On- and off-line ethanolamine and ammonia emission monitoring in PCCC

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Materials and methods used

On-line measurement of organics (MEA, aldehydes,...) and inorganics (NH$_3$, CO$_2$, H$_2$O, ...) at ppm level

**FTIR**

On-line measurement of PM/aerosol size distribution & concentration between 6 nm & 10 µm

**ELPI+**

Off-line measurement of the gas phase: mostly used for NH$_3$, MEA, aldehydes, nitrosamines

**Manual sampling**
Materials and methods used

On-line measurement of organics (MEA, aldehydes, ...) and inorganics (NH$_3$, CO$_2$, H$_2$O, ...) at ppm level
High MEA emissions have been observed during different pilot plant campaigns at different locations

High MEA emissions measured using FTIR at different pilots in EU:


High emissions measured also in US:

Project NCCC in Alabama

<table>
<thead>
<tr>
<th>Test</th>
<th>Beds</th>
<th>Inter-Coolers</th>
<th>Max Temp °F</th>
<th>MEA in Wash Water, %</th>
<th>MEA Emission Rate Total, lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0</td>
<td>174</td>
<td>1.05 (1)</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2</td>
<td>160</td>
<td>0.98 (2)</td>
<td>7.3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>162</td>
<td>1.06 (2)</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>163</td>
<td>0.22 (3)</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0</td>
<td>174</td>
<td>0.92 (1)</td>
<td>1.1</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>1</td>
<td>164</td>
<td>5.58 (1)</td>
<td>5.9</td>
</tr>
</tbody>
</table>

From 0.25 to 1.6 g/Nm³

http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/T%20Carter-NCCC-Post-combustion.pdf
High MEA emissions are linked to the presence of very fine aerosols and particulate matter in the power plant flue gases

Change in Power plant load (see $O_2$ concentration change):

→ sharp increase in MEA emissions

Can be linked to:

→ increase in PM/SO$_3$ aerosol emissions from power plant

→ formation of MEA aerosols inside absorber

Confirmed by other studies eg.:


Knudsen; J. and O. Bade; 2012: Emission Reduction Technologies; CLIMIT Workshop 5-6 December 2011, Oslo, Norway. Available at [www.akercleancarbon.com](http://www.akercleancarbon.com)
Water wash not successful in removing all MEA emissions → indicates the presence of MEA in the form of aerosols

Water wash has no effect on NH₃

Water wash only reduces MEA emissions to around 50 %:

→ not all MEA is gaseous

→ MEA aerosols
Materials and methods used

On-line measurement of organics (MEA, aldehydes, ...) and inorganics (NH$_3$, CO$_2$, H$_2$O, ...) at ppm level

On-line measurement of PM/aerosol size distribution & concentration between 6 nm & 10 µm
Characterisation of the amount and size of aerosols using ELPI+

- **ELPI = Electrical Low Pressure Impactor**

- Real-time measurement of particle size distribution and concentration between 6 nm to 10 µm

- Working principle:
  1. Particle charging
  2. Size classification in a cascade impactor (15 size classes)
  3. Electrical detection with sensitive electrometers

<table>
<thead>
<tr>
<th>Stage</th>
<th>D50% [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>6.8</td>
</tr>
<tr>
<td>13</td>
<td>4.4</td>
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<tr>
<td>12</td>
<td>2.5</td>
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<tr>
<td>11</td>
<td>1.6</td>
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<td>10</td>
<td>1.0</td>
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<td>9</td>
<td>0.64</td>
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<td>8</td>
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<td>0.26</td>
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<tr>
<td>6</td>
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</tr>
<tr>
<td>5</td>
<td>0.108</td>
</tr>
<tr>
<td>4</td>
<td>0.060</td>
</tr>
<tr>
<td>3</td>
<td>0.030</td>
</tr>
<tr>
<td>2</td>
<td>0.017</td>
</tr>
<tr>
<td>1</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Different types of flue gas filters and their effect on PM/aerosol size and numbers are being evaluated.

→ Clear correlation between the number of PM/aerosols entering the absorber and the MEA emissions.
Correlation between ELPI+ (PM/aerosol number concentration) and FTIR measurements (MEA) allows a better understanding of the aerosol issue.

<table>
<thead>
<tr>
<th>Type of flue gas</th>
<th>High MEA emission measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas 1</td>
<td>Yes</td>
</tr>
<tr>
<td>Flue gas 2</td>
<td>Yes</td>
</tr>
<tr>
<td>Flue gas 2 filtered</td>
<td>No</td>
</tr>
<tr>
<td>Flue gas 3</td>
<td>No</td>
</tr>
</tbody>
</table>
Aerosol total number only slightly affected but aerosol size increases significantly as they move through the absorber

Aerosols mainly grow inside the absorber through the take-up of water (and amine)

→ Take care interpreting the absolute value of the measured sizes due to dilution!
Challenge of the ELPI measurement = effect of dilution on measured size distribution:

Dilution necessary to avoid water condensation on the different ELPI+ stages → electrical shortcutting!

Dilution has effect (shrinking) on aerosol size distribution if aerosols contain a lot of water!

Dilution no effect if aerosols are close to dry droplet diameter or PM that contain no water!

Materials and methods used

On-line measurement of organics (MEA, aldehydes, ...) and inorganics (NH$_3$, CO$_2$, H$_2$O, ...) at ppm level

Off-line measurement of the gas phase: mostly used for NH$_3$, MEA, aldehydes, nitrosamines

Manual sampling
No standardized methodology for manual sampling and consequent analysis of the gas phase in PCCC

- Challenges:
  - Many components at different concentration levels (ppb – ppm)
  - Water saturated flue gases
  - Emissions possibly under aerosol form

- 3 aspects to be considered for an accurate and precise measurement:
Significant discrepancies observed at several sites between FTIR and manual measurements & amongst manual measurements
MEA analysis accuracy depends on the analytical method, the chemical concentration and matrix effect

Round Robin Test results for MEA (Care, only based on 1 RRT):

→ One laboratory gives unsatisfactory results
→ As the matrix is getting more complex, higher deviations are observed for all laboratories
Effect of the sampling flow rate

LOW FLOW

- Oven (80 °C)
- Ice Bath
- Absorbing solution
- Silica gel

HIGH FLOW

- Oven (80 °C)
- Ice Bath
- Absorbing solution
- Silica gel

FTIR

FID

Small pump (3 l/min)

Gas counter

Main gas flow

bubblers

impingers
Effect of sampling flow rate
Effect of sampling on MEA emissions

- In absence of aerosols, MEA measured concentration are higher than compared to FTIR but same order of magnitude between laboratories.
- In presence of aerosols, MEA measured concentration are much lower than compared to FTIR but increases when increasing the sampling flow rate.
- Improved capture efficiency when using impingers instead of bubblers and the higher flow.

Possible explanations:

⇒ In the manual sampling set-up, a part of the aerosols travels without being captured contrary to FTIR where all aerosols are evaporated at 180 °C.

⇒ Overestimation by FTIR in the high MEA value range? (only calibrated up to 55 mg.Nm⁻³)
Conclusions & future research

Amine aerosol formation is linked to the number of PM/aerosols entering the absorber

Aerosols grow as they move through the absorber taking up water (and amine)

Accuracy of MEA and NH$_3$ measurements is function of the matrix
  ⇒ Cross-checking of laboratories measurement recommended
  ⇒ Spiked solution

In presence of aerosols, high discrepancy between FTIR and manual measurements are noticed
  ⇒ Aerosols potentially travel across the manual samplings set-up without being captured
Conclusions & future research

Characterize further the size and number of aerosols that enter and leave the absorber at different sites and their relation with MEA emissions

The effect of the capture plant’s operational settings to minimise aerosol emissions

Further evaluation of flue gas filters and their effectiveness in avoiding aerosol emissions

Standardisation work is urgently needed for the emission monitoring in CCS
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