ELECTROANALYTICAL TECHNIQUES

Karl Fischer titration

Karl Fischer was the scientist who in 1935 developed the original Karl Fischer method for water determination

Fundamental principle:

- Bunsen Reaction between iodine and sulfur dioxide in an aqueous medium (Iodometric titration of SO_2 in water)

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

- Modified to determine water in non-aqueous medium, excess of sulfur dioxide
- Using methanol as solvent, base (pyridine as buffering agent)

Basic concept: water reacts with iodine until the water is consumed and the endpoint is reached

Karl Fischer reaction

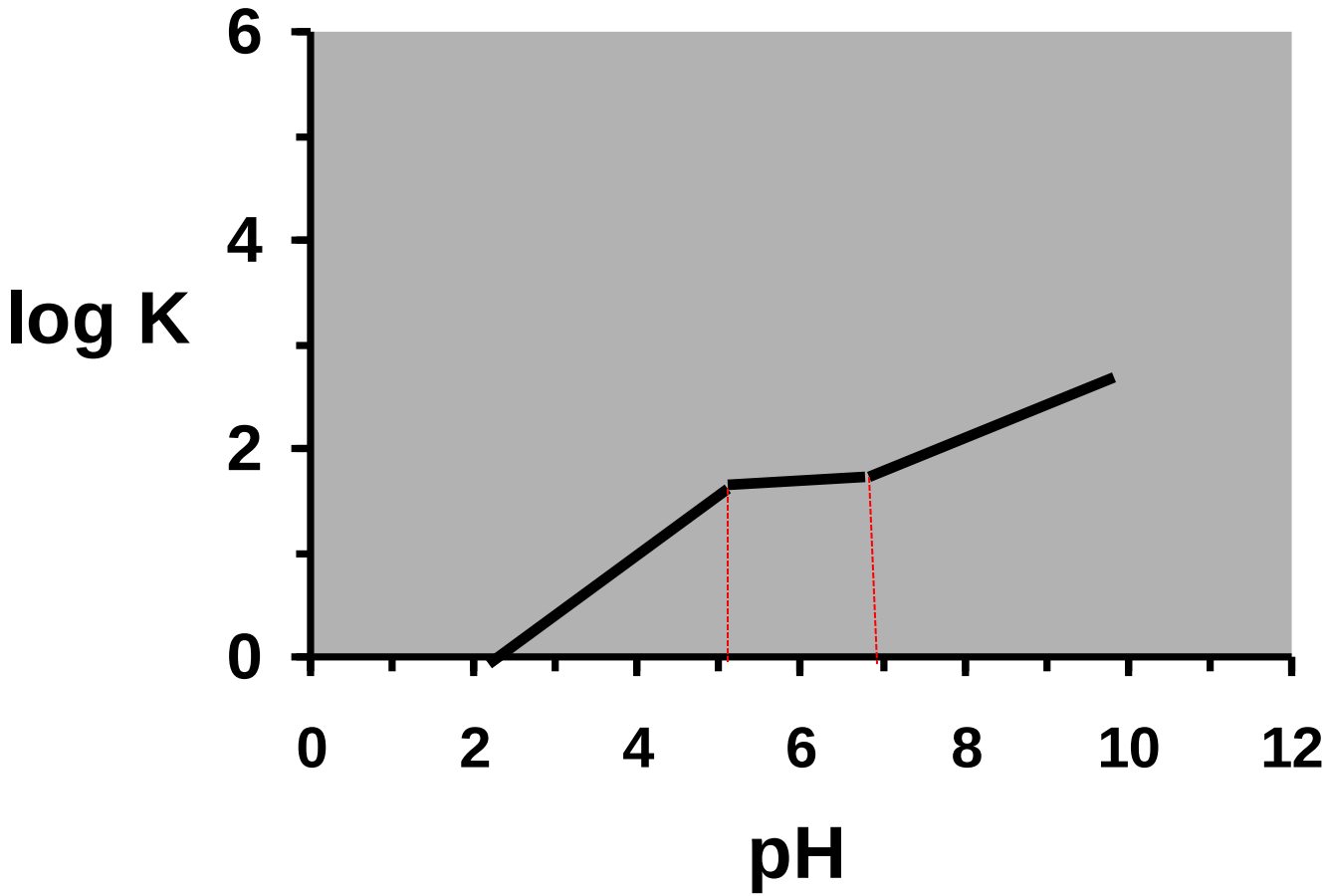
- Step 1:The alcohol reacts with sulfur dioxide (SO_2) and base to form an intermediate alkylsulfite salt

$$ROH\ (Alcohol) + SO_2 + R'N \rightarrow R'NHSO_3R$$
(alkylsulfite salt)

- Step 2:Alkylsulfite salt oxidized by iodine to an alkylsulfate salt.

$$R'NHSO_3R + H_2O + I_2 + 2R''N \rightarrow 2[R''NH]I + [R'NH]SO_4R$$

pH dependency



Optimum: pH range between 5 and 7

$ROH\ (Alcohol) + SO_2 + R'N \rightarrow RN'HSO_3R$

$RN'HSO_3R + H_2O + I_2 + 2R''N \rightarrow 2[R'NH]I + [R''NH]SO_4R$

- This oxidation reaction consumes water
- Water and iodine are consumed in a 1:1 ratio in the above reaction
- All of the water present in sample is consumed by iodine
- Excess iodine is then detected voltametrically by the titrator's indicator electrode or visually

Two types of methods (differ in how iodine is generated):

1- **Volumetric Titration method**:

Iodine directly added, reagent volume measured

$$\%\ \text{Water(W/W)} = \frac{\text{Volume(ml) of TS for Water Determination consumed} \times \text{f (mg/mL)}}{\text{Weight of the sample(mg)}} \times 100\%$$

f = Water mg/ml

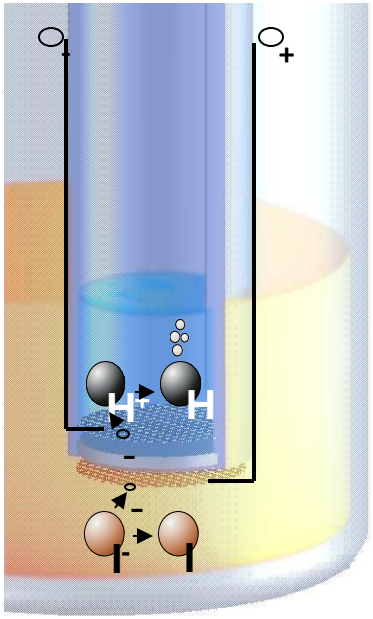
TS = Titrant standard

2-**Coulometric Titration method**:

- Iodine generated electrochemically during the titration

- Water is quantified on the basis of the total charge passed (Q), as measured by current (amperes) and time (seconds)

Q = 1 C (Coulomb) = 1 A x 1 s
where 1 mg H2O = 10.72 C



Karl Fischer reagent

- Original reagent prepared by action of sulphur dioxide on iodine in a mixture of anhydrous pyridine and anhydrous methanol

- Methanol unstable, different alcohols used instead: methoxyethanol, trifluoroethanol, cholorethanol

- Pyridine , too weak, is replaced these days (imidazole or primary amines)

$$ROH\ (Alcohol) + SO_2 + R'N \rightarrow RN'HSO_3R$$

$$RN'HSO_3R + H_2O + I_2 + 2R'N \rightarrow 2[R'NH]I + [R'NH]SO4R$$

ROH The solvent is generally methanol.

Methanol is the common solvent used as media

When analyzing Aldehydes and ketones, do not use methanol as a media. These compounds reacts with methanol to form additional water.

Number of iodines is equivalent to number water molecules in the reaction of iodine consumption.

KF degrades itself with atmospheric air and moisture, since the oxidation happening to sulfur dioxide.

so that the standardization of KF should be done frequently(Daily once).

Each ml of KF can neutralize (here react to consume) 5-6 mg of water. This will be exactly known by standardization of KF with DST(Disodium tartarate dihydrate) or Water.

Commercially KF reagents available in two types with respect to concentration.
1) 2 mg/ ml
2) 5 mg/ml

Karl Fischer reagent (Standardisation Procedure)

Standardisation:

1. 36 ml methanol + sufficient KF reagent to end point

2. Add 150 – 250 mg sodium tartarate ($C_4H_4Na_2O_6 \cdot 2H_2O$ MWt.= 230.08) and titrate with KF to end point

$2H_2O$ (MWt. 36.04)/ $C_4H_4Na_2O_6 \cdot 2H_2O$ (MWt.= 230.08)= 0.1566

3. Water equivalence factor (f) = 0.1566 x W/V

f = Water mg/ml reagent

W = weight of sodium tartarate in mg

V = volume of KF reagent in ml

Determination of Water by KFR

- Procedure:

1. Add 25 ml of titrant standard to titration flask
2. Titrate to end point with KFR
3. Weigh/measure sufficient sample to contain 10-50 ml of H_20
4. Quickly transfer to flask, stir vigorously, titrate with KFR
5. Water content in sample

$$\%\ \text{Water(W/W)} = \frac{\text{Volume(ml) of TS for Water Determination consumed} \times \text{f (mg/mL)}}{\text{Weight of the sample(mg)}} \times 100\%$$

Advantages of Analysis

1. High accuracy and precision - typically within 1% of available water, i.e. 3.00% appears as 2.97 - 3.03%

2. Selectivity for water

3. Small sample quantities required

4. Easy sample preparation

5. Short analysis duration

6. Nearly unlimited measuring range (1ppm to 100%)

7. Volumetric method:range of application 0.1%-100%
depends on sample size

8. Coulometric method: range of application 0.001 % - 1 % (10 µg - 200 mg absolute water content), mainly liquids and gases

9. Suitability for analyzing: solids, liquids , gases

Challenges with KF Method

Water has to be accessible and easily brought into methanol solution. Foods such as chocolate, release water slowly and with difficulty and this requires additional efforts to reliably bring the total water content into contact with the Karl Fischer reagents