

# ABC of Titration



Titration Theory

## ABC of Titration

in Theory and Practice

METTLER TOLEDO

# Content

|          |   |           |
|----------|---|-----------|
| <b>1</b> | <b>Definition of Titration</b>                | <b>5</b>  |
| <b>2</b> | <b>Historical development</b>                 | <b>6</b>  |
| <b>3</b> | <b>Fields of use</b>                          | <b>7</b>  |
| <b>4</b> | <b>Advantages of titration</b>                | <b>8</b>  |
| <b>5</b> | <b>Titration theory</b>                       | <b>9</b>  |
| 5.1      | Types of chemical reaction                    | 9         |
| 5.2      | Indication principles                         | 10        |
| 5.2.1    | Manual titration                              | 10        |
| 5.2.2    | Semi or automated titration                   | 11        |
| 5.3      | Titration Mode – Endpoint / Equivalence point | 13        |
| 5.3.1    | Endpoint titration (EP)                       | 13        |
| 5.3.2    | Equivalence point titration (EQP)             | 14        |
| 5.4      | Titration types                               | 15        |
| 5.4.1    | Direct titration                              | 15        |
| 5.4.2    | Blank compensated titration                   | 15        |
| 5.4.3    | Back titration                                | 16        |
| <b>6</b> | <b>Titration control</b>                      | <b>18</b> |
| 6.1      | Manual titration                              | 18        |
| 6.2      | Automated titration                           | 18        |
| 6.2.1    | Titrant addition                              | 19        |
| 6.2.2    | Measured value acquisition                    | 19        |
| <b>7</b> | <b>Calculations</b>                           | <b>20</b> |
| 7.1      | Stoichiometry and equivalent number           | 20        |
| 7.2      | Result calculation                            | 21        |

|           |   |           |
|-----------|---|-----------|
| <b>8</b>  | <b>Components involved in the titration</b>         | <b>23</b> |
| 8.1       | Titrant   | 23        |
| 8.1.1     | Titrant concentration determination                 | 23        |
| 8.2       | Sensor  | 24        |
| 8.2.1     | pH sensor and measurements (Acid/Base titrations)   | 24        |
| 8.2.1.1   | pH Sensor and Temperature                           | 25        |
| 8.3       | Burette   | 26        |
| 8.4       | Sample  | 26        |
| <b>9</b>  | <b>Performance Verification of titration</b>        | <b>27</b> |
| <b>10</b> | <b>Karl Fischer Titration</b>                       | <b>28</b> |
| 10.1      | Titration principle                                 | 29        |
| 10.2      | Endpoint indication of a Karl Fischer titration     | 29        |
| 10.3      | Prerequisites for volumetric Karl Fischer titration | 29        |
| 10.4      | Drift   | 30        |
| 10.5      | Volumetric Karl Fischer reagents                    | 30        |
| 10.5.1    | One-component KF reagent                            | 30        |
| 10.5.2    | Two-component KF reagent                            | 30        |
| 10.6      | Concentration determination                         | 31        |
| 10.7      | Sample handling                                     | 32        |
| 10.7.1    | Solid samples                                       | 33        |
| 10.7.2    | Liquid samples                                      | 33        |
| 10.7.3    | Solubility of sample                                | 34        |
| 10.8      | Execution of a volumetric Karl Fischer titration    | 35        |
| 10.9      | Interferences of Karl Fischer titration             | 35        |
| 10.9.1    | Influence of pH                                     | 35        |
| 10.9.2    | Side reactions                                      | 36        |
| <b>11</b> | <b>Glossary</b>                                     | <b>37</b> |

# ABC of Titration

## Introduction

This booklet is intended as a first introduction to the theory and practice of general and Karl Fischer titration. The basic knowledge that is needed to understand a titration is given. Different kinds of chemical reactions, indication principles and titration types for general titration are explained and manual titration is compared to automated titration.

The Karl Fischer titration, as a special variant of titration for water content determination, is discussed in a separate chapter.

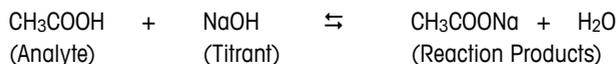
Finally, some practical tips & hints are given for general and Karl Fischer titration.

# 1 Definition of Titration

Titration is the determination of the quantity of a specific substance (analyte) contained in a sample by the controlled addition of a reagent (titrant) of known concentration based on a complete chemical reaction between the substance and the reagent. The titrant is added until the reaction is complete. In order to determine the end of the titration, the reaction has to be monitored (indicated) by an appropriate technique. The measurement of the dispensed titrant volume allows the calculation of the analyte content, based on the stoichiometry of the chemical reaction.

The reaction involved in a titration has to be fast, complete, unambiguous and observable.

A well-known example is the titration of acetic acid ( $\text{CH}_3\text{COOH}$ ) in vinegar with sodium hydroxide ( $\text{NaOH}$ ) according to the following equilibrium:



The classical way of the monitoring of a titration reaction was carried out by the usage of a suitable color indicator, which changes color when the chemical reaction is complete (end of titration). Today, there is the possibility to monitor the reaction and end point by means of an electrochemical sensor.

## 2 Historical development

### From manual to automated titration

The classical way to perform a titration is using a graduated glass cylinder (burette). With a tap the titrant addition is regulated manually. A change in color indicates the end of the titration reaction (endpoint).

At first, only those titrations showing a significant color change upon reaching the endpoint were performed. Today, titrations are colored artificially with an indicator dye. The precision achieved depends mainly on the chemist's skills and, in particular, on his ability for perception of different colors.

Titration has experienced a strong development: manual and later motor-driven piston burettes allow accurate and repeatable titrant addition. Electrochemical sensors replace the color indicators, thus achieving higher precision and accuracy of results. The graphical plot of potential versus titrant volume and mathematical evaluation of the resulting titration curve provides a more exact statement about the reaction than the color change at the endpoint. With microprocessors the titration can be controlled and evaluated automatically. This represents an important step towards automation.



### 3 Fields of use

Titration is a widely applied analytical technique used in various fields. A few examples are given below:

- Chemical industry
- Food & beverages
- Electronics industry
- Universities / Schools
- Other segments exist



## 4 Advantages of titration

There are several reasons why titration is used in laboratories world-wide. A comparison of manual and automated titration is shown below:

### Manual titration

- Well-established analytical technique
- Fast
- Accurate and precise
- Good price/performance ratio compared to more sophisticated techniques

### Automated titration

- Well-established analytical technique
- Fast
- Higher precision, repeatability and accuracy compared to manual titration
- Good price/performance ratio compared to more sophisticated techniques
- Operator independent
- Saves analyst time
- Simple operation, easy to learn
- Can even be used by semi-skilled operators



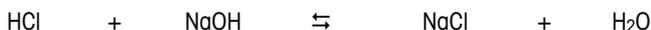
## 5 Titration theory

Titrations can be classified according to the chemical reactions occurring and the indication principles used to monitor the reaction.

### 5.1 Types of chemical reaction

Mainly three different kinds of chemical reactions are used in titration. The reactions are listed below with an example and some typical applications:

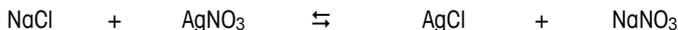
#### Acid/Base reactions:



Applications: Acid content in juices, milk and wine  
Acid content in vinegar, ketchup  
p- and m-value in water  
Acidity/Alkalinity

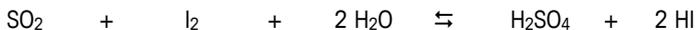
METTLER TOLEDO's **Titration EasyPlus™ Easy pH** includes everything needed for a successful acid/base titration.

#### Precipitation reactions:



Applications: Chloride/salt content in food  
Silver content determination

METTLER TOLEDO's **Titration EasyPlus™ Easy Cl** includes everything needed for a successful chloride determination.

**Redox reactions:**

Applications: Reducing sugars in juices  
 Vitamin C in juices  
 SO<sub>2</sub> content in wine  
 Peroxide number in edible oils

METTLER TOLEDO's **Titration EasyPlus™ Easy Ox** includes everything needed for a successful redox titration.

METTLER TOLEDO's **Titration EasyPlus™ Easy Pro** combines all three reaction types in one instrument.

For Water content determination, i.e. Karl Fischer titration, refer to chapter 10.

## 5.2 Indication principles

### 5.2.1 Manual titration

In manual titration the reaction is monitored using a color indicator. When the reaction is completed the color of the indicator changes and indicates the end of the titration (i.e. endpoint).



The table below shows some typical color indicators used for pH titration, the color change and the corresponding pH range including application examples.

| <b>Indicator</b>                          | <b>Color change</b> | <b>pH range</b> | <b>Application example</b> |
|---|---------------------|-----------------|----------------------------|
| Methyl orange                             | red - yellow        | 3.1 - 4.4       | Base content<br>m-Value    |
| Phenolphthalein                           | colorless - pink    | 8.3 - 10.0      | Acid content<br>p-Value    |
| Mixed Indicator<br>(e.g. Merck5, Tashiro) | violet - green      | 4.4 - 6.2       | Kjeldahl Nitrogen          |

### 5.2.2 Semi or automated titration

The **potentiometric principle** is most commonly used for automated or semi-automated titrations (manual titration with a sensor and a measuring unit). The concentration dependent potential (mv) of a solution is measured against a reference potential.

This includes pH measurements, redox measurements and silver ion measurements. Typically a combined sensor (electrode) including reference is used.

A list with application examples and the corresponding sensor is shown below.

#### **Acid/Base (aqueous)**

Examples:

#### **Combined pH glass sensor**

Acid content in wine, milk and juices  
p- and m-value in water

METTLER TOLEDO sensor for EasyPlus™ Titration: **EG11-BNC**

#### **Acid/Base (non-aqueous) Combined pH glass sensor**

Examples:

Free fatty acid content in edible oils  
Total acid-/base number

METTLER TOLEDO sensor for EasyPlus™ Titration: **EG13-BNC**



**Precipitation**

Examples:

**Combined silver sensor**

Argentometric titrations in aqueous media  
Chloride content in food  
Silver content determination

METTLER TOLEDO sensor for EasyPlus™ Titration: **EM45-BNC**

**Redox  
(aqueous/non-aqueous)**

Examples:

**Combined platinum sensor**

Peroxide number in edible oils  
Reducing sugars in juices

METTLER TOLEDO sensor for EasyPlus™ Titration: **EM40-BNC**

For some Redox reactions the **voltametric indication** is more suitable, where the concentration dependent potential of a solution is measured with a double platinum pin sensor at a constant polarization current.

**Redox (Ipol)**

Examples:

**Double platinum pin sensor**

Sulfur dioxide in wine  
Vitamin C in beverages

METTLER TOLEDO sensor for EasyPlus™ Titration: **EM43-BNC**

This indication principle is also used in Karl Fischer titration (Water content determination), refer to chapter 10.2.

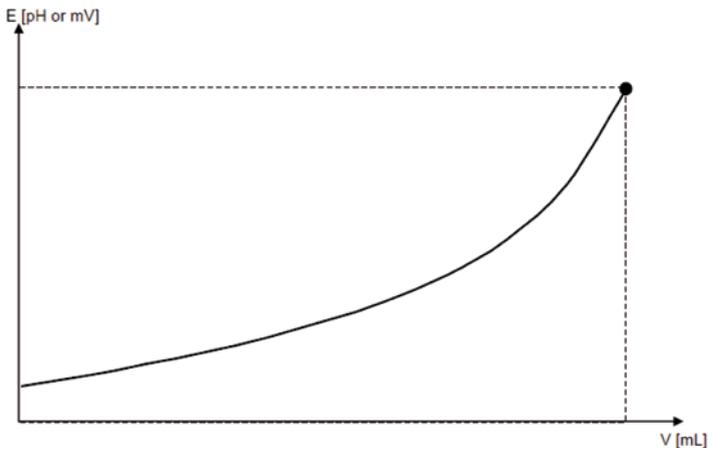
## 5.3 Titration Mode – Endpoint / Equivalence point

There are basically two titration modes which can be distinguished: Endpoint titrations (EP) and Equivalence point titrations (EQP).

### 5.3.1 Endpoint titration (EP)

The endpoint mode represents the classical (manual) titration procedure, where the titrant is added until the end of the reaction is observed by a color change of an indicator. Using potentiometric indication this means the sample is titrated until a predefined measured value is reached, e.g.  $\text{pH} = 8.2$  or  $E = 100 \text{ mV}$ .

Figure 1 shows a typical endpoint titration curve.



**Figure 1**  
Endpoint titration curve

The color change of an indicator typically correlates to a certain pH range; therefore this mode is typically used for Acid/Base titrations. The actual endpoint/pH value is often based on an historical definition.

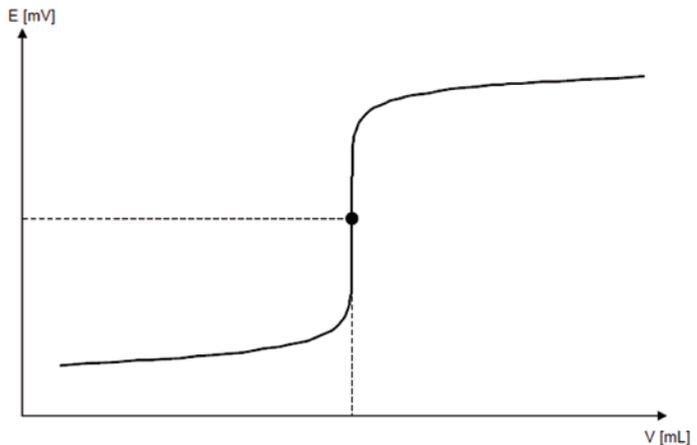
For accurate pH endpoint titrations it is absolute necessary to perform a proper sensor calibration before titration. An incorrect pH reading will lead to wrong titrant consumption and thus a wrong result.

Furthermore, the pH of a sample is temperature dependent. Therefore the sample determination/titration has to be performed at the same temperature as during the sensor calibration or an additional temperature sensor should be used for temperature compensation.

### 5.3.2 Equivalence point titration (EQP)

The equivalence point is the point at which the analyte and the reagent (titrant) are present in exactly the same (equivalent) concentration. In most cases it is virtually identical to the inflection point of the titration curve, for example titration curves obtained from acid/ base titrations. The inflection point of the curve is defined by the corresponding pH or potential (mV) and titrant consumption (mL).

Figure 2 shows a typical equivalence point titration curve.



**Figure 2**  
Equivalence point  
titration curve

## 5.4 Titration types

In practice three different types of titration are used:

- Direct titration
- Blank compensated titration
- Back titration

### 5.4.1 Direct titration

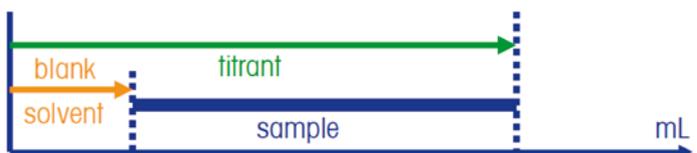
In a direct titration the titrant reacts directly with the analyte. The titrant consumption equates directly to the analyte content and is used for calculations.



An example for a direct titration is the determination of acid content in vinegar. An aliquot of the sample is diluted and then directly titrated with sodium hydroxide.

### 5.4.2 Blank compensated titration

In this case the sample is dissolved in a solvent which also reacts with the titrant and leads to a certain consumption. Therefore a blank value of the solvent has to be determined. The total consumption minus the consumption for the solvent (blank value) equates to the analyte in the sample.



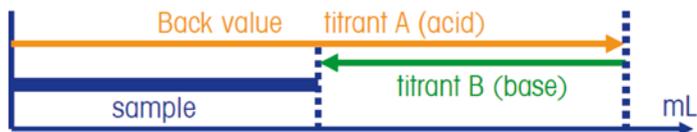
An example for a blank compensated titration is the determination of the acid number or free fatty acids in edible oil. The sample is dissolved in a mixture of solvents and titrated with potassium hydroxide in ethanol. Acidic impurities in the solvent also react with the titrant. To determine the blank value, first the solvent is titrated without sample. In a second titration the sample dissolved in the solvent is titrated. The titrant consumption for the sample equates to the total consumption (sample + solvent) minus the consumption for the solvent without sample (= blank value) and is used for calculations.

Always use the same amount of solvent for sample and blank determination.

**EasyPlus™ Titration:** The Blank value is stored in the general settings of the instrument.

### 5.4.3 Back titration

In a back titration an exactly known excess of titrant/reagent is added to the sample. After a sufficiently long reaction time, this excess is then back titrated with a second titrant. The difference between the added amount of the first and second titrant then gives the equivalent amount of the analyte.



An example of a back titration is the determination of reducing sugars. An excess of copper(II) solution is added to the sample. The reducing sugar reacts with the copper(II) to reduce it to copper(I). The copper(II) which is not reduced by the sample is then titrated with sodium thiosulfate. The exact amount of copper(II) added to the sample has to be

known or determined accordingly. This amount is called the back value. The back value minus the titrant consumption (after reaction of the sample with the copper(II) solution) equates to the actual consumption for the sample and is used for the calculations.

The back value, i.e. the exact amount of titrant/reagent added to the sample must be known.

**EasyPlus™ Titration:** The Back value is stored in the individual method of the instrument.

## 6 Titration control

### 6.1 Manual titration

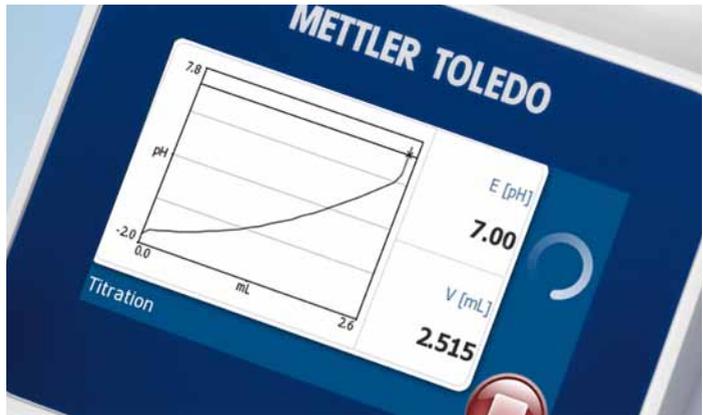
A manual titration is controlled by the operator himself. The titrant addition is regulated manually and the monitoring of the reaction and indication of the endpoint are mostly done visually.



### 6.2 Automated titration

A titrator allows the automation of all operations involved in the titration, i.e. titrant addition, monitoring of the reaction (measured value acquisition), recognition of the endpoint, including evaluation and calculation of the result.

The titration curve shows the measured signal  $E$  [mV or pH] against the volume  $V$  [ml] of the added titrant. The signal indicates the progress of the titration reaction versus the titrant addition.



### 6.2.1 Titrant addition

The titrant can be added in two ways: continuously at a defined dispensing rate or incrementally with individual volume steps. The volume steps are either defined as fixed increments or dynamically, dependent on the actual change in measured potential.

### 6.2.2 Measured value acquisition

After each addition of a volume increment a measured value must be acquired. This is generally obtained equilibrium controlled.

**EasyPlus™ Titration:** A set of tested and approved control parameters for each reaction type is already preprogrammed in the instrument.

These are:

**Normal** to achieve high accuracy with average speed.

**Fast** if analysis requires high titrant consumption, analysis speed may lead to lower accuracy.

**Cautious** highest accuracy, especially for low contents, analysis speed may be prolonged.

In addition a **user defined** control can be selected.

## 7 Calculations

The calculation of the final result is based on the consumption of the titrant as well as the stoichiometry of the chemical reaction between analyte and titrant.

### 7.1 Stoichiometry and equivalent number

The stoichiometry describes the ratio of analyte and reagent (titrant) in a chemical reaction, i.e. how many molecules or moles of a reagent are needed for a complete reaction with a certain number of molecules or moles of the analyte.

The stoichiometric information is always included in any chemical equation, e.g.:



For titration the ratio of analyte and reagent is usually expressed by the equivalent number, abbreviated as "z".

In the above example 2 mol of sodium hydroxide (NaOH) are required to neutralize 1 mole of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), therefore the equivalent number is z=2. That means the equivalent number indicates how many mol of the titrant react with the analyte.

The equivalent number z is used in calculation along with the molar mass of the analyte. This applies if the titrant has been prepared as a molar solution of the reactive part, e.g.  $c(1/2 \text{ H}_2\text{SO}_4) = 0.1 \text{ mol/L}$  or  $c(1/5 \text{ KMnO}_4) = 0.1 \text{ mol/L}$ .

The following table shows some typical examples of analytes, their titrants and the corresponding equivalent number.

| <b>Analyte (Sample)</b>  | <b>Titrant (Reagent)</b> | <b>Equivalent number (z)</b> |
|--------------------------|--------------------------|------------------------------|
| HCl                      | NaOH                     | 1                            |
| NaCl                     | AgNO <sub>3</sub>        | 1                            |
| Acetic acid              | NaOH                     | 1                            |
| Tartaric acid            | NaOH                     | 2                            |
| Sulfur dioxide           | I <sub>2</sub>           | 2                            |
| Vitamin C/ Ascorbic acid | DPI                      | 2                            |
| Citric acid              | NaOH                     | 3                            |

## 7.2 Result calculation

The content of the analyte in the sample is calculated according to the following formula:

$$\text{Content} = \frac{\text{VEQ} * c * M * f}{m * z}$$

VEQ = Consumption of titrant [mL]

c = Equivalent concentration of titrant [mol/L]

M = Molar mass of analyte [g/mol]

m = Sample size [g] or [mL]

z = Equivalent number of the analyte

f = Factor for calculation in the desired unit, e.g. g/L or %

The following shows a calculation example of the sodium chloride content in ketchup expressed as a percentage or mg/100g respectively:

Sample size: m = 1.071 g

Titrant concentration (AgNO<sub>3</sub>): c = 0.1 mol/L

Consumption of titrant: VEQ = 6.337 mL

Molar mass (NaCl): M = 58.44 g/mol

Equivalent number: z = 1

Factor: f = 0.1

$$\text{Content [\%]} = \frac{6.337 \text{ mL} * 0.1 \text{ mol} * 58.44 \text{ g} * 0.1}{1.071 \text{ g} * 1 * \text{L} * \text{mol}}$$

$$\text{VEQ [mL]} * c [\text{mol/L}] = \text{Consumption in mmol} = Q = 0.6337 \text{ mmol}$$

$$Q [\text{mmol}] * M [\text{g/mol}] / m [\text{g}] = \text{Content [mg/g]} = 34.578 \text{ mg/g}$$

The factor 'f' is used to convert the result into the desired unit :

$$[\text{mg/g}] * 100 / 1000 \text{ (or } [\text{mg/g}] * 0.1) = 3.458 \% \text{ or g/100g}$$

(Divided by 1000 to convert mg into g and multiplied with 100 per 100g)

**EasyPlus™ Titration:** The titrator includes predefined calculation formulas for the most commonly used measurements. Simply select the desired result unit.

# 8 Components involved in the titration

## 8.1 Titrant

The titrant is a solution of a certain reagent with known concentration which reacts with the analyte in the sample. Its nominal concentration is usually expressed in mol/L of equivalents. The actual concentration is determined by a titrant concentration determination (standardization or titer determination) using a primary standard.

The nominal concentration of commercially available titrant solutions is reliable after freshly opened and thus can be used directly for titration. Usually Titrants are stable up to two weeks depending on storage/usage and protection. If a titrant solution is prepared from its chemical it is recommended to determine the actual concentration by titrant determination.

### 8.1.1 Titrant concentration determination

The titrant concentration determination (standardization or titer determination) is performed under standard conditions using a primary standard of high purity. The molar mass of this standard is used to calculate the actual concentration of the titrant and the actual concentration is related to the nominal concentration. This results in the "Titer" which is the quotient of the determined concentration and the nominal concentration, and is usually approximately 1.

The relation between nominal concentration, titer and actual concentration is described below:

Actual concentration = Nominal concentration \* Titer

$$\text{Titer} = \frac{c(\text{Titrant}) \text{ determined}}{c(\text{Titrant}) \text{ nominal}}$$

Some titrants such as sodium and potassium hydroxide, react with carbon dioxide. Use carbon dioxide free water or solvent for preparation and protect them from ambient air with a suitable absorbent (e.g. NaOH on carrier). Many titrants e.g. DPI, iodine and permanganate are light sensitive and must be protected by storing them short term in brown glass bottles and long term in the dark. Do not expose titrants to high temperature fluctuations to prevent evaporation and condensation because this may affect their concentration.

## 8.2 Sensor

In case a potentiometric sensor is used for monitoring a titration, the following basic conditions have to be considered:

- The sensor including diaphragm must be immersed properly
- Consistent stirring during measurement
- The level of the internal electrolyte must be higher than the sample level.
- The electrolyte refill opening must be open during the measurement

Depending on usage and treatment of a sensor, the lifetime varies from 6 months to about 3 years. For further instructions, maintenance, care and storage refer to the corresponding operation instructions of the sensor used.

### 8.2.1 pH sensor and measurements (Acid/Base titrations)

For accurate pH measurements, in particular pH endpoint titrations, a sensor calibration (adjustment) is imperative.

The correlation between mV and pH measurement is described by the Nernst equation, where the slope and zero point (offset) are outlined as follows:

|             |                     |        |
|-------------|---------------------|--------|
| Slope:      | - 59,16 mV/pH       | @ 25°C |
| Zero point: | +/- 0 mV or pH 7.00 |        |

Since pH sensors are usually manufactured manually (mouth blown) each sensor needs to be calibrated to obtain correct pH measurements. The calibration adjusts the individual slope and zero point of a pH sensor.

A calibration is performed using buffer standards with a defined pH value. At least two buffers are required. The mV values of the buffers are measured subsequently. The slope and zero point are calculated and stored automatically by the instrument itself (i.e. pH meter or titrator).

### **8.2.1.1 pH Sensor and Temperature**

The pH of a buffer or sample is temperature dependent. Therefore the temperature has to be indicated with each measurement.

The temperature dependence of a buffer is known. The buffer values for different temperatures are typically stored with each buffer in the instrument or can be entered and used for calibration. In case an additional temperature sensor is connected, the actual measured temperature and the corresponding buffer value are used for calibration. If no temperature sensor is used, the calibration refers to a global ambient temperature, which is usually 25°C.

The temperature dependence of a sample is not known. Therefore the sample determination/titration has to be performed at the same temperature as the sensor calibration.

**EasyPlus™ Titration:** The global temperature is entered in the general settings of the instrument. A separate temperature sensor can be connected and used for temperature compensation.

### 8.3 Burette

In general the burette size for a titration is chosen to achieve a total consumption of approx. 20 to 90% of the total burette volume.

Always assure that the burette – including tubes (i.e. suction, connection and dispensing tube) in case of automated burette – is/ are clean and filled with titrant with no gas bubbles present. Eliminate bubbles by rinsing the burette (and tubing if applicable) several times.



Gas bubbles in the burette and tubing can be minimized by heating or ultrasonic degassing of the titrant before usage.

### 8.4 Sample

The sample size can be used either as weight [g] for solid samples or volume [mL] for liquid samples.

Since the burette size is chosen to achieve a total consumption of approx. 20 to 90% of the total burette volume, the sample size should be adjusted accordingly. Choose an appropriate solvent to dissolve the sample completely.

For better accuracy it is recommended to use sample weight for any sample type (i.e. solid and liquid). The density of the sample is used for correction to volume if applicable.

## 9 Performance verification of titration

Performance verification is achieved by a standard titration of a reference sample with a known content. Hereby the entire titration procedure including titrant addition, measured value acquisition and endpoint detection is verified and analysis accuracy is verified.

It is recommended to carry out a performance verification at regular time intervals. At least three samples should be measured to enable the determination of the relative standard deviation.

To get an unbiased statement confirming accuracy of analysis, use EasyPlus™ performance verifications kits including certificates. Ready-to-use standard solutions are available for acid, base and chloride titrations.

## 10 Karl Fischer Titration

The Karl Fischer method for water content determination is one of the most frequently used titration methods.

The titration is based on the reaction described by R. W. Bunsen:



Karl Fischer, a German petro-chemist, discovered that the reaction performed in a non-aqueous system, i.e. methanol, containing an excess of sulfur dioxide, is suitable to determine the water content. In order to achieve an equilibrium shift to the right, it is necessary to neutralize the acids (HI and H<sub>2</sub>SO<sub>4</sub>) formed during the reaction. Karl Fischer used pyridine for this purpose.

Later investigations revealed that the reaction actually follows two-steps and that methanol not only acts as a solvent, but also participates directly in the reaction. Today commercial reagents are available from different suppliers where the pyridine has been replaced by imidazole.

The determination of the water content according to Karl Fischer is nowadays performed by two different techniques, i.e. by volumetric and coulometric titration. Whereas the coulometric titration determines trace amounts of water, the volumetric titration is suitable to measure a range of 100 ppm to 100% and is the most widespread technique.

METTLER TOLEDO's Easy KFV titrator enables volumetric Karl Fischer titration for a wide variety of samples from different industries.



## 10.1 Titration principle

The sample (liquid or solid) is dissolved in a suitable water free solvent, e.g. methanol. The titrant, containing iodine, is added by a burette and reacts with the  $\text{H}_2\text{O}$  in the sample. The endpoint of the titration, i.e. an excess of iodine, is determined by a double platinum pin sensor using voltametric indication.

## 10.2 Endpoint indication of a Karl Fischer titration

The voltametric indication is used for endpoint detection of a Karl Fischer titration. Hereby, a small constant current (so called polarization current =  $I_{\text{pol}}$ ) is applied to a double platinum pin sensor. To maintain the set polarization current a high voltage (i.e. 400 – 600 mV) is necessary at the double pin sensor. As soon as all the water of the sample has reacted with the iodine, there will be free iodine in the titration solution. The iodine reacts at the platinum pins of the sensor causing an "ionic conduction". Now, only a low voltage (approx. 100 mV) is required to keep the polarization current constant. When the voltage drops below a defined value, the titration is terminated.

Thorough mixing of the titration solution is necessary in order to achieve constant "ionic conduction" i.e. a proper endpoint indication.

## 10.3 Prerequisites for coulometric Karl Fischer titration

There are two main prerequisites for the coulometric KF titration:

- A tight system, in particular titration vessel to be able to achieve a low drift
- The water from the sample must be completely releasable.

## 10.4 Drift

No titration cell is completely tight; the water from atmospheric humidity will find a way into the titration vessel. The drift is the amount of water entering the titration cell per time interval, usually expressed as microliter per minute ( $\mu\text{L}$  Titrant/min).

In this respect, it is necessary to quantify the drift, to be able to correct for the sample.

Protect the titration cell from ingress of water by connecting a drying tube filled with molecular sieve.

The water absorption capacity of molecular sieve is limited. It therefore has to be exchanged frequently.

## 10.5 Volumetric Karl Fischer reagents

To perform a volumetric Karl Fischer titration a solvent and titrant is needed. There are two different types of reagents available, i.e. One-component KF reagent and Two-component KF reagent.

### 10.5.1 One-component KF reagent

The titrant contains iodine, sulfur dioxide and imidazole, dissolved in a suitable alcohol. The solvent is usually methanol.

### 10.5.2 Two-component KF reagent

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

Because of easy handling and moderate price the one-component reagent is more commonly used.

The concentration of the titrant is typically expressed as milligram water per milliliter titrant, e.g. 5 mg/mL. Different concentrations from different suppliers are available. Since the KF titrants are not stable over longer time periods after opening, a concentration determination has to be performed regularly.

To be able to guarantee the concentration of a titrant over a longer period of storage, the reagent suppliers usually adjust the concentration to 5-10% higher than the nominal concentration. Therefore a concentration determination has to be performed even when a fresh bottle is opened.

Titration and solvent have to be protected against the ingress of moisture from ambient air using a drying tube filled with molecular sieve on the top of the bottle.

## 10.6 Concentration determination

A concentration determination (titrant determination) is performed using a primary standard with defined water content. Different standards are available for concentration determination, these are:

- Di-Sodium-Tartrate Dihydrate
- Liquid Water Standard (certified)
- Water Tablet (defined concentration per tablet)
- Pure water

Liquid standards are the easiest to use. For solid standards assure sufficient pre-mixing duration to dissolve completely the standard.

Di-Sodium-Tartrate has a limited solubility in methanol. Therefore the solvent (i.e. methanol) has to be exchanged at least after three determinations.

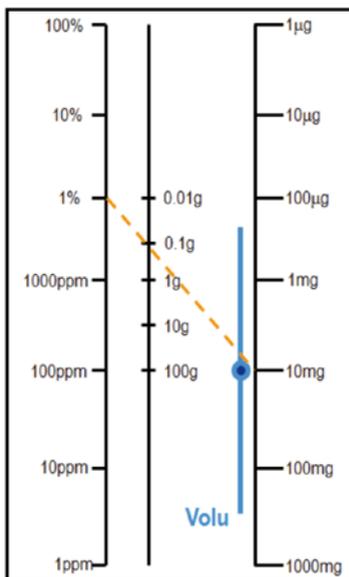
## 10.7 Sample handling

The amount of sample used for titration mainly depends on two factors, i.e.:

- the expected water content
- the required accuracy and precision

For volumetric titrations the optimum amount of water to be added is approximately 10-30 mg. The accuracy increases with the amount of sample, due to higher titrant consumption and less influence of air moisture during sampling and addition.

The recommended sample size can be determined as a function of the expected water content for optimum KF analysis, as shown in the following graphic:



The optimum point, e.g. 10 mg water is connected by a straight line to the expected water content.

The intersection point of this line with the "Amount of sample" scale (\*) in the middle represents the recommended amount of sample to be used.

(\*) Logarithmic scale

In general the sample size is measured by weight. Hence, the back weighing technique is the most suitable way to determine the correct sample size of the sample actually transferred into the titration cell. The procedure is described below for individual sample types.

### 10.7.1 Solid samples

Solid samples can be directly transferred into the titration vessel. The sample should be quickly weighed and added to minimize air exposure.

Back weighing principle: The sample is weight into a weighing boat and placed on the balance. Tare the balance to zero. Add the sample into the titration vessel and return the empty weighing boat to the balance and back-weigh the empty weighing boat. The absolute value of the weight shown on the balance equates to the sample size.

Brittle hard or coarse-grained samples may be ground or crushed with an analytical mill or a mortar and pestle before weighing. Soft samples can be cut into small pieces using a knife or scissors. Pieces can also be added using a pair of tweezers.



### 10.7.2 Liquid samples

Liquid samples are usually handled with a syringe and injected into the titration vessel through a septum.

Rinse the syringe and needle 2-3 times with sample before addition. For higher viscosity samples use a thick needle or even use the syringe

without needle. In this case the sample is filled into the syringe from the back e.g. with the help of a spatula.

The weighing procedure for liquids is the same as for solid samples, i.e. back weighing and is described in chapter 10.7.1 above.

Liquids with heterogeneous water distribution, e.g. non-polar liquids like oils must be thoroughly mixed before sampling.

### 10.7.3 Solubility of sample

To be able to determine the water content in a sample, the sample must release its water completely. Only freely available water undergoes the reaction with the Karl Fischer reagent. Additional solvents can be used as co-solvents to achieve complete dissolution of the sample. In such cases, a large part of the solvent mixture, at least 30%, must always be an alcohol (most preferably methanol) to ensure that the Karl Fischer reaction is strictly stoichiometric.

The following table shows various solvents used as co-solvent for different sample types and the maximum amount:

| Solvent    | Max. amount | Samples   |
|------------|-------------|---|
| Methanol   | 100%        | Solvents: toluene, dioxane, alcohols, ester<br>Organic products: urea, salicylic acid<br>Foods: honey, yogurt, beverages<br>Cosmetics: soaps, creams, emulsions |
| Chloroform | 70%         | Petrochemical products: crude oil, hydraulic oil, transformer oil, fat  |
| Decanol    | 50%         | Oils: edible oil, massage oil, ethereal oils  |
| Octanol    |             | Petrochemical products: gasoline, diesel  |
| Hexanol    |             | oil, kerosene   |
| Dodecanol  |             | Pharmaceutical products: ointments, fatty creams  |



|           |     |   |
|-----------|-----|---|
| Toluene   | 50% | Waxes, tar products, suppositories  |
| Formamide | 50% | Sugar products: jelly, caramel, jelly bears<br>Starch products: flour, corn, noodles,<br>potato chips |

The dissolving capacity of the solvent is a crucial factor in Karl Fischer titration. If exhausted, the water will no longer be completely released. This will lead to incorrect results, i.e. too low water content. It is therefore necessary to replace the solvent frequently.

## 10.8 Execution of a volumetric Karl Fischer titration

The cell needs to be conditioned after freshly filled with solvent, i.e. the existing water in the solvent is titrated. As soon as there is no more water in the cell the titrator is ready for sample determination. The sample (liquid or solid) is added into the titration vessel. During prestir duration the water in the sample is released and subsequently titrated. The calculation including drift compensation is automatically performed and the result is shown on the display (or printed).

## 10.9 Interferences in Karl Fischer titration

### 10.9.1 Influence of pH

The Karl Fischer reaction rate is pH dependent. The optimum pH range is between 5.5 and 8. At a pH below 4 the reaction is very slow and at a pH above 8.5, side reactions occur which lead to a higher iodine consumption.

Use suitable buffers to adjust the pH value in the titration vessel for water content determination of acidic or basic samples, e.g. imidazole for acids and salicylic acid for bases.

### 10.9.2 Side reactions

There are mainly three side reactions known that can affect the result, in addition to the pH effect described above.

| <b>Problem</b>  | <b>Solution</b>   |
|---|---|
| <ul style="list-style-type: none"><li>• Aldehydes and ketones react with methanol resulting in the formation of water which will lead to a too high result.</li><li>• Aldehydes and ketones react with SO<sub>2</sub>, consuming water which will lead to lower water contents.</li><li>• Samples which are easily oxidizable e.g. ascorbic acid, hydroxide, peroxide, sulfite etc. react with the iodine in the titrant.</li></ul> | <ul style="list-style-type: none"><li>• Use special reagents for aldehydes and ketones for these samples. These reagents – so called K-reagents – contain an alcohol other than methanol.</li><li>• Perform a quick titration, i.e. immediate start after sample addition and fast titrant addition to prevent the side reaction.</li><li>• Most of these samples can be analyzed by using external extraction or the indirect Karl Fischer oven technique.</li></ul> |

# 11 Glossary

|                        |   |
|------------------------|---|
| Titration              | Quantitative chemical analysis. The amount of titrant which reacts quantitatively with the sample compound to be analyzed is determined. From this volume (titrant consumption) the amount of sample compound is calculated. The calculation is based on the stoichiometry of the assay reaction (Synonyms: volumetry, titrimetry). |
| Titrant                | Solution of a certain chemical reagent. Its concentration is accurately known by standardization.   |
| Primary standard       | Certified high purity substance which is used for the accurate determination of the titrant concentration.  |
| Indication             | Procedure to follow the reaction and to detect the end of the titration, e.g. potentiometry (electrochemical sensor), or use of color indicators.   |
| End of titration       | A titration is terminated when the desired endpoint or the equivalence point is reached. The consumption of titrant to this point is evaluated. Depending on the chemistry, more than 1 equivalence point may occur during the same titration.  |
| Equivalence point      | The point at which the number of entities (equivalents) of the added titrant is the same as the number of entities of sample analyte.   |
| Analyte                | Specific chemical species of which the content in the sample can be determined by titration.  |
| Standardization        | Determination of the titrant concentration by using a highly pure reference chemical substance (standard).  |
| Stoichiometry          | Mole/mass relationships between reagents and products. The reagents always react according to fixed relationships.  |
| Karl Fischer Titration | Special titration for water content determination   |
| Drift                  | The amount of water entering the titration cell per time interval. Needs to be quantified, to be able to correct for sample determination.  |





# ABC of Titration

This booklet provides an introduction to the analytical technique of titration.

The basic knowledge that is needed to understand a titration is given and the manual titration is compared with automatic titration.

Specifically, different chemical reactions, indication principles and titration types for general are illustrated and explained.

Finally, some practical hints & tips are given.

The Karl Fischer Titration, as a special variant of titration, is discussed in a separate chapter.

[www.mt.com/easyplustitration](http://www.mt.com/easyplustitration)

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

© 03/2013 Mettler-Toledo AG

Printed in Switzerland 30084349

Global MarCom Switzerland