

# Karl Fischer Titration

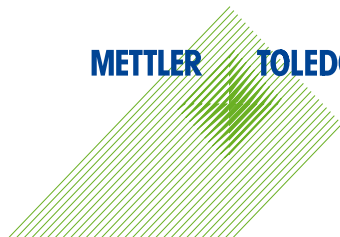


KF Guide 1

The Techniques

## **Introduction** to Karl Fischer Titration

**METTLER TOLEDO**





# Editorial

Dear Reader,

The Karl Fischer method for the water content determination is one of the most frequently used titration methods. Published by German petrochemist Karl Fischer in 1935, it has become well renowned for a wide variety of applications and samples.

This brochure presents a short, historic overview of the development of Karl Fischer's method. It explains the chemical reaction and the two major measuring techniques: Volumetry and coulometry.

Learn from METTLER TOLEDO's extensive knowledge of moisture and water content determination from 1 ppm to 100%.

<b>Content</b>	<b>4</b>
<b>1. The Karl Fischer Titration</b>	<b>5</b>
1.1. A historic overview	5
1.2. The Karl Fischer chemical reaction	7
1.3. Consequences for practical applications	9
<b>2. Volumetric and Coulometric Karl Fischer Analyses</b>	<b>11</b>
2.1. Volumetric KF analysis	12
2.1.1 One-component KF reagent	12
2.1.2 Two-component KF reagent	12
2.1.3 Pyridine-containing reagents	13
2.1.4 Special reagents for aldehydes and ketones	13
2.1.5 Karl Fischer reagents with ethanol	13
2.2. Coulometric KF analysis	14
2.2.1 KF coulometry	14
2.2.2 Stoichiometry of the coulometric KF reaction	16
2.2.3 Iodine generation	16
2.2.4 Generator electrode without diaphragm	17
2.2.5 Limitations for the use of the cell without diaphragm	18
<b>3. Further Information</b>	<b>19</b>

# 1. The Karl Fischer Titration

## 1.1. A historic overview

- 1935 Publication: "Neues Verfahren zur massanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und festen Körpern" by Karl Fischer.
- 1943 Publication: "The Dead-Stop End Point", by G. Wernimont and F.J. Hopkinson.
- 1950 Pyridine-containing two-component reagents and dead-stop titration instruments are commercially available.
- 1952 Use of Karl Fischer method spreads, promoted by publications by E. Eberius.
- 1955 Publication on stabilized single-component Karl Fischer reagent by E. D. Peters and J. L. Jungnickel.
- 1956 First German DIN standard for the Karl Fischer titration (DIN 51777, April 1956, "Testing of mineral oil hydrocarbons and solvents: Determination of water content according to Karl Fischer - Direct method").
- 1959 Publication: Coulometric Karl Fischer Titration by A. S. Meyer and C. M. Boyd.
- 1960 KF titration instruments with piston motorized burettes. Enormous spread of the use of KF titration.
- 1970 First coulometric KF titration instruments are commercially available.
- 1980 Pyridine-free KF reagents are commercially available.
- 1984 First microprocessor controlled KF titrator (METTLER DL18) with automatic drift compensation, and solvent dispensing and removal.
- 1985 First fully automatic KF titration with laboratory robots (METTLER DL18 and ZYMARK); DO185 Drying Oven for the DL18 Karl Fischer Volumetric Titrator.
- 1989 First diaphragm-less cell for coulometric KF titration.
- 1990 DL37 KF Coulometer from METTLER TOLEDO.
- 1995 Water standards (10.0, 1.0, 0.1 mg/g) with test certificate according to DIN 50049-2.3  
First titrator (METTLER TOLEDO DL55) with online curves  $E = f(t)$  and  $V = f(t)$  for Karl Fischer titration.

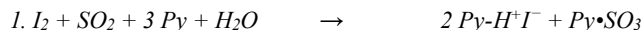
- 1997 New DV705 KF Titration Stand with very low drift value ( $< 2\mu\text{g}/\text{min}$ ) for the METTLER TOLEDO DL53/55/58, and DL67/70ES/77 Titrators
- 1998 Introduction of the METTLER TOLEDO DL31/DL38 KF Titrators with dedicated fuzzy logic control, titrant specific standard parameters and LEARN titration. They replaced the DL18/35 KF Volumetric Titrators.  
Introduction of less poisonous KF reagents based on ethanolic solution.
- 2000 METTLER TOLEDO RONDO Sample Changer with Karl Fischer Kit for automated KF volumetric determination.
- 2001 Improved METTLER TOLEDO DO307 KF Manual Drying Oven. Solid KF Oven Standards with water contents of 5.5% and 1%, respectively.
- 2002 Introduction of the METTLER TOLEDO DL32/39 KF Coulometers (generating cell with and without diaphragm).  
Introduction of the METTLER TOLEDO STROMBOLI KF Oven Sample Changer.
- 2008 Introduction of the METTLER TOLEDO Titration Compact Line V20/V30 and C20/C30 Karl Fischer Instruments.

## 1.2 The Karl Fischer chemical reaction

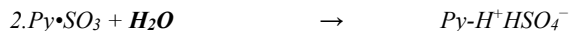
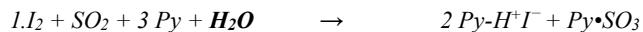
The water content determination is based on the reaction described by R. W. Bunsen:



Karl Fischer discovered that this reaction could be used for water determinations in a non-aqueous system containing an excess of sulfur dioxide. Methanol proved to be suitable as a solvent. In order to achieve an equilibrium shift to the right, it is necessary to neutralize the acids that are formed during the process (HI and H<sub>2</sub>SO<sub>4</sub>). Karl Fischer used pyridine for this purpose. Smith, Bryanz and Mitchell formulated a two-step reaction:

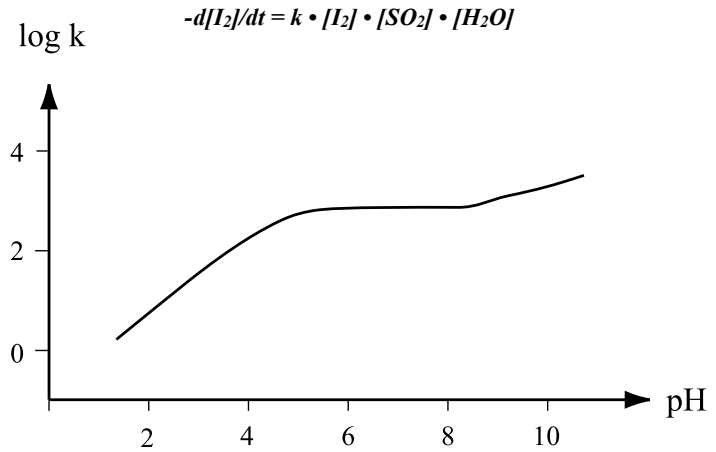


According to these equations, methanol not only acts as a solvent but also participates directly in the reaction itself. In an alcoholic solution, the reaction between iodine and water takes place in the stoichiometric ratio of 1:1. In an alcohol-free solution, the reaction between iodine and water takes place in the stoichiometric ratio of 1:2:

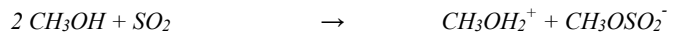


Further studies conducted by J. C. Verhoef and E. Barenrecht on the subject of the Karl Fischer reaction have revealed that:

- Pyridine is not directly involved in the reaction, i.e., it only acts as a buffering agent and can therefore be replaced by other bases,
- The rate of the Karl Fischer reaction, described by the rate constant *k*, depends on the pH value of the medium (see graphics below)



One possible explanation for the influence of pH on the reaction rate is that it is not the sulfur dioxide itself that is oxidized by iodine under the influence of water, but rather the methyl sulfite ion. This is formed from sulfur dioxide and methanol according to the equation:



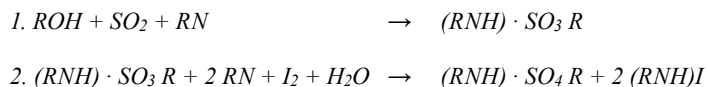
The higher the pH of the solution, the more methyl sulfite is formed by the capture of protons, and the faster the rate of the Karl Fischer reaction.

In the pH range 5.5 to 8, all the sulfur dioxide is present as methyl sulfite; the maximum reaction rate is reached here and cannot increase further. At pH values above 8.5, the reaction rate increases due to side



reactions between iodine and hydroxide or methylate ions; in a titration, this results in a more sluggish endpoint and higher iodine consumption. On the basis of this knowledge, E. Scholz developed a pyridine-free Karl Fischer reagent with imidazole as base. This reagent not only replaced the toxic, pungent pyridine, but also facilitated faster and more accurate titrations because imidazole buffers in a more favorable pH range than pyridine.

Studies by E. Scholz resulted in the following reaction scheme being proposed for the Karl Fischer reaction:



This resulted in the general chemical equation:



E. Scholz was also able to confirm the existence of basic methylsulfite in methanol/SO<sub>2</sub>/I<sub>2</sub> solutions during the titration. In 1988, A. Seubert identified methylsulfite in KF solutions with the aid of IR spectroscopy and isolated and identified methyl sulfate as the secondary product of the KF reaction.

Experiments on the stoichiometry of the reaction showed that methanol can in fact be replaced by other alcohols (e.g. ethanol, 2-propanol, methoxyethanol, diethylene glycol monoethylether). This improves the titer stability.

### 1.3 Consequences for practical applications

#### • Influence of pH on the Karl Fischer reaction

Since the maximum rate of the Karl Fischer titration is in the pH range 5.5 to 8, pH values less than 4 and greater than 8 should be avoided in practice. With acidic or basic samples, you should adjust the pH value to the ideal range by adding buffering agents (for acids: imidazole, and for bases: salicylic acid).

#### • Influence of the solvent on the Karl Fischer reaction

The stoichiometry (molar ratio of H<sub>2</sub>O:I<sub>2</sub>) depends on the type of solvent:

Alcoholic solvent	H <sub>2</sub> O:I <sub>2</sub> = 1:1	(e.g. methanol)
Non-alcoholic solvent	H <sub>2</sub> O:I <sub>2</sub> = 2:1	(e.g. dimethylformamide)

Studies by Eberius showed that iodine and water react in the ratio of 1:1 if the percentage of methanol in the solvent is 20% or more. Methanol should therefore always be present in the minimum required amount. If a methanol-free titrant has to be used (e.g. for determination in ketones or aldehydes), you can use other alcohols such as, for instance, ethylene glycol monomethyl ether.

- **Influence of the water content of the sample on the Karl Fischer reaction**

The water content of the sample also influences the  $\text{H}_2\text{O}:\text{I}_2$  molar ratio. J.C. Verhoef and E. Barendrecht observed an increase in the titer with water contents greater than 1 mol/L. This, however, is not a serious limitation because the water concentration in the solvent is usually much less.

## 2. Volumetric and Coulometric Karl Fischer Analyses

The determination of the water content according to Karl Fischer is nowadays performed by two different techniques:

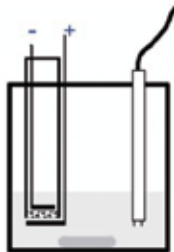
- Volumetric Karl Fischer Titration, where a solution containing iodine is added using a motorized piston burette;
- Coulometric Karl Fischer Analysis, where iodine is generated by electrochemical oxidation in the cell

The selection of the appropriate technique is based on the estimated water content in the sample:



### Volumetric Karl Fischer Titration

Iodine is added by a burette during titration. Suitable for samples where water is present as a major component: **100 ppm - 100%**



### Coulometric Karl Fischer Analysis

Iodine is generated electrochemically during titration. Suitable for samples where water is present in trace amounts: **1 ppm - 5%**

## 2.1 Volumetric KF reagents

### 2.1.1 One-component KF reagent

The **titrant** contains iodine, sulfur dioxide and imidazole, dissolved in a suitable alcohol. The **solvent** is methanol. You can also use a methanolic solvent mixture specially adapted to the sample as the solvent.

The reagent can be stored for approximately two years. The drop in titer, i.e., the decrease in concentration, is approximately 0.5 mg/mL per year in a sealed bottle. The reagent is available in three different concentrations:

- 5 mg/mL for samples with a water content of 1000 ppm to 100%,
- 2 mg/mL for samples with a water content of less than 1000 ppm,
- 1 mg/mL for samples with a water content of less than 200 ppm.

### 2.1.2 Two-component KF reagent

The **titrant** contains iodine and methanol. The **solvent** contains sulfur dioxide, imidazole and methanol.

A titration speed two or three times as high can be achieved with the two-component reagent. Both the components are very stable in storage. The titrant has a stable titer, provided that the bottle is tightly sealed. It is available in two different concentrations:

- 5 mg/mL for samples with a water content of 1000 ppm to 100%,
- 2 mg/mL for samples with a water content of less than 1000 ppm.

Reagents	+	-
One-component	Simple handling, favorably priced.	Titer less stable, titration speed slower.
Two-component	High titration speed, stable titer.	Solvent capacity restricted.

### 2.1.3 Pyridine-containing reagents

Despite the existence of pyridine-free reagents, which allow for fast and accurate Karl Fischer titrations, reagents containing pyridine are still used because they are cheaper and can be made in-house.

One-component reagent:

The titrant contains iodine, sulfur dioxide and pyridine, dissolved in methanol. The solvent is either methanol or consists of methanol mixtures. Some manufacturers have slightly increased the pyridine content

in the titrant to achieve a higher titration speed. This reagent is declared as "rapid". To improve stability, some manufacturers also sell the titrant separated into solution A (sulfur dioxide, pyridine, methanol) and B (iodine, methanol). These solutions are mixed 1:1 just before use to form the one-component titrant.

Two-component reagent:

The titrant contains iodine dissolved in an alcohol, e.g. methanol, whereas the solvent consists of sulfur dioxide and a base, e.g. imidazole, dissolved in an alcohol (usually methanol), or an alcoholic mixture. The separation into titrant and solvent improves stability of the KF reagents, increases their lifetime, and results in higher titration speed.

#### **2.1.4 Special reagents for aldehydes and ketones**

Aldehydes (R-CHO) and ketones (R-CO-R) form acetals and ketals if titrated with standard methanol-containing reagents. As a result, additional water is produced and titrated at the same time, leading to higher water contents and a vanishing end point. Special methanol-free KF one-component reagents such as e.g. HYDRANAL® (Composite 5K and Working Medium K, from Sigma-Aldrich) and e.g. apura® (CombiTitrant 5 Keto with CombiSolvent Keto, from VWR/MERCK) are commercially available to prevent this problem.

One-component reagent:

The titrant contains iodine, imidazole, sulfur dioxide and 2-methoxyethanol, whereas the solvent contains 2-chloroethanol and trichloromethane. The titration takes slightly longer than with the standard KF reagent. Note that it may be necessary to adapt the end point value in the titration method to these reagents. This special reagent is also suitable for substances that react with methanol, such as amines.

#### **2.1.5 Karl Fischer reagents with ethanol**

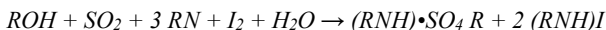
Since ethanol is less toxic than methanol, two-component, ethanol-based reagents were launched in 1998. These reagents also allow for titration of several ketones which form ketals considerably more slowly in ethanol than in methanol.

The titrant contains iodine and ethanol, whereas the solvent contains sulfur dioxide, imidazole, diethanolamine and ethanol.

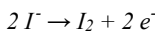
## 2.2 Coulometric KF analysis

### 2.2.1 KF coulometry

Coulometric KF determination of water is based on the standard reaction equation for the KF reaction.

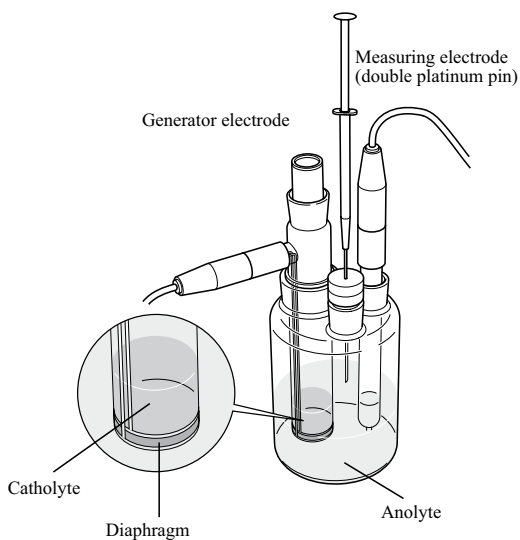


In coulometry, however, the iodine is generated electrochemically by anodic oxidation in the coulometric cell according to the following half-reaction:



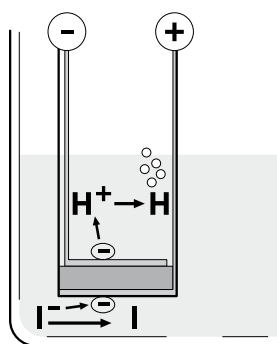
Iodine generation occurs at a generator electrode\* (also called "generator cell", or "inner burette") incorporated into the glass titration cell. The generator is close to the measuring electrode\*, a double pin platinum electrode, which is monitoring the potential of the sample solution by voltametric technique during coulometric titration.

The classical coulometric cell consists of two parts, the anode compartment and the cathode compartment. Both parts are separated by a diaphragm.



\* The terms "generator electrode" and "measuring electrode" mean an arrangement of two electrodes (anode and cathode) to form an electrolytic cell.

The anode compartment contains the anolyte, i.e. the KF electrolyte which is required for the oxidation in order to generate iodine by applying a current at the generating electrode. This consists of sulfur dioxide, imidazole and iodide salts. Methanol or ethanol is used as solvent. Depending on the application, other solvents such e.g. as chloroform, octanol, hexanol or ethylene glycol may be added. The cathode compartment contains the catholyte, i.e. the reagent that enables completion of the whole electrochemical reaction: the oxidation reaction in the anolyte compartment is completed by a reduction reaction in the catholyte compartment. The catholyte is either a manufacturer-specific special reagent, or the same reagent as used in the anode compartment.



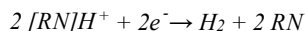
#### **Anode reaction**

At the anode, iodine is generated from iodide by electrochemical oxidation. The negative iodide ions release electrons at the anode and form iodine, which subsequently reacts with water.

#### **Cathode reaction**

At the cathode, the positive hydrogen ions are reduced to hydrogen. This is the main product formed.

An ammonium salt is added to the catholyte in order to promote hydrogen production.



Ammonium ions are then reduced with the formation of hydrogen and a free amine.

Note that methyl sulfonic acid,  $CH_3SO_3H$ , present in the anolyte compartment, can reach the cathode where it is reduced to a sulfide compound (obnoxious smell!). This can cause the cathode to become black.

To avoid this, the catholyte should be replaced once in two weeks.

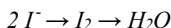
### 2.2.2 Stoichiometry of the coulometric KF reaction

The amount of water titrated by coulometric technique is determined by the amount of electrical current given in Coulomb, C, used to generate iodine. To calculate it, it is necessary to first recall the definition of 1 Coulomb: one coulomb, C, is the quantity of charge that is transported by a current of 1 ampere in one second.

$$1 \text{ C} = 1 \text{ A} \cdot 1 \text{ s}$$

On the other hand, it is known that to produce **one** mole of a chemical substance that requires **one** electron, 96485 C of current are needed. The value 96485 C/mol is known as the Faraday constant.

In Karl Fischer reaction **two** iodide ions, I<sup>-</sup>, are oxidized to one molecule of iodine, I<sub>2</sub>, releasing **two** electrons at the anode. Subsequently, iodine reacts with water.



Therefore, 2 x 96485 C/mol is required for 1 mole of water. Since the molar mass of water is 18.015 g/mol, this calculation can be expressed as follows:

**1 mg of water** corresponds to a consumption of **10.712 C** electrical current.

For an electrochemically optimized Karl Fischer cell, the current conversion efficiency for iodine production is assumed to be 100%. Since current and time can be accurately measured, no standardization of the coulometric KF reagents is necessary. For this reason, coulometry is designated as absolute method. As a consequence, it is used as a reference method for the determination of water content. Nevertheless, it is strongly recommended that the coulometer is regularly checked by measuring a certified water standard.

### 2.2.3. Iodine generation

Iodine is generated by means of current pulses of 400, 300, 200 and 100 mA. The rate of iodine generation is adjusted by varying the pulse duration and frequency and the pulse height (in mA). The maximum pulse height depends on the following factors:

- conductivity of the anolyte
- voltage at the generator electrode
- surface of the generator electrode

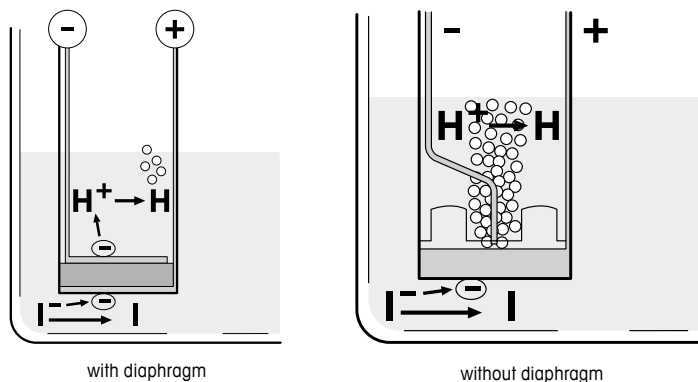


The voltage at the generator electrode and the surface of the electrode depend on the type of coulometer. In addition, the conductivity of the analyte is influenced by the samples and additional solvents (chloroform, hexanol, etc.).

With standard conductivity values, the coulometer operates with current pulses of 400 mA. This gives an iodine generation rate which corresponds to a maximum of 2240  $\mu\text{g}$  water/min.

At very low conductivities (i.e. less than 3–4  $\mu\text{S}/\text{cm}$ ), the maximum possible current applied by the instrument is 100 mA.

### 2.2.4 Generator electrode without diaphragm



The first commercially available diaphragmless cell for KF coulometry was introduced in 1989. The main advantages compared to cells with diaphragms are:

- no contamination or blockage of the diaphragm
- easier cleaning
- lower drift

Originally, the generator cell was first built with a porous ceramic frit (diaphragm) separating the inner cathode compartment from the anode compartment. The purpose is to prevent that iodine molecules generated at the anode are immediately reduced to iodide ions at the cathode instead of reacting with water.

To avoid this concurring reaction, a different geometry is used for the generating cell without diaphragm. The cathode is smaller and made in such a way that iodine cannot reach the cathode (i.e. the cathode is

a small-size pin). In addition, a relatively high stirrer speed allows for more rapid distribution of the generated iodine molecules. The latter can thus react more efficiently with water.

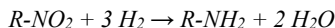
Note that hydrogen gas generated at the cathode is forming gas bubbles around its surface. Thus, this makes it almost impossible for iodine to reach the cathode and be reduced to iodide. This effect is further enhanced by the small dimensions of the cathode.

Nevertheless, it is still possible for a very small amount of iodine to reach the cathode. However, the relative error due to this effect can be minimized by using a larger amount of sample.

In practice, for measurement of samples having a very low water content (e.g., lower than 50 µg water/sample), and for very accurate determinations, the cell with diaphragm may yield more precise results.

### 2.2.5 Limitations for the use of the cell without diaphragm

The cell without diaphragm is not suitable for samples that are easily reduced. Nascent hydrogen is formed at the cathode. This is a very good reducing agent, especially for nitro compounds such as nitrobenzene.



Besides this, other easily reducible substances such as unsaturated fatty acids, etc. may also be reduced at the cathode by the formation of water.

The diaphragmless cell is ideal for the determination of the water content of the following compounds:

- hydrocarbons - chlorinated hydrocarbons
- alcohols - phenols (most)
- esters - ethers
- ketones (with special reagent) - acetamides
- etheric oils and essences - edible oils
- petroleum oils

A cell with diaphragm is required for:

- samples with a very low water content (< 50 µg water/sample)
- very accurate determinations
- nitro compounds
- unsaturated hydrocarbons, especially when easily reducible.

## 3. Further Information

**3.1 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.

**3.2 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

**3.3 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).

# 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.



### 1. Evaluation

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

### 2. Selection

Choose the ideal combination of instrument and measuring technology to best match your process needs.

### 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.

► [www.mt.com/gtp](http://www.mt.com/gtp)

[www.mt.com/karl-fischer](http://www.mt.com/karl-fischer)

For more information

#### Mettler-Toledo AG, Analytical

CH-8603 Schwerzenbach, Switzerland

Tel. +41-44-806 77 11

Fax +41-44-806 73 50

Subject to technical changes

© 08/2012 Mettler-Toledo AG

Printed in Switzerland 30056831

Global MarCom Switzerland