How It Works: The Karl Fischer Titration

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History of Karl Fischer Titration

• Karl Fischer (March 24, 1901 – April 16, 1958) was a German chemist

• Published a method in 1935 to determine trace amounts of water in samples. This method is now called Karl Fischer titration. **Abbreviations: KF or KFT**

• It remains the **primary method of water content determination** used worldwide by:
  – Government – Food Science
  – Academia – Research
  – Industry – Quality Control
Karl Fischer Reaction

• Bunsen Reaction:

\[
2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI
\]

\[
ROH + SO_2 + R’N \rightarrow [R’NH]SO_3R + H_2O + I_2 + 2R’N \rightarrow 2[R’NH]I + [R’NH]SO_4R
\]

alcohol base alkylsulfite salt hydroiodic acid salt alkylsulfate salt

• Once the intermediate alkylsulfite salt is produced, it is oxidized by iodine to the alkylsulfate salt

• *Oxidation reaction consumes water*

• pH sensitive: optimal range \( p\text{H} 5 – 8 \) otherwise buffer highly acidic/basic samples

http://www.emdmillipore.com/chemicals/aquastar-karl-fischer-faqs-and-tech-notes/c_yPab.s1OEMgAAAEiPkg7mMef
Water and iodine are consumed in a 1:1 mole ratio in the KF reaction.

Once the reaction consumes all of the water present, the presence of excess iodine is detected by the indicator electrode.

Percent water is calculated based on the [I₂] in the Karl Fischer titrating reagent (i.e. titer) and the amount of KF reagent consumed.
Two Types of Karl Fischer Titration

• **Volumetric**
  
  – Iodine is added mechanically to a solvent containing the sample
  
  – Water is quantified from the volume of KF reagent consumed
  
  – 100 to $1 \times 10^6$ ppm (0.01 – 100%)

• **Coulometric**
  
  – Iodine is generated electrochemically *in situ* during the titration
  
  – Water is quantified from the total charged passed
    
    $Q = 1 \ C = 1 \ A \times 1 \ s$ where $1 \ mg \ H_2O = 10.72 \ C$
  
  – 1 to 50,000 ppm (0.0001 – 5%)
## General Sample Size Requirements

<table>
<thead>
<tr>
<th>SAMPLE WATER CONTENT</th>
<th>VOLUMETRIC SAMPLE SIZE</th>
<th>COULOMETRIC SAMPLE SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>0.02 to 0.05 g</td>
<td>NOT RECOMMENDED</td>
</tr>
<tr>
<td>50%</td>
<td>0.05 to 0.25 g</td>
<td>0.01 g</td>
</tr>
<tr>
<td>10% (100,000 PPM)</td>
<td>0.25 to 0.50 g</td>
<td>0.01 to 0.05 g</td>
</tr>
<tr>
<td>5% (50,000 PPM)</td>
<td>0.50 to 2.50 g</td>
<td>0.05 to 0.10 g</td>
</tr>
<tr>
<td>1% (10,000 PPM)</td>
<td>2.50 to 5.00 g</td>
<td>0.10 to 0.50 g</td>
</tr>
<tr>
<td>0.5% (5,000 PPM)</td>
<td>5.00 to 7.50 g</td>
<td>0.20 to 1.00 g</td>
</tr>
<tr>
<td>0.1% (1,000 PPM)</td>
<td>7.50 to 10.0 g</td>
<td>1.00 to 2.00 g</td>
</tr>
<tr>
<td>0.01% (100 PPM)</td>
<td>10.0 to 15.0 g</td>
<td>2.00 to 5.00 g</td>
</tr>
<tr>
<td>0.001 (10 PPM)</td>
<td>15.0 to 20.0 g</td>
<td>5.00 to 10.0 g</td>
</tr>
<tr>
<td>0.0001% (1 PPM)</td>
<td>NOT RECOMMENDED</td>
<td>10.0 g OR MORE</td>
</tr>
</tbody>
</table>
Metrohm 716 DMS Titrino