Retrospectively Evaluating Employee Exposures During an Accidental Chlorine Release Using Tracer Gas Technology

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Alleged Exposure

- Semiconductor manufacturing facility

- Accidental chlorine release from “Dry Etch Tool” process exhaust pump discharge

- Pump in basement underwent maintenance
  - Exhaust ducting inadvertently not reconnected
 Alleged Exposure

- Process equipment started – 50 ccpm Cl\textsubscript{2} release for 30 seconds
  - Chlorine monitor activated/shut down process
  - Personnel on floor above evacuated

- Operator on floor above allegedly overcome
  - Taken to hospital; alleged permanent damage to health
  - Filed workers’ compensation claim
Tracer Gas Technology

- In use for over 30 years
  - Semiconductor industry developed standard in 1993 (F-15)

- Wide range of applications
  - Industrial hygiene
  - Environmental

- Excellent tool for recreating chemical release events
What is Tracer Gas Technology?

- The marking of air with a gas
- Monitoring for its presence and concentration
- Data useful in evaluating:
  - Various parameters of ventilation systems
  - Chemical migration patterns
- Numerous ASTM, ANSI, ASHRAE Standards
A Good Tracer Gas?

- Non-toxic
- Colorless and odorless
- Inert
- Not normally present in the environment?
Common Tracer Gases Used

- Carbon Dioxide (CO$_2$)
- Freons
- Helium
- Sulfur Hexafluoride (SF$_6$)
Semiconductor Industry
SEMI F-15 Test Method

- Simulation of an accidental chemical release
  - Prediction of employee exposures
- Industry Concerns-Equipment failures
  - Piping/processes using highly hazardous gases and vapor-laden gas streams under pressure
  - Arsine, chlorine, fluorides
SEMIF-15 Testing
Tracer Gas Test Method

- Chemical of Concern
  • Most Hazardous
### Chemicals of Most Concern

<table>
<thead>
<tr>
<th>HPM</th>
<th>Concentration (Pc)</th>
<th>OEL&lt;sup&gt;(a)&lt;/sup&gt; (ppb)</th>
<th>OEL/Pc Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>100%</td>
<td>25,000</td>
<td>250</td>
</tr>
<tr>
<td>Oxygen</td>
<td>NA</td>
<td>None</td>
<td>NA</td>
</tr>
<tr>
<td>Ozone</td>
<td>28%</td>
<td>100</td>
<td>3.57</td>
</tr>
<tr>
<td>Argon</td>
<td>NA</td>
<td>None</td>
<td>NA</td>
</tr>
<tr>
<td>Helium</td>
<td>NA</td>
<td>None</td>
<td>NA</td>
</tr>
<tr>
<td>Water</td>
<td>NA</td>
<td>None</td>
<td>NA</td>
</tr>
<tr>
<td>Nitrogen Trifluoride</td>
<td>100%</td>
<td>10,000</td>
<td>100</td>
</tr>
<tr>
<td>Boron Trichloride</td>
<td>100%</td>
<td>5,000</td>
<td>50</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> Source: Guide to Occupational Exposure Values – 2006. Compiled by the American Conference of Governmental Industrial Hygienists (ACGIH).
SEMIF-15 Testing
Tracer Gas Test Method

- Worst-case Injection Point
  - Usually fitting closest to an opening and fitting of highest pressure
SEMI F-15 Testing
Tracer Gas Test Method

- Injection Rate
  - Worst Possible Release
    - Formula for calculating release from pressurized line in F-15 Standard.
    - Most gas supply systems have flow control valves or orifices 2-3 times maximum process required.
SEMIMI F-15 Testing
Tracer Gas Test Method

- Measurement Location
  - Worst-case exposure
ERC = \frac{Q_p \cdot C_p \cdot T_m}{Q_t \cdot C_t}

- ERC = Equivalent Release Concentration
- \( Q_p \) = Worst-case release rate of process gas of concern
- \( Q_t \) = Tracer gas injection rate
- \( C_p \) = Concentration of process gas of concern in %
- \( C_t \) = Concentration of tracer gas of concern in %
- \( T_m \) = Concentration of level of SF\(_6\) at measurement location
Simulation Plan/Strategy

- Inject SF$_6$/nitrogen blend at discharge of process pump
  - Blend to have similar mole weight (MW) as chlorine gas
    - MW of 100% Cl$_2$ = 70
    - MW of 100% SF$_6$ = 146
    - MW of 100% N$_2$ = 28
    - Chosen blend
      - 40% SF$_6$ + 60% N$_2$ = 75
Simulation Plan/Strategy

- Start with 200 ccpm for 30 seconds and progressively increase injection duration
  - Record SF$_6$ levels at various locations at workstations on operating floor
    - For the different injection times
    - Breaks in between injection periods
- Maintain same facility ventilating conditions as day of incident.
# Measurements Recorded

<table>
<thead>
<tr>
<th>Measurement Location</th>
<th>Max. $T_m^{(1)}$</th>
<th>OEL ppb$^{(2)}$</th>
<th>ERC ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location #1:</td>
<td>28.69</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Location #2</td>
<td>55.23</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Location #3:</td>
<td>29.01</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Location #4:</td>
<td>66</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Location #5</td>
<td>25.72</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Location #6:</td>
<td>32.62</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Location #7:</td>
<td>60.87</td>
<td>500</td>
<td></td>
</tr>
</tbody>
</table>

ERC = $Q_p \frac{C_p T_m}{Q_t C_t}$
### Measurement Correction

<table>
<thead>
<tr>
<th>Measurement Location</th>
<th>Max. $T_m^{(1)}$</th>
<th>OEL ppb$^{(2)}$</th>
<th>ERC ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location #1</td>
<td>28.69</td>
<td>500</td>
<td>71.8</td>
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<tr>
<td>Location #2</td>
<td>55.23</td>
<td>500</td>
<td>138.1</td>
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<tr>
<td>Location #3</td>
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<td>500</td>
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<tr>
<td>Location #4:</td>
<td>66</td>
<td>50</td>
<td>165</td>
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<td>500</td>
<td>64.3</td>
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<td>Location #6</td>
<td>32.62</td>
<td>500</td>
<td>81.6</td>
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<tr>
<td>Location #7:</td>
<td>60.87</td>
<td>500</td>
<td>152.2</td>
</tr>
</tbody>
</table>

- ERC = $Q_p C_p T_m / Q_t C_t$
  
  = (100%) (200ccpm) $T_m$ / (40%) (200ccpm)
  
  = 2.5 $T_m$
Conclusions

- Chlorine releases “Dry Etch Tool” on the Fab level
  - Larger release durations
    - During the alleged exposure incident
    - Resulted in employee exposures
    - Well below recognized exposure criteria levels