

Water Determination by Karl Fischer Titration



KF TITRATOR FOR LIQUID SAMPLES

Thermal sample preparation



KF oven

KF TITRATOR FOR SOLID SAMPLES

Determination of water content is important

Two Methods

A – **Drying methods** (drying ovens, infrared lamps and infrared balances).

B – **Titration methods** : Specific to water and rapid.

KFT methods

Two Methods: based on I_2 -providing principles

A – Volumetric KFT: I_2 required for reaction is added from a burette and water is quantified based on volume of KFR.

Advantages: High Water content (*100 ppm to 100%.*)

Disadvantages: Expensive, lengthy, KFR calibration

B – Coulometric titration methods : I_2 is produced by electrolysis of I^- ions and the quantity of electricity used in electrolysis is measured.

Advantages: Cheap, fast, absolute method

Disadvantages: Low water content *Water range 1 ppm to 5%*

How does a Volumetric Titrator work?

The volumetric titrator performs the following three key functions:

- 1) It dispenses KF titrating reagent containing iodine into the cell using the burette
- 2) It detects the endpoint of the titration using the double platinum pin indicator electrode
- 3) It calculates the end result based on the volume of KF reagent dispensed using the onboard microprocessor.

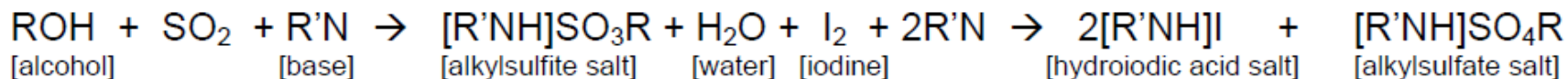
How does a Coulometric Titrator work?

The Coulometric titrator performs the following three key functions:

- 1) It generates iodine at the anode of the titration cell, instead of dispensing KF reagent as in volumetric titration.
- 2) It detects the endpoint of the titration using the double platinum pin indicator electrode.
- 3) It calculates the end result based on the total charge passed (Q), in Coulombs, using the on-board microprocessor.

Volumetric KFT

Principle-The titrimetric determination of water is based upon the quantitative reaction of water with an a solution of excess sulfur dioxide and known iodine concentration (mg H₂O/mL KFR) in a suitable medium (methanol) in the presence of a base (buffering agent) that reacts with hydrogen ions. The water content is determined by measuring the amount of iodine consumed as a result of reaction with water in a sample.



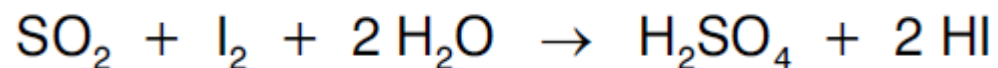
Karl Fischer Titration

- ▶ This is a specific method. Only water will be determined. The method is rapid (a few minutes).
- ▶ With KF titration both free and bound water can be determined, e.g. surface water on crystals or the water contained inside them.

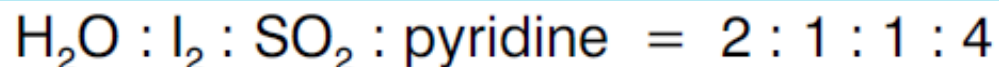
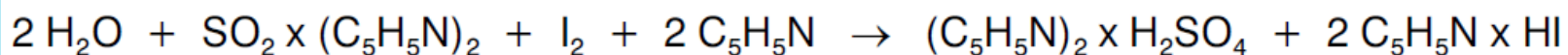


The Story of KFT Reaction

Bunson Reaction:

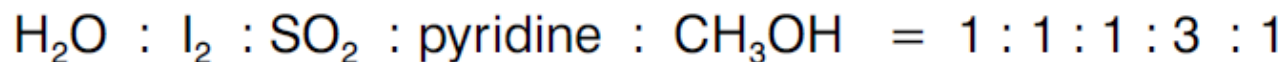


This reaction can be used to determine H_2O if SO_2 is in excess and H_2SO_4 is neutralized by a base. **Karl Fisher** did that.

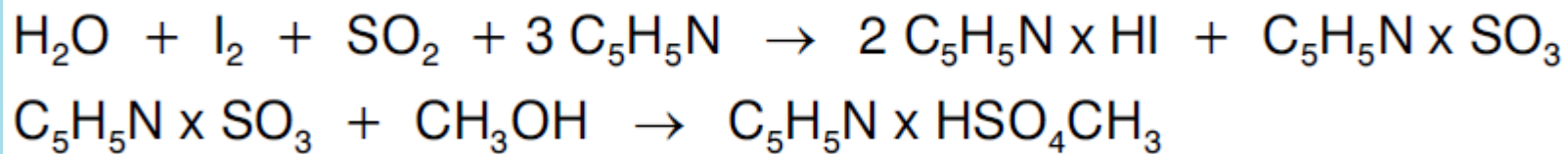


Smith, Bryant and Mitchell Showed that:

The molar ratios were:



In a first partial reaction water forms the (hypothetical) pyridine sulfur trioxide, which then further reacts with methanol



Verhoef and Barendrecht noted that in the KF reagent it is not the SO_2 that functions as the reactive component, but rather the intermediate monomethyl sulfite ion that is formed from SO_2 and methanol:



this intermediate alkylsulfite salt is then oxidized by iodine to an alkylsulfate salt. The reaction consumes H_2O .



Verhoef, J. C. and Barendrecht, E. Mechanism and Reaction Rate of the Karl-Fischer Titration Reaction. J. Electroanal. Chem. 1976, 71, 305-315

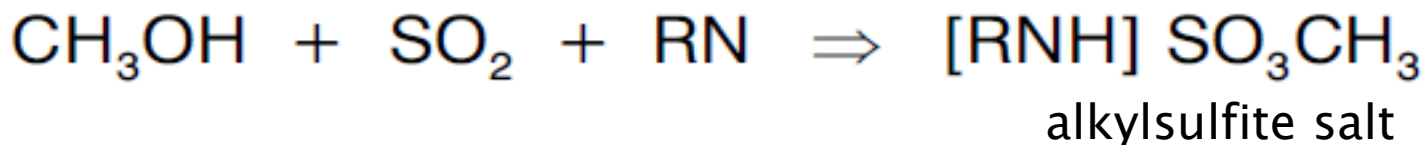
KF Reagent

A solution of iodine and sulfur dioxide in a mixture of pyridine and methanol.

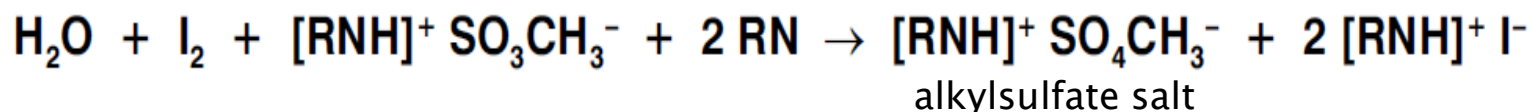
254 g of g iodine + 5.0 L of CH_3OH +
790 g pyridine+ 192 g liquid SO_2 .
(F= 3)

Basic ingredients of KF reagents

- ▶ Iodine I_2
- ▶ Sulfur dioxide SO_2
- ▶ Buffer Imidazol
- ▶ Solvent Methanol



this intermediate alkylsulfite salt is then oxidized by iodine to an alkylsulfate salt. The reaction consumes H_2O .



alkylsulfite salt

hydroiodic acid salt

KF reagents

▶ HYDRANAL® Karl Fischer Reagents

Advantage.....

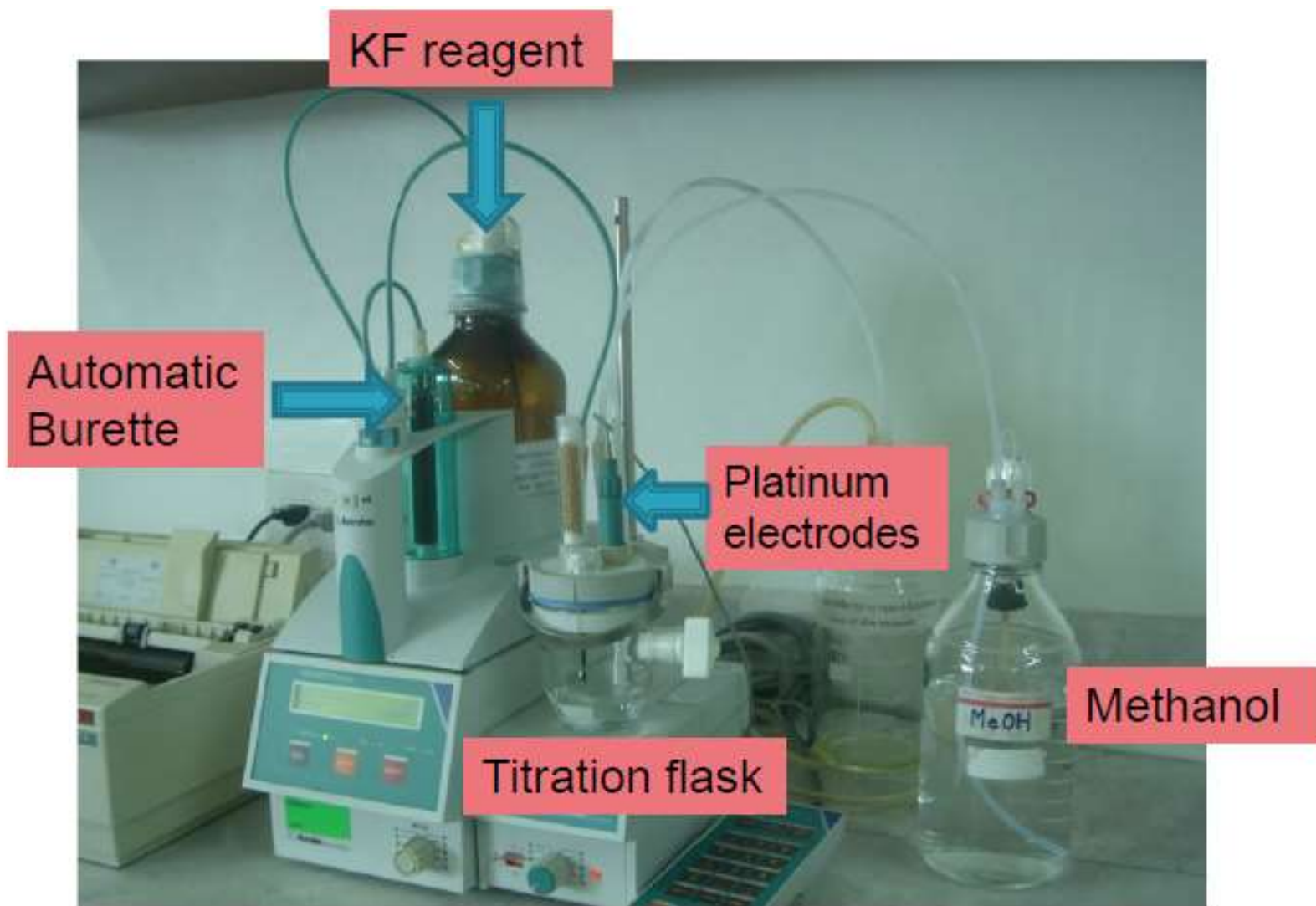
The HYDRANAL® reagents uses imidazole or diethanolamine as a base, rather than noxious pyridine. Imidazole and diethanolamine are both safe and effective and guarantee reliable analyses.

Replacement of noxious pyridine with bases that are both safer and more effective.

HOW to perform
a KF Titration ? ? ?



Volumetric KFT



The titration apparatus should be protected from atmospheric moisture.

KF Titration

Accessories and reagent required

- Analytical balance (min resolution 0.1 mg)
- Syringe with long, thin needle
- Karl Fischer reagents for volumetric water determination

Requirements

KF instrument should not be set up in areas that are subject to large temp fluctuations, high humidity. They must not be placed in the proximity of heating, cooling devices.

Method for Karl Fischer Titration

2 Steps

1. Standardization of the reagent
(Titer determination)
2. Water determination

Homogenization of the KFR

It is important to homogenize the KFR by circulating between Burette and KFR container.



Step 1. Standardization



Fill MeOH in the titration flask to cover the electrodes.
Condition system to conditioning drift OK ($<20 \mu\text{L}/\text{min}$).
Quickly add the water standard, accurately weighed containing
20 to 25 mg of water into the titration flask, stir and titrate until
the endpoint.

Step 1. Standardization

Calculate **the water equivalency factor, F**, in mg of water per mL of reagent, by the formula:

$$F = W/V$$

W = the weight, in mg, of water contained in aliquot of standard use.

V = the volume, in mL, of the Reagent used in the titration.

Step 1. Standardization

Titer of KF reagent = mg H₂O/ mL

Hydranal composite-5[®] : One mL of KF solution when freshly prepared is equivalent to approx. 5 mg of water, but it deteriorates gradually; therefore, Standardize the titrant before the first use and at suitable intervals thereafter. Protect from light while in use.

Step 2. Water determination

- ▶ Quickly transfer the Test Preparation into the titration flask, stirring. And again titrate the solution with KF reagent to the end point under vigorous stirring.

Step 2. Water determination

Calculate the water content of the specimen, in mg, taken by the formula:

$$SF$$

S = the volume, in mL, of the Reagent consumed in the second titration.

F = the water equivalence factor of the Reagent.

Step 2. Water determination

Water content (%)

$$= \frac{SF \times 100}{\text{mg of Test Preparation}}$$

S = the volume, in mL, of the Reagent consumed in the second titration.

F = the water equivalence factor of the Reagent.

Endpoint indication

Bivoltametry $I_{\text{pol}} = 50 \mu\text{A}$
Current applied to a double Pt electrode

During titration: **Excess H_2O**
→ High voltage between the Pt wires

At the end of titration: **Small excess of free iodine**
→ Voltage decreases sharply

Example

- ▶ 0.0244 g of Standard water is equivalence to KFR 5.249 mL

$$\text{Titer} = \frac{0.0244 \times 1000}{5.249} = 4.6485 \text{ mg/mL}$$

- ▶ 0.1564 g of Lidocaine HCl is eq. to KFR 2.094 mL

$$\text{water content(\%)} = \frac{2.094 \times 4.6485 \times 100}{156.4} = 6.22\%$$

Limit USP34 (Lidocaine HCl) : between 5.0% and 7.0%

Conclusion: ☒ Pass

Coulometric KFT

In coulometric Karl Fischer, iodine is generated electrochemically *in situ during the titration*. Water is quantified on the basis of the total charge passed (Q), as measured by current (amperes) and time (seconds), according to the following relationship:

$$Q = 1\text{C (coulomb)} = 1\text{A} \times 1\text{S}$$

$$\text{Where } 1\text{mg H}_2\text{O} = 10.72 \text{ C}$$

Additional Details of the Technique

Influence of Water Content

Influence of the organic solvent

Kinetics of KF reaction

Effect of pH

Sample Size

Influence of Water content

The water content of the working medium influences the stoichiometry of the KF reaction.

High water content (aqueous media):

If H_2O content $> 1\text{mol/L}$ (18 g/L) then the reaction behavior changes to favour the Bunsen reaction for aqueous solutions. This means that two H_2O are consumed for one I_2 or one SO_2 .

Influence of Organic Solvent

Protic Solvent (methanol or ethanol): $\text{H}_2\text{O} : \text{I}_2 = 1:1$

Aprotic Solvent (DMF): $\text{H}_2\text{O} : \text{I}_2 = 2:1$

Long chain alcohols: intermediate values (fractional values)

Reason: reactivity of alcohols plays a role— In methanol about 100%, in propanol approx. 80% and in butanol only approx. 50% is present as sulfite ester.

Choice of Organic Solvent

A best solvent is one that assures Stoichiometry of KF reaction and dissolve both Reactant and product of the reaction.

Methanol–the first natural choice:

Known stoichiometry, rapid reaction, Good solubility of most samples but side reactions may occur

2-methoxyethanol (ethylene glycol monomethyl ether):

Suitable for aldehydes and Ketones samples little side reactions (esterification, acetal/ketal formation) occur

Long-chain alcohols (ethanol, propanol)

Better solubilizing agents than methanol for lipophilic molecules

Chloroform :

good solvent for solubilizing fats and can be used with methanol. The methanol content should comprise at least 25 % of the total volume, preferably 50 %. 100% chloroform changes the stoichiometry of KF Reaction.

Formamide (for Proteins):

improves the solubility of polar substances and can be mixed with methanol (70% methanol) for the determination of water in proteins.

Kinetics of the KF reaction

Cedergren investigated the KF reaction sequence and establish that

- the reaction rate increases as the concentrations of SO_2 , I_2 and H_2O increase.
- The reaction is first order referring to each individual component.
- For the rate constant K he used the equation :

$$-d[\text{I}_2] / dt = K [\text{I}_2] \times [\text{SO}_2] \times [\text{H}_2\text{O}]$$

And obtained the values

$$K = (1.2 \pm 0.2) \times 10^3 \times \text{l}^2 \times \text{mol}^{-2} \times \text{s}^{-1} \quad \log K = 3.08 \pm 0.08$$

Kinetics of the KF reaction...

Verhoef and Barendrecht confirmed the results of **Cedergren** but at the same time found that the reaction constant K depends on the pH of the solution:

pH < 5

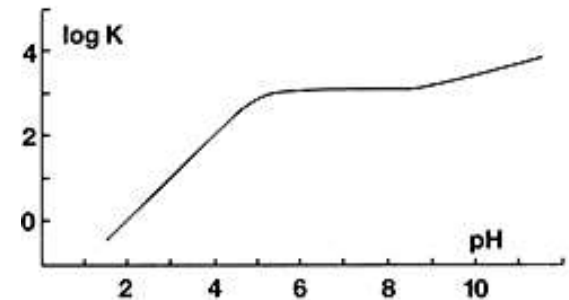
log K increases linearly with the pH.

pH = 5.5 - 8

the reaction rate is constant

pH > 8

the reaction rate again increases slightly
(side reactions probably occur).



Important:

From the increases in K under acidic conditions the authors conclude that it is not SO_2 , but the sulfite base that is the reactive component.

Effect of pH

The rate of the reaction depends on the pH value of the solvent, or working medium.

at pH = 5-8 the titration proceeds normally (**OPTIMAL**)

at pH < 5 the titration speed is very slow

at pH > 8 the titration speed is fast (side reaction-esterification-
produces water, diffuse end point.

Comments:

Highly acidic or basic samples need to be buffered to bring the overall pH into that optimal (5-8) range.

What sample size should be used?

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

What sample size should be used?

Sample	Approximate sample size [g] for 10 mL buret		
	Titrant 1	Titrant 2	Titrant 5
0.5%	0.2-1.8	0.4-3.6	–
1.0%	0.1-0.9	0.2-1.8	0.5-4.5
5.0%	0.02-0.18	0.04-0.36	0.1-0.9
10.0%	–	0.02-0.18	0.05-0.45
25.0%	–	–	0.02-0.18
50.0%	–	–	0.02-0.09

How can Titrator performance be monitored?

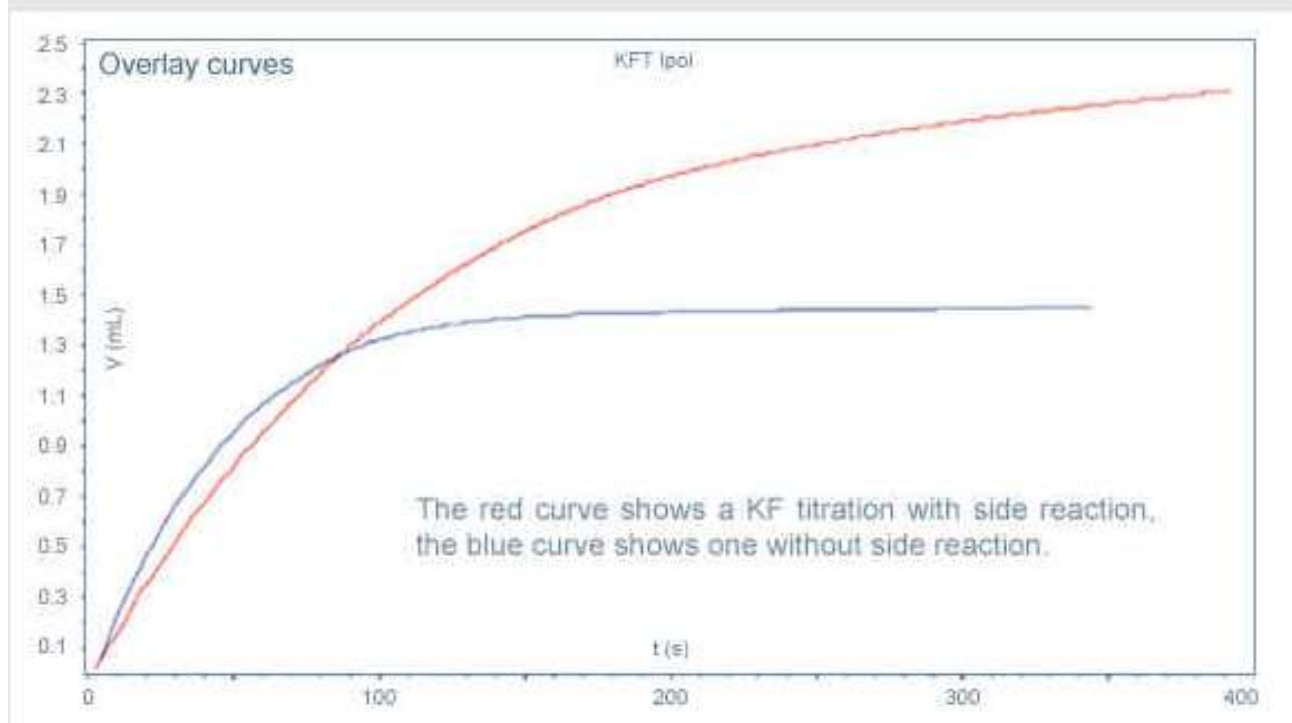
Standard	Cat. No.	Form	Application(s)
Water Standard Oil 15-30ppm NIST	1.88055	liquid	Coulometry of oils, Oil Evaporators
Water Standard 0.01% NIST	1.88050	liquid	Coulometry
Water Standard 0.1% NIST	1.88051	liquid	Coulometry, Volumetry
Water Standard 1.0% NIST	1.88052	liquid	Coulometry, Volumetry
Water Standard 5mg/ml	1.09259	liquid	Volumetry
Water Standard Oven 1%	1.88054	solid	KF Ovens
Lactose Standard 5%	1.12939	solid	Coulometry, Volumetry, KF Ovens
Sodium Tartrate Dihydrate 15.66%	1.06664	solid	Volumetry

General Considerations

- Changing the molecular sieves every 6 weeks is appropriate in the presence of medium humidity.
- Molecular sieve can be regenerated at 300 degree C for 24h.
- Clean the platinum pins on the indicator electrode with a soft paper tissue, scrub softly with toothpaste. Afterwards, flush it with ethanol or methanol.
- If drift vlaues is very high during pre-titration (conditioning), change the molecualr sives, check leakage, ensure no side reaction or pH change has occured and the sample is soluble in solvent.
- The cell solution should be replaced after approximately 30 mL of titrant have been used in the case of cell solutions with 20...25 mL of solvent

How to recognize a side reaction?

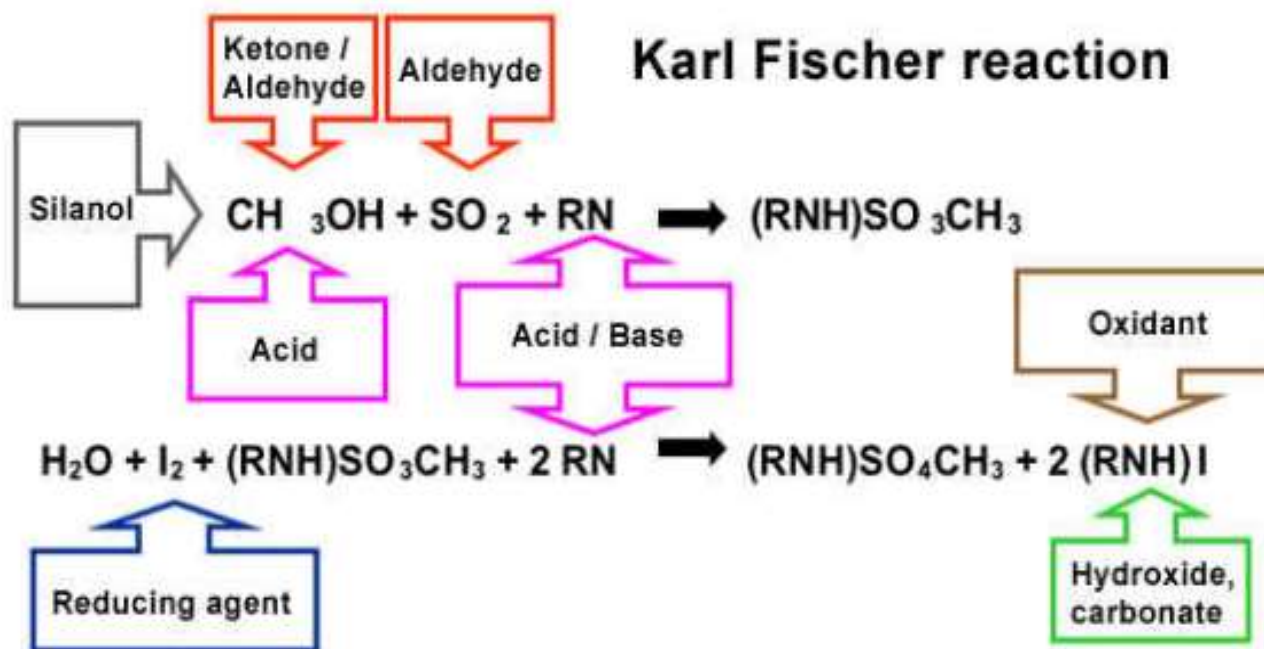
See Figure 1: Curve for a titration with side reaction.



The following characteristics indicate the presence of a side reaction:

- High drift after the titration has been completed, slow endpoint recognition or no endpoint found at all
- The water contents determined are not independent of the sample weight
- The results are (depending on the type of side reaction) too high or too low
- The water recovery rate found when spiking samples is not within $100 \pm 3\%$

The Possibilities of side reaction?



Detection of END POINT in KFT

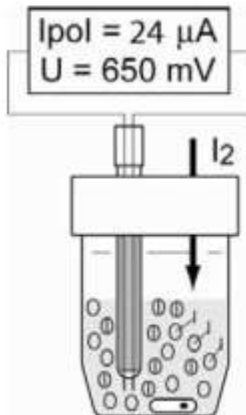
The Titration termination/control parameters

- The Change in Potential (E)
- The Drift Criterion
- Rate of reagent addition
- Delay time

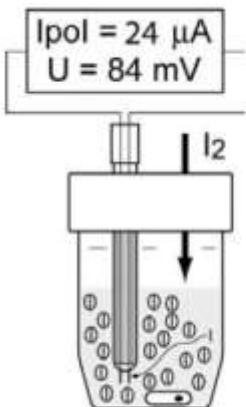
1-Change in Potential Criterion

3.1.1 Principle of bipotentiometric indication

A bipotentiometric indication is used for the volumetric Karl Fischer titration as well as for the coulometric analysis (in electrochemical terminology this is also called "2-electrode potentiometry"). A small, constant AC current – the polarization current " I_{pol} " – is applied to a double pin platinum electrode.

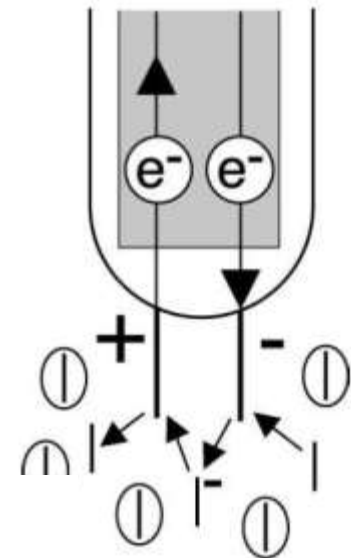


- As long as the added iodine reacts with the water, there is no free iodine in the titration/anolyte solution.
- A high voltage is necessary to maintain the specified polarization current at the electrode.



- As soon as all the water has reacted with iodine, there will be free iodine in the titration solution.
- Free iodine causes ionic conduction and the voltage needs to be reduced to keep the polarization current constant.
- When the voltage drops below a defined value, the titration is terminated.

- The ionic conduction takes the following course: an iodine molecule is attracted by the negatively charged platinum pin.
- It then acquires two electrons and turns into iodide ions (2 I^-).
- The two negatively charged iodide ions are attracted by the positively charged platinum pin, where they donate the electrons and form an iodine molecule, I_2 , again.



At the beginning and during the titration:

As long as the iodine generated reacts with the water, there is no free iodine in the titration/anolyte solution. A voltage of ca. 400 mV to 650 mV is necessary to maintain the set polarization current at the double pin electrode.

At the end of the titration:

As soon as all the water in the sample has reacted with the iodine, free iodine is present in the titration/anolyte solution. This free iodine gives rise to "ionic conduction". Now a low voltage of 50 mV to 100 mV is required to keep the polarization current constant. This drop in voltage is used to indicate the end of the titration.

Ionic conduction

Iodine takes up an electron at the negatively charged platinum pin of the indicator electrode and is thereby reduced to iodide (I^-). Iodide ions, which are present in excess in the titration solution, then release the electron again at the positively charged platinum pin and is again oxidized to iodine.

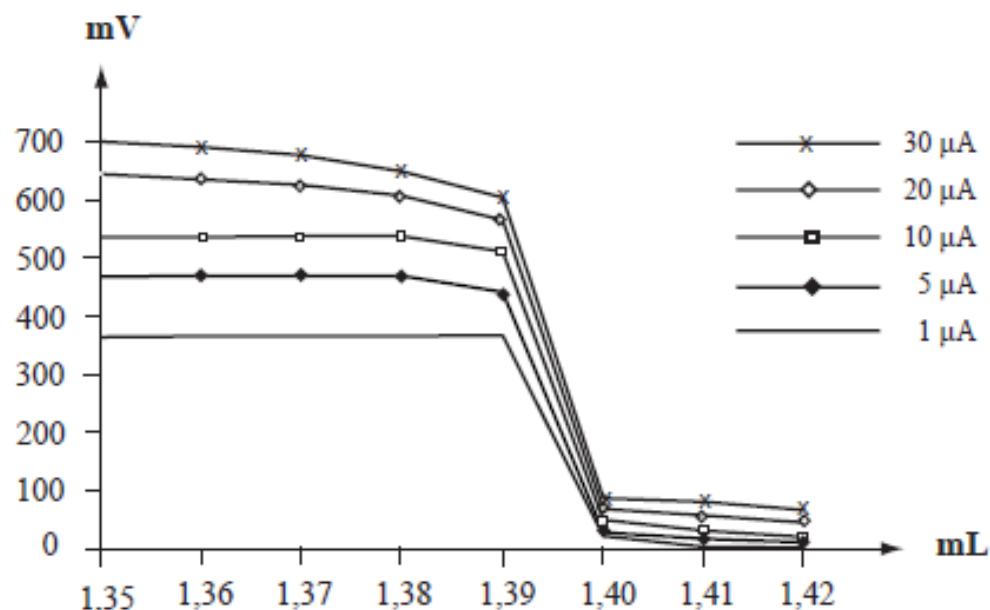
Thorough mixing of the titration/anolyte solution is necessary in order to achieve constant "ionic conduction". The iodine is present only at low concentration. If mixing is poor, no iodine reaches the negatively charged platinum pin. This leads to a termination of "ionic conduction" and the measurement signal becomes unstable.

3.1.2 End point and polarization current

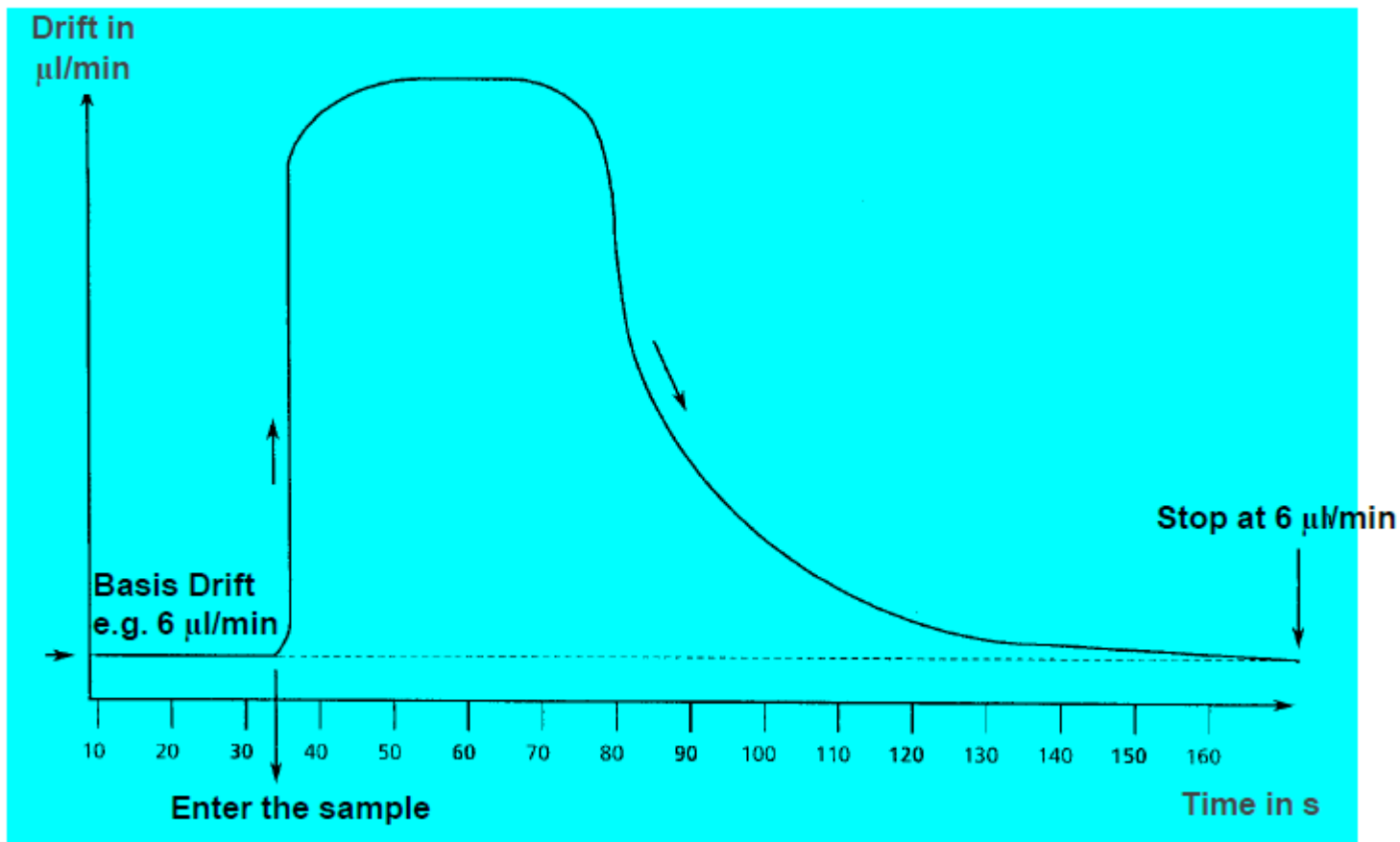
The Karl Fischer titration is terminated when free iodine is detected in the titration solution, i.e., the titration end point is reached when the potential at the polarized, double platinum pin electrode drops below a defined value. This value depends, above all, on the polarization current and to a lesser extent on the type of electrode as well as on the solvent that is used.

The following end points have been defined for reagents containing methanol (with double platinum pin electrode, pin length: 3 to 4 mm, pin diameter: 1 mm):

I_{pol}	End point
1 μ A	20 to 30 mV
5 μ A	50 to 70 mV
10 μ A	80 to 100 mV
20 μ A	100 to 120 mV
30 μ A	130 to 150 mV
40 μ A	150 to 170 mV



2 "Drift"- criteria



In addition to a predefined voltage (or current), a certain drift value must also be achieved. The drift is the amount of KF reagent per unit time that is consumed to keep the titration cell dry. In general, the drift value for titration cells titrated to dryness is in the order of a few $\mu\text{L}/\text{min}$.

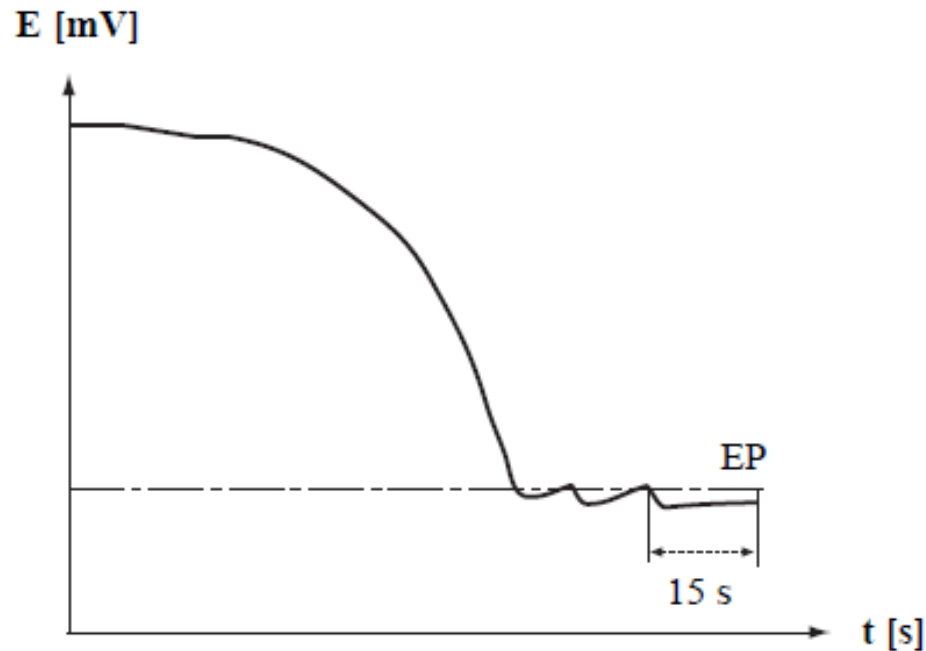
3. Rate of Reagent additon

The Titrant additon rate depends on

- the *distance from the end point*—the closer the End Point, the slower the addition rate
- the Potential change with each additon

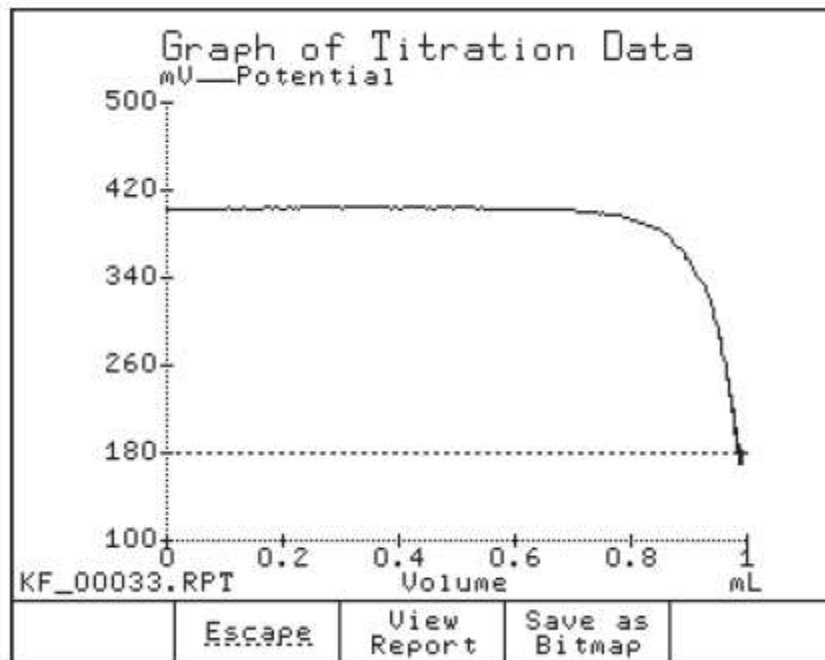
The Delay time

The Titration is terminated when E remains below the end point for a defined time (e.g 15 seconds) following the addition of a titrant increment



Titration Termination

The titration is terminated when the conditions of the Termination Criteria have been met. The default Termination Criterion is mV value, in which the titration is terminated after the mV value remains below the end point potential for the selected stability time.



Additional Details of the Technique

Influence of Water Content

Influence of the organic solvent

Kinetics of KF reaction

Effect of pH

Sample Size

Influence of Water content

The water content of the working medium influences the stoichiometry of the KF reaction.

High water content (aqueous media):

If H_2O content $> 1\text{mol/L}$ (18 g/L) then the reaction behavior changes to favour the Bunsen reaction for aqueous solutions. This means that two H_2O are consumed for one I_2 or one SO_2 .

Influence of Organic Solvent

Protic Solvent (methanol or ethanol): $\text{H}_2\text{O} : \text{I}_2 = 1:1$

Aprotic Solvent (DMF): $\text{H}_2\text{O} : \text{I}_2 = 2:1$

Long chain alcohols: intermediate values (fractional values)

Reason: reactivity of alcohols plays a role— In methanol about 100%, in propanol approx. 80% and in butanol only approx. 50% is present as sulfite ester.

Choice of Organic Solvent

A best solvent is one that assures Stoichiometry of KF reaction and dissolve both Reactant and product of the reaction.

Methanol-the first natural choice:

Known stoichiometry, rapid reaction, Good solubility of most samples but side reactions may occur

2-methoxyethanol (ethylene glycol monomethyl ether):

Suitable for aldehydes and Ketones samples little side reactions (esterification, acetal/ketal formation) occur

Long-chain alcohols (ethanol, propanol)

Better solubilizing agents than methanol for lipophilic molecules

Chloroform :

good solvent for solubilizing fats and can be used with methanol. The methanol content should comprise at least 25 % of the total volume, preferably 50 %. 100% chloroform changes the stoichiometry of KF Reaction.

Formamide (for Proteins):

improves the solubility of polar substances and can be mixed with methanol (70% methanol) for the determination of water in proteins.

Kinetics of the KF reaction

Cedergren investigated the KF reaction sequence and establish that

- the reaction rate increases as the concentrations of SO₂, I₂ and H₂O increase.
- The reaction is first order referring to each individual component.
- For the rate constant K he used the equation :

$$- d [I_2] / dt = K [I_2] \times [SO_2] \times [H_2O]$$

And obtained the values

$$K = (1.2 \pm 0.2) \times 10^3 \times l^2 \times mol^{-2} \times s^{-1} \quad \log K = 3.08 \pm 0.08$$

Kinetics of the KF reaction...

Verhoef and Barendrecht confirmed the results of **Cedergren** but at the same time found that the reaction constant K depends on the pH of the solution:

pH < 5

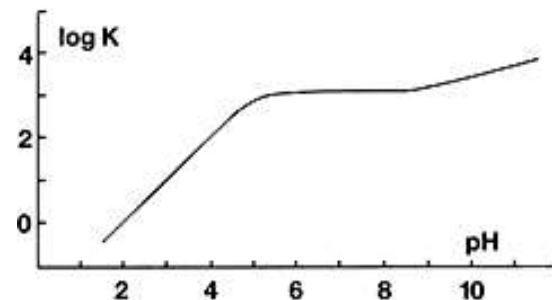
log K increases linearly with the pH.

pH = 5.5 - 8

the reaction rate is constant

pH > 8

the reaction rate again increases slightly
(side reactions probably occur).



Important:

From the increases in K under acidic conditions the authors conclude that it is not SO_2 , but the sulfite base that is the reactive component.

Effect of pH

The rate of the reaction depends on the pH value of the solvent, or working medium.

at pH = 5-8 the titration proceeds normally (**OPTIMAL**)

at pH < 5 the titration speed is very slow

at pH > 8 the titration speed is fast (side reaction-esterification-
produces water, diffuse end point.

Comments:

Highly acidic or basic samples need to be buffered to bring the overall pH into that optimal (5-8) range.

What sample size should be used?

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

What sample size should be used?

Sample	Approximate sample size [g] for 10 mL buret		
	Titrant 1	Titrant 2	Titrant 5
0.5%	0.2-1.8	0.4-3.6	–
1.0%	0.1-0.9	0.2-1.8	0.5-4.5
5.0%	0.02-0.18	0.04-0.36	0.1-0.9
10.0%	–	0.02-0.18	0.05-0.45
25.0%	–	–	0.02-0.18
50.0%	–	–	0.02-0.09

How can Titrator performance be monitored?

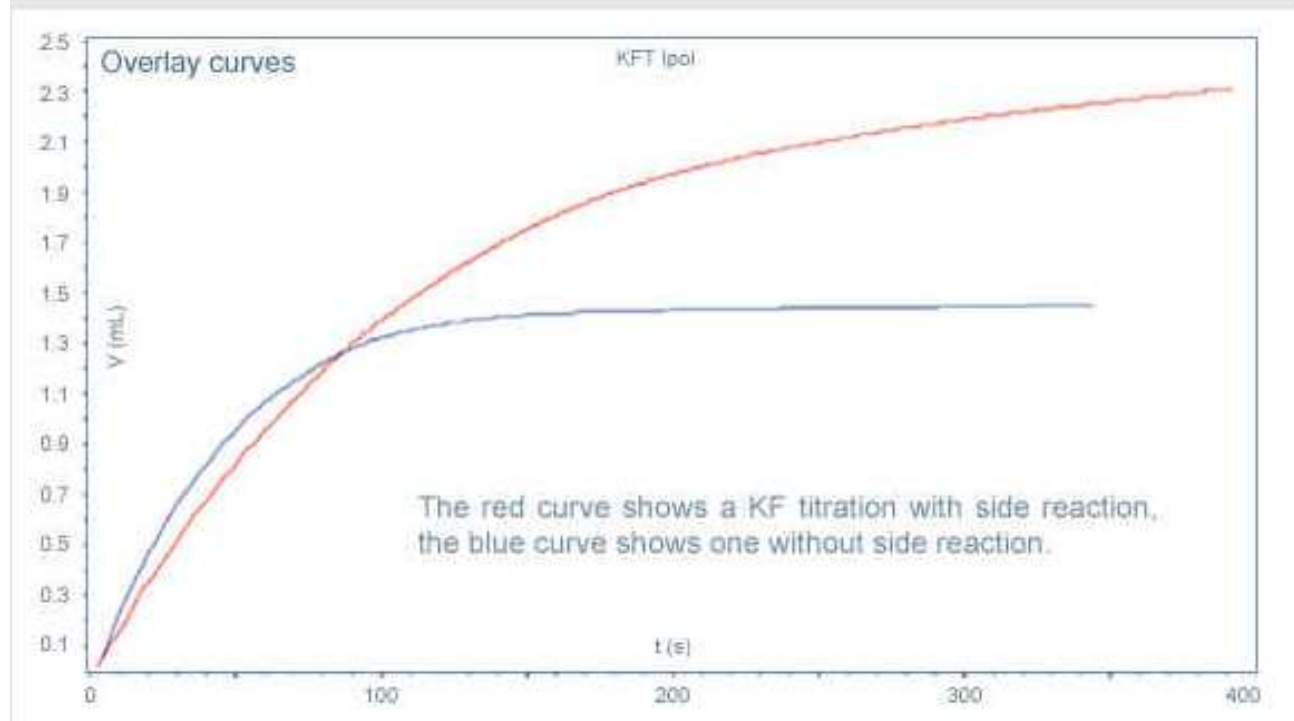
Standard	Cat. No.	Form	Application(s)
Water Standard Oil 15-30ppm NIST	1.88055	liquid	Coulometry of oils, Oil Evaporators
Water Standard 0.01% NIST	1.88050	liquid	Coulometry
Water Standard 0.1% NIST	1.88051	liquid	Coulometry, Volumetry
Water Standard 1.0% NIST	1.88052	liquid	Coulometry, Volumetry
Water Standard 5mg/ml	1.09259	liquid	Volumetry
Water Standard Oven 1%	1.88054	solid	KF Ovens
Lactose Standard 5%	1.12939	solid	Coulometry, Volumetry, KF Ovens
Sodium Tartrate Dihydrate 15.66%	1.06664	solid	Volumetry

General Considerations

- Changing the molecular sieves every 6 weeks is appropriate in the presence of medium humidity.
- Molecular sieve can be regenerated at 300 degree C for 24h.
- Clean the platinum pins on the indicator electrode with a soft paper tissue, scrub softly with toothpaste. Afterwards, flush it with ethanol or methanol.
- If drift values is very high during pre-titration (conditioning), change the molecular sieves, check leakage, ensure no side reaction or pH change has occurred and the sample is soluble in solvent.
- The cell solution should be replaced after approximately 30 mL of titrant have been used in the case of cell solutions with 20...25 mL of solvent

How to recognize a side reaction?

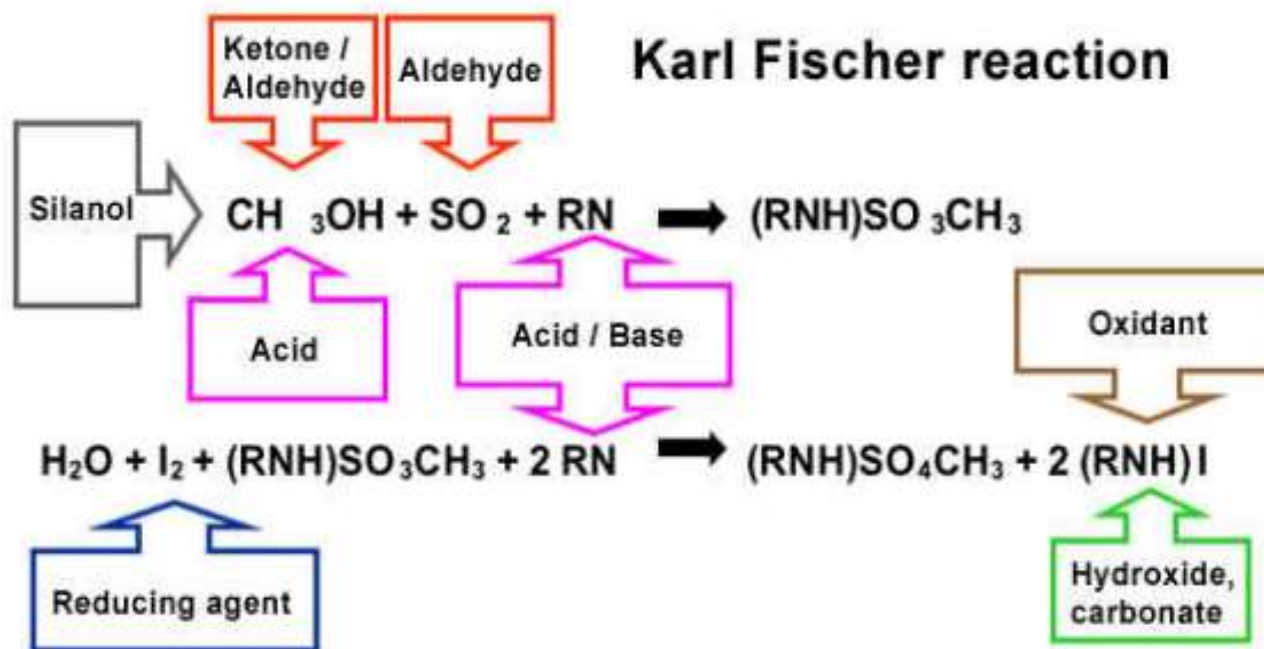
See Figure 1: Curve for a titration with side reaction.



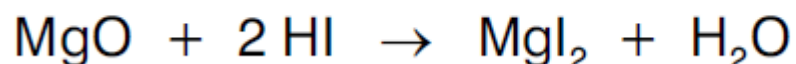
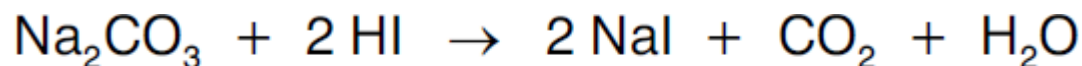
The following characteristics indicate the presence of a side reaction:

- High drift after the titration has been completed, slow endpoint recognition or no endpoint found at all
- The water contents determined are not independent of the sample weight
- The results are (depending on the type of side reaction) too high or too low
- The water recovery rate found when spiking samples is not within $100 \pm 3\%$

The Possibilities of side reaction?

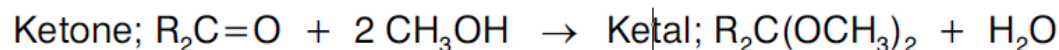
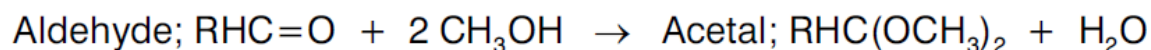


Carbonates, hydroxides and oxides

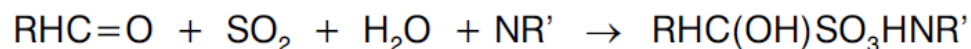


7.2. Aldehydes and ketones

These two classes of compound combine with the methanol in the KFR to form acetals and ketals respectively with the release of water.

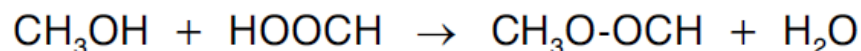
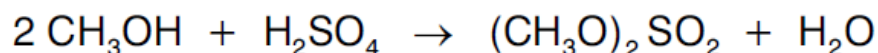


With aldehydes a second reaction – bisulfite addition – can also interfere. In this case H_2O is consumed, so that the water content determined could be too low.



7.3. Strong acids

Strong acids can react with the methanol contained in the KF reagent and release water:

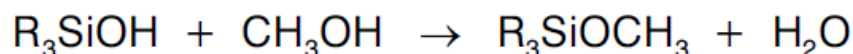


Among the organic acids the strongest esterification is shown by formic acid; acetic acid only undergoes partial esterification. Methanol esterifies the quickest. With propanol and/or 2-methoxyethanol slower reaction rates are achieved.

However, strong acids also lower the pH of the reaction solution so much that the KF reaction either no longer takes place or proceeds unsatisfactorily. The reaction mixture can be buffered by the addition of a base (e.g. imidazole) and the pH brought back to the optimal range again. If this measure is taken then no esterification occurs even with strong mineral acids (e.g. H_2SO_4 or HNO_3).

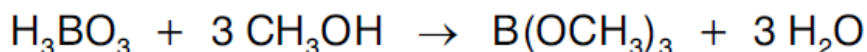
7.4. Silanols/Siloxanes

The terminal silanol groups esterify with the methanol contained in the KF reagents and release water. This means that methanol-free reagents must be used to determine the water content of these substances.



7.5. Boron compounds

Boric acid reacts with methanol with esterification and the release of water:



Boron trioxide (B_2O_3), metaboric acid (HBO_2) and borax / sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) all react in the same way.

The esterification rate decreases as the chain length of the alcohol increases (methanol esterifies the quickest).

7.7. Reducing agents

Reducing or oxidizing agents can react directly or indirectly with the iodine in the KF reagents and simulate a water content that is too high or too low, respectively.

0.5 mol H₂O / mol substance in the sample is simulated by:

