Towards a TDLAS based optical gas standard for the absolute HCl measurements in flue gases from combustion process

Introduction
Accurate measurement of emissions of pollutants from industrial combustion processes to the atmosphere is vital in enabling action to control and reduce air pollution. Industry needs to measure and report emissions for regulatory purposes including assessing stack emissions against concentration limit values.

The EMPIR IMPRESS 2 project [1] goes beyond state of the art in measuring the emissions of HCl with lower emission limit values (2 mg/m³ ~1.4 ppm HCl), to achieve directly traceable measurements. Here, we present the spatial heterogeneity effects on the method of direct TDLAS (dTDLAS) method for absolute HCl concentration measurement in real applications.

HCl in N₂ spectra
- Gas sample: HCl in N₂ (R2735703, N₂ 6.0, HCl 5.5)
- Flow rate: 200 sccm (constant gas flow through the cell)
- Temperature: 294 K
- 500 ppm HCl in N₂
  - Measured HCl spectra in balance gas of N₂ →
  - Peak OD: 1.35
  - SNR: 1500
  - LOD: 0.26 ppm
  - Limit of detection: 0.016 ppm m⁻¹ Hz⁻¹/²
  - Single shot without average, 7 ms
  - our 0.26 ppm is lower than EU emission limit values
  - can be scaled with pathlength to even lower LOD

Heterogeneity effects
We developed a heterogeneity effect simulation model and applied to our 2.7 µm CO₂ and 4.6 µm CO-TDLAS systems.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Simulation info:</th>
<th>Concentration deviation</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Experiment &amp; simulation</td>
<td>3%</td>
<td>Ref [4]</td>
</tr>
<tr>
<td>CO</td>
<td>Experiment &amp; simulation</td>
<td>15%</td>
<td>Ref [8]</td>
</tr>
<tr>
<td>HCl</td>
<td>Simulation</td>
<td>2%</td>
<td>This work</td>
</tr>
</tbody>
</table>

Summary
- dTDLAS spectrometer for HCl
  - ICI laser
  - Light source:
    - ICI laser at 3.6 µm
    - Swept at 139 Hz (time resolution 0.007s)
  - Gas cell:
    - single pass 77 cm (coated)
    - Vigo Mid-IR detector
  - Sensors:
    - T-sensor: PT100
    - P-sensor: capacitive pressure gauge
  - Operation ranges:
    - Pressure: 0–1 bar
    - Temperature: 20–30 °C (gas in cell) (possible for high T)

Results
- a dTDLAS spectrometer was developed for absolute HCl concentration measurements
  - a LOD of 0.26 ppm at 0.007s time resolution was achieved
  - the temperature gradient effects on the dTDLAS HCl concentration measurement was analyzed using our simulation model showed a max. 8% deviation of T gradient
- Plans
  - bring this HCl Optical Gas standard in operation
  - to improve the measurement uncertainty

References
[8] Z. Qu et al., GAS Analysis 2019, NL.