ANALYTICAL CHEMISTRY

- Karl Fischer Titration

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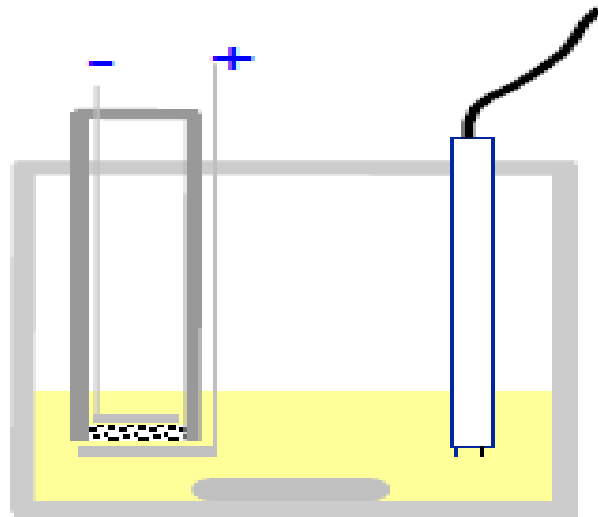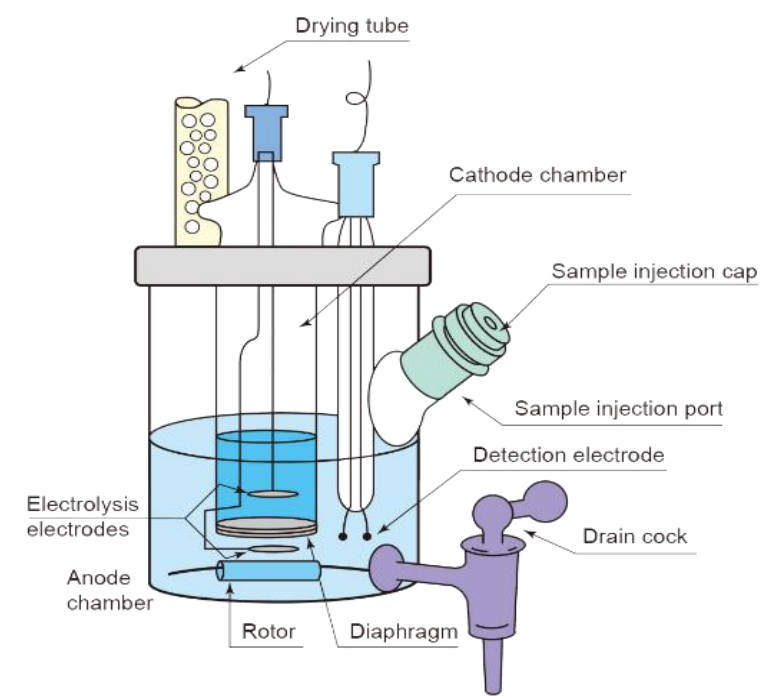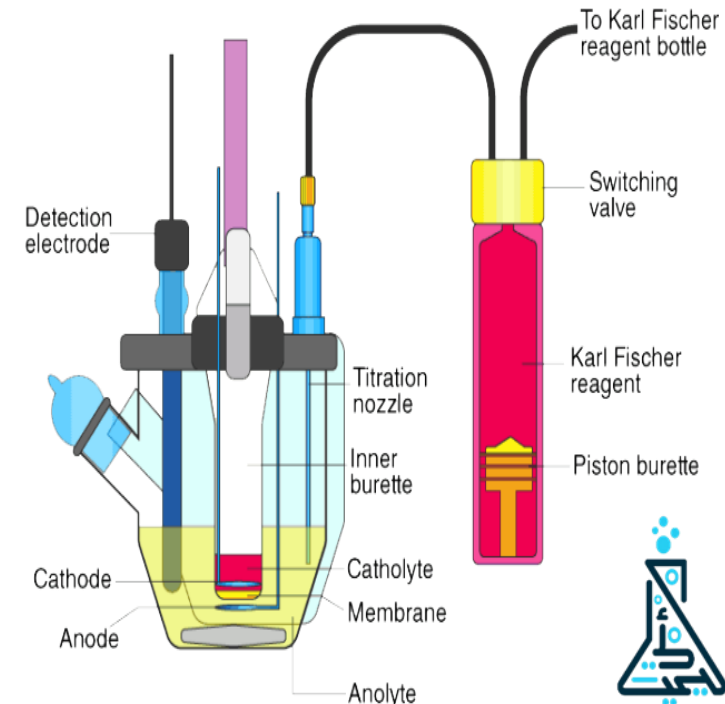
Volumetric & Coulometric Karl Fischer Titration
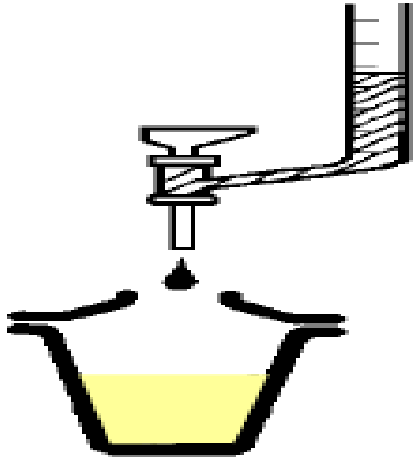
Volumetric Karl Fischer **Iodine** is added by burette during titration.
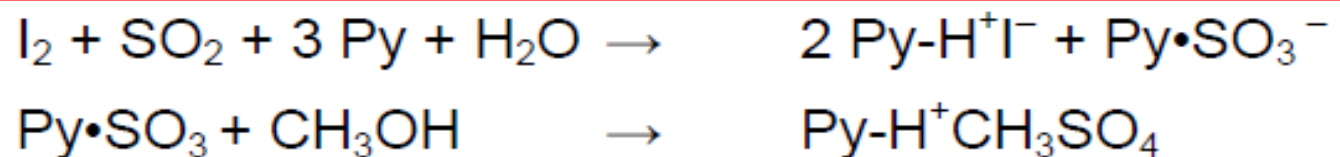**Water as a relevant component: 100 ppm - 100 %**

Coulometric Karl Fischer **Iodine** is generated electrochemically during titration.
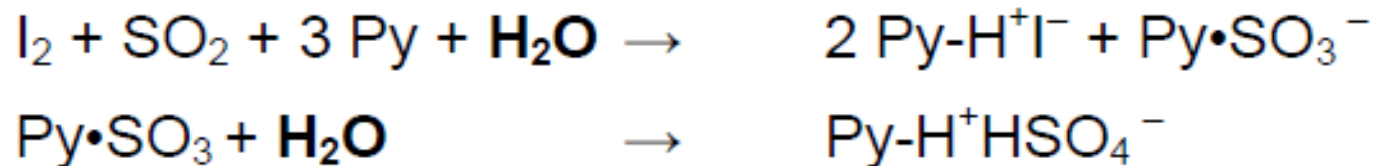**Water in trace amounts: 1 ppm-5 %**

Volumetric Karl Fischer

The Karl Fischer chemical reaction

● Karl Fischer discovered that this reaction could be used for water determinations in a no aqueous system containing an excess of sulphur dioxide.

● Methanol proved to be suitable as a solvent. In order to achieve an equilibrium shift to the right, it is necessary to neutralize the acids that are formed during the process (HI and H_2SO_4) Karl Fischer used pyridine for this purpose.

$$I_2 + SO_2 + 3\,Py + H_2O \rightarrow 2\,Py\text{-}H^+I^- + Py\bullet SO_3^-$$

$$Py\bullet SO_3 + CH_3OH \rightarrow Py\text{-}H^+CH_3SO_4$$

● According to these equations, methanol not only acts as a solvent but also participates directly in the reaction itself.

● In an alcoholic solution, the reaction between iodine and water takes place in the stoichiometric ratio of **1 : 1**
● In an alcohol-free solution, the reaction between iodine and water takes place in the stoichiometric ratio of **1 : 2**

$$I_2 + SO_2 + 3\,Py + \mathbf{H_2O} \rightarrow 2\,Py\text{-}H^+I^- + Py\bullet SO_3^-$$

$$Py\bullet SO_3 + \mathbf{H_2O} \rightarrow Py\text{-}H^+HSO_4^-$$

Volumetric Karl Fischer

● **E.ScholZ** developed a **pyridine**-free Karl Fischer reagent with **imidazole** as base.

● This reagent not only replaced the toxic, pungent pyridine, but also facilitated faster and more accurate titrations because imidazole **buffers** in a more favourable pH range than pyridine.

1. $ROH + SO_2 + RN \rightarrow (RNH) \cdot SO_3 R$

2. $(RNH) \cdot SO_3 R + 2 RN + I_2 + H_2O \rightarrow (RNH) \cdot SO_4 R + 2 (RNH)I$

This resulted in the general chemical equation:

$$ROH + SO_2 + 3 RN + I_2 + H_2O \rightarrow (RNH) \cdot SO_4 R + 2 (RNH)I$$

Volumetric Karl Fischer

Influence of pH on the Karl Fischer reaction

● Since the maximum rate of the Karl Fischer titration is in the pH range **5.5 to 8**.

● pH values less than 4 and greater than 8 should be avoided in practice.

● With acidic or basic samples, you should adjust the pH value to the ideal range by adding buffering agents (for acids: imidazole, for bases: salicylic acid).

Influence of the solvent on the Karl Fischer reaction

● The stoichiometry (molar ratio of $H_2O : I_2$) depends on the type of solvent:
  ❑ Alcoholic solvent $H_2O : I_2 = 1:1$ (e.g. methanol)
  ❑ Non-alcoholic solvent $H_2O : I_2 = 2:1$ (e.g. dimethyl formamide)

● Studies by Eberius showed that iodine and water react in the ratio of 1:1 if the percentage of methanol in the solvent is **20% or more.**

● Methanol should therefore always be present in the minimum required amount.

● If a methanol-free titrant has to be used **(e.g. for determination in ketones or aldehydes)**, you can use other alkohols.

Volumetric Karl Fischer

Volumetric KF reagents

One-component KF reagent

The titrant
- ❑ iodine
- ❑ sulfur dioxide
- ❑ imidazole, dissolved in a suitable alcohol.

The solvent
- ❑ methanol.

● **The reagent available in three different concentrations:**
- ❑ 5 mg/mL for samples with water content of 1000 ppm to 100%.
- ❑ 2 mg/mL for samples with water content of less than 1000 ppm.
- ❑ 1 mg/mL for samples with water content of less than 200 ppm.

Two-component KF reagent

The titrant
- ❑ Iodine
- ❑ methanol.

The solvent
- ❑ sulfur dioxide
- ❑ imidazole
- ❑ methanol

● **It is available in two different concentrations:**
- ❑ 5 mg/mL for samples with a water content of 1000 ppm to 100%.
- ❑ 2 mg/mL for samples with a water content of less than 1000 ppm.

Reagents	+	–
One-component	Simple handling, favorably priced.	Titer less stable, titration speed slower.
Two-component	High titration speed, stable titer.	Solvent capacity restricted.

Volumetric Karl Fischer

Pyridine-containing reagents

● Despite the existence of pyridine-free reagents, which allow for fast and accurate Karl Fischer titrations, reagents containing pyridine are still used because they are cheaper and can be made in-house.

One-component reagent:

● Some manufacturers have slightly increased the pyridine content in the titrant to achieve a higher titration speed.

Two-component reagent:

● The titrant contains iodine dissolved in an alcohol, e.g. methanol, whereas the solvent consists of sulfur dioxide and a base, e.g. imidazole, dissolved in an alcohol (usually methanol), or an alcoholic mixture.

● The separation into titrant and solvent improves stability of the KF reagents, increases their lifetime, and results in higher titration speed.

Volumetric Karl Fischer

Special reagents for aldehydes and ketones

● Aldehydes (R-CHO) and ketones (R-CO-R) form acetals and ketals if titrated with standard methanol-containing reagents.

● As a result, additional water is produced and titrated at the same time, leading to higher water contents and a vanishing end point.

Special methanol-free KF one-component reagents are commercially available to prevent this problem.

One-component reagent:

● The titrant contains iodine, imidazole, sulfur dioxide and 2-methoxyethanol, whereas the solvent contains 2-chloroethanol and trichloromethane.

The titration takes slightly longer than with the standard KF reagent.

● **Note** that it may be necessary to adapt the end point value in the titration method to these reagents. This special reagent is also suitable for substances that react with methanol, such as amines.

Volumetric Karl Fischer

Karl Fischer reagents with ethanol

● Since ethanol is less toxic than methanol

● These reagents also allow for titration of several ketones which form ketals considerably more slowly in ethanol than in methanol.

● The titrant contains iodine and ethanol, whereas the solvent contains sulfur dioxide, imidazole, diethanolamine and ethanol.

Titration control and end point determination

● The addition or generation of iodine must be controlled. Ideally, iodine should be added or generated as quickly as possible, and the addition or production stopped exactly at the end point.

● Only then can the titrant consumption or the generated iodine amount be determined with the desired accuracy, and hence, the water content.

● The control of the titration is only possible if the end point is indicated. The resulting titration speed depends on the following factors:
   ❖ the addition speed or generation rate of iodine.
   ❖ the reaction rate of the Karl Fischer reaction.
   ❖ the stirring speed and mixing of the sample solution.
   ❖ the viscosity of the solution and its temperature.
   ❖ the control algorithm and its parameters.
   ❖ the termination of the analysis.

Volumetric Karl Fischer

Indication

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**.
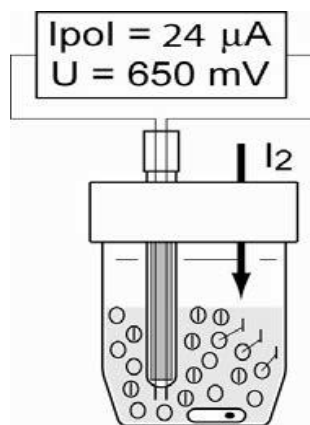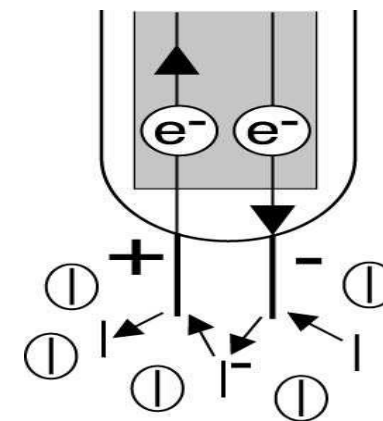

As long as the added iodine reacts with the water, there is no free iodine in the titration / anolyte solution.

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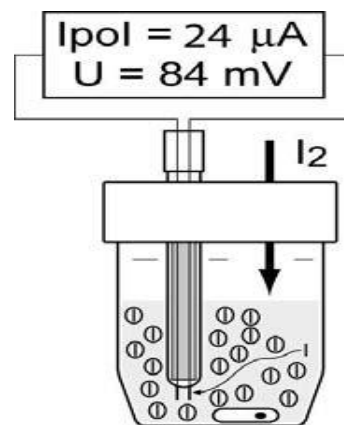
As soon as all the water has reacted with iodine, there will be free iodine in the titration solution.
• Free iodine causes ionic conduction and the voltage needs to be reduced to keep the polarization current constant.
• When the voltage drops below a defined value, the titration is terminated.

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.

Volumetric Karl Fischer

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 releases 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.

Volumetric Karl Fischer

End point and polarization current

● The Karl Fischer titration is terminated when an **excess of iodine** is detected in the titration cell, i.e. the titration end point is reached if the potential at the polarized platinum double pin electrode drops below a specific predefined value.

● **The end point value mainly depends on**

❑ the polarization current, I_{pol}

❑ (to a lesser extent) the type of electrode (i.e. geometry and dimensions of the metal parts)

❑ the solvent or anolyte used in the instrument, respectively.

❑ this value depends on the polarization current.

● For the **volumetric KF titration**, the following end points have been defined for methanolic **one-component and two-component** KF reagents using a V20/V30 volumetric KF titrator or T70/T90 Excellence titrator (double pin platinum electrode, pin length: 3 to 4 mm, pin diameter: 1 mm):

AC Polarization current / µA	Endpoint / mV
24	100

● For the **coulometric KF analysis**, the following values have been obtained with a C20/C30 KF Coulometer (double pin platinum sensor; pin length: 3 - 4 mm, pin diameter: 1 mm):

AC Polarization current / µA	Endpoint / mV
5	100

Volumetric Karl Fischer

Reaction rate

● The reaction rate of the Karl Fischer titration depends on:
- the water concentration, **[H₂O]**
- the sulfur dioxide concentration, **[SO₂]**
- the iodine concentration, **[I₂]**

$$d[I_2] / dt = k \cdot [I_2] \cdot [SO_2] \cdot [H_2O]$$

● In addition, the pH value of the solution has a strong influence on the rate and in particular on the stoichiometry of the Karl Fischer reaction.

● At the beginning, the water content is high, which gives a high reaction rate. Iodine generation or addition can proceed rapidly because iodine immediately reacts with water. Towards the end of the titration, the water concentration is lower, and the reaction rate also Decreases.

● iodine must be generated or added more slowly because a small water amount is still present. Iodine generation or addition is usually the **rate determining factor.**

● In the **volumetric KF titration**

one component titrant

sulfur dioxide is added only in *slight* **excess** with the iodine titrant

two component reagents

a **large excess** of sulfur dioxide is present in the solvent.

● This results in a reaction rate up to 2 times *faster* for the two component reagent than for the one component reagent.

Volumetric Karl Fischer

Control parameters in the volumetric KF titration

● Several parameters can be defined in the titration method in order to optimize the method for the samples and the reagents.

● An overview of the control parameters is given as follows:

Volumetric KF Titration

Control	Tasks
Methods » Method » Titration (KF Vol) » Control	

End point	100.0 mV	1 2 3
Control band	400.0 mV	1 2 3
Dosing rate (max)	5 mL/min	1 2 3
Dosing rate (min)	80 µL/min	1 2 3
Start	Normal	▼

Cancel   OK

End point

Control band

Dosing rate (max)

Dosing rate (min)

Start: Normal, Cautious

Volumetric Karl Fischer

Polarization current and end point

● Each end point is valid for a specific polarization current, if the polarization current changes, the end point must be adjusted.

● The end point for a specific polarization current is influenced by the sensor and the solvent.
In particular, longer titration times and poorer repeatability are resulting by selecting a higher end point potential value.

● The following points represent possible contributing factors:

❑ contaminated or old sensors,

❑ sensors with very short platinum pins (< 3 mm)

long alkyl chain alcohols, e.g. 2-propanol, used as solvent, instead of methanol or ethanol.

● The consequences of choosing a too low end point value are illustrated in the figures:
On the right side, the titration curve is more or less flat towards the end; this results in an illdefined titration end point, which will lead to long titration times and to low precision.
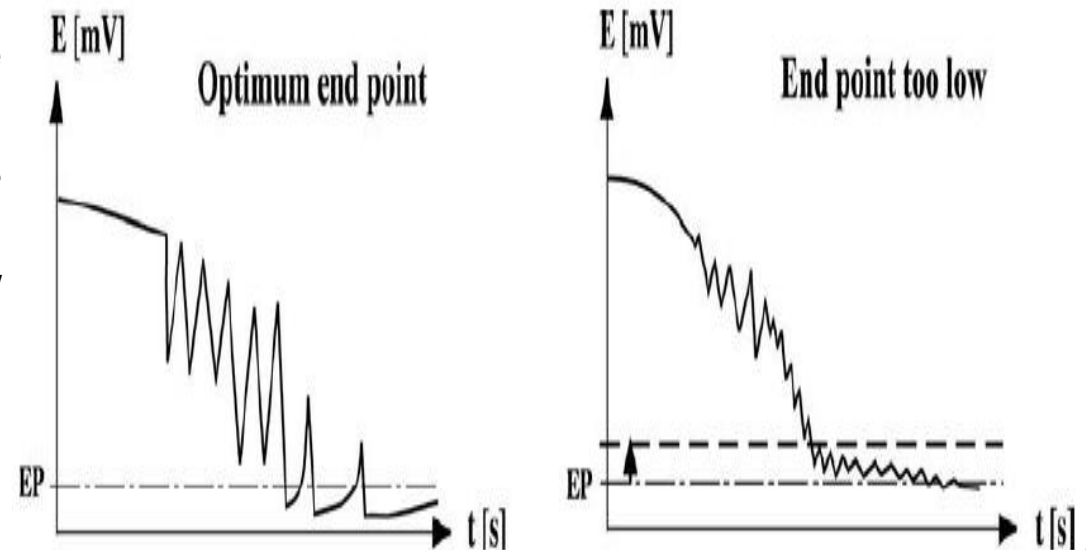
Volumetric Karl Fischer

The Karl Fischer titration

Various factors must be taken into account with Karl Fischer titration.

- The factors include:

  ❑ the atmospheric humidity

  ❑ the working medium

  ❑ the pH of the sample

  ❑ the side reactions between the sample and the Karl Fischer reagent

Volumetric Karl Fischer

Atmospheric humidity (drift determination)

● Atmospheric humidity represents the most relevant source of error in Karl Fischer titration.

● Moisture can enter the sample, the titrant and the titration stand.

● This problem is particularly relevant in tropical climates or in coastal regions, where the relative humidity can achieve values of more than 80%.

● The assumption that air-conditioned rooms have a lower atmospheric humidity is often not true: the majority of air-conditioning systems simply cool the air. However, since cold air cannot absorb as much moisture, the relative humidity increases. Briefly, the higher the atmospheric humidity in the laboratory, the greater is its influence on the results of the Karl Fischer titration.

● The air-conditioning system should therefore be equipped with a moisture condenser.

● The Karl Fischer titrator should never be installed close to a ventilator of the air conditioning system!

Volumetric Karl Fischer

Titration stand

● The titration stand must be sealed as tightly as possible against atmospheric moisture.

● The following rules should be observed:
  ❑ Close all openings in the titration stand.
  ❑ Condition the titration cell before use.

● When you assemble the titration stand for the first time, there will be moisture on:
  ❑ The glass surface of the titration cell and the inserts.
  ❑ The air within the titration vessel also contains moisture.

● After the anolyte (coulometer) or the solvent (volumeter) has been added, it is titrated to dryness during pretitration, until it is absolutely free of water.

The drift, however, remains high because the moisture present on the glass walls and the air in the titration cell diffuse only slowly into the anolyte (solvent). This can take 1 - 3 hours.

● The total moisture can be titrated more quickly by gently moving the vessel from side to side so that solvent swirls up the side of the vessel to pick up moisture adsorbed on the glass walls.

  In this way, the residual moisture dissolves more rapidly into the anolyte (solvent).

  Do not shake too vigorously to avoid solvent gets on the cover of the vessel.

● Protect the titration cell with a desiccant (3 A molecular sieve and silica gel).

The desiccant absorbs the moisture and protects the titration cell against the ingress of moisture. The drying capacity of the desiccant is limited and it depends on the humidity and can be exhausted after 2 - 4 weeks (indicated by a colour change of the indicator of the silica gel).

● Silica gel can be regenerated over night at 150 °C, whereas molecular sieves require temperatures up to 300 °C.

Volumetric Karl Fischer

The drift

● No titration stand is completely water tight

● On the other hand, this water amount is also titrated during analysis. Therefore it must be taken into account when calculating the water content.

● In this respect, it is necessary to quantify the amount of water entering the titration cell during titration.

● The **drift** indicates the quantity of water that enters the titration stand over a defined period **(t)** and is given in **μg water/minute**.

● This is achieved by titration of the dry solvent for a defined time **(drift determination).**

● At the start of a sample titration, the last measured drift value is automatically stored, if it is defined as the parameter "**Source for drift: Online**" in method function "Titration stand (KF stand)".

● On the other hand, it is also possible to use the value of a previously performed drift determination ("**Determination**"), or a fixed value can be defined into the titration method ("**Fix value**"), or it can be entered by the user ("**Request**"):

● The drift value is subsequently used in the calculation of the result in order to compensate for the moisture that entered the titration cell according to the following formula:

Sample result = Total amount of water determined - (drift * titration time)

For accurate results,drift value should therefore be as low as possible and stable before the start of a titration!

Volumetric Karl Fischer

Titrant concentration

The titrant concentration can change due to the following reasons:

1. The titrant is not chemically stable, the one-component titrant.

2. The titrant may absorb moisture from atmosphere reducing its concentration

(anhydrous methanol in titrant is very hygroscopic)

- if the desiccant on the titrant bottle is "used up",

- if the titrant bottle is not tightly sealed.

3. A significant change in temperature may occur: The Karl Fischer titrants consist of approximately 90% methanol or ethanol. Their volume increases considerably with temperature, so that there is a sharp drop in concentration.

Volumetric Karl Fischer

Concentration determination with di-sodium tartrate dihydrate

General

Di-sodium tartrate dihydrate (the primary standard for Karl Fischer titration)

$Na_2C_4H_4O_6 \cdot 2H_2O$

(M = 230.08 g/mol)

Stable

Non-hygroscopic

Contains 15.66% of water.

Slowly dissolves in methanol So you should first grind it to a fine powder before using

Procedure

❑ Use the optimized METTLER TOLEDO method M301

❑ Weigh between 0.04 and 0.08 g di-sodium tartrate dihydrate with the aid of a weighing boat. This sample size yields an optimum titrant consumption of 1.3 to 2.5 mL with a 5 mL burette (26-50 % of burette volume)

❑ Add it into the titration vessel. Make sure that nothing adheres to the beaker wall or to the electrode.

❑ Determine the weight by back weighing and enter it as sample size.

❑ Mix for 3 minutes to achieve complete dissolution before you start the titration.

Volumetric Karl Fischer

Concentration determination with Water Standard 10.0 mg/g

General

● Water standards consist of a mixture of organic solvents containing a specific amount of water

● Ex **"HYDRANALR-Water** Standard 10.0" from **Sigma-AldrichR** with 10 mg water in 10 g standard.

● This content is confirmed by the test certificate enclosed with every package.

● The water standards are supplied in glass ampoules. They are thus protected against the ingress of moisture and can be stored for up to five years.

Procedure

● To achieve an optimum consumption of 2 to 3 mL titrant with a concentration of 5 mg/mL, you should weigh in 1.0 to 1.5 g of water standard 10.0.

❑ Use the **METTLER TOLEDO** method M300

❑ Open the ampoule shortly before the measurement in accordance with the enclosed instructions.

❑ Rinse a 10 mL syringe with approximately 1 mL of water standard.

❑ Draw the whole content of the ampoule into the 10 mL syringe.

❑ Inject 1 to 1.5 mL at a time as an aliquot.

❑ Determine the weight by back weighing. The content of an ampoule is sufficient for 3 to 5 determinations.

❑ Start the titration without any mixing time.

Volumetric Karl Fischer

Concentration determination with pure water

General

● When using pure water to determine the concentration, a very good deal of practice and precise working is required to obtain repeatable, accurate results.
● This is due to the *very small amount of sample* (10 to 20 µL) that has to be injected.
● Thus, it is strongly recommended determining the concentration either with di-sodium tartrate dihydrate, or with a 10.0 mg/g water standard.

Procedure

❏ You should weigh between 10 and 20 µL of deionized water or water according to ISO 3696 to achieve a consumption of 2 to 4 mL titrant with a concentration of 5 mg/mL.
❏ The sample should be weighed either using a balance *with a resolution of 0.01 mg* **(METTLER TOLEDO XP205 balance)** or with a *10 or 20 L* precision syringe **(e.g. with a Hamilton microliter syringe).**
❏ A balance with a resolution of 0.1 mg does not satisfy the requirements for a repeatable titration.
❏ Inject exactly 10.0 µL deionized water with a 10 µL syringe.
❏ Enter 0.01 g as the sample size.
❏ Start the titration without any mixing time.

Volumetric Karl Fischer

The solvent

● To determine the water content in a sample, the sample must release water completely. Only freely available water undergoes reaction with the Karl Fischer reagent.

● You can use mixture of solvents to achieve complete dissolution.

● However, the largest part of the solvent mixture must always be an alcohol (most preferably methanol) to ensure that the Karl Fischer reaction is strictly stoichiometric.

Notes

❑ The solvents that are used should contain as few water as possible (< 100 ppm), or the titration will take too long and titrant will be wasted.

❑ If acidic or basic samples are titrated, buffering agents are first added to the solvent to ensure that the titration is quick and without side reactions.

❑ imidazole is used for acidic samples, and salicylic or benzoic acid for basic samples.

Solvent	Max. amount	Samples
Methanol	100%	Solvents: toluene, dioxane, alcohols, ester Organic products: urea, salicylic acid Foods: honey, yogurt, beverages Cosmetics: soaps, creams, emulsions
Chloroform	70%	Petrochemical products: crude oil, hydraulic oil, transformer oil, fat
Decanol Octanol Hexanol Dodecanol	50%	Oils: edible oil, massage oil, ethereal oils Petrochemical products: gasoline, diesel oil, kerosene Pharmaceutical products: ointments, fatty creams
Toluene	50%	Waxes, tar products, suppositories
Formamide	50% (30%)	Sugar products: jelly, caramel, jelly bears Starch products: flour, corn, noodles, potato chips

Volumetric Karl Fischer

Dissolving capacity of the solvent

● The dissolving or extraction capacity of the solvent is a crucial factor in Karl Fischer titration. If exhausted, the water will no longer be completely released. This will lead to incorrect results, so too low water content. Therefore, it is necessary to replace the solvent timely.

● The solvent for the two-component reagent contains SO_2, which may be completely expended if you titrate a large number of samples with high water content. In this case, the titration of subsequent samples will then be very slow. Once again, you must replace the solvent timely.

● The Compact Line KF titrators are able to monitor the solvent capacity: the user can define when the solvent should be replaced by specifying the usable life, the amount of water in mg which has been titrated, or by indicating the maximum number of samples to be titrated.

● The titrator accumulates the total water amount continuously during titrations and reports "Solvent capacity exhausted" as soon as the specified value is exceeded.

Volumetric Karl Fischer

Sampling

● When taking samples for water determination, you must be extremely careful to exclude atmospheric moisture - the most common source of error. If the water content of a sample changes during sampling due to moisture being absorbed or desorbed, you will no longer be able to determine its true water content.

"An analysis cannot be better than the actual sample!"

When sampling, you should take into account the following points:

❑ The sample must be representative, it must contain the same average amount of water as the material as a whole.

❑ The sample should be taken quickly to exclude, or at least minimize, the absorption or release of moisture.

❑ Heterogeneous water distribution in samples:

non-polar liquids, e.g. oils, the water is *not uniformly dispersed*. It floats on the surface or sinks to the bottom. Liquids of this type must be thoroughly mixed (by shaking) before a sample is taken.

non-polar solids, such as butter, which cannot be mixed as thoroughly as liquids, the sample should be larger the more heterogeneous the distribution of the water.

❑ Hygroscopic solids may exhibit *higher water content* on the surface than inside if they have absorbed atmospheric moisture during storage.

Substances with very low water content:

● Substances with a very low water content are frequently extremely hygroscopic. The sample must therefore be taken very quickly and with a syringe or a spatula that is absolutely dry.

Volumetric Karl Fischer

Amount of sample

The amount of sample used depends on
- ❑ The expected water content
- ❑ Required accuracy and precision.

Volumetric titrations

● the optimum amount of water is approximately **10 mg** per sample. As a rule of thumb, the accuracy increases with the amount of sample, because the absorption of air moisture during sampling and sample addition becomes less important.

● If a high level of accuracy is required, the amount of sample should require a titrant consumption between **30 and 70%** of the nominal burette volume.

● This corresponds to *7.5 to 17.5 mg* water per sample for a *5 mL* burette with a titrant concentration of *5 mg/mL*.

● Water content determinations below 1000 ppm are not required to be quite as accurate:

● A relative standard deviation srel of 1 to 5% is generally considered as acceptable for such values.

● A titrant consumption of *0.1* to *0.05 mL* is thus still acceptable when using a *5 Ml* burette.

● This corresponds to *0.1* to *0.05 mg* water per sample with a titrant concentration of *1 mg/mL*.

● For a more accurate determination of water traces (10 ppm to 1000 ppm) by volumetric KF titration, a KF titrant with a lower concentration (1 or 2 mg/mL) has to be used, and the following minimum sample sizes should be used:

Water content	[ppm]	10	50	100	200	500	1000
Min. sample size	[g]	8	7	5	4	3	2

Volumetric Karl Fischer
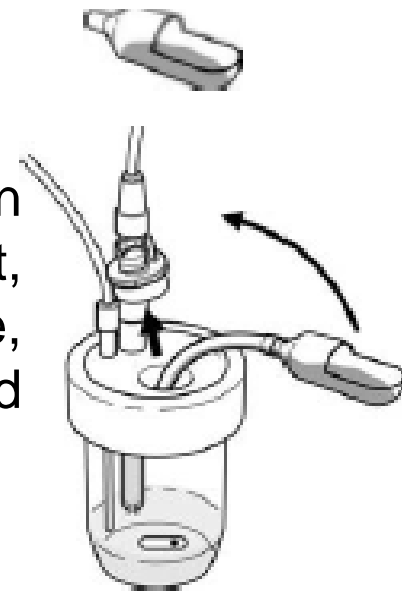
Solid samples

KF coulometry

It is not possible to directly titrate solid samples using KF coulometry when the titration cell is opened to add the sample, about 50-100 µg water enter the anode compartment, depending on the ambient humidity. With an optimum sample size of 1 mg water/sample, this would lead to an error of 5% to 10%. For this reason, other methods have to be used for the determination of low water content by KF coulometry in solid samples:
- ❏ External extraction
- ❏ External dissolution
- ❏ Drying oven

Volumetric KF titrator

solids can be directly transferred into the titration vessel. The sample should be quickly weighed and added to minimize air exposure.

If possible, it should be added under the same conditions as it was transported and stored. For instance, the storage of samples in a refrigerator may cause water to condense; thus, it is necessary to warm up such samples to room temperature in a closed vessel before weighing.

Volumetric Karl Fischer

Weight of solid samples with the back-weighing technique

❑ Weigh the sample in
the weighing boat.

❑ Tare the balance to zero.

❑ Add the sample into the titration vessel.

❑ Use weighing boat with attached flexible tubing to prevent the sample

from adhering to the vessel wall or to the electrode.

❑ Back-weigh the empty weighing boat.

❑ Enter the weight in the titrator or transfer it automatically.

❑ Start the titration.
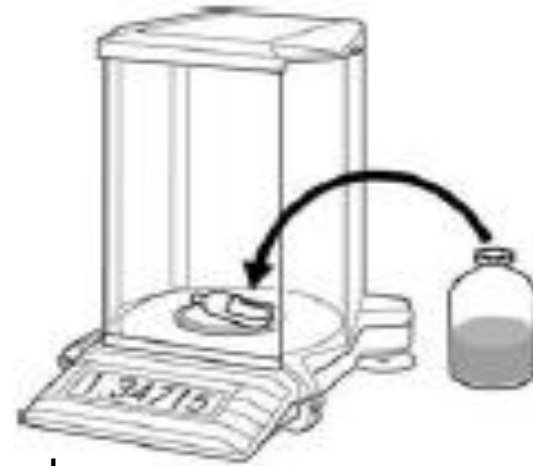
Volumetric Karl Fischer

Measurement accuracy

The accuracy strongly depends not only on the technical specifications of the instruments, but also on the several factors that have been already mentioned in the previous chapters:

- ❑Sampling

- ❑Selection of optimum sample size

- ❑Condition of the KF reagents fresh reagents, pre-titration, low drift value

- ❑Sealed titration vessel and tight tubing,

- ❑Condition of the indication electrode

Volumetric Karl Fischer

Interferences

Effects of temperature

● The Karl Fischer titrants consist of approximately 90% methanol or ethanol.

● Their volume increases if the temperature increases, and their concentration decreases accordingly.

● S. Eberius specifies a correction factor of 0.0012 per degree Celsius for methanolic Karl Fischer solutions.

● According to ISO 760, a temperature increase of 1 °C causes a drop of 0.1% in the concentration. The titrant (in particular, the two-component KF solvent) may loose sulfur dioxide if the temperature rises.

● This causes bubbles to form in the titrant tubing.

Volumetric Karl Fischer

Titration at low temperatures

● You can perform Karl Fischer titrations at low temperature to eliminate undesired side reactions.

● The water content of *peroxides*, can be determined at - 40 °C.

● You must use the two-component reagent to do so, because the reaction rate of the one component reagent is too slow at this temperature.

Titration at high temperatures

● Increasing the titration temperature speeds up the dissolution of the sample or the extraction of the water from it, resulting in shorter titration times.

● Titrations at elevated temperature have proved particularly effective for *foodstuffs.*

● The maximum temperature depends on the boiling point of the reagent

    ❑ methanol: 64 °C

    ❑ ethanol: 78 °C

Volumetric Karl Fischer

Side reactions

There are mainly three side reactions that can affect the result:

1. Reaction with methanol, CH_3OH

- Aldehydes and ketones react with methanol leading to *additional water*
- Esterification with carboxylic acids leading *to additional water*

2. Reaction with water, H_2O

- Ketones and aldehydes react with sulphur dioxide, a base and water (i.e. *water is consumed*)

3. Reaction with iodine, I_2

- The reaction of iodine with:

Oxides   Hydroxides   Carbonates   Amines

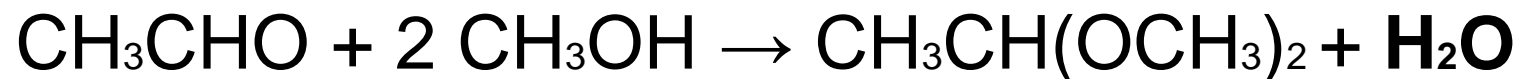leads to a higher *consumption of iodine* giving higher water content.
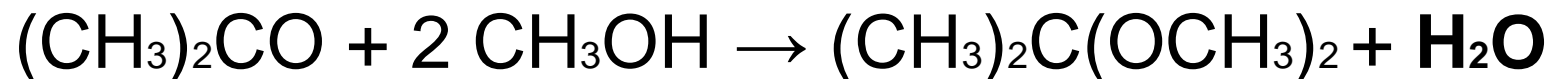
Volumetric Karl Fischer
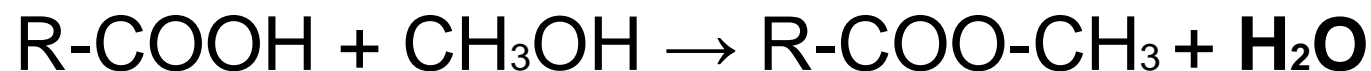
Reaction with methanol

Aldehydes and ketones:

Formation of acetals:

$$CH_3CHO + 2\ CH_3OH \rightarrow CH_3CH(OCH_3)_2 + \mathbf{H_2O}$$

Formation of ketals:

$$(CH_3)_2CO + 2\ CH_3OH \rightarrow (CH_3)_2C(OCH_3)_2 + \mathbf{H_2O}$$

Esterification:

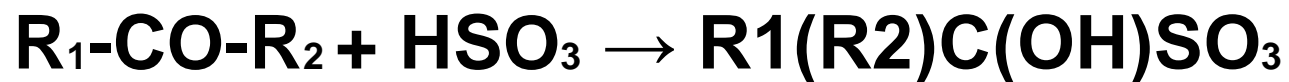$$R\text{-}COOH + CH_3OH \rightarrow R\text{-}COO\text{-}CH_3 + \mathbf{H_2O}$$

Volumetric Karl Fischer

Reaction with water

Another side reaction, the bisulfite addition, occurs with aldehydes and ketones in the presence of SO2.

Bisulfite addition:

$$CH_3CHO + H_2O + SO_2 + NR \rightarrow HC(OH)SO_3HNR$$

$$R_1\text{-}CO\text{-}R_2 + HSO_3 \rightarrow R1(R2)C(OH)SO_3$$

Note: $SO_2 + H_2O = HSO_3 + H^+$

Solution:
- ❏ Start the titration immediately after adding the sample.
- ❏ Perform a fast titration by predispensing 90% of titrant consumption
- ❏ This causes water to titrate quickly, before any bisulfite addition can take place.
- ❏ The **"Autostart"** parameter allows for the automatic start of the titration as soon as the sample has been added and water is detected.

Volumetric Karl Fischer Questions & Answers

1.What is the primary principle of the Karl Fischer Titration?

(a) To determine the boiling point of a given analyte

(b) To determine the moisture content of a given analyte

(c) To determine the ash value of a given analyte

(d) To determine the optical rotation of a given analyte

Answer:

(b) The primary principle of the Karl Fischer Titration is to determine the moisture content of a given analyte.

2.Which of the following can be used as a reagent in the Karl Fischer titration?

(a) Iodine, sulfur dioxide and a solvent

(b) Chlorine, nitrogen dioxide and a solvent

(c) Both (a) and (b)

(d) None of the above

Answer:

(a) Iodine, sulfur dioxide and a solvent can be used as a reagent in Karl Fischer titration.

Volumetric Karl Fischer Questions & Answers

3.Which of the following can be used as a buffering agent in the Karl Fischer titration?

(a) Pyridine

(b) Methanol

(c) Both (a) and (b)

(d) None of the above

Answer:

(a) Pyridine can be used as a buffering agent in the Karl Fischer titration.

4.Which of the following can be used as a solvent in the Karl Fischer titration?

(a) Pyridine

(b) Methanol

(c) Both (a) and (b)

(d) None of the above

Answer:

(b) Methanol can be used as a solvent in the Karl Fischer titration.

5.Which of the following is the correct chemical equation for the reaction between iodine and sulphur dioxide?

(a) $I_2 + NO_2 + H_2O \rightarrow 2\ HI + NO_3$
(b) $Cl_2 + SO_2 + H_2O \rightarrow 2\ HCl + SO_3$
(c) $I_2 + SO_2 + H_2O \rightarrow 2\ HI + SO_3$
(d) $Cl_2 + NO_2 + H_2O \rightarrow 2\ HCl + NO_3$

Answer:

(c) $I_2 + SO_2 + H_2O \rightarrow 2\ HI + SO_3$ is the correct chemical equation for the reaction between iodine and sulphur dioxide.

6.What is DST? What is it used?
Answer:

DST is the abbreviation for disodium tartrate dihydrate.
It is primarily used for the standardization of Karl Fischer's Titration. Under standard conditions, DST is stable and non-hygroscopic.

Volumetric Karl Fischer Questions & Answers

7.Mention some factors that affect the Karl Fischer Titration?

Answer:

Karl Fischer titration is a method used to determine the water concentration in a given analyte sample by using coulometric or volumetric titration. Various factors that affect the Karl Fischer Titration are mentioned below.
1. Humidity
2. pH of sample
3. Medium
4. K_F reagent

8.What are the pieces of equipment of the Karl Fischer Titration?

Answer: Various pieces of equipment of the Karl Fischer Titration are mentioned below.
1. Drying tube
2. K_F reagent
3. Sample injection cap
4. Anode chamber
5. Electrode analysis
6. Rotor
7. Cathode chamber
8. Drain cook
9. Detection electrode
10. Magnetic stirrer

Volumetric Karl Fischer Questions & Answers

9.What is the primary discrepancy between coulometric and volumetric titration?
Answer:

The primary difference between coulometric and volumetric titration is that in the coulometric titration, the titrant is produced electrochemically inside the titration cell. In contrast, in the volumetric titration, the titrant is added directly to the sample with the help of a burette.

10.What is the difference between Karl Fischer's titration and loss on drying?
Answer:

Both Karl Fischer's titration and loss on drying are used to determine the water concentration in a given analyte sample by using coulometric or volumetric titration. But, loss on drying can also determine the volatile matter in a given analyte sample.

اللهم لا سهل
إلا ما جعلته سهلا
وأنت تجعل الحزن إذا شئت سهلا

Best regards
Chemist
Ahmed Talaat Elnagar