CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #17

**Kinetic Modeling:** Computer Models

**Case Study:** Chloramination II

Brezonik, pp.
HAAs: Chlorine vs Chloramine

- Dihalo products, but little trihalo

**Diagram:**
- NOM
  - Oxidation & Substitution (chlorine & chloramines)
  - Hydrolysis
  - Hydrolysis & Oxidation
  - Substitution (free chlorine only)
  - Hydrolysis
  - Oxidative Hydrolysis

**Reactions:**
- DCAA
- TCAA
- THM
- CHCl₃
- Cl₃C
- Cl₂HC
- Cl₂HC—C—OH
- O
- Cl₂HC
- C—OH
- R'' — C — CCl₂ C — R'
- R'' — C — CHCl₂
- R'' — C — CCl₃
- R'' — C — CCl₂ C — OH
THMs: Chlorination followed by Chloramination

The UMass-MWRA Study
HAAs: Chlorination followed by Chloramination

The UMass-MWRA Study

- pH 6, temp=2°C, 1.5 mg/L Cl₂
- pH 6, temp=2°C, 3.5 mg/L Cl₂
- pH 6, temp=20°C, 1.5 mg/L Cl₂
- pH 6, temp=20°C, 3.5 mg/L Cl₂
- pH 8, temp=2°C, 1.5 mg/L Cl₂
- pH 8, temp=2°C, 3.5 mg/L Cl₂
- pH 8, temp=20°C, 1.5 mg/L Cl₂
- pH 8, temp=20°C, 3.5 mg/L Cl₂
- pH 7.6, temp=20°C, 3.5 mg/L Cl₂

4 hr. chlorination
4 hr. chlorination plus 48 hr. chloramination
### Precursors & Behavior

<table>
<thead>
<tr>
<th>Mono &amp; Dihalo-DBPs</th>
<th>Trihalo-DBPs</th>
<th>Precursor Origins</th>
<th>Coag. or Oxidation</th>
<th>Biodgradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haloacids (DCAA)</td>
<td>THMs</td>
<td>General NOM</td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Aldehydes</td>
<td>Oxidized NOM</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Ketones (Dichloropropanone)</td>
<td>Ketones</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Nitroalkanes</td>
<td>Nitroalkanes</td>
<td>reactive Nitrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitriles</td>
<td>Nitriles</td>
<td>Algal (autochthonous)</td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td>(Dichloroacetonitrile)</td>
<td>(Trichloroacetonitrile)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amides (Dichloroacetamide)</td>
<td>Amides (Trichloroacetamide)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyanogen Halides (CNCl, CNBr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haloenzoquinones?</td>
<td>Haloacids (TCAA)</td>
<td>Terrestrial - Lignin (allochthonous)</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>

**General Trends**

- **Removal by:**
  - **Coag. or Oxidation:**
    - Average
  - **Biodgradation:**
    - Average

**Notes:**
- Haloacids (TCAA): Terrestrial - Lignin (allochthonous)
- Haloacids (DCAA): Preferentially formed by Chloramination

**Other Information:**
- **David A. Reckhow**
- **CEE697K Lecture #17**
### DBP control with DS management

**Para-m**eter | THM | Tri-HAAs | Di-HAAs | HANs | TCP | DCP | CP | Iodo-DBPs
---|---|---|---|---|---|---|---|---
Time↓ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↓ | ↑
Cl₂ Dose↓ | ↓ | ↓~ | ↓ | ↑ | ↑ | ↑↑ | ↓ | ↑
pH↓ | ↓ | ↑ | ~ | ↑ | ↑ | ↑ | | ↑
Cl₂ to NH₂Cl↑ | ↓ | ↓↓ | ↓~ | ~ | ~ | ↑ | ↑ | ↑
Temp↓ | ↓ | ~ | ↓ | ↑ | ↑ | ↑ | ↓ | ↑

**Driven by Regulations**

**Notes:**

- **HANs:** haloacetantriles, including DCAN
- **TCP:** trichloropropanone, a haloketone
- **DCP:** dichloropropanone: a haloketone
- **CP:** chloropicrin: a halonitromethane
- **Iodo-DBPs:** include iodinated THMs, HAAs, etc
Chloramines vs Free Chlorine

- DBPs
  - Lower levels of trihalogenated byproducts
    - Easier to meet current DBP regulations
  - Less impact on dihalogenated compound
    - Some are higher with chloramines
  - More of some types of N-DBPs
    - Organic chloramines, nitriles, amides, nitro compds

- Other concerns
  - Growth of ammonia oxidizing bacteria
    - Loss of residual, formation of reactive intermediates
  - Reduction of Lead (IV)
  - Public perception & direct health effects
Theoretical Breakpoint Curve

Chlorine Residual
mg Cl₂/mg NH₄-N

Chlorine Dose, mg Cl₂/mg NH₄-N
0 2 4 6 8 10 12 14 16

NH₂Cl
NHCl₂
HOCl + OCl⁻
NCl₃

David A. Reckhow
Distribution Diagram for Chloramine Species with pH

- Monochloramine
- Dichloramine
- Nitrogen Trichloride

Total Combined Chlorine (%) vs. pH


Table I. Reactions and Associated Constants

<table>
<thead>
<tr>
<th>reaction stoichiometry</th>
<th>rate expression</th>
<th>rate constant (25 °C)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) HOCl + NH₃ → NH₂Cl + H₂O</td>
<td>$k_{am}[HOCl][NH₃]$</td>
<td>$k_{am} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>18</td>
</tr>
<tr>
<td>(2) NH₂Cl + H₂O → HOCl + NH₃</td>
<td>$k_{ma}[NH₂Cl]$</td>
<td>$k_{ma} = 7.6 \times 10^{-2} \text{ h}^{-1}$</td>
<td>18</td>
</tr>
<tr>
<td>(3) HOCl + NH₂Cl → NHCl₂ + H₂O</td>
<td>$k_{md}[HOCl][NH₂Cl]$</td>
<td>$k_{md} = 1.0 \times 10^{6} \text{ M}^{-2} \text{ h}^{-1}$</td>
<td>4, 17</td>
</tr>
<tr>
<td>(4) NHCl₂ + H₂O → HOCl + NHCl₂</td>
<td>$k_{dm}[NHCl₂]$</td>
<td>$k_{dm} = 2.3 \times 10^{-3} \text{ h}^{-1}$</td>
<td>17</td>
</tr>
<tr>
<td>(5) NH₂Cl + NH₂Cl → NHCl₂ + NH₃</td>
<td>$k_{mmd}[NH₂Cl]^2$</td>
<td>$k_{mmd} = k_H[H^+] + k_{H₃PO₄}[H₂PO₄^-] + k_{H₃PO₄}[H₃PO₄]$</td>
<td>20, 21</td>
</tr>
<tr>
<td>(6) NHCl₂ + NH₃ → NH₂Cl + NH₂Cl</td>
<td>$k_{dmm}[NHCl₂][NH₃][H^+]$</td>
<td>$k_{dmm} = 2.16 \times 10^{6} \text{ M}^{-2} \text{ h}^{-1}$</td>
<td>9</td>
</tr>
<tr>
<td>(7) NHCl₂ + H₂O → I</td>
<td>$k_{di}[NHCl₂][OH^-]$</td>
<td>$k_{di} = 4.0 \times 10^{-5} \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>20, 28</td>
</tr>
<tr>
<td>(8) I + NHCl₂ → HOCl + products $^b$</td>
<td>$k_{idp}[I][NHCl₂]$</td>
<td>$k_{idp} = 1.0 \times 10^{6} \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>(9) I + NH₂Cl → products $^b$</td>
<td>$k_{imp}[I][NH₂Cl]$</td>
<td>$k_{imp} = 3.0 \times 10^{-7} \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>(10) NH₂Cl + NHCl₂ → products $^b$</td>
<td>$k_{mdd}[NH₂Cl][NHCl₂]$</td>
<td>$k_{mdd} = 55.0 \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>6, 8</td>
</tr>
<tr>
<td>(11) HOCl + NHCl₂ → NCl₃ + H₂O</td>
<td>$k_{dt}[NHCl₂][HOCl]$</td>
<td>$k_{dt} = k_{H₃PO₄}[HPO₄^{2-}] + k_{OCO}[OCO^-] + k_{OH}[OH^-]$</td>
<td>9</td>
</tr>
<tr>
<td>(12) NHCl₂ + NCl₃ + 2H₂O → 2HOCl + products $^b$</td>
<td>$k_{dtp}[NHCl₂][NCl₃][OH^-]$</td>
<td>$k_{dtp} = 2.0 \times 10^{14} \text{ M}^{-2} \text{ h}^{-1}$</td>
<td>9, d</td>
</tr>
<tr>
<td>(13) NH₂Cl + NCl₃ + H₂O → HOCl + products $^b$</td>
<td>$k_{mtp}[NH₂Cl][NCl₃][OH^-]$</td>
<td>$k_{mtp} = 5.0 \times 10^{12} \text{ M}^{-2} \text{ h}^{-1}$</td>
<td>d</td>
</tr>
<tr>
<td>(14) NHCl₂ + 2HOCl + H₂O → NO₃⁻ + 5H⁺ + 4Cl⁻</td>
<td>$k_{dhp}[NHCl₂][OCO^-]$</td>
<td>$k_{dhp} = 8.3 \times 10^{5} \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>d</td>
</tr>
</tbody>
</table>

$^a k_H = 2.5 \times 10^7 \text{ M}^{-2} \text{ h}^{-1}$; $k_{H₃PO₄} = 1.3 \times 10^3 \text{ M}^{-2} \text{ h}^{-1}$; $k_{H₃PO₄} = 3.2 \times 10^6 \text{ M}^{-2} \text{ h}^{-1}$. In carbonate-buffered systems additional terms include $k_{H₃CO₃[H₂CO₃]} + k_{HCO₃⁻[HCO₃⁻]}$, where $k_{H₃CO₃} = 2.7 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$ and $k_{HCO₃⁻} = 7.2 \text{ M}^{-2} \text{ h}^{-1}$ (21). $^b$ Products may include N₂, H₂O, Cl⁻, H⁺, NO₃⁻, and unidentified reaction products. For purposes of $d[H^+]$ calculation, products were assumed to contain $3H^+$ for each reaction, consistent with N₂ formation. $^c k_{H₃PO₄} = 5.72 \times 10^7 \text{ M}^{-2} \text{ h}^{-1}$; $k_{OCO} = 3.24 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$; $k_{OH} = 1.18 \times 10^{13} \text{ M}^{-2} \text{ h}^{-1}$. In carbonate-buffered systems additional term is $k_{CO₃[CO₃^{2-}]}$, where $k_{CO₃} = 2.16 \times 10^{10} \text{ M}^{-2} \text{ h}^{-1}$ (9). $^d$ This work.
# Model Equations

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate coefficient/equilibrium constant (25°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$</td>
<td>$k_{1.1} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>Morris and Isaac (1981)</td>
</tr>
<tr>
<td>1.2</td>
<td>$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$</td>
<td>$k_{1.2} = 7.6 \times 10^{-2} \text{ h}^{-1}$</td>
<td>Morris and Isaac (1981)</td>
</tr>
<tr>
<td>1.3</td>
<td>$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$</td>
<td>$k_{1.3} = 1.0 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>Margerum et al. (1978)</td>
</tr>
<tr>
<td>1.4</td>
<td>$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_2\text{Cl}$</td>
<td>$k_{1.4} = 2.3 \times 10^{-3} \text{ h}^{-1}$</td>
<td>Margerum et al. (1978)</td>
</tr>
<tr>
<td>1.5</td>
<td>$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$</td>
<td>$k_{d}^{a}$</td>
<td>Vikesland et al. (2001)</td>
</tr>
<tr>
<td>1.6</td>
<td>$\text{NHCl}_2 + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_2\text{Cl}$</td>
<td>$k_{1.6} = 2.2 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$</td>
<td>Hand and Margerum (1983)</td>
</tr>
<tr>
<td>1.7</td>
<td>$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{I}$</td>
<td>$k_{1.7} = 4.0 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>Jafvert and Valentine (1987)</td>
</tr>
<tr>
<td>1.8</td>
<td>$\text{I} + \text{NHCl}_2 \rightarrow \text{HOCl} + \text{products}$</td>
<td>$k_{1.8} = 1.0 \times 10^8 \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>Leao (1981)</td>
</tr>
<tr>
<td>1.9</td>
<td>$\text{I} + \text{NH}_2\text{Cl} \rightarrow \text{products}$</td>
<td>$k_{1.9} = 3.0 \times 10^7 \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>Leao (1981)</td>
</tr>
<tr>
<td>1.10</td>
<td>$\text{NH}_2\text{Cl} + \text{NHCl}_2 \rightarrow \text{products}$</td>
<td>$k_{1.10} = 55.0 \text{ M}^{-1} \text{ h}^{-1}$</td>
<td>Leao (1981)</td>
</tr>
<tr>
<td>1.11</td>
<td>$\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-$</td>
<td>$pK_a = 7.5$</td>
<td>Snoeyink and Jenkins (1980)</td>
</tr>
<tr>
<td>1.12</td>
<td>$\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$</td>
<td>$pK_a = 9.3$</td>
<td>Snoeyink and Jenkins (1980)</td>
</tr>
<tr>
<td>1.13</td>
<td>$\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$</td>
<td>$pK_a = 6.3$</td>
<td>Snoeyink and Jenkins (1980)</td>
</tr>
<tr>
<td>1.14</td>
<td>$\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$</td>
<td>$pK_a = 10.3$</td>
<td>Snoeyink and Jenkins (1980)</td>
</tr>
</tbody>
</table>

Modified version of equation #5 for carbonate

- $k_d = k_+^+[H^+] + k_{H_2CO_3}[H_2CO_3] + k_{HCO_3}[HCO_3]$

Where

- $k_+^+ = 2.5 \times 10^7 \text{ M}^{-2}\text{h}^{-1}$
- $k_{H_2CO_3} = 4 \times 10^4 \text{ M}^{-2}\text{h}^{-1}$
- $k_{HCO_3} = 800 \text{ M}^{-2}\text{h}^{-1}$
- I is the unidentified monochloramine auto-decomposition intermediate

## Temperature Effects

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient/equilibrium constant</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl+NH₃→NH₂Cl+H₂O</td>
<td>( k_{1,1} = 2.37 \times 10^{12} \exp(-1510/T) \text{ M}^{-1} \text{ h}^{-1} )</td>
<td>Morris and Isaac (1981)</td>
</tr>
<tr>
<td>NH₂Cl+H₂O→HOCl+NH₃</td>
<td>( k_{1,2} = 6.7 \times 10^{11} \exp(-8800/T) \text{ h}^{-1} )</td>
<td>Morris and Isaac (1981)</td>
</tr>
<tr>
<td>HOCl+NH₂Cl→NHCl₂+H₂O</td>
<td>( k_{1,3} = 1.08 \times 10^9 \exp(-2010/T) \text{ M}^{-1} \text{ h}^{-1} )</td>
<td>Margerum et al. (1978)</td>
</tr>
<tr>
<td>NH₂Cl+NH₂Cl→NHCl₂+NH₃</td>
<td>( k_{1,5} = kH^+[H^+] + kHCO_3[HCO_3^-] + kH_2CO_3[H_2CO_3] )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( k_{H^+} = 3.78 \times 10^{10} \exp(-2169/T) \text{ M}^{-2} \text{ h}^{-1} )</td>
<td>Granstrom (1954)</td>
</tr>
<tr>
<td></td>
<td>( k_{HCO_3} = 1.5 \times 10^{35} \exp(-22144/T) \text{ M}^{-2} \text{ h}^{-1} )</td>
<td>Vikesland et al. (2001)</td>
</tr>
<tr>
<td></td>
<td>( k_{H_2CO_3} = 2.95 \times 10^{10} \exp(-4026/T) \text{ M}^{-2} \text{ h}^{-1} )</td>
<td>Vikesland et al. (2001)</td>
</tr>
<tr>
<td>H₂CO₃⇌HCO₃⁻+H⁺</td>
<td>( \text{pK}_a = 1.48 \times 10^{-4} (T)2 - 9.39 \times 10^{-2} (T) + 21.2 )</td>
<td>Snoeyink and Jenkins (1980)</td>
</tr>
<tr>
<td>HCO₃⁻⇌H⁺+CO₂⁻</td>
<td>( \text{pK}_a = 1.19 \times 10^{-4} (T)2 - 7.99 \times 10^{-2} (T) + 23.6 )</td>
<td>Snoeyink and Jenkins (1980)</td>
</tr>
<tr>
<td>NH₄⁺⇌NH₃+H⁺</td>
<td>( \text{pK}_a = 1.03 \times 10^{-4} (T)2 - 9.21 \times 10^{-2}(T) + 27.6 )</td>
<td>Bates and Pinching (1950)</td>
</tr>
<tr>
<td>HOCl⇌OCl⁻+H⁺</td>
<td>( \text{pK}_a = 1.18 \times 10^{-4} (T)2 - 7.86 \times 10^{-2}(T) + 20.5 )</td>
<td></td>
</tr>
</tbody>
</table>
Chloramine Decay

\[
\begin{align*}
\text{NH}_3 & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{NH}_2\text{Cl} \\
\text{NH}_2\text{Cl} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{NHCl}_2 \\
\text{NHCl}_2 & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{NCl}_3 \\
\text{HOCl} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{NOH} \\
\text{NOH} & \quad \xrightarrow{\text{H}_2\text{O} + \text{HCl}} \quad \{\frac{1}{2} \text{NO}_3\} \\
\end{align*}
\]
Chloramine Formation and Decay pathway

\[ \text{NH}_3 \xleftrightarrow{\text{HOCl}} \text{NH}_2\text{Cl} \]

\[ \text{NH}_2\text{Cl} \xrightarrow{k_d} \text{NHCl}_2 \]

\[ \text{NHCl}_2 \xrightarrow{k_3} \text{HOCl} \]

\[ \text{HOCl} \xrightarrow{k_2} \text{H}_2\text{O} \]

@ Equilibrium

Rate Limiting Step

Fast

Valentine Model #1
Looking at the Rate Limiting Step

\[
- \frac{d[NH_2Cl]}{dt} = 3k_d[NH_2Cl][NH_2Cl] + 2k_3[NH_2Cl][HOCl]
\]
Valentine Model #3

- Re-arranging:

\[- \frac{d[NH_2Cl]}{dt} = 3k_d[NH_2Cl][NH_2Cl] + 2k_3[NH_2Cl][HOCl]\]

\[- \frac{d[NH_2Cl]}{dt} = 3k_d[NH_2Cl]^2 + 2k_3[NH_2Cl][HOCl]\]

\[- \frac{d[NH_2Cl]}{dt} = \left(3k_d + 2k_3 \frac{[HOCl]}{[NH_2Cl]} \right)[NH_2Cl]^2\]
Looking at the first step

- Forward reaction rate equals reverse rate
  - equilibrium
  \[ k_1 [HOCl][NH_3] = k_2 [NH_2Cl] \]

- Which leads to
  \[ \frac{[HOCl]}{[NH_2Cl]} = \frac{k_2}{k_1} \frac{[NH_3]}{[NH_3]} \]
Valentine Model #5

- **Combining**

\[- \frac{d[\text{NH}_2\text{Cl}]}{dt} = \left( 3k_d + 2k_3 \right) \frac{[\text{HOCl}]}{[\text{NH}_2\text{Cl}]} [\text{NH}_2\text{Cl}]^2 \]

- **We get:**

\[- \frac{d[\text{NH}_2\text{Cl}]}{dt} = \left( 3k_d + \frac{2k_3(k_2)}{[\text{NH}_3]} \right) [\text{NH}_2\text{Cl}]^2 \]
pH effects

- Ammonia and chloramine species are prone to protonation
- Dichloramine is more prevalent at low pH
  - Why?
    - The protonated form of monochloramine reacts more quickly than the neutral form or the reverse reaction is slower

\[ \text{NH}_3\text{Cl}^+ + \text{NH}_2\text{Cl} \rightleftharpoons \text{NHCl}_2 + \text{NH}_4^+ \]
Nitrogen Trichloride

- Acute Human toxicity ??
  - Drinking Water, showers and swimming pools
  - Blatchley’s group:

  "Trichloramine (NCl$_3$), which is often associated with the ‘chlorine odor’ of swimming pools, has been identified as a common by-product of chlorination of many organic-N compounds that are common to swimming pools, including urea, creatinine, and amino acids.

  NCl$_3$ is a respiratory irritant to mice, and more recent studies have indicated NCl$_3$ to contribute to acute ocular and respiratory irritation symptoms in lifeguards and swimming pool workers.

  Retrospective studies have shown positive correlation between irritation symptoms among swimmers and patrons and high gas-phase NCl$_3$ concentration at indoor pool facilities."

Measuring chloramines

- DPD titrimetric method

![Chemical reaction diagram showing the DPD titrimetric method](image_url)
Oxidation of DPD

- Reaction with free chlorine or iodine

\[ \text{C}_2\text{H}_5\text{N}-\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{N}-\text{C}_2\text{H}_5 \]

\[ \text{C}_2\text{H}_5\text{N}^-\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{N}^-\text{C}_2\text{H}_5 \]

From Gordon et al., 1987

Figure 2.6 Oxidation-reduction/acid-base reaction of DPD
Speciation with DPD

- **FRC**
  - Direct reaction of HOCl/OCl\(^-\) with DPD

- **Monochloramine**
  - Oxidation of I\(^-\) to I\(_3^-\) by NH\(_2\)Cl, and subsequent oxidation of DPD
    - Require only a small amount of iodide

- **Dichloramine**
  - Oxidation of I\(^-\) to I\(_3^-\) by NHCl\(_2\), and subsequent oxidation of DPD
    - Require a large amount of iodide and longer reaction time
DPD titrimetric method

\[
\begin{align*}
C_2H_5 & \quad C_2H_5 \\
\text{N} & \quad \text{N} \\
\text{I3-} & \quad \text{I-, 2HI} \\
\text{HCl} & \quad \text{H2O, HCl} \\
\text{HOCl} & \\
\text{Fe(+III)} & \quad \text{Fe(+II), H+} \\
\text{Colorless} & \quad \text{Red}
\end{align*}
\]
DPD titrimetric method

- **pH control**
  - Low pH leads to protonated forms
  - High pH catalyzes DPD oxidation by atmospheric oxygen

- **Potential interference**
  - Any substance that can directly oxidize DPD
    - MCA can do this a bit, so we sometimes add HgCl₂
  - Any substance that can oxidize iodide
    - Hydrogen peroxide, persulfate
Figure 1 Schematic representation of the MIMS system (a) and configuration of the membrane cell (b).
Figure 2 Representative EI mass spectra (35 ≤ m/z ≤ 125) of:

(a) free chlorine (2000 mg/L as Cl2),
(b) monochloramine (40 mg/L as Cl2),
(c) dichloramine (20 mg/L as Cl2), and
(d) trichloramine (20 mg/L as Cl2).

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DOI: 10.1021/es9812103
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Figure 3 Effects of membrane temperature and liquid flow rate on the MIMS system performance (dichloramine at 9.2 and 8.5 mg/L as Cl₂, respectively): ○, signal abundance; □, signal response time; ▵, signal noise.

gas flow rate, 0.459 mL/min; liquid flow rate, 0.9 mL/min; and ion source temperature, 156°C.
Figure 4 (a) Quantification of monochloramine by the MIMS method at $m/z = 53$: concentrations refer to titrimetrically determined values (as Cl$_2$) up to the limit of detection (see insert). (b) Linear response curves of the MIMS method for chloramines: □, monochloramine ($m/z = 53$); ○, dichloramine ($m/z = 87$); △, trichloramine ($m/z = 119$).
Figure 5 Residual chlorine concentrations as a function of Cl:N mass ratio after 30 min chlorination of an aqueous solution containing (a) ammonia and (b) glycine (0.5 mg/L as N) at pH 7. For each Cl:N ratio, residual chlorine was measured by DPD/FAS titration (left bar) and MIMS/EI (right bar).
<table>
<thead>
<tr>
<th>Chlorine dose</th>
<th>species</th>
<th>mean</th>
<th>RSD&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>mean</th>
<th>RSD&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>DPD</th>
<th>MIMS</th>
<th>DPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 free</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.38</td>
<td>0</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>mono</td>
<td>0.12</td>
<td>4 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0</td>
<td>0.08</td>
<td>0.07</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>di</td>
<td>0.05</td>
<td>12 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0.03</td>
<td>2 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td></td>
<td>tri</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.16</td>
<td>14 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0.17</td>
<td>5 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0.16</td>
<td>0</td>
<td>4.28</td>
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<tr>
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<td>2 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0.22</td>
<td>1 (&lt;i&gt;n&lt;/i&gt; = 6)</td>
<td>0.08</td>
<td>0.03</td>
<td>0</td>
</tr>
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<td>tri</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>10.0 free</td>
<td>2.92</td>
<td>2 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>2.58</td>
<td>1 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>0.16</td>
<td>0</td>
<td>9.00</td>
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<td>0.15</td>
<td>15 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>0.13</td>
<td>5 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>4.64</td>
<td>5.17</td>
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<tr>
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<td>0.77</td>
<td>8 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>0.37</td>
<td>0 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>0.40</td>
<td>0.24</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>tri</td>
<td>0</td>
<td>0.08 3 (&lt;i&gt;n&lt;/i&gt; = 3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
<td></td>
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<tr>
<td>chlorine dose</td>
<td>species</td>
<td>mean</td>
<td>RSD&lt;sup&gt;b&lt;/sup&gt; (%)</td>
<td>mean</td>
<td>RSD&lt;sup&gt;b&lt;/sup&gt; (%)</td>
<td>DPD</td>
<td>MIMS</td>
<td>DPD</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>0.38</td>
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<tr>
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<td>0.12</td>
<td>4 (n = 6)</td>
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<td>12 (n = 6)</td>
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<td>0.04</td>
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<td>0</td>
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<tr>
<td>5.0</td>
<td>free</td>
<td>0.16</td>
<td>14 (n = 6)</td>
<td>0.17</td>
<td>0.16</td>
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<td>1.94</td>
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<td>0.26</td>
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<td>2 (n = 6)</td>
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<td>10.0</td>
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<td>2 (n = 3)</td>
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<td>1 (n = 3)</td>
<td>0.16</td>
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<td>15 (n = 3)</td>
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<td>4.64</td>
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<td>0 (n = 3)</td>
<td>0.40</td>
<td>0.24</td>
<td>0</td>
</tr>
</tbody>
</table>
DPD based method for NCl₃

- Schematic of impinger method for gas-phase NCl₃ measurement. The arrows indicate the air flow pattern.
- Validation experiment setup. A gas-washing bottle containing an aqueous solution of the target compound was prepared and connected to the air entrance of measuring impinger system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Typical liquid-phase concentration (mg/l)(^a)</th>
<th>Henry’s law constant (atm, 20°C)(^b)</th>
<th>Equilibrium gas-phase Concentration (mg/m(^3))</th>
<th>Reported gas-phase concentration at pool area (mg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl(^c)</td>
<td>1.2</td>
<td>0.060</td>
<td>0.053</td>
<td>N.A</td>
</tr>
<tr>
<td>Cl(_2)(^c)</td>
<td>0.000012</td>
<td>767</td>
<td>0.0067</td>
<td>N.A</td>
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<tr>
<td>NH(_2)Cl</td>
<td>0.30</td>
<td>0.45</td>
<td>0.10</td>
<td>N.A</td>
</tr>
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<td>NHCl(_2)</td>
<td>0.10</td>
<td>1.52</td>
<td>0.11</td>
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<tr>
<td>NCl(_3)</td>
<td>0.070</td>
<td>435</td>
<td>23</td>
<td>0.1–0.7(^d)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>0.080</td>
<td>185</td>
<td>11</td>
<td>0.009–0.058(^e)</td>
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<td>CHBr(_2)Cl</td>
<td>0.0040</td>
<td>57.3</td>
<td>0.17</td>
<td>0.002–0.003(^e)</td>
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<tr>
<td>CHBr(_3)</td>
<td>0.0010</td>
<td>21.5</td>
<td>0.016</td>
<td>0.0008(^e)</td>
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<tr>
<td>CNCl</td>
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<td>108</td>
<td>0.24</td>
<td>N.A</td>
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<tr>
<td>CNCHCl(_2)</td>
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<td>0.21</td>
<td>0.00013</td>
<td>N.A</td>
</tr>
<tr>
<td>CH(_3)NCl(_2)</td>
<td>0.020</td>
<td>154</td>
<td>2.3</td>
<td>0.016–0.07(^f)</td>
</tr>
</tbody>
</table>
Dynamics of gas-phase trichloramine (NCl₃) in chlorinated, indoor swimming pool facilities
Dynamics of gas-phase trichloramine (NCl₃) in chlorinated, indoor swimming pool facilities
Dynamics of gas-phase trichloramine (NCl₃) in chlorinated, indoor swimming pool facilities
Relationship between DPD-based liquid-phase NCl₃ concentration and gas-phase NCl₃ concentration in Pool A facility. The results showed no significant correlation between these two parameters for this facility. The correlation coefficients between liquid-phase and gas-phase NCl₃ concentrations were -0.140 and 0.154 for the diving well and competition pool, respectively.
Loss in Tedlar bag

- Comparison of gas-phase NCl₃ measurement at pool deck and in the laboratory with a Tedlar gas-sampling bag. The results showed apparent loss of NCl₃ from the gas-sampling bag during transport.

![Graph showing gas-phase NCl₃ concentration over time.](image_url)
To next lecture