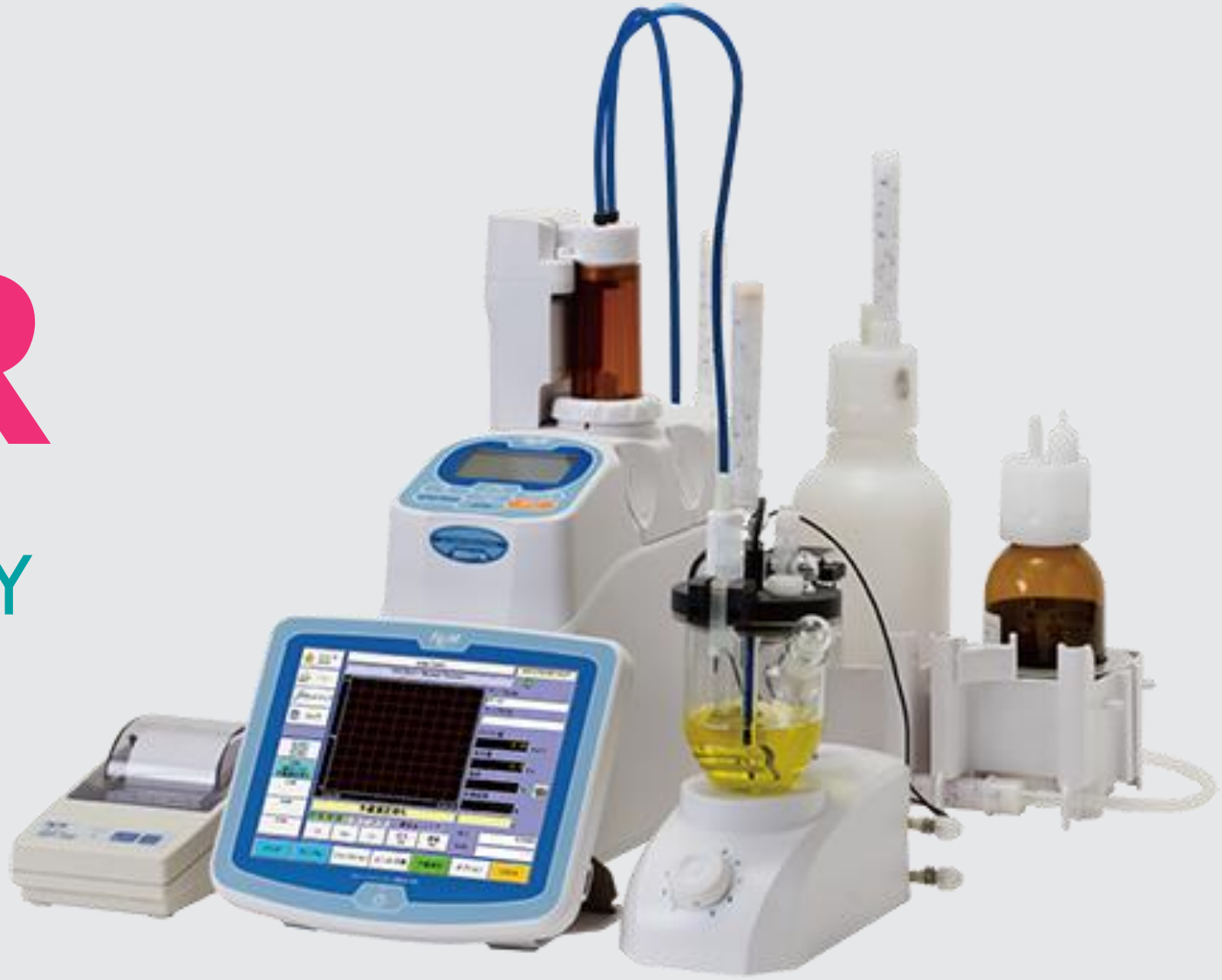
KARL FISCHER

BASICS OF CHEMISTRY



RECAP

UNITS

NORMALITY

STANDARDIZATION

PURITY

EXPERIMENT
Std. OF HCL
& KOH
PURITY

pH Meter

CONTENTS

INTRODUCTION

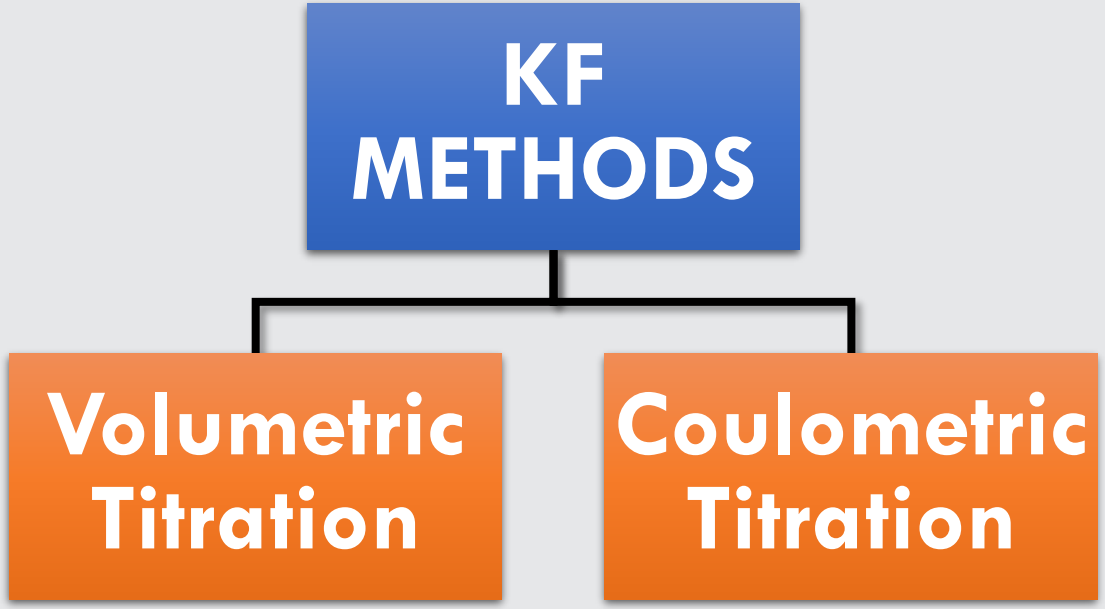
DEFINITION

1. Karl Fischer Titration Is A Technique For The Determination Of Moisture Content.
2. The Technique Was Developed By A Chemist Named Karl Fischer.
3. It Is Based On A Reagent (Karl Fischer Reagent) Which Reacts With Water And Converts The Water Into A Non-conductive Chemical.

INTRODUCTION

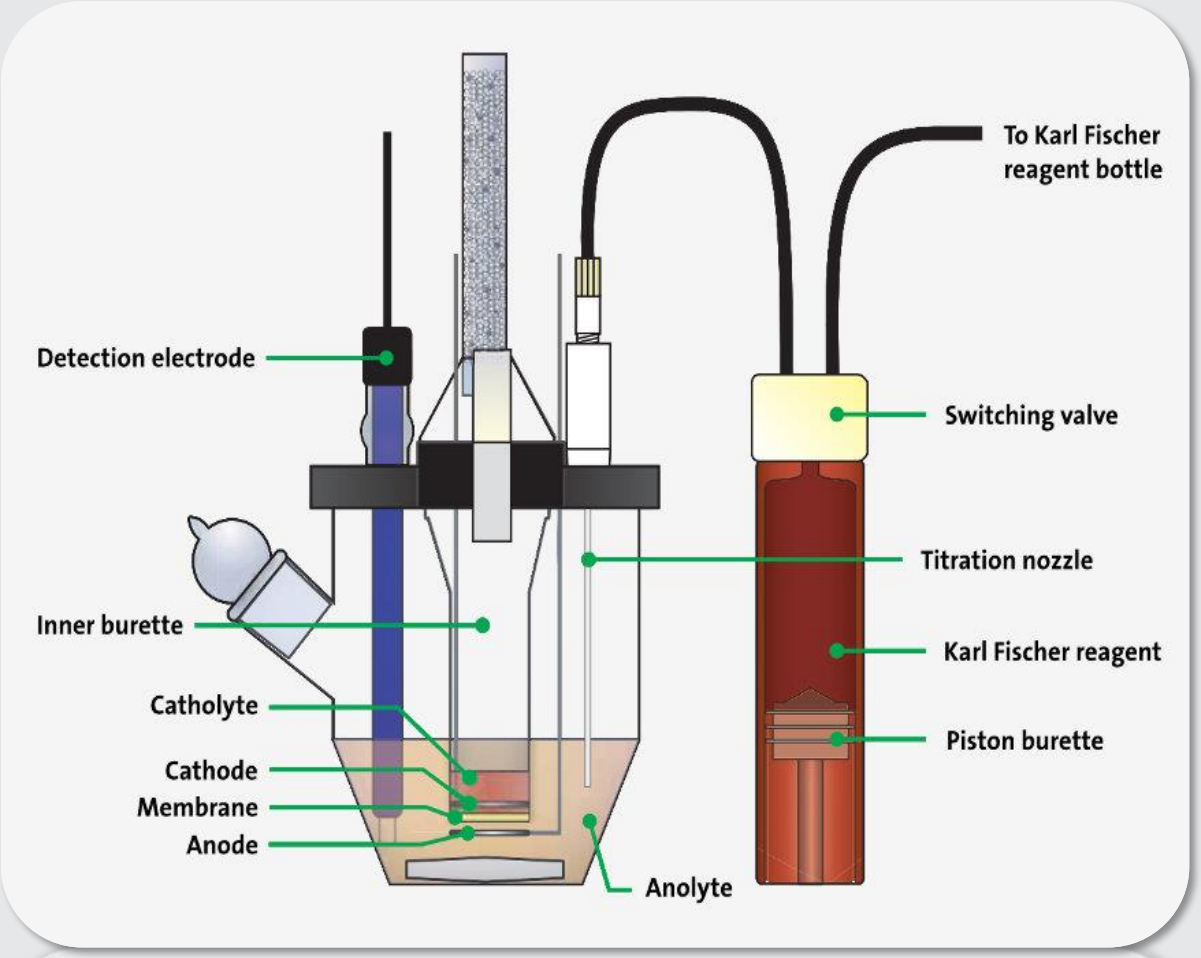
DEFINITION

4. There Are Two Methods Used To Perform The Karl Fischer Titration Test.
5. One Is Known As Volumetric Karl Fischer Titration. The Other Method Is Known As Coulometric Karl Fischer Titration.

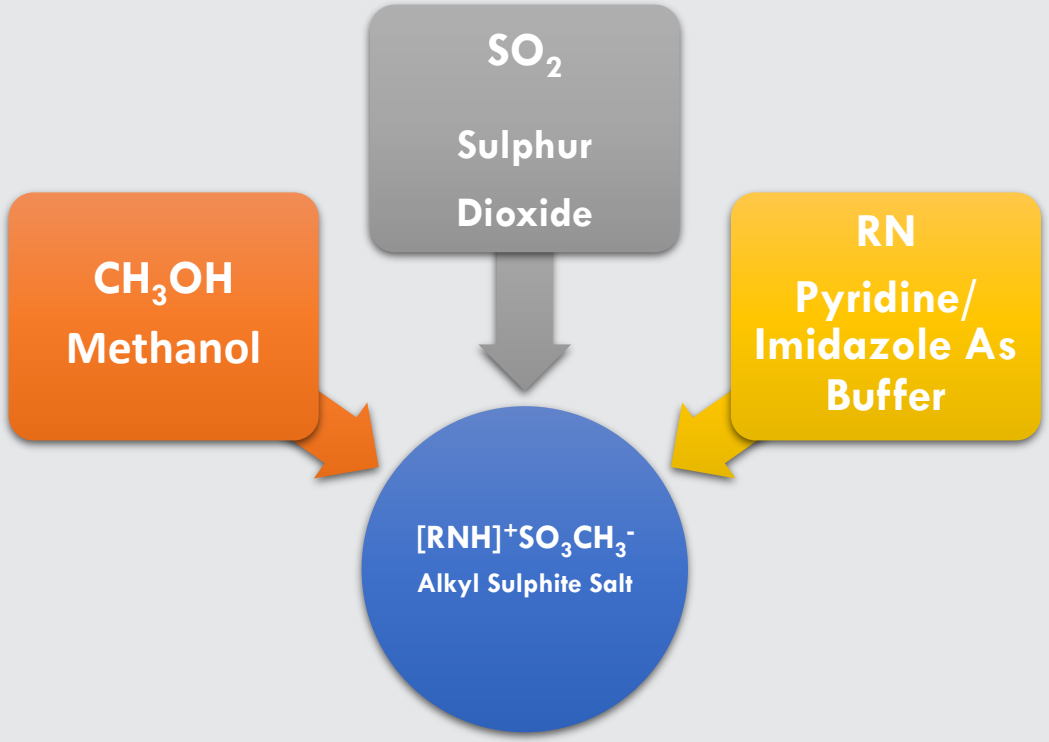


PRINCIPLE OF WORKING

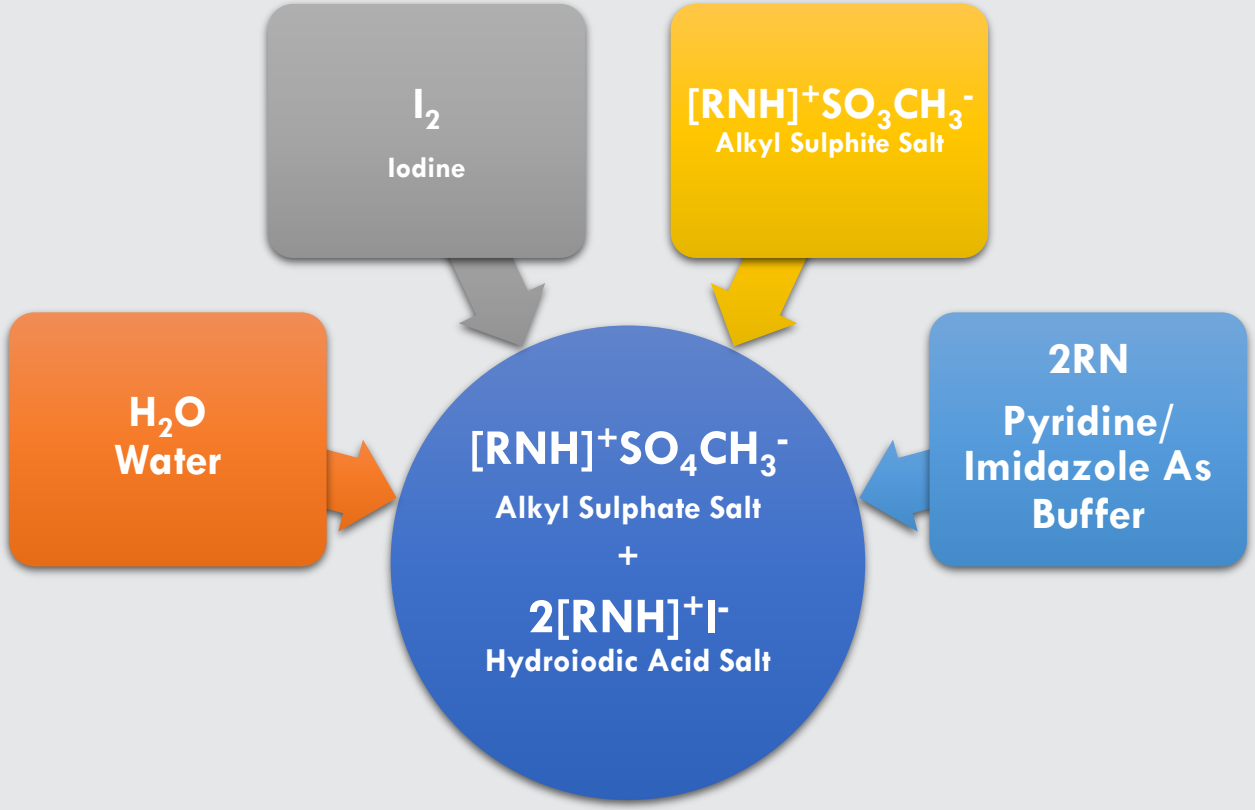
1. The Principle Of Karl Fischer Titration Is Based On The Oxidation Reaction Between Iodine And Sulfur Dioxide.
2. Water Reacts With Iodine And Sulfur Dioxide To Form Sulfur Dioxide And Hydrogen Iodide. An Endpoint Is Reached When All The Water Is Consumed.
3. This Chemical Rection Generates Iodine Ions Which Cause Flow Of Electric Current Which Is Measured And Used For the Calculating Water Content.



PRINCIPLE OF WORKING



STEP 1



STEP 2

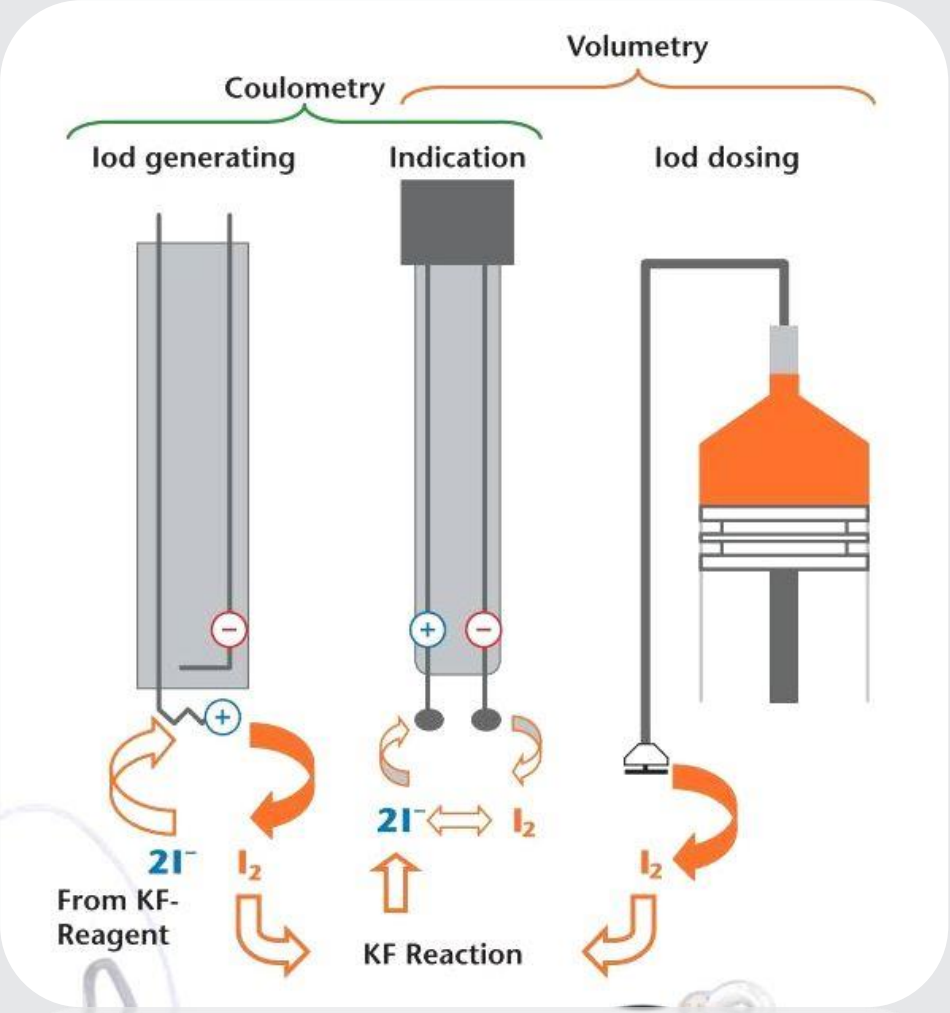
PRINCIPLE OF WORKING

$2[RNH]^{+}I^{-}$
Hydroiodic Acid Salt

$2[RNH]^{+}$

$2I^{-}$

STEP 3



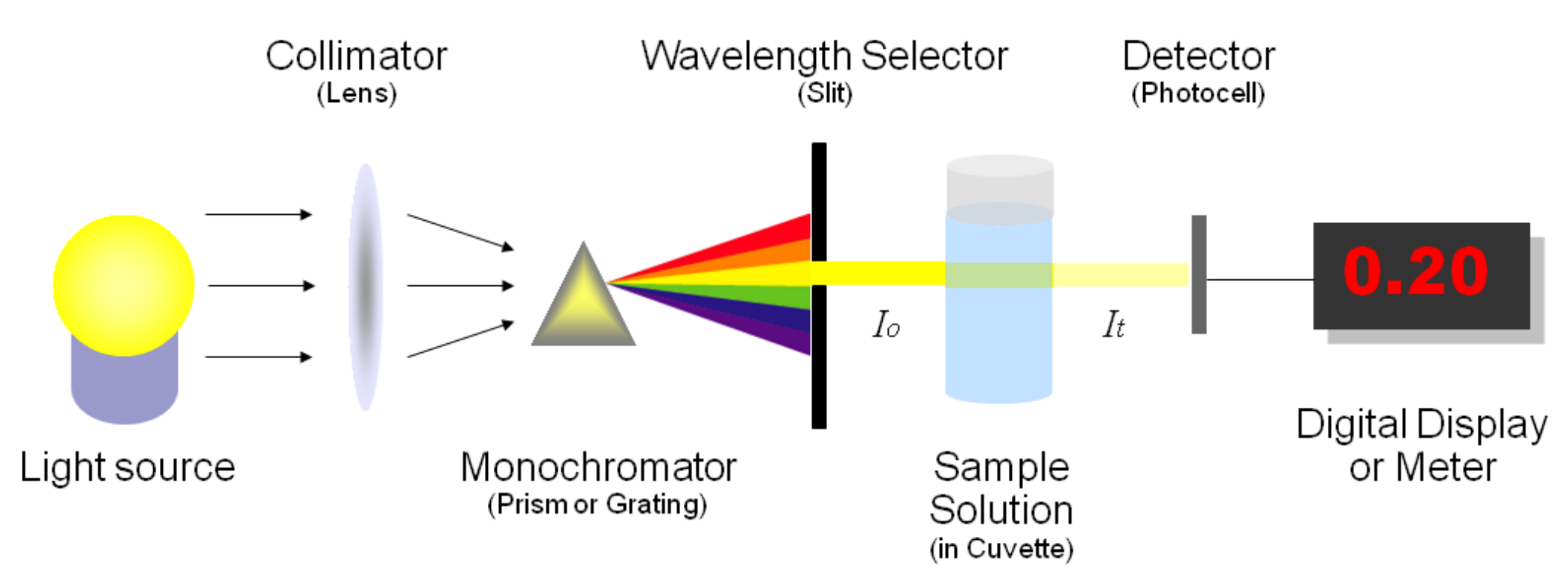
ENDPOINT DETECTION

VISUAL INSPECTION METHOD TO DETECT END POINT

Highly Inaccurate In Detecting Colour Change. Rarely Used.

ENDPOINT DETECTION

SPECTROPHOTOMETRY METHOD TO DETECT END POINT



Impractical Method. Other Easier And Less Complicated Methods Available Insitu.

ENDPOINT DETECTION

ELECTROMETRIC INDICATION METHODS

1. Endpoint Indication Methods Using Two Polarized (Polarizable) Electrodes Are Most Popular.
2. Double Pt-wire Or Double Pt-ring Electrodes Are Commonly Used.

ENDPOINT DETECTION

ELECTROMETRIC INDICATION METHODS

ELECTROMETRIC INDICATION METHODS

- BIAMPEROMETRIC INDICATION
- BIVOLTAMETRIC INDICATION

BIAMPEROMETRIC INDICATION

1. Also Called Dead Stop Indication Of Endpoint.
2. A Constant Voltage Of Max. 500 mv Is Applied To The Electrodes And The Resulting Current Is Measured.

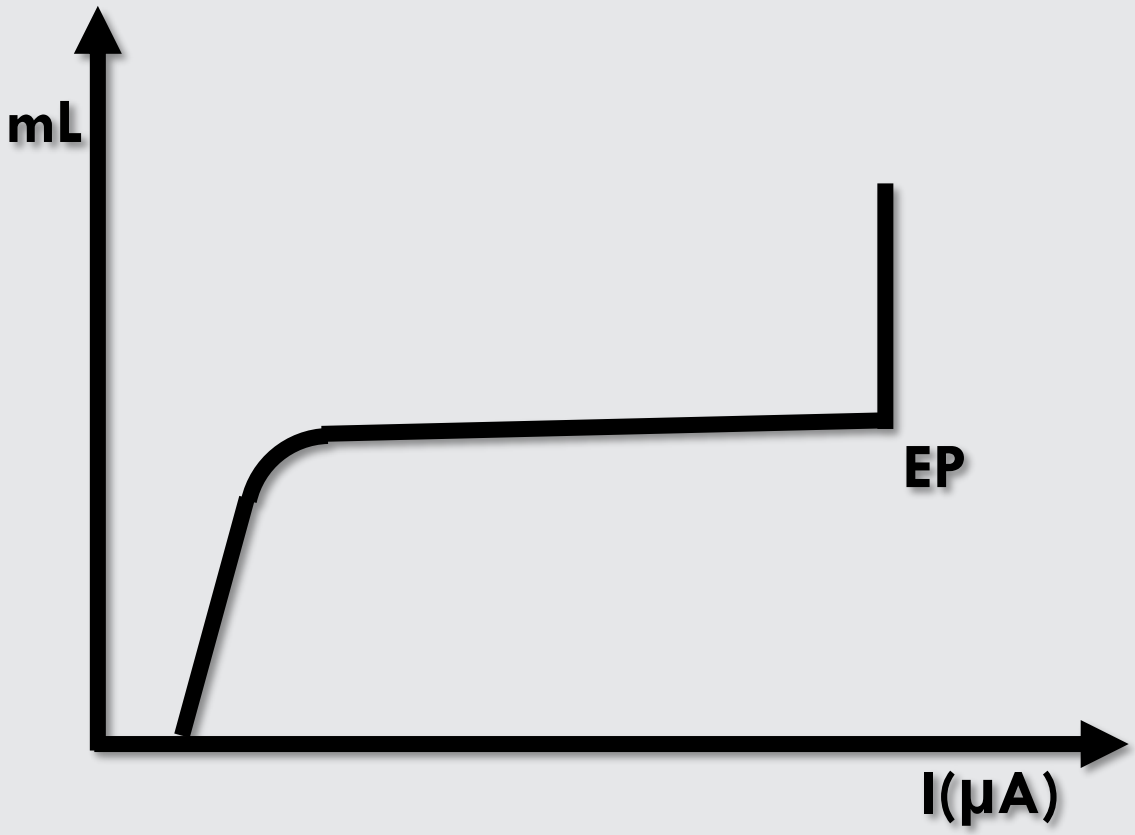
The Following Reactions Occur At The Electrodes:

CATHODE	ANODE
$I_2 + 2\,e^- \rightarrow 2\,I^-$ (reduction)	$2\,I^- - 2\,e^- \rightarrow I_2$ (oxidation)

3. Initially Only Low Voltages Are Required To Produce A Flow Of Current. Then The Voltage Increases Steeply – As A Function Of The Iodine Concentration.

ENDPOINT DETECTION

ELECTROMETRIC INDICATION METHODS

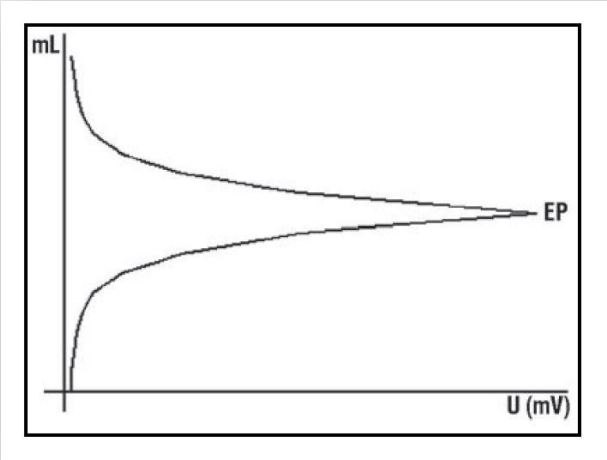


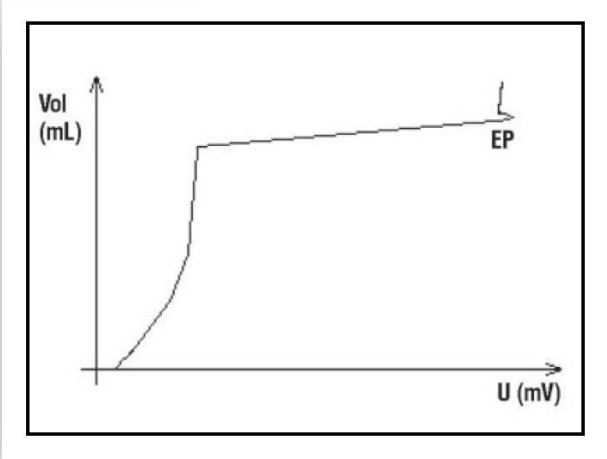
BIAMPEROMETRIC INDICATION

3. Initially Only Low Voltages Are Required To Produce A Flow Of Current. Then The Voltage Increases Steeply – As A Function Of The Iodine Concentration.
4. This Means That A Current Flows For As Long As Iodine Is Present.
5. When The Iodine Has Been Consumed The Current Falls Abruptly To 0 (Hence Called Dead Stop Endpoint), The Resistance Between The Electrodes Increases Strongly And The Electrodes Are Again Polarized.

ENDPOINT DETECTION

ELECTROMETRIC INDICATION METHODS





BIVOLTAMETRIC INDICATION

1. A Small Direct Or Alternating Current Is Applied Between The Electrodes.
2. If The Sample Solution And Titrant Are Electrochemically Active Then Peak-shaped Or V-Shaped Titration Curves Are Obtained.
3. If Only One Partner Is Electrochemically Active (The KFR With Excess Iodine) Then L-Shaped Curves Are Obtained.

KARL FISCHER REAGENT

KARL FISCHER REAGENT STANDARDISATION

1. Place Adequate Quantity Of Methanol In The Titration Vessel And Add Sufficient Amount Of Karl Fischer Reagent To Reach The Characteristic Endpoint.
2. Weight Accurately 150 - 350 Mg Of Sodium Tartrate ($Na_2C_4H_4O_6,2H_2O$ – Certified Water Standard Grade) Accurately Weighed, By Difference And Titrate To The Endpoint.
3. The Water Equivalence Factor 'F' In mg Of Water Per ml Of KF Reagent Should Be Calculated Using The Formula.

$$F = 0.1566^{*} \times \frac{W}{V}$$

Where,

W = Weight Of Sodium Tartrate Expressed In mg.

V = Volume Of Kf Reagent Expressed In ml.

$$* \textit{Each mg of Sodium Tartrate Is Equivalent To} = \frac{2H_2O}{Na_2C_4H_4O_6,2H_2O} = \frac{36.04}{230.08} = 0.1566$$

TYPES OF KARL FISCHER TITRATORS

VOLUMETRIC

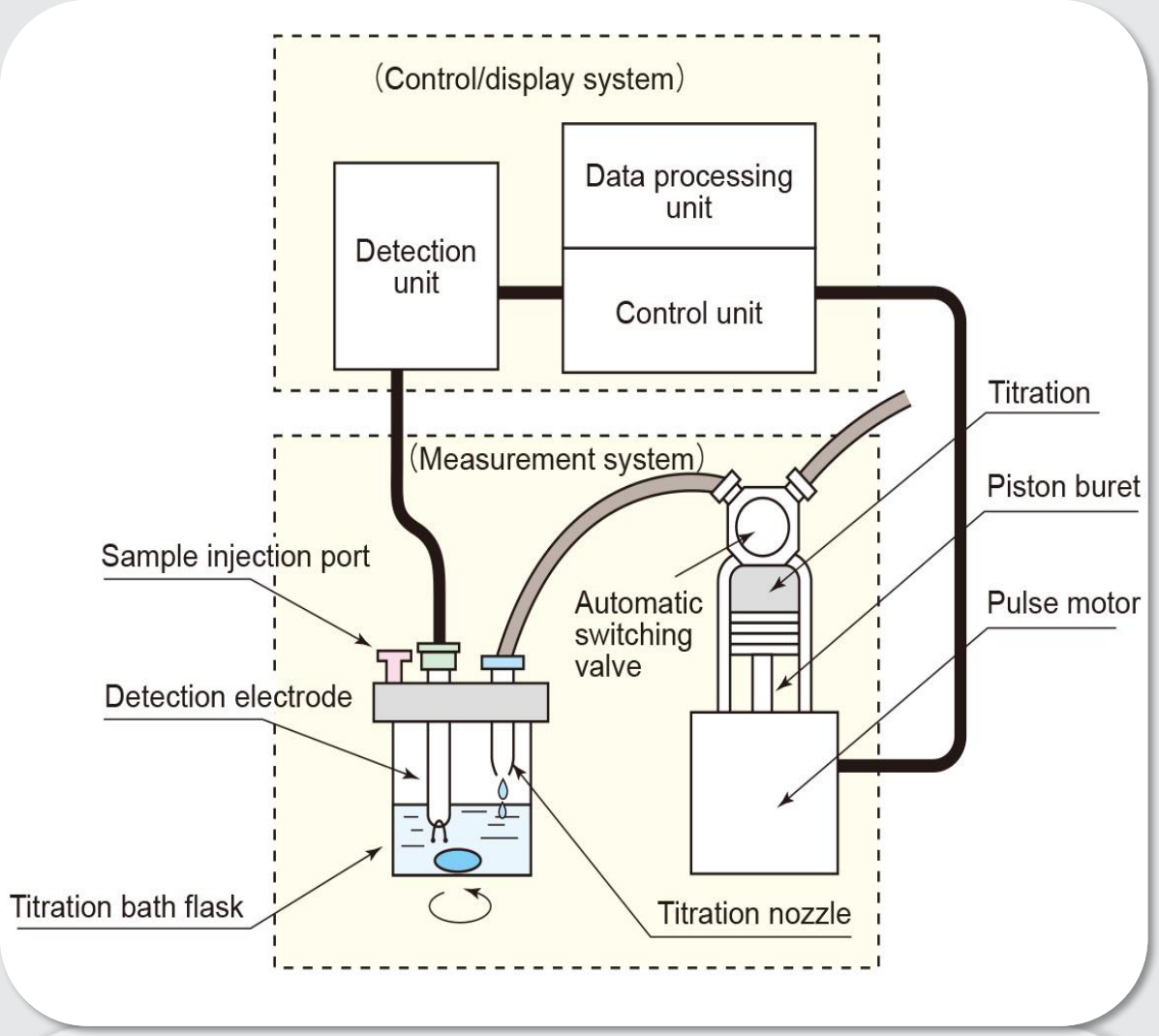
COULOMETRIC

HYBRID

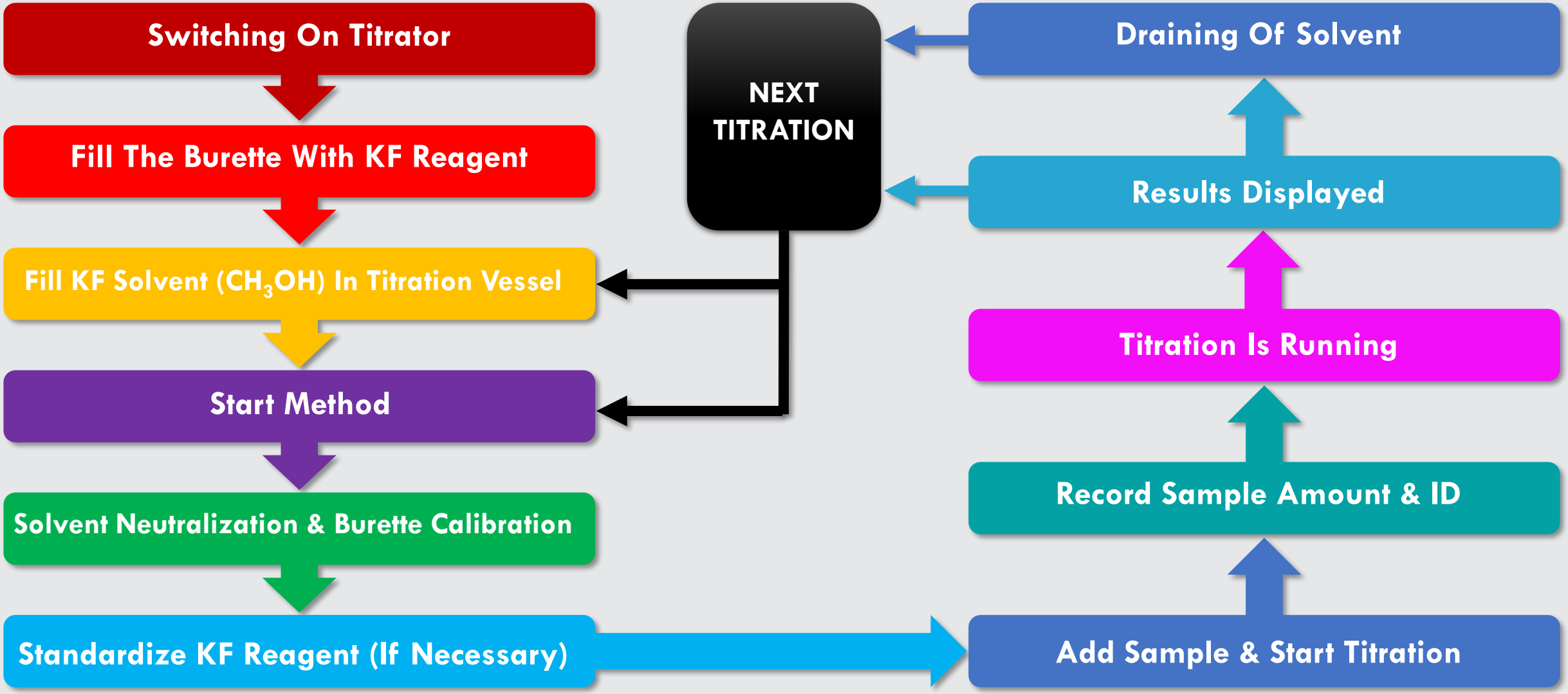
ABLE TO DO VOLUMETRIC & COULOMETRIC KF TITRATION

VOLUMETRIC KARL FISCHER METHOD

- In Volumetric Karl Fischer, Iodine Is Added Mechanically To A Solvent Containing The Sample By The Titrator's Burette During The Titration.
- Water Is Quantified On The Basis Of The Volume Of Karl Fischer Reagent Consumed.
- Volumetry Is Best Suited For Determination Of Water Content In The Range Of 100 ppm To 100%.



VOLUMETRIC KARL FISCHER METHOD



VOLUMETRIC KARL FISCHER METHOD

% WATER MEASUREMENT

1. Add 30 ml Of Methanol Into Titration Flask.
2. Neutralize With Karl Fischer Reagent To The Electrometric End Point.
3. Weigh Accurately Specified Quantity Of Sample & Transfer It In To A Titration Flask Stir For 1 Minute & Titrate The Solution With Karl Fischer Reagent To The Electrometric Endpoint.
4. Record The Volume Of Karl Fischer Reagent Consumed In ml.

CALCULATION FORMULA

$$\%\,Water = \frac{B.R. \times F \times 100}{wt \times 1000}$$

Where,

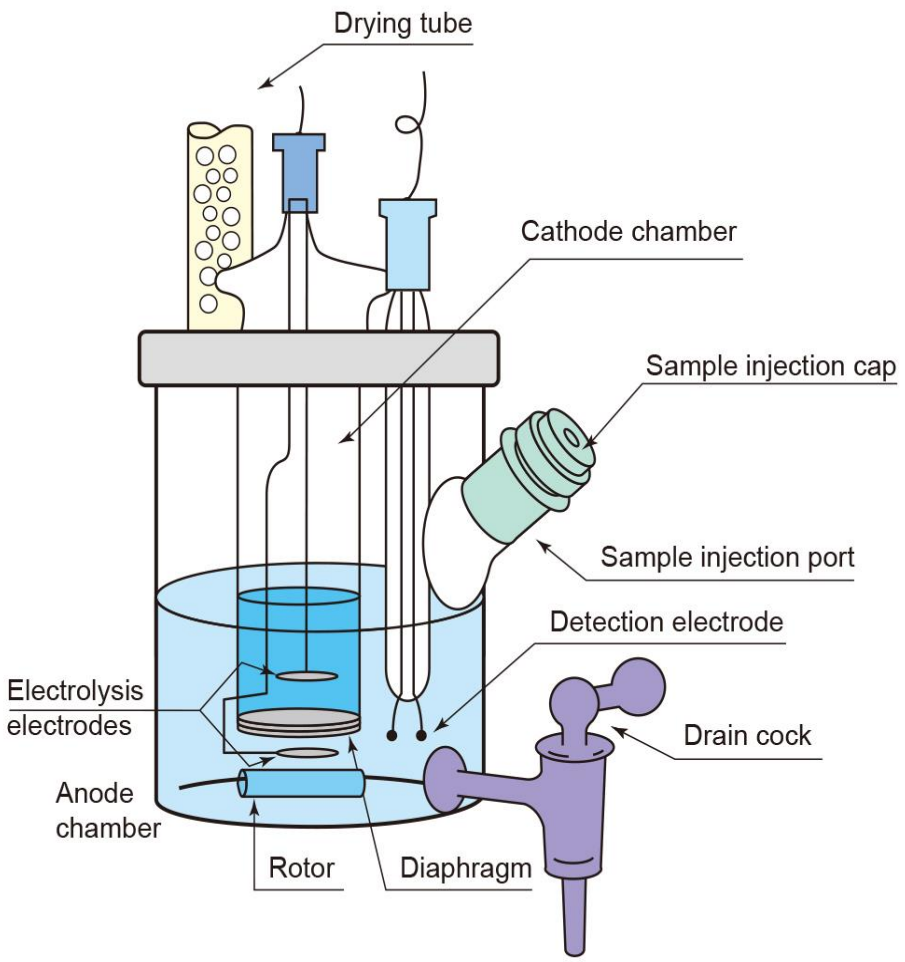
B.R. = Vol. Of KF Reagent.

F = KF Reagent Factor mg/ml.

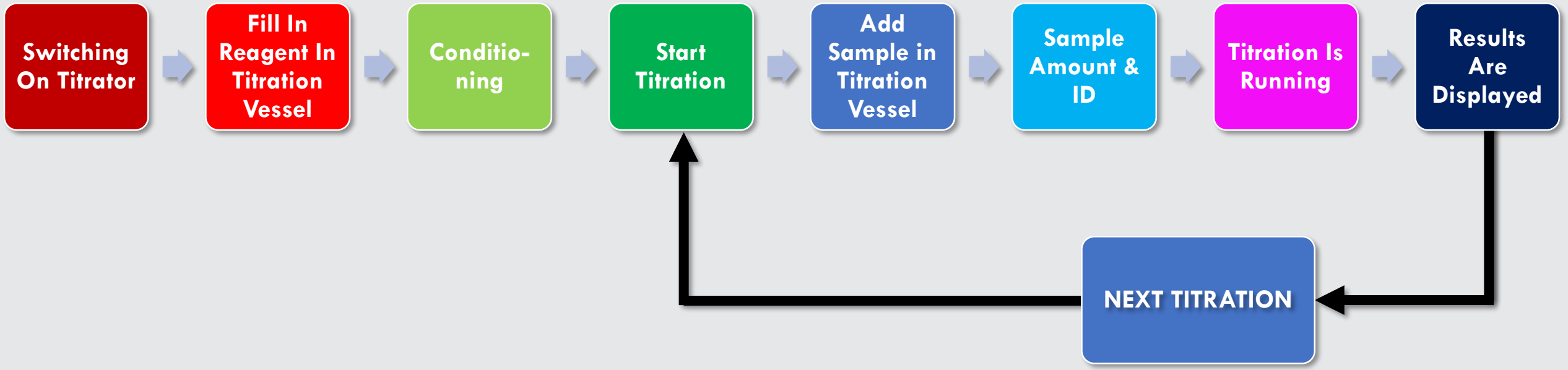
wt. = Weight Of Sample Taken in g.

COULOMETRIC KARL FISCHER METHOD

1. In Contrast To Volumetric Karl Fischer Titration, In KF Coulometry No Titrant Is Added But The Required Iodine Is Generated Directly In The Iodide-containing Electrolyte By Electrochemical Means (Electronic Burette).
2. There Is A Strictly Quantitative Relationship Between The Amount Of Electric Charge And The Amount Of Iodine Generated. This Relationship Allows The Extremely Precise Addition Of The Iodine.



COULOMETRIC KARL FISCHER METHOD

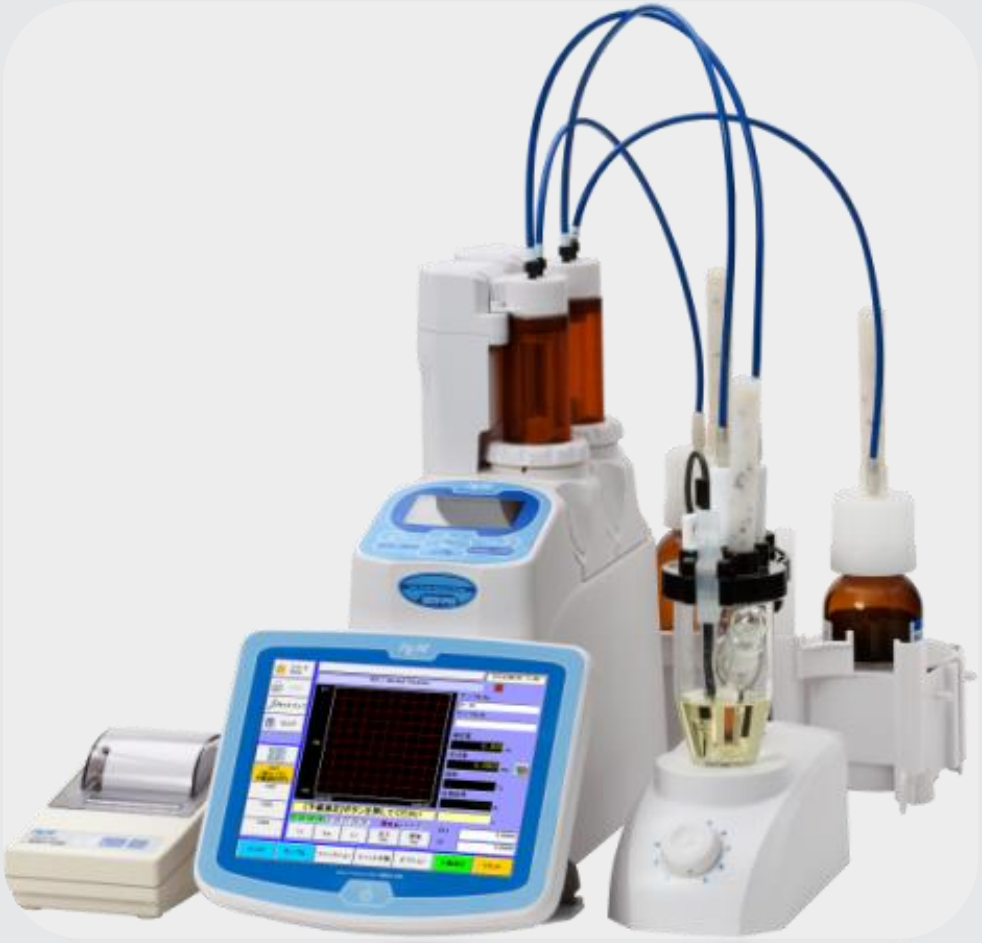


COULOMETRIC GENERATOR ELECTRODES

A. GENERATOR ELECTRODE WITHOUT DIAPHRAGM
   1. The Generator Electrode Without Diaphragm Is Easy To Handle And Easy To Clean.
   2. Only A Single Reagent Is Required.
   3. Specific For Reagents Other Than Aldehydes & Ketones.
B. GENERATOR ELECTRODE WITH DIAPHRAGM
   1. Used Whenever Your Samples Contain Ketones And Aldehydes, As The Special Reagents Used For Them Are Only Available For Generator Electrodes With Diaphragms.
   2. Also Useful For Reagents With Low Conductivity.

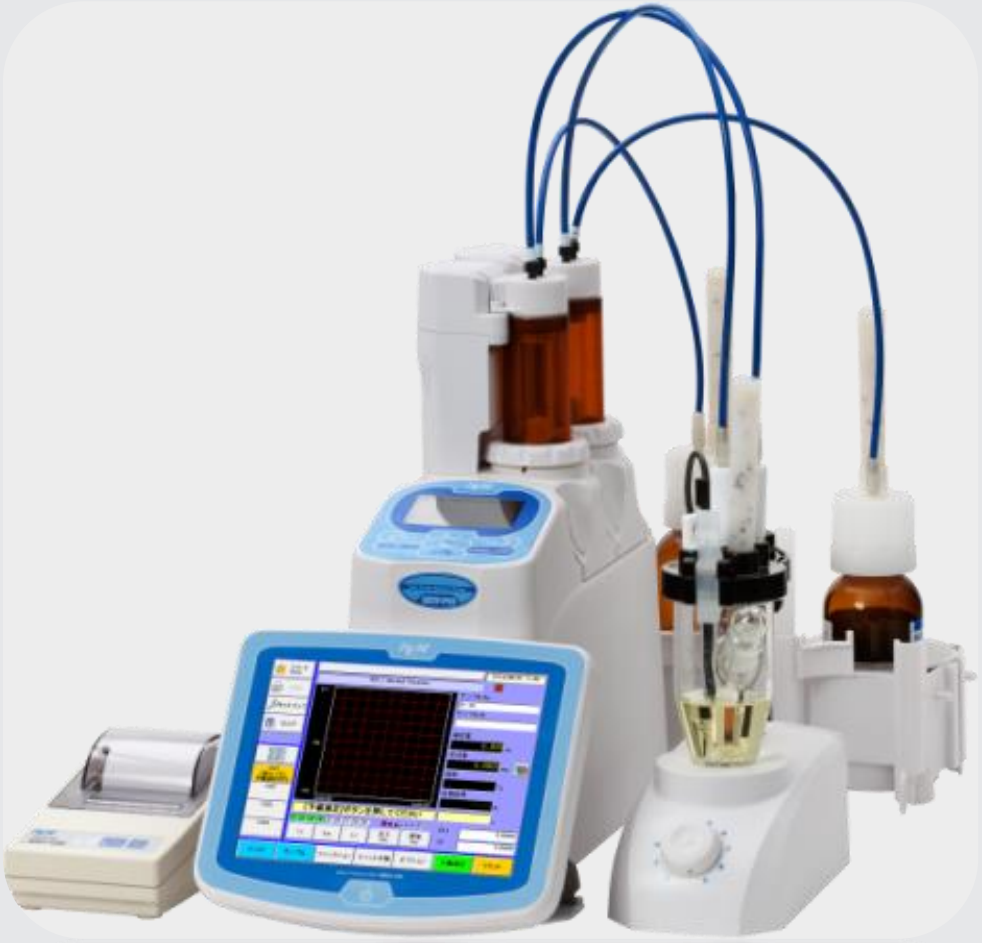
ADVANTAGES OF KARL FISCHER

1. It Is Fitted For Determining Water In Gases, Liquids And Solids.
2. The Coulometric Titrator Helps In Detecting Free Water, And Emulsified Water.
3. It Is A Quick Process Which Demands A Minimal Amount Of Sample Preparation
4. Extremely Accurate Method



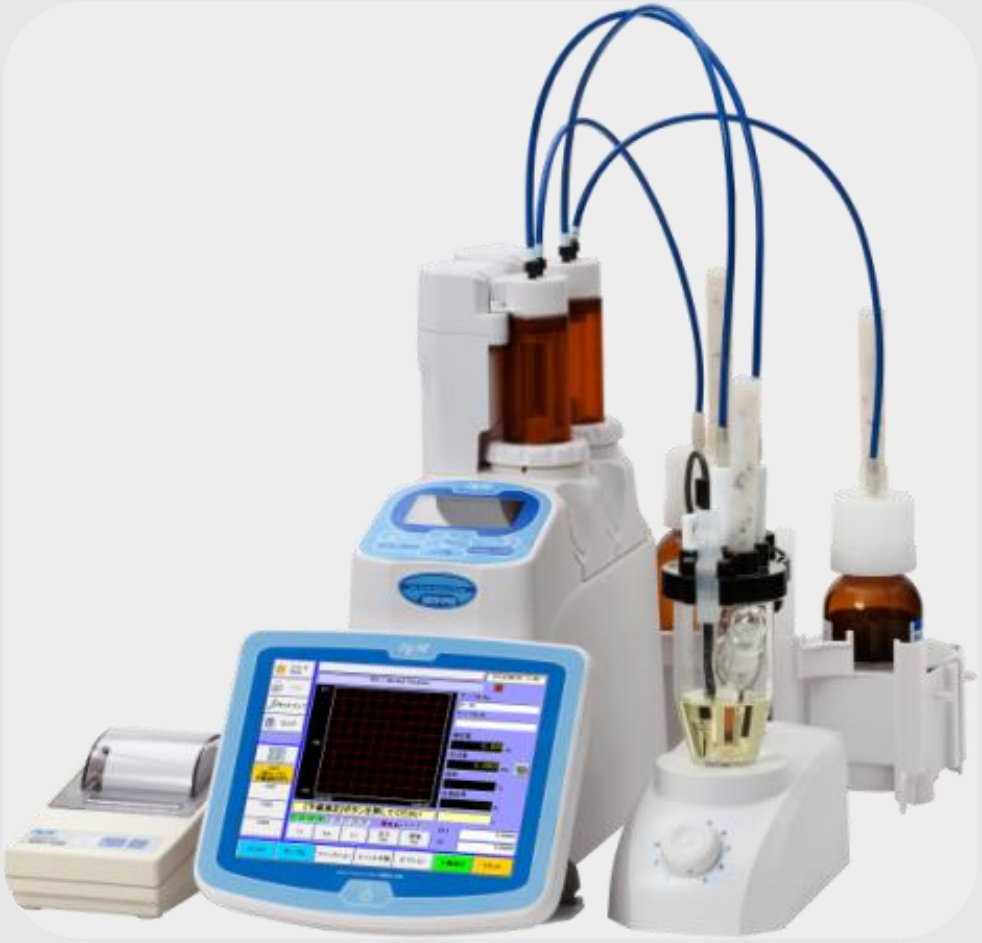
ADVANTAGES OF KARL FISCHER

5. Specificity For Water Determination Because It Does Not Detect The Loss Any Other Volatile Substances. Unlike Other Methods Such As Loss On Drying Which Are Based Upon The Heat Induced Loss Of Moisture With Respect To Reduction In Weight Of The Sample.
6. It Works With Small Samples Unlike Several Other Methods, And This Makes It More Accurate And Repeatable.
7. The Process Lends Itself To Automation, Making Water Determination A Matter Of Minutes.



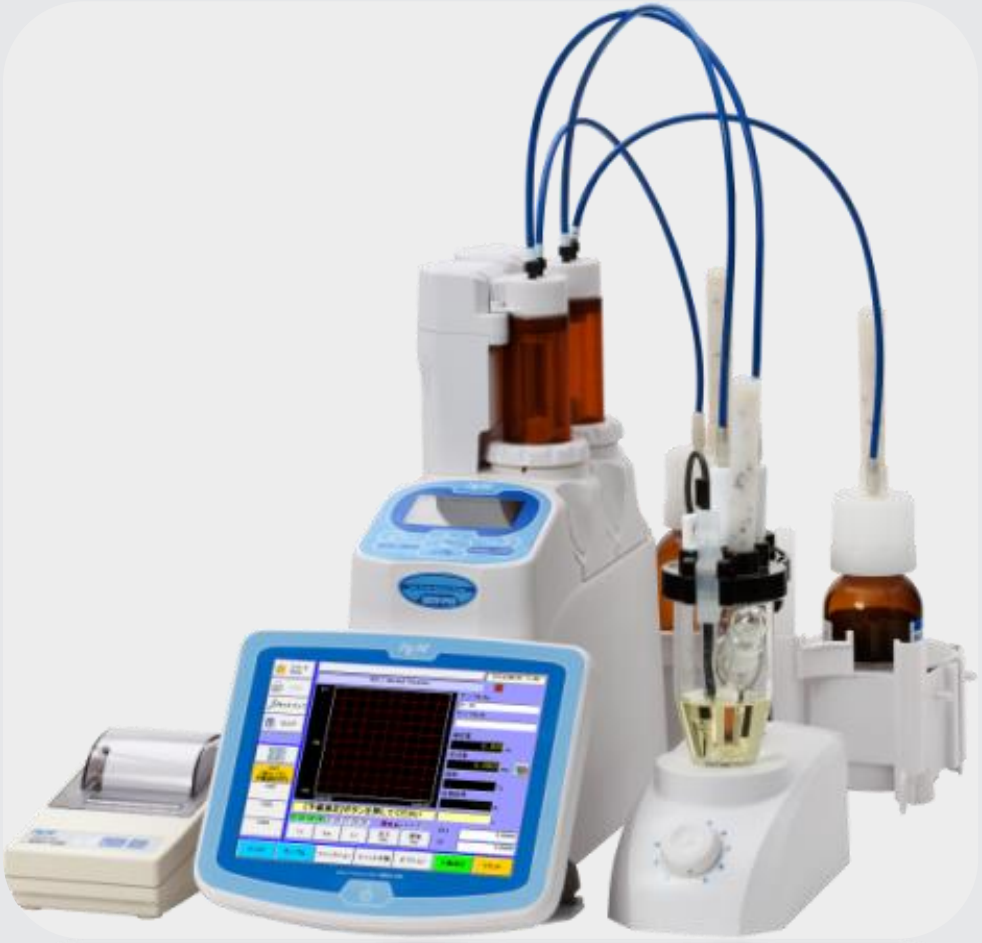
LIMITATIONS OF KARL FISCHER

1. It Is A Destructive Technique.
2. The Solvent Consumption Is High As The Manual Volumetric Titration Demands Reloading During Each Determination.
3. Coulometric Titration Is Fitted Only For Samples That Contain A Small Amount Of Water
4. Coulometric Titration Takes Extremely Long Periods To Determine



LIMITATIONS OF KARL FISCHER

5. The Manual Titration Requires Considerable Operator Input.
6. Compounds Like Lithium Chloride Have Tightly Bound Water Or Hydration, So When They Are Part Of The Solvent, It Is Difficult To Use With KF Titration.
7. KF Titration Depends Upon A Redox Reaction And Thus Any Component Of The Sample Which Is As Dimethyl Sulfoxide Will React With The Iodine In The Reagent And Generate False Results.



APPLICATIONS OF KARL FISCHER

FOOD INDUSTRY

CHEMICAL INDUSTRY

PHARMACEUTICAL INDUSTRY

GAS ANALYSIS

COSMETICS


CEMENT INDUSTRY


PETROL & DIESEL

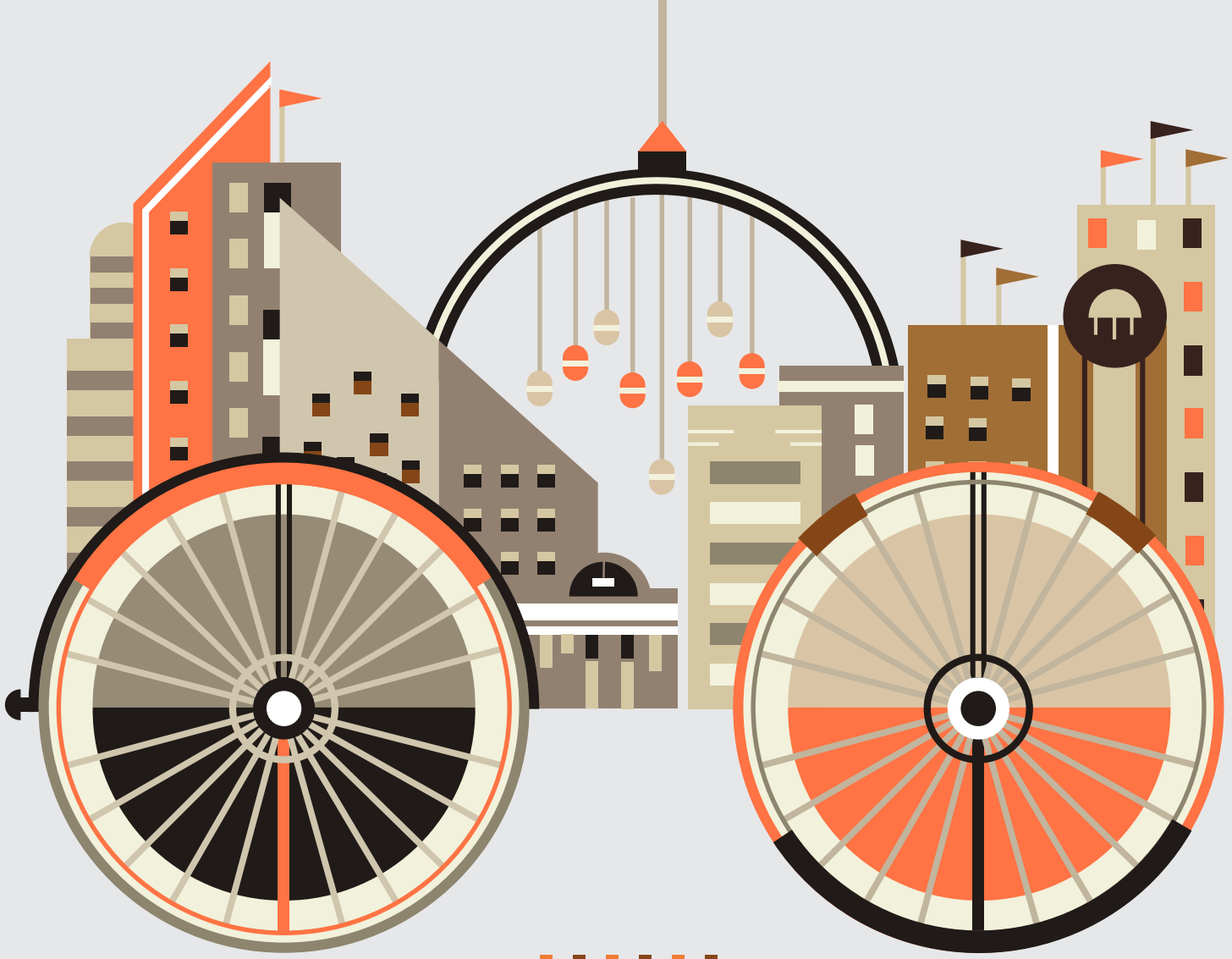

POLYMER INDUSTRY


PETROLEUM REFINERY


PAINT & DYE INDUSTRY

SUMMARY

1. INTRODUCTION
2. PRINCIPLE OF WORKING
3. END POINT DETECTION
4. KARL FISCHER REAGENT
5. VOLUMETRIC KF TITRATION
6. COULOMETRIC KF TITRATION
7. ADVANTAGES
8. LIMITATIONS
9. APPLICATIONS OF KF
10. SUMMARY



THANK YOU VERY MUCH