Safe Container unloading procedures, an obligation or not important?
Introduction on how to perform risk assessment on inbound cargo – upstream approach – root cause analysis

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Occupational Hygiënist Mensura
President BeCOH
INTRODUCTION

• Cf. Session last year
• Downstream risk assessment is possible
• Follow up by selective and nonselective measurements is feasible

→ Not really possible to solve the problem
GOALS

ROOT CAUSE ANALYSIS
1. Which chemicals of concern are present in different parts of the produced goods
2. Identify the high risk chemicals compared with downstream measurements
3. Define action items to reduce or eliminate VOC content in products

PREDICTIVE ANALYTICS
1. Correlate Upstream & Downstream nonselective and selective measurement Results
2. Set up an upstream limit value \(\rightarrow\) decision chart if cargo can leave the factory
Root Cause Analysis Procedure

**Factory Visit**
- Selection of shipped product
- Sampling on Finished Product, Material and Chemical Usage

**Lab Testing**
- Product Non-selective PID Measurement with Chamber Aging
- Product Selective Measurement with Chamber Aging
- Materials & Chemicals Selective Measurement by Solvent Extraction

**Identify Root Causes & Follow Up Actions**
- Identify Root Causes of Concerned VOCs
- Define Action Items to Reduce or Eliminate Concerned VOCs Content in Products
# Root Cause Analysis – Upstream Statistics

<table>
<thead>
<tr>
<th>Concerned VOCs</th>
<th>Range (mg/m³)</th>
<th>No. of Goods at high risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Ethenyl Cyclohexene</td>
<td>0.3864 – 2.7517</td>
<td>2</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.282 – 3.61</td>
<td>0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>22.83 - 1167</td>
<td>10</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.8050</td>
<td>1</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>1.71 – 23.285</td>
<td>13</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>11.98 – 30.65</td>
<td>5</td>
</tr>
<tr>
<td>Chloroform</td>
<td>7.73 – 18.28</td>
<td>2</td>
</tr>
<tr>
<td>Hexane</td>
<td>18.68</td>
<td>1</td>
</tr>
<tr>
<td>Methyl Vinyl Ketone</td>
<td>0.15 - 1.68</td>
<td>3</td>
</tr>
</tbody>
</table>
Root Cause Analysis – Upstream Statistics

No. of Goods at high risk

- 4-Ethenyl Cyclohexene
- Acetonitrile
- Ammonia
- Benzene
- Carbon disulfide
- Cyclohexanone
- Chloroform
- Hexane
- Methyl Vinyl Ketone
# Root Cause Analysis – components

<table>
<thead>
<tr>
<th>Components / Chemicals</th>
<th>Identified Concerned VOCs</th>
<th>Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component 1</td>
<td>Carbon Disulfide 4-Ethenyl Cyclohexene</td>
<td>5.91 – 35.5 0.88 – 1.01</td>
</tr>
<tr>
<td>Component 2</td>
<td>Carbon Disulfide</td>
<td>2.52</td>
</tr>
<tr>
<td>Component 3</td>
<td>Chloroform</td>
<td>303 - 1457</td>
</tr>
<tr>
<td>Solvent 1</td>
<td>Cyclohexanone</td>
<td>513</td>
</tr>
<tr>
<td>Solvent 2</td>
<td>Cyclohexanone</td>
<td>Declared to contain cyclohexanone</td>
</tr>
<tr>
<td>Component 4</td>
<td>Ammonia</td>
<td>15 – 112</td>
</tr>
<tr>
<td>Component 5</td>
<td>Ammonia</td>
<td>4.91 – 82.5</td>
</tr>
</tbody>
</table>
Upstream & Downstream Predictive Analytics

Upstream Lab Testing
- Product Non-selective PID Measurement with Chamber Aging
- Product Selective Measurement with Chamber Aging

Downstream Container Testing
- Container Non-selective PID Measurement
- Container Selective Measurement

Set Up Factory Upstream Limit Value
- Correlate Upstream & Downstream PID and Selective Measurement Results
- Set Up Upstream Factory Limit Value by Downstream Safe Container Unloading (SCU) Limit Value using Predictive Formula
## Upstream & Downstream Testing Results

<table>
<thead>
<tr>
<th>Concerned VOCs</th>
<th>Cas No.</th>
<th>Downstream Container LV (mg/m3)</th>
<th>Upstream Chamber Results, Concentration (mg/m3)</th>
<th>Downstream Container Results, Concentration (mg/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Ethenyl cyclohexene</td>
<td>100-40-3</td>
<td>0.45</td>
<td>0.043</td>
<td>ND</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>75-05-8</td>
<td>34.00</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ammonia</td>
<td>7664-41-7</td>
<td>14.00</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
<td>3.25</td>
<td>0.037</td>
<td>ND</td>
</tr>
<tr>
<td>CS2</td>
<td>75-15-0</td>
<td>3.16</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>108-94-1</td>
<td>40.80</td>
<td><strong>15.7</strong></td>
<td><strong>11.4</strong></td>
</tr>
<tr>
<td>Hexane</td>
<td>110-54-3</td>
<td>72.00</td>
<td>0.683</td>
<td>0.015</td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>78-94-4</td>
<td>0.58</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>67-66-3</td>
<td>10.00</td>
<td>0.205</td>
<td>ND</td>
</tr>
<tr>
<td>PID Results</td>
<td></td>
<td></td>
<td><strong>TVOC: 40</strong></td>
<td><strong>TVOC: 0.9</strong></td>
</tr>
</tbody>
</table>
Predictive analytics

Upstream – Downstream predictive analytics

Upstream measurement

Downstream measurement

Downstream SCU Limit Value

Upstream PRODUCT PID limit value
Predictive analytics

- Formula – algorithm to set SITE/PRODUCT limit value

Upstream & Downstream PID Correlation

\[ y = 32.353 \ln(x) + 29.922 \]

\[ R^2 = 0.7029 \]
Predictive analytics

• Formula – algorithm to set SITE/PRODUCT limit value
  Upstream PID LV = 32,353ln(Downstream PID LV) + 29,922

• A clear procedure

- Measurement SOP Off-gas VOC’s by PID
- PID measurement < FCTY LV
  Safe for shipment
- PID measurement > FCTY LV
  "Special case" - selective upstream product testing results showing high specific component concentrations
  Not safe for shipment - actions required
## Predictive analytics – results (1)

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Downstream PID Limit value (ppm)</th>
<th>Measured PID</th>
<th>Conclusion</th>
<th>Upstream PID Limit value (ppm)</th>
<th>Measured PID</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43,3</td>
<td>5,2</td>
<td></td>
<td>151,8</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>23,0</td>
<td>1,4</td>
<td></td>
<td>131,6</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>23,0</td>
<td>1,4</td>
<td></td>
<td>131,6</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>23,0</td>
<td>1,9</td>
<td></td>
<td>131,6</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6,8</td>
<td>1,73</td>
<td></td>
<td>91,9</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6,8</td>
<td>1,1</td>
<td></td>
<td>91,9</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>24,8</td>
<td>2,00</td>
<td></td>
<td>134,0</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>39,8</td>
<td>21,7</td>
<td></td>
<td>149,0</td>
<td>126</td>
<td></td>
</tr>
</tbody>
</table>
## Predictive analytics – results (2)

<table>
<thead>
<tr>
<th>FCTY/STYLE</th>
<th>Downstream PID Limit value (ppm)</th>
<th>Measured PID</th>
<th>Conclusion</th>
<th>Upstream PID Limit value (ppm)</th>
<th>Measured PID</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>84,5</td>
<td>29,2</td>
<td></td>
<td>173,0</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>84,5</td>
<td>62,4</td>
<td></td>
<td>173,0</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>17,3</td>
<td>27,1</td>
<td></td>
<td>122,0</td>
<td>160,0</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>17,3</td>
<td>4,7</td>
<td></td>
<td>122,0</td>
<td>159,0</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>22,7</td>
<td>1,7</td>
<td></td>
<td>131,0</td>
<td>46,0</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>22,7</td>
<td>4,3</td>
<td></td>
<td>131,0</td>
<td>38,0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>39,8</td>
<td>74,7</td>
<td></td>
<td>149,0</td>
<td>195,0</td>
<td></td>
</tr>
</tbody>
</table>

**False positive ➔ conservative**
CONCLUSION

• Root cause analysis can identify chemicals of concern → replacement advice can be given at R&D level → workers exposure at production site will decrease

• Predictive analytics can provide clear upstream limit values and can be used prior to shipment → less problems at unloading site
Production SITE

At Production / Pre-shipment Stage

Models Completed Root Cause Analysis Protocol?

Yes

Meet PID Limit Value (LV)?

Yes

Ship Product

No

Run Chamber Selective VOC Risk Assessment

> Limit Value ; or

Change in production process

Low Risk

<Limit Value

High Risk

Long term solution

Short term solution

No

Consult for Pre-shipment Treatment

Take Pre-Shipment Actions Such as Ventilating, Aging...etc

At Product Development Stage

Conduct Non-Selective PID Analysis

Yes

Conduct Non-Selective PID Analysis

No

Move to Production / Shipment

At Product Development Stage

Move to Production / Shipment

Long term solution

Short term solution

Yes

Root Cause Analysis & Correlation Study

Corrective Actions Such as Using Alternatives for Improvement

Consult for Pre-shipment Treatment

Take Pre-Shipment Actions Such as Ventilating, Aging...etc

Belgian Society for Occupational Hygiene
DISCUSSION & NEXT STEPS

• Information necessary to improve the predictive analytics:
  – Product chamber test results
  – Downstream related product results

• Changes of chemicals/products used need to be identified in the development stage NOT in the production stage.

• Information needed from the production sites:
  – Dates and shipment detail of upstream tested products
  – Communicate results of the upstream measurement results
DISCUSSION & NEXT STEPS

• Information needed from the suppliers
  – Technical and Safety data sheet to perform a modelled SCU risk assessment → conclusion: good for improvement or not good enough as an improvement

• What are the production sites receiving
  – Updated limit values for container air prior to shipment
  – Updated Risk Assessment files
REFERENCES


Thank you for your attention

mensura.be; becoh.be; bsoh.be

Mensura; BeCOH; BSOH

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