On-site Quantification of Monoethanolamine in Crude Oils

Sai R Pinappu
COQA 2014 Fall Meeting
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Outline

- Tramp amine sources
- Challenges processing tramp amine contaminated crudes
- Tramp monitoring technologies
- Today’s tramp amine monitoring requirements
- Improved solution: TOPGUARD™ field amine measurement services (FAMS)
- Field application
Tramp Amine Sources

Quality of incoming crude oils – Tramp amines from H₂S scavengers is the major source.

- Tramp amines in slops (Example: Amine unit)
- Tramp amines in desalter wash water
Tramp Amines Increase Desalter pH

- Increased partitioning of amines to crude oil
- Stabilized emulsion layer
  - Increased BS&W in the desalted crude
  - Higher chloride concentration in the overhead water
  - \( \text{RNH}_2 + \text{HCl} \rightleftharpoons \text{RNH}_3\text{Cl} \)
# Current Industry Standard Tramp Amine Monitoring Methods

<table>
<thead>
<tr>
<th>Analytical Technique</th>
<th>Detection Limit</th>
<th>Lab/Field</th>
<th>Interferences/ Limitations</th>
<th>Typical Analysis Time</th>
<th>Specialist Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>0.1 ppm</td>
<td>Lab</td>
<td>Other aliphatic amines, high conductivity, not specific</td>
<td>1-2 days</td>
<td>Yes</td>
</tr>
<tr>
<td>ASTM D6919-09, E1151</td>
<td></td>
<td></td>
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<tr>
<td>GC/GC-MS\textsuperscript{1,2}</td>
<td>0.4 ppm</td>
<td>Lab</td>
<td>Nitriles, aromatic amines, derivatization required</td>
<td>1-2 days</td>
<td>Yes</td>
</tr>
<tr>
<td>LC\textsuperscript{3}</td>
<td>0.2 ppm</td>
<td>Lab</td>
<td>Derivatization required</td>
<td>1-2 days</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Current Baker Hughes Monitoring and Modelling Capabilities

- Ion Chromatography
  - Modified ASTM method
  - Often takes several days to receive results

- Total Nitrogen method
  - Relies on subtraction of N from neutralizer and NH$_3$ from the total N
  - If excess N remains, it is labeled “tramp”
  - Does not specify whether tramp N is from MEA

- Cases where MA is the primary source

Baker Hughes recognized the need for a new, fast, on-site method to quantify MEA to support enhanced corrosion risk prediction and mitigation.
Today’s Tramp Amine Monitoring Requirements

- Fast onsite quantification
- Lower detection limits
- Onsite prediction of corrosion risk potential
- Timely mitigation strategies
- Flexibility to use for multiple analytes
- Portable
- Ease of use
TOPGUARD Field Amine Measurement Services

- Field asymmetric ion mobility spectrometry was identified as potential technology platform

- Developed customized methodology to determine MEA in crude oils
  - Proprietary sample preparation protocols were developed
  - Minimized interferences and increased sensitivity
  - Instrument operating parameters were optimized
  - Proprietary data processing and modeling capabilities are applied

MEA peak location identified and quantified down to 1 ppm with excellent reproducibility (RSD ≤ 10%)
TOPGUARD FAMS Correlates with IC

• Good agreement with IC data on crude samples, ± 20% of the IC result

• Calculated overhead MEA using TOPGUARD FAMS in agreement with IC

• Detection of MEA down to 1 ppm in crude oils
TOPGUARD FAMS Features & Benefits

**Features**
- On-site measurement
- Portable
- Fast: 1 hour per sample
- MEA sensitivity down to 1 ppm in crude oil
- Ease of use

**Benefits**
- Real-time screening of feedstock for amine content
- Improved prediction of corrosion risk potential
- Flexibility to use for multitude analytes
TOPGUARD FAMS – Analysis Process

Step 1 - Sample Collection & Preparation

- Adjust neutralizer rate to control pH
- Adjust caustic to control chlorides
- Modify tower, OH operations to avoid salt

Mitigation Strategies

Step 2 - TOPGUARD FAMS Analysis

- Adjust desalter pH to remove MEA, avoid salt

Step 3 - TOPGUARD CRM Calculations

Step 4 – Determine Appropriate Mitigation Strategy

- Adjust pH to remove MEA, avoid salt
- After Wash: Wash time excess over saturation 71.5%
- Required wash rate: 48 gpm
- Exchanger:
  - Water flow point temperature: 210°F
  - Ammonia salt 0.7% -75°F
  - Neutralizer salt 0.7%
  - Tunza amine salt 0.7%
Mitigation Options

• **Apply caustic**
  – Reduces overhead chlorides, thus reducing MEA –HCl salt formation temperature

• **Use EXCALIBUR™ contaminant removal program**
  – Reduces MEA to the overhead, thus reducing MEA – HCl salt formation temperature

• **Make operational changes (e.g. increase tower operating temperature)**
  – Increases “Salt ΔT,” thus reducing the risk of salt deposition
  – Often a costly and undesirable option

• **Adjust crude blend ratio**
  – Reduces contaminants to the overhead, thus reducing the risk for salt deposition
  – Often a costly and undesirable option
Process Refining Application

Gulf Coast Refinery
Corrosion Risk Free - No Mitigation Required

64% of data required **NO MITIGATION**
What to Do when Mitigation is Needed

Mitigation Required
Mitigation: MEA ~15ppm, ΔT ~ (0 – 5)°F
**Mitigation: Apply Caustic**

- **MEA**: 15
- **Brine pH**: 8.5
- **OVHD Cl⁻ (ppm)**: ~5
- **Tower T (°F)**: 260

**LOW RISK**

- Increasing Corrosion Risk

**Corrosion Risk = Medium**

**HIGH RISK**

- Default

**Corrosion Risk = High**
Mitigation: Apply Caustic + EXCALIBUR program

- **MEA**: 4
- **Brine pH (controlled)**: 5.5 – 6.0
- **OVHD Cl⁻ (ppm)**: ~5
- **Tower T (°F)**: 260

**Low Risk**
- Control: Corrosion Risk = Low

**Increasing Corrosion Risk**

**High Risk**
- Default: Corrosion Risk = High
Tramp MEA, MEA-HCl Risk Management

TOPGUARD field amine measurement services provides refiners:

• Quick identification of amine-contaminated crude oils
• Quantification of tramp amines and translation to corrosion risk potential
• Timely implementation of mitigation programs to minimize corrosion
  – Adjustments to crude tower operations
  – Optimization of EXCALIBUR contaminant removal program
  – Proactive planning and blending optimization
• Achievement of targeted operating efficiency and profitability goals
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