ELECTROANALYTICAL TECHNIQUES-6

Lecture 6

By

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Who is Karl Fischer ??

- 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)

What is a Karl Fischer titration ?

- A Karl Fischer titration **determines the water content** in a sample

- Titration based on an iodine/iodide redox reaction
- **Basic concept:** water reacts with iodine until the water is consumed and the endpoint is reached

Karl Fischer reaction

- <u>Step 1:</u>
- ROH (Alcohol) + SO_2 + R'N = RN'HSO_3R (alkylsulphite salt)

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

- <u>Step 2:</u>
- RN'HSO_3R + H_2O + I_2 + 2R'N = 2[R'NH]I + [R'NH]SO_4R

- Alkylsulfite salt oxidized by iodine to an alkylsulfate salt.

Karl Fischer reaction

- ROH (Alcohol) + SO_2 + R'N = RN'HSO_3R (alkylsulphite salt)

- RN'HSO_3R + H_2O + I_2 + 2R'N = 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

Different Karl Fischer titration Methods

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

- Volumetric titration method:
  - Iodine directly added, reagent volume measured

- 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 H_2O = 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)

Karl Fischer reagent (Preparation)

- Steps:

1. Dissolve 63 g of Iodine in 100 ml of dehydrated pyridine
2. Cool in ice , pass SO_2 until gain of 32.3 g
3. Add sufficient Me_2OH to make 500 ml
4. Allow stand for 24 hrs
5. 1 ml reagent = 5 mg of H_2O
6. Standardize within 1 hr or daily before use

Karl Fischer reagent (Standardisation Procedure)

- Primary Standardisation:

1. 36 ml methanol + sufficient KF reagent to end point
2. Add 150 – 250 mg sodium tartarate and titrate to end point
3. Water equivalence factor (F) = 0.1566 W/V

F = Water mg/ml reagent

W = weight of sodium tartarate in mg

V = volume of reagent in ml

- Secondary Standardisation:

1. 2 ml + 1000 ml methanol
2. 25 ml of this solution titrated with KF
3. Blank titration on 25 ml methanol
4. F (Water mg/ml reagent) = V*F/25

Determination of Water by KFR

- Procedure:

1. Add 25 ml 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 = S x F

   S = Volume of KFR

   F = water equivalence factor (mg of water

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%)
    1. Volumetric method: 100 ppm – 100 %
    2. Coulometric method: 1ppm – 5 %
7. Suitability for analyzing: solids, liquids , gases
8. In contrast, loss on drying will detect the only volatile substances

Challenges with KF Method

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