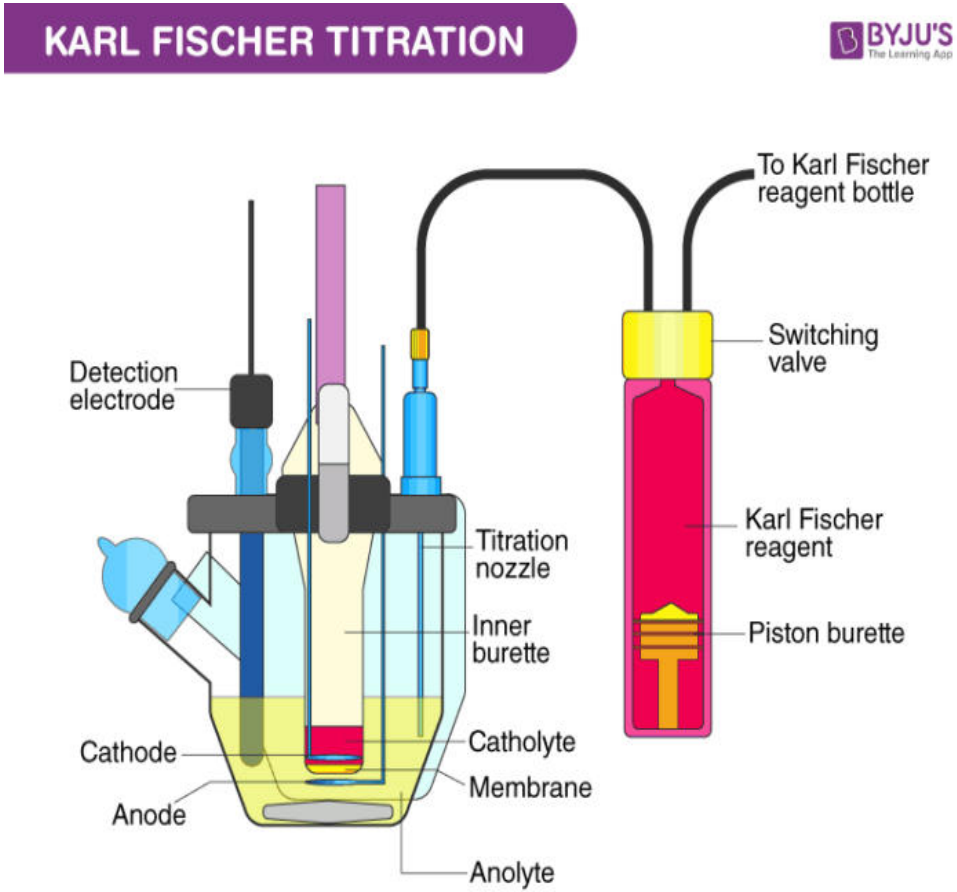
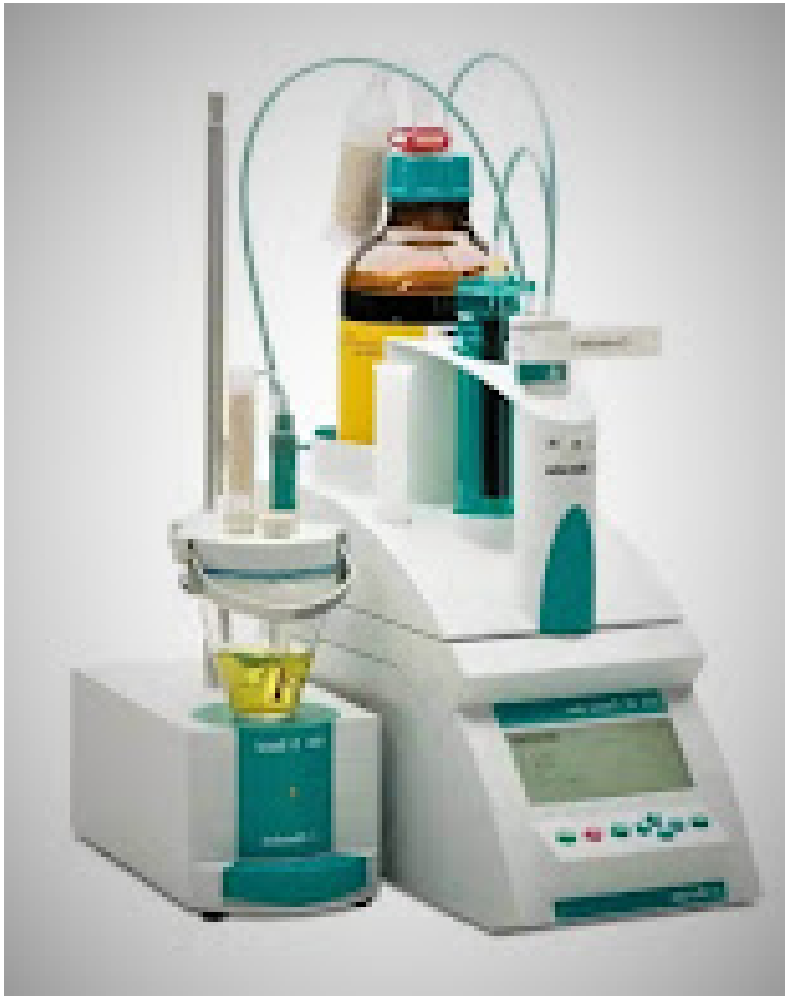
Karl Fischer Titration





Topics

- KF reaction
- Volumetric KF Titration
- Coulometric KF Titration
- Endpoint indication
- Drift as second endpoint indication
- Parameters
- KF Instruments

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Method for water determination

- in technical products

  (oil, plastics and gases)
- in cosmetic products
- in pharmaceutical products
- in food industry

The KF reaction

I.

$$CH_3OH + SO_2 + RN \rightarrow [RNH]SO_3CH_3$$

II.

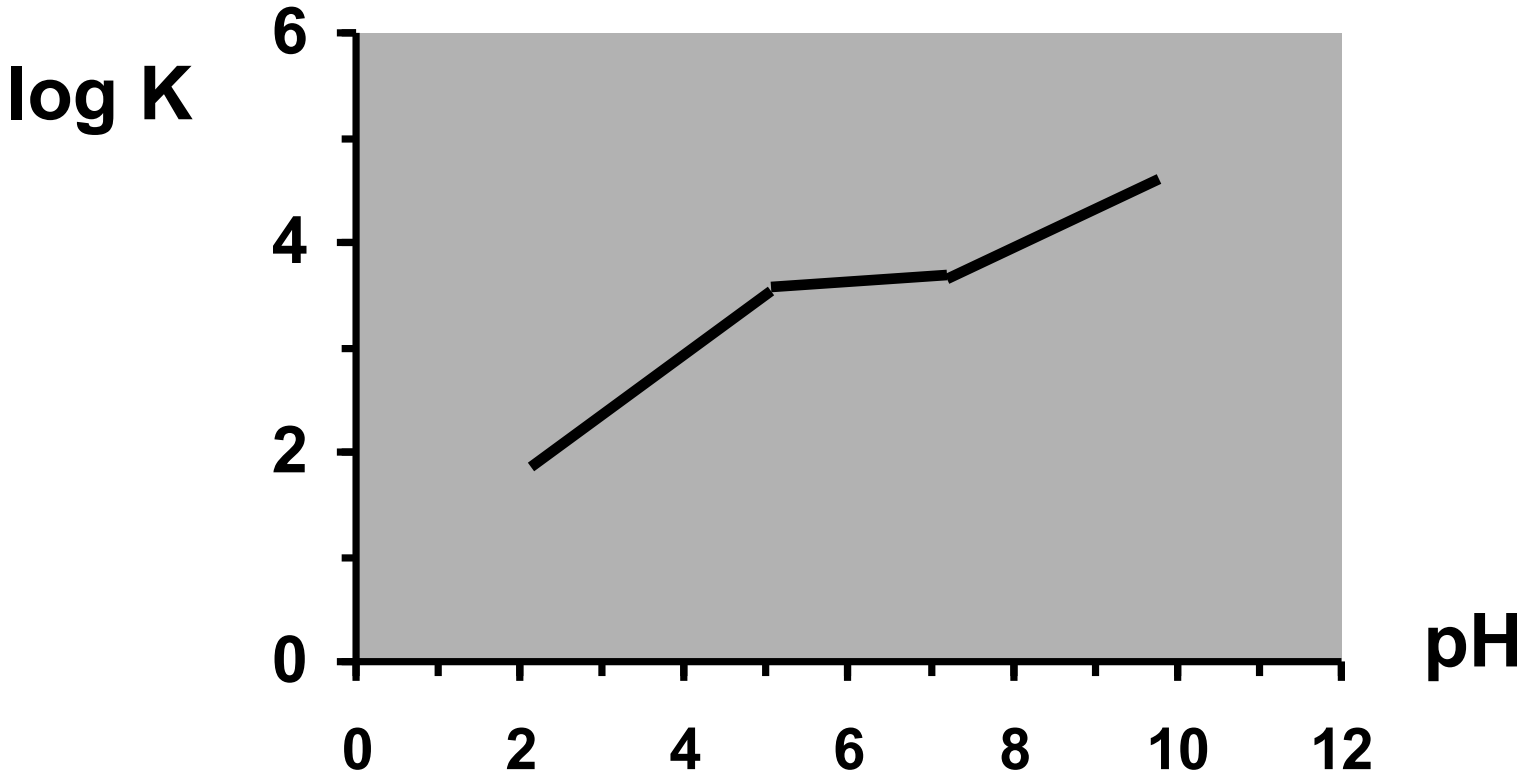
$$H_2O + I_2 + [RNH]SO_3CH_3 + 2RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

(RN = Base)

Basic ingredients of KF reagents

Iodine	I_2
Sulphur dioxide	SO_2
Buffer	Imidazole
Solvent	Methanol

pH dependency



Optimum: pH range between 5 and 7

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KF titration methods

Volumetric KF titration

Working medium & titrant

Coulometric KF titration

Iodine is generated in titration cell (anodic oxidation)

Volumetric KF titration step by step

- Fill titration vessel with solvent
- Pretitration with KF reagent
- Add the sample
- Titrate with KF reagent

Volumetric KF reagents

One component reagents

- Titrant contains iodine, sulphur dioxide, buffer and methanol/ethanol
- Working medium contains only the methanol/ethanol
- Disadvantage: the titre decreases 5% per year in the closed bottle!

Two component reagents

- Titrant contains iodine
- Solvent contains buffer and sulphur dioxide
- Advantages: pH optimum in the solvent / fast reaction / titre is very stable

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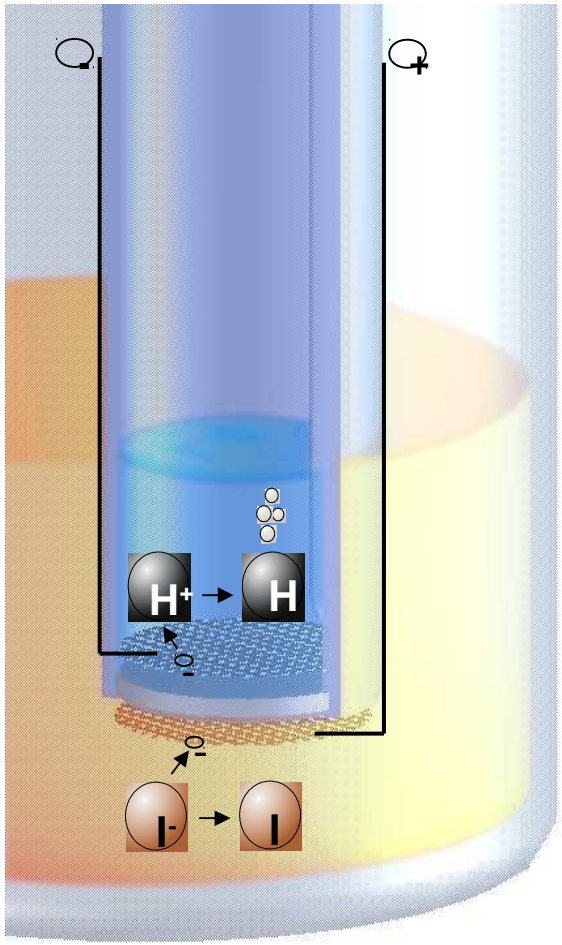
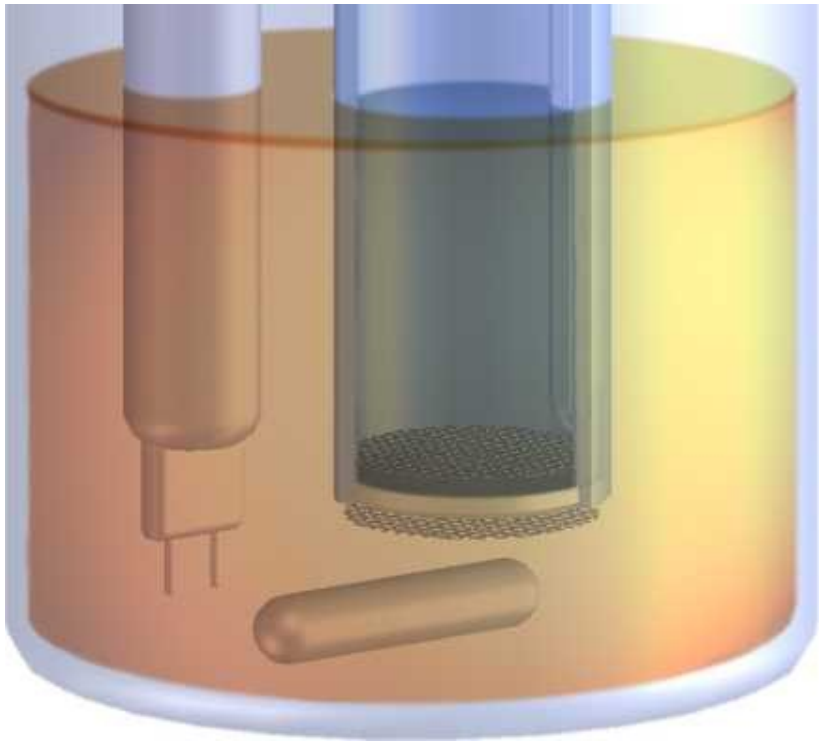
Coulometric KF titration step by step

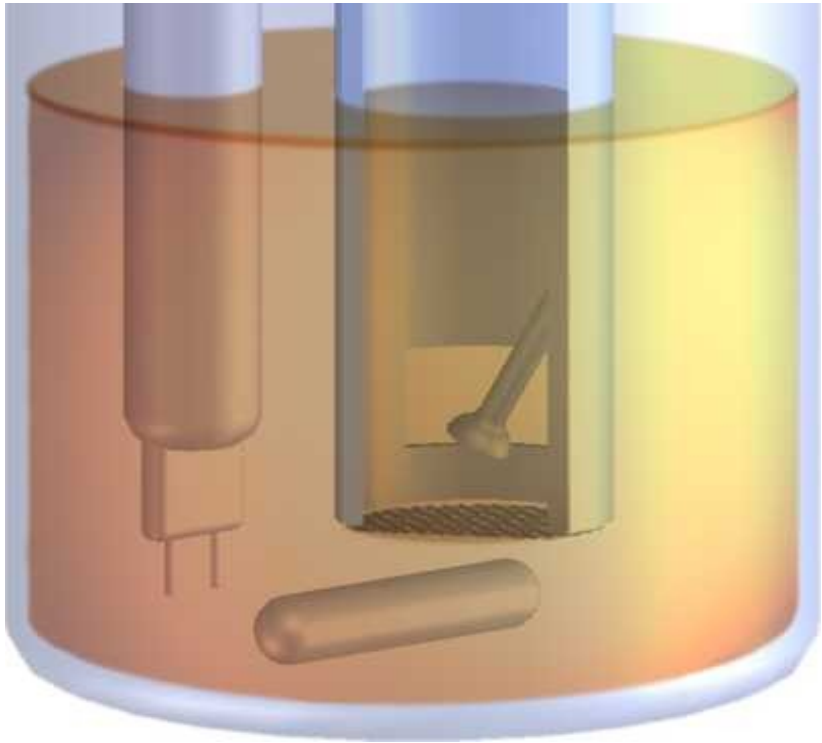


- current is our burette
- iodine is produced from a iodide containing solvent by anodic oxidation
- generating current is switched off as soon as a slight excess of free iodine is present
- free iodine is indicated by a double platinum electrode

Coulometric KF titration

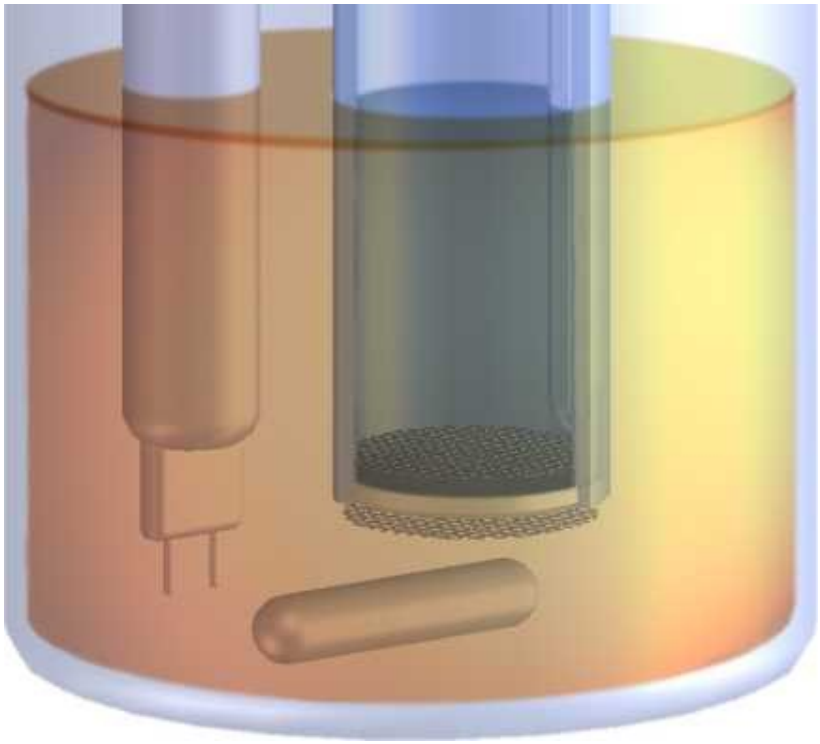


Cell with diaphragm



Cell without diaphragm

How to fill coulometric cell with diaphragm?



- **Catholyte 5 mL**

  Reduction: $2\ H^+ + 2\ e^- = H_2$

  change catholyte weekly!

- **Anolyte: about 100 mL**

  $2\ I^- = I_2 + 2\ e^-$

Comparison with and without diaphragm

Without diaphragm	With diaphragm
Recommendable for most applications, sample should have a good solubility in alcohol	Reagents with low conductivity (the addition of chloroform or xylene > 10%), with ketone reagents absolute water content < 50 ppm
Generator I: 400 mA	Generator I: auto

Coulometric KF reagents

- Capacity of more than 1000 mg of water (100 mL KF reagent)
- Anodic and cathodic reagents
- Combined reagents
- Special reagents for ketones

Which is the right method for my application?

- Volumetric titration
  range of application 0.1 % - 100 %
  depends on sample size

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

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Endpoint indication

Bivoltametry I_{pol} = 50 uA

Constant current applied to double Pt electrode

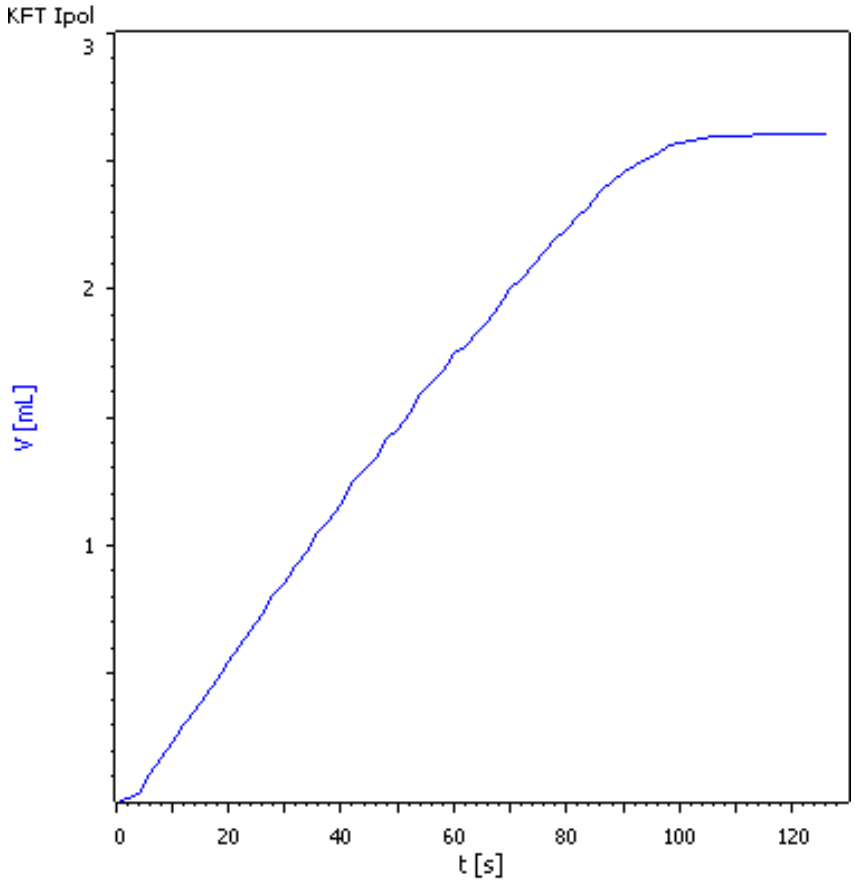
During titration: Excess H_2O

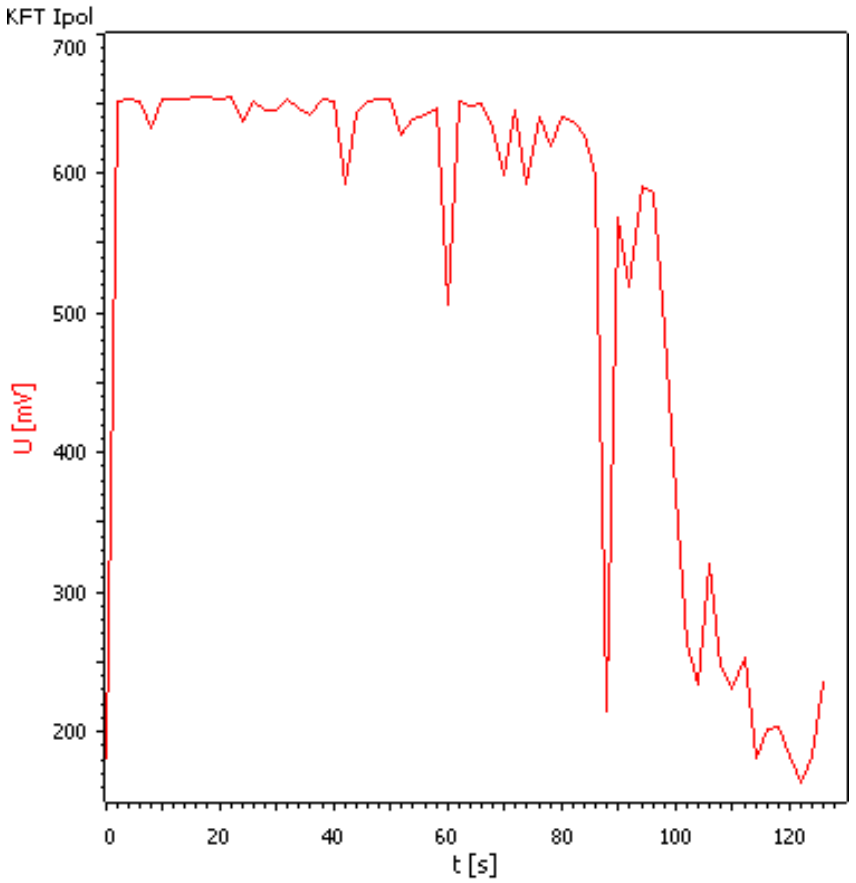
→ High voltage between Pt wires

At end of titration: Small excess of free iodine

→ Voltage decreases sharply

Endpoint indication





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KF Titration

permanent consumption of KF reagent

→ *Drift*

Aim:	constant and low drift	
Optimal:	Volumetry	<10 µL/min
	Coulometry	2...10 µg/min

- Influence on the results → drift correction

Drift

- Start drift – acceptable drift value for start of determination (cond. OK)
- Stop criteria drift – absolute or relative drift value
  - Absolute drift– the entered value is the stop drift
  - Relative drift – the stop drift is calculated from the measured drift value (start) and the entered value

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Titration parameter

Volumetry

EP at U	**250 mV**
Dynamics	**100 mV**
Stop criteria	**drift/time**
Stop drift	**20 uL/min**
Delay time	**10 s**

$I_{(pol)}$: 50 uA

Coulometry

EP at U	**50 mV**
Dynamics	**70 mV**
Stop criteria	**drift/rel drift**
Stop drift	**5 ug/min**
Rel. Drift	**5 ug/min**
Start drift	**20 ug/min**

$I_{(pol)}$: 10 uA

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Volumetric KF Titration

Titrinos:

787 KF Titrino
795 KFP Titrino

Titrandos:

841 Titrando
PC Control / tiamo
Touch Control

Volumetric KF Titration

Modi	841 Titrando
KFT	X
SET	X
Meas	X

Only a version with dosing units ?

- **Advantages:**

  The dosing unit can be totally emptied that means:

  - **No crystallisation in cock and tubings**
  - **Rinsing the buret several times after changing the titrant is no longer necessary**

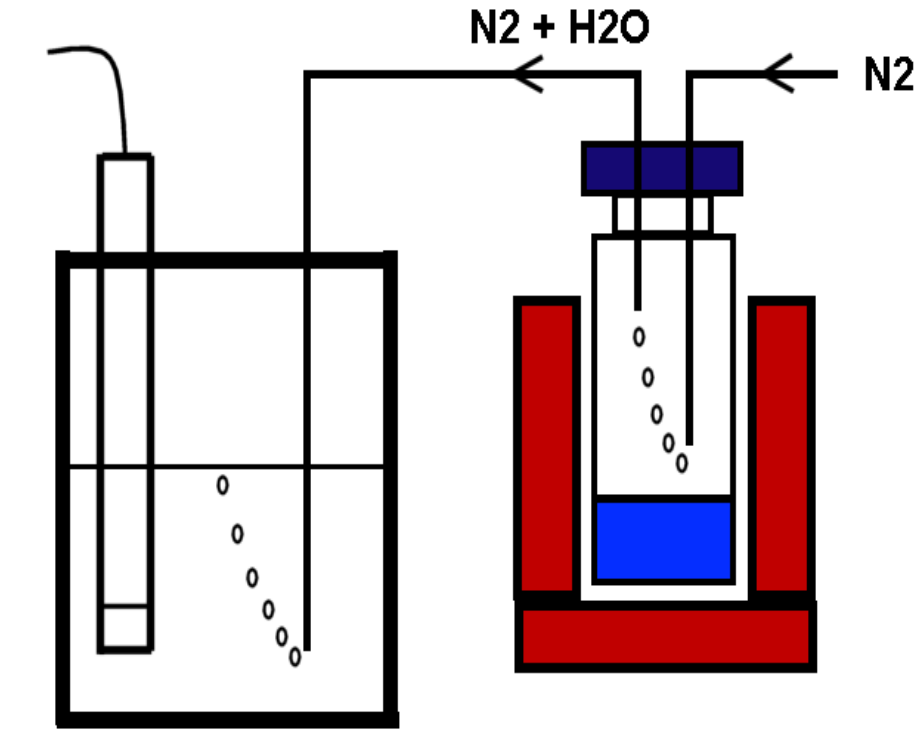
Coulometric KF titration

756 Coulometer

– with internal printer

831 Coulometer

Principle of the oven technique



Coulometric cell

Vial placed in the oven

KF Titration

832 Thermoprep

774 Oven Sample Processor