

Karl Fischer Titration



KF Guide 2

Release the Water

Sample Preparation for Karl Fischer Titration

METTLER  **TOLEDO**

Editorial

Dear Reader,

The Karl Fischer method determines water content specifically and is easily applied to a huge variety of samples. It is a common standard method in R&D, quality control and production monitoring.

However, the method requires adequate sample preparation in order to release entrapped, capillary-bound or water of crystallization. The water molecules need to be 'freely available' in order to undergo the chemical reaction with the KF reagents.

This brochure uses METTLER TOLEDO's expert knowledge of Karl Fischer titration to explain more advanced sample preparation procedures than the simple sample dissolution in the titration cell.

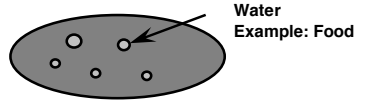
Apply these well-proven applications to your samples for quick, simple and accurate water content titrations.

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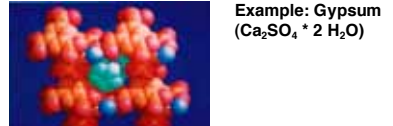
1. Release of Water from the Sample

1.1 Introduction Karl Fischer titration is only possible if the water in the samples is freely available. This is not the case with solids if the water is bound as, e.g.:

- entrapped water



- water of crystallization (salts)



- water of crystallization (salts)



- capillary bounded water
(e.g. in plants)



Thus, suitable sample preparations and special Karl Fischer methods are necessary to release water in these samples.

Sample preparation

First of all, it is necessary to crush insoluble solids in order to gain access to the trapped water. The following methods are available:

Sample characteristic	Procedure
Very hard	e.g. minerals, hard salts: Grind in a closed, cooled analytical mill.
Hard, brittle	e.g. inorganic salts, grain, noodles, coffee beans: Crush in a mixer.
Moderately hard, brittle	e.g. organic salts, crystalline products: Pulverize in a mortar.
Viscous	e.g. jellied fruits, almond paste ("marzipan"): Cut into small pieces with scissors or a knife.
Hard, fatty	e.g. chocolate, solid fat: Grate the product.
Soft, fatty	e.g. sausage, meat, cheese: Mince the product, then reduce it further with a homogenizer in an external solvent.
Fibrous natural products	e.g. dried fruit and vegetables, berries: Reduce with a homogenizer in an external solvent.
Suspensions	e.g. fruit juice extracts, vegetable juices: Reduce with a homogenizer.

1.2 Internal extraction

Internal extraction is suitable for **insoluble solids** that release water **quickly** when crushed:

- Add the crushed samples into the titration vessel, using either methanol or a mixture of it as the solvent.
- Water is then extracted providing the mixing time defined in the titration method is sufficiently long.

You can speed up the extraction of water from the sample by

- heating the solution with a thermostating titration beaker,
- grinding the sample additionally with a built-in homogenizer (see photos below).

In many cases, the homogenizer eliminates the need to use auxiliary reagents such as formamide with, e.g. hazelnuts, potato chips, sugar, etc.



Thermostatable vessel



High-speed homogenizer

Examples:

Sample	Result / %	srel / %	Solvent
Flour	12.1	0.4	Formamide:methanol 2:3 at 50 °C
Potato chips	4.8	0.8	Formamide:methanol 2:3 at 50 °C
Ground hazelnuts	4.8	1.2	Formamide:methanol 2:3 at 50 °C
Chocolate	1.3	1.1	Methanol / Homogenizer
Instant coffee	2.5	1.4	Methanol / Homogenizer
Dried chives	8.0	1.0	Methanol / Homogenizer
Dried tarragon	7.3	1.4	Methanol / Homogenizer
Aspirin	1.5	1.9	Methanol / Homogenizer
Sweetener tablets	1.1 mg/pc	0.9	Methanol / Homogenizer
Optical bleaching agent	3.9	0.8	Methanol

1.3 External extraction

External extraction is suitable for **insoluble solids** that release water only **slowly** when crushed as well as for samples with an extremely **inhomogeneous water distribution**. In particular, water is extracted from the sample by means of a defined quantity of solvent of known water content.

Briefly, the finely crushed sample is added to a solvent with **very low** water content and is left to stand until the water has been released from the sample. The extraction of water can be improved

- by shaking the solution (mechanical shaker, shaking bath)
- placing the solution in an ultrasonic bath for a certain time
- or reducing the sample further with a built-in homogenizer.

The organic solvents most commonly used are:

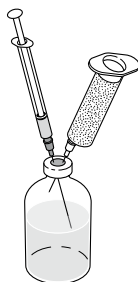
- methanol for insoluble organic solids
- decanol / octanol for fatty and dairy products (butter, butter milk, edible fat)
- formamide for natural substances (almonds, pepper, curry) for dehydrated products
- chloroform for sugar (total water), sugar and starch products for sugar (surface water)

The external extraction is carried out in four steps:

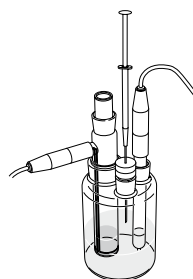
Step 1: Blank value determination of the extraction solvent



Solvent in septum bottle



Take a solvent aliquot

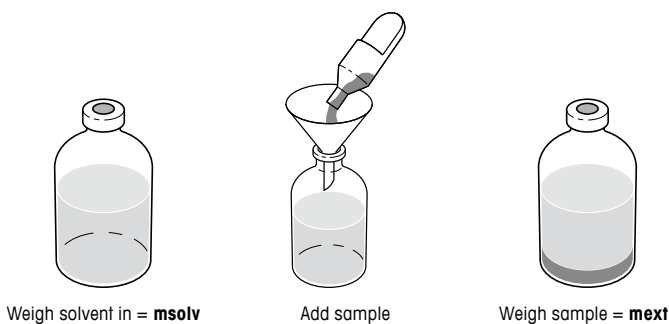


Water content determination of solvent =
blank value B

- The water content of the solvent must be **much less** than the one of the sample.

- Pay attention to the water capacity of chloroform (max. 350 ppm) and toluene (max. 600 ppm).
- Provide sufficient solvent for the blank value determination so that enough solvent is available for the extraction.

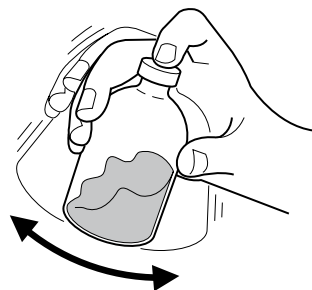
Step 2: Weigh in solvent and sample



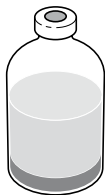
- Cut the sample into small pieces so that it releases its water more quickly and efficiently.
- Add a sufficient amount of sample. The larger the sample, the smaller the relative error because the total error is calculated with respect to the sample size.
- A dilution factor of **10 - 20** is normally used.

Step 3: Extraction

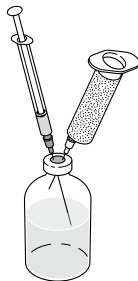
- Shake, or use an ultrasonic bath with heating, or use a homogenizer.
- Shaking is the method generally used for extraction.
- A mechanical shaker is normally used because the extraction time is often long (at least two hours or overnight).
- For the extraction of tablets, the addition of **dry quartz sand** has proven useful for improving and speeding up the extraction.



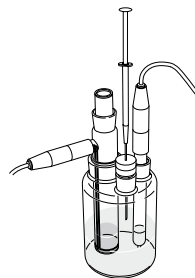
Step 4: Allow settling, take an aliquot and titrate



Allow to settle



Take an aliquot of the extraction solution



Titrate sample

The following equations are used to calculate the water content of the extracted sample:

For %:
$$R(\%) = \frac{100}{100 - C} \cdot \left(C \cdot \frac{msol}{mext} - \frac{B \cdot msol}{mext} \right)$$

For ppm:
$$R(ppm) = \frac{10^6}{10^6 - C} \cdot \left(C \cdot \frac{msol}{mext} - \frac{B \cdot msol}{mext} \right)$$

R: Water content in the sample P (% or ppm).

C: Water content of the supernatant extraction solvent (% or ppm)
 %: $C = (VEQ \cdot CONC \cdot TIME \cdot DRIFT / 1000) \cdot 0.1 / m$
 ppm: $C = (VEQ \cdot CONC \cdot TIME \cdot DRIFT / 1000) \cdot 1000 / m$

B: Blank value (water content of the solvent, % or ppm).

msol: Amount of solvent (g)

mext: Amount of sample (g) extracted with the solvent

m: Weight of the sample aliquot (g)

Note:

The detailed calculations which lead to these formulas are given in the appendix.

Examples for the external extraction:

KF Coulometry

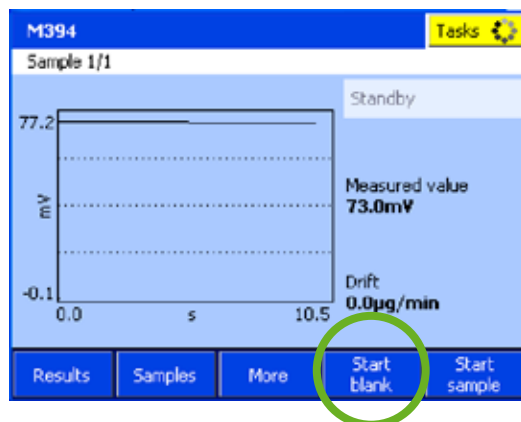
Sample	Result/ppm	srel / %	Extraction solvent
Sucrose (surface water)	72	4.2	Chloroform

Volumetric KF Titration


Sample	Result/ppm	srel / %	Extraction solvent
Cheese	27.6	0.4	Decanol:formamide: methanol 8:2:1
Liver sausage	61.6	0.4	Decanol:formamide: methanol 8:2:1
Mustard	72.4	0.6	Decanol:formamide 1:1
Chicken broth	4.9	0.3	Decanol:formamide: methanol 8:2:1
Tobacco	11.5	0.5	Methanol
Wool	9.8	0.4	Methanol
Acrylic paint	54.3	0.5	Formamide

There is a dedicated KF method type 'External Extraction'. The METTLER TOLEDO methods M305 for the volumetric KF titrator and M394 for the coulometric KF titrator are available with optimized method parameters for immediate execution.












The solvent blank is determined directly from the method running in standby by pressing the 'Start blank' button.



The weight of the solvent (msol), the weight of the sample (mext) and the weight of the aliquot of the supernatant solution containing the extracted water (sample size m) is entered into the respective sample data fields:

Sample 1/1 Tasks 

Sample list > Sample data

Number	1		
ID 1	--		
sample size m 	Sample size	0 g	
	Density	1.0 g/mL	
msol 	Solvent weight	0.0 g	
mext 	Wt. extracted sample	0.0 g	
Cancel		OK	

The equation for the calculation of the water content of the extracted sample is predefined in the calculation method function. In particular, by selecting the appropriate calculation (i.e. "External extraction") in the method function "Calculation", the formula is automatically given.

Note:

1. The water content of the solvent should be as low as possible, in order to maximize the extraction effect and ensure that the difference between the water contents before and after extraction is as large as possible.
2. The amount of sample should be sufficiently large to ensure that the amount of water in the sample is significantly greater than that in the solvent prior to extraction.
3. The amount of sample should also take account of the absorption capacity of the solvent. Chloroform, for instance, reaches the saturation limit for water already at 350 ppm!

1.4 External dissolution

External dissolution is defined as the **complete dissolution** of a sample in a defined amount of solvent of known water content. External dissolution is suitable for soluble solids

- with an extremely inhomogeneous water distribution, or
- with a very low water content, or
- with a high water content

Pure solvents can be used to dissolve the samples; the addition of methanol is not necessary. The following solvents are commonly used:

- methanol for organic solids
- formamide for sugar products
- chloroform for petroleum oils and adhesives
- toluene for tar, waxes and suppositories

Example:

Sample	Result/ppm	srel / %	Extraction solvent
Sucrose (total water)	533	4.2	formamide
Naphthalene	35	10.2	methanol
Phenol	174	1.8	methanol
Salicylic acid	116	2.9	methanol
Contact adhesive ("Rubber cement")	278	5.3	chloroform

The method corresponds to external extraction except that the sample dissolves completely in the external solvent. The dedicated method type 'External Extraction' and the METTLER TOLEDO methods M305 for the volumetric KF titrator and M394 for the coulometric KF titrator can be used as templates; only the calculation method function has to be adapted to by selecting the corresponding calculation from the list of proposed results.

$$\text{For \% AND ppm: } R(\%, \text{ppm}) = C \cdot \left(\frac{msol + mext}{mext} \right) - \left(\frac{B \cdot msol}{mext} \right)$$

R: Water content in the sample P (% or ppm)

C: Total water content (sample + solvent), in % or ppm.

$$\%: C = (VEQ * CONC * TIME * DRIFT / 1000) * 0.1/m$$

$$\text{ppm: } C = (VEQ * CONC * TIME * DRIFT / 1000) * 1000/m$$

- B:** Blank value (water content in % or ppm) of the solvent.
msol: Amount of solvent (g) after determining the blank value
mext: Amount of sample (g) extracted with the solvent
m: Weight of the sample aliquot (g)

To obtain accurate results a large sample amount is used for substances with an inhomogeneous water distribution. Direct titration is not suitable, because a large sample amount leads to a too long titration time, and too much titrant is consumed.

If the solid has a low water content (<200 ppm), the error obtained by direct titration if the titration stand is opened to add the sample is too large. If 1 g of sample has a water content of 100 ppm ($= 100 \mu\text{g}$) for instance, the error as a result of opening the titration stand will be between 10 and 30 μg . Since you are able to work with larger amounts of sample when working with this technique, this error is reduced.

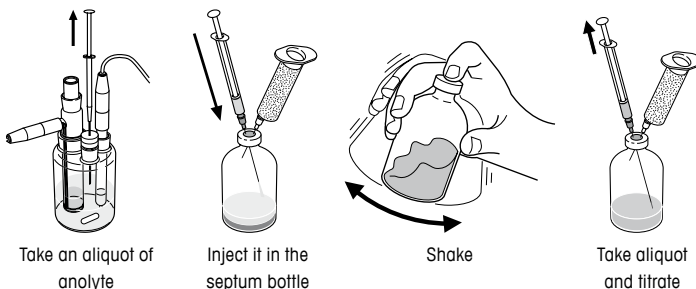
On the other hand, KF coulometry is not suitable for samples with water contents of 10-100% because a very small amount of sample would have to be used. Thus, the sample is previously diluted through external dissolution to be able to titrate a larger sample aliquot.

1.5 Lyophilized substance in septum bottles

The extremely low water content of freeze-dried substances (e.g. biological tissue, serum, foodstuffs) in septum bottles means that external extraction or external dissolution as described in the previous sections are not recommended.

In fact, the blank value correction is too large compared to the amount of water in the sample. You should therefore proceed as it follows:

Procedure:



1. Remove approx. 10 mL of anolyte titrated to dryness from the titration cell using a 20 mL syringe with a long needle and then return it to the titration cell.
2. Rinse the syringe two or three times in this way.
3. Draw 10 - 20 mL of anolyte titrated to dryness into the syringe, weigh it and inject it into the septum bottle.
4. Determine the weight of anolyte injected by back weighing.
5. Shake the bottle or place it in an ultrasonic bath for 5 minutes so that the lyophilized substance dissolves or forms a suspension.
6. Draw an aliquot into the same syringe again, weigh it and inject it into the titration cell.
7. Determine the weight by back weighing.

If the sample is completely dissolved: use the method type "External extraction" and the calculation for the "External dissolution"

If a suspension is formed: use the method type "External Extraction" and the calculation for the "External extraction"

Note:

In both cases, zero must be entered for the blank value (B), because the anolyte titrated to dryness has a blank value of "0".

Alternative procedure:

1. Remove approx. 10 mL of anolyte titrated to dryness from the titration cell using a 20 mL syringe with a long needle and then return it to the titration cell.
2. Rinse the syringe two or three times in this way.
3. Draw exactly 20 mL of anolyte titrated to dryness into the syringe and inject it into the septum bottle. The accuracy of a plastic syringe is enough.
4. Shake the bottle or place it in an ultrasonic bath for 5 minutes so that the lyophilized substance dissolves or forms a suspension.
5. Draw exactly 5 mL from the septum bottle into the same syringe again and inject it into the titration cell. The water amount in μg is determined.
6. With a standard method calculation and calculate the water amount in μg .
7. Since $\frac{1}{4}$ of the total amount was injected, the water amount in

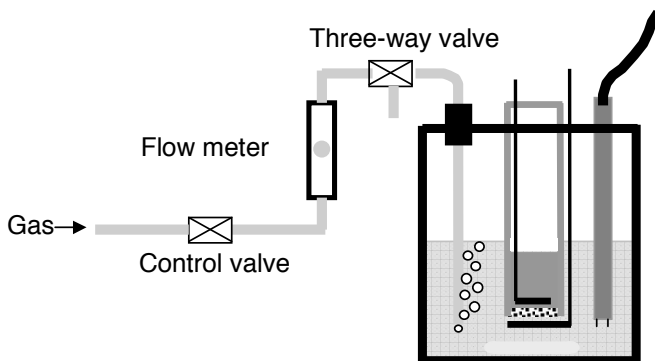
the septum bottle is 4 times larger. Thus, the final result must be multiplied by 4 (factor $f = 4$).

8. If you know the lyophilized sample amount in the septum bottle, then you can additionally calculate the result can be given in ppm.

In this way, neither the calculation for the external extraction nor for the external dissolution are needed for this procedure using the volume instead of the mass.

1.6 Determination of water in gases

To determine the water content of gases, the gas must be directed through the titration vessel for a defined period of time. The flow rate has to be constant to determine the volume necessary to calculate the water content: $\text{gas volume} = \text{gas flow rate} \times \text{time}$.



The water content in ppm is calculated by entering the volume and the density.

Sampling/sample addition

- If possible, you should titrate the gas sample directly from the source. If not, you must fill the gas either into special gas sample tubes or into small steel cylinders.
- Purge the sample vessel and the tubings thoroughly beforehand with the gas.
- With sample vessels the gas amount gas can be determined by differential weighing.

Determination

- Adjust the gas stream to a constant flow rate with the control valve: 50 to 200 mL/min, depending on the water content of the gas.
- Purge the system with the gas before you start the determination.
- Turn the three-way valve, to prevent the gas from flowing into the titration vessel.
- As soon as the drift is stable again, start the titration and reset the three-way valve to its original position in order to direct the gas into the titration vessel.
- Stop the gas flow after 1 to 2 mL titrant has been consumed.
- Calculate the volume from the time and the gas flow rate.

Notes

- Add a sufficient amount of buffer solution into the titration vessel to determine the water content of acid gases such as e.g. hydrochloric acid.
- When titrating large quantities of gas in the same solvent, evaporated methanol lost in the gas stream must be replaced depending on titration time and number of determinations.
- CO₂ gas can not be titrated directly since iodine reacts with CO₂. The gas must be directed through a water-dissolving, water-free absorption liquid in which CO₂ itself does not dissolve. The water contained in the gas is then absorbed by the liquid and can be determined by means of Karl Fischer titration in a process similar to external extraction.
- Select “Max. time” and a “Delay time” of e.g. 600 s as termination parameters, to ensure that the titration is **terminated** after the maximum time.

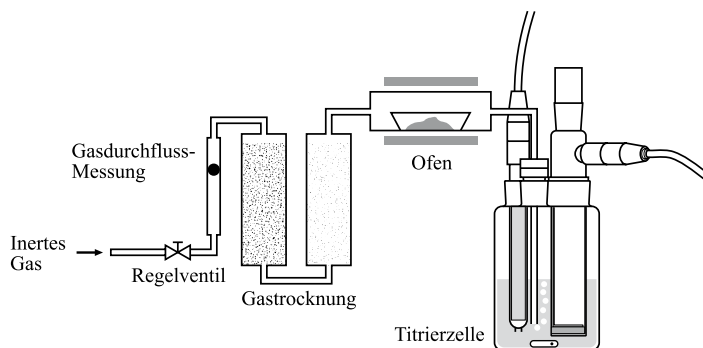
1.7 Determination using the drying oven

This method is suitable for solids and liquids that

1. cause side reactions with the Karl Fischer reagent,
or
2. that release water very slowly.

1.7.1 Principle

The sample is heated in an oven, causing the water in the sample to vaporize. The water is transferred to the titration cell in a current of dry inert gas (purge gas), and the amount of water is determined.



1.7.2 Purge gas

- Air contains oxygen, which could react with the sample at higher temperatures. Air should therefore only be used for non-oxidizable, inorganic samples.
 - If you use air for organic samples, the oven temperature should not exceed 160 °C.
 - If you use nitrogen from a gas cylinder, you should use a two-stage pressure regulator so that the final pressure is in the range 0.5 - 1 bar (cf. chapter 1.6.4)
 - A gas stream of approx. 150 mL/min is ideal for DO308 and 70 mL/min for Stromboli (automated KF drying oven, cf. chapter 1.6.5).
- Experiments with various gas flow rates yielded the following results:

Gas flow rate [mL/min]:	108	166	500
Recovery [%]:	99.9	99.7	97.1

- The recovery rate is **clearly decreasing** with **increasing** gas flow rate. Thus, for accurate results do not select a too high gas flow rate.
- The purge gases commonly used contain moisture, e.g.:
 - ° air with 50% humidity: approx. 11 mg/L
 - ° nitrogen gas from a cylinder: 1.4 – 8.0 mg/L

Therefore, the purge gases must be **first dried** before entering the KF oven. For Karl Fischer titration, the residual moisture in the purge gas should be less than at least 10 µg/L (for coulometric determination) and 20 µg/L (for volumetric KF titration) in order to obtain accurate and repeatable results. Several agents are available to dry the purge gas:

Several agents are available to dry the purge gas:

Method	Residual moisture	Residual moisture for 200 mL/min gas flow rate (drift)
Sulfuric acid, 100%	50 - 80 µg H ₂ O/L	10 – 15 µg H ₂ O/min
Phosphorous pentoxide, P ₂ O ₅	40 - 50 µg H ₂ O/L	8 – 10 µg H ₂ O/min
KF one-component reagent	15 – 20 µg H ₂ O/L	3 – 4 µg H ₂ O/min
Silica gel	50 – 60 µg H ₂ O/L	10 – 12 µg H ₂ O/min
Molecular sieves 3 Å	5 – 10 µg H ₂ O/L	1 – 2 µg H ₂ O/min

You can use the following desiccants to dry the purge gas:

- Molecular sieves are the best drying agent as far as residual moisture is concerned, but their water absorption capacity is low, i.e. they are rapidly exhausted.
- Silica gel is appreciably better in this respect. It is therefore recommended to dry the gas with a combination of silica gel and molecular sieves. Start off with the silica gel to absorb the bulk of the water and then use molecular sieves to reduce the residual moisture to a minimum.

Silica gel and molecular sieves have the advantage that they can be regenerated, in contrast to other desiccants. Silica gel can be regenerated over night at 150 °C, whereas molecular sieves requires temperatures up to 300 °C.

1.7.3 Procedure

There are two different methods to perform a KF titration with the drying oven:

1. Method 1: The water evolved is continuously titrated

After a short mix time (20 - 60 s), the titration starts and the released water is continuously titrated. The short mix time is necessary so that a delayed vaporization of water does not lead to premature termination of the titration. In order to avoid the latter you may also use the minimum time as termination parameter.

At the end of the titration, the vaporization is often very irregular. To ensure that the determination is repeatable, you should set the maximum titration time as the termination parameter (i.e. deactivate the drift stop).

2. Method 2: The water is first vaporized and then titrated afterward

During a defined long mix time, all the water is vaporized and transferred to the titration cell. The KF titration is then started. The relative drift stop or the maximum titration time can be used as the termination criterion. With some samples the drift at the end of the titration is significantly higher than the initial drift. This is caused by a slow release of the final traces of water or slow thermal decomposition of the sample. In such cases you should use the maximum titration time as termination parameter (i.e. deactivate the drift stop).

Evaporation of solvents

Passing the gas stream into the titration cell causes the analyte (in the KF coulometer) and solvent (generally methanol in KF volumetric titrator) to vaporize, especially methanol. The amount depends on the gas flow rate and the type of KF reagent present in the titration cell.

In the case of KF coulometers, there are two types of analyte solutions:

- Standard analyte solutions containing methanol (e.g. Coulomat AG or CombiCoulomat frit):

Analyte loss at **150 - 200 mL/min**, oven temperature **200 °C**:
approx. 3,5 - 4,5 mL/hour

- Analyte containing ethylene glycol, i.e. dedicated analyte to be used with a KF Oven (e.g. Coulomat AG Oven):

Analyte loss at **150 - 200 mL/min**, oven temperature **200 °C**:
approx. 1 mL/hour

From time to time, you should replace the analyte lost through vaporization with new anhydrous methanol. Make sure that the level of the analyte does not fall below that of the catholyte (higher drift!).

Due to the vaporization of the methanol, there is a small loss of water, i.e. the recovery is not 100%. The recovery therefore depends on the amount of methanol vaporized and the method used. As an example data from coulometric determinations are indicated here:

Method	Anolyte	Gas flow rate	Recovery %
1	Coulomat AG	166 mL/min	99.7
1	Coulomat AG Oven	183 mL/min	99.95
2	Coulomat AG	166 mL/min	98.2
2	Coulomat AG Oven	106 mL/min	99.1

Briefly:

The less methanol is vaporized, the faster the water is titrated, and the better the recovery.

1.7.4 Manual Karl Fischer drying oven

The METTLER TOLEDO DO308 drying oven can be operated in a temperature range from 50 to 300 °C. It has a large glass sample boat capable of holding up to 10 cm³ of sample. This is particularly important with low-weight samples (e.g. fibers) or with samples of low water content.

The DO308 oven is equipped with a gas drying unit with two bottles for silica gel and molecular sieve, as well as a gas flow meter. An air pump is available as an optional accessory.

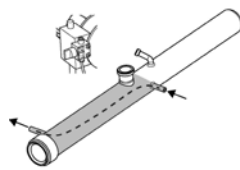
The procedure for the determination of water content is described in the operating instructions.

Examples:

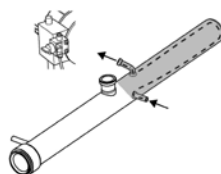
Sample	Result ppm	No. of samples	srel %	T °C	Time min	Comments
Polyamide	5547	6	0.8	190	15	Max. time
Polyethylene	68	6	6.9	280	10	Max. time
Motor oil	842	6	9.9	140	15	Max. time
Cement	8200	6	2.2	300	20	Max. time
Cooking salt	360	5	4.2	300	10	Max. time
Carbon black	3583	5	1.5	200	15	Max. time

Comments:

1. Set a gas flow rate of 150-200 mL/min.
2. Always start the titration before you place the sample in the oven to ensure that the correct drift value is adopted by the method (online drift).
3. The drift should be **5-10 $\mu\text{g H}_2\text{O/min}$** at a gas flow of 150 mL/min. If the drift is higher than 15 $\mu\text{g H}_2\text{O/min}$, replace the silica gel and molecular sieves of the gas drying unit, and/or replace the anolyte of the KF coulometer.
4. Coulometer KF: The internal drying tube of the generator electrode has to be replaced with an external, bent drying tube. Then, evaporated solvent does not condense in the drying tube, and does not drop into the cathode compartment/titration cell.
5. Some samples require some time before water starts evaporating. Here a short mixing time (15 to 60 s) or the minimum titration time should be defined to prevent the titration from being terminated too early. For the same reason, do not select the parameter "Auto start".
6. Some samples have surface water that is lost as soon as the oven is purged with dry gas. This leads to a too low result. In such cases, you should proceed as follows:
 - Open the stop cock, purge the "cold zone",
 - Close the stop cock and purge the "hot zone".
 - If the drift is constant, start the titration so that the drift value is automatically entered.
7. Add the sample through the tapered joint and slide the glass boat with the sample into the oven.

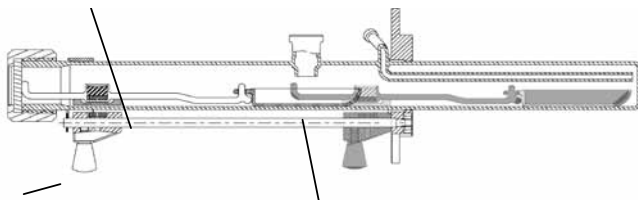


Cold zone or back purging



Hot zone or cell purging

8. To check the performance of the titrator/drying oven system, you may use the SIGMA-ALDRICH HYDRANAL® water standard KF oven 5.55% or VWR/VWR/MERCK water standard KF oven 1%.



9. A large amount of evaporated water cannot be fully absorbed by the solvent. This can happen when the titration is started only after complete evaporation. Experiments using methanol as the solvent gave a recovery rate of 98% for a stream of 166 mL/min. If the water is titrated as soon as it begins to evaporate, the recovery increases to 99.7%.
10. If several determinations are performed in the same solvent, the evaporated solvent lost in the gas stream has to be replaced. For instance, in volumetric KF titration the methanol loss is approx. 3.5 to 4 mL/h for an oven temperature of 200 °C and a flow rate of 200 mL/min. The evaporation is reduced by adding ethylene glycol (higher boiling point) to a maximum solvent ratio of 20-30%.

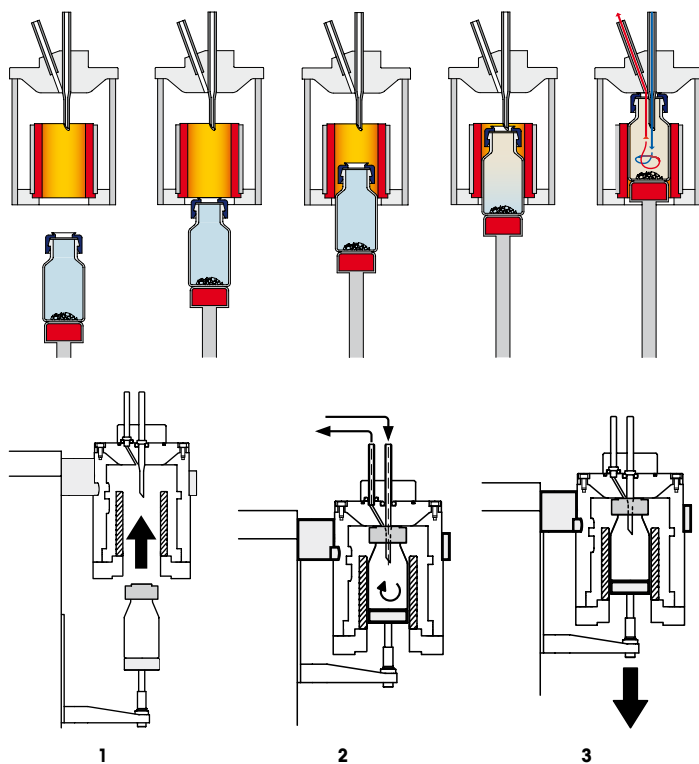
1.7.5 STROMBOLI automatic oven sample changer

The METTLER TOLEDO STROMBOLI oven sample changer is a drying oven for automatic Karl Fischer titration with the KF Compact Volumetric V30 and Coulometric Titrators C30 as well as with the Titration Excellence Titrators T70 and T90.

The drying oven can be operated in the temperature range from 50 to 300°C. STROMBOLI is completely controlled by the titrator: all the parameters for the determination, including the oven temperature, are included in the titration method.

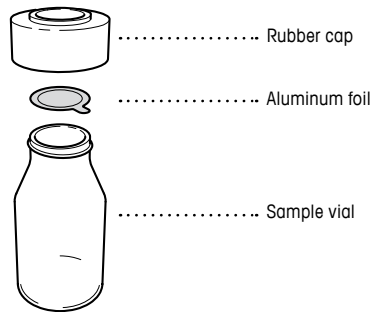
Besides 14 places for glass sample vials, STROMBOLI offers one fixed place on the sample rack for an empty sample vial in order to determine the drift value.



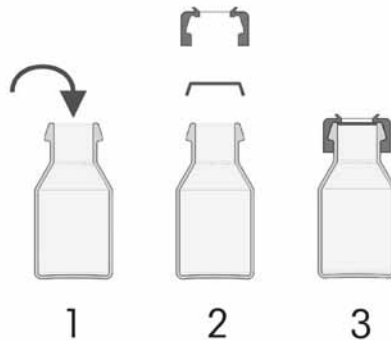
**During a sample series:**

1. The sample vials are moved upward into the oven by a lift. The blue rubber cap seals the sample vial tightly against the oven, while a glass tube pierces the aluminum foil cover. The oven heats the sample to the set temperature.
2. The purge gas flows through the sample vial and the water vaporized is transported via the transfer tube into the titration cell of the coulometer.
3. After the analysis, the lift is moved downward and gravity facilitates the removal of the sample vial from the oven.

Sample vials:



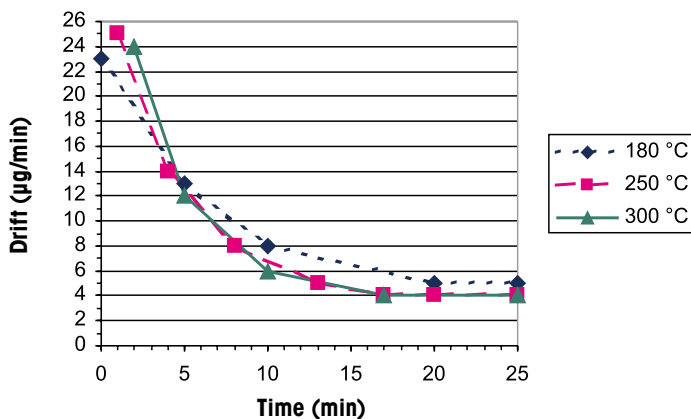
The glass sample vials have a large volume (up to 25 mL). This is particularly important with light samples (e.g. fibers) or with samples of low water content. The sample vials are sealed with self-sealing aluminum foil and a rubber cup.



Drift determination:

The drift determination is performed with an empty vial on the first position of the sample rack. The drift value is defined as the moisture entered into the titration cell by the purge gas.

To determine the drift value accurately, the moisture in the empty sample vial has first to be removed. This takes 10-20 minutes as can be seen in the following diagram:

Development of drift at 180 - 300 °C / 150 mL/min**Blank value determination:**

The blank value is the amount of water contained in an empty sample vial (i.e. the moisture in the air present in the vial, and the adsorbed moisture on the glass walls of the vial) minus the amount of water due to the drift (i.e. drift value x time).

The blank value should be determined before each series because the humidity can change, and thus the moisture adsorbed on the glass walls is not always the same.

The **optimum blank value** is in the range of **70 - 300 µg water**.

Important: After a blank value determination, the vial used no longer has the same properties as the "fresh" sample vials, i.e. the moisture content is somewhat lower. Thus, it is important to use a new sample vial for each blank value determination (i.e. one with the same properties as the sample vials into which the samples have been filled in).

Performing the drift and blank value determination

In general, a blank value determination should be performed before each series of samples since the ambient conditions (humidity, moisture in the sample vial, gas flow, etc.) are always slightly different.

If the **maximum titration time** is used as termination criterion in the method -which is what we recommend- the analysis times for the determination of the blank value and for each sample are the same. In this case, the blank value determination also takes the actual drift into account. It is therefore not necessary to perform a drift determination before each series. This means that the stored drift value of the previous determination will be used.

Nevertheless, a drift determination should still be performed at least once a day in order to check whether the drift is too high (e.g. > 15 µg H₂O/min). If this is the case, the silica gel and molecular sieves in the bottles of the gas drying unit can be replaced, as well as the anolyte in a coulometric analysis.

Multiple sample series at different temperatures

Several series can be started on the same sample turntable – even at different temperatures. If, for example, different plastic samples have to be analyzed, whose optimum bake-out temperatures differ, they can be measured at different temperatures using the same method. For each series, the method contains a so-called sample loop. At the start of the method, you can enter the number of samples the series includes for each loop. The loops run through one after the other and the samples are processed sample for sample. If the temperatures of successive loops are different, the last sample vial that was baked out remains in the oven until the temperature has stabilized at the temperature of the next loop and the drift is low and stable. The first sample of the next loop is then transferred into the oven and the water determination begins. There are dedicated METTLER TOLEDO multi-loop methods available in the V30 (M313) and in the C30 (M396). These method templates are based on a dedicated KF method type called ‘Stromboli’.

The blank value can also vary as a function of temperature. In this case, a blank determination can be performed between two sample loops. The new blank value is automatically used for the blank correction. To determine the blank value as accurately as possible, several blank value determinations can be performed one after the other in the same loop and the mean value calculated from the results. In the same way, at the end of a series the blank value can be measured again and compared with the value determined at the beginning.

With rapidly changing, suboptimum conditions, the drift value can change with time. By performing a drift determination at the end of the series or between several series, you can check whether the drift is constant and the new drift value can be used for the next series.

Comments on the operation with the STROMBOLI oven sample changer:

1. Set a gas flow of 40–60 mL/min. The delivery tube has a T-piece that causes a small leak flow. This is necessary so that the KF solvent or analyte is not aspirated into the hot sample vial if Stromboli is not properly shut down while it is still hot.
2. An optional 3/2 way valve which is automatically controlled by STROMBOLI can be used instead of the T-piece mentioned in 1. This valve shall be used especially if inert gas sources are used, since it provides a leak free inert gas stream during normal operation. A sudden shutdown of power immediately switches the valve in that way, that the inert gas stream to the gas source is closed and the system is ventilated with ambient air. Therefore no precious inert gas is lost and no vacuum is applied to the system which may result in a back aspiration of the analyte into the hot oven.
3. KF Coulometer C30: The internal drying tube of the generator electrode has to be replaced with an external, bent drying tube. In this way, evaporated solvent is not condensing in the drying tube, and therefore it does not drop into the cathode compartment.
4. With STROMBOLI, you can not only determine solids but also liquid samples. These are partially vaporized (e.g. motor oil) or completely vaporized (e.g. toluene, see also list of results). A special (longer) gas inlet glass tube is provided to bubble gas into the liquid.
5. The amount of moisture adhering to the glass surface of the sample vials strongly depends on how the vials were treated beforehand (cleaning, drying and storage). This has a large effect on the blank value and thus on the result. Vials that have undergone different treatment can show differences in the blank value of 50-150 µg water.
6. Use the same vials for a sample series as well as for the blank value determination.

Sample	Result [ppm]	No. of samples	srel [%]	T [°C]	Max. Time [s]	Comments
Polylactic acid 0.5 g	2589	3	1.1	160, air	—	Stir time: 600 s Max. time: 300 s rel. drift: 3 µg/min
Polymer ABS-50 T 10014 3 g	736	5	1.1	190, N ₂ - gas	300	Stir time: 900 s Delay time: 300 s
Polymer ABS-50 F10014 2 g	1312	13	0.9	170, N ₂ - gas	300	Stir time: 900 s Delay time: 300 s
Motor oil 1120/03 (AA) 2 g	241	3	4.4	165, air	1500	Stir time: 60 s Delay time: 300 s Very slow evapora- tion, not faster with 180°C, above 180°C decomposition
	261	4	7.9			
Motor oil 1034/03 (AA) 1.5 g	426	4	2.7	180, air	1800	Stir time: 60 s Delay time: 300 s Very slow evapora- tion, above 180°C decomposition
	438	3	4.5			

7. Allow sample vials that have been used or cleaned to stand overnight in the atmosphere for conditioning before starting measurements.
8. To check the titrator/drying oven system, you can use SIGMA-ALDRICH HYDRANAL® water standard KF oven 5.55% or VWR/VWR/MERCK water standard KF oven 1%. This test also serves to check the tightness of the oven and the connection tubing

2. Further Information

2.1 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 GmbH, Darmstadt / Germany, 1985.

2.2 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

2.3 Application brochure Many more details regarding the Karl Fischer titration are published in the application brochure Good Titration Practice™ in Karl Fischer Titration (ME 517252145).

2.4 Product Information Details about the volumetric and coulometric Karl Fischer titrators of METTLER TOLEDO you can find on:

► www.mt.com/karl-fischer

or at any of the local sales and service organisations.

Good Measuring Practices

For Balances, Titrators and Pipettes

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1. Evaluation

Analyze your process flows and its associated criteria to consistently assure the highest quality of your application and your data.

2. Selection

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3. Installation & Training

Enjoy every confidence in your new device and master it with full professional skills right from day one.

4. Calibration & Qualification

Trust the manufacturer-trained METTLER TOLEDO Service Team when it comes to calibrating and qualifying your instruments.

5. Routine Operation

Benefit from tangible recommendations for optimal performance verification, calibration and maintenance.

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