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

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Karl Fischer Reaction

- Bunsen Reaction:

$$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$$

$$ROH + SO_2 + R'N \rightarrow [R'NH]SO_3R + \mathbf{H_2O} + I_2 + 2R'N \rightarrow 2[R'NH]I + [R'NH]SO_4R$$

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 ***pH 5 – 8*** otherwise buffer highly acidic/basic samples

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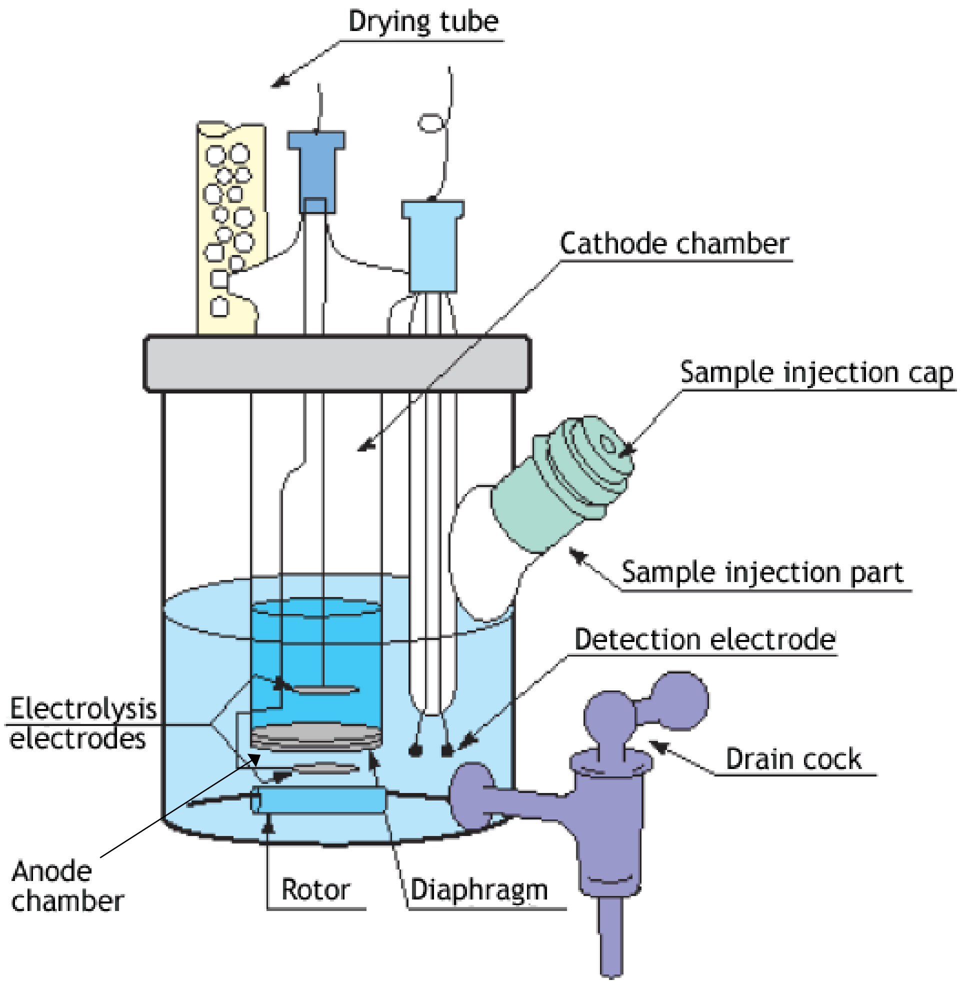
Cartoon Karl Fischer Cell



- 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 [I_2] in the Karl Fischer titrating reagent (i.e. titer) an the amount of KF reagent consumed

http://www.wako-chem.co.jp/english/labchem/product/analytical/aquamicron/index.htm

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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 1×10^6 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 x 1 s **where 1 mg H_2O = 10.72 C**
  - 1 to 50,000 ppm (0.0001 – 5%)

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General Sample Size Requirements

SAMPLE WATER CONTENT	VOLUMETRIC SAMPLE SIZE	COULOMETRIC SAMPLE SIZE
100%	0.02 to 0.05 g	NOT RECOMMENDED
50%	0.05 to 0.25 g	0.01 g
10% (100,000 PPM)	0.25 to 0.50 g	0.01 to 0.05 g
5% (50,000 PPM)	0.50 to 2.50 g	0.05 to 0.10 g
1% (10,000 PPM)	2.50 to 5.00 g	0.10 to 0.50 g
0.5% (5,000 PPM)	5.00 to 7.50 g	0.20 to 1.00 g
0.1% (1,000 PPM)	7.50 to 10.0 g	1.00 to 2.00 g
0.01% (100 PPM)	10.0 to 15.0 g	2.00 to 5.00 g
0.001 (10 PPM)	15.0 to 20.0 g	5.00 to 10.0 g
0.0001% (1 PPM)	NOT RECOMMENDED	10.0 g OR MORE

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Metrohm 716 DMS Titrino