MOISTURE DETERMINATION IN CRUDE OIL

by

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BRINKMANN INSTRUMENTS
• METROHM
  manufactures titration equipment

• BRINKMANN
  distributes & supports Metrohm titration equipment in the US & Canada
WHY IS MOISTURE DETN. IMPORTANT?

• Economic ramifications for:
  – Supplier
  – Transporter
  – Refineries
  – Consumer
“Over 400,000 barrels of material were annually unaccounted for due to centrifuge readings versus Karl Fischer combined with sediment-by-extraction numbers”.


\[400,000 \times \$30.00/\text{barrel} = \$12,000,000.00\]
PROFIT SHARING!
CURRENT METHODS
(Attachment Discussion Paper 11/26/00)

- Centrifuge 30 minutes
- Distillation 120 minutes
- Karl Fischer 10 minutes
- Online Water Devices
WHY KARL FISCHER?

• Very specific for water
• Fast analysis time
• Higher degree of accuracy & precision
• Easy sample handling
• Relatively inexpensive
TWO TECHNIQUES

Volumetric (1mg - 100%)  Coulometric (10ug - 10mg)
Volumetric Karl Fischer Titration

- Add titrant with automatic dosing unit
- Excess iodine indicates the endpoint has been reached
- 1 unit $I_2 = 1$ unit water

Titrant from buret

Solvent in vessel
COULOMETRIC KF

- Iodine generated electrochemically in the titration vessel.

- Generator electrode (electrochemical cell)
  \[2I^- + 2e^- = I_2\]

- 1 unit I$_2$ = 1 unit water
Detection of the endpoint

- Measurement of the potential at constant current.
- Excess iodine is sensed with polarized, double platinum pin electrodes
- Endpoint potential is preset in method.
VOLUMETRIC KF

- Similar equipment used for TAN, TBN.
- Easy maintenance.
- Some flexibility with solvent mix.
**Titrant:**
Hygranal Composite 2 or equivalent.

**Solvent:**
Methanol / Xylene mixture or Hygranal solvent oil / Xylene
Current Karl Fischer Formulation

Non-pyridine based reagent

Imidazole
DEGmonoethylether
Iodine (I₂)
Sulfur dioxide
Two methods are stored in the Titrator.
Built-in safe guards will not allow operator to start analysis until the cell is ready.
Just three steps:

“START TITRATOR”
“ENTER SAMPLE INFORMATION”
“WAIT FOR RESULTS”
VOLUMETRIC KF CELL
• Perform check on titrant value at least once per week and whenever a new bottle is used.
  Hydranal water standards available.

• Introduce well mixed sample to vessel using a dry syringe (without needle).

• Determine sample weight by differential weighing using an analytical balance.

• Monitor cell condition from “drift” display.
TO EMPTY VESSEL

- 703 Built-in Pump
- Vessel with stopcock
COULOMETRIC KF
GENERATOR ELECTRODES

WITHOUT DIAPHRAGM

WITH DIAPHRAGM
COULOMETRIC KF

- Cell without diaphragm designed and patented by Metrohm.
- Uses one solution e.g. Hydranal Coulomat AGH.
- Much less maintenance compared to cell with diaphragm.
- More sensitive to interferences cf volumetric.
- Can add max. 15% xylene to enhance solubility.
- Less tolerance for co-solvent - change reagent more frequently.
INTERFERENCES

- Sulfides & mercaptans consume titrant and give high water values.

  100 ppm mercaptan  ~  30 ppm water
  100 ppm sulfide    ~  50 ppm water
Add a *masking* agent to solvent. Allow sample to react for about 5 minutes before starting the analysis.

Time delay is built into the method for consistency.
<table>
<thead>
<tr>
<th></th>
<th>VOL.</th>
<th>COUL.</th>
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<tbody>
<tr>
<td>900 OK 76-69</td>
<td>0.15%</td>
<td>0.15%</td>
</tr>
<tr>
<td>586 BP 90-63/81</td>
<td>0.13%</td>
<td>0.13%</td>
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<tr>
<td>751 OK 142-55</td>
<td>0.08%</td>
<td>0.08%</td>
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<tr>
<td>835-EJ 52-12</td>
<td>0.18%</td>
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<tr>
<td>875-OK 992-63</td>
<td>0.31%</td>
<td>0.32%</td>
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<tr>
<td>885-NN 791-12/24</td>
<td>0.05%</td>
<td>0.04%</td>
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THANK YOU!