabile chlorine.

1 Introduction

Nitryl chloride ($ClNO_2$) is an important nighttime reservoir of two highly reactive atmospheric species: atomic Cl and NO_2. Atomic Cl radicals play multifaceted roles in oxidation chemistry throughout the boundary layer (Simpson et al., 2015),

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

including hydrocarbon oxidation (Atkinson et al., 2006a, and references therein), ozone production and destruction (Halfacre and Simpson, 2022; Liao et al., 2014; Sarwar et al., 2012, 2014; Simon et al., 2009; Wang et al., 2016), and mercury depletion (Driscoll et al., 2013). However, the quantitative magnitude to which they affect these processes remains an open question. On the other hand, NO_2 is one of the principal components of photochemical smog and the major anthropogenic precursor for ozone production. Accounting for all sources of NO_2 is therefore important for accurately informing chemical and air quality models.

The first in situ observation of ambient $ClNO_2$ was reported by Osthoff et al. (2008) utilising chemical ionization mass spectrometry (CIMS) in the polluted marine boundary layer. CIMS has since been used in a multitude of studies for additional $ClNO_2$ observations worldwide, including North America (Jaeglé et al., 2018; Lee et al., 2018a, b; Mielke et al., 2011; Riedel et al., 2012, 2013; Thornton et al., 2010; Wagner et al., 2013; Young et al., 2012), Europe (Bannan et al., 2015; Phillips et al., 2012; Sommariva et al., 2018; Tan et al., 2022), Asia (Le Breton et al., 2018; Liu et al., 2017; Tham et al., 2016, 2018; Wang et al., 2022, 2016, 2017; Xia et al., 2020; Ye et al., 2021; Yu et al., 2020; Zhou et al., 2018), in the presence of snow/ice (Kercher et al., 2009; McNamara et al., 2020), and in indoor air quality studies (Moravek et al., 2022). Limits of detection are often reported at 10^0 pptv under 25-30 s averaging times, (Bannan et al., 2015; Kercher et al., 2009; McNamara et al., 2020; Mielke et al., 2011), and has been recently reported at sub-pptv for 1 s measurements (Decker et al., 2024). Typical observed mixing ratios range from $10^1 – 10^3$ pptv, with the highest levels observed in coastal polluted regions, where sources of nitrogen oxides and Cl^--rich aerosols are plentiful (Wang et al., 2019, 2021, and references therein).

While CIMS is a highly effective technique, $ClNO_2$ quantitation involves non-trivial calibration work. A laboratory source of $ClNO_2$ may be readily generated by flowing a known amount of N_2O_5 across a Cl^--containing salt bed (or Cl_2 across NO_2^--containing salt bed), but its quantitation assumes unit conversion out of the salt bed (e.g., Osthoff et al., 2008) or requires additional equipment to observe $ClNO_2$ thermal dissociation products, such as a N_2O_5-cavity ring down spectrometer (CRDS) (Thaler et al., 2011) or a cavity attenuated phase shift spectrometer (CAPS) (e.g., Tan et al., 2022). Further, I^- based CIMS demonstrates variable sensitivities based on the temperature and relative humidity of the ion-molecule reactor, thereby requiring substantial laboratory work to develop humidity- and temperature-dependent calibration factors (Lee et al., 2014; Robinson et al., 2022). Thus, there is an opportunity to innovate a method that can detect $ClNO_2$ directly without the need for supplemental instrumentation.

The advantages of optical methods include analyte specificity and near absolute detection, utilizing well-defined physical absorption properties, and requiring only infrequent calibrations or method validation procedures. Thaler et al. (2011) previously used a CRDS system (tuned for the detection of peroxyacyl nitrates) to detect $ClNO_2$ under laboratory conditions, achieving CIMS-competitive metrics (e.g., reported 20 pptv limit of detection for 1 minute averaging). This was achieved by flowing sample air through both an unheated reference pathway and a heated (450 ^oC) sample pathway, under which $ClNO_2$ would thermally dissociate into Cl radicals and NO_2 (Reaction R1).

$$ClNO_2 + heat \rightarrow Cl + NO_2 \quad (R1)$$

The difference in observed NO_2 signal between the two channels provided a quantitative $ClNO_2$ measurement. However, its use for conducting field measurements was reported to be limited, as the thermal degradation of alkyl nitrates (i.e., PAN) into NO_2 cannot be distinguished from NO_2 originating from $ClNO_2$ due to overlapping thermal dissociation profiles.

For this same thermal-dissociation setup, product chlorine radicals will react quickly (e.g., Cl radical lifetime of 0.2 s for typical CH_4 mixing ratios of 2 ppmv and k_{298} = 1 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Bryukov et al., 2002)) with ambient

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

hydrocarbons (e.g., methane) to form hydrogen chloride (HCl), which is a stable reservoir species for reactive chlorine (Reaction R2).

$$Cl + RH \rightarrow HCl + R \quad (R2)$$

Several optical methods for the high-frequency and precise detection of HCl have recently been reported that overcome historical challenges with its sampling (Furlani et al., 2021; Hagen et al., 2014; Halfacre et al., 2023; Wilkerson et al., 2021), making them attractive candidates for an alternative thermal dissociation approach for the detection of $ClNO_2$. In this work, we demonstrate the coupling of a thermal dissociation furnace to HCl-TILDAS (TD-TILDAS) for quantitative detection of $ClNO_2$ as HCl. Compared with CIMS, TD-TILDAS is a lower cost method for determining $ClNO_2$ mixing ratios, involving less experimental calibration work and simpler data processing as a direct method.

2 Methods

2.1 $ClNO_2$ Generation

$ClNO_2$ was synthesized by flowing Cl_2 across a nitrite-rich slurry, as described by Thaler et al. (2011) and shown by Reaction R3.

$$Cl_2(g) + NO_2^-(aq) \leftrightarrow ClNO_2(g) + Cl^-(aq) \quad (R3)$$

However, it is believed the $ClNO_2$, once produced, may react further by dissolving into the water, hydrolyzing, and producing nitronium and chloride ions (R4) (Frenzel et al., 1998).

$$ClNO_2 \leftrightarrow Cl^- + NO_2^+ \quad (R4)$$

The nitronium ion can then react with NO_2^- to produce N_2O_4, which exists in equilibrium with NO_2 (R5).

$$N_2O_4 \leftrightarrow NO_2 + NO_2 \quad (R5)$$

As detailed by Thaler et al. (2011), this chemistry can be mitigated by minimizing the residence time of $ClNO_2$ in the reaction vessel and, to a lesser extent, by increasing the Cl^- content of the slurry to encourage the equilibrium in R4 towards $ClNO_2$. Therefore, we composed our slurry using sodium chloride (>99.5% pure, BioXtra, Sigma Aldrich product no S7653-5KG, USA) and sodium nitrite (99%, extra pure, Acros Organics Code 196620010, Belgium) at a mole ratio of 100:1 Cl^-:NO_2^-, wetting with 18MΩ deionized water (Millipore). The slurry was housed in ~10 cm of 1.25 cm diameter PFA tubing. Varied flow rates (0.5-5 mL min^{-1}) of 10 ppmv Cl_2 (diluted in nitrogen, BOC product no. 150916-AV-B, United Kingdom) were injected into a dilution flow (ranging from 200-2499.5 mL min^{-1}) of NO_x-scrubbed compressed air (using trap composed of 50% Sofnofil (Molecular Products Ltd., Essex, United Kingdom) and 50% activated carbon) that was subsequently passed over the slurry, generating $ClNO_2$. A portion of the dilution flow was directed into a bubbler containing 18MΩ deionized water prior to entering the slurry to maintain a humid environment and prevent the slurry from drying out. A schematic diagram of this setup is presented in Fig. 1a.

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

2.2 TD-TILDAS

The TILDAS instrument and operation technique have been well-described previously (McManus et al., 2011, 2015). HCl-TILDAS was developed by Aerodyne Research, Inc. and characterized by Halfacre et al. (2023). Briefly, air is sampled at 3.0 L min^{-1} through a heated (50 ºC) quartz "inertial inlet," which is a type of virtual impactor used to remove particles >300 nm from the sample matrix. Sample air continues its flow through 3 m of heated (50 ºC) tubing into the Herriott cell (204 m pathlength) inside the TILDAS. HCl is then detected via a mid-IR inter-band cascade laser that probes the strong R(1) $H^{35}Cl$ absorption line at 2925.89645 cm^{-1} within the (1-0) rovibrational absorption band (Guelachvili et al., 1981).

Nitryl chloride was converted to HCl for detection by TILDAS via thermal dissociation and the subsequent reaction of Cl radicals with hydrocarbons, namely methane (Reactions R1-R2) (Thaler et al., 2011). The sample flow was additionally spiked with propane (BOC Limited, product no. 34-A) to a mixing ratio of 5 ppmv to ensure reaction completeness and outcompete Cl wall losses. Next, the sample was directed to a 90 cm length of quartz tubing (9.5 mm OD, 7.5 mm ID) housed within a furnace (Carbolite Gero TS1 12/60/450) upstream of the inertial inlet. Sixty centimetres of this tubing is held within the heated region of the furnace, resulting in a residence time of ~500 ms under a flow rate of 3 L min^{-1}. To mitigate HCl surface interactions after $ClNO_2$-conversion, perfluorobutane-1-sulfonic acid (PFBS; Merck, product no. 562629, United Kingdom) vapor was introduced just after the furnace to improve HCl transmission to the TILDAS inlet (Halfacre et al., 2023; Roscioli et al., 2016). As detailed by Halfacre et al. (2023), a flow (50-75 mL min^{-1}) of oxygen-free nitrogen was flowed into the headspace of a Teflon bubbler containing 5 g of PFBS, thereby flushing the PFBS vapor into the sample line. A schematic diagram of this setup is presented in Fig. 1b.

The major sources of uncertainty with using TD-TILDAS to detect $ClNO_2$ include the degree of $ClNO_2$ conversion to HCl, instrument noise, background drifts, and potential line losses of HCl. Confirmation of the unit conversion of $ClNO_2$ to HCl was confirmed by modelling and laboratory experiments (see Sects. 3.1 and 3.2). Instrument noise and background drifts were assessed regularly from blanks. For laboratory experiments, blanks were performed by sampling the $ClNO_2$ standard (Sect. 2.1) diluted in NO_x-scrubbed compressed air through the unheated furnace. This dilution air was generated using an air compressor and dehumidifying system (dew point approximately −60 ◦C, absolute water vapor concentration ∼ 0.01%). To vary sample humidity, carrier gas flow was split such that varied amounts were passed through a bubbler containing deionized water. Concerning line losses of HCl, the only source of HCl will be from $ClNO_2$ conversion during laboratory experiments, and therefore line losses were assessed between the furnace and the inertial inlet. As detailed in Fig. 1b, 30 mL min^{-1} of flow from a homemade HCl permeation source (Furlani et al., 2021; Halfacre et al., 2023) was injected alternatingly before the furnace and just before the inertial inlet to determine loss of HCl over this region. So long as unit conversion of $ClNO_2$ to HCl can be confirmed and blank / line losses are corrected, this method will be as accurate as the TILDAS is for detecting HCl, which was previously found to be within the 5% tolerance of a commercial HCl cylinder with a certified concentration (Halfacre et al., 2023).

For ambient sampling (Fig. 1c), an additional 5m of 1.25 cm OD PTFA Teflon was added before the tee that splits the CIMS and TILDAS flow paths to sample outside air. A 5 µm PFA Teflon filter was also installed to collect particulates, reducing the potential for HCl displacement through thermodynamic partitioning of particulate Cl^- that would otherwise enter the heated furnace (Huffman et al., 2009). Blank air was generated by pumping ambient air through a 50% activated carbon / 50% Sofnofil scrubber, which was found to effectively remove $ClNO_2$ from the sample stream. The pump (KNF model N035.1.2AN.18) was able to overblow the sample inlet at a flow rate of ~25 L min^{-1}. This approach is favoured over the use of synthetic cylinder air as significant changes in sample humidity can result in release of HCl from surfaces (Halfacre et al., 2023). Blanks were performed for 10 minutes every 30 minutes to ensure the instrument had enough time to respond and adjust

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

to a stable background value. Additionally, ambient measurements will include HCl, which would act as an interference for $ClNO_2$ observations. To obviate this, a denuder (coating of 2% Na_2CO_3 and 2% glycerol dissolved in 50% water and 50% methanol) was installed before the furnace to selectively remove acidic gases (e.g., HCl, HNO_3) that may influence quantitation. While effective for this purpose, the denuder was also found to affect $ClNO_2$ throughput, with a freshly coated denuder causing as much as 55% loss of the $ClNO_2$ standard mixing ratio. As such, the $ClNO_2$ standard (Sect. 2.1) was sampled in dry air before and after overnight experiments to estimate how this loss process evolved over the course of an experiment. In contrast to the laboratory experiment configuration, permeation source HCl in blank air was only injected just downstream of the furnace mid-experiment. Losses were assessed by comparing this observed HCl injection value to pre- and post-experiment injections over dry compressed air. Injections of HCl and $ClNO_2$ standards was controlled using 3-way Teflon solenoid valves (MasterFlex Model no. 01540-18, Cole Parmer, United Kingdom).

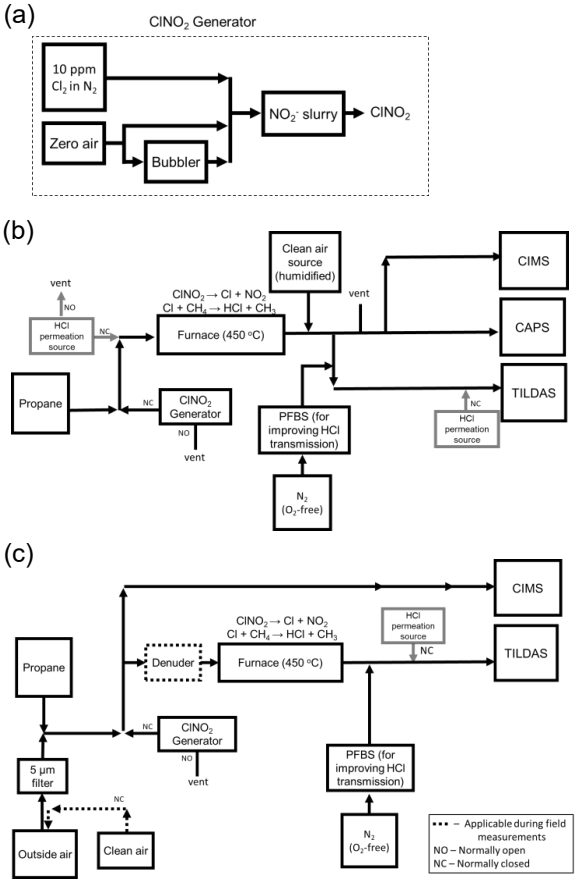

Figure 1 Experimental schematic diagrams for (a) generating $ClNO_2$, b) laboratory comparison measurements between CIMS, TILDAS, and CAPS NO_2, and (b) calibration/field sampling between CIMS and TILDAS. Note that "NO" stands for "normally open" and "NC" stands for "normally closed" in reference to solenoid valves that control the flow direction for these items.

2.3 Supporting Instrumentation

To confirm the efficacy of TD-TILDAS as a valid quantitative method for $ClNO_2$ detection, testing was performed simultaneously with a Cavity Attenuated Phase Shift (CAPS) NO_2 instrument (Sect. 2.3.1) and Time of Flight-Chemical Ionization Mass Spectrometer (Sect. 2.3.2), both of which have previously reported as $ClNO_2$ detection methods.

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

2.3.1 Cavity Attenuated Phase Shift (CAPS) NO_2

$ClNO_2$ mixing ratios observed by the TILDAS were confirmed via simultaneous detection of the NO_2 product of $ClNO_2$ thermal dissociation using a commercial Cavity Attenuated Phase Shift NO_2 detector (Teledyne T500U CAPS). Briefly, emission from a LED (emission centred around 425 nm) is reflected across two spherical mirrors and absorbed by NO_2 in the optical cell. This difference in light is detected by a photodiode and quantified based on its absorbance via the Beer-Lambert Law. The instrument was calibrated using gas-phase titration of NO by O_3 to produce varied concentrations of NO_2. A 1ppm NO in nitrogen cylinder (certified 982 ppb, NPL) was used to verify the concentration of NO in a 25ppm NO in nitrogen working standard (BOC). A multigas blender (Environics S6100) was used to generate a range of O_3 concentrations (range 0-130 ppbv) for titrating some of the NO (NO in excess, 200 ppbv) into NO_2, and the decrease in the NO concentrations was measured using a calibrated NO_x instrument (Teledyne API Chemiluminescence T200). The NO_2 introduced to the CAPS instrument is thus the sum of the drop of NO from the added ozone and the NO_2 already present in the working standard. The T200 NO_x instrument was also used to measure ambient air alongside the CAPS (range 0-25 ppbv), and these data are presented in Fig. A1.

2.3.2 Time of Flight Chemical Ionisation Mass Spectrometry (CIMS)

$ClNO_2$ was additionally detected using a VOCUS high-resolution chemical ionization time-of-flight CIMS (Tofwerk, Switzerland) with a VOCUS AIM reactor and using iodide (I^-) as a reagent ion gas. A complete description of this instrument and its operational principles are described in detail by Riva et al. (2024). Briefly, sample gas is drawn into the sampling inlet and pulled through a critical orifice (0.475 mm) and PFA Teflon sample flow guide into a conical ion-molecule reactor (IMR) at a flow rate of 1.8 L min^{-1}. The IMR was held at a constant pressure of 50 mbar using a vacuum pump (IDP3, Agilent Technologies) and temperature controlled to 50 °C. The reagent ion source was a permeation tube containing trace amounts of CH_3I dissolved in benzene (Tofwerk). Ultra-high purity, oxygen-free N_2 gas (generated by flowing compressed air through gas with a commercial N_2 generator, Infinity NM32L, Peak Scientific Instruments, UK) is continually flowed over the permeation tube to flush the gaseous CH_3I/benzene mixture into a compact vacuum ultraviolet ion source (VUV). Within the VUV, UV light emitted from a Kr lamp (116.486 nm and 123.582 nm) is absorbed by benzene, generating low energy photoelectrons that can react with CH_3I to produce I^- (Ji et al., 2020). The I^- reacts with analytes for approximately 30 ms before being drawn through another critical orifice where the sample travels through four differentially pumped chambers before reaching the drift region of the ToF-CIMS. Ions in the ToF chamber are extracted and converted into mass spectra via an MCP detector with a preamplifier over a mass range of 7-510 Th. The extracted packets are averaged over a period of 1 second and the resolution of the instrument is ≈ 5000. Data was collected at a rate of 1 Hz. Data averaging, mass calibration, peak assignment, peak fitting and peak integration are all performed using the software package Tofware (version 4.0.0, TOFWERK) used in Igor Pro 9 software (Wavemetrics). Peak fitting focused on $I^{35}ClNO_2^-$ (m/z 207.8668) and $I^{37}ClNO_2^-$ (m/z 209.8638), and isotope abundances were manually confirmed to be ~1:0.32, based on the natural abundance of chlorine isotopes. CIMS signals were normalized against the sum of the total number of reagent ions, which is equivalent to $I^- + I(H_2O)^-$. Additionally, as the CIMS sensitivity to $ClNO_2$ varies with humidity in the ion-molecule reactor region, we define an additional term equal to ratio of the iodide water cluster ($I(H_2O)^-$) to the reagent ion sum ($I^- + I(H_2O)^-$), hereafter referred to as the Iodide Water Ratio (IWR). Instrument backgrounds were assessed using air scrubbed of $ClNO_2$, as described in Sect. 2.2.

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

2.4 Data Analysis

Data analysis was conducted using the R language for statistical computing (R Core Team, 2021). Linear regressions were calculated using the York method (Cantrell, 2008) when possible so as to incorporate uncertainties in compared variables.

2.5 Chemical Modelling

The 0-D box model Kintecus (Ianni, 2003, 2022) was used to predict the timescales for the thermal-dissociation of $ClNO_2$ and the subsequent formation of HCl after reaction with hydrocarbons (Reaction R2), as well as to identify potential interferents that could prevent unit conversion of $ClNO_2$ to HCl. The results of the model were used to guide the experimental set-up. The modelled species, reaction list, and initial concentrations are included in the Appendix (Tables A1-A3). Reaction kinetics were sourced from the NIST Chemical Kinetics Database and IUPAC Evaluated Kinetic Data websites (Manion et al., 2015; Wallington et al., 2021), and primary literature references are listed next to each reaction. The model integration time was set to 1 ms, and the entire simulation was set to last 150 ms. The model initiated with a temperature of 25 ^{o}C (held for 10 ms) before increasing to 450 ^{o}C over the course of 22 ms. The temperature was held at 450 ^{o}C for 40 ms, before gradually decaying back to 25 ^{o}C over 70 ms.

3 Results & Discussion

3.1 Modelling TD Chemistry

Box model simulations predicted the rapid, virtually unit conversion of $ClNO_2$ to HCl after increasing temperature to 450 ^{o}C (Fig. 2). Ninety percent conversion was calculated to occur within 23 ms from a starting $ClNO_2$ concentration of 2.46 x 10^{10} molecules cm^{-3} (1 ppbv at 25 ^{o}C), and ambient mixing ratios of methane (i.e., 2 ppmv at 25^{o}C) were found to be sufficient for facilitating this chemistry. While Cl-mediated hydrocarbon oxidation was shown to produce a modest enhancement of hydroxyl radical concentrations (Fig. 2b), it was not enough to compete meaningfully with Cl to mitigate or retard Reaction R1. Similarly, an initial O_3 concentration of 9.84 x 10^{11} molecules cm^{-3} (40 ppbv at 25^{o}C) did not significantly inhibit the desired chemistry by the direct reaction of O_3 with Cl radicals.

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

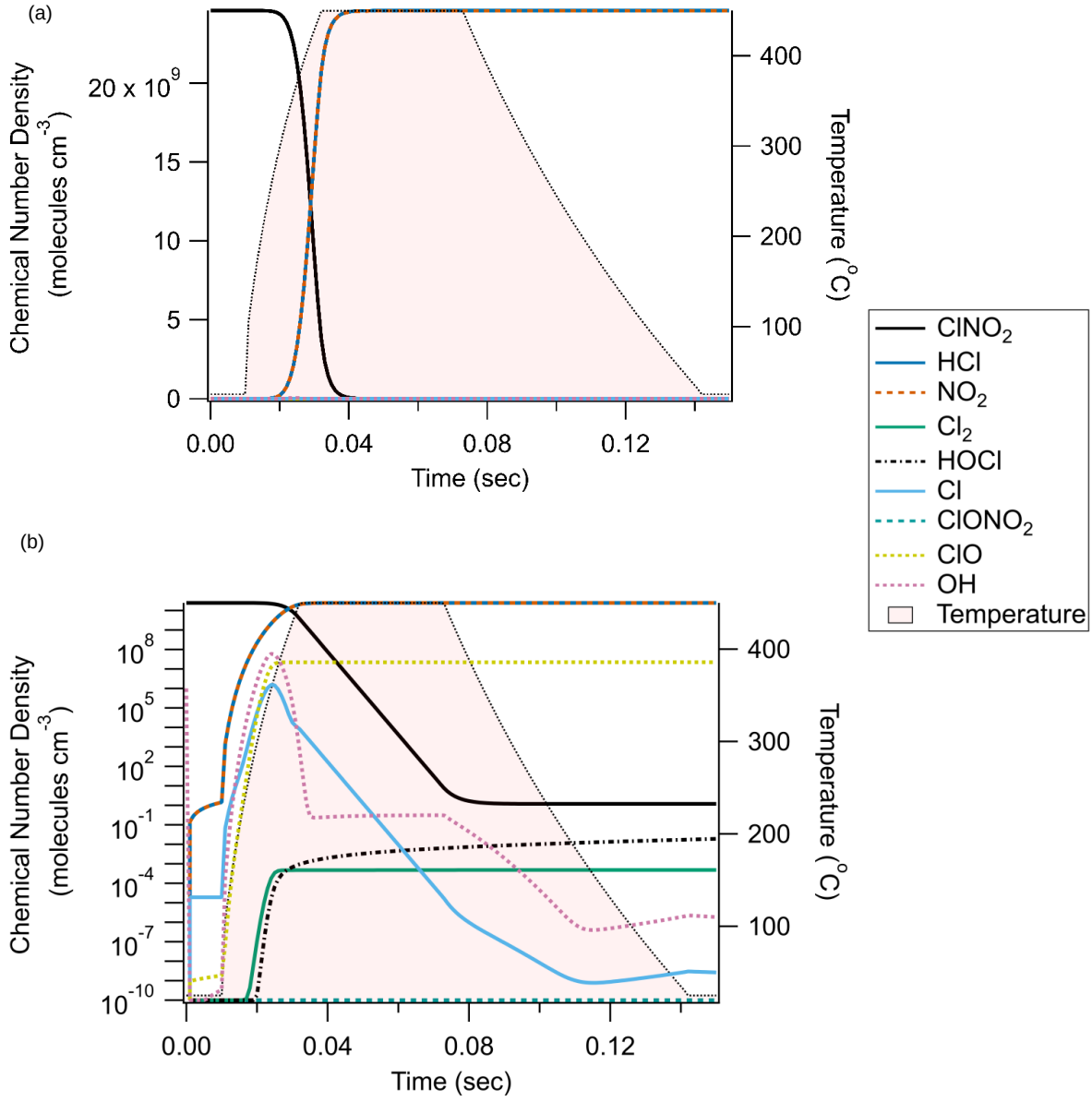

Figure 2: Chemical modelling results of the thermal dissociation of $ClNO_2$ and its subsequent conversion to HCl. Panel A presents results on a linear y-axis, while Panel B features the same data on a logarithmic y-axis.

Concerning potential interferents, $ClNO_2$ was predicted to be the only source of inorganic chlorine to thermally dissociate at 450 °C. This is consistent with the relative bond dissociation energies found for $ClNO_2$ (142 kJ mol^{-1}) relative to the various other forms of inorganic chlorine simulated (Cl-NO_2 < Cl-Cl < Cl-O < Cl-R < Cl-H) (Darwent, 1970). Finally, production of other inorganic chlorine compounds (e.g., Cl_2, HOCl, $ClONO_2$, or reformation of $ClNO_2$) was orders of magnitude less than the resulting HCl and is therefore not believed to influence HCl production. One notable class of compounds that could not be

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

simulated were chloramines, which have recently received increased attention as relevant daytime sources of Cl atoms (A. Angelucci et al., 2023; Wang et al., 2023). Trichloramine, dichloramine, and monochloramine have reported bond dissociation energies of 381, 280, 251 kJ mol^{-1}, respectively (Darwent, 1970), and so would not be expected to produce free Cl radicals in the temperature range simulated herein if its thermochemistry is consistent with the above bond dissociation energy trend. However, to the authors' knowledge no information is available regarding its thermal stability in the gas phase at atmospherically relevant conditions, and this potential source of positive interference for our proposed method cannot be discounted via the model at this time.

3.2 Laboratory Characterization of TD-TILDAS

For laboratory characterization, a stable source of $ClNO_2$ was generated (Sect. 2.1) for assessing TD-TILDAS performance in comparison with other established $ClNO_2$ sampling techniques, including CAPS NO_2 and CIMS (Sect. 2.3). One key change between model simulations and this experimental setup is the inclusion of propane to the sample stream (estimated mixing ratio of 5 ppmv within the heated section of sample configuration). While the model predicted the pertinent chemistry will occur in ~23 ms using only ambient methane as the hydrocarbon (Sect. 3.1) and the residence time in the heated furnace is ~500 ms, adding propane ensures complete conversion of $ClNO_2$ to HCl and ensures wall losses are negligible, as Cl radicals react with propane approximately 3 orders of magnitude faster than with methane (Atkinson et al., 2006a). The fact that no additional HCl signal was observed on addition of propane at varying levels (not shown) supports our calculations that unit conversion is achieved and competitive loss of Cl radicals to walls is negligible.

A schematic diagram of these experiments is shown in Fig. 1a. Figure 3 represents a typical comparison experiment in which $ClNO_2$ was sampled by all three instruments simultaneously. First, $ClNO_2$ was introduced into the flow stream with the furnace unheated, yielding a positive CIMS signal for $ICl NO_2^-$ (~1100 ncps for the example in Fig. 3), while TILDAS HCl and CAPS NO_2 mixing ratios remained at background levels. As the furnace temperature approached 450 °C, Reactions R1-R2 began to occur. HCl and NO_2 mixing ratios rose, plateauing at similar values (~2.2 ppbv in Fig. 3) while $ICl NO_2^-$ decreased to the instrument baseline, implying both Reactions R1-R2 proceeded to completion. Signals returned to their original positions once the furnace was allowed to cool back to room temperature (e.g., from 16:45 in Fig. 3). Note that HCl signal spike during the furnace's temperature ramp was seen consistently across experiments, and was most likely caused by a shift in HCl molecule partitioning between the surface of the quartz tubing toward the gas phase (Halfacre et al., 2023). Allan-Werle deviation calculations demonstrate favourable performance metrics for TILDAS while sampling $ClNO_2$, with 1 Hz precision of 11.8 pptv, and as good as 1.2 pptv with an integration time of 96 seconds (Fig. 4).

A summary of comparison experiments across varied humidities is presented in Fig. 5. The changes in HCl as observed by TILDAS correlated strongly with the changes in NO_2 observed by the CAPS instrument (Pearson correlation coefficients of 0.999, 0.997, and 0.987 for relative humidities of 11%, 44%, and 66%, respectively). However, the slopes were consistently less than unity (0.95 ± 0.01, 0.93 ± 0.02, and 0.91 ± 0.02 at 11%, 44%, and 66%, respectively), indicating observed HCl mixing ratios were less than corresponding NO_2 mixing ratios. One potential explanation for this could be loss of Cl radical loss in the furnace, but we do not believe this to be the case (as detailed above). While physical losses of HCl to sampling lines would not be unexpected as HCl has a high affinity for sorbing to physical surfaces, experiments were designed to minimize these interactions, and line loss experiments were performed to quantify any losses observed at tested humidities. Experimentally, a small flow (50-75 mL min^{-1}) of PFBS vapour was injected into the TILDAS sampling line downstream of the furnace to reduce HCl affinity for surfaces (Sect. 2.2) (Note that PFBS was not introduced to the entirety of the flow path to avoid sampling of PFBS by other instruments. Additionally, there is evidence that PFBS degrades at temperatures above 400°C (Xiao et al., 2020), and so its ultimately efficacy and reproducibility within the furnace system would be uncertain).

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

Further, the high operating temperature of the furnace would also be expected to minimize HCl-wall interactions within the quartz tubing. Indeed, no lines losses were found at 11% relative humidity between when the HCl permeation source standard was injected into the sampling line before the furnace (2.95 ± 0.02 ppbv) and when HCl was injected just before the inertial inlet (accounting for dilution factors) (2.95 ± 0.02 ppbv), consistent with Halfacre et al. (2023). Similar results were found at 44% relative humidity (pre-furnace value of 2.68 ± 0.03 ppbv vs 2.66 ± 0.03 ppbv when HCl was introduced at inlet), and real HCl loss was quantified at 66% relative humidity (pre-furnace value of 1.87 ± 0.03 ppbv vs 1.97 ± 0.03 ppbv when HCl introduced at inlet). Having accounted for these line losses, ANOVA calculations found no significant differences between these three slopes as presented in Fig. 3 ($F(2,19) = 0.10$, $p = 0.902$), indicating consistent performance between TILDAS and CAPS for detecting $ClNO_2$. However, it does not appear to explain the deviation from unity, which will be discussed below.

As discussed in Sect. 2.1, chemistry may occur within the slurry to produce N_2O_4, which can easily degrade at room temperature to produce two NO_2 molecules. If the N_2O_4 output from the NO_2^-/Cl^- slurry is constant over the timescale of an experiment (< 1 hr), it would be expected this additional NO_2 is readily accounted for during blank subtraction calculations. While we believe this is largely true for the experiments presented above, discrepancies in $ClNO_2$ signals were observed as the slurry aged (> ~3 weeks), with CAPS-observed NO_2 mixing ratios growing in significant excess of TILDAS-observed HCl mixing ratios (Fig. A2). Separate applications of TILDAS- and CAPS-based calibration factors (using data from Fig. 5) to concurrent CIMS $ClNO_2$ observations show closer resemblance to the TILDAS-observed mixing ratios (Fig. A2), suggesting additional chemistry may be occurring within the salt bed that produces stable reservoirs of NO_2 that thermally dissociate in the furnace to produce undesired NO_2. This NO_2 artefact serves as a likely explanation for the sub-unity slopes presented in Fig. 5, as it would positively bias the CAPS measurements but not the TILDAS, which is only sensitive to HCl. We are not aware of such chemistry being addressed in the literature for this $ClNO_2$ generation method and do not propose potential reactions as it is outside the scope of this paper.

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Preprint. Discussion started: 26 February 2025

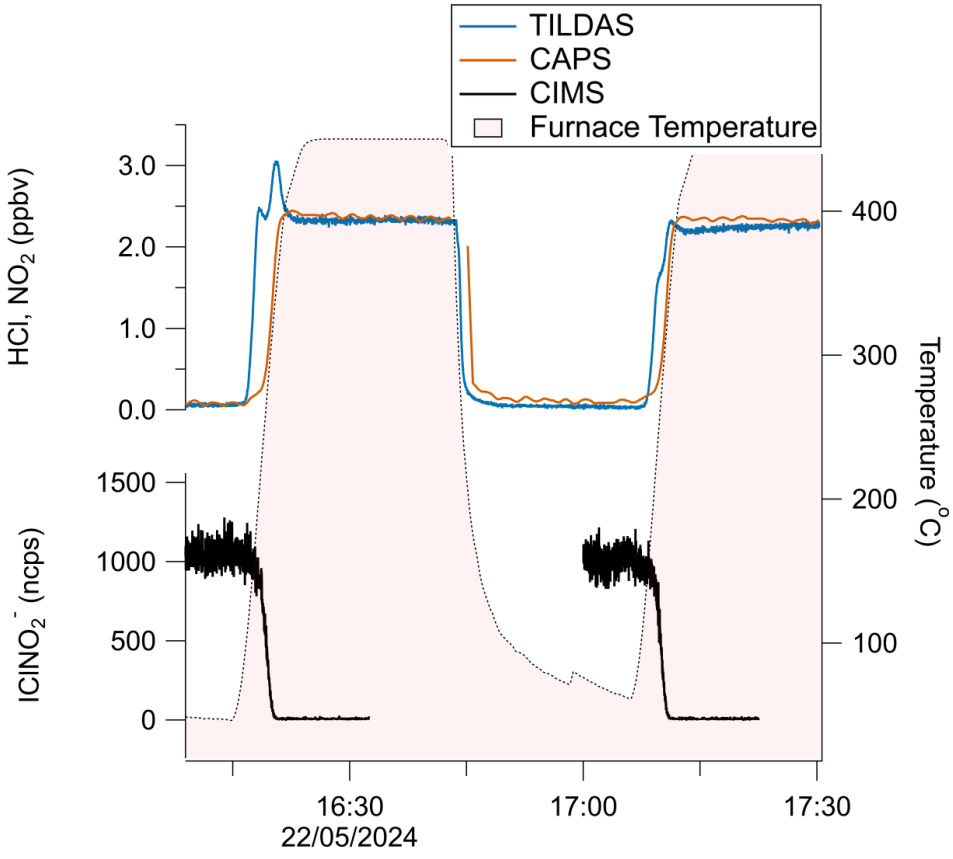

Figure 3: a) Time series demonstrating the reversible thermal conversion of $ClNO_2$ to NO_2 (red trace, CAPS) and HCl (blue trace, TILDAS), as evidenced by changes in CIMS-observed $ICINO_2^-$ (black). Gaps in CIMS data are from internal CIMS tests not pertinent to this work.

Both HCl and NO_2 mixing ratios independently correlated strongly with the CIMS measurement of $ICINO_2^-$ (Fig. 5b, c), and the I^- CIMS sensitivity for $ICINO_2^-$ was found to vary strongly with humidity, as previously reported (Kercher et al., 2009; Mielke et al., 2011). The weakest Pearson correlation coefficient was for NO_2 and $ICINO_2^-$ at 66% relative humidity ($r = 0.988$), virtually matching that of NO_2^- and HCl at the same humidity. Due to the uncertainty / unreliability of the NO_2 as it relates to $ClNO_2$ quantitation, we do not further consider the relationship between CAPS and CIMS.

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Preprint. Discussion started: 26 February 2025

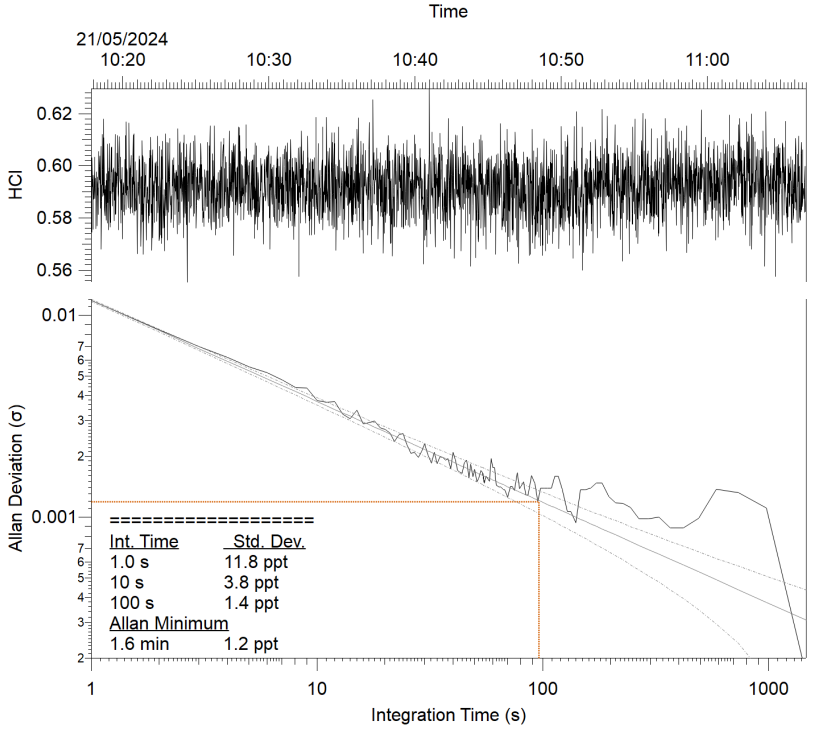
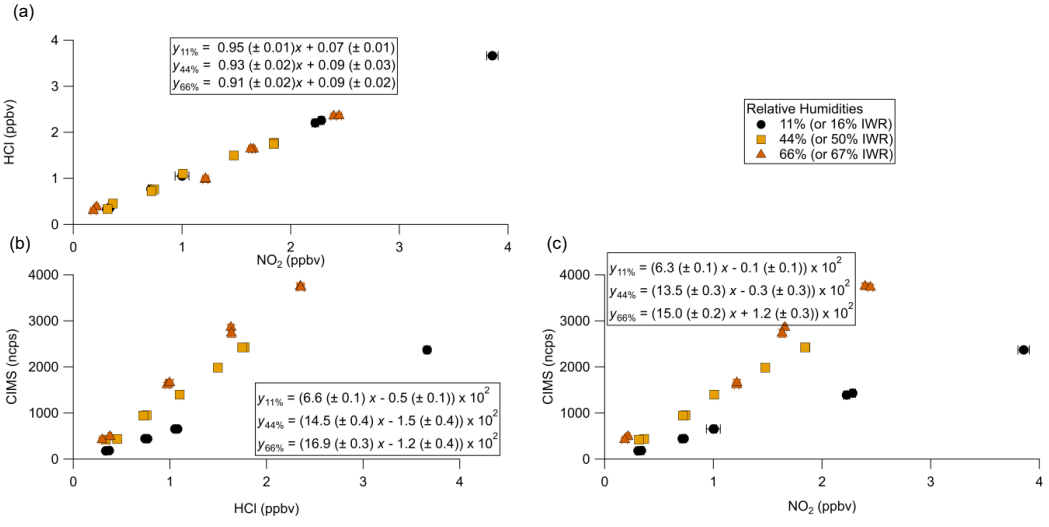


Figure 4: Allan-Werle plot for TD-TILDAS during addition of $ClNO_2$ standard into the sample line. The Allan minimum is indicated by the dotted red lines.



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Preprint. Discussion started: 26 February 2025

Figure 5 – Comparison curves of a) TILDAS vs CAPS, b) CIMS vs TILDAS, and c) CIMS vs CAPS for injections of varied mixing ratios of $ClNO_2$ across different relative humidities. Regressions involving TILDAS data have been corrected for line losses observed at 66% relative humidity.

The linear equations from Fig. 5a present significant intercepts that suggest a source of positive error for the TILDAS, and the similarity of these intercepts suggest a relatively constant/consistent source (values are statistically the same $F(4,19) = 0.624$, $p = 0.546$ per ANOVA). For these experiments, TILDAS blanks were obtained by sampling slurry air flowed through an unheated furnace; in this scenario, Reactions R1-R2 are unable to occur, and therefore any signal observed by TILDAS could be considered background. It is possible that a small amount of HCl forms in the slurry system from the aqueous disproportion reaction between Cl_2 and H_2O. When the furnace is unheated, some amount of HCl interaction with the quartz tubing is expected given there is no PFBS flow through this portion of the plumbing, biasing this blank measurement low. Then, once the furnace is heated to 450 °C, this HCl will be liberated from the quartz tubing, possibly then biasing the heated measurement high. This is supported by the presence of a peak in observed HCl as the furnace reheats (e.g., as in the second temperature ramp in Fig. 3), as some of the HCl sorbed to the furnace tube walls under room temperature is forced into the gas phase. The statistical similarity in intercepts implies this effect is constant across these experiments, leading to a consistent offset. While an ideal blank would sample the gas downstream of the slurry while selectively scrubbing $ClNO_2$, this was not practical to achieve without simultaneously scrubbing HCl. Therefore, we propose the y-intercept in these cases is a good estimate of the systematic error present in these comparison experiments.

3.3 Applicability as Field Instrument

The applicability of TD-TILDAS as a field method for $ClNO_2$ detection was tested by sampling ambient air from outside the Wolfson Atmospheric Chemistry Laboratory building on the University of York campus (York, United Kingdom) from the morning of 13 January 2025 (Fig. 6). Compared with the laboratory-based configuration described in Sect. 3.2, ambient air will contain varied amounts of HCl that would interfere with accurate quantification of $ClNO_2$ via the TILDAS method. To address this, a base-coated denuder (Sect. 2.2) was installed in the HCl sampling line. $ClNO_2$ throughput was found to be hindered when flowed through the denuder but increased over the course of the observation period (pre-experiment estimation of 55% loss vs 31% measured directly after the experiment). This loss was accounted for by applying a time-varying, linearly interpolated correction factor for the denuder. In addition, line losses affecting HCl between the heated furnace and TILDAS inlet were estimated as 2.7%, which was added back into the TILDAS measurements. CIMS observations of $ICl NO_2^-$ were calibrated against TD-TILDAS using a mid-experiment $ClNO_2$ addition, yielding a sensitivity factor of 1982 ncps ppb^{-1} (measured with a corresponding IWR of 42%). We note that this factor is ~35% greater than the value of 1450 ncps $ppbv^{-1}$ as presented in Fig. 5b for a comparable IWR (44%); this is likely due to the replacement of the reagent ion permeation source and change in CIMS inlet configuration between the experiments from Sect. 3.2 and this section. Application of this sensitivity factor across this measurement period can be justified as the IWR was found to be stable (38 ± 2%). Limits of detection, based on instrument blanks, were found to average 10 ± 5 pptv for TD-TILDAS and 1 ± 1 pptv for CIMS (using 60 second data averaging).

As seen in Fig. 6a, TILDAS- and CIMS-observed $ClNO_2$ demonstrate very good agreement for these ambient observations in both signal magnitude and structure. This is quantitatively supported by regression calculations during this period that yield a slope of 0.97 ± 0.01 (Fig. 6b), which is well within the averaged combined uncertainty for this period of 9%. While the sub-unity slope could indicate small losses on the TILDAS method, pre- and post-experimental losses were tested and corrected for as detailed above, and so this is not believed to be a large source of error in this case. It is otherwise not unexpected that this slope is found to deviate from unity given the uncertainty in the application of a single-point CIMS

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

sensitivity factor. Nevertheless, this agreement gives us confidence that it is appropriate for these measurements and provides proof-of-concept for this TILDAS method.

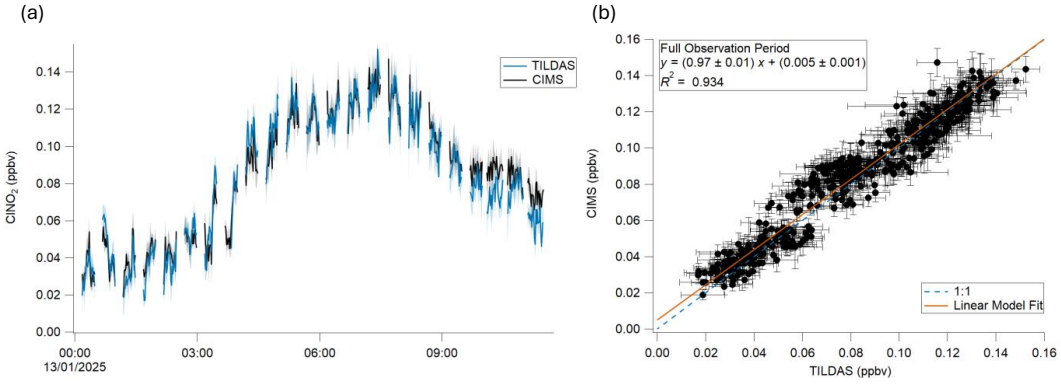

Figure 6 – a) Time series comparison of TILDAS and CIMS observations of $ClNO_2$. b) Scatter plot of data shown in panel (a). The error shading in (a) and bars in (b) represent the standard deviation of the 60 s averaged measurements.

Additional sources of measurement uncertainty include unaccounted-for thermolabile chlorine reservoirs that could cause positive interference in the TILDAS-method. As stated above, the TD-TILDAS method functions on the assumption that $ClNO_2$ is the only inorganic chlorine source that thermally dissociates at 450 °C. However, relevant thermochemistry information is unavailable for chloramines, which therefore cannot be ruled out as possible interferences. Indeed, while CIMS signals of chloramines did not rise above their baselines during the period shown in Fig. 6, a separate measurement period demonstrates multiple occurrences where signal increases in iodide-tri- and di-chloramine adducts ($INCl_3^-$, $INHCl_2^-$) correspond with TILDAS-observed signal increases (Fig. A3). This is most dramatic at ~08:15, where ~115 ncps of $INCl_3^-$ and 18 ncps of $IHNCl_2^-$ corresponds with an increase of 100 pptv in the TILDAS signal. Synthesis and calibration of chloramine standards is a non-trivial task (Wang et al., 2023), and so further experiments are required to investigate 1) to what extent the chloramine signals can be quantified by TILDAS and 2) if the chloramine signal can be dissected from the $ClNO_2$ signal through temperature scans. The results of such experiments may therefore allow this method to be extended for the quantification of both chloramines and $ClNO_2$.

Conclusions

This work demonstrates the viability of TD-TILDAS as an independent $ClNO_2$ detection method at performance metrics comparable to quadrupole CIMS, which are more than adequate for commonly observed mixing ratios in the boundary layer. While modern CIMS instruments can achieve lower limits of detection and higher precision, the major advantage of TD-TILDAS over CIMS is that it does not require external $ClNO_2$ calibration experiments, as this work demonstrates the unity conversion of $ClNO_2$ to HCl that is subsequently detected based on well-understood spectroscopic principles. The TD method described here can thus be used effectively in laboratory settings to measure $ClNO_2$ in related experiments, or even to calibrate CIMS for $ClNO_2$ directly without needing to make assumptions regarding Cl_2 conversion on salt slurries. Additionally, use of a denuder allows this method to be readily applied to other HCl optical instruments, such as those based on CRDS.

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

As a field method, TD-TILDAS demonstrated excellent agreement with a co-located CIMS for $ClNO_2$ detection. However, the TD-TILDAS method appears susceptible to positive interference, potentially resulting from chloramines or other unaccounted-for thermolysable chlorine compounds. More work is required to confirm and quantify the response of this method to chloramines, and if so, identify an appropriate method to mitigate this potential interference. Experimental adjustments could be further made for the TILDAS to alternate its sampling between a heated channel (as described in this paper) for $ClNO_2$ detection and an unheated pathway that allows for the additional detection of HCl. Doing so would require careful characterization of physical HCl losses inherent to both sampling pathways, as well as consideration of the likely hysteresis in detected HCl mixing ratios resulting from changes to the sampled air temperature that would affect the partitioning of HCl between surfaces and the gas phase.

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

Appendix 1

Table A1 – Bimolecular reactions and parameters used for the modelling described in Sect. 2.5. Reactions follow the rate expression $k(T) = A\,(T/298)^n\,e^{-Ea/RT}$ (Burkholder et al., 2015)

Reaction	A	n	Ea (kJ mol^{-1})	Reference
$ClNO_2 + M \Rightarrow Cl + NO_2$	9.13×10^{-10}	0	106	(Baulch et al., 1981)
$Cl + Cl \Rightarrow Cl_2$	6.15×10^{-34}	0	-7.53	(Baulch et al., 1981)
$M + ClONO_2 \Rightarrow NO_2 + ClO$	2.76×10^{-5}	0	94.78	(Anderson and Fahey, 1990)
$CH_4 + Cl \Rightarrow CH_3 + HCl$	8.24×10^{-13}	2.49	5.06	(Bryukov et al., 2002)
$HCl + OH \Rightarrow H_2O + Cl$	3.74×10^{-12}	0	4.27	(Baulch et al., 1981)
$HCl + M \Rightarrow H + Cl$	7.31×10^{-11}	0	342	(Baulch et al., 1981)
$CH_3 + HCl \Rightarrow CH_4 + Cl$	3.89×10^{-13}	0	9.64	(Baulch et al., 1981)
$CH_3 + NO_2 \Rightarrow CH_3O + NO$	3.44×10^{-11}	0	0	(Srinivasan et al., 2005)
$O_3 + M \Rightarrow O + O_2$	7.6×10^{-10}	0	93.12	(Heimerl and Coffee, 1979)
$CH_3 + O \Rightarrow CH_2O + H$	2.26×10^{-11}	0	0	(Baulch et al., 1992)
$HCl + O \Rightarrow OH + Cl$	7.07×10^{-14}	2.87	14.72	(Mahmud et al., 1990)
$OH + CH_4 \Rightarrow CH_3 + H_2O$	4.16×10^{-13}	2.18	10.24	(Srinivasan et al., 2005)
$Cl_2 + M \Rightarrow Cl + Cl$	3.85×10^{-11}	0	196	(Baulch et al., 1981)
$Cl + Cl \Rightarrow Cl_2$	6.15×10^{-34}	0	-7.53	(Baulch et al., 1981)
$Cl_2 + O \Rightarrow ClO + Cl$	4.17×10^{-12}	0	11.39	(Baulch et al., 1981)
$Cl_2 + H \Rightarrow HCl + Cl$	1.43×10^{-10}	0	4.91	(Baulch et al., 1981)
$Cl_2 + OH \Rightarrow HOCl + Cl$	3.60×10^{-12}	0	9.98	(Atkinson et al., 2007)
$CH_3 + O_2 \Rightarrow CH_3O + O$	2.19×10^{-10}	0	131	(Baulch et al., 1992)

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

$ClO + O ==> O_2 + Cl$	2.50×10^{-11}	0	-0.91	(Atkinson et al., 2007)
$OH + ClO ==> HO_2 + Cl$	6.86×10^{-12}	0	-2.49	(Atkinson et al., 2007)
$OH + ClO ==> HCl + O2$	4.38×10^{-13}	0	-2.49	(Atkinson et al., 2007)
$CH_3O + NO ==> CH_2O + HNO$	4.00×10^{-12}	-0.7	0	(Atkinson et al., 1992)
$CH_3O + O_2 ==> CH_2O + HO_2$	7.20×10^{-14}	0	8.98	(Atkinson et al., 1992)
$HOCl + O ==> OH + ClO$	1.70×10^{-13}	0	0	(Atkinson et al., 2007)
$ClCO + M ==> CO + Cl$	4.10×10^{-10}	0	24.6	(Atkinson et al., 2007)
$O_3 + NO ==> O_2 + NO_2$	1.40×10^{-12}	0	10.9	(Atkinson et al., 2004)
$CH_3O_2 + NO ==> CH_3O + NO_2$	2.30×10^{-12}	0	-2.99	(Atkinson et al., 2006b)
$HO2 + NO ==> NO_2 + OH$	3.6×10^{-12}	0	-2.24	(Atkinson et al., 2004)
$CH_2O + Cl ==> HCl + HCO$	8.20×10^{-11}	0	0.28	(Atkinson et al., 1992)
$CH_2O + OH ==> HCO + H_2O$	4.73×10^{-12}	1.18	-1.87	(Baulch et al., 1992)
$CH_3O_2 + HO_2 ==> CH_3OOH + O_2$	3.80×10^{-13}	0	-6.49	(Atkinson et al., 1992)
$CH_3OOH ==> CH_3O + OH$	6.00×10^{14}	0	177	(Baulch et al., 1994)
$HCO + O_2 ==> CO + HO_2$	5.20×10^{-12}	0	0	(Atkinson et al., 2006b)
$CO + OH ==> CO_2 + H$	5.40×10^{-14}	1.5	-2.08	(Baulch et al., 1992)
$Cl + HO_2 ==> HCl + O_2$	1.80×10^{-11}	0	-1.41	(Atkinson et al., 1992)
$Cl + HO_2 ==> ClO + OH$	6.30×10^{-11}	0	4.74	(Atkinson et al., 2007)

https://doi.org/10.5194/egusphere-2025-831
Preprint. Discussion started: 26 February 2025

$Cl + O_3 ==> ClO + O_2$	2.80×10^{-11}	0	2.08	(Atkinson et al., 2007)
$CO + Cl ==> ClCO$	1.33×10^{-33}	-3.8	0.00	(Atkinson et al., 2007)
$OH + HOCl ==> H_2O + ClO$	5.00×10^{-13}	0	0	(Atkinson et al., 2007)
$ClO + HO_2 ==> HOCl + O_2$	2.20×10^{-12}	0	-2.8	(Atkinson et al., 2007)
$ClO + ClO ==> Cl_2 + O_2$	1.00×10^{-12}	0	13.22	(Atkinson et al., 2007)
$ClO + ClO ==> OClO + Cl$	3.50×10^{-13}	0	11.39	(Atkinson et al., 2007)
$ClO + ClO ==> ClOO + Cl$	3.00×10^{-11}	0	20.37	(Atkinson et al., 2007)
$ClO + NO ==> Cl + NO_2$	6.20×10^{-12}	0	-2.45	(Atkinson et al., 2007)
$CH_2O + O ==> HCO + OH$	1.78×10^{-11}	0.57	11.56	(Baulch et al., 1992)
$OH + NO_2 ==> HNO_3$	2.70×10^{-11}	0	0	(Troe, 2012)

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Preprint. Discussion started: 26 February 2025

Table A2 – Termolecular reactions and parameters used for the modelling described in Sect. 2.5. The effective rate constant is calculated by combing the low- and high-pressure limit expressions into the following formula: $k_f(T,[M]) = \left\{\frac{k_\infty(T)k_0(T)[M]}{k_\infty(T)+k_0(T)[M]}\right\} 0.6^{\{1+[log_{10}(\frac{k_0(T)[M]}{k_\infty(T)})]^2\}^{-1}}$

Reaction	Low-Pressure Limit $k_0 = k_0^{298}(T/298)^{-n}$		High Pressure Limit $k_\infty = k_\infty^{298}(T/298)^{-n}$		Reference
	k_0^{298}	n	k_∞^{298}	m	
$Cl + NO_2 + M ==> ClNO_2 + M$	1.8×10^{-31}	2	1.1×10^{-10}	1	(Burkholder et al., 2015)
$CH_3 + O_2 + M ==> CH_3O_2 + M$	4.1×10^{-31}	3.6	1.2×10^{-12}	-1.1	(Burkholder et al., 2015)

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Preprint. Discussion started: 26 February 2025

402 **Table A3 – Initial concentrations for specified species simulated in model. All other compounds were initialised with a concentration**
403 **of 0 molecules cm^{-3}.**

Species	Initial Concentration (molecules cm^{-3})
$ClNO_2$	2.46×10^{10} (1 ppbv)
N_2	1.92×10^{19} (78%)
O_2	5.17×10^{19} (21%)
CH_4	4.92×10^{13} (2 ppmv)
OH	1×10^{6}
O_3	9.84×10^{11} (40 ppbv)

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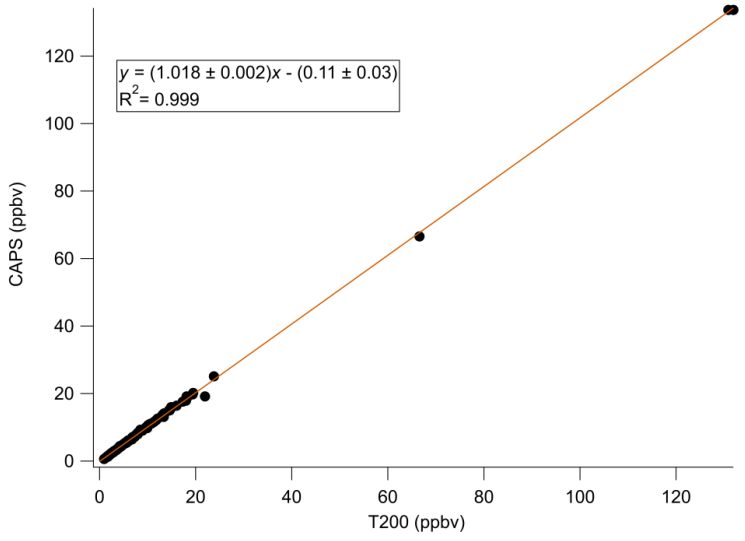

Figure A1 – Laboratory calibration curve for CAPS NO_2

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Preprint. Discussion started: 26 February 2025

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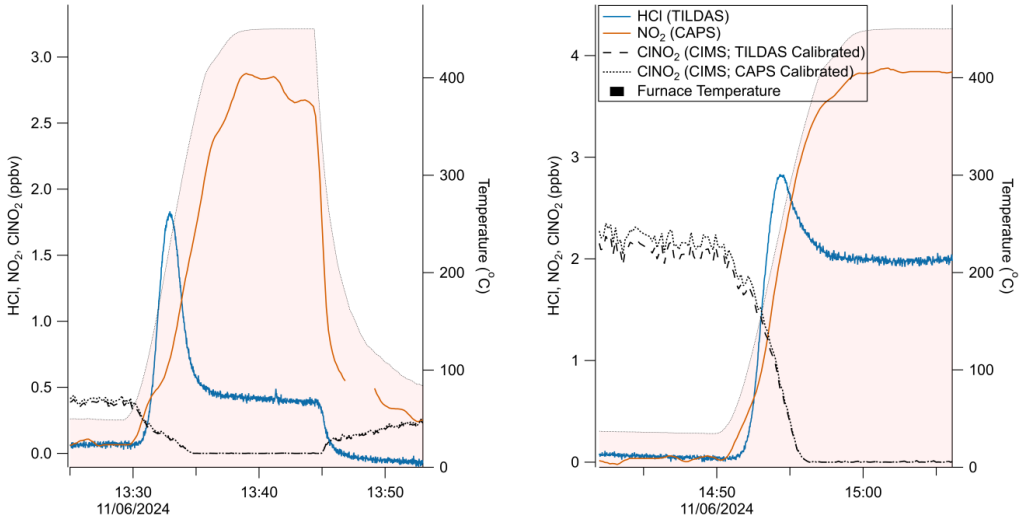

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413 **Figure A2 – a) Comparison plot of $ClNO_2$ observations with an apparent excess of NO_2 formed after aging/processing of the same**
414 **slurry used for generating Fig. 3-4. (b) Additional comparison using a freshly made slurry. CIMS signal was calibrated using**
415 **humidity-dependent calibration factors as presented in Fig. 5.**

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Preprint. Discussion started: 26 February 2025

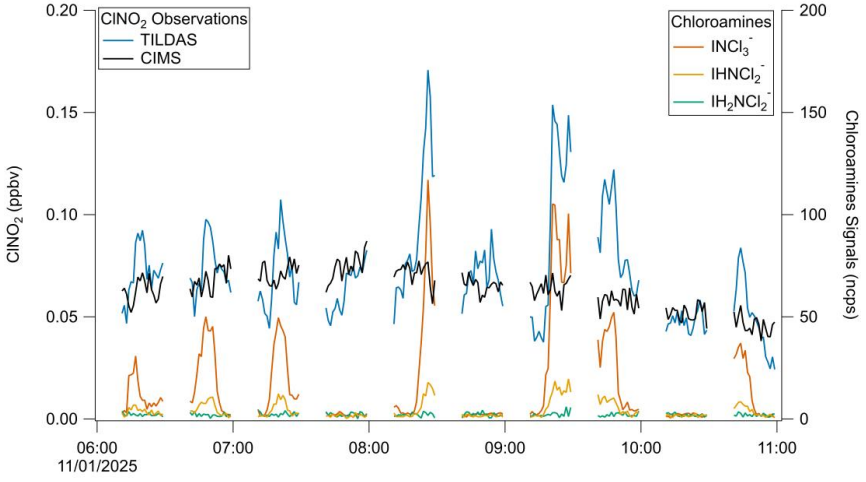

Figure A3 –Field data showing apparent coincident signal increases TILDAS-observed $ClNO_2$ with CIMS-observed chloramines (uncalibrated).

Code availability

Code used for this analysis is available from the corresponding author on request.

Data availability

Data are available from the corresponding author on request.

Author contribution

PRV, MAR, SSB designed and performed proof-of-concept experiments to demonstrate potential of the method.
SCH, HRR, CD, TIY designed, built, and tested the HCl TILDAS at Aerodyne Research, Inc. SCH, HRR, CD, TIY, and PME designed initial laboratory experiments.
JWH and PME designed laboratory and field experiments, and JWH conducted laboratory and field experiments presented in this work.
LM, MDS, LJC provided support for laboratory use of CIMS. EM, TJB, HC provided support for field CIMS observations.
JWH prepared the manuscript, and all authors reviewed the manuscript.

Competing interests

The authors declare that they have no conflicts of interest.

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Preprint. Discussion started: 26 February 2025

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