Measuring Indoor HCl at the parts-per-trillion (ppt) level with novel Picarro CRDS Gas Concentration Analyzer

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ABSTRACT

The Picarro SI2108 gas concentration analyzer can provide real-time monitoring of hydrogen chloride (HCl) at a parts-per-trillion (ppt) sensitivity for a variety of applications, including indoor and outdoor air quality, atmospheric science, and hazard assessment.

The Picarro SI2108 operates using Cavity Ring-Down Spectroscopy (CRDS). CRDS utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify isotope ratios and concentrations. Using a small 3-mirrored cavity with a long effective path-length of up to 20 km, measuring the decay rate rather than absolute absorbance, and using a patented wavelength monitor which provides highly accurate measurement and control of the laser's wavelength, allows the instrument to measure HCl at <15 ppt level precision, with a maximum drift over 24 hours of ±50 ppt.

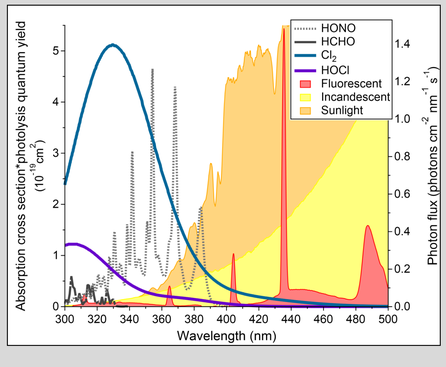
Here we present examples of Picarro instruments being used to define sources of HCl indoors. HCl levels inside are generally a few hundred pptv. Using Picarro analyzers, HCl was observed from dishwasher use and electric stovetop use. Reproducible increases in HCl concentrations (~100 pptv) were also observed from bleach applications on a house floor at night, with room lights turned on. The possibility of direct emission or chemical formation of HCl via chlorine atoms is indicated by these observations of HCl derived from household activities.

PICARRO SI2108 CRDS ANALYZER

- ≤45 ppt HCl LDL (3σ, 100 sec)
- ±50 ppt HCl zero drift (peak-to-peak, 50-minute average)
- 15 ppt HCl precision @ 1σ, 100 sec
- Coated critical gas pathway components reduces HCl adherence to internal surfaces, which improves response time

RADICALS INDOORS

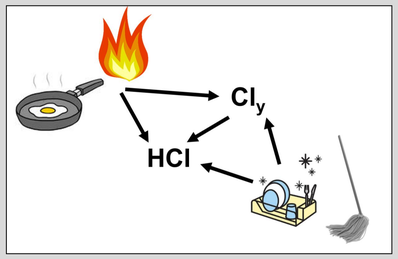
- Lower light available indoors.
  - Photolytic source of OH are less active.
- Indoors, expect greater importance of:
  - NO_3, which forms in the absence of light.
  - Cl, which has more photolabile precursors.
- Possible that Cl_y could have an impact on indoor air quality.



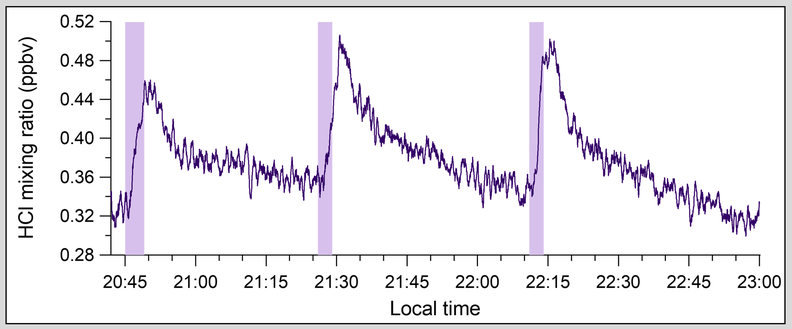
Young et al. 2019 ESPI; Weschler 1992 ES&T

DIRECT SOURCES OF HCl INDOORS

- Possible direct sources of Cl_y include cooking and cleaning activities.
- Measurements of HCl made indoors in an occupied home.



SOURCES OF HCl INDOORS

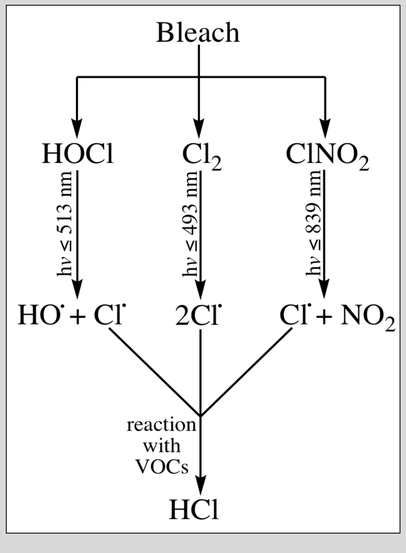


- HCl levels inside generally a few hundred pptv (typically higher than outside).
- HCl observed from dishwasher use (Cl-containing detergent), electric stovetop use.
- Reproducible HCl increases (~100 pptv) observed from repeated bleach applications on a house floor at night, with room lights turned on.
- Calculated HCl production rate ~1.2 x 10^7 molecules cm^{-3} s^{-1}.
- Direct emission or chemical formation possible.

Dawe et al. 2019 Indoor Air

COULD Cl_y PHOTOLYZE INDOORS?

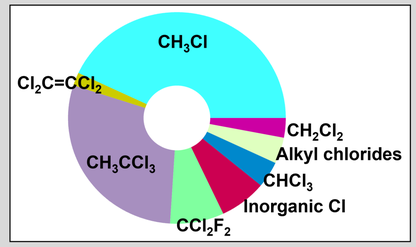
- Sunlit windows could lead to photolysis of some components of Cl_y.
- Radiation emitted from LED (>400 nm), halogen (>308 nm), and covered fluorescent tubes (>363 nm) could photolyze reactive Cl.
- Estimated instantaneous Cl production rates:
- 2 x 10^2 – 3 x 10^6 molecules cm^{-3} s^{-1}
- Similar to predicted OH production rates indoors from HONO photolysis (10^5 - 10^7 molecules cm^{-3} s^{-1}).
- Chemical formation of HCl is possible.
- We need indoor measurements of all Cl_y species simultaneously.

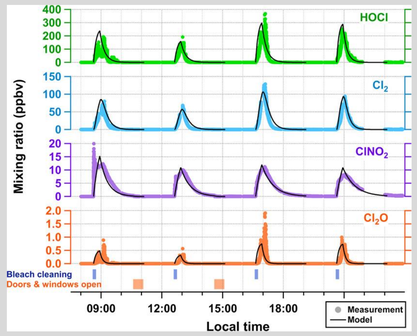


Wong et al. 2017 Indoor Air, Dawe et al. 2019 Indoor Air

TOTAL GASEOUS Cl (TCl_g) MEASUREMENT

- In recent years, atmospheric chemists have developed methods to measure total C (as CO2) and N (as NO).
- Coupling different inlets/chemistry can allow simple analyzers to make more complex measurements.
- Analogous to other total elemental measurements, the HCl CRDS can be coupled to a converter to give a total gaseous Cl (TCl_g) measurement.
  - Potential applications to outdoor and indoor environments.

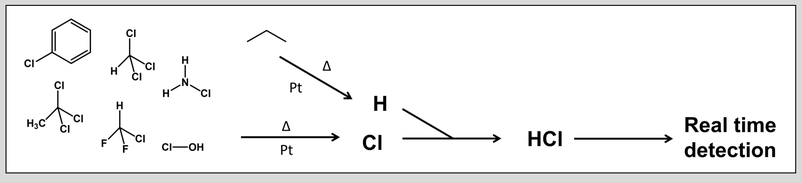




Khalil et al. 1999 JGR Atmos, Mattila et al. 2020 ES&T

APPROACH TO MEASURING TCl_g

- Approach:
  1. Heated platinum catalyst (825°C) converts TCl_g to Cl atoms.
  2. Cl atoms react with H (from C_3H_8 provided in excess) to form HCl.

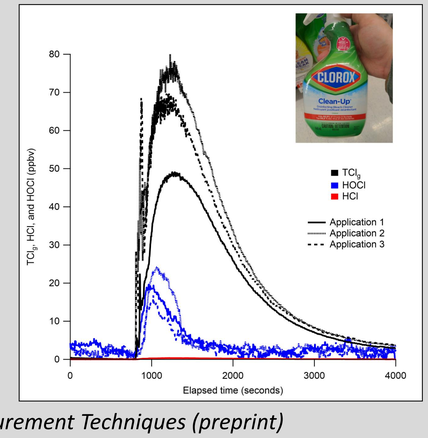


- Ambient air pulled through instrument with residence time of 1.5 seconds.
- Time response of measurement depends on detection limit of HCl method.
- Quantitative response determined using 6 chemicals.

Furlani et al. 2023 AMT

TCl_g IN THE INDOOR ATMOSPHERE

- Application of Cl-based spray to floor surface (x 3).
- Co-located HOCl CRDS measurement.
  - 50 – 80 ppbv TCl_g.
  - 15 – 25 ppbv HOCl.
  - 400 pptv HCl (separate analysis).
  - Generally consistent with previous measurements.
- Large quantity (~80%) of "missing" chlorine.



Furlani et al. 2022 Atmospheric Measurement Techniques (preprint)