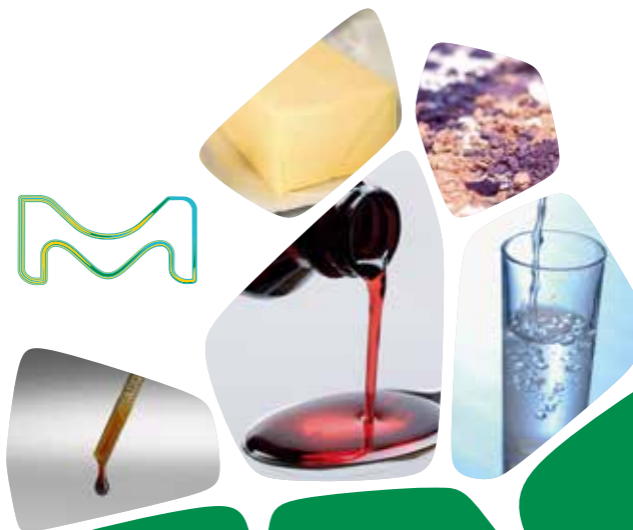


# Titripur<sup>®</sup> The Measure of all Things

Titration Guide for  
Titer Determination



The life science business  
of Merck KGaA, Darmstadt,  
Germany operates as  
MilliporeSigma in the  
U.S. and Canada.

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# 1. General information

The titer determination of volumetric solutions is one of the most important preconditions to receive reliable and transparent results in titration.

The following points influence the titration results:

- Measuring method
- Instrument (instrument uncertainty/abrasion of the burette)
- Electrodes (electrode uncertainty/alteration of electrodes)
- Handling (e.g. preparation of dilution)
- Balance (weighing error)
- Temperature
- Concentration change of volumetric solution because of influence through environmental oxygen, carbon dioxide, microbes, evaporation of water/solvent.

## 1.1 Titration and quality assurance according to DIN EN ISO 9001 and DIN EN ISO/IEC 17025

As with other analytical procedures it is also essential with titrimetry to determine results with high accuracy. The method used must be adapted to the sample matrix; suitable working procedures and a reproducible and traceable documentation of results must be present.

It cannot be described as a whole how a quality management system for titrimetric analyses must be arranged. The respective circumstances and requirements have to be considered: who titrates what, by which means and with which accuracy? This must be documented in a traceable way. Erroneously quality management is sometimes understood as:

- the request of usability data and additional quality relevant data per certificate from the reagent manufacturer,
- the presentation of technical tolerances of the instrument available from the manufacturer.

These not very expensive activities are, for the following reasons, only a small basis for comprehensive analytical results:

1. Usability data of standard solutions, supplied by the manufacturer, are only valid for originally closed containers. After opening other influences play a role.
2. The effective concentration indicated on the certificate refers only to the standard solution and is determined independently of the instrument. Specific properties of the analytical instrument used cannot be considered. The indicated titer can directly be applied by the user only with certain limitations.
3. Technical data of analytical instruments can only be used in a quality-related way when they are confirmed by regular control. The obvious prerequisite is periodical maintenance and service.

It is the better way that each user of titration systems establishes his own procedures for the quality assurance. This is the only possibility to recognize the limits of the analytical system used. For such a procedure it is necessary to define and to consider all quality relevant parts of the instruments employed.

Fundamental parts of the system are:

- a) Weighing devices,
- b) Volume gauges (volumetric flasks, pipettes, burettes, also mechanically driven),
- c) Standard solutions,
- d) Automatic titrators (instruments for the determination of the equivalent point as well as for the calculation of the analytical result),
- e) Electrodes,
- f) Other reagents (as e.g. indicators, buffer substances, acids, bases),
- g) Further instruments (as e.g. drying ovens, heating furnaces, densimeters).

According to the condition of the analytical system this list can be extended by one or the other topic which has to be considered as mentioned above.

## 2. standardization of volumetric solutions

In all following examples of the titer determination the initial weight was planned for a final consumption of approx. 19 mL of titrant which is the ideal consumption for a 20 mL burette. Direct initial weight of about 200 mg of a volumetric standard may, however, result in up to 0.2% weighing error. In such cases it is recommended to use the division into aliquots by gravimetry (see 4.2). For titrations which hardly allow a division into aliquots by gravimetry (e.g. non-aqueous titrations; perchloric acid titration 2.5) an improvement of the precision can only be reached by increase of the initial weight and use of 50 mL burettes.

### 2.1 di-Sodium EDTA solution 0.1 mol/L (Catalog No. 1084311000)

**Reaction type:** Complexometry

**Kind of titration:** Direct titration

**Volumetric**

**standard:** Zinc metal (Catalog No. 1024090100)

**Method of initial**

**introduction:** Division into aliquots by gravimetry

#### Indication

**a) visual:** indicator buffer tablet

(Catalog No. 1084300500); colour change from red to green (mixed colour),

**b) potentiometrical:** ion selective copper electrode with reference electrode and automatic titrator using 1 mL of copper EDTA solution 0.1 mol/L per determination instead of the indicator buffer tablet.

## Analytical procedure

### a) Preparation of a zinc chloride solution 0.1 mol/L volumetric standard

Approx. 6.54 g of zinc (Volumetric Standard) are analytically exactly weighed, transferred to an exactly weighed 1-L volumetric flask and dissolved in approx. 70 mL of hydrochloric acid 25% GR for analysis overnight. The volumetric flask is then made up to approx. 1 L and the total weight is determined to the second decimal.

### Calculation of the mass fraction $w$ (Zn) introduced in mg/g solution:

$$w \text{ (mg Zn/g solution)} = \frac{\text{weight of Zn (mg)} \cdot Cf}{\text{total weight (g)}}$$

$Cf$  = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

### b) Titration:

In a titration vessel of about 150–200 mL, approx. 19 g of zinc chloride volumetric standard solution are analytically exactly weighed per difference weighing using a plastic syringe. The solution is diluted to approx. 100 mL with water GR for analysis, one indicator buffer tablet and 10 mL of ammonia solution 25% GR for analysis are added and the solution is titrated with the  $\text{Na}_2\text{EDTA}$  solution to be tested.

### Calculation

$$t = \frac{\text{weight of ZnCl}_2\text{-solution (g)} \cdot w \text{ (Zn mg/g)}}{f \text{ (6.538 mg/mL)} \cdot \text{consumption (mL)}}$$

$t$  = titer

$w$  (Zn) = mass of zinc in 1 g of zinc chloride volumetric standard solution

$f$  = stoichiometric factor (volumetric equivalent in mg/mL).

## Standard solutions which can be tested with the standardized Na<sub>2</sub>EDTA solution:

- Barium chloride solution 0.05 mol/L\*
- Barium perchlorate solution 0.05 mol/L\*
- Copper nitrate solution 0.1 mol/L
- Copper sulfate solution 0.1 mol/L
- Mercury(II) nitrate solution 0.05 mol/L
- Zinc chloride solution 0.1 mol/L

## 2.2 Sodium thiosulfate solution 0.1 mol/L (0.1 N) (Catalog No. 1091471000)

**Reaction type:** Redox titration/iodometry

**Kind of titration:** Back-titration based on substitution

**Volumetric standard:** Potassium iodate  
(Catalog No. 1.02404)

Potassium iodate should be preferred to the toxic potassium dichromate which is suspected to be carcinogenic.

### Method of initial

**introduction:** Division into aliquots by gravimetry

### Indication

**a) visual:** with starch solution 1%; colour change from blue to colourless,

**b) potentiometrical:** with platinum single rod measuring chain and automatic titrator.

### Analytical procedure

#### a) Preparation of a potassium iodate solution 1/60 mol/L (0.1 N) (Catalog No. 1024040100)

Approx. 3.57 g of potassium iodate (Volumetric Standard), dried for 2 h at 130 °C, are exactly weighed, transferred to a 1-L volumetric flask, dissolved in water GR for analysis and made up to 1 L with water. The total weight is determined to the second decimal.

\*via back-titration with copper nitrate solution 0.1 mol/L



## Calculation of the mass fraction $w$ ( $\text{KIO}_3$ ) in mg/g solution:

$$w \text{ (mg KIO}_3\text{/g solution)} = \frac{\text{weight of volumetric standard (mg)} \cdot C_f}{\text{total weight (g)}}$$

$C_f$  = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

### b) Titration:

In a titration vessel of about 300 mL, approx. 19 g of potassium iodate volumetric standard solution are analytically exactly weighed per difference weighing using a plastic syringe. 150 mL of water GR for analysis, 3 g of potassium iodide and 5 mL of hydrochloric acid 25% are added and the iodine liberated is titrated immediately with the sodium thiosulfate solution to be tested.

### Calculation

$$t = \frac{\text{weight of KIO}_3\text{-solution (g)} \cdot w \text{ (KIO}_3 \text{ mg/g)}}{f \text{ (3.5667 mg/mL)} \cdot \text{consumption (mL)}}$$

$t$  = titer

$w$  ( $\text{KIO}_3$ ) = masse  $\text{KIO}_3$  in 1 g volumetric standard solution

$f$  = stoichiometric factor (volumetric equivalent in mg/mL).

### Standard solutions which can be checked with the standardized sodium thiosulfate solution:

- Bromate solution 1/60 mol/L
- Bromide-bromate solution 0.05 mol/L
- Iodide-iodate solution 1/64 mol/L
- Iodine solution 0.05 mol/L
- Potassium dichromate solution 1/60 mol/L
- Potassium iodate solution 1/60 mol/L
- Potassium permanganate solution 0.02 mol/L (for use in iodometry)

## 2.3 Iodine solution 0.05 mol/L (0.1 N) (Catalog No. 1090991000)

**Reaction type:** Redox titration/iodometry

**Kind of titration:** Direct titration

**Volumetric standard:** Sodium thiosulfate solution 0.1 mol/L  
(Catalog No. 1091471000)  
(standardized with the initial burette)

Arsenic (III) oxide should not be used as volumetric standard because of the high toxicity and the difficult handling. Atmospheric oxygen oxidizes the alkaline solution of  $\text{As}_2\text{O}_3$  very easily.

**Method of initial introduction:** Using the measurement of volume  
(under consideration of the temperature)

### Indication

**a) visual:** with starch solution 1%; colour change from colourless to blue,

**b) potentiometrical:** with platinum single rod measuring chain and automatic titrator.

### Analytical procedure

In a titration vessel of about 150–200 mL exactly 19.00 mL of sodium thiosulfate solution 0.1 mol/L (standardization see 5.4.4.2) are transferred from the initial burette, diluted to approx. 100 mL with water GR for analysis and titrated to the end point with the iodine solution to be tested.

### Calculation

$$t = \frac{\text{amount of Na-thiosulfate solution (mL)} \cdot t \text{ Na-thiosulfate}}{\text{consumption (mL)}}$$

### Standard solution which can be checked with the standardized iodine solution:

Sodium arsenite solution 0.05 mol/L.

### Further applications:

Determination of sulfur dioxide, arsenium compounds.

## 2.4 Cerium(IV) sulfate solution 0.1 mol/L (0.1 N) (Catalog No. 1090921000)

**Reaction type:** Redox titration/cerimetry

**Kind of titration:** Direct titration

**Volumetric standard:** Iron(II) ethylenediammonium sulfate (Catalog No. 1024020080)

Arsenic (III) oxide should not be used as volumetric standard because of the high toxicity and the difficult handling. Atmospheric oxygen oxidizes the alkaline solution of  $\text{As}_2\text{O}_3$  very easily.

**Method of initial introduction:** Direct weighing

### Indication

**a) visual:** with ferroin indicator solution (Catalog No. 1091610100); colour change from orange to faint blue,

**b) potentiometrical:** with platinum single rod measuring chain and automatic titrator.

### Analytical procedure

Approx. 700–750 mg of iron (II) ethylenediammonium sulfate (Volumetric Standard), dried for 24 h over silica gel, are exactly weighed into a titration vessel of approx Catalog No. 1090721000. 150–200 mL, dissolved in 50 mL of sulfuric acid 0.5 mL/L and titrated to the colour change with the cerium (IV) sulfate solution 0.1 mol/L (Catalog No. 1090921000) to be tested.

### Calculation

$$t = \frac{m(\text{Iron(II)-ethylenediammonium sulfate in mg}) \cdot Cf}{f (38.215 \text{ mg/mL}) \cdot \text{consumption (mL)}}$$

t = titer

m = weight of volumetric standard

f = stoichiometric factor (volumetric equivalent in mg/mL)

Cf = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

## 2.5 Perchloric acid in anhydrous acetic acid 0.1 mol/L (0.1 N) (Catalog No. 1090651000)

**Reaction type:** Acid-base titration in non-aqueous medium

**Kind of titration:** Direct titration

**Volumetric standard:** Tris(hydroxymethyl)aminomethane (TRIS) (Catalog No. 1024080080)

Alternative: Potassium hydrogen phthalate using the same analytical procedure. Tris(hydroxymethyl)aminomethane does not require drying, avoids the precipitation of potassium perchlorate and shows identical results when used for the potentiometric titration.

### Method of initial

**introduction:** Direct weighing

### Indication

**a) visual:** with 1-Naphtolbenzein (Catalog No. 1062020005); colour change from yellow to green.

If for the following application of perchloric acid a different indicator is used, this indicator must also be utilized for the calibration.

**b) potentiometrical:** pH-electrode.

### Analytical procedure

Approx. 220–230 mg of tris(hydroxymethyl)aminomethane (Volumetric Standard), stored for 24 h over silica gel, are exactly weighed into a titration vessel of approx. 150–200 mL, dissolved in 80 mL of acetic acid anhydrous GR for analysis and titrated to the colour change with the perchloric acid 0.1 mol/L to be tested.

## Calculation

$$t = \frac{m \text{ (Tris(hydroxymethyl)aminomethane in mg)} \cdot Cf}{f \text{ (12.114 mg/mL)} \cdot \text{consumption (mL)}}$$

t = titer

m = weight of volumetric standard

f = weight of volumetric standard

Cf = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

## 2.6 Sodium hydroxide solution 0.1 mol/L (0.1 N) (Catalog No. 1091411000)

### a) Determination of the NaOH content

**Reaction type:** Acid-base titration/alkalimetry

**Kind of titration:** Direct titration

**Volumetric standard:** Potassium hydrogen phthalate (Catalog No. 1024000080)

**Method of initial introduction:** Direct weighing

### Indication

**a) visual:** with phenolphthalein (Catalog No. 1072270250); colour change from colourless to faint pink,

**b) potentiometrical:** pH-electrode like e.g. single rod measuring chain and automatic titrator.

### Analytical procedure

Approx. 380 mg of potassium hydrogen phthalate (Volumetric Standard), dried at 120 °C to constant weight, are exactly weighed into a titration vessel of approx. 200 mL, dissolved in approx. 100 mL of water GR for analysis and titrated to the colour change with sodium hydroxide solution 0.1 mol/L to be tested.

## Calculation

$$t = \frac{m \text{ (K hydrogen phthalate in mg)} \cdot Cf}{f \text{ (20.423 mg/mL)} \cdot \text{consumption (mL)}}$$

t = titer

m = weight of volumetric standard

f = stoichiometric factor (volumetric equivalent in mg/mL)

Cf = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

### a) Determination of the total content of alkali (hydroxide and carbonate)

**Reaction type:** Acid-base titration/acidimetry

**Kind of titration:** Direct titration

**Volumetric standard:** Volumetric standard: Hydrochloric acid 0.1 mol/L tested against tris (hydroxymethyl) aminomethane (Volumetric Standard) (Catalog No. 1090601000)

**Method of initial introduction:** Volumetric using the burette provided for the sodium hydroxide solution

## Indication

**a) visual:** with mixed indicator 4.5 acc. to Mortimer (Catalog No. 1013590250); colour change from blue to red (mixed colour),

**b) potentiometrical:** pH-electrode like e.g. single rod measuring chain and automatic titrator.

## Analytical procedure

Exactly 19.00 mL of sodium hydroxide solution to be tested, using a burette provided for the base, are initially introduced into a titration vessel of approx. 200 mL, diluted with approx. 80 mL of water GR for analysis and titrated to the colour change with hydrochloric acid 0.1 mol/L just tested.

For bases with an increased carbonate content – recognizable by the delayed colour change – or for a very exact determination, it is recommended to boil the solution in order to remove the carbon dioxide dissolved after the addition of approx. 18.5 mL of hydrochloric acid 0.1 mol/L.

### Calculation

$$t = \frac{\text{consumption (mL HCl)} \cdot t_1 (\text{HCl})}{V_1 (\text{mL NaOH})}$$

Consumption of mL hydrochloric acid 0.1 mol/L

$t_1$  = titer of hydrochloric acid 0.1 mol/L

$V_1$  = mL of the sodium hydroxide solution 1 mol/L initially introduced.

## 2.7 Sodium hydroxide solution 1 mol/L (1 N) (Catalog No. 1091371000)

### a) Determination of the NaOH content

**Reaction type:** Acid-base titration/alkalimetry

**Kind of titration:** Direct titration

**Volumetric standard:** Potassium hydrogen phthalate  
(Catalog No. 1024000080)

**Method of initial introduction:** Direct weighing

### Indication

**a) visual:** with phenolphthalein  
(Catalog No. 1072270250); colour change from colourless to faint pink,

**b) potentiometrical:** pH-electrode like e.g. single rod measuring chain and automatic titrator.

### Analytical procedure

Approx. 3,800 mg of potassium hydrogen phthalate (Volumetric Standard), dried at 120 °C to constant weight, are exactly weighed into a titration vessel of approx. 200 mL, dissolved in approx. 100 mL of water GR for analysis and titrated to the colour change with sodium hydroxide solution 1 mol/L to be tested.

## Calculation

$$t = \frac{m \text{ (K hydrogen pththalate in mg)} \cdot Cf}{f \text{ (20.423 mg/mL)} \cdot \text{consumption (mL)}}$$

t = titer

m = weight of volumetric standard

f = stoichiometric factor (volumetric equivalent in mg/mL)

Cf = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

### b) Determination of the total content of alkali (hydroxide and carbonate content)

**Reaction type:** Acid-base titration/acidimetry

**Kind of titration:** Direct titration

**Volumetric standard:** Hydrochloric acid 0.1 mol/L (Catalog No. 1090571000) tested against tris (hydroxymethyl) aminomethane (Volumetric Standard) (Catalog No. 1024080080)

**Method of initial introduction:** Volumetric using the burette provided for the sodium hydroxide

## Indication

**a) visual:** with mixed indicator 4.5 acc. to Mortimer (Catalog No.101359); colour change from blue to red (mixed colour),

**b) potentiometrical:** pH-electrode like e.g. single rod measuring chain and automatic titrator.

## Analytical procedure

Exactly 19.00 mL of sodium hydroxide solution to be tested are initially introduced into a titration vessel of approx. 200 mL using a burette provided for the base, diluted with approx. 80 mL of water GR for analysis and titrated to the colour change with hydrochloric acid 0.1 mol/L just tested.



For bases with an increased carbonate content – recognizable by the delayed colour change – or for a very exact determination, it is recommended to boil the solution in order to remove the carbon dioxide dissolved after the addition of approx. 18.5 mL of hydrochloric acid.

### Calculation

$$t = \frac{\text{consumption (mL)} \cdot t_1 (\text{HCl})}{V_1 (\text{mL})}$$

Consumption of mL hydrochloric acid 0.1 mol/L

$t_1$  = titer of hydrochloric acid 0.1 mol/L

$V_1$  = mL of the sodium hydroxide solution 0.1 mol/L initially introduced.

## 2.8 Silver nitrate solution 0.1 mol/L (0.1 N) (Catalog No. 1090811000)

**Reaction type:** Precipitation titration/argentometry

**Kind of titration:** Direct titration

**Volumetric standard:** Sodium chloride  
(Catalog No. 1024060080)

**Method of initial introduction:** Division into aliquots by gravimetry

### Indication

**a) visually possible with potassium chromate**  
(Catalog No. 1049520250); colour change from yellow to red-brown; this indication is only possible after change of the analytical procedure corresponding to the determination acc. to Mohr in neutral solution.

**b) potentiometrical:** combined silver electrode and automatic titrator.

### Changes in connection with the visual indication:

- closeable titration vessel (Erlenmeyer flask),
- no nitric acid present,
- the titration vessel must be shaken vigorously after each addition of the titrant.

## Analytical procedure

### a) Preparation of a sodium chloride solution approx. 0.1 mol/L (Volumetric Standard solution) (Catalog No. 1024060080)

Approx. 5.85 g of sodium chloride (Volumetric Standard), dried at 150 °C to constant weight, are exactly weighed and transferred to a weighed 1-L volumetric flask, dissolved in water GR for analysis and made up to 1 L. The total weight is determined to two decimals.

### Calculation of the mass fraction $w$ (NaCl) in mg/g solution:

$$w \text{ (mg NaCl/g solution)} = \frac{\text{weight of volum. std. (mg)} \cdot Cf}{\text{total weight (g)}}$$

Cf = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

### b) Titration:

Approx. 19 g of sodium chloride solution (Volumetric Standard) are weighed exactly into a titration vessel of 150–200 mL (e.g. beaker), using the difference weighing of a plastic syringe, and diluted to approx. 100 mL with water GR for analysis, 5 mL of nitric acid 25% are added and the solution is titrated with the silver nitrate solution to be tested with vigorous stirring.

### Calculation

$$t = \frac{\text{weight of NaCl solution (g)} \cdot w \text{ (NaCl mg/g)}}{f \text{ (5.8443 mg/mL)} \cdot \text{consumption (mL)}}$$

t = titer

w (NaCl) = mass of NaCl in 1 g of volumetric standard solution

f = stoichiometric factor (volumetric equivalent in mg/mL).

## 2.9 Potassium permanganate solution 0.02 mol/L (0.1 N) (Catalog No. 1091221000)

<b>Reaction type:</b>	Redox titration/manganometry
<b>Kind of titration:</b>	Direct titration
<b>Volumetric standard:</b>	Sodium oxalate (Catalog No. 1024070060)
<b>Method of initial introduction:</b>	Division into aliquots by gravimetry

### Indication

- a) visual:** without indicator using the intrinsic colour; first visible pink coloration,
- b) potentiometrical:** with platinum single-rod measuring chain and automatic titrator.

### Analytical procedure

#### a) Preparation of a sodium oxalate solution 0.05 mol/L (Volumetric Standard solution)

Approx. 6.70 g of sodium oxalate (Volumetric Standard), dried at 110 °C to constant weight, are exactly weighed and transferred to a weighed 1-L volumetric flask, dissolved in water GR for analysis and made up to 1 L. The total weight is determined to two decimals.

#### Calculation of the mass fraction $w$ (sodium oxalate) in mg/g solution:

$$w \text{ (mg sodium oxalate/g solution)} = \frac{\text{weight of volum. std. (mg)} \cdot C_f}{\text{total weight (g)}}$$

$C_f$  = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

#### b) Titration:

Approx. 19 g of sodium oxalate solution (Volumetric Standard) are weighed exactly into a beaker or titration vessel of 300 mL, using the difference weighing of a plastic syringe. To this solution 10 mL of sulfuric acid 96% (attention: heating!) and approx. 170 mL of water

GR for analysis, warmed to 80–85 °C, are added and the solution is titrated at this temperature with the potassium permanganate solution 0.02 mol/L to be tested under permanent stirring until the colour change.

The pink coloration appearing immediately must disappear after the addition of a few mL of the titrant. The decolourized solution is titrated carefully and slowly until again a noticeable faint pink coloration appears.

### Calculation

$$t = \frac{\text{weight Na-oxalate solution (g)} \cdot w (\text{Na-oxalat mg/g})}{f (6.700 \text{ mg/mL}) \cdot \text{consumption (mL)}}$$

t = titer

w (sodium oxalate) = mass of sodium oxalate in 1 g of volumetric standard solution

f = stoichiometric factor (volumetric equivalent in mg/mL).

### Standard solution which can be checked with the standardized potassium permanganate solution:

Oxalic acid solution 0.05 mol/L.

## 2.10 Hydrochloric acid 0.1 mol/L (0.1 N) (Catalog No. 1090601000)

**Reaction type:** Acid-base titration/acidimetry

**Kind of titration:** Direct titration

**Volumetric standard:** Tris(hydroxymethyl)-aminomethane (TRIS) (Catalog No. 1024080080)

**Method of initial introduction:** Division into aliquots by gravimetry

### Indication

**a) visual:** mixed indicator 4.5 acc. to Mortimer; colour change from blue to red (mixed colour),

**b) potentiometrical:** pH-electrode like e.g. single-rod measuring chain and automatic titrator.

## Analytical procedure

### a) Preparation of a tris(hydroxymethyl)-aminomethane solution 0.1 mol/L (0.1 N) (Volumetric Standard solution)

Approx. 12.114 g of tris(hydroxymethyl)aminomethane (volumetric Standard), stored for 24 h over a neutral drying agent in a desiccator and exactly weighed, are transferred to a dry, weighed 1-L volumetric flask, dissolved in water GR for analysis and made up to approx. 1 L. The total weight is determined to two decimals.

#### Calculation of the mass fraction w (TRIS) in mg/g solution:

$$w \text{ (mg TRIS/g solution)} = \frac{\text{weight of volumetric standard (mg)} \cdot C_f}{\text{total weight (g)}}$$

$C_f$  = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

### b) Titration:

Approx. 19 g of tris(hydroxymethyl)aminomethane solution (Volumetric Standard solution) are weighed exactly into a beaker or titration vessel of approx. 150–200 mL using difference weighing of a plastic syringe, diluted to approx. 100 mL with water GR for analysis and titrated to the colour change with hydrochloric acid 0.1 mol/L to be tested.

#### Calculation

$$t = \frac{\text{weight of TRIS-solution (g)} \cdot w \text{ (TRIS mg/g)}}{f \text{ (12,114 mg/mL)} \cdot \text{consumption (mL)}}$$

$t$  = titer

$w$  (TRIS) = mass of TRIS in 1 g of volumetric standard solution

$f$  = stoichiometric factor (volumetric equivalent in mg/mL).

## Standard solutions which can be checked with the standardized hydrochloric acid 0.1 mol/L:

All strong and weak bases in the concentration range of 0.01 to 0.25 mol/L considering the choice of the suitable indicator resp. the pH range.

For the titration of the content of the total alkali of strong bases it is recommended to use methyl orange with an end point in the pH range of approx. 4.5. The exact determination of the carbonate content requires a boiling just before the end of the titration, as described in the analytical procedure. Here the mixed indicator 4.5 acc. to Mortimer is recommended. For the determination of the hydroxide only, methyl red with a transition range of pH 4–6 or, better, phenolphthalein with a transition range of pH 8–10 can be utilized.

For the titration of weak bases, the use of indicators with a transition range of between pH 4 and 6 is recommended. For specific ranges mixed indicators are available like, e.g. mixed indicator 5 for ammonia titrations.

## 2.11 Hydrochloric acid 1 mol/L (1 N) (Catalog No. 1090571000)

<b>Reaction type:</b>	Acid-base titration/acidimetry
<b>Kind of titration:</b>	Direct titration
<b>Volumetric standard:</b>	Tris(hydroxymethyl)aminomethane (TRIS) (Catalog No. 1024080080)
<b>Method of initial introduction:</b>	Direct weighing

### Indication

- a) visual:** mixed indicator 4.5 acc. to Mortimer (Catalog No. 1013590250; colour change from blue to red (mixed colour),
- b) potentiometrical:** pH-electrode like single-rod measuring chain and automatic titrator.

## Analytical procedure

Approx. 2.3 g of tris(hydroxymethyl)aminomethane (Volumetric Standard), stored for 24 h over a neutral drying agent in a desiccator, are exactly weighed in a 150 mL beaker or titration vessel and dissolved in approx. 100 mL of water GR for analysis. The solution is titrated to the colour change resp. the end point with hydrochloric acid 1 mol/L to be tested.

## Calculation

$$t = \frac{m \text{ (TRIS in mg)} \cdot Cf}{f \text{ (121.14 mg/mL)} \cdot \text{consumption (mL)}}$$

t = titer

m = mass of TRIS

f = stoichiometric factor (volumetric equivalent in mg/mL)

Cf = correction factor, calculated from the effective content of the volumetric standard acc. to the certificate divided by 100.

## Important standard solutions which can be checked with the standardized hydrochloric acid 1 mol/L:

All strong and weak bases in the concentration range of 0.5 to 2 mol/L considering the choice of the suitable indicator resp. the pH range.

For the titration of the content of the total alkali of strong bases it is recommended to use the mixed indicator 4.5 acc. to Mortimer or methyl orange with a pH transition point of abt. 4.5. For the determination of the hydroxide portion of the base, methyl red with a transition range of pH 5–6 or phenolphthalein with a pH transition range of 8–10 can also be used.

For the titration of weak bases, the use of indicators with a transition range of between pH 4 and 6 is recommended. Here mixed indicators are available for specific ranges like e.g. mixed indicator 5 for ammonia titrations.

## 3. VOLUME GAUGES

### 3.1. Limits of error of volume gauges

The deviation of volume gauges can be taken from the following tables. The volume errors of the measuring instruments are, compared to the other possible errors, not insignificant and multiply through series dilutions (Motor piston burettes).

Table 1

#### Volumetric flasks and their error limits acc. to DIN

Nominal volume (mL)	Class A max. permissible error		Class B max. permissible error	
	mL	%	mL	%
50	±0.06	±0.12	±0.12	±0.24
100	±0.1	±0.1	±0.2	±0.2
250	±0.15	±0.06	±0.3	±0.12
500	±0.25	±0.05	±0.5	±0.1
1,000	±0.4	±0.04	±0.8	±0.06

Table 2

#### Volumetric pipettes and their error limits acc. to DIN

Nominal volume (mL)	Class A max. permissible error		Run-off time s	Class B max. permissible error		Run-off time s
	mL	%		mL	%	
1	±0.007	±0.7	10–20	±0.015	±1.5	5–20
5	±0.015	±0.3	15–30	±0.03	±0.6	5–20
10	±0.02	±0.2	15–40	±0.04	±0.4	8–40
20	±0.03	±0.15	25–50	±0.06	±0.3	9–50
25	±0.033	±0.13	25–50	±0.08	±0.32	10–50
50	±0.05	±0.1	30–60	±0.1	±0.2	13–60
100	±0.08	±0.08	40–60	±0.16	±0.16	25–60



### 3.2 Calibration of volume gauges with water (determination of a correction factor)

When a volume gauge cannot be included in the titer, it is necessary for an exact titration to carry out a calibration.

The calibration of volume is always recommended in case in which calibrated volumetric solutions are used in combination with different burettes or pipettes. Likewise a check of burettes, pipettes and volumetric flasks is suggested when an accuracy of  $<0.2\%$  (relative) is aimed at.

When a titrimetric standard solution (Volumetric Standard) is initially introduced using a volume gauge, the deviation of the dosing device must also be known and considered accordingly for the calculation.

For exact values the calibration has to be carried out under identical conditions as for the later analysis.

Important topics in this connection are the cleanliness of the instruments, the ambient temperature and personal influences of the operator (e.g. differing handling of the pipette regarding the efflux speed, run-on time, strip-off etc.).

The easiest way of checking happens through weighing of a certain volume of water which is measured with the volume gauge to be calibrated. Here the buoyancy of the air during the weighing process has to be considered.

The water used must be analytically pure, double distilled or of analytical grade. In addition it is of advantage to boil up the water shortly before use for degassing. For the final use the water should be cooled down to ambient temperature again.

The temperature must be kept constant during dosing. The temperature does not play a role during the weighing procedure.

The function of the instruments must not be affected; i.e. they must be clean and fat-free.

Further it is of importance to dimension the quantity of water measured (eventually through multiple dosing) in such a way that the weighing error present does not affect the measuring result. It is recommended to weigh 50–100 g on the analytical balance.

In order to avoid the loss of liquid through evaporation, closed glass vessels are used (like e.g. volumetric flasks), the ground joint resp. the closure of which may not be wetted. The burette tip must be stripped off after the dosing process in order to receive reproducible conditions.

Instead of a self-attached calibration mark it is recommended to determine a factor for the device concerned: the adaptation factor  $f$  for the corresponding volume gauge. The adaptation factor multiplied with the volume indicated results in the volume actually dosed.

Using a longer term control, good proof does exist about the dosing stability of the volume gauges when utilized permanently. A continuous enhancement of the factor is to be expected for e.g. bases.



### 3.3 Testing of burettes and motor piston burettes

The check of burettes can be carried out according to two methods because they are used within a variable range:

- a) A burette is used predominantly in a certain volume range of e.g. 40 mL. In this case it is recommended to check at 40 mL by weighing 2 amounts of volume (2 x 40 mL in a tared out container). The result is guaranteed through a triple determination. This adaptation factor can be indicated as "burette factor" for 40 mL.

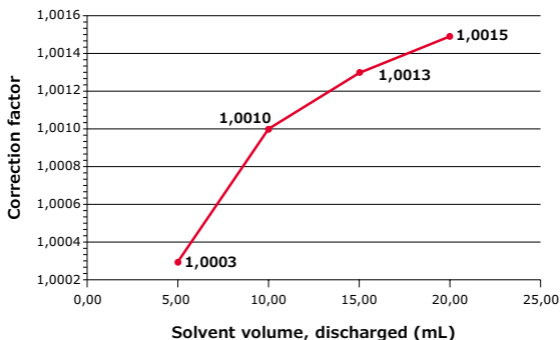
#### **Example for labelling:**

**Factor 40 mL:** 1.0025

Date: 30.01.05      No. of burette: 18

Next test: 01/06

- b) If burettes are used over the whole range, the calibration should also be carried out advantageously over the same range. In this case a burette of 25 mL is checked at 5, 10, 15, 20 and 25 mL. In order to reach guaranteed results each single value is checked several times. With the values determined, a burette-error curve can be established for the whole range of volume measurements.



**Figure: Burette-error curve:**

Development of a correction factor of a burette at different discharge volumes.

### 3.4 Testing of pipettes and piston pipettes

Using the clean pipettes a multiple measurement, according to volume size, is carried out in a tared out container. After pipetting the amount of water is weighed. Through the determination of the mass of one pipetting process and the comparison with the volume listed in Table 3, the calculation of the correction factor is possible. Here, too, a sufficient number of measurements has to be carried out in order to obtain a guaranteed result.

### 3.5 Testing of volumetric flasks

The dry and clean measuring flask is tared out using a balance with the corresponding maximum load and readability of 10 mg. Thereafter, the volumetric flask is filled exactly to the mark with water of known temperature and weighed again. The mass of the content can be calculated from the difference of the weighings

which is compared with the value stated in Table 3 – at the corresponding temperature. From that a correction factor can be calculated. The determination should be carried out at least in triplicate.

### 3.6 Calculation example for a burette

The weight  $m$  of 100 mL of water at 21.2 °C is 99.938 g.

The value stated in Table 3 for 21.2 °C = 996.89 g/1,000 mL.

#### Adaptation factor for the volume gauge:

$$\text{Burette factor } f = \frac{99.938 \text{ g} \cdot 1,000 \text{ mL}}{996.89 \cdot 100 \text{ mL}} = 1.0025 \quad f = 1.0025$$

**Result:** The volume discharged is 1.0025 times larger than the volume indicated.

It can be taken directly from the following Table 3 at which temperature  $t$  (°C) the stated weight  $m$  (g) corresponds to the volume  $V = 1,000$  mL. Here the buoyance of the air is already included. This table was calculated with a brass weight of the density  $\nu = 8.4 \text{ g/cm}^3$ . Table 3 can, however, also be used for the calculation for newer balances with stainless steel weights with a density  $\nu = 8.0 \text{ g/cm}^3$  because the difference between the two densities results in a relative error of 0.001%.

Table 3

**The determination of volume using the weighing with water at different temperatures<sup>2</sup> (V = 1,000 mL)**

t (°C)	m (g)	t (°C)	m (g)	t (°C)	m (g)	t (°C)	m (g)
0	998.78	17.2	997.68	23.2	996.43	29.2	994.82
1	998.84	17.4	997.64	23.4	996.38	29.4	994.76
2	998.88	17.6	997.61	23.6	996.33	29.6	994.70
3	998.91	17.8	997.57	23.8	996.28	29.8	994.64
4	998.91	18.0	997.53	24.0	996.23	30.0	994.58
5	998.91	18.2	997.50	24.2	996.18	30.2	994.52
6	998.88	18.4	997.46	24.4	996.13	30.4	994.46
7	998.84	18.6	997.42	24.6	996.08	30.6	994.40
8	998.78	18.8	997.38	24.8	996.03	30.8	994.34
9	998.72	19.0	997.34	25.0	995.98	31.0	994.28
10	998.63	19.2	997.30	25.2	995.93	31.2	994.21
11	998.55	19.4	997.26	25.4	995.88	31.4	994.15
12	998.44	19.6	997.22	25.6	995.83	31.6	994.09
13	998.32	19.8	997.18	25.8	995.77	31.8	994.02
14	998.18	20.0	997.14	26.0	995.72	32.0	993.96
14.2	998.16	20.2	997.10	26.2	995.67	32.2	993.90
14.4	998.13	20.4	997.06	26.4	995.61	32.4	993.83
14.6	998.10	20.6	997.02	26.6	995.56	32.6	993.77
14.8	998.07	20.8	996.97	26.8	995.50	32.8	993.70
15.0	998.04	21.0	996.93	27.0	995.45	33.0	993.64
15.2	998.01	21.2	996.89	27.2	995.38	33.2	993.57
15.4	997.98	21.4	996.84	27.4	995.34	33.4	993.51
15.6	997.95	21.6	996.80	27.6	995.28	33.6	993.44
15.8	997.91	21.8	996.75	27.8	995.23	33.8	993.37
16.0	997.88	22.0	996.71	28.0	995.17	34.0	993.30
16.2	997.85	22.2	996.66	28.2	995.11	34.2	993.24
16.4	997.82	22.4	996.62	28.4	995.05	34.4	993.17
16.6	997.78	22.6	996.57	28.6	995.00	34.6	993.10
16.8	997.75	22.8	996.52	28.8	994.94	34.8	993.03
17.0	997.71	23.0	996.48	29.0	994.88	35.0	992.97

## 4. preparation and taking aliquots of standard and volumetric standard solutions

### 4.1 Procedure for taking volumetric aliquots

- Use only Standard Reference Materials (SRM) or Certified Volumetric Standard substances; reagents of at least analytical quality only as exception.
- Take notice of the effective content of the batch of the Volumetric Standard and consider this value for the calculation.
- Volumetric flasks have to comply with class A and must be calibrated resp. of certified conformity.
- Dry, if required, the Standard Reference Material or the Volumetric Standard substance according to the instructions of the manufacturer. In this case temperatures and durations indicated – mostly 1–2 hours are sufficient until constant weight – should be adhered to.
- Use an analytical balance with a readability of 0.0001 g. Utilize only weighing boats or tubes or beakers made of glass and no sheets of paper or plastic (electrostatic charge).
- Transfer the weighed sample quantitatively to the volumetric flask. For safety reasons a funnel should always be used. Rinse well beaker, weighing boat and scoop and funnel. If substance or solution is lost start again from the beginning.
- Close the measuring flask for the dissolution of the weighed sample and rinse the stopper briefly after withdrawal.
- Fill the volumetric flask to about 80% with the solvent and adjust the temperature with the help of a thermometer. The calibration temperature of the flask has to be considered. Rinse the thermometer again after withdrawal.

- Make up the volumetric flask exactly to the mark.
- Close the volumetric flask with the stopper and mix thoroughly by repeated turns.
- Label the flask unambiguously with:
  - contents,
  - concentration resp. amount of material weighed in,
  - date of preparation,
  - expiry date,
  - safety instructions,
  - initials of the person who prepared the solution.
- When using the Volumetric Standard solution do not leave open unnecessarily the flask for too long.
- Mix the Volumetric Standard solution and check the temperature each time before use.
- Withdraw your sample by first transferring each time a sufficient amount into a clean beaker. Avoid entering the flask with pipettes or other objects; only by this means the quality of the standard and Volumetric Standard solution is guaranteed right to the end, in spite of frequent usage.

## 4.2 Procedure for taking gravimetric aliquots

- Use only Standard Reference Materials (SRM) or Volumetric Standard substances; reagents of at least analytical quality only as exception.
- Glassware must be closeable (volumetric or Erlenmeyer flasks with ground joint). This equipment must not fulfil specific quality requirements.
- Determine the tare weight of the dry and clean flask including the stopper.
- For this determination use a precision balance with a readability of 0.01 g.
- Dry, if required, the Standard Reference Material or the Volumetric Standard substance according to the instructions of the manufacturer. In this case temperatures and durations indicated – mostly 1–2 hours are sufficient until constant weight – should be adhered to.



- Use an analytical balance with a readability of 0.0001 g. Utilize only weighing boats or tubes or beakers made of glass and no sheets of paper or plastic (electrostatic charge).
- Transfer the weighed sample quantitatively to the volumetric flask. For safety reasons a funnel should always be used. Rinse well beaker, weighing boat and scoop and funnel.
- If substance or solution is lost start again from the beginning.
- Close the measuring flask for the dissolution of the weighed sample and rinse the stopper briefly after withdrawal.
- Fill the flask with the solvent approximately up to the total desired volume.
- Dry stopper and ground joint, close the flask and weigh it back using a precision balance (gross weight).
- Calculate the total initial weight (gross weight – tare weight) and determine the mass fraction  $w$  of the standard reference material per gram of the initial weight of the solution considering the effective content of the batch of the Volumetric Standard (initial weight of SRM  $\times$  effective content/total initial weight  $\times$  100).
- Label the flask unambiguously with:
  - contents,
  - concentration resp. amount of material weighed in,
  - date of preparation,
  - expiry date,
  - safety instructions,
  - initials of the person who prepared the solution.
- When using the Volumetric Standard solution do not unnecessarily leave the flask open for too long.
- Mix the Volumetric Standard solution and check the temperature each time before use.

- Withdraw your sample by first transferring each time a sufficient amount into a clean beaker. Avoid entering the flask with pipettes or other objects. Only by this means the quality of the Volumetric Standard solution is guaranteed right to the end, in spite of frequent usage.
- Use for weighing out portions preferably a plastic single-use syringe and determine the weight by differential weighing using an analytical balance.
- Calculate the actual amount of Volumetric Standard by multiplying the weight of the portion with the mass fraction previously calculated.

The gravimetric procedure<sup>3</sup> described in the following can be carried out in the analytical laboratory using conventional instruments and balances and is by factor of 10 more exact than the volumetric procedure.

## 5. preparation of the 1% starch solution

A slurry 5 g of starch in a small amount of water is added to 500 mL of boiling water (attention: delayed boiling!). Boil the solution for a short while and allow to cool. The indicator solution formed should show only a slight opalescence. Starch solutions tend to be attacked by microorganisms and should, therefore, be renewed regularly.

3 W. Gernand, K. Streckenreuter, G. Wieland, Z. Anal Chem. 334, 534-539 (1989)

# 6. Traceability of certipur<sup>®</sup> volumetric solutions and volumetric standards to standard-reference-material (SRM) from NIST

NIST = National Institute of Standards and Technology, USA

Volumetric-method	Standard-Reference-material (SRM)	Volumetric Solution	Volumetric standards MilliporeSigma
<b>Acidimetry</b>	Tris(hydroxymethyl)-aminomethane (NIST)	Hydrochloric acid	Tris(hydroxymethyl)-aminomethane (NIST) Order No. 1.02408.0080
		Hydrochloric acid	Sodium carbonate Order No. 1.02405.0080
<b>Alkalimetry</b>	Potassium hydrogen-phthalate (NIST)	Sodium hydroxid solution	Potassium hydrogen phthalat Order No. 1.02400.0080
	Benzoic acid (NIST)	Sodium hydroxid solution	Benzoic Acid Order No. 1.02401.0060
<b>Argentometry</b>	Potassium chloride (NIST)	Silver nitrate solution	Sodium chloride Order No. 1.02406.0080
<b>Reductometry</b>	Potassium dichromate (NIST)	Sodium thiosulfate solution	Potassium dichromate Order No. 1.02403.0100
		Sodium thiosulfate solution	Potassium iodate Order No. 1.02404.0100
<b>Oxidimetry</b>	di-Sodium oxalate (NIST)	Potassium permanganate solution	Fe(II)-ethylen-diammonium sulfate Order No. 1.02402.0080
		Potassium permanganate solution	di-Sodium oxalate Order No. 1.02407.0060
<b>Complexometry</b>	Zinc (NIST)	EDTA (Titriplex <sup>®</sup> III-solution)	Zinc (NIST) Order No. 1.02409.0100
		EDTA (Titriplex <sup>®</sup> III-solution)	Calcium carbonate Order No. 1.02410.0100

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