Good Titration Practices (GTP)

METTLER TOLEDO

Agenda

Basic of Titration

Terminology and Definition

- **Qualitative chemical analysis:** Determine the chemical composition in a sample using chemical reactions and interactions.
  Example: Test for halides with Beilstein test (green flame if halides are present).
- **Quantitative chemical analysis:** Determine the content in a sample of one or more chemical substances using chemical reactions and interactions.
  Example: Vitamin C content in orange juice by titration.
- **Sample:** A small representative portion of the entity that should be analyzed.
  Example: Feed
- **Analyte:** The chemical substance to be determined with the analysis.
  Example: Protein
- **Matrix:** Everything in the sample besides the analyte(s).
  Example: Fat, Carbohydrate, Additive, ... in Protein analysis of feed
- **Titrant**: Solution of known concentration which is added to the sample (titration) and reacts with the analyte. The analyte content is calculated from the consumption of the titrant.

Basic of Titration

What is titration?

- **Titration is the determination of the quantity of a specific substance (analyte) contained in a sample by controlled addition of a reagent (titrant) of known concentration based on a complete chemical reaction between the substance and the reagent.**

- ***Example:***

  Determination of acetic acid (CH_3COOH) by titration with sodium hydroxide (NaOH)

$$\underset{\text{(analyte)}}{CH_3COOH} + \underset{\text{(titrant)}}{NaOH} \rightleftharpoons \underset{\text{(reaction products)}}{CH_3COONa} + H_2O$$

Basic of Titration

- ***Practical Procedure:***
  - *The sample (e.g. vinegar) is diluted → sample solution with low pH value (= acidic).*
  - *A NaOH solution of known concentration (titrant) is carefully added to the acidic solution (titration).*
  - *The analyte (CH_3COOH) reacts with the titrant (NaOH) → pH rises slowly (from acidic to basic)*
  - *As soon as all analyte has reacted, the pH rises immediately (excess of NaOH in the solution) → equivalence point*

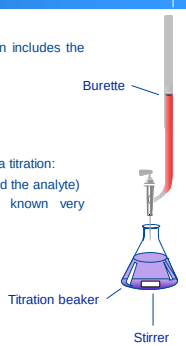
- ***Content calculation:***
  - *Sample size is known.*
  - *Concentration of titrant is known.*
  - *Titrant consumption (volume) until the equivalence point is measured during titration.*

  → The acetic acid content in the sample can be calculated from these three variables.

Basic of Titration

- **Apparatus** : The standard equipment for a manual titration includes the following :
  - Burette: for accurate titrant addition
  - Titration beaker
  - Stirrer

- Several prerequisites have to be fulfilled in order to perform a titration:
  - **Suitable reaction** needed (reaction between the titrant and the analyte)
  - **Titrant concentration** and **used volume** must be known very accurately
  - Equivalence point must be **detectable**

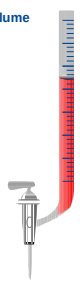


Reaction must be …

- **Selective:**
  The chemical reaction between the analyte and the titrant must be selective (only the analyte should react with the titrant).
- **Fast:**
  The reaction should be fast in order to guarantee that the added titrant reacts immediately with the analyte.
- **Complete:**
  The equilibrium of the reaction should lie strongly on the product side of the reaction to guarantee a complete reaction.
- **Unambiguous:**
  The stoichiometry of the reaction must be known and unambiguous.

Titrant

- The key point of a good titration is the **accurate determination of the volume** of titrant used until the equivalence point.
- For this reason the following two requirements have to be fulfilled:
  - A titrant addition in **small quantities** must be possible.
  - An **accurate reading** for the volume used is needed.
- A manual burette fulfills these requirements
  - Stopcock: add small volumes
  - Grading: accurate volume reading



Indication

- The equivalence point (when all analyte has reacted with the titrant) of a titration should be easily visible or measurable.
- The two basic indication principles are:
  - **Indicator**
  - **Electrode**

- Indicator:
  - An indicator is a substance which **changes its color at the equivalence point**.
  - Small amounts of an indicator are added to the solution prior to the analysis.
  - *Example:*
    Phenolphthalein is an indicator which is pink under basic conditions and colorless under acidic conditions. At the equivalence point of an acetic acid titration by sodium hydroxide, the color will immediately change from colorless to pink.

Indication

- Electrode:
  - An electrode is an instrument that measures a specific property of a solution **electrochemically**.
  - A suitable electrode has to be chosen for each type of reaction. The electrode must measure a **property which is related to the titration reaction**.
  - The whole titration procedure can be followed with an electrode → titration curve

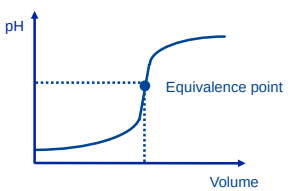
  - *Example:*

    For the titration of acetic acid by sodium hydroxide a pH electrode is used. The pH electrode measures the H+ concentration related to acetic acid that hasn't reacted. The equivalence point is reached when the pH value changes suddenly from acidic to basic.

Titration Curve

- If an electrode is used for a titration the **signal vs. titrant volume** can be plotted.
- Such a plot is called a **titration curve**.
- The equivalence point can be determined directly from a titration curve and is the **inflection point** of the curve.

- *Example: Titration curve (pH vs. volume) of acetic acid titration with sodium hydroxide. The equivalence point is clearly visible.*

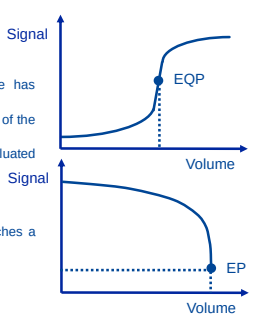


Titration Modes

- Two different titration modes are used:
  - **Equivalence point titration (EQP)**
  - **Endpoint titration (EP)**

- EQP:
  - The EQP is reached as soon as all analyte has reacted with the titrant.
  - In a titration curve the EQP is the inflection point of the curve.
  - The titration is carried out over the EQP and evaluated afterwards.

- EP:
  - The EP is reached as soon as the signal reaches a predefined value.
  - The titration is usually stopped at the EP



Titration Types and Calculation – Direct Titration

- The most common and basic titration type is: **direct titration**.
- In a direct titration the analyte reacts directly with the titrant.
- *Example: In the titration of acetic acid with sodium hydroxide the acetic acid reacts directly with sodium hydroxide by exchanging a proton. The content of acetic acid can be calculated directly from the used sodium hydroxide (titrant) volume (consumption).*

$$\underset{\text{(analyte)}}{CH_3COOH} + \underset{\text{(titrant)}}{NaOH} \rightleftharpoons \underset{\text{(reaction products)}}{CH_3COONa} + H_2O$$

Titration Types and Calculation – Direct Titration

- The analyte content in a direct titration is calculated from the titrant consumption at the equivalence or end point using the following formula:

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m}$$

R: Result
VEQ: Titrant consumption at the equivalence or end point (in mL)
c: Titrant concentration (in mol/L)
t: Titrant titer (no unit)
C: Constant for unit conversion (unit part, unit is dependent on the result needed)
m: Sample size (in g or mL)

- The constant *C* is dependent on the result unit wanted and on the unit of the sample size.

Titration Types and Calculation – Direct Titration

- Examples of constants:

Sample size entry unit	g	mL	
Result unit	%		$C = \frac{M}{10 \cdot z}$
	mg/g	g/L	$C = \frac{M}{z}$
	ppm	mg/L	$C = \frac{M \cdot 1000}{z}$
	mmol/kg	mmol/L	$C = \frac{1000}{z}$
	mol/kg	mol/L	$C = \frac{1}{z}$

M: Molar mass of the analyte (in g/mol)
z: Equivalent number (no unit)

Titration Types and Calculation – Direct Titration

- *Example: For the titration of the acetic acid (M = 60.04 g/mol) in a 1 g sample of vinegar, 5 mL sodium hydroxide (c = 0.1 mol/L, titer: 0.9900) were consumed until the equivalence point. To calculate the acetic acid content in % you have to use the following formula:*

$$C = \frac{M}{10 \cdot z} = \frac{60.04\ \mathrm{g/mol}}{10 \frac{\mathrm{mg}}{\mathrm{g \cdot \%}} \cdot 1} = 6.004 \frac{\mathrm{g \cdot \%}}{\mathrm{mmol}}$$

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m} = \frac{5\ \mathrm{mL} \cdot 0.1\ \frac{\mathrm{mol}}{\mathrm{L}} \cdot 0.9900 \cdot 6.004\ \frac{\mathrm{g \cdot \%}}{\mathrm{mmol}}}{1\ \mathrm{g}} = 2.97\ \%$$

Titration Types and Calculation – Titer

- The **titer** is usually determined by a direct titration, but the calculation is a little different.
- The titer (*t*) is defined as the actual concentration (c_{act}) divided by the nominal concentration (c_{nom}) of a titrant:

$$t = \frac{c_{\mathrm{act}}}{c_{\mathrm{nom}}}$$

- The following formula can be used to calculate the titer of a titrant, if this titrant was used to titrate a titer standard by a direct titration:

$$t = \frac{m}{VEQ \cdot c \cdot C}$$

t: Titrant titer (no unit)

m: Titer standard sample size (in g or mL)

VEQ: Titrant consumption at the equivalence or end point (in mL)

c: (Nominal) titrant concentration (in mol/L)

C: Constant for unit conversion (unit part, unit is dependent on the titer substance form)

Titration Types and Calculation – Titer

- If the titer standard substance is a solid, use the following formula for the constant C:

$$C = \frac{M}{10 \cdot p \cdot z}$$

- For liquid titer standards the following constant is used:

$$C = \frac{1}{cst \cdot z}$$

M: Molar mass of the analyte (in g/mol)

p: Purity of the solid titer standard (in %)

z: Equivalent number of the titer standard (no unit)

cst: Concentration of the liquid titer standard (in mol/L)

Titration Types and Calculation – Titer

- *Example: Potassium hydrogen phthalate (KHP, M= 204.23 g/mol) was used as a solid titer standard to determine the titer of sodium hydroxide (c = 0.1 mol/L). 0.0931 g of KHP (purity: 99 %) was weighed into a titration beaker and diluted with deionized water. This solution was titrated with sodium hydroxide. The equivalence point was detected at a titrant consumption of 4.5238 mL. For this measurement the titer can be calculated as follows:*

$$C = \frac{M}{10 \cdot p \cdot z} = \frac{204.23\ \frac{\text{g}}{\text{mol}}}{10\ \frac{\text{mg}}{\text{g} \cdot \%} \cdot 99\ \% \cdot 1} = 0.206\ \frac{\text{g}}{\text{mmol}}$$

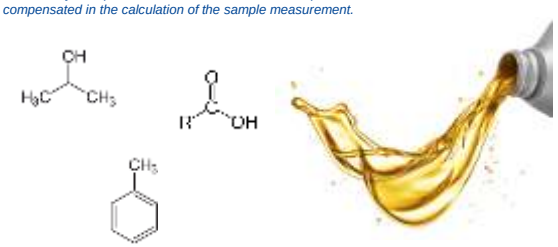
$$R = \frac{m}{VEQ \cdot c \cdot C} = \frac{0.0931\ \text{g}}{4.5238\ \text{mL} \cdot 0.1\ \frac{\text{mol}}{\text{L}} \cdot 0.206\ \frac{\text{g}}{\text{mmol}}} = 0.9990$$

Titration Types and Calculation – Blank Titration

- In some titrations it may happen that the solvent itself also reacts with the titrant. The amount of titrant used for the solvent is called the **blank value**.
- The blank value has to be **compensated t**o get the correct result.
- To determine the blank value a titration of the **solvent without any sample** has to be performed. The blank value is the volume of the titrant used until the equivalence or endpoint is reached.
- For a titration where a blank value is used, take care to always use the same solvent volume!

Titration Types and Calculation – Blank Titration

- *Example: The acid number of motor oil is determined by a non-aqueous acid/base titration with potassium hydroxide (in 2-propanol) as titrant. As solvent a mixture of toluene, 2-propanol and water is used. Before titrating the sample, the solvent mixture without any sample is titrated. The titrant consumption of this blank measurement is compensated in the calculation of the sample measurement.*



Titration Types and Calculation – Blank Titration

- The calculation of a blank value compensated titration is similar to the direct titration:

$$R = \frac{(VEQ - B) \cdot c \cdot t \cdot C}{m}$$

R: Result

VEQ: Used titrant volume until the equivalence or end point (in mL)

B: Blank value, titrant volume used for the titration of the solvent (in mL)

c: Titrant concentration (in mol/L)

t: Titrant titer (no unit)

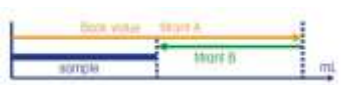
C: Constant for unit conversion (unit part, unit is depending on the result needed)

m: Sample size (in g or mL)

- The constant *C* is the same as for the direct titration

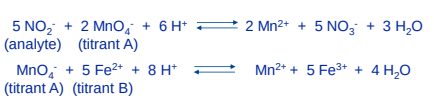
Titration Types and Calculation – Back Titration

- In a **back titration** a known excess amount of reagent (titrant A with known concentration) is added to the sample. This titrant reacts with the analyte. Afterwards the amount of non-reacted titrant A will be titrated with a second titrant (titrant B).
- The added volume of titrant A has to be known very precisely.
- For accurate measurements a so called **back value** is determined by titrating the added volume of titrant A without any sample. The result is based on the used volume of titrant B without any sample.
- Such titrations are often used when the reaction between the analyte and the first titrant is slow.



Titration Types and Calculation – Back Titration

- *Example: For the titration of nitrite in soya sauce a known volume of potassium permanganate (titrant A) is added to the sample. Potassium permanganate will react with the nitrite and the excess of the permanganate is titrated with ammonium ferrous sulfate(II) (titrant B).*



Titration Types and Calculation – Back Titration

- The analyte content in a back titration is calculated using the following formula:

$$R = \frac{(Bk - VEQ) \cdot c \cdot t \cdot C}{p \cdot m}$$

R: Result

Bk: Back value, volume of titrant B used for the titration of titrant A without sample (in mL)

VEQ: Volume of titrant B used to back titrate the excess of titrant A after sample addition (in mL)

c: Concentration of titrant B (in mol/L)

t: Titer of titrant B (no unit)

C: Constant for unit conversion (unit part, unit is depending on the result needed)

p: Stoichiometric proportion between titrant A and titrant B of the second reaction, stoichiometric factor of titrant B divided by factor of titrant A (no unit)

m: Sample size (in g or mL)

- The constant *C* is the same as for the direct titration

1. Acid / Base

- **Reaction:**
  - This type of titration is based on the reaction between an acid (AH) and a base (B), where a proton (H^+) is exchanged.

$$AH + B \rightleftharpoons A^- + BH^+$$

  - If the analyte is an acid the titrant will be a base and vice versa.
- **Analytes:**
  - Weak or strong acid / base
  - *Examples: Hydrochloric acid, sulphuric acid, acetic acid, sodium hydroxide, ammonia, …*
- **Titrants:**
  - Strong base / acid solution
  - *Examples: Sodium hydroxide 0.1 mol/L, hydrochloric acid 0.1 mol/L*
- **Indication:**
  - pH indicators: pH dependent dyes (for manual titration), *examples*: phenolphthalein, methyl orange, …
  - pH sensor (for automated titration)

Reaction types in Titration

1. Acid / Base

- The parameter which changes during a acid / base titration is the pH value.
- The pH value is defined as the negative decadic logarithm of the H^+ (or H_3O^+) concentration in a solution:

$$pH = -\log\left(c(\mathrm{H^+})\right) = -\log\left(c(\mathrm{H_3O^+})\right)$$

- Even in pure deionized or distilled water a small amount of ions is present due to the amphoteric properties of water (it can react as a acid or a base). Water molecules react with each other to build H_3O^+ and OH^-:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

- In pure deionized water the concentration of H_3O^+ and OH^- ions are both 10^{-7} mol/L. The product of these two concentrations is called the ionic product of water (K_w) and this value is a constant:

$$K_w = c(\mathrm{H_3O^+}) \cdot c(\mathrm{OH^-}) = 10^{-7}\frac{\mathrm{mol}}{\mathrm{L}} \cdot 10^{-7}\frac{\mathrm{mol}}{\mathrm{L}} = 10^{-14}\frac{mol^2}{L^2}$$

Reaction types in Titration

1. Acid / Base

- If we calculate the pH value for pure water ($c(H_3O^+)$ = 10^{-7} mol/L) it is 7. **A pH value of 7 is neutral.**
- If an acid (AH) is added to an aqueous solution, it will react (dissociation) with water to form more H_3O^+ ions (and less OH^- ions due to K_w):

$$AH + H_2O \rightleftharpoons A^- + H_3O^+$$

The H_3O^+ concentration will increase and the pH value will decrease. **A pH value below 7 is acidic.**

- If a base (B) is added to an aqueous solution, it will react with water to form more OH^- ions (and less H_3O^+ ions due to K_w):

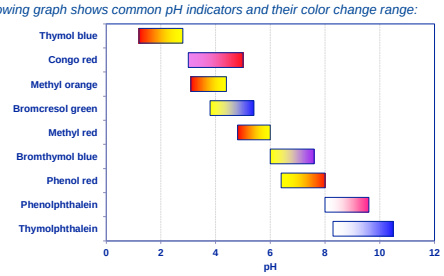
$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

The H_3O^+ concentration will decrease and the pH value will increase. **A pH value above 7 is alkaline.**

Reaction types in Titration

1. Acid / Base

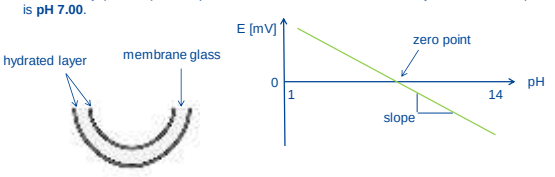
- For a manual titration various pH indicators exist. The selection must be based on the pH range where the equivalence point occurs: the indicator has to be chosen such that its color change occurs at the equivalence point.
- *The following graph shows common pH indicators and their color change range:*



Reaction types in Titration

1. Acid / Base

- For **automated titration** the pH value is measured by a **pH sensor** (usually combined sensor), which consists of a reference system (usually Ag/AgCl) and a glass membrane which is sensitive to H^+ (or H_3O^+).
- Since the measured signal is a potential (mV) and not pH, the sensor has to be calibrated (correlate the mV signal to a pH value).
- The calibration is done by measuring the potential of various calibration buffers with defined pH value. From these measurements (calibration points) a calibration line is calculated.
- Theoretically (at 25°C) the slope of the calibration line is **-59.16 mV/pH** and the zero point is **pH 7.00**.



Reaction types in Titration

1. Acid / Base

Example 1: Titration of acetic acid in vinegar with sodium hydroxide

- The acetic acid concentration of a vinegar sample should be determined. Since acetic acid is an acid this will be done by titrating with sodium hydroxide. The reaction for this titration is

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

- For this sample an acetic acid content of 5 % is expected. From this value one can calculate the sample size by re-arranging the calculation formula so that the sample size can be calculated

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m} \quad \rightarrow \quad m = \frac{VEQ \cdot c \cdot t \cdot C}{R}$$

- If we use a 20 mL burette, a titrant consumption of about 10 mL (half of burette volume) would be perfect. We use a sodium hydroxide solution with c = 0.1 mol/L and assume a titer of 1. Form these values the approximate sample size can be calculated.

Reaction types in Titration

1. Acid / Base

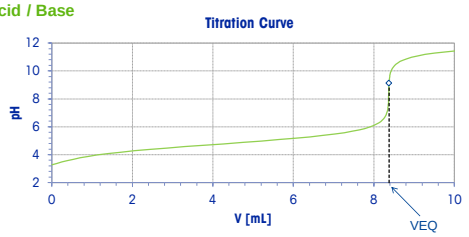
$$C = \frac{M}{10 \cdot z} = \frac{60.04\ \mathrm{g/mol}}{10 \frac{\mathrm{mg}}{\mathrm{g} \cdot \%} \cdot 1} = 6.004 \frac{\mathrm{g} \cdot \%}{\mathrm{mmol}}$$

$$m = \frac{VEQ \cdot c \cdot t \cdot C}{R} = \frac{10\ \mathrm{mL} \cdot 0.1 \frac{\mathrm{mol}}{\mathrm{L}} \cdot 1 \cdot 6.004 \frac{\mathrm{g} \cdot \%}{\mathrm{mmol}}}{5\ \%} = 1.2\ \mathrm{g}$$

- Based on this calculation 1.3134 g of vinegar was weighed on an analytical balance into a titration beaker and diluted in 50 mL deionized water. This solution was titrated with sodium hydroxide (c = 0.1 mol/L and t = 0.9877) on an automated titrator equipped with a pH sensor until the equivalence point was recognized.

Reaction types in Titration

1. Acid / Base



- From the titrant consumption (8.3784 mL) the content of acetic acid in the sample was calculated:

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m} = \frac{8.3784\ \text{mL} \cdot 0.1\ \frac{\text{mol}}{\text{L}} \cdot 0.9877 \cdot 6.004\ \frac{\text{g} \cdot \%}{\text{mmol}}}{1.3134\ \text{g}} = 3.78\ \%$$

Reaction types in Titration

1. Acid / Base

Example 2: Simultaneous titration of sodium hydroxide and carbonate

- If a sodium hydroxide solution is not closed and not protected against carbon dioxide intake, carbon dioxide will be dissolved and will react to carbonate. If one performs a titration, this carbonate will also be titrated.
- During the titration three different bases are present: sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$). Since NaOH is the strongest base this species will react first with the titrant (hydrochloric acid, HCl). Afterwards Na_2CO_3 will react to $NaHCO_3$ and this base will react at the end to CO_2.

1. $NaOH + HCl \rightleftharpoons NaCl + H_2O$
2. $Na_2CO_3 + HCl \rightleftharpoons NaHCO_3 + NaCl$
3. $NaHCO_3 + HCl \rightleftharpoons CO_2 + NaCl + H_2O$

Reaction types in Titration

1. Acid / Base

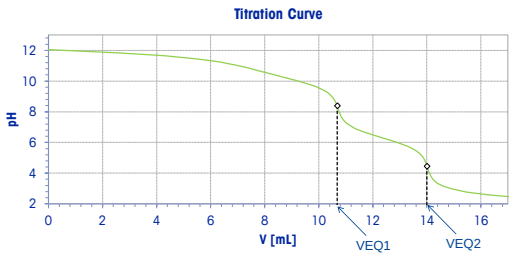
- Theoretically, we should observe three equivalence points but the first point will be very flat and only two points will be clearly visible:
  - 1. EQP: Reaction of NaOH and Na_2CO_3
  - 2. EQP: Reaction of $NaHCO_3$

- From these two EQP's the NaOH and Na_2CO_3 concentrations can be determined.

- To perform this titration 7 mL of sodium hydroxide sample is added with a accurate pipette into a titration beaker and the solution is diluted with 50 mL of deionized water. This solution is titrated with hydrochloric acid (c = 0.1 mol/L and t = 0.9932) until two equivalence points are recognized (automatic titrator with pH sensor).

Reaction types in Titration

1. Acid / Base



Reaction types in Titration

2. Precipitation

- **Reaction:**
  - The analyte (A) and the titrant (T) react and form a compound which precipitates.

$$A + T \rightleftharpoons \underset{\downarrow}{AT}$$

  - Usually silver nitrate ($AgNO_3$) is used as a titrant, which forms hardly soluble silver salts (e.g. AgCl)
- **Analytes:**
  - Ions which form hardly soluble silver salts
  - *Examples: chloride, cyanide, thiocyanate*
- **Titrants:**
  - Silver nitrate
- **Indication:**
  - Indicators: Potassium dichromate (for manual titration)
  - Silver ring electrode (for automated titration)

Reaction types in Titration

2. Precipitation

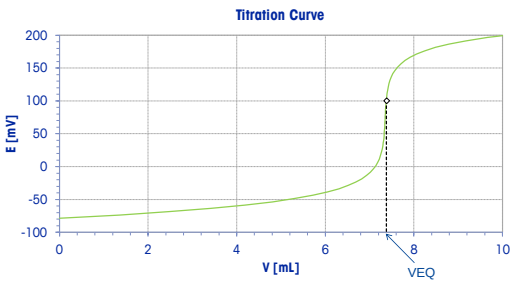
Example: Titer determination of silver nitrate

- The titer of silver nitrate ($AgNO_3$) is determined by sodium chloride (NaCl) as standard substance.

$$NaCl + AgNO_3 \rightleftharpoons \underset{\downarrow}{AgCl} + NaNO_3$$

- To determine the titer, 43.2 mg of NaCl standard (purity: 99.5 %) is weighed into a titration beaker and dissolved in 50 mL nitric acid (c = 0.02 mol/L). The nitric acid is needed to keep a pH value of 4.5 in the sample solution, since the precipitation reaction takes place under slightly acidic conditions.
- The sample solution is titrated with $AgNO_3$ (c = 0.1 mol/L) while the signal is measured with a silver ring sensor (measures Ag^+ concentration). The titration is stopped as soon as the equivalence point is recognized.
- During the titration the precipitation of AgCl is clearly visible.

2. Precipitation



3. Redox

- **Reaction:**
  - The analyte and the titrant exchange electrons during this reaction and the oxidation state of both changes.
  - If the analyte is an oxidizing agent (O) the titrant is a reducing agent (R) and vice versa.

Oxidation: $R \longrightarrow R^+ + e^-$

Reduction: $O + e^- \longrightarrow O^-$

Redox reaction: $R + O \rightleftharpoons O^- + R^+$

- **Analytes:**
  - Oxidizing and reducing agents
  - *Examples: Sulphurdioxide, Nitrite, Iron, …*
- **Titrants:**
  - Oxidizing and reducing agents
  - *Examples: Iodine, Sodium thiosulfate, potassium permanganate, …*
- **Indication:**
  - Color change due to colored titrant, starch solution (for Iodine)
  - Platinum sensor (for automated titration)

3. Redox

Example 1 : Titer determination of potassium permanganate

- The titer of potassium permanganate ($KMnO_4$) is determined by using Di-sodium oxalate ($Na_2C_2O_4$) as the standard. During this titration $Na_2C_2O_4$ is oxidized to CO_2 and $KMnO_4$ is reduced to Mn^{2+}:

Oxidation: $Na_2C_2O_4 \longrightarrow 2\ CO_2 + 2\ Na^+ + 2\ e^-$

Reduction: $KMnO_4 + 8\ H^+ + 5\ e^- \longrightarrow Mn^{2+} + 4\ H_2O + K^+$

Redox reaction:

$5\ Na_2C_2O_4 + 2\ KMnO_4 + 16\ H^+ \rightleftharpoons 10\ CO_2 + 10\ Na^+ + 2\ Mn^{2+} + 8\ H_2O + 2\ K^+$

- Since two electrons are released by the oxidation of $Na_2C_2O_4$ the equivalent number of this substance is $z = 2$.
- Since 5 electrons are needed for the reduction of the titrant $KMnO_4$ the concentration of the titrant will be given as $c(1/5\ KMnO_4)$ which is five times higher than the concentration $c(KMnO_4)$.

$$c = c(1/5\ \mathrm{KMnO_4}) = c(\mathrm{KMnO_4}) \cdot 5$$

3. Redox

Example 2: Iodometric determination of Cr^{6+}

- Cr^{6+} should be determined in an electroplating bath. This is done in a two step reaction. First Cr^{6+} is reduced to Cr^{3+} using iodide (I^-) which is oxidized to iodine (I_2). The iodine produced is then titrated with sodium thiosulfate ($Na_2S_2O_3$):

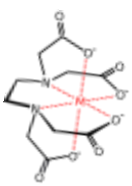
1. $2\ Cr^{6+} + 6\ I^- \rightleftharpoons 2\ Cr^{3+} + 2\ I_2$
2. $2\ Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2\ I^-$

- Since three electrons are needed to reduce Cr^{6+} to Cr^{3+} the equivalent number is $z = 3$.
- 5 mL of a 1:100 diluted bath sample (m = 0.05 mL) is added into a titration beaker. The sample is diluted in
  - 5 mL of 50 % H_2SO_4 solution to acidify the solution
  - 40 mL deionised water.
- To have an excess of iodide in the solution 5 mL of 10 % potassium iodide (KI) solution was added. This iodide reacts with the Cr^{6+} and a corresponding amount of iodine is produced.

4. Complexometric

- **Reaction:**
  - Analyte (A) and titrant (T) react together to build a complex ([AT]).

$$A + T \rightleftharpoons [AT]$$



- **Analytes:**
  - Metal ions with a charge > 1
  - *Examples: Zinc ion, magnesium ion, calcium ion, …*
- **Titrants:**
  - Ligands which build complexes with the analyte
  - *Example: Ethylenediaminetetraacetic acid (EDTA)*
- **Indication:**
  - Indicators (also ligands) that change color if they are not bound to the analyte, *examples: Murexide, Eriochrome Black T*
  - Indicators and a photometric sensor (for automated titration)

4. Complexometric

- In a manual titration the color change of the indicator is observed visually with the **naked eye**.
- In an automated titration an indicator is also added, but the color change is observed by a **photometric sensor**.

4. Complexometric

Example: Total hardness of water

- Total hardness of water is expressed as the $CaCO_3$ (M = 100.09 g/mol, z = 1) content in water. It is a typical analysis done as a complexometric titration of calcium and magnesium at pH 10.
- 50 mL of tap water, 10 mL of 5 % ammonia solution (for pH 10), and 1 mL of 1 % Eriochrome Black T indicator solution were added into a titration beaker. This solution was titrated by EDTA (c = 0.1 mol/L, t = 0.9763) and the color change, from violet to blue, was observed with a photometric sensor at pH 10. The equivalence point was found at a titrant consumption of 0.7392 mL.
- The hardness (as $CaCO_3$ content) can be calculated as follows:

$$C = \frac{M \cdot 1000}{z} = \frac{100.09\ \frac{\text{g}}{\text{mol}} \cdot 1000\ \frac{\text{mg}}{\text{g}}}{1} = 100090\ \frac{\text{mg}}{\text{mol}}$$

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m} = \frac{0.7392\ \text{mL} \cdot 0.1\ \frac{\text{mol}}{\text{L}} \cdot 0.9763 \cdot 100090\ \frac{\text{mg}}{\text{mol}}}{50\ \text{mL}} = 144.47\ \text{ppm}$$

5. Karl Fischer

- **Reaction:**
  - Karl Fischer titration is a special type of redox titration for water determination.

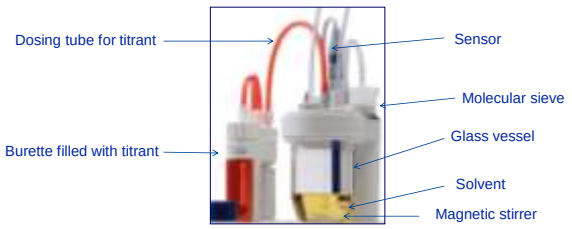
  - The Karl Fischer reaction needs an alcohol (ROH, usually methanol), sulfur dioxide, a base (imidazole or pyridine), iodine and the analyte water.
- **Analyte:** Water
- **Titrants and Solvents:**
  - One-component reagent: contains iodine, sulfur dioxide and a base dissolved in methanol. The solvent is methanol.
  - Two-component reagent: Contains iodine dissolved in methanol. The solvent contains sulfur dioxide, a base and methanol.
- **Indication:**
  - Polarized double pin platinum electrode (voltammetry)

5. Karl Fischer

- The Karl Fischer reaction is a two step reaction:
  1. ROH + SO_2 + R'N ⇌ (R'NH)·SO_3R
  2. (R'NH)·SO_3R + I_2 + H_2O + 2 R'N ⇌ (R'NH)·SO_4R + 2 (R'NH)I
- From this reaction it can be seen that **water reacts with iodine** attaining **1:1 stoichiometry**.
- The solvent ROH (usually methanol) is also involved in the reaction, this means that at least 50 % of the solvent should always be methanol.
- A suitable base (R'N, usually imidazole, in the past: pyridine) keeps the pH value between 5 and 7. This is the optimal pH range so that the reaction is fast and yet no side reactions occur.

5. Karl Fischer

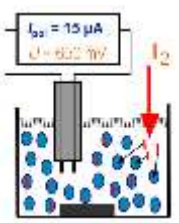
- Karl Fischer titration needs a special setup: The titration vessel has to be protected from humidity as it has an influence on the result. For this reason Karl Fischer titrations are almost always done using an automatic titrator.
- A typical setup for a Karl Fischer titration is shown below:



5. Karl Fischer

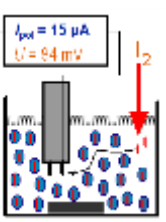
- Karl Fischer titration is an endpoint titration.
- The endpoint is detected with a polarized double platinum pin sensor. A fixed polarization current (I_{pol}) is applied to this sensor and the voltage (U in mV), which is used to maintain this current is measured.

- **During the titration:**
  The iodine from the titrant reacts directly with the water
  → No free iodine in the solution
  → High voltage is needed to maintain the polarization current

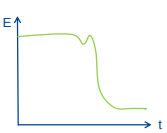


5. Karl Fischer

- **At the end of the titration:**
  No water is available for the reaction with iodine
  → Free iodine in the solution causes ionic conduction
  → Low voltage is needed, signal drop



- As soon as the voltage signaldrops below a defined endpoint the titration stops



Reaction types in Titration

5. Karl Fischer

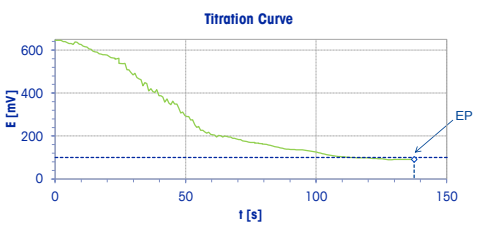
Example: Water content determination in ethanol

- The titration is started. Once the pretitration is done the titrator goes into standby mode. A stable and low drift value (typically < 25 µg/min) is awaited.
- The drift value read just before the sample determination starts is noted.
- Since ethanol is completely soluble in methanol, the sample can be directly inserted into the titration vessel. For this purpose about 5 mL of ethanol is drawn up into a syringe, placed on a balance and tared.
- The sample determination is started (drift value: d = 11.3 µg/min, titrant concentration: c = 4.8976 mg/mL). About 1 mL of ethanol is added with the syringe into the titration beaker. The syringe is once again placed on the balance. The sample size is the difference between the weight of the syringe before and after the sample addition (back weighing): 1.0348 g

Reaction types in Titration

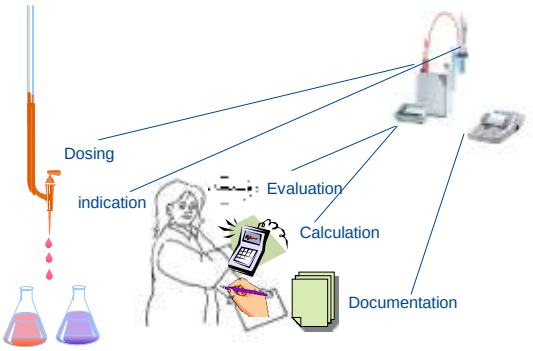
5. Karl Fischer

- The titration ends (endpoint was set to 100 mV) after 2.1865 mL and a titration time of 2.293 min.



Agenda

Manual vs Automatic Titration

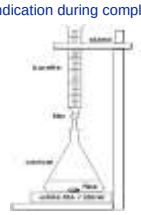


Manual vs Automatic Titration

Dosing

Manual Titration

- Open and close tap of manual burette
- Wait in between to allow reaction to take place
- Check indication during complete titration



Automatic Titration

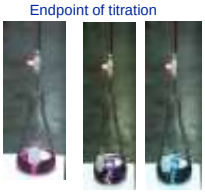
- Automatic dosing via precision glass burettes and high-resolution motor driven piston
- High dosing accuracy
- Fully controlled by titrator via method parameters
- Automatic preparation and refill
- Burette volume and piston stroke can be calibrated with traceable standards


Manual vs Automatic Titration

Indication

Manual Titration

- Color indicator
- Color change indicates Endpoint of titration



Before | End point | After

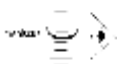
Automatic Titration

- Automatic indication via sensors of different kind
- High measurement accuracy
- Measured value recorded after every volume increment added
- Fully controlled by titrator via method parameters
- Big application range (not just color-indicated EP titrations)
- Independent from operator
- Sensor inputs as well as sensors can be calibrated with traceable standards

Evaluation

Manual Titration

- Read off dispensed volume when endpoint is reached
- Only for endpoint titration
- Equivalence point titration not possible



Automatic Titration

- Automatic evaluation of endpoint and equivalence point by optimized algorithms
- Mathematically, based on measured value table
- High analysis accuracy and repeatability
- Big application range (not just color-indicated EP titrations)
- Independent from operator

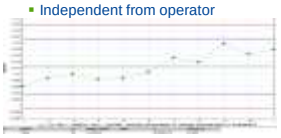
Calculation

Manual Titration

- Calculate content or concentration
- Inputs
  - Dispensed volume to endpoint
  - Concentration of titrant
  - Sample size (weight or volume)
  - Molecular weight and equivalence number of analyzed substance
- Calculate by hand, calculator, PC etc

Automatic Titration

- Automatic calculation of result
- Various results simultaneously available
- Predefined or user defined calculation formulas
- Automatic calculation of statistics, outlier test etc.
- No typing or calculation mistakes
- Independent from operator



Documentation

Manual Titration

- Write calculated result on paper
- Archive paper
- Type result into electronic file
- Archive files

Automatic Titration

- Automatic print-out
- Slip or A4 printer
- Contains all data, not just result
  - Who did what when and how
  - Fully GLP compliant
  - Guarantees traceability
- Archive paper still manually
- Type result into electronic file
- Archive files
- Transfer data to LIMS

Manual vs Automatic Titration

Automatic Titration Benefit

- **Accurate and precise** results - due to the automatic titrant addition and the possibility of adding very small amounts of titrant (lower than 0.001 mL).
- **Fast** but still precise titrations - due to the controlled titrant addition determined by an algorithm (small increments near the equivalence point).
- Highly **reproducible results** - since no operator interaction is needed the results are highly reproducible even if another operator performs the analysis.
- **Full titration curve** is recorded, which allows a titration to the equivalence point and post-processing.
- The results can be **calculated and printed automatically** by the titrator.
- **Traceability -** the titration curve and the results can be stored (e.g. on a computer if the titrator is connected) or printed directly.
- Operator has **minimal contact with chemicals** since the titrant and the reagents can be added directly from the bottle.
- Depending on the titrator, the analysis can be **fully automated** thus saving time

Agenda

Titration Innovations at Mettler-Toledo

DV/DK

The first METTLER TOLEDO titrator

1973

- Analogue titrator
- Modular system
- Up to 16 modules for EP, EQP, KF etc.
- Innovative, especially for photometric titration

SR10 1st computerised system

1974

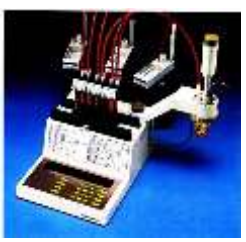
- Controlled by microprocessor (PDP 9-bit)
- Largest in the world
- Sample preparation included
- 100-position sample changer
- 10 automated burettes
- 25 systems sold worldwide
- Price then: 90'000 CHF for the basic unit, 330'000 CHF for the complete system
- Displayed in the Technical Museum in Munich

Light-years ahead of the times

DL40 MemoTitrator

1st compact general and KF titrator

1979



- Z8 processor
- 1st titrator with memory
- 40 programmable methods
- Data storage
- Processing software
- Propeller stirrer
- Automatic titration
- MemoCard

The first modern microprocessor titrator

DL25 Titrator

Introduces dynamic addition of titrant

1985

- 50 programmable methods
- EQP detection with non-linear regression

Simple, quick and flexible

Titration Innovations at Mettler-Toledo

DL70 Line Autotitrators

1989

- Online titration curve
- Flexible method creation
- Logic conditions
- 4 automated burettes
- 4 processing criteria
- Titrant database
- Automatic titrations
- 2 titrations in parallel

Great application flexibility. The first for safety and GLP functions

Titration Innovations at Mettler-Toledo

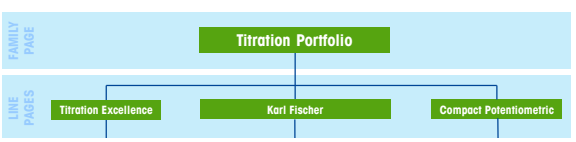
DL50 Family of titrators

1996

- 1st titrator with memory card (results, methods, config.)
- Expandable
- Online titration curve
- Automated 2-phase titration
- Titrant expiry verification
- Routine/Expert mode
- Intuitive and easy to use

The most modern operator interface. The first with online help.

MT Automatic Titrator Today...



Introduction Titration Excellence

METTLER TOLEDO

Introduction Titration Excellence

One Click® Titration **Simple**

One Click® offers easy to understand simplicity

Introduction Titration Excellence

One Click® Titration Excellence

Efficient

Secure

Modular

Introduction Titration Excellence

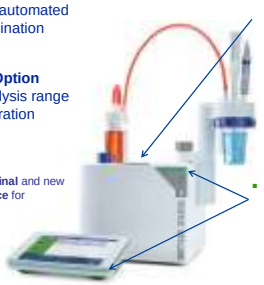
Titration Excellence approach to modularity:

1. **Tailored Exactly to Your Needs.**
   - → with segment specific applications
   - → with a huge variety of accessories
2. **Get all You Need in One Box.**
   - → expand efficiency all in one device
3. **Be Future Ready.**
   - → simple addition of accessories
   - → upgradability (T7 to T9)

New Titration Excellence Line Highlights

METTLER TOLEDO

- **Multiple Standard Addition** for completely automated sodium determination
- **Coulometric Option** expanding analysis range with KF coul titration
- **Touchscreen terminal** and new **One Click® interface** for increased efficiency
- **SmartSample™** reader for efficient and secure data transfer
- **PDF writer** and new data export for more flexibility
- **StatusLight™** for increased efficiency



New features emphasize Titration Excellence utmost modularity

New Titration Excellence Line Highlights

METTLER TOLEDO

- **Touchscreen terminal** with a new look and increased efficiency.
  - Large 7 inch WVGA color TFT screen
  - USB connection on right hand side
  - Built in StatusLight™

- **New One Click® User Interface**
  - Save up to 24 shortcuts
  - User management with color skinning
  - Scrolling and Swiping

Modern appearance, more comfort and attractive for demos!

New Titration Excellence Line Highlights

METTLER TOLEDO

- **Coulometric Option** enables Titration Excellence to perform potentiometric, KF vol and KF coul analyses.
  - All-in-one system integrated
  - Improved accuracy of Bromine Index determination
  - Simultaneous KF Vol and KF Coul analysis on T9
  - Overflow protection for KF Vol

Coulometer Board
Always in the 4th slot

No Y cable anymore!

Potentiometric and Karl Fischer titration in one device

New Titration Excellence Line Highlights

METTLER TOLEDO

- **SmartSample™ reader** to offer efficient and secure data transfer for single samples

- Installed SmartSample reader on the titrator as standard
- Enables wireless data transfer from balance to titrator
- Elimination of transcription errors

Intelligent choice for single- and automated multi-sample titration

New Titration Excellence Line Highlights

METTLER TOLEDO

The integration of the **Sodium Analyzer** functionalities on Titration Excellence offers:

- Ion determination based on multiple standard addition
- Completely automated sodium analysis
- Accurate ion specific analysis

Strong feature for Food and Beverage industry

New Titration Excellence Line Highlights

METTLER TOLEDO

- **StatusLight™** supports you in routine operations and daily work by visual and acoustic signaling.

- StatusLight™ on titrator and terminal
- StatusLight™ concept aligned with InMotion™, UV/VIS and Excellence Balances
- Built-in loudspeaker for acoustic signals

Stay in touch with your titration

New Titration Excellence Line Highlights

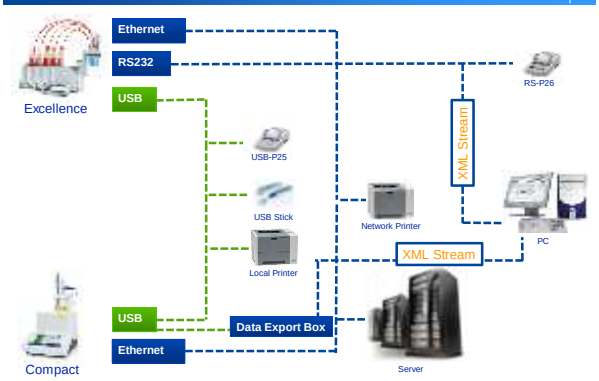
METTLER TOLEDO

- Flexible Data Export
  - CSV
  - PDF
  - XML

More flexibility in data export

Data Export

METTLER TOLEDO



LabX

LabX connectivity:

- **New LabX Version 2016 with launch**
- **New titrators can be connected**

- **New features not yet compatible with Version 2016**
  - **→ Compatibility will be assured with Version 2017!**
  - **→ Launch Version 2017: JULY 2016**

Agenda

1	Basic of Titration
2	Reaction types in Titration
3	Manual VS Automatic Titration
4	Titrator Instrument
5	Aplication in F&B
6	Tips and Hints

Salt Content

As chloride or sodium chloride

- Titrant: 0.1 mol/L $AgNO_3$
- Solvent: water
- Auxiliary reagent: HNO_3
- Sensor: DMi141-SC or DMi145-SC or DMi148

$$NaCl + AgNO_3 \longrightarrow AgCl + Na^+ + NO_3^-$$

Tips & Hints

- pH must be below pH 6 (ideal pH 4.5) to prevent AgOH formation.
- pH should not be below pH 2 - it dissolves the silver ring of the electrode.
- For high chloride content take care not to titrate too fast: co-precipitation
- Can add PVA to prevent co-precipitation
- To clean sensor, stirrer and burette tip, dip in ammonium hydroxide (Automation – use conditioning beaker)

Salt Content

Sodium, Na^+

- Sodium has been linked to high blood pressure.
- High blood pressure can increase the risk of heart disease, kidney disease and stroke.
- Na-content is relevant
- Determination of Na-content by standard addition technique

Salt Content

- **Examples**
  - Ketchup
  - Dairy product (cheese, butter)
  - Vegetable juice (carrots, tomato, etc.)
  - Soup, meat and vegetable bouillon
  - Sauces, meat extract
  - Bread and pastries
  - Snack food (potato chip)
  - Breakfast cereals
  - Seasoning powders
  - Spices
  - Bean paste sauce
  - Pasta sauces

Acid Content

Acid content as:

- Acetic acid, Tartaric acid, Citric acid, Malic acid, Free fatty acid, etc.

Acetic acid	M = 60.01z	= 1
Tartaric acid	M = 150.09	z = 2
Citric acid	M = 192.13	z = 3
Malic acid	M = 134.09	z = 3

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

- Titrant: 0.1 mol/L NaOH
- Solvent: water
- Sensor: DGi115 or DGi114 or DGi111

Acid Content

- **Examples**
  - Vinegar
  - Juices (apple, orange)
  - Wine
  - Coca Cola
  - Yoghurt drink
  - Milk
  - Sour cream
  - Honey
  - Edible oil








Calcium content

Calcium

- Titrant:0.1 mol/L EDTA
- Solvent: water
- Sensor: DP5 Phototrode™ or DX240 Ca-ISE

Ca^{2+} + EDTA → $[Ca\text{-}EDTA]^{2+}$

Tips & Hints

- pH must be adjusted to pH 10 with ammonia or borate buffer
- Not suitable to use the DP5 Phototrode™ for beverage samples due to opacity, natural colors and protein suspensions
  - Alternative sensor – Ca ISE
- Indicator not necessary when Ca ISE sensor is used


Calcium content

- **Examples**
  - Milk
  - Soy Milk
  - Cheese
  - Yoghurts
  - Juices





Vitamin C determinations

- **Three ways to titrate**
  - **Potentiometric**
    - Titrant: Iodine (direct titration) or sodium thiosulfate (back-titration)
    - Reaction: Redox reaction
    - Sensor: DMi140-SC or DM147i-SC
  - **Voltametric**
    - Titrant: DPI
    - Reaction: Redox reaction
    - Sensor: DM143-SC Polarized sensor
  - **Amperometric**
    - Titrant: DPI
    - Reaction: Redox reaction
    - Sensor: DM143-SC Polarized sensor

Vitamin C determinations

Potentiometric Indication

- Titrant: 0.05 mol/L I_2
- Solvent: water
- Auxiliary reagent: 5% H_2SO_4
- Sensor: DMi140-SC or DMi147-SC

$$C_6H_8O_6\ (aq) + I_2\ (aq) \longrightarrow C_6H_6O_6\ (aq) + 2\ HI$$

- Direct titration with Iodine (Iodimetric titration)
  - Quantitative oxidation of ascorbic acid to dehydroascorbic acid by iodine in acid solution.
- Back titration with sodium thiosulfate
  - Adding KI and KIO_3 to generate I_2
  - Excess iodine is titrated with $Na_2S_2O_3$
  - Results more reliable than direct titration (less I_2 is lost to the environment).

- Disadvantages:

Iodine is not selective to Vitamin C; other components will be oxidized, e.g. SO_2.

Vitamin C determinations

- **Voltametric or amperometric Indication**

- Titrant: 0.01 mol/L 1/2 DPI (2,6-Dichlorophenolindophenol)
- Solvent: water
- Auxiliary reagent: Oxalic acid or NaOH to adjust pH to 3
- Sensor: DM143-SC

$$C_6H_8O_6 + DPI \rightarrow C_6H_6O_6 + H_2\text{-}DPI$$

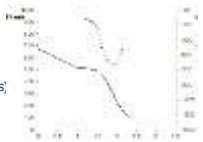
Advantages:

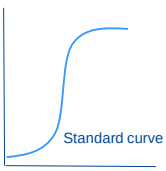
- DPI is more selective for Vitamin C than iodine
- DPI gives a higher jump at the EQP compared to the titration with iodine.

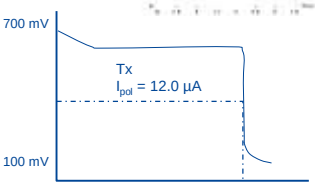
Vitamin C determinations

Voltametric Indication

- Titration curve: "sudden" jump
  - Accurate results requires incremental addition.
    Fixed increment = 0.03 – 0.1 mL
    (In same cases also dynamic titrant addition works)
  - Evaluation: Standard or asymmetric



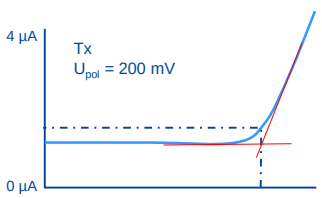




Vitamin C determinations

Amperometric Indication

- Segmented titration curve:
  - Evaluation: segmented
  - Segmented evaluation allows (requires) the use of larger increments.
    Fixed increments 0.1 – 0.2 mL
    → faster titration; titration time 1 to 3 minutes



Vitamin C determinations

- **Examples**
  - Juices
  - Canned fruits
  - Dried fruits

Vitamin C determinations

Tips & Hints I

- Titrant DPI preparation.
  - Use DPI sodium salt monohydrate, which dissolves good in water.
    DPI sodium salt dihydrate does not dissolve very good in water (Filtration needed.)
- Titrant DPI is not stable.
  - Titrant DPI is unstable and should be prepared freshly, at least every 2nd day, and should be stored in the dark when not used.
  - Run a titer determination every day.
- Titer determination (Standard: Ascorbic acid).
  - Since the sample size is very small (20 mg) use a stock solution.
  - Make a fresh stock solution for every titer determination, since ascorbic acid is not stable.
- pH adjustment to pH 3 is very important.
  - For the titer determination, the pH should also be adjusted to pH 3, because deionized water has a pH between 6 and 7, which is too high.

Vitamin C determinations

Tips & Hints II

- Clean sensor between samples for better precision.
- Vitamin C is not stable against light and oxygen.
  - For accurate work bubble nitrogen through sample during titration and titrate with red titration beakers to protect against light.
- Iodine and DPI are not selective for Vitamin C
  - Iodine is less selective than DPI.
    If orange juice contains also SO_2,
    - with Iodine: Vitamin C and SO_2 will be titrated.
    - with DPI: Vitamin C and approx. 20 % SO_2 will be titrated.
  - It is possible to selectively titrate Vitamin C in a sample which also contains SO_2 by masking SO_2 with glyoxal (ethane-1,2-dione, $C_2H_2O_2$).

Free and Total SO_2

Free sulphur dioxide, SO_2

- Titrant: 0.1 mol/L ½ I_2
- Auxiliary reagent: 5 mL KI 10 % and 5mL 25% H_2SO_4
- Sensor: DM143-SC

$$SO_2 + I_2 + 2\ H_2O \longrightarrow H_2SO_4 + 2\ HI$$

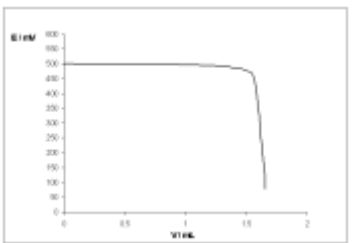
Total sulphur dioxide, SO_2

- Add 5mL 5 M NaOH and allow to react for 15 minutes to release bound SO_2 (Swiss Food Manual)
- Acidify with 7mL 25% H_2SO_4 and add 5 mL KI 10 %.
  (KI addition to delay reduction of I_2 by other components in sample)
- Titrate with I_2 as for free SO_2

Free and Total SO_2

METTLER TOLEDO

- Voltametric titration to endpoint EP=100 mV (similar to KF)



Free and Total SO_2

METTLER TOLEDO

Tips & Hints

- SO_2 is volatile
  - In order to avoid loss of SO_2, the samples must be taken from freshly opened bottle.
  - Working with sample changer leads to small SO_2 losses from the samples already prepared.
- Iodine is not selective for SO_2
  - These competing reactions can partially be delayed by addition of KI. (not ascorbic acid).
- SO_2 Standard
  - Sodium metabisulfite, $Na_2S_2O_5$, can be used as a SO_2 Standard ($Na_2S_2O_5$ → 2 SO_2)
- Very low content of SO_2 in wine (< 20-50 ppm)
  - Titrate with EQP und Iodine solution (for 3 ppm VEQ ca. 0.2 mL)

Free and Total SO_2

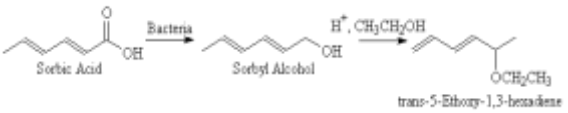
METTLER TOLEDO

Examples

- Wine
- Cider
- Fruit based drinks
- Dried fruit
- Flour
- Sausages

Free and Total SO_2

- Use of SO_2
- Used as a preservative in wine for its antibacterial properties
  - Sorbic acid in wine is reduced by bacteria to foul smelling ether



- Bleaching agent in flour
- Fumigate fruit and vegetables to extend their shelf life

Kjeldahl Nitrogen

Principle of Nitrogen Determination according to Kjeldahl

- Digestion
  Sample strongly heated for 2 – 3 hours in digestion flask containing sulfuric acid 98 %.
- Distillation of ammonia
  NaOH solution 30 % is added. Ammonia is generated according:

  $(NH_4)_2SO_4 + 2\ NaOH \rightarrow 2\ NH_3 + Na_2SO_4 + H_2O$

  Ammonia is distilled using water steam and collect in 1 – 2 % boric acid solution

  $2\ NH_3 + 4\ H_3BO_3 \rightarrow (NH_4)_2B_4O_7 + 5\ H_2O$
- Titration
  Ammonium tetraborate, $(NH_4)_2B_4O_7$, can be titrated with HCl.

  $(NH_4)_2B_4O_7 + 2\ HCl + 5\ H_2O \rightarrow 2\ NH_4Cl + 4\ H_3BO_3$

- Titrant: 0.1 mol/L HCl
- Solvent: Water
- Sensor: DGi111 or DGi115

Johan Gustav Christoffer Thorsager Kjeldahl
(Danish chemist, 1849 - 1900)

Kjeldahl Nitrogen

TTL I/O (RS232) for automated Kjeldahl analysis

Büchi (KjelFlex K-360)

Communication between Distillation unit

- Compact Titrator G20
- Titration Excellence T50 T70 and T90

via TTL I/O (and RS232 for Txx)

Büchi K-360 with T50

Kjeldahl Nitrogen

- **Examples**
  - Milk
  - Cheese
  - Yogurt
  - Butter

Additional Applications

- Reducing sugar acc. Rebelein (M496* – furthermore M568, M341, M342)
- Peroxide Value (M624* - M369)
- Iodine Value (M617*)
- Saponification Value (M618* - M090*)
- Formol Value (M493* - M061, M240)

* with Titration Excellence

Saponification value

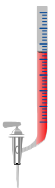
Agenda

1	Basic of Titration
2	Reaction types in Titration
3	Manual VS Automatic Titration
4	Titrator Instrument
5	Aplication in F&B
6	Tips and Hints

Tips and Hints

- **Titration beakers**
  - Use absolutely **clean** titration beakers.
  - Clean titration beakers in a dishwasher and rinse at least 2 times with deionised water.
  - The material of the beakers (plastic or glass) should be **resistant** to all chemicals used for the titration.
  - If the analytes are sensitive to light use special beakers which **protect the sample** from UV radiation.

- **Burette**
  - Choose the **appropriate burette size**. The titrant consumption should be within 20 % to 90 % of the burette volume for an accurate measurement
  - Estimate the burette size by calculating the titrant consumption from the expected value or perform a fast test titration.
  - **Avoid bubbles** in the burette or remove them before starting the titration (rinsing) as they will produce results that are too high. De-gas the titrant or reduce the titration speed if bubbles start coming from the titrant.



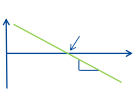
Tips and Hints

- **Tubes (automated titration)**
  - **Remove all bubbles** from the tubes (or the results will be too high) by tapping gently during rinsing.
  - Use a **siphon** to avoid diffusion of titrant into the titration solution.

- **Indicator (manual titration)**
  - Choose an indicator with a **color change range** within the range of the equivalence jump.
  - **Don't add too much indicator**; the indicator may influence the analyte/titrant reaction. Just a few drops of indicator solution usually suffice.

Tips and Hints

- **Sensor (automated titration)**
  - **Store and maintain** the sensor as described in the operating instructions.
  - Ensure that the **electrolyte level** is high enough, namely higher than internal elements and titration solution
  - **Poor sensor response** results in titrant consumption and results that are too high.
  - Perform a **sensor test** periodically to check slope, offset and drift value of sensors which need calibrating (pH sensor).
  - Perform a **sensor calibration**, especially before endpoint titrations and after every maintenance action.
  - Some sensors need **conditioning** (see operating instructions) before they can be used or after they have not been used for a long time.
  - **Reference electrodes** (which are also part of a combined electrode) need to be in contact with the sample solution by a junction (diaphragm). Avoid junction blockage for correct and stable results. When required clean the junction using an appropriate solution (see operating instructions).



Tips and Hints

- **Sample solution**
  - The overall sample solution (sample, reagents and solvent) should be enough to **cover the sensor**, typically 50 mL. Add solvent (water for aqueous titrations) if the volume is too small.
  - The **amount of sample** should be chosen such that the titrant consumption is within 20 % to 90 % of the burette volume.
  - Use **accurate measuring tools** (analytical balances, pipettes, …) to measure the sample size.
  - Perform a **blank** value determination if the solvent isn't pure.
  - Depending on the titration reaction (e.g. redox and precipitation titration) make sure that the **pH value** of the sample solution is within the requested range.

Tips and Hints

- **Titrant**
  - Perform a **titer determination** to know the titrant concentration accurately.
  - Use high purity, stable, non-hygroscopic substances with a high molecular weight (for a high sample size) as the **titer standard substance**.
  - A titer determination interval (**usable life**) and a **lifespan** should be defined depending on the stability of the titrant.
  - **Protect titrant** from CO_2, UV radiation, humidity or other factors which may have an influence on the concentration.