

Karl Fischer Titration



KF Guide 3

The Right Sample

Taking Samples for Karl Fischer Titration

METTLER  **TOLEDO**

Editorial

Dear Reader

Taking the right sample in the right way is a prerequisite to obtaining accurate and reliable results. In the case of water and moisture content determinations, avoiding water absorption from atmospheric moisture, sampling tools or sample vials and vessels is a paramount sampling objective.

Different sampling techniques have been developed to accommodate the varying nature of samples since the first Karl Fischer titrations were carried out in 1935.

This brochure explains some important rules and guidelines for drawing samples to determine water content according to Karl Fischer. Our tips and tricks incorporate the experience of METTLER TOLEDO's application chemists and are well proven through daily practice and application.

Rely on good sampling techniques as the starting point of reliable results.

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1. Sampling

1.1 Taking the sample

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:

1. The sample must be representative, i.e. it must contain the same average amount of water as the material as a whole.
2. The sample should be taken quickly to exclude, or at least minimize, the absorption or release of moisture.
3. Heterogeneous water distribution in samples:
In 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.
In the case of 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.
4. Hygroscopic solids may exhibit higher water content on the surface than inside if they have absorbed atmospheric moisture during storage.
5. 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.

1.2 Storing the sample

After you have taken the sample, you should determine its water content **as soon as possible**. If you have to store the sample, keep it in a tightly sealed bottle:

- Glass bottles are preferable to plastic bottles because plastic is not completely gas-tight, and thus air moisture can penetrate the plastic and be absorbed by the sample.
- Use sample bottles with small openings to minimize the ingress of moisture.
- Use bottles with a septum stopper for liquids of very low water content.

- Use a bottle with an optimum volume for the amount of sample: the smaller the gas space above the sample, the lower the amount of moisture.
- With **liquid samples**, rinse the bottles two or three times with the sample beforehand.

With liquid samples that do not dissolve water such as oils, water may be separated from the sample if it is left to stand for a long time. This can happen when a sample cools and the water solubility is decreased. In such cases, the solubility of water in the sample can be increased using a solubility promotion agent such as 2-propanol.

1.3 Amount of sample

The amount of sample used depends on

- the expected water content, and the
- required accuracy and precision.

For **coulometric analyses**, the optimum amount of water is in the range from **0.5 to 2 mg** water per sample. Repeatable results can be obtained even with 0.1 mg water per sample. Under optimum measurement conditions, approx. 10-50 µg water can be detected if the demand for repeatability is not too high.

In general, the accuracy is improved if larger sample amounts are used, because the absorption of atmospheric moisture during sampling or sample addition becomes less important.

For optimum accuracy with determinations in the range from **1 ppm to 1% water**, it is recommended to use the minimum sample size given in the following table:

Water content [ppm]	1	10	50	100	500	1000	5000	10000 = 1%
Min. sample size [g]	10	8	5	4	2	1	0.2	0.1
Amount of water [mg]	0.01	0.08	0.25	0.4	1.0	1.0	1.0	1.0

For **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.

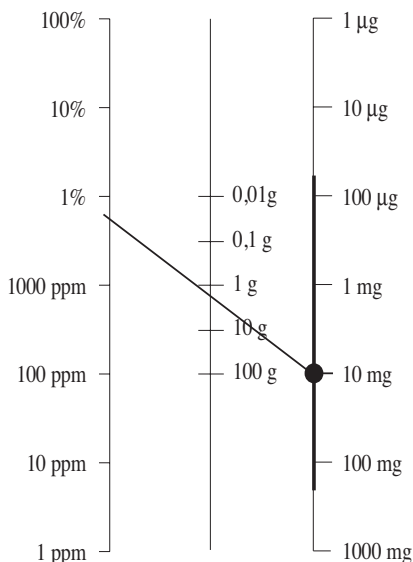
If a high level of accuracy is required, the amount of sample should require a titrant consumption between **30 and 70%** of the nominal burette volume. This corresponds to 7.5 to 17.5 mg water per sample for a 5 mL burette with a titrant concentration of 5 mg/mL.

Water content determinations below 1000 ppm are not required to be quite as accurate: a relative standard deviation s_{rel} 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

Determination of the amount of sample for a water content in the range from 1000 ppm to 100%



Principle:

The recommended sample size can be determined as a function of the expected water content for optimum KF analysis.

Procedure:

- Start from the optimum point (10 mg for volumetric KF, 1 mg for coulometric KF) or the recommended range
- The optimum point is connected by a straight line to the expected water content.
- The intersection point of this line with the "Amount of sample" scale represents the recommended amount of sample to be used.

Note: Logarithmic scale!

Example:

Expected water content:	5000 ppm
Optimum amount of water:	10 mg/sample
Optimum sample amount:	2 g

The Compact volumetric and colometric KF titrators support the user with a sample size calculation routine, which is accessible in the online titrations screen:

Suggested sample size		Tasks 
Sample 1/1 » KF functions » Sample size		
Determination	Sample	▼
Content	5	¹ 2 ₃
Unit	%	▼
→ Lower limit	0.15 g	
→ Upper limit	0.35 g	
Cancel Calculate OK		

Dependent on the expected water content, an optimum sample weight range is recommended.

2. Sample Addition

2.1 Liquid samples

When adding liquid samples, you must take suitable precautions to prevent atmospheric moisture from being absorbed, especially with samples of low water content. The following procedures are suitable for the different types of liquid samples:

Sample characteristics	Examples	Procedure
High water content Low viscosity	perfumes, aqueous emulsions, alcoholic beverages	Inject the sample into the titration vessel either through a septum (KF coulometer) or through the needle hole in the three-hole adapter (volumetric KF titrator) using a 1 mL syringe with needle.
Low water content Low water content Hygroscopic	methanol, edible oils hexane, toluene, benzene	Store the sample in a bottle with a septum stopper to avoid moisture absorption from the air. Rinse a 10 mL syringe 2-3 times with the sample Inject the sample using a 1 mL or 10 mL syringe through a septum cap.
Viscous	glycerol, hydraulic oils, silicone oil, mineral oils massage oil	Inject the sample using a 5 or 10 mL syringe with a thick needle into the titration cell. Possibly warm the sample slightly to lower the viscosity. In the case of a volumetric Karl Fischer titrator, you can use a syringe without needle since the sample can be added via the larger hole of the three-hole adapter.
Very viscous	ointments, creams, yoghurt, honey	Fill the 5 or 10 mL syringe with sample after removal of the piston. Inject it into the cell using a wide-bore needle. In the case of a volumetric Karl Fischer titrator, you can use a syringe without needle since the sample can be added via the larger hole of the three-hole adapter.
Waxy	candle wax, paraffin, ski wax, suppositories	Liquefy the sample in an oven at approx. 50 °C and fill it into a syringe. The syringe is heated together with the wax. This prevents the sample from solidifying in the syringe during the weighing.



a



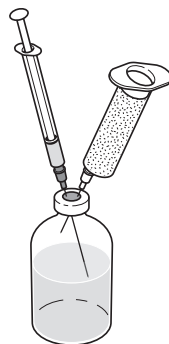
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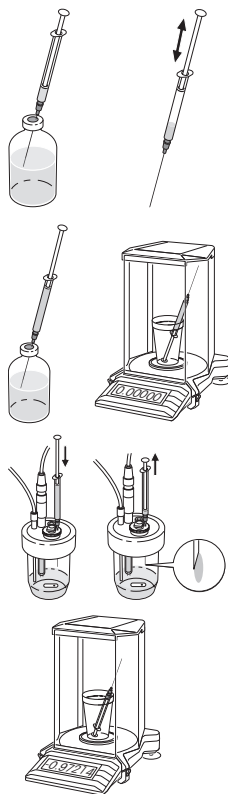
Taking samples from a bottle with septum stopper

After several samples have been taken, a vacuum develops in the bottle with septum stopper and it will no longer be possible to take a sample aliquot. To avoid this, you must aerate the bottle with dry air (equalize the pressure). Fill a syringe without a plunger with molecular sieves, seal it with cotton wool and insert it into the septum bottle using a short needle. Air flows through the molecular sieve into the bottle when you take a sample aliquot.



Sample addition of liquids with the back weighing technique

- Fill the syringe to a quarter with sample. If the sample is hygroscopic or has a low water content (< 1000 ppm), use bottles with a septum stopper and pressure equalization.
- Withdraw the plunger and rinse the syringe with the sample by shaking it.
- Empty the syringe (into the waste bottle) and repeat the rinsing two or three times.
- Fill the syringe with sample and wipe the needle with a paper tissue.
- Place the syringe (upside down) in a beaker on the balance pan and tare the balance to "0".
- Start the titration method by pressing the <Start> button.
- Inject the sample into the titration cell through the septum stopper.
- Withdraw the plunger so that the drop at the tip of the needle is sucked back into the needle. Otherwise when the syringe is removed, the drop will adhere to the septum.
- Replace the syringe with the remaining sample on the balance and back weigh it.
- Enter the sample size in the titrator or transfer it automatically.
- Start the titration.

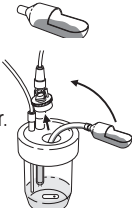


2.2 Solid samples

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

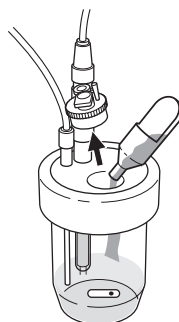
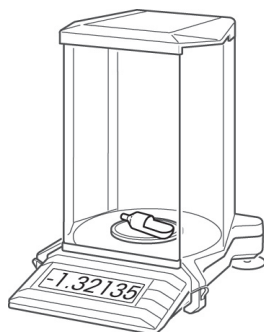
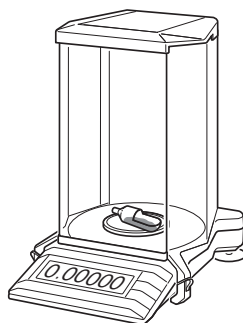
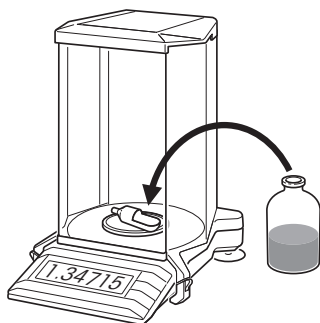
On the other hand, in a **volumetric KF titrator** solids can be directly transferred into the titration vessel. The sample should be quickly weighed and added to minimize air exposure. If possible, it should be added under the same conditions as it was transported and stored. For instance, the storage 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.

Sample characteristics	Procedure
Brittle Hard/soft Pourable	e.g. salts, crystalline samples: Weighing boat – Grind hard, coarse-grained samples in a closed, cooled analytical mill; pulverize less hard samples in a mortar. – Add the sample with a weighing boat. 
Finely powdered Dusty	– Use a weighing boat with an attached flexible tubing to add the sample: it prevents the sample from adhering to the wall of the titration vessel or to the electrode.
Finely powdered with very low water content	e.g. salicylic acid, cellulose powder: – Either weigh the sample in a dry box or extract it externally.
Soft	e.g. jellied fruits, jelly bears, almond paste: – Cut into small pieces with scissors or a knife and add the sample with a spatula.

Sample characteristics	Procedure
Hard, fatty	e.g. chocolate, solid fat: – Grate the product and add the sample with a spatula.
Soft, fatty, inhomogeneous	e.g. butter, margarine, edible fat: – Homogenize the sample well: the water is heterogeneously distributed. The water content is often lower at the surface than inside the sample. – Add the sample with a spatula. Do not use a syringe, because the water is released if it is pressurized
Waxy	e.g. candles, paraffin, ski wax, suppositories: – Liquefy the samples in a drying oven at approx. 50 °C and fill them into a syringe. – The syringe is heated up together with the wax. This prevents the sample from hardening inside the syringe during the weighing process
Creamy Highly viscous	e.g. chocolate cream, honey, sugar products – The METTLER TOLEDO Visco-Spoon™ simplifies the handling with creamy samples since it can be directly mounted into the titration stand. 

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 a weighing boat with attached flexible tubing if necessary, 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.

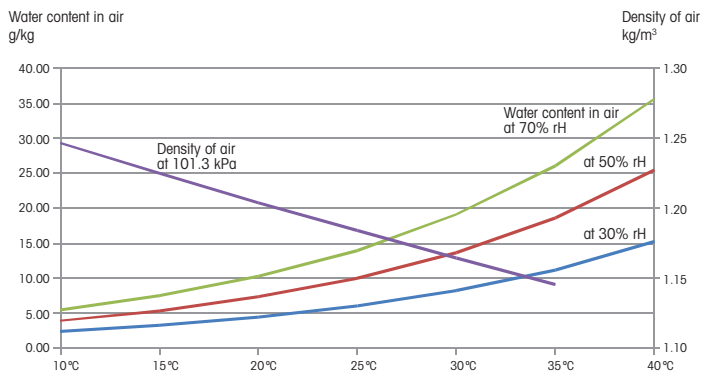


3. The Influence of Atmospheric Humidity

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!



Ambient air at 20 °C and 101.3 kPa contains water in the range of 5 - 10 g/m³ depending on the relative humidity (rH).

3.1 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, i.e. 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 Å 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.

3.2 The drift

No titration stand is completely water tight; traces of water will always find a way into the titration cell. 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. Therefore, 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).

In the standby titration, the KF titrator continuously titrates the water that diffuses into the cell, and its value is displayed on the screen. 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"**):

Source for Drift	Explanation
Online	Last measured value of standby
Determination	The drift is determined and stored as raw result DRIFT
Fix value	A fixed value is defined into method
Request	The value can be entered immediately after starting sample titration

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

4. More Information

4 .1 Literature HYDRANAL®- Manual, „Eugen Scholz Reagents for Karl Fischer Titration“, Sigma -Aldrich Laborchemikalien GmbH, D- 30918 Seelze / Germany, 2006.

SCHOLZ. E., „Karl Fischer Titration“, Springer Verlag Berlin, 1984.

WIELAND, G., „Wasserbestimmung durch Karl-Fischer-Titration – Theorie und Praxis“, GIT Verlag G mbH, Darmstadt / Germany, 1985.

4 .2 More guides METTLER TOLEDO has prepared a set of guides for the Karl Fischer titration. They explain basics, methods and techniques and provide tips and hints for the daily practice.

1	Introduction to Karl Fischer Titration
2	Sample Preparation for Karl Fischer Titration
3	Taking Samples for Karl Fischer Titration
4	The Method at a Glance

4 .3 Application brochure Many more details regarding the Karl Fischer titration are published in the application brochures

- Good Titration Practice™ in Karl Fischer Titration (ME 517252145).
- METTLER TOLEDO Methods for Water Content Determination, Application Brochure Nr. 38 (ME 51725075A).

Good Measuring Practices

For Balances, Titrators and Pipettes

METTLER TOLEDO's risk-based guidelines for titration, weighing and pipetting empowers you to take the right decision when and where it really matters. The five steps of Good Measuring Practices cover the entire lifecycle of your instruments and provide you with practical guidance to implement a sound quality management system.



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2. Selection

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4. Calibration & Qualification

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5. Routine Operation

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