

Tips and Hints
For a Successful
Water Content
Determination

Titration Excellence
KF Compact Titrators

Water Content by Karl Fischer Titration Essentials and Troubleshooting

METTLER TOLEDO

Editorial

The presence of water in petroleum products, pharmaceutical substances or foodstuffs is often undesirable. A water content that is too high can reduce the shelf life of rice, make the processability of pharmaceutical products more difficult, or lead to quality problems with plastic products. The determination of the water content in different materials is therefore crucial in production processes and quality control.

Chemical methods for the water content determination include techniques where a chemical reaction takes place between water and a suitable reagent. The amount of water converted during the reaction is determined from the amount of reagent consumed. The most well-known method based on this principle is the Karl Fischer titration. The main advantages of this quantitative analytical technique are its

- high selectivity to water
- wide measuring range
- short analysis time
- accuracy and repeatability
- directness i.e. no additional reference method necessary

METTLER TOLEDO offers you a complete portfolio of solutions for successful water content determination by Karl Fischer titration, including autosamplers and dedicated accessories for the unattended analysis of a high number of samples. Detailed information can be found at [Volumetric and Coulometric Karl Fischer Titrators – For Accurate and Precise Water Determinations \(mt.com\)](https://www.mt.com).

This Competence Guide covers the most relevant points to be considered when performing a Karl Fischer titration - without starting from basics. Beside a brief overview, this Guide will focus on three parts:

- **The four key questions for a successful KF titration:**

To achieve accurate and correct results by the KF titration it is necessary to first completely understand what are the goal, the needs and the water content determination to be performed. Four specific questions will support and guide you in the right direction.

- **Sample preparation:**

The water content can be successfully determined only if water is freely available to undergo the chemical reaction according to Karl Fischer. If water is not freely available, dedicated sample preparation has first to be applied to release water molecules from the sample matrix.

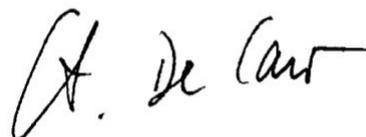
- **Frequently asked questions:**

A selection of the most relevant frequently asked questions

We are convinced that this document is a valuable support for your work on water content determination.



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Overview

Karl Fischer (KF) Titration

Titration is a straightforward, easy and affordable technique for the content determination of a specific analyte in sample solutions. If the analyte is water, then the titration according to Karl Fischer is the method of choice. Briefly, the water content is determined by addition of an iodine I_2 solution of known concentration to the sample dissolved in an alcoholic solution e.g. in methanol. Iodine reacts with water in a 1:1 ratio in a two-step reaction involving methanol, an organic base and sulfur dioxide (SO_2). This chemical reaction is designated according to the German Chemist Karl Fischer who developed this analytical technique for the determination of the water content in petroleum products i.e. the so-called Karl Fischer (KF) reaction.

During titrant addition, the potential difference is monitored with a polarized double pin platinum potentiometric sensor (a redox electrode), such that the process can be visualized in a graph showing a titration curve. The iodine titrant solution is added until a predefined potential endpoint is reached i.e. until a potential of 100 mV is reached. The titrant consumption in mL up to this point allows for calculation of the water content in the sample (**Volumetric KF titration**). Alternatively, the iodine needed for the KF reaction can be generated directly in the titration vessel by electrochemical processes (**Coulometric KF titration**).

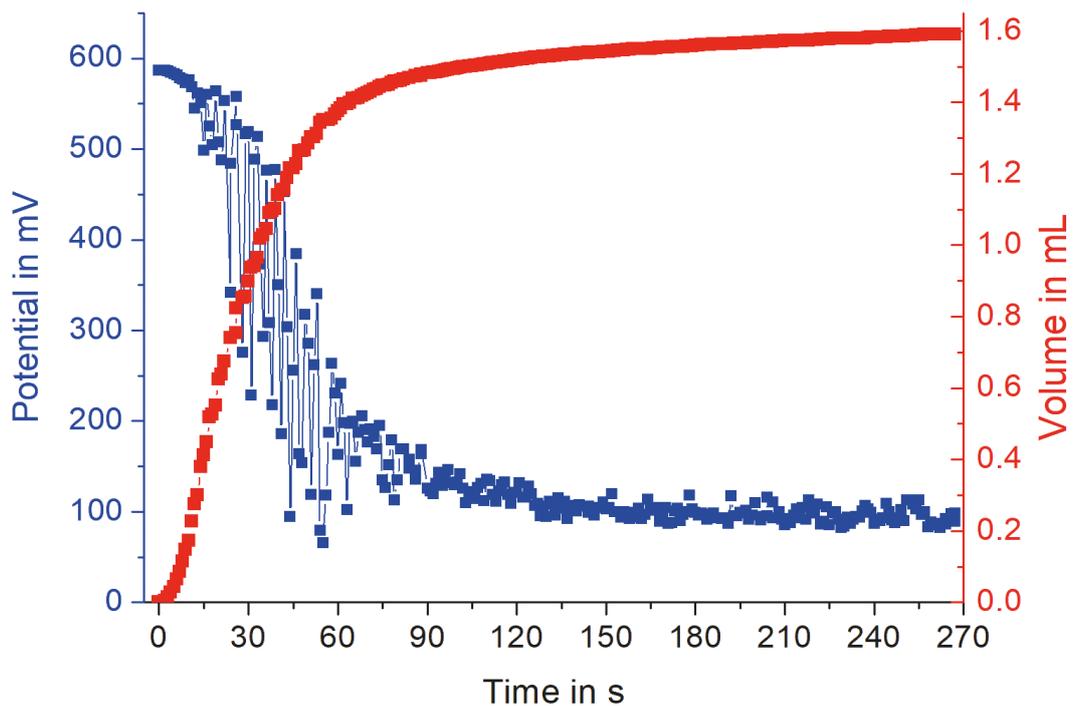


Figure 1: Titration curves showing the determination of water in cellulose by volumetric KF titration. 0.15 g cellulose was added directly in the vessel of a volumetric KF titrator, stirred during 120 s to achieve complete dissolution, and subsequently titrated. The potential (blue curve) and the titrant volume (red curve) are plotted versus time.

Ready-to-use checklist for KF titrations

The following points has to be verified to perform successful titrations:

Environment	<ul style="list-style-type: none"> – Temperature – Humidity – Pressure – Ventilation / air conditioning – Sun exposure – Use 	<ul style="list-style-type: none"> – Ambient temperature – i.e. 5-40 °C – non-condensing environment – Standard pressure approx. 1 atm – Avoid exposition to air flows – Avoid exposition to direct sunlight – Inside / interior spaces
Equipment	<ul style="list-style-type: none"> – Balance – Titration vessel / titration stand – Molecular sieve / silica gel – Burette, tubes – Sensor – Automation and accessories 	<ul style="list-style-type: none"> – Correct weighing range, connected – Check tightness, grease the junctions if needed – Fresh / regenerated in the oven to eliminate absorbed water – Eliminate gas bubbles before titration by rinsing once – Connected and defined in the titrator setup – Connected and defined in the titrator setup
Chemicals and Samples	<ul style="list-style-type: none"> – Titrant – Solvent – Coulometric electrolyte – Water standards – Sample – Auxiliary solvents and reagents 	<ul style="list-style-type: none"> – Fresh, new titrant / tightly closed, not wet – Fresh, dry – Fresh, new electrolyte / tightly closed, not wet – Suitable concentration, use new standards – Sufficient amount, homogeneous sample – Very low water content
Users	<ul style="list-style-type: none"> – Assistant – Operator – Chemist – Lab manager 	<ul style="list-style-type: none"> – Administrator – Check correct role – Verify access rights
Documentation	<ul style="list-style-type: none"> – Operating instructions – Qualification documents – Standard operating procedures – Titration method validation – Available and up-to-date 	<ul style="list-style-type: none"> – Available – Documented proof of correct working – Available and up-to-date – Documented evidence of method correctness

The four key questions in Karl Fischer titration

What is the expected water content of the sample?

Two determination techniques are used in KF titration depending on the water content of the sample:

- Coulometric KF titration 1 ppm - 5%
- Volumetric KF titration 100 ppm - 100%

The techniques differ in the way they provide iodine for the Karl Fischer reaction with water. Based on the expected water content, the most suitable instrument i.e. a coulometric or a volumetric KF titrator is selected:

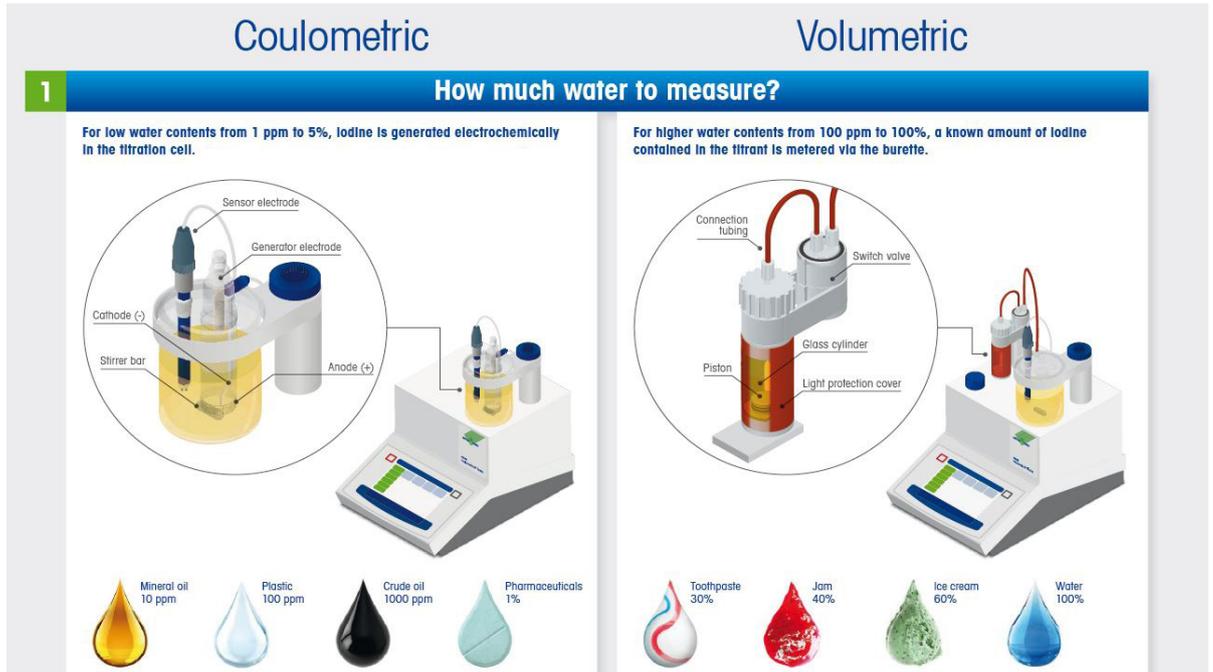


Figure 2A: Coulometric (left, [Coulometric KF Titration - Tutorial - YouTube](#)) and volumetric (right, [13. Run titration - Karl Fischer Volumetric Titrator - YouTube](#)) KF titrators. Typical samples are indicated below each instrument.

When measuring several aliquots of the same sample in a sample series, the repeatability – expressed as relative standard deviation S_{rel} in % - is changing depending on the water content, as shown in figure 2 B. In particular, decreasing water contents lead to poorer repeatability i.e. the relative standard deviation is increasing:

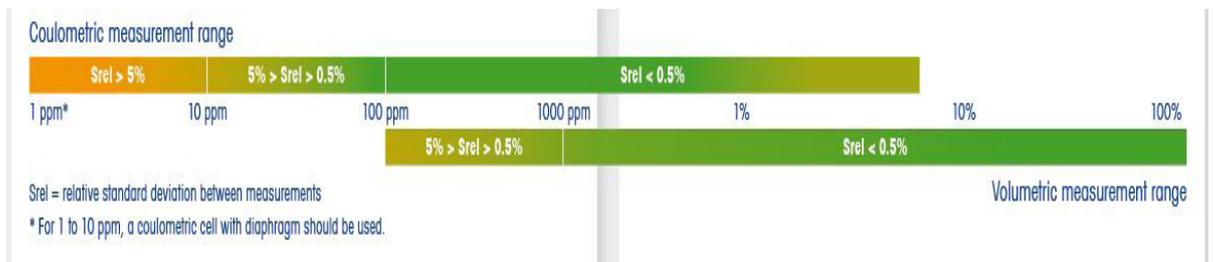


Figure 2B: Measurement range for coulometric and volumetric KF titration. The repeatability (rel. std. deviation S_{rel} , %) is also given as a function of the water content.

How much sample has to be weighed?

Select the suitable sample size for accurate and precise measurement i.e. small deviation from expected value and low relative standard deviation:

Coulometric KF titration

- The ideal coulometric titration sample contains 1 mg of water.
- The recommended practical working range is 0.1 to 5 mg.

**The ideal coulometric titration sample contains 1 mg of water.
Recommended practical working range is 0.1 to 5 mg.**

Water content of the sample	Sample size (g)	Absolute water quantity (mg)
5%	0.1	5.0
1%	0.2	2.0
0.1% (1000 ppm)	1.0	1.0
0.01% (100 ppm)	5.0	0.5
0.001% (10 ppm)	10.0	0.1
0.0001% (1 ppm)	10.0	0.01

- Recommended conditions
- Borderline conditions for accuracy or sample size

Figure 3A: Optimal sample size for coulometric KF titration.

Volumetric KF titration

- The ideal volumetric titration uses ½ of the burette volume.
- The recommendations below use a standard burette size of 5 mL.

**The ideal volumetric titration uses ½ of the burette volume.
Recommendations below use a standard burette size of 5 mL.**

Titrant concentration	5 mg/mL	2 mg/mL	1 mg/mL
For burette volume: 5 mL	Sample size (g)		
100%	0.015	—	—
60%	0.020	0.008	—
40%	0.030	0.013	—
30%	0.040	0.017	—
10%	0.125	0.05	0.025
1%	1.25	0.5	0.25
0.1% (1000 ppm)	12.5	5	2.5
0.01% (100 ppm)	25	25	25

- Recommended conditions
- Borderline conditions for accuracy or sample size
- = not recommended

Figure 3B: Optimal sample size for volumetric KF titration.

How is water released from the sample matrix?

Obtaining accurate results requires extracting all water from the sample. Many liquid samples dissolve easily in the classical KF solvent methanol, and thus the titration can be performed after direct injection of the liquid sample in the vessel. On the other hand, viscous oils, pastes or solid samples requires additional preparation steps to release water from the sample matrix. These steps can include the use of auxiliary solvents, increased dispersion e.g. longer (stirring times) or even higher temperatures to extract water completely:

Mixing

Many liquid or solid samples dissolve in methanol or in methanol mixtures using a normal magnetic stirring bar:

- Methanol: liquid foods, cosmetics, organic solids
- Chloroform: petroleum products, fats, organic solids
- Long-chain alcohols (e.g. octanol): edible oils, fuels, creams
- Toluene/xylene: tars, waxes, crude oil
- Formamide: sugars, starches, solid foods, pharmaceuticals



Figure 4A: Dissolution by stirring with magnetic stirrer bar.

Dispersion

Thicker, viscous liquids, pastes or powders may require more intense dispersion with a high-speed homogenizer to fully dissolve them.

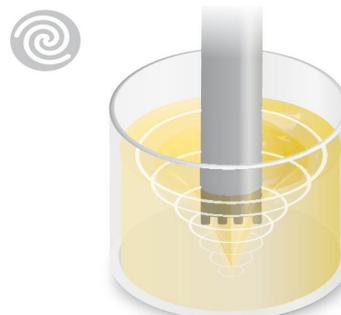


Figure 4B: Dispersion using a high-speed homogenizer.

Warming

A thermostatable titration vessel allows warming up to 50°C with an external silicon oil or water bath to improve dissolution and extraction of water from the sample.

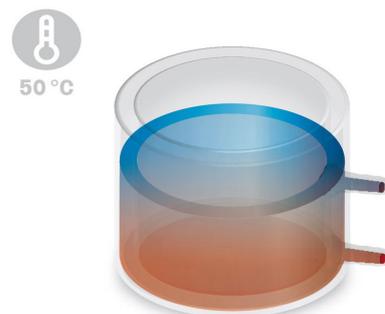


Figure 4C: Improving dissolution by warming up.

KF Oven

For solids or liquids causing side reactions or releasing water very slowly, a drying oven heats samples up to 280°C to drive water out of the sample and into the titration beaker.

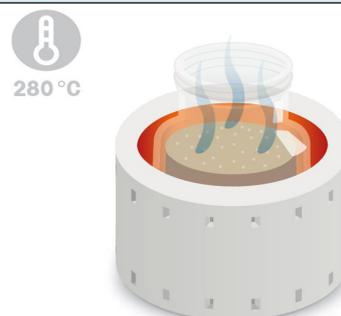


Figure 4D: Water extraction in the gas phase by heating.

Which KF reagents should I use?

Easily soluble samples can be titrated by injection (addition) directly into the titration cell:

Alcohols, ethers, aliphatic and aromatic hydrocarbons, etc.						
One-component KF volumetric reagents			Two-component KF volumetric reagents			
Honeywell	Titrant: Solvent:	HYDRANAL HYDRANAL	Composite 5 / 2 / 1 Methanol Dry Methanol Rapid	Titrant: Solvent:	HYDRANAL HYDRANAL	Titrant 5 / 2 Solvent NEXTGEN Solvent FI
Merck	Titrant: Solvent:	Aquastar Aquastar	CombiTitrant 5 / 2 / 1 CombiMethanol	Titrant: Solvent:	Aquastar Aquastar	Titrant 5 / 2 Solvent
With ethanol (E) or methanol-free – KF kinetics with E-reagents is slower than with methanolic reagents						
Honeywell	Titrant: Solvent:	HYDRANAL HYDRANAL	Composite 5 / 2 / 1 CompoSolver E	Titrant: Solvent:	HYDRANAL HYDRANAL	Titrant 5 / 2 E Solvent E NEXTGEN Solvent E-FI
Merck	Titrant: Solvent:	Aquastar Aquastar	CombiTitrant 5 / 2 / 1 CombiSolvent (methanol-free)	--		
KF coulometric reagents						
Honeywell	Anolyte: Catholyte:	HYDRANAL HYDRANAL	Coulomat A Coulomat AG Coulomat AD NEXTGEN Coulomat AG-FI NEXTGEN Coulomat A-FA Coulomat CG NEXTGEN Coulomat C-FA		cell with diaphragm cell with and without diaphragm cell without diaphragm with and without diaphragm/free of imidazole with diaphragm – Li-batteries, Ketones cell with diaphragm cell with diaphragm – Li-batteries, Ketones	
Merck	Anolyte:	Aquastar	CombiCouloma frit CombiCoulomat fritless		with diaphragm: anode and cathode compartment cell with and without diaphragm	
With ethanol (E) or methanol-free – KF kinetics with E-reagents is slower than with methanolic reagents						
Honeywell	Anolyte:	HYDRANAL	Coulomat E		cell with and without diaphragm	
Merck	--					

Ketones (e.g. acetone) and aldehydes react with methanol to form water. To suppress this undesired side reaction, dedicated KF reagents are needed when dealing with these samples.

Ketones (e.g. acetone) and aldehydes					
One-component KF volumetric reagents			Two-component KF volumetric reagents		
Honeywell	Titrant: Solvent:	HYDRANAL HYDRANAL	Composite 5K KetoSolver (halogen-free) Medium K (with chloroform) Working Medium K (CHCl ₃ , CH ₂ ClCH ₂ OH)	--	
Merck	Titrant: Solvent:	Aquastar Aquastar	CombiTitrant 5 Keto CombiSolvent Keto	--	
KF coulometric reagents					
Honeywell	Anolyte: Catholyte:	HYDRANAL HYDRANAL	NEXTGEN Coulomat A-FA Coulomat AK NEXTGEN Coulomat C-FA Coulomat CG-K		cell with diaphragm – Ketones, Li-batteries cell with diaphragm cell with diaphragm – Ketones, Li-batteries cell with diaphragm
Merck	Anolyte: Catholyte:	Aquastar Aquastar	Anolyte K Catholyte K		cell with diaphragm cell with diaphragm

Many samples cannot be easily dissolved or are very difficult to be completely dissolved due to their non-polar nature. Mixtures of organic solvents are used to improve the dissolution process. This is achieved either by adding auxiliary solvents (e.g. decanol, formamide, chloroform) to methanol, or by using dedicated KF solvent mixtures:

Diesel oil, petroleum, edible oil, ethereal oils, ointments, butter, fats, etc.				
Solvents for one-component KF volumetric reagents		Solvents for two component KF volumetric reagents		
Honeywell	HYDRANAL	Methanol Dry + max. 50% v/v decanol or hexanol	HYDRANAL	Solvent Oil (with chloroform)
	HYDRANAL	LipoSolver CM (with chloroform) LipoSolver MH (with hexanol)		Solvent CM (with chloroform) Solver (Crude) Oil (xylene, chloroform)
Merck	Aquastar	CombiSolvent Fats (butyl acetate, decanol) CombiSolvent Oils (with toluene)	Aquastar	Solvent Oils & Fats (hexanol, 2-propanol)

Mineral oils are very difficult to be completely dissolved. Auxiliary solvents (chloroform, toluene, xylene and mixtures thereof) added to methanol or dedicated KF solvents can cope with these challenging samples:

Mineral oil, transformer oil, silicon oil, grease, glue				
Solvents for one-component KF volumetric reagents		Solvents for two component KF volumetric reagents		
Honeywell	HYDRANAL	Methanol Dry + up to 70% v/v chloroform Solver (Crude) Oil (xylene, chloroform)	HYDRANAL	Solvent + up to 70% v/v chloroform Solvent CM (with chloroform) Solver (Crude) Oil (xylene, chloroform)
	Merck	Aquastar	CombiMethanol + up to 70% v/v chloroform CombiSolvent Oils (with toluene)	Aquastar Solvent + up to 70% v/v chloroform CombiSolvent Oils (with toluene)

Products containing sugar, starch or gelatin also need the use of formamide as auxiliary solvent to be completely dissolved in the titration cell:

Sugars, sugar-and starch-based products				
Solvents for one-component KF volumetric reagents		Solvents for two component KF volumetric reagents		
Honeywell	HYDRANAL	Methanol Dry + up to max. 50% v/v formamide	HYDRANAL	Solvent + up to max. 50% v/v formamide
Merck	Aquastar	CombiMethanol + up to max. 50% v/v formamide	Aquastar	Solvent + up to max. 50% v/v formamide

Sample preparation in Karl Fischer titration

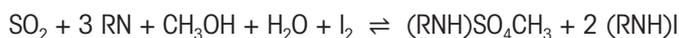
Complete release of water from the sample matrix

Water determination in liquid samples is generally straightforward and does not involve any challenges other than improving the sample solubility to achieve a complete release of water into the KF solvent. The situation is different when the water content has to be determined in solid samples.

In fact, water molecules present in solid samples are bound to the sample matrix in different ways i.e. water molecules can be

- Entrapped in cavities of the sample structure, or
- Weakly bound in capillaries of biological samples, or
- Adsorbed on the sample surface, or
- Tightly bound in crystal structure.

Hence, water must be first completely released from solid samples to be available for the Karl Fischer titration:



The Karl Fischer reaction consists of two steps: first, sulfur dioxide SO_2 reacts with a base RN and methanol CH_3OH to a methyl sulfite, $(\text{RNH})\text{SO}_3\text{CH}_3$. Subsequently, methyl sulfite reacts with water H_2O , iodine I_2 and a base giving methyl sulfate as a product.

The methods to efficiently release water from the sample matrix have been summarized in the following list:

- By dissolution in the Karl Fischer solvent,
- By mechanically crushing the sample in the titration vessel,
- By extraction from the sample matrix with a suitable solvent, or
- By evaporation in a dedicated KF oven connected to the titrator.

Based on these methods, different sample preparation techniques have been developed:

- Direct titration
- Internal extraction
- External extraction
- External dissolution
- Gas-phase extraction

The choice of the suitable technique depends on the sample to be titrated. The different techniques will be presented in the next chapters.

Direct titration

The direct titration of a sample to determine its water content is possible if

- The sample is soluble,
- It does not undergo side reactions with the KF reagents, and
- No additional sample preparation steps are needed.

Alcohols, esters, ethers, aliphatic and aromatic hydrocarbons:

These organic solvents such as do not cause any solubility issues when directly titrated.

Sugars, starch and starch containing products:

The dissolution is cumbersome or slow, hence an auxiliary solvent is used to improve it. In this case, formamide is used in a volume ratio between 30% and max. 50% v/v with the KF solvent to achieve complete dissolution.

Hydrocarbons with long aliphatic chains:

They cannot be easily dissolved in the KF solvent – which is generally methanol. This is because they are mainly non-polar substances - in contrast to methanol. Auxiliary solvents and warming up may become necessary.

Diesel fuel, petroleum edible oils and fats, ethereal oils, ointments:

These samples are difficult to dissolve in the KF solvent. The solubility is improved by mixing decanol or hexanol up to 50% v/v with methanol. Both alcohols have long non-polar chains, thus improving the dissolution.

Mineral oils, transformer and silicon oils, greases and glues:

Chloroform is the auxiliary solvent used for complete dissolution of these samples. Note that the amount of chloroform should not be higher than 70% v/v to avoid interferences during the Karl Fischer reaction.

pH value adjustment:

When the samples are acidic or basic, the optimum pH for the Karl Fischer Titration i.e. between pH 5 and 7 is achieved by adding buffers (imidazole, or benzoic acid) to the KF solvent before starting the titration.

Procedure for direct titration:

In the direct titration, the sample is introduced directly in the titration vessel using the back-weighing technique:

1. A sample aliquot is taken with the syringe/weighing boat.
2. The syringe/weighing boat is placed on the balance pan and the balance is tared.
3. Subsequently, the syringe/weighing boat is taken from the balance, and the sample is rapidly injected.
4. Back weighing of the empty syringe/weighing boat, the value entered in the instrument before starting titration.

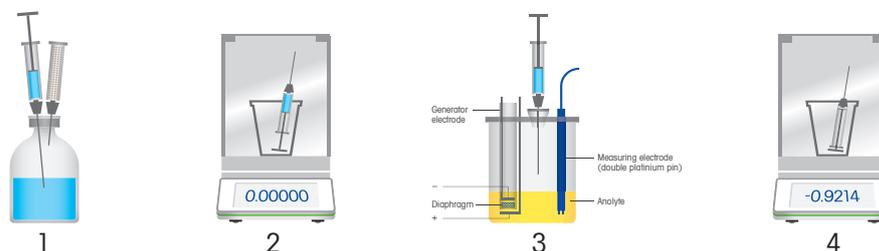


Figure 5: Back-weighing procedure

Summary :

Direct titration			
Sample	Soluble	If required:	Adjust pH value
	No side reactions		Improve solubility - Auxiliary solvents - Warming/heating
	No specific sample preparation		

Internal extraction

The internal extraction technique -more precisely: the direct titration with internal extraction- is applied when the water is extracted directly in the titration vessel by means of e.g.

- A long stir time (e.g. 5-10 min), and/or
- Speed (e.g. 80%), or
- High-speed homogenizer for a short but intensive dispersion action,
- Use of auxiliary solvents, or a combination of all previous steps.

The sample preparation by internal extraction is applied when

- the sample is not soluble,
- It does not undergo side reactions with the KF reagents, and
- The water release is fast.



Figure. 6A: The high-speed mixer is mounted on the top of the titration stand of the instrument.

The use of a high-speed homogenizer allows for an efficient and quick dispersion of the sample. Consequently, the water is released completely and fast from the sample matrix:



Figure. 6B/6C: Homogenizer before (left, B) and during action (right, C) in the titration vessel of the KF volumetric instrument.

Summary :

Internal extraction			
Sample	Insoluble e.g. almonds	Extraction by	Long stir time = 5-10 min
	No side reactions e.g. instant coffee		High-speed mixer
	Fast water release e.g. tablets		Improve solubility - Aux. solvents

External extraction

This sample preparation technique is needed when the water is extracted from the sample in an external vessel containing a solvent of known water content during a defined time e.g. 1-2 hours. Subsequently, an aliquot of the extraction solvent is titrated by injection in the KF titration vessel. Briefly:

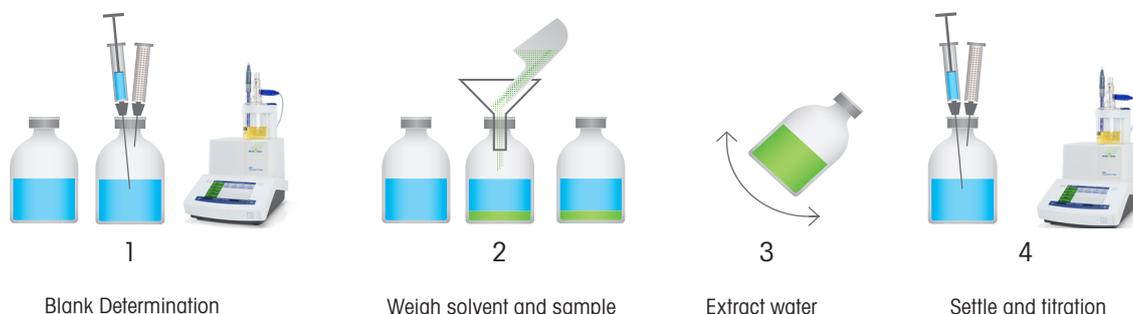


Figure. 7: The sequence for the external extraction

To achieve accurate and precise results it is necessary that

- The amount of water present in the extraction solvent is very low.
- The extraction capacity of the solvent is large enough (typical values: chloroform can extract max. 350 ppm, and toluene max. 600 ppm)
- The quantity of extraction solvent is large enough to allow for blank determination and for the extraction.

The sample preparation by external extraction is required when

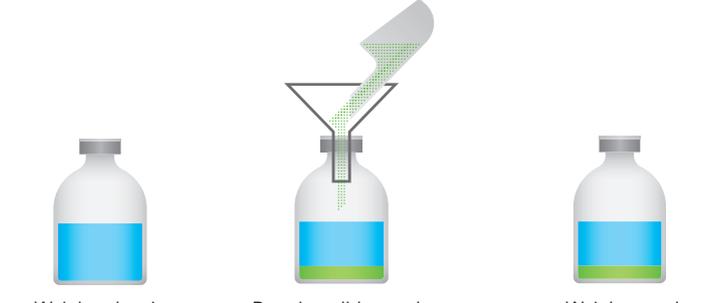
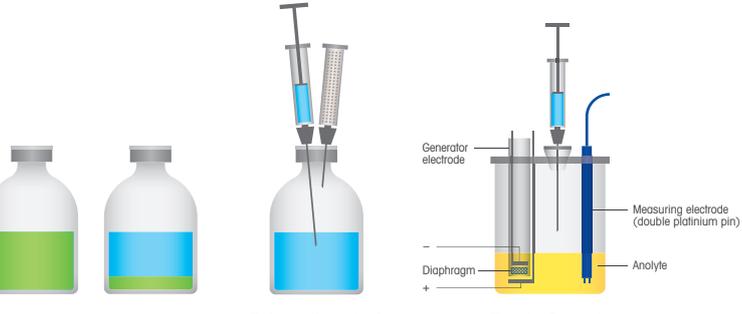
- The samples are not soluble,
- The water release is slow,
- The water content of the samples is very low, thus a large sample size is needed
- The samples do not undergo side reactions with the KF reagents, and
- The samples cannot be titrated in the coulometric titration vessel since they are solid.

Summary :

External extraction				
Sample	Not soluble e.g. tobacco	Extraction by	Suitable solvent or solvent mixture	water content << sample water content
	Slow water release e.g. cheese		Long extraction time	1-2 h and more
	Very low water content e.g. surface water of sugar		Large sample size	Large sample size for the extraction to get a large sample water amount with respect to the solvent water content
No side reactions e.g. wool				
	Solid sample – Direct coulometric titration not possible e.g. plastic pellets		NEVER enter solid sample in a coulometric KF titration vessel	Generator cell will be damaged!

External extraction in four steps

The workflow of the external extraction consists of four steps:

<p>1</p> <ul style="list-style-type: none"> Place the extraction solvent in a flask and close the flask with a septum Take an aliquot of the solvent with a syringe Determine the water content (blank value) 	 <p>Solvent in bottle with septum Take an aliquot of the solvent Determine water content of solvent = Blank value</p> <p>Figure. 8A: Blank determination</p>
<p>2</p> <ul style="list-style-type: none"> Weigh the solvent Pour the solid sample in the flask and close the flask with the septum (dilution factor: 10-20, sample size: 5-20 g) Weigh the sample in the flask with the septum 	 <p>Weigh solvent Pour in solid sample Weigh sample</p> <p>Figure. 8B: Weigh solvent and sample</p>
<p>3</p> <p>Extract water from the sample</p> <ul style="list-style-type: none"> overnight with shaking with ultrasonic and/or heating bath 	 <p>Overnight With shaking With ultrasonic and/or heating bath</p> <p>Figure. 8C: Water extraction</p>
<p>4</p> <ul style="list-style-type: none"> Wait for settling of the insoluble sample Take an aliquot of the supernatant liquid Titrate the aliquot to determine the extracted water amount 	 <p>Settling Take a liquot of extraction sample Titrate Sample</p> <p>Figure. 8D: Water extraction</p>

The calculation for the water content in ppm of the extracted sample is defined in the following formula:

$$\text{Water content (ppm)} = \frac{10^6}{10^6 - x} \cdot \left[x \cdot \frac{f_2}{f_3} - \frac{f_1 \cdot f_2}{f_3} \right]$$

where

x	Water content (ppm) of titrated sample/aliquot	ppm
f ₁	Water content of extraction solvent (blank)	ppm
f ₂	Weight of extraction solvent used	grams
f ₃	Total weight of sample used for extraction	grams

Similarly, the calculation for the water content in % of the extracted sample is defined in the following formula:

$$\text{Water content (\%)} = \frac{100}{100 - x} \cdot \left[x \cdot \frac{f_2}{f_3} - \frac{f_1 \cdot f_2}{f_3} \right]$$

where

x	Water content of titrated sample/aliquot	%
f ₁	Water content of extraction solvent (blank)	%
f ₂	Weight of extraction solvent used	grams
f ₃	Total weight of sample used for extraction	grams

External extraction of lyophilized substances

Lyophilized substances (or freeze-dried substances) have a very low water content in the order of e.g. 10-50 ppm. For this reason, they are very hygroscopic when exposed to air, i.e. they easily absorb moisture from the air as soon as the sealed vials are opened.

To avoid this, the extraction of water from the lyophilized sample is performed directly into the sealed vial by adding dried coulometric anolyte during pretitration:

1. Fill the KF coulometer with fresh anolyte
2. Start the pretitration
3. The anolyte is dried and the instrument has reached stand-by status
4. While in stand-by, aspire 1-2 mL of dried anolyte with a 10 mL syringe from the cell
5. Shake the syringe to eliminate water present on the inner wall of the cylinder
6. Discard the aspirated solution
7. Aspire 5-10 mL of dried anolyte with the same syringe
8. Inject the dried electrolyte in the sealed vial through the septum
9. Shake the vial to allow for water release from the lyophilized sample
10. Let the solution settle down
11. Aspirate an aliquot and titrate it.
12. Form the water amount determined with the KF coulometer and the sample mass given on the label of the vial, the water content of the freeze-dried sample can be calculated.

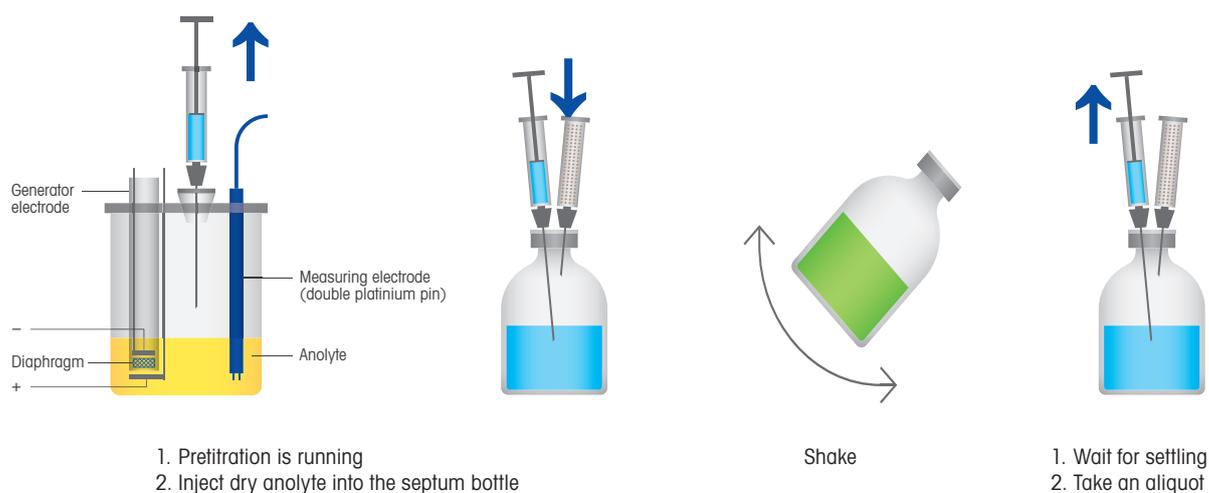


Figure 9: External extraction of water in lyophilized (freeze-dried) substances

External dissolution

In the case when the water content is extremely low, a much too large sample mass (e.g. 30-40 g) has to be used to achieve accurate and precise results. This will quickly fill up the titration vessel, and not more than 1-2 samples could be titrated. Thus, the KF solvent must be often replaced. In the worst case, it has to be replaced even after one single KF titration since the vessel is too full to accommodate other samples.

A large amount of the sample is dissolved in a flask containing a suitable solvent. Subsequently, an aliquot of the extraction solvent is titrated by injection in the KF titration vessel. The whole procedure is similar to the external extraction, however the calculations are slightly different:

$$\text{Water content (\%, ppm)} = x \cdot \left(\frac{f_2 + f_3}{f_3}\right) - \left(\frac{f_1 \cdot f_2}{f_3}\right)$$

where

x	Water content of titrated sample/aliquot	%, or ppm
f ₁	Water content of extraction solvent (blank)	%, or ppm
f ₂	Weight of extraction solvent used	grams
f ₃	Total weight of sample used for dissolution	grams

The sample preparation by external dissolution is applied when

- The samples are soluble,
- The water distribution in the sample is inhomogeneous,
- The water content of the samples is very low, thus a large sample size is needed
- The samples do not undergo side reactions with the KF reagents, and
- The samples cannot be titrated in the coulometric titration vessel since they are solid.

As in the case for the external extraction, to achieve accurate and precise results it is necessary that

- The amount of water present in the dissolution solvent is very low.
- The dissolution capacity of the solvent is large enough
- The solvent amount used is large enough to allow for blank determination as well as for the dissolution.

Summary :

External dissolution				
Sample	Soluble e.g. phenol	Dissolution	Suitable solvent or solvent mixture	water content << sample water content
	Non-homogeneous water distribution e.g. sucrose		Long extraction time	1-2 h and more
	Very low water content e.g. petroleum products		Large sample size	large water amount
No side reactions e.g. phenol				
	Solid sample e.g. sugar		Direct coulometric titration not possible	

Automated calculation for external extraction and dissolution

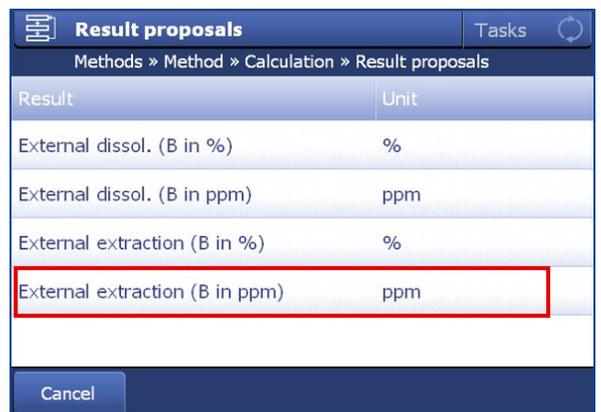
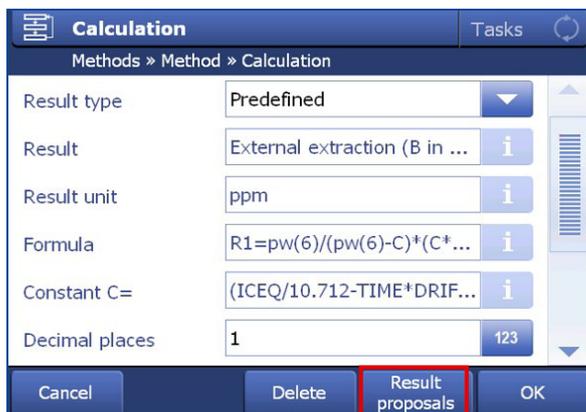
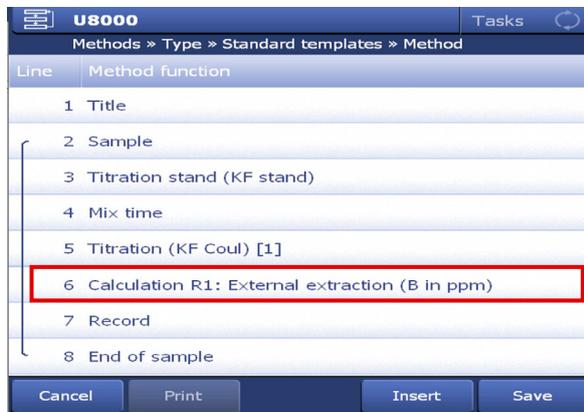
The specific calculations for both sample preparations are built-in in the high-end KF titrators to improve easy-of-use and reduce errors when performing these techniques prior to the KF titration.

In fact, these KF instruments have preprogrammed standard method templates as well as tested titration methods to perform automatically the whole procedure including the calculations. Depending on the analysis to be performed, the corresponding template is selected:

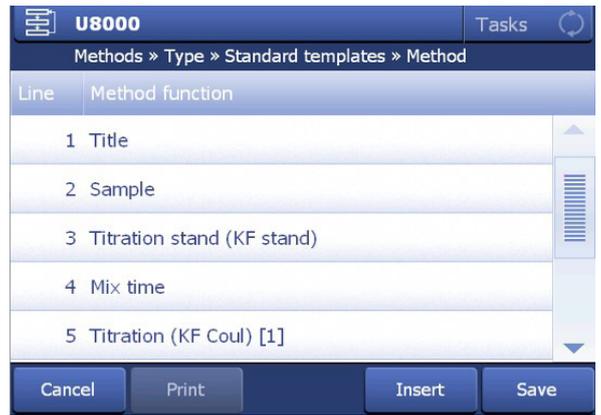
From the list of templates the method KFC002 is selected to develop a KF titration with external extraction (or dissolution)



In the method function "Calculation" you can select the corresponding procedure sample preparation procedure, as well as and the desired units i.e. "ppm" or "%"



Select the method function "Sample"



1. Under the function "Sample", select "Blank" to first determine the water content (blank) of the extraction (dissolution) solvent.
2. Subsequently, the sample is determined (select "sample")

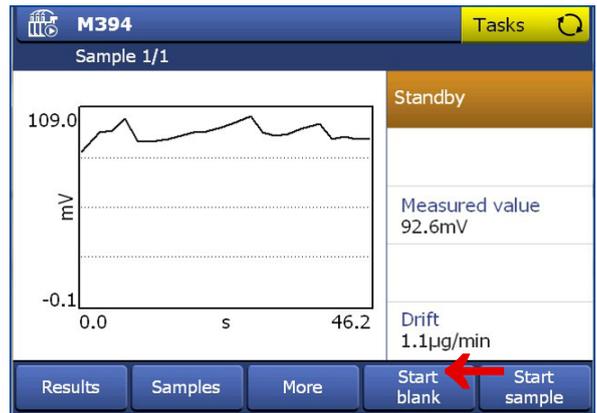


Briefly, the operator is guided through all steps of the analysis. In the case of an external extraction followed by coulometric Karl Fischer Titration, the detailed workflow is given in the next page.

Titration workflow for external extraction/dissolution

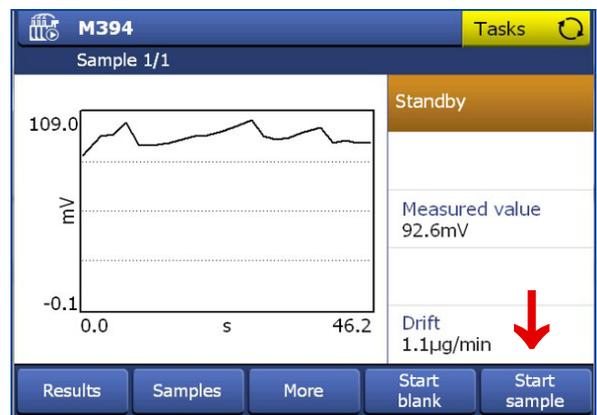
1. Start blank determination

- 1.1 Press "Start blank" when the corresponding button is active.
- 1.2 After the blank has been determined, the value is automatically stored in the instrument.

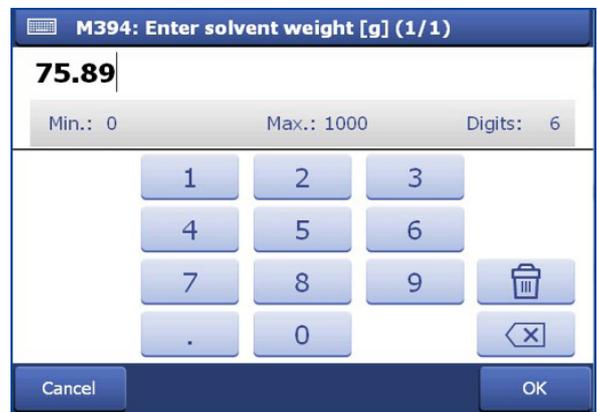


2. Start sample titration

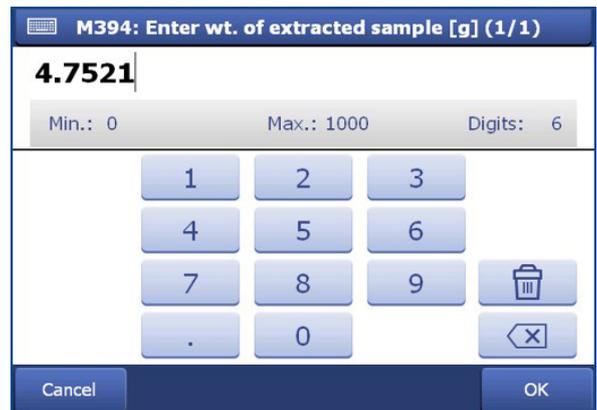
- 2.1 Press "Start sample" when the corresponding button is active.



- 2.2 The solvent mass is requested to be entered in the instrument.



- 2.3 The mass of the extraction sample is entered in the instrument.



Gas-phase extraction

When the sample undergoes side reactions with the KF reagents, water has first to be released by heating the sample in an oven with subsequent transfer into the titration vessel. The KF oven is connected to the KF titrator with a transfer tube with an inlet in the titration cell, and the evaporated moisture is transferred using a stream of dry and inert gas such as nitrogen.

The gas-phase extraction is used when

- The samples are insoluble,
- The samples undergo side reactions with the KF reagents,
- The water release from the sample matrix is very slow, and
- The samples do not decompose when heated i.e. they are thermally stable.

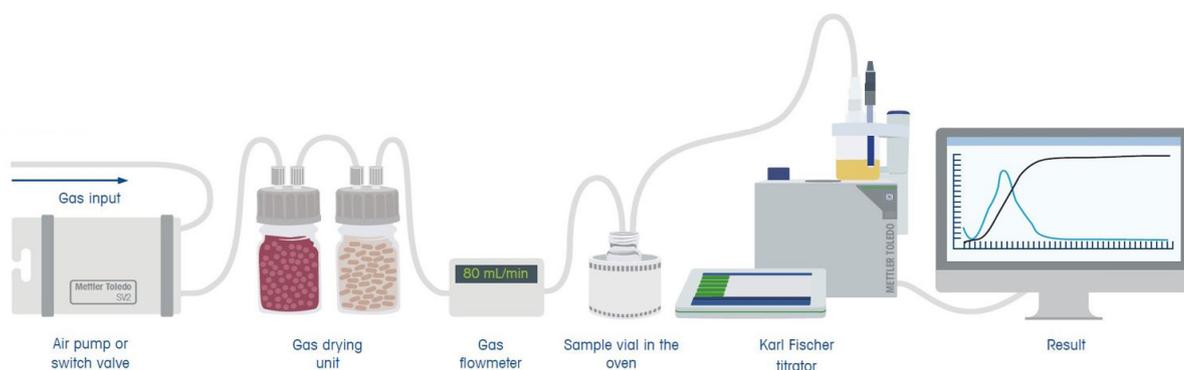


Figure 10: A continuous flow of dry gas enter the sample vial in the oven and transport the evaporated water into the KF titration vessel.

Summary :

Gas-phase extraction			
Sample	Side reactions with the KF reagents e.g. motor oil	Heating and collecting the vapor	No contact with reagents
	Insoluble e.g. plastic chips		
	Slow water release e.g. polymers		Heating time Recommendation: <ul style="list-style-type: none"> • At least 10 min • max. 30 min
	Thermally stable – no decomposition e.g. polylactic acid (sutures)		Heating temperature <ul style="list-style-type: none"> • Select heating temperature 10-20°C below melting point • Avoid oxidation by using nitrogen as inert transfer gas

Water content in gases

To determine the water content of gases, the gas is purged through the titration vessel for a defined time period. During this time, the KF solvent absorbs the gas humidity. First, the gas is passing through a flow meter to ensure a constant flow rate to achieve an accurate determination of the total gas volume. Subsequently, the gas transfer is stopped, and the titration is started.:

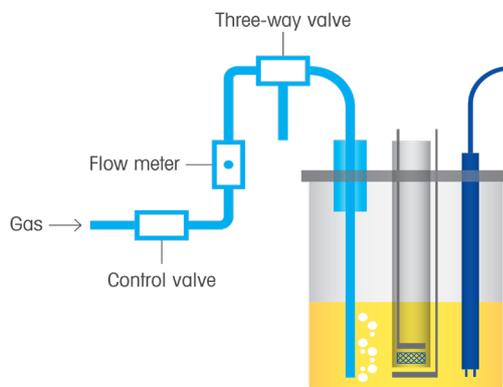


Figure 11: The gas humidity is collected in the titration vessel during a specific time e.g. 5 min before titration.

The amount of water m_{water} determined by KF titration allows for the calculation of the water content:

1. The total gas volume V is determined by multiplying the gas flow rate (mL/min) with the time (min):
2. The water content is determined according to:

$$\text{Total gas volume} = V = \text{gas flow rate} \left(\frac{\text{mL}}{\text{min}} \right) \times \text{time (min)}$$

1. The water content is determined according to:

$$\text{Water content} = \frac{m_{\text{water}}}{V} = \frac{\text{water amount } (\mu\text{g})}{\text{Total volume (mL)}}$$

Summary :

Determination of water in gases			
Sample	Gaseous samples e.g. nitrogen	Purge the gas into the titration vessel	Constant flow rate
	No side reaction with the KF reagents e.g. liquefied petroleum gas		

Troubleshooting: The most frequently asked questions

The drift does not decrease to a low and stable value even after 1-2 hours. Any hints?

The air humidity is the big enemy of a Karl Fischer titration! Measures are implemented to reduce the influence of air moisture on the KF reaction. More specifically, the penetration of air humidity in the titration vessel has to be limited by checking the following points:

- Connections to openings of the KF titration vessel have to be greased i.e. tube inserts, electrode, adapters, septum and generator cell (KF coulometer), as well as stoppers.
- Use dry and fresh molecular sieve and silica gel in the drying tubes to ensure an efficient absorption of moisture from the air.
- KF coulometer: the ceramic frit of a generator cell with diaphragm has to be dry.



Figure 12: Grease and tighten all connections (green arrows)

Explanation:

During pretitration, the titrator adds (generates) iodine to react with water present in the KF solvent. When the KF solvent is dry, the titrator switches from pretitration to stand-by mode. At this point, the online drift is still too high to start a sample analysis. In general, it takes additionally 20-30 min to get a low and stable drift value of 10 µg/min.

To decrease the drift value it is also important to use fresh drying agents in the drying tubes. We recommend exchanging molecular sieves every 6 weeks. The molecular sieves are regenerated by drying them in the oven overnight at e.g. 250-300°C (check product data sheet).

Furthermore, if you use a cell with diaphragm, wash the diaphragm with dry methanol and store it for at least one night in an oven at max. 80°C, or at a well-ventilated place to evaporate water trapped inside the ceramic diaphragm.

Solution:

How to quickly achieve low and stable online drift values

1. Work in suitable working spaces (low humidity, room temperature, no strong ventilation)
2. Check tightness of the system
3. Use fresh KF reagents, solvents and molecular sieve
4. Regularly renew and dry exhausted molecular sieve
5. Gently shake the titration vessel to collect traces of water from the glass walls
6. Coulometric generator cell: Dry it in the oven if the ceramic frit is too wet (max. 80°C)

What to do if after 20-30 min the online drift is still too high e.g. 20-30 µg/min
Check again points 1.-6. (1.-7.)

What is the smallest amount of water that can be determined by Karl Fischer titration?

In volumetric KF titration, this mainly depends on

- The equipment used,
- The burette size,
- The KF titrant concentration, and
- The sample size.

A KF Compact Volumetric Titrator can determine the smallest amount (LOD) of 62.5 µg water in a 5 g sample, using a 5 mL burette with a 5 mg/mL KF titrant. This corresponds to a water content of 12.5 ppm under optimal conditions.

A KF Compact Coulometer can determine the smallest amount of 10 µg water. This corresponds to a water content of 1 ppm for a 10 g sample – under optimal working conditions.

	KF Volumetric Titrator	KF Coulometer
Theoretical smallest increment	Resolution: 20'000 burette steps 5 mL burette: 0.25 µL 5 mg/mL: 1.25 µg H ₂ O/step	0.1 mC (100 mA x 1 ms) Theoretical: 0.01 µg H ₂ O Resolution: < 0.1 µg H ₂ O
Limit of detection (LOD)	50 x resolution 5 mL burette: 12.5 µL 5 mg/mL: 62.5 µg H ₂ O Example: 5 g sample → determination of 12.5 ppm	10 µg Example: 10 g sample → determ. of 1 ppm Assumptions: - Current is used for iodine generation - Iodine is reacting with water only.

Explanation:

The highest dosing accuracy is reached when the titrant consumption is within 10-90% of the absolute burette volume.

Hence, the most accurate results will be obtained using half of the burette volume for one titration. For instance, best results for a sample with an expected water content of 5% are achieved if you use a sample size of 0.25 g in combination with a 5 mL burette and a 5 mg/mL KF one-component titrant.

If the water content is very low e.g. 0.1%, a much bigger sample size is required to obtain best results, or the sample has to be titrated by a KF Coulometer.

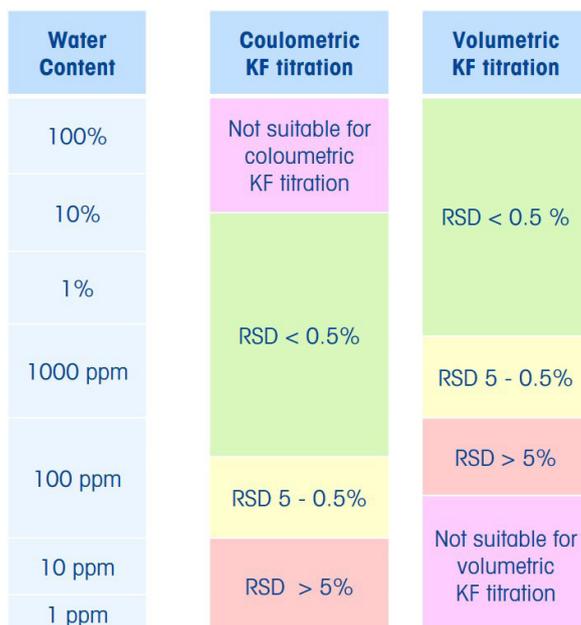


Figure 13: Suitability of KF coulometric and volumetric titrators.

Is it mandatory to check the concentration of a new Karl Fischer titrant bottle?

Indeed, it is always necessary to determine the concentration of the Karl Fischer titrant since the value printed on the label is a nominal value, and not the current concentration. Thus, if one calculate the water content using the nominal titrant concentration after a sample determination, the result will not be accurate. The determination procedure is shown in a short film under [Determine titrant concentration - Karl Fischer Titrator - YouTube](#).

Explanation:

The concentration of e.g. the one-component 5 KF titrant is always slightly higher than 5 mg/mL to allow for a longer storage time of the bottle. Moreover, the titer is always changing with time even in a closed bottle due to air moisture still penetrating into the bottle.

The concentration value indicated in the Certificate of Analysis is determined just after production of the reagent. As soon as you open the bottle, air humidity reacts with it, thus decreasing its value. Hence, it is necessary to perform a concentration determination value.

Note that the concentration determination using reference materials is a straightforward way to verify the correct working of the whole titration instrument.

Solution:

Once the new KF titrant bottle has been connected to the titrator, a concentration determination is performed using

- 1 mg H₂O/g and 10 mg H₂O/g liquid water standards
It is recommended to work with liquid water standards for the concentration determination of the KF titrants due to their straightforward use.

- Sodium tartrate dihydrate (15.66 % water content)
Use a sample size of 50 mg for each titration, and exchange the KF solvent after performing three determinations in the same solvent i.e. max. 150 mg.

- Pure water (100% water content)
It is not recommended to use pure water since the weighing uncertainty is too high due to the very small amount of water needed (10-30 mg). Thus, the accuracy and repeatability are strongly affected by it.

The concentration value affects the speed of the Karl Fischer reaction: in fact, the titration time is increased with decreasing titrant concentration.

To achieve optimum titration time, it is recommended to define tolerances for the concentration determination:

- 5 mg/mL: min. 4.5 mg/mL
- 2 mg/mL: min. 1.5 mg/mL

Parameter	Value	Action
Titrant	KF 1-comp 5	Info
Nominal conc.	5 mg/mL	Info
Standard	Water-Standard 10.0	Menu
Entry type	Weight	Dropdown
Lower limit	0.0 g	123
Upper limit	2.0 g	123
Temperature	25.0 °C	Info
Mix time	10 s	123
Autostart	<input checked="" type="checkbox"/>	
Entry	After addition	Dropdown
Conc. lower limit	4.5 mg/mL	123
Conc. upper limit	5.6 mg/mL	123

Which water standards do you recommend for the concentration determination?

The use of liquid water standards is strongly recommended since they allow for seamless determination of the KF titrant concentration.

Two liquid water standards for the volumetric KF titration are commercially available with a concentration 10 H₂O mg/g and 1 mg H₂O/g. Ready-to-use titration methods developed for these standards are stored in the KF titrator, hence no additional steps are needed.

Explanation:

Beside liquid water standards, also certified solid standards are available for the concentration determination of the KF titrants. The reference material of choice is sodium tartrate dihydrate, an organic compound with an exact water content of 15.66%. Briefly, water is tightly bound in the crystal structure of sodium tartrate. The dissolution in the KF solvent allows for release of water from the structure, and thus water can be subsequently titrated.

However, sodium tartrate dihydrate is only partially soluble in the KF solvent, hence the solvent must be replaced as soon as it becomes turbid when titrating several samples:

- Max. 0.15 g sodium tartrate in 40 mL KF methanolic solvent i.e. max. three samples of each 0.05 g can be titrated in the same solvent.
- Max. 0.05 g sodium tartrate in 40 mL KF methanolic i.e. after one sample of 0.05 g sodium tartrate the solvent should be replaced.

Hence, the best results and most convenient use will be obtained with the liquid water standards. In fact, liquid standards are soluble in most solvents without any problem when compared to sodium tartrate. When using liquid standards, you can even perform six determinations in the same solvent. Moreover, you get a lower standard deviation and the analysis time is much faster since no long stirring time is needed as for a solid water standard, which requires a stir time of 120-180 s prior titration.

It is also possible to perform the concentration determination using pure water. However, the accuracy is strongly affected due to very small sample size used i.e. 10-30 µL. Thus, the influence of sample handling will be highly increased. As an example, if you lose e.g. 5 µL of your 10 µL pure water sample, then there will be a huge error of 50%. On the other hand, the sample size with liquid standard is in the order of 1000 µL, and therefore a loss of 5 µL is not so relevant as in the case of pure water.

Solution:

How to perform the titer determination of a KF titrant:

1. Flush the whole system i.e. the burette and tubes three times, and discard the dispensed reagent using the manual operations of the titrator. This will remove any bubbles in the tubes and also guarantees that the titer in the dosing unit and also in the tubes will be the same.
2. Use the 10 and/or 1 mg/g liquid water standard for the concentration determination.
3. If the ambient conditions are changing during the day, e.g. due to a humidity increase and/or a temperature increase by more than 3-5°C, the concentration determination must be repeated.

Are liquid water standards hygroscopic?

Certified liquid water standards consist of an exact amount of water dissolved in a solvent mixture. The composition of the water standards has been optimized to reduce the absorption of air humidity. In any case, Good Titration Practice (GTP) strongly recommends not to leave the ampoules open with liquid standard inside. The liquid standard should be completely aspirated and transferred from the ampoule in a gas-tight syringe (e.g. a glass syringe).

Explanation:

Every solvent that is exposed to air may absorb humidity until saturation is reached i.e. until chemical equilibrium between the liquid and the gaseous phase is achieved. The amount of water absorbed from the air in the liquid standard mainly depends on the

- Relative humidity of air,
- The polarity of the solvent, and
- The temperature

Solvents such as

- Ethanol, methanol and isopropanol i.e. alcohols (R-OH),
- Acetone $\text{CH}_3\text{-CO-CH}_3$ and methyl isobutyl ketone MIBK i.e. ketones (R₁-CO-R₂)
- Diethyl ether $\text{CH}_3\text{CH}_2\text{-CO-CH}_2\text{CH}_3$ and tetrahydrofuran $(\text{CH}_2)_4\text{O}$ i.e. ethers (R₁-O-R₂)

easily absorb water from the air due to the presence of oxygen atoms in their chemical structure leading to electrical polarity. The water molecule H_2O is strongly polar, where the oxygen atom O is negatively charged and the two hydrogen atoms H are positively polarized. Thus, water is easily absorbed in a polar solvent because polar substances tend to mix up.

On the other hand, solvent like toluene $\text{CH}_3\text{C}_6\text{H}_6$ and chloroform CHCl_3 are weakly polar or even non-polar. Hence, the absorption of water is extremely small.

By selecting suitable solvents for the production of the water standards, the stability of these standards can be optimized.

Solution:

How to use a liquid water standard

1. Open the glass vials containing 5-6 mL of water standard
2. Aspirate 0.5-1 mL liquid standard into the syringe
3. Pull the piston to the maximum position
4. Shake the syringe to wash the inner wall
5. Discard the liquid standard
6. Aspirate the whole content from the glass vial
7. Start the concentration determination.

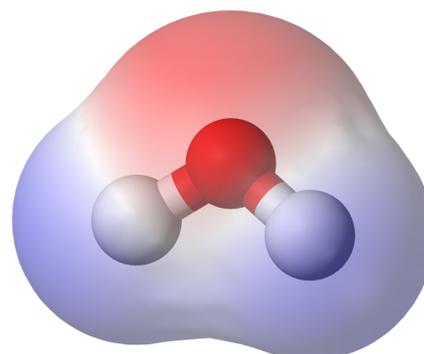


Figure 15: The water molecule H_2O contains two strong polar chemical bonds between hydrogen H and oxygen O atoms. The negative electrical charge shifts towards the central red oxygen atom.



Figure 16: Aspirate the whole content in the syringe.

How often should the concentration of the KF titrant be determined?

The Karl Fischer titrant is very sensitive to air humidity; thus, its concentration must be determined every time before determining the water content of a sample by volumetric Karl Fischer titration. The procedure of the concentration determination for KF titrants is shown in a short film under [Determine titrant concentration - Karl Fischer Titrator - YouTube](#).

Explanation:

The determination of the titrant concentration is a crucial step in titration workflow. Without knowing the exact concentration it is not possible to achieve correct results. Thus, the determination must be performed at least every time before starting a series of measurements. Moreover, KF titrants are sensitive to air humidity and their concentration slowly decreases with time – even if the titrant bottle is tightly closed. It is estimated that the decrease in concentration of the KF titrant is in the order of -0.1 mg/mL per week.

Therefore, depending on the ambient conditions, the concentration of the KF titration have to be determined more frequently. For instance, if the temperature and humidity are changing a lot during the day, it is necessary to repeat the determination even during the daily routine.

How do you determine the titer for the coulometric KF reagent?

It is not necessary to determine the concentration of the coulometric KF reagent since coulometry is an absolute method because the amount of current used to generate iodine by electrochemical processes is directly measured by the electronics in the titrator. Thus, the generated current does not have to be compared to any reference material.

Explanation:

The amount of electrical charges (Coulomb, C) needed for the iodine generation is used in the calculation of the water content through the Faraday constant (96847 C/mol). It is required that the generator and electronics in the instrument are correctly working to achieve accurate results.

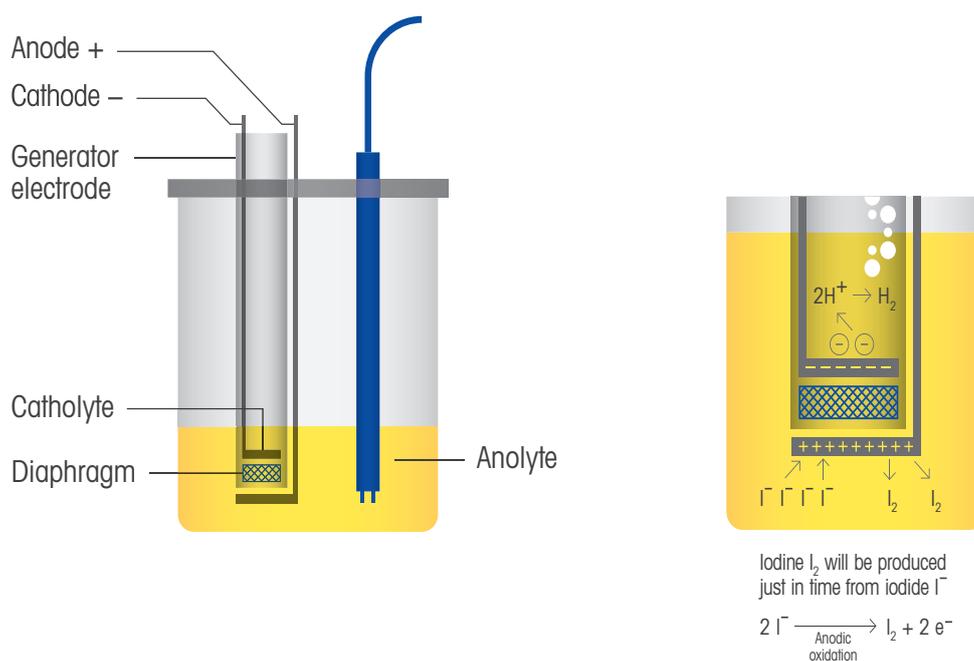


Figure 17: Working principle of the coulometric determination of water by KF titration.

Calculation of the water content:

- 96487 C are required to produce 1 mol of a chemical compound with 1 mol of electrons.
- Iodine I_2 is generated from two iodide ions I^- by oxidation at the anode of the generator cell.
- 1 mol I_2 reacts with 1 mol H_2O , i.e. 1 mole H_2O (18 g H_2O) is equivalent to 2×96487 C.
This corresponds to 10.712 C/ mg H_2O (Assumption: 100% electrochemical conversion).

It is recommended to periodically verify the performance of the KF coulometer. This is achieved by checking the recovery (%) of certified liquid water standards 1 and 0.1 mg H_2O/g .

The verification with standards is outside the uncertainty in the certificate of analysis. Any suggestions?

In general, if the results are outside the tolerances stated in the certificate of analysis (CoA) of the water standards or they differ too much from the certified value, there is nothing left but to systematically check the whole titration system step-by-step to limit or suppress the influence of all possible sources of uncertainty. Additionally, most errors come from handling problems, especially when working with the lowest water standard with 0.1 mg/g (100 ppm).

Explanation:

The measurement uncertainty indicated on the CoA of the water standard e.g. $0.99\% \pm 0.02\%$ only indicates the uncertainty of the specific water standard measured just after production at the production site of the provider of liquid standards. Thus, it indicates the calibration uncertainty of the water standard obtained at production plant of the provider.

This means that the uncertainty of the CoA refers only to the conditions of content determination at the provider's site, i.e. to the analytical methods, instruments procedures, standard operating procedures SOPs, ambient conditions etc. used at provider's site. The uncertainty value is only valid under the same working conditions and instruments at the provider's site. However, this is never the case, and thus it is not related to the result uncertainties of measurements. Therefore, it is not correct to state that a value is wrong if it outside the tolerances of the CoA.

To assess if a measurement is acceptable or not, note that the providers of reference materials give recommendations, as given below:

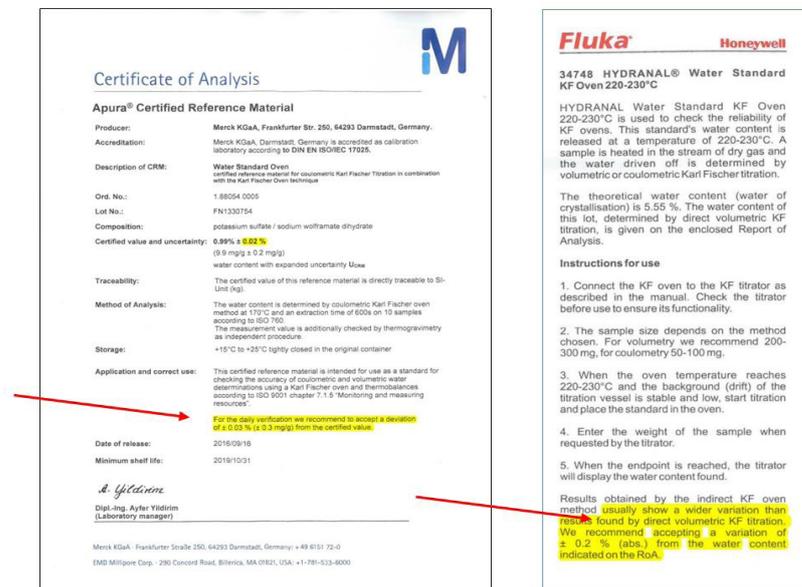


Figure 18: Certificates of analysis (CoAs) indicating both a) the calibration uncertainty of the water standard determined after production at provider's site, as well as b) recommendations for the assessment of tolerances for the determination of water by KF titration.

Solution:

How to reduce handling errors:

Most errors come from handling problems, especially with the low water standards that have only 100 ppm. It is recommended to use airtight glass syringes with long needles since glass is not absorbing air moisture as plastic:

1. Shake the liquid standard glass ampoule before opening it.
2. Snap of the top tag of the ampoule.
3. Rinse the needle and the plunger by taking approx. 0.5 mL standard into the syringe. Avoid taking any air into the syringe while doing this step.
4. Discard the solution and do not pull the plunger up and down.
5. Wipe the needle dry and draw the rest of the standard immediately into the syringe.
6. Remove any air bubble from the syringe and wipe the needle dry. Now your standard is well protected and ready for use.
7. Add an aliquot to the titration vessel by back-weighing, and carry out the titration.
8. Before further use, remove few drops of standard from the tip of the syringe and wipe the needle dry again.

Suggestion:

How to define the tolerances for your measurements:

Use the limits recommended by the providers of the water standards as highlighted in yellow at the end of the certificates in figure 18, and also of additional documents related to the standards.

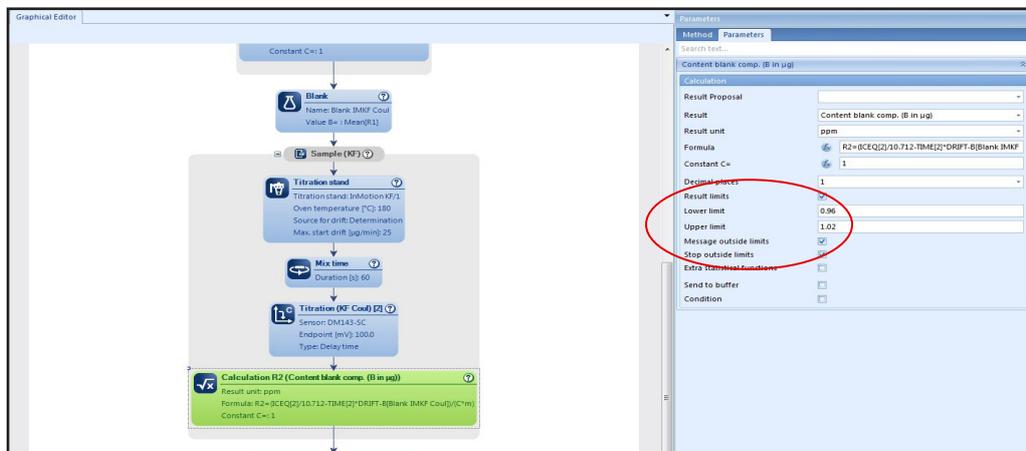


Figure 19A: Definition of result limits in the method function "Calculation".



Figure 19B: Warning message on the titrator display if the result is outside the limits.

What do you do if the result is not correct?

It is expected that the titrator has been adjusted and its performance verified with water standards. Thus, the most important point to be checked is related with the applied sample preparation i.e. if the sample preparation has achieved a complete release of water from the sample matrix. In other words: Has all water been released from the sample? Is it completely dissolved in the KF solvent?

Explanation:

For a successful water content determination by the Karl Fischer titration, the sample needs to be fully dissolved or dispersed to completely release water. Moreover, no side reactions should take place, and the correct pH for the KF reaction should be between 5.5 and 8.

For example, the determination of water content in lubricants requires the use of a KF oven to evaporate water, since the additives present in these samples lead to side reactions that affect the result. Thus, a direct titration is not the method of choice. In fact, the direct injection of oil samples containing additives such as thiols R-SH lead to higher results because the thiol group R-SH reacts with iodine giving an erroneous higher consumption.

Note that there are also some oils and lubricants without additives, therefore they can be titrated by direct injection in a mixture consisting of the KF solvent and auxiliary solvents such as e.g. chloroform facilitating the dissolution of the oil samples.

The KF Titration is only possible if water is freely available

■ Samples contain water as :

- Entrapped water
- Crystal water
- Surface/adherent water
- Capillary bound water

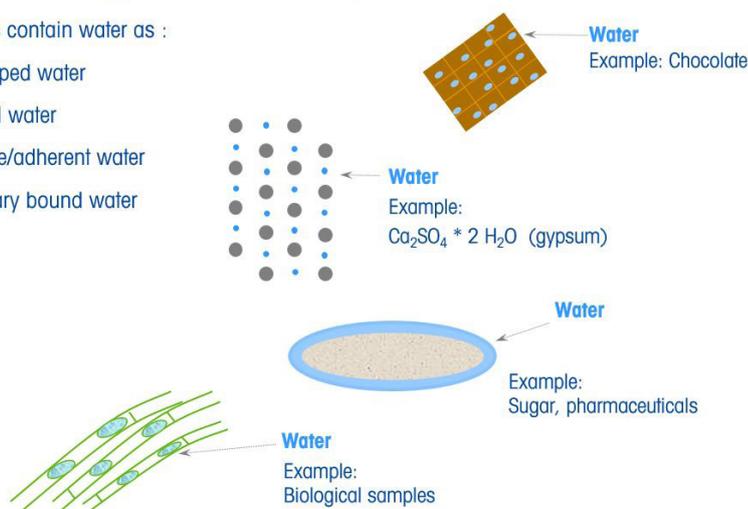


Figure 20: Water is bound to the sample matrix and it has first to be released before starting the KF titration.

Solution:

Always select the suitable sample preparation first

In general, deviations from the expected results are due to incomplete release of water from the sample. Depending on the sample nature, there are different preparation techniques for the complete release of water as well as for the handling of the sample:

1. Direct titration
2. Internal extraction (inside titration cell)
3. External extraction
4. External dissolution
5. Gas-phase extraction
6. Water content in gases

How long should the stand-by take until the online drift reaches a low level?

In general, the stand-by (or conditioning) of the KF titration cell should take no longer than 20- 30 minutes to reach low online drift values. This can be achieved if the KF coulometric electrolyte or the KF volumetric titrant and solvent used are fresh and the titrator is well tight, i.e. all apertures and connections of the cell are slightly greased, correctly assembled and tighten.

To decrease the online drift value it is also important to use fresh drying agents in the drying tubes. We recommend exchanging molecular sieves every 6 weeks. Furthermore, if you use a cell with diaphragm, wash the porous ceramic diaphragm with dry methanol and store it at least for one night in an oven at max. 80°C, or at a well-ventilated place to evaporate water trapped inside the ceramic diaphragm.

Explanation:

After assembling and filling the titration cell, the pretitration is started to eliminate the water present in the KF solvent or the coulometric electrolyte. When the solvent is dried, the titrator switches from pretitration in the stand-by mode. However, at this point the online drift is generally still too high to start a sample analysis.

During stand-by, the online-drift is slowly but continuously decreased since the titrator automatically reacts to any potential change caused by the presence of humidity e.g. from air. This step may require 20-30 minutes in general.

To speed up the process, it is beneficial to gently shake the titration vessel in order to efficiently collect traces of water adsorbed on the glass wall of the titration cell.

Low drift values are necessary to achieve accurate and precise results. The following table gives indicative values that can be reached with a KF titrator:

	Suitable online drift for titration start
KF Volumetric Titration	1 - 10 µg/min
KF Coulometric Titration	1 - 5 µg/min

Solution:

How to achieve low drift values

1. Work in suitable working spaces (low humidity, room temperature, no strong ventilation)
2. Check tightness of the system
3. Use fresh KF reagents, solvents and molecular sieve
4. Regularly renew and/or dry exhausted molecular sieve
5. Gently shake the titration vessel to collect traces of water from the glass walls
6. Coulometric generator cell: Dry it again in the oven

What to do if after 20-30 min the online drift is still too high e.g. 20-30 µg/min
Check again points 1.-6. (1.-7.)

The online drift is still very high after titration end. How can this problem be solved?

A too high drift value e.g. 60 µg/min after sample titration can be attributed either to

1. Side reactions with the KF reagents, or
2. The sample is not completely dissolved,
3. Water is not completely released.

Thus, either special KF reagents have to be used, or the sample must be heated with the KF oven, or the sample preparation has to be improved to achieve the complete release of water.

Explanation:

Side reactions are caused by interfering chemical reactions between the sample and the KF reagents. Most of these side reactions can be almost completely suppressed by using special KF reagents. For instance, in the case of samples containing ketone groups e.g. R_1-CO-R_2 , the use of so-called K-reagents allows to achieve correct results by suppression of the side reactions.

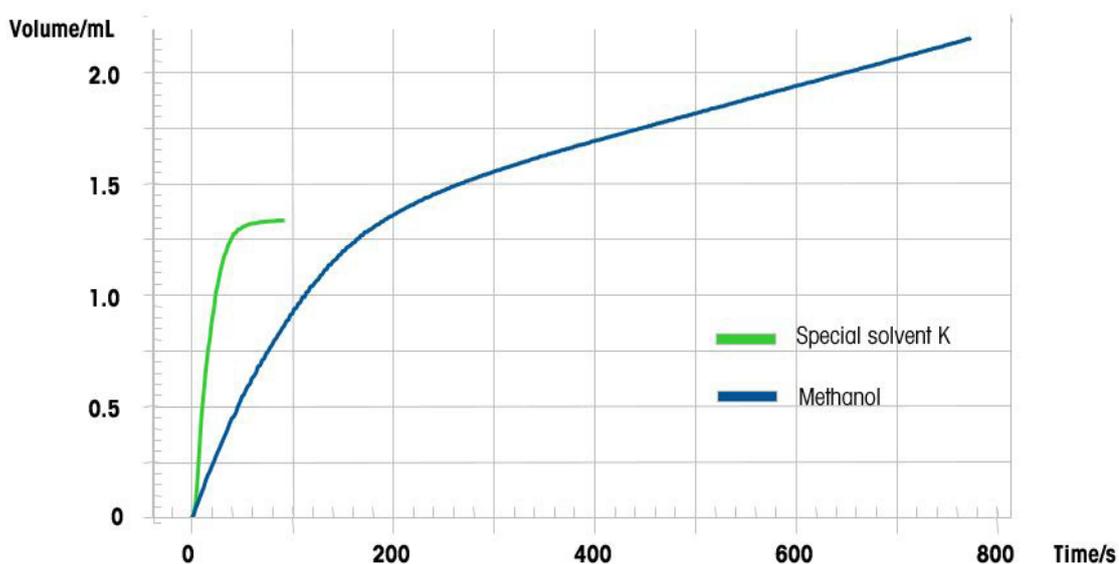


Figure 21: KF titration of 5 mL acetone using two different solvent: blue line - classical KF solvent, green line - solvent for ketones and aldehydes. The titration in methanol is not stopping even after 600 due to side reactions.

Another possibility to avoid side reactions is to heat up the sample in a KF oven and thus to evaporate water to be titrated in the KF vessel.

In many cases, a longer stir time, a higher stir speed and the use of selected auxiliary solvents have proven to be very beneficial to improve dissolution or extraction allow for complete release of water.

Solution:

Improve the sample preparation techniques

1. Select the correct KF reagent to avoid side reactions
2. Evaporate the water from the sample in a KF oven
3. Optimize the stir time, the stir speed and the use of auxiliary solvents to improve sample dissolution or water extraction from sample matrix.

Sometimes we get negative results when using the automated KF oven – Why?

The KF instrument always determines the total amount of water present in the titration vessel, i.e. the water present in the sample, the air humidity entering the vessel with time (drift) as well as adherent water on the glass surface of the sample vials (blank).

Drift and blank values are subtracted from the total amount of water. If the sum of both contributions are bigger than the total amount of water, then the result becomes negative.

Explanation:

To calculate the water content of the sample, the contributions due to the air humidity (i.e. the drift) and – where needed - of the adherent water on inner surfaces of the vials (i.e. blank value) have to be subtracted from the determined water amount:

$$\text{Volumetric KF titration: } \text{Water content (\%)} = \frac{(VEQ \times CONC - \frac{B(\text{Blank})}{1000} - \frac{TIME \times DRIFT}{1000})}{M \times 0.1}$$

VEQ: KF Titrant consumption mL

CONC: KF titrant concentration mg/mL

B[Blank]: Blank value μg

TIME: Titration time min

DRIFT: Drift value $\mu\text{g}/\text{min}$

m: sample mass g

1000: Conversion factor from μg to mg

0.1: Conversion factor from mg/g to %

$$\text{Coulometric KF titration: } \text{Water content (\%)} = \frac{(\frac{ICEQ}{10.712} - B(\text{Blank}) - TIME \times DRIFT)}{M \times 10000}$$

ICEQ: Current consumption mC

B[Blank]: Blank value μg

TIME: Titration time min

DRIFT: Drift value $\mu\text{g}/\text{min}$

m: sample mass g

10.712: Conversion factor from mC to μg

water ($96485.33 \text{ C/mol} \cdot 2 (\text{I}_2) / 18 \text{ g/mol} / 1000$)

10000: Conversion factor from $\mu\text{g}/\text{g}$ to %

Solution:

1. Drift:

- Start the KF titration only when the online drift is very low e.g. below $5 \mu\text{g}/\text{min}$. It may be necessary to wait at least 15-20 min in stand-by to achieve low drift values.
- Take into account or the drift by determining the blank using the same heating time as for the sample. In this case, the drift value is set to $0 \mu\text{g}/\text{min}$.

2. Blank value:

- Use dry glass vials – previously dried in an oven,
- Perform the blank determination for at least three vials, and calculate the average
- Be sure that the inert gas used is correctly dried

3. Heating time:

Do not use too long heating time for the sample determination: a too long time increases the influence of the drift value. Recommendation: 10-30 min.

Literature

"GTP Brochure – Good Titration Practice in Karl Fischer Titration", METTLER TOLEDO Brochure No. 51725145, October 2014.

"METTLER TOLEDO Methods for Water Content Determination", Titration Applications Brochure No. 38, ME-51725075B, August 2012.

"Karl Fischer Titration with a Homogenizer – Practical Examples", Titration Applications Brochure No. 27, ME-51725053B, April 2013.

"Validation of Titration Methods - A Guideline for Customers", Titration Applications Brochure No. 16, ME-51724912C, March 2017.

"Selected Applications with Karl Fischer Oven Autosampler", Titration Applications Brochure No. 49, 30452052, November 2017.

Links

[InMotion Karl Fischer Titration Oven Autosampler - METTLER TOLEDO – YouTube](#)

[Volumetric KF Titration - Tutorial - YouTube](#)

[Coulometric KF Titration - Tutorial - YouTube](#)

[Determine titrant concentration - Karl Fischer Titrator – YouTube](#)

[Automated Titration of the Water Content in Candies – YouTube](#)

This application bulletin represents selected, possible application example. These have been tested with all possible care in our lab with the analytical instrument mentioned in the bulletin. The experiments were conducted and the resulting data evaluated based on our current state of knowledge.

However, the application bulletin does not absolve you from personally testing its suitability for your intended methods, instruments and purpose. As the use and transfer of an application example are beyond our control, we can not accept responsibility therefore.

When chemicals and solvents are used, the general safety rules and the directions of the producer must be observed.

Titration Guide

Tips and hints for a successful water content determination by Karl Fischer Titration

This Titration Competence Guide is dedicated to the water content determination by Karl Fischer (KF) titration. Focus has been put on the practical aspects rather than on theoretical knowledge.

After a short introduction on Karl Fischer titration, the main points affecting result accuracy such as low drift determination, tightness of the instrument, fresh KF reagents and specific sample preparation will be presented in detail. In addition, frequently asked troubleshooting questions will be presented and answered.

Several KF applications have been developed by the Market Support Group Analytical Chemistry. They are available for download on the METTLER TOLEDO website www.mt.com.



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