

## Application Bulletin 77/3 e

# Volumetric water content determination according to Karl Fischer

## Tips and tricks for volumetric Karl Fischer titration

### Branch

All branches

### Keywords

Titration; Karl Fischer titration; volumetric; KFT; KFV; water content determination; volumetry; ASTM E203

### Summary

In addition to the determination of pH, weighing and acid-base titration, the determination of the water content is one of the most frequently used methods in laboratories worldwide. Two methods in particular have become dominant in the market:

#### A – Drying methods (drying ovens, infrared balances...)

Various standards mention this method. However, it suffers from the following disadvantages:

- Loss on drying is determined and not necessarily the water content. Apart from water, also other volatile components of the sample are determined.
- It takes a long time to obtain the results (several hours in a drying oven).

#### B – Titration methods

- In contrast to drying, Karl Fischer titration is a specific method. If no side reactions occur, only water will be determined.
- The method is rapid and normally takes a few minutes only.
- The method can be validated and fully documented.

Higher water contents (> 1%) are preferably determined by volumetric titration. Volumetry has the advantages that solid or pasty samples can be introduced directly into the titration vessel. In contrast to coulometry, opening a volumetric titration cell for a short period of time does not falsify the results. Additionally, volumetry allows carrying out a titration with various suitable organic solvents depending on the sample at hand.

Of course, it is also possible to determine small amounts of water volumetrically, e.g., in solvents. If an appropriate

amount of sample and diluted KF reagents are used, then the determination limit is approx. 50 – 100 ppm of water.

KF titrants do not have a stable titer. Therefore, one of the minor disadvantages of volumetry is that the titer has to be determined on a regular basis. Titer determination is crucial to obtain correct results as the titer has a significant influence on the calculation of the samples water content.

This Application Bulletin gives an overview of the volumetric water content determination according to Karl Fischer. Amongst others, it describes the handling of electrodes, samples, and water standards. The described procedures and parameters comply with the ASTM E203.

### Instruments

- Titrator with a KFT mode

### Electrodes

Double Pt wire-electrode (indicator electrode for volumetric Karl Fischer titration)

### Reagents

For volumetric KF titration, there is a general distinction between one- and two-component reagents.

#### A - One-component reagents

The titrant of one-component reagents contains all the reactants necessary for the Karl Fischer reaction. The solvent component is in most cases pure methanol. To improve solubility of the sample, suitable organic solvents (e.g., chloroform, toluene, ...) can be mixed with methanol.

#### B – Two-component reagents

The two-component reagents consist of all necessary reactants as well, but the components are divided in two different solutions, the titrant and solvent component.

A large variety of KF reagents is available from various manufacturers (e.g., Honeywell, Merck, ...).

Additionally, solid and liquid water standards are available. These standards can be used to determine the titer of the used titrant or to validate the titration system.

## Parameters

Table 1: Default method parameter for a volumetric KF titration

	Parameter	Setting
General	I(pol)	50 $\mu$ A
Control parameter	EP at	250 mV
	Titration rate	optimal
	Stop criterion	drift
Titration parameters	Stop drift	20 $\mu$ L/min
	Titration direction	-
Conditioning	Start drift	20 $\mu$ L/min

For most applications, the parameters mentioned in Table 1 are suitable.

If ketone reagents (methanol free reagents for water content determination in aldehydes and ketones) or methanol deficient reagents are used, then the endpoint, start and stop drift must be adjusted, as those reagents influence the reaction rate of the Karl Fischer reaction.

Table 2: Control and titration parameter for ketone reagents

	Parameter	Setting
General	I(pol)	20 $\mu$ A
Control parameter	EP at	500 mV
	Titration rate	optimal
	Stop criterion	drift
Titration parameters	Stop drift	20 $\mu$ L/min
	Titration direction	-
Conditioning	Start drift	20 $\mu$ L/min

## Conditioning and drift

The titration cell must be dry before the determination start. Conditioning removes water contained in the reagent and water on the surfaces of the equipment (inside of titration cell, electrodes, ...). The water content determination of the sample should only be started once a low and stable drift is reached.

A constant drift equal or lower than 10  $\mu$ L/min is acceptable. Lower values are certainly possible. If higher and stable drift values occur, then the results are normally still good as the drift can be compensated. However, a high drift value can also indicate a leak in the setup (see also section troubleshooting).

## Titer determination

Please refer to AB-424 for a detailed description of a Karl Fischer titer determination.

## Sample addition

### Sample size

The sample size depends on the water content of the sample (see tables 3 to 5). In principle, the sample size should be selected in such a way that the titrant consumption lies between 10% and 90% of the buret volume. For a 10 mL buret, the consumption of titrant should therefore be between 1 and 9 mL.

In addition, the selected sample weight should not be too low. For recommended sample sizes, see tables 3 to 5. On the one hand, the weighing error can be significant, while on the other hand the sample will no longer be representative. In cases of high water content, it may be better to use a buret with a larger volume in order to avoid filling the buret during the titration.

If the sample does not dissolve completely in the working medium, then the selected sample size may be too high and exceeds the dissolving capacity of the working medium. This can be avoided by reducing the sample size and using a smaller buret or a titrant with a lower water equivalent, e.g., 2 mg/mL or 1 mg/mL. Despite the lower initial weight, the titrant consumption will then be in the range of 10 to 90% of the buret volume.

Generally when the titrant consumption is low, you should work with a lower titer (e.g., Titrant 1, Titrant 2), and with a high titer when titrant consumption is high (Titrant 5).

Table 3: Approximate sample size in [g] for a 5 mL buret depending on the titer of the titrant and the expected water content of the sample

Expected water content	Titrant 1	Titrant 2	Titrant 5
0.5%	0.1-0.9	0.2-1.8	0.5-4.5
1.0%	0.05-0.45	0.1-0.9	0.25-2.25
5.0%	-	0.02-0.18	0.05-0.45
10.0%	-	-	0.03-0.23
25.0%	-	-	-
50.0%	-	-	-

Table 4: Approximate sample size in [g] for a 10 mL buret depending on the titer of the titrant and the expected water content of the sample

Expected water content	Titrant 1	Titrant 2	Titrant 5
0.5%	0.2-1.8	0.4-3.6	-
1.0%	0.1-0.9	0.2-1.8	0.5-4.5
5.0%	0.02-0.18	0.4-0.36	0.1-0.9
10.0%	-	0.02-0.18	0.05-0.45
25.0%	-	-	0.02-0.18
50.0%	-	-	0.02-0.09

Table 5: Approximate sample size in [g] for a 20 mL buret depending on the titer of the titrant and the expected water content of the sample

Expected water content	Titrant 1	Titrant 2	Titrant 5
0.5%	0.4-3.6	-	-
1.0%	0.2-1.8	0.4-3.6	-
5.0%	0.04-0.36	0.8-0.72	0.2-1.8
10.0%	0.02-0.18	0.04-0.36	0.1-0.9
25.0%	-	0.02-0.14	0.04-0.36
50.0%	-	-	0.02-0.18

### Liquid samples

Liquid samples are usually added with the aid of a syringe. Either a syringe with a long needle is used with the needle being immersed beneath the surface of the reagent during injection or a short needle can be used, with the last drop being drawn back into the needle. The best way of determining the actual sample weight is by weighing the syringe before and after injection.

Volatile or low-viscosity samples should be refrigerated before the sample is taken, in order to prevent handling losses. In contrast, the syringe itself should not be directly refrigerated as this could cause the formation of condensate. For the same reason aspirating air into a syringe that has been cooled by taking up a refrigerated sample should be avoided.

Highly viscous samples can be warmed to lower their viscosity, but the syringe must also be warmed. The same goal (lower viscosity) can be reached by dilution with a suitable solvent. In this case, the water content of the solvent must be determined and deducted as a blank value correction. Alternatively, viscous samples can be added using a spoon for paste (figure 1).



Fig. 1: OMNIS spoon for paste (6.02711.000)

The sample can be weighed directly on the spoon and the spoon can be left in the titration cell until the end of the titration.

### Solid samples

To add solid samples, the septum stopper of the titration cell is removed. The sample can then be added using a weighing boat (see figure 2), a weighing paper or any other suitable tool.



Fig. 2: Glass weighing boat (6.2412.000) for addition of solid samples

To avoid any influence of atmospheric moisture on the results, the sample should only be exposed to the ambient air as short as possible and added as quickly as possible before the titration cell is closed again quickly.

### Tips and tricks

#### Reagent exchange

In the following cases, the reagent should be exchanged:

- When the titration vessel is too full.
- When the capacity of the reagent is exhausted (unstable drift values).
- If the drift is too high and shaking the cell does not result in any improvement.
- If a two-phase mixture is formed in the titration vessel.
- If the sample does not dissolve anymore in the solvent.

### **Indicator electrode**

The two Pt wires of the indicator electrode should be as parallel to one another as possible. Check on insertion.

#### Cleaning

The indicator electrode can be cleaned by rinsing it with methanol or ethanol. Please make sure that the ethanol does not contain any ketone additives, as ketones cause side reactions with KF reagents.

If rinsing does not help, the indicator electrode can be carefully cleaned with an abrasive cleansing agent (e.g., aluminum oxide (6.2802.000 Polishing Set) or toothpaste). Care should be taken not to bend the two Pt wires during the cleaning. After cleaning, it should be rinsed with methanol or ethanol. Please make sure that the ethanol does not contain any ketone additives.

Dry all parts thoroughly after cleaning. If the parts are dried in a drying oven, take care that the temperature does not exceed 70 °C (plastic components!).

#### Storage

The indicator electrode can either be stored dry or directly in the titration cell immersed in the Karl Fischer reagent.

### **Handling of standard**

#### **Liquid water standard**

1. Open the ampoule containing the standard as recommended by the manufacturer.
2. Aspirate approximately 1 mL of the standard into the syringe.
3. Take the tip of the needle out of the liquid and pull back the plunger to the maximal volume. Sway the syringe to rinse it with standard. Then eject the standard into the waste.
4. Aspirate the remaining content of the ampoule into the needle (in case air is aspirated, eject the air out of the syringe).
5. Remove excess liquid from the outside of the needle with a paper tissue.
6. Place the needle on a balance and tare the balance.
7. Then start the determination and inject a suitable amount of standard (see table in AB-424) through the septum into the titration vessel. Do not inject the whole content of the syringe! Please take care that the standard is injected into the reagent and not onto the electrode or the wall of the titration vessel. This leads to unreproducible results.
8. After injecting the standard, place the syringe again on the balance.

9. Enter the injected sample weight in the software.

Repeat steps the required number of times. If the complete content of an ampoule has been injected, the needle can be filled with fresh standard (same batch). In this case, the needle does not need to be rinsed again. Start directly with step 4.

There are two possibilities to add liquid standard. It can be injected with the tip of the needle above the reagent level. Then, the last drop must be aspirated back into the syringe. Otherwise, it is wiped off at the septum and might not be determined although the weight of it is taken into account.

If the needle is long enough, it can be immersed in the reagent directly. In this case, there is no last drop and the needle can be pulled out of the titration vessel without aspirating back any liquid.

#### **Solid water standard**

1. Place the weighing spoon on the balance and tare the balance. Weigh an appropriate amount of solid standard. Tare the balance again.
2. Start the titration, quickly remove the stopper with septum, add the solid standard and put the stopper back. When adding the standard, take care that no standard sticks to the electrode or the walls of the titration vessel. In case parts of the solid standard are not dissolved in the reagent, gently swirl the titration vessel to wash down the standard.
3. After the addition of the standard, place the weighing spoon on the balance again.
4. Enter the sample weight in the software.

Repeat steps the required number of times.

#### **Pure water**

##### By weight

1. An insulin syringe is filled with water. Due to the very small amounts of pure water added for the titer determination, we recommend to use a very thin needle. This helps to add small sample sizes.
2. After filling the syringe, place the syringe on a balance and tare the balance.
3. Then start the titration and inject an appropriate amount of water through the septum into the titration vessel. Aspirate the last drop back into the syringe.
4. Then pull out the needle and place the syringe on the balance again.
5. Enter the sample weight in the software.

Repeat steps 2 to 5 at least three times.

### By volume

1. A microliter syringe is filled with an appropriate volume of water. Make sure there are no air bubbles in the syringe. Air bubbles will falsify the result.
2. After filling the syringe, start the titration and inject the content of the syringe through the septum into the titration vessel.
3. Enter the added volume in the software.

Repeat steps the required number of times.

### **Troubleshooting**

#### ***Drift too high***

- Depots containing water in the titration vessel → shake titration cell.
- Reagent exhausted or contaminated → exchange reagent.
- Moisture penetrating into titration cell:
  - Molecular sieve exhausted?
  - Septum pierced?
  - Seals not OK?
- Sample matrix consumes iodine. Change reagent more often.
- When working with Oven/Oven Sample Processor:
  - Molecular sieve of Oven/Oven Sample Processor exhausted?
  - Gas flow too high?
  - Allow to run overnight.
  - Screw seals tight?

#### ***Drift unstable***

- Poor stirring → Stir in such a way, that mixing is efficient, but without the formation of air bubbles.
- Reset the control parameters to standard values.

#### ***Result too high***

- Titration cell not properly conditioned → shake and wait until drift has stabilized.
- Sample contains substances that are oxidized.
- Set stop drift higher.

#### ***Result too low***

- Stop drift too high.
- Minimal titration rate too slow.
- Sample releases iodine.

### ***Results are widely scattered***

- Inhomogeneous sample? Poor reproducibility of sample addition?
- Drift unstable.

### ***Titration times too long***

- Wait until drift during conditioning becomes stable.
- Amount of water in sample aliquot too large
- Set stop drift higher.
- Set control range smaller.
- Set maximal titration rate faster.

### **Literature**

- Metrohm Monograph  
Water determination by Karl Fischer Titration.  
8.026.5003
- Metrohm Application Bulletin AB-280 – Automatic water content determination using gas extraction
- Metrohm Application Bulletin AB-407 – Automated volumetric Karl Fischer titration
- Metrohm Application Bulletin AB-417 – Automated volumetric Karl Fischer titration including sample preparation
- Metrohm Application Bulletin AB-418 – Utilization of the Polytron PT 1300 D (Metrohm version)
- Metrohm Application Bulletin AB-424 – Titer determination in volumetric Karl Fischer titration

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### **Author**

Competence Center Titration  
Metrohm International Headquarters