Accuracy and Interface Classification in Sediment and Water Testing in the Field

May 2019
Presentation Overview

1. Comparison of test methods for water content in the lab and field

2. Quantifying interface layers (wax, emulsion, asphaltene, etc.) with UV imaging in centrifuge tests

3. How much water do interface layers contain? Lab studies assessing if interface analysis can explain the bias between water cuts measured by centrifuge vs. Karl Fischer Titration
Why water content is measured in crude

1. **Production accounting:** volume of water subtracted from total volume paid for at custody transfer

2. **Pipeline integrity:** Too much water in crude accelerates corrosion and other problems in pipelines and reduces pipeline efficiency

3. **Specification limits:** Most pipelines have specification limits for water and sediment (typically 0.5%-2%)
Comparison of test methods
Methods of measuring water content

1. **Centrifuge test (ASTM D4007 or API MPMS Ch. 10.4)**
   a. Cited in most pipeline specs and custody transfer agreements in North America today
   b. Most widely used method in the field
   c. Only method for water content that also measures sediment

2. **Karl Fischer Titration (ASTM D4928)**
   a. Used for custody transfer at a few locations in North America
   b. Miniaturized and automated units available
   c. Some field use

3. **Distillation method (ASTM D4006)**
   a. Historical referee method recommended by ASTM for disputes (replaced with ASTM 7829 guidelines)
   b. Not practical for field use
## Repeatability and Reproducibility

<table>
<thead>
<tr>
<th>Method</th>
<th>Repeatability at 0.5% (ASTM lab studies)</th>
<th>Reproducibility at 0.5% (ASTM lab studies)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centrifuge method (ASTM D4007)</td>
<td>±0.12%</td>
<td>±0.28%</td>
</tr>
<tr>
<td>Karl Fischer Titration (ASTM D4928)</td>
<td>±0.04%</td>
<td>+0.07%</td>
</tr>
</tbody>
</table>

Karl Fischer Titration shows more consistent results in the lab
### Bias between test methods on clean oil (S&W < 1%) - bias

<table>
<thead>
<tr>
<th>Study</th>
<th>Distillation vs. Centrifuge</th>
<th>Karl Fischer Titration vs. Centrifuge</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCQTA study (150 samples)</td>
<td>+0.12%</td>
<td>+0.28%</td>
</tr>
<tr>
<td>Validere study - light crude (29 samples)</td>
<td>N/A</td>
<td>+0.11%</td>
</tr>
<tr>
<td>Validere study - heavy crude (52 samples)</td>
<td>N/A</td>
<td>+0.18%</td>
</tr>
</tbody>
</table>

Centrifuge testing produces lower results than other methods for water cut. KFT shows higher results than distillation.
Centrifuge measures free water and sediment. KFT measures total water.
## Common sources of error and bias in the field

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Bias direction</th>
<th>Source of error</th>
<th>Bias direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling and subsampling</td>
<td>Either high or low</td>
<td>Sampling and subsampling</td>
<td>Either high or low</td>
</tr>
<tr>
<td>Moisture on the sampling or measurement apparatus</td>
<td>High</td>
<td>Insufficient spinning (speed or duration)</td>
<td>Low</td>
</tr>
<tr>
<td>Interference from mercaptans</td>
<td>High</td>
<td>Insufficient heating</td>
<td>Low</td>
</tr>
<tr>
<td>Improper reagent preparation</td>
<td>Either high or low</td>
<td>Tight emulsions</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td></td>
<td>User interpretation</td>
<td>Either high or low</td>
</tr>
</tbody>
</table>

Spread between centrifuge and KFT likely larger in the field
Quantifying interface layers
What is ‘interface’?

1. **Definition:** Anything that phase separates from oil phase in a centrifuge, but is lighter than water

2. **Most common types of interface:**
   a. Waxes
   b. Tight emulsions
   c. Asphaltenes
   d. Production chemicals

3. **Significance:**
   a. Many interfaces have little commercial value
   b. High wax content can damage pipeline/refinery instrumentation, and accumulate in pipes and in tanks
Quantifying interfaces with the Centrifuge Tube Reader (CTR)

- Tubes imaged under white light and UV light
- Sediment, water and interface layers quantified using image analysis
CTR images

White light image  UV fluorescence image
Interface Seen in UV Images
Interface Seen in UV Images
Interface Seen in UV Images
Large-scale field study: Significant interface layers found in most samples

>1000 samples
% of samples with interface: 55%
Mean interface value: 0.4%
Median interface value: 0.115%
How much water do interface layers contain?
Study design and goals

1. Centrifuge tests with CTR imaging and KFT tests done on samples from several production and midstream sites

2. Determine if there is a correlation between interface content and the difference between centrifuge and KFT water measurements

3. Determine if machine can associate fluorescence patterns in interface layers with their water content

4. Try to develop a centrifuge method that will give higher agreement with KFT
Definitions

- **WSI** = Water + sediment + interface measured by centrifuge (CTR)
- **WS** = Water + sediment measured by centrifuge (CTR)
- **KFT** = Total water content measured by Karl Fischer Titration
Wet interface (WSI > KFT >> WS)
Dry Interface (WSI >> KFT, WS)
Dissolved Water (KFT > WSI)

KFT

WSI = WS
Results (Lab 1)

Overall
34 samples
% of samples with interface: 47%
Mean interface value: 0.20%
Median interface value: 0.00%

Heavy Oil
24 samples
% of samples with interface: 38%
Mean interface value: 0.07%*
Median interface value: 0.00%

Med. Oil
10 samples
% of samples with interface: 90%
Mean interface value: 0.20%
Median interface value: 0.11%
Results (Lab 2)

Overall
46 samples
% of samples with interface: 74%
Mean interface value: 0.20%
Median interface value: 0.00%

Heavy Oils
27 samples
% of samples with interface: 59%
Mean interface value: 0.04%
Median interface value: 0.05%

Light/Med. Oils
19 samples
% of samples with interface: 95%
Mean interface value: 0.38%
Median interface value: 0.14%
KFT-Centrifuge Bias

Bias between Karl Fischer and Centrifuge (with and without including interface)

- **Light/Med Crudes (<0.9g/mL)**
  - KFT - S&W: 0.11% ± 0.04%
  - KFT - WSI: -0.27% ± 0.42%

- **Heavy Crudes (>0.9g/mL)**
  - KFT - S&W: 0.18% ± 0.10%
  - KFT - WSI: 0.14% ± 0.10%
Little consistency of implied water content in interface layer

- Average max water content in light oils: 59%, range from 10% - 100%. Standard deviation: 39%

- No stream dependance and little consistency from sample to sample.
Summary

- Karl Fischer Titration (KFT) gives higher water content results than centrifuge tests in the lab. This gap likely increases in the field due to bias introduced by most common errors.

- KFT measures total water. Centrifuge measures free water and sediment.

- Significant interface content found in majority of production samples in a large-scale study across several sites.

- UV imaging and image analysis enables quantification and classification of interface layers (waxes, emulsions, asphaltenes, etc.). Some interface layers contain water.

- In heavy crudes (density > 0.9g/mL or < 26 API), total water generally exceeds water extractable by centrifuge tests, even when accounting for interface.

- In light/med crudes (density < 0.9g/mL or > 26 API), interface can account for difference between total water and free water, but implied water content of interface layers are not consistent enough to easily quantify.