

# Webinar 1: Fundamentals of Karl Fischer Titration

■ Michael Margreth

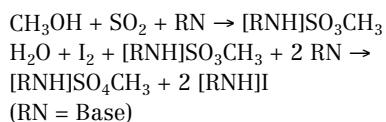
Karl Fischer titration is one of the world's most frequently applied laboratory methods. It is used to determine the water content not only of liquids, but also of gases and solids. Water determination by Karl Fischer titration is specific, rapid, and requires very little apparatus.

## Why Karl Fischer Titration?

Probably the biggest advantage of Karl Fischer titration is its selectivity. In contrast to other water determination methods, e.g., loss on drying, Karl Fischer titration determines water – and only water. No other volatile components are included in the determination. Additionally, Karl Fischer titration covers a large measuring range starting at ppm levels and ending at 100% water. The obtained results are highly accurate and reproducible. Last but not least, the results are usually available within 2 to 3 minutes.

## Volumetry or Coulometry?

Volumetric Karl Fischer titration is used for the determination of water contents in the range of 0.1 to 100%. It is a classical titration, where an iodine-containing titrant is added to react with the water of the dissolved sample. Based on the stoichiometry of the Karl Fischer reaction (see equation below), the volume of titrant dosed allows the calculation of the water content of the sample.



Coulometric Karl Fischer titrators allow a much more sensitive water determination than volumetric titrators and are therefore used to determine water contents in the range of 0.001 to 1%. While the chemical processes underlying coulometry and volumetry are the same, the iodine required for coulometric titration is not added by a buret and a titrant, but is electrochemically generated in the titration cell. An electric current releases iodine from an iodide-containing reagent by electrolysis. The coulometer measures the time and the

current flow that is required to reach the endpoint. According to Faraday's law, the product of time and current is directly proportional to the amount of iodine generated and therefore to the amount of water determined.

## Is a titer Determination Required?

Volumetric Karl Fischer titration being a classical titration, a titrant is added to the titration cell using a buret. Since the titer (or water equivalent) of a Karl Fischer titrant is subject to changes (it gradually decreases), the titer needs to be determined regularly, using pure water or a water standard with known water content. A titer determination is indispensable to guarantee correct results. By contrast, the coulometric technique does not require a titer determination because it is an absolute method and the iodine is generated electrolytically from iodide in the Karl Fischer reagent.

## Drift and drift Compensation

The drift serves several important functions in Karl Fischer titration.

First off all, it makes visible the permanent consumption of iodine during the conditioning phase (drying of titration cell before sample determination), but also during the titration. The higher the drift value, the more water is present in the titration cell.

Secondly, the drift value is used to define the start conditions. As soon as a predefined value is undercut, a message informs the user that the system is ready for sample addition. An essential part of a titration is the detection of the endpoint. In addition to the voltage, which is measured with a double Pt-wire electrode, the drift is used to define the end of a titration.

The longer the titration takes, the bigger is the influence of the drift (consumption of iodine per time) on the result. To minimize the influence, the drift value at the start of the titration is multiplied with the determination time. The resulting amount of water is subtracted from the water content of the sample..

Two Webinars on Karl Fischer Titration  
October 11 and 13, 2016 2 p.m. CET

Part 1: Fundamentals, Oct 11  
Part 2: TROUBLESHOOTING, TIPS AND TRICKS, Oct 13

Learn all you need to know about "Karl Fischer Titration" in the joint webinar series of G.I.T. Laboratory Journal and Metrohm. On Oct 11, we will explain how the technique works and on Oct. 13, troubleshooting and error prevention are the core topics. Following the webinars, there will be a Q&A where your specific questions will be answered. Register now at:  
<http://bit.ly/GIT.KFT>



# Webinar 2: Karl Fischer Titration – Troubleshooting, tips, and tricks

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Karl Fischer titrations are easy to carry out. The titration is started and the sample added to the titration cell. All subsequent steps like the addition of the titrant, the evaluation, and the calculation of the result are done by the KF titrator and the software.

Nevertheless, some questions regarding operation, handling, and maintenance of KF equipment arise from time to time. Following, you find some of these questions answered. The webinars will answer all remaining questions.

the reagent needs to be exchanged after a few determinations. To avoid this, the use of liquid water standards is recommended.

## Is the Sample completely dissolved? How much Sample should be added to the Titration Cell?

Before an analysis is started, the titration cell needs to be absolutely dry, otherwise water in the titration cell is included in the determination. Therefore, the titration cell is dried and kept dry by conditioning, i.e., by adding or generating iodine..

## How is an Electrode Cleaned and Stored?

Karl Fischer indicator electrodes are virtually maintenance-free. However, from time to time, they should be cleaned. In most cases, it is sufficient to wipe the Pt pins with a methanol-moist paper tissue. Take extra care not to bend the Pt pins, as this could lead to permanent damage of the sensor. Generator electrodes without diaphragm are rinsed with or immersed in a suitable solvent to remove sample residues. To clean a generator electrode with diaphragm, it is filled with nitric acid. The acid is allowed to flow through the diaphragm, thus cleaning it. Afterwards, the diaphragm is rinsed several times with water and finally the water is rinsed off with methanol. An important point to consider when cleaning Karl Fischer electrodes and equipment is the solvent used. Never use ketones, because ketones undergo a reaction with Karl Fischer reagents which releases water and falsifies the results. Karl Fischer electrodes can be stored dry.

To determine the water content, the sample has to be fully dissolved. Various sample preparation techniques can improve the solubility of samples. Very simple and effective is the addition of a solubility promoter. Solubility promoters, e.g., formamide for sugar-containing samples, can be added to the Karl Fischer reagent to improve dissolution of the sample. But what if a sample persistently refuses to dissolve? Try extracting the water, either with a solvent or with a gas. The water in samples that are not soluble in organic solvents can be extracted with, e.g., methanol. To determine the water content, an aliquot of the methanol is injected into the titration cell. The oven method (gas extraction) is the ideal technique for insoluble samples or samples causing side reactions. The sample is weighed into a headspace vial which is tightly closed with a septum cap. The vial is then placed in an oven and heated. Via a needle system which is pierced through the septum, a dry carrier gas flows through the sample vial and transports the evaporated water into the titration cell, where the water content is determined. This way, water and sample matrix are separated. Side reactions, matrix effects, and contaminations are avoided and thus a lot of reagent is saved.

Our webinars will enable you to perform better, more effective and faster analyses and to avoid errors. We look forward to your participation!

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