



Titration Handbook

THEORY AND PRACTICE OF TITRATION

SI Analytics

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Dr. Robert Reining
Managing Director

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Since 2011, SI Analytics has been part of the publicly traded company Xylem Inc., headquartered in Rye Brook, N.Y., USA. Xylem is a world leader in solving water related problems. In 2016, the German companies were finally merged to Xylem Analytics Germany and continue to represent the established brands at the known locations.

We herewith present to you our Titration handbook.

The focus has been consciously put on linking application information with our lab findings and making this accessible to you in a practical format.

If you have any questions about the very large field of titration, we look forward to helping you with words and deeds.

We at Xylem Analytics Germany in Mainz would be happy to keep on working successfully together with you in the future.

Xylem Analytics Germany

Sincerely,
Robert Reining

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Titration guide

INTRODUCTION AND DEFINITION

Titration is one of the oldest methods for content determination in chemistry.

In contrast to gravimetry, no sparingly soluble compounds are dried and weighed, but a reagent of known concentration is added to the dissolved sample until the chemical conversion is complete. For the definition of titration, there are a number of formulations that have changed over time. The IUPAC (Compendium of chemical Technology) defines titration as:

Quantitative analysis method in which a sample of known composition but unknown content is converted with a reagent of known concentration (also called standard solution) in a chemical reaction of known stoichiometry.

From the very precisely added volume of the reagent, the unknown content in the sample can be calculated on the basis of the calculation factors.

Titration finds broad use in chemical analysis. On the one hand, a titration can be performed very easily and quickly, on the other hand, the titration provides a very accurate measurement result after only a few minutes - under optimal conditions. A relative standard deviation of below one percent is normal. It is not without reason that numerous standards require titration as a method.

Even with a very common and proven method of analysis, there is a need for support. This guide builds on the basic principles of titration and addresses the user of potentiometric titration. Therefore, the basics of potentiometry is discussed with the Nernst equation. The "manual titration" is almost completely left out. A general overview of titration can be found in the classic standard work of titration, the Jander / Jahr [1].

Titration guide

This guide requires chemical knowledge, e.g. the reading of reaction equations, knowledge of important technical terms, basic knowledge of working in the chemical laboratory, as well as the handling of devices such as scales, burettes, pipettes, electrodes and the safety regulations in the laboratory.

Titration is also called volumetry. Even when working with a pH electrode, the measurement unit of the titration remains the volume and not the pH value. The correctness of the volume is thus essential for every titration. Coulometry is an exception, which is a titration method, but which is not performed volumetrically.

In the first step, this guide deals with the volume and its correctness. Thereafter, the focus is on the sample and its handling. Subsequently, the used reagents, electrodes and the titration parameters are dealt with in detail.

Furthermore, application areas are mentioned and various titration methods are presented. The individual calculations always give rise to questions and are therefore explained and summarized with the most important formulas. Typical titrations with their titration curves and calculations are presented by means of examples.

Evaluation and quality are more and more in the foreground. Therefore, the final chapter is devoted to the qualification of the devices, verification and validation of results, as well as measurement uncertainty.

SECTION 1

BASICS

1.1 Definitions and foundations

The definition of titration is valid unchanged in its core: We need a stoichiometric reaction, a precisely dosable, stable reagent and a detection of the end of the reaction end or a curve showing the course of the reaction.

The standard work for Volumetric Analysis [1] also falls back on these characteristics and defines:

- *The chemical reaction on which the titration is based must proceed rapidly, quantitatively and unambiguously in the manner indicated by the reaction equation.*
- *It must be possible to prepare a reagent solution of defined concentration or to determine the concentration of the solution in a suitable way.*
- *The endpoint of the titration must be clearly recognizable. It should coincide with the equivalence point at which the reagent amount equivalent to the substance amount of the searched substance was added or at least come very close to it.*

This definition has to be extended or limited nowadays: there are many reactions that do not take place stoichiometrically. In the Karl Fischer reaction, this has been discussed controversially for decades (1: 1 or 2: 1). With some reactions it is completely unclear how they actually take place. It is only certain that they run equally under the same conditions (e.g., the determination of chondroitin sulphate). Validations are then performed by means of linearity tests with standards, which enable a quantification of the sample. There are also numerous applications that go beyond simple content determination. These include stability studies, long-term extractions and monitoring of crystallizations (sometimes over months), determination of pK_s values, pK_b values and still further methods with very specific statements.

Titration guide

When validating a titration method, the following aspects must be observed:

- chemical reaction
- accurately adjusted reagent
- the sensor for detection.

The chemical reaction must be fast, clear and quantitative. An indication of whether a reaction is suitable for the titration is given by the law of mass action:



with the equilibrium constant K

$$K = [C]^c * [D]^d / [A]^a * [B]^b$$

For the titrations, the reaction equilibrium should be on the right side of the reaction equation, thus $K \gg 1$.

After the reaction has been determined, particular attention must be paid in the laboratory to the exact dosage of the set reagent and the selection of a suitable sensor. The core function of a modern titrator is the exact dosage of the titrant. The standard [ISO 8655 \[2\]](#) describes the requirements and check of the exact dosing.

The detection can be carried out by colour indicators or by means of electrochemical methods, which are dealt with here in essence.

The predominant method is potentiometry using e.g. pH and redox sensors with indicator and reference electrodes, which can detect potentials according to the electrochemical series.

The Nernst equation is the basis of potentiometry. It describes this electrochemical potential at an electrode as a function of the activity of the ions in the solution.

$$E = E^\circ + \frac{RT}{z_e F} \ln \frac{a_{\text{ox}}}{a_{\text{Red}}}$$

- E Electrode potential
- E° Standard electrode potential
- R Universal or molar gas constant,
 $R = 8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$
- T absolute temperature in Kelvin
- z_e Number of electrons transferred
(also equivalence number)
- F Faraday constant,
 $F = 96485.34 \text{ C mol}^{-1}$
- a Activity of the respective redox partner

A pH electrode is used in most cases. In order to establish a comparability with previous results obtained manually by colour indicators, it is possible to titrate to a fixed pH value, which corresponds to a colour change. For such an endpoint titration (EP = endpoint) to a fixed pH value, a calibration of the electrode is required.

Other titrations are carried out to an equivalence point (EQ = Equivalence Point). Here, it depends only on the change of the potential or the pH value. The calibration of a pH electrode serves only for quality monitoring in this case.

The measured value of the titration is the volume. The correctness of the volume must be verifiable for each consumption. Consumption at the EQ, EP or colour change thus indicates the equivalence of sample substance and added reagent.

1.2 Titration reactions

Acid-base titration

In acid-base or neutralization titration, acids are titrated with a base (or vice versa). The detection of the equivalence point can take place by colour indicators or potentiometrically with a glass electrode. The reaction is the same for all acid/base titrations, water results from a proton and a hydroxide ion



If several acids with different $\text{p}K_s$ values are contained in a solution, they show several equivalence points in a potentiometric titration and can be determined next to each other if the alkalinity values are distinguished by at least 2 - 3 powers of ten.



with

$$K_s = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{X}^-)}{c(\text{HX})}$$

Titration guide

Precipitation titration

The precipitation titration is based on the formation of hardly soluble salts of sample and reagent. The solubility of salts can be described by the solubility product K_L . For the dissociation of a salt M_mX_x in saturated solution, the following applies:



with

$$K_L = c(M^{x+})^m * c(X^{m-})^x$$

If several ions are contained in a solution, which form products which are hardly soluble with different solubility product with the reagent, they show several equivalence points in a potentiometric titration and can be determined next to each other if the K_L values differ by at least 2 - 3 powers of ten.

A classic application of the precipitation titration is the determination of the halogenides (Cl^- , Br^- und I^-) by means of $AgNO_3$ solution or the determination of the silver content with a $NaCl$ solution.

Complexometric titration

In the complexometric titration, metal ions are titrated with a strong complexing agent. The equivalence point is detected by a colour indicator (also a complexing agent) or by ion-sensitive electrodes. For the formation of the complex from a divalent metal ion and probably the most commonly used 6-tooth complexing agent ethylene diamine tetra acetic acid (EDTA) the following applies:



with

$$K = \frac{c([MEDTA]^{2-})}{c(M^{2+}) + c(EDTA^{4-})}$$

Divalent metal ions are determined often during complexometric titration. The stability of these complexes depends on the pH value (a buffer must therefore be added to the sample if necessary). An important application for complexometric titration is e.g. the determination of water hardness in drinking water.

Redox titration

In a redox titration, oxidizing components are titrated with a reducing agent, or vice versa. The oxidation states of the reactants and thus the redox potential of the sample change. The detection of the EQ can be carried out by colour change (of colour indicators or the sample solution), potentiometrically with a redox electrode (usually a Pt electrode) or biamperometrically with a double platinum electrode.



An important application for redox titration is e.g. the determination of vitamin C in fruit juices or the Karl Fischer titration.

Charge transfer titration

In charge transfer titration, negative charges are titrated with positive charges (or vice versa) to a charge transfer neutral point. An important application for this is the characterization of pulp suspensions by polyelectrolyte titration in paper manufacture.

Chemical / visual

A classification of the titrations is also often carried out according to the type of detection of the titration end. The oldest type of equivalence point determination is the chemical/ visual type. Hereby, the detection of the end or equivalence point is takes place by a colour change of the sample solution (or of the precipitate with precipitation titrations). This usually requires the addition of a colour indicator, but there are also reactions where the sample or titrant changes colour at the EQ. This type of EQ determination is mostly used in manual titrations.

Titration guide

Potentiometric

With the potentiometric titration, the determination of the end or equivalence point takes place by the chemical potential that is established at a suitable electrode.

This potential depends on the concentration of ions to which the electrode responds. If the electrode is "inert", that is, not sensitive to ions contained in the solution, the redox potential of the solution can be determined. The electrode potentials follow the Nernst equation:

$$U = U_N \cdot \lg a_1/a_2$$

The potential which adjusts itself at an individual electrode cannot be measured directly. All that can be measured is a voltage U as the difference between two electrode potentials in a closed circuit. In the example (Fig. 1), two electrodes made of the same metal are immersed in solutions of one of their salts.

The dependence of this voltage on the concentrations c_1 and c_2 or the ion activities a_1 and a_2 in the individual half-cells can be formulated according to the Nernst equation:

$$a = f_c \cdot c$$

- a = activity
- f_c = activity coefficient
(dependent on concentration)
- c = concentration

By measuring the electrode potential, it is therefore not possible to determine a concentration directly with the Nernst equation, but only the ion activity. At very high dilution, the activity coefficient is about 1 and therefore the activity is approximately equal to the concentration. Fig. 2 shows the course of a typical titration curve.

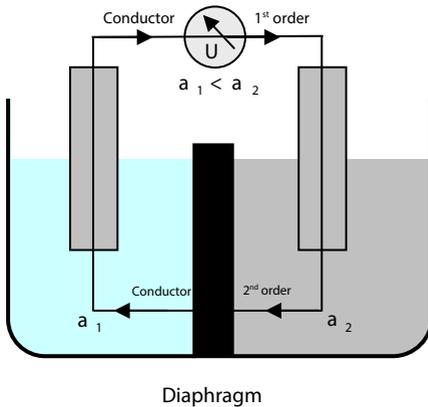


Fig. 1 Circuit in an electrochemical measurement cell [5]

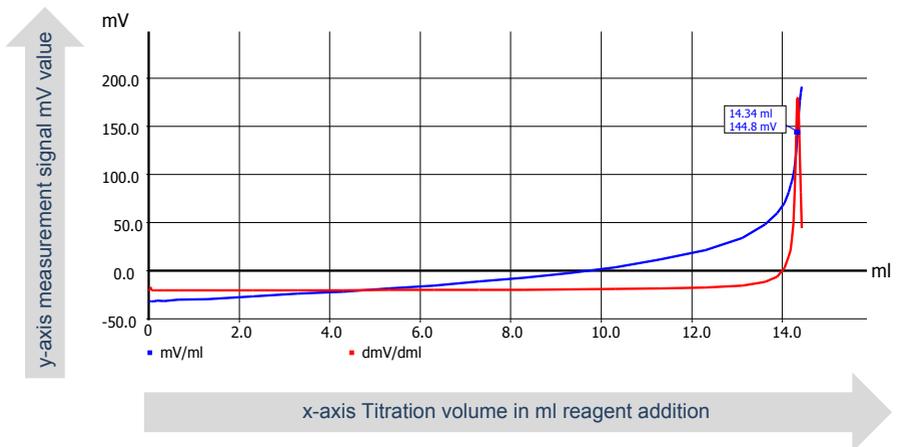


Fig. 2 mV titration curve of a chloride titration

Titration guide

Biamperometric

Biamperometric or Dead Stop titrations can be carried out if reversible redox systems are formed or consumed in the course of the reaction. In this type of detection, a double platinum electrode is used which is polarized at a low voltage. If a reversible redox couple is present, a current flows between the electrodes. As long as no reversible redox couple is present, no current flows between the two electrodes.

Important examples for this are the Karl Fischer titration and iodometric titrations. The reversible redox system, which is used to detect the endpoint, is hereby:



Iodide is oxidized to iodine at the anode, while iodine is simultaneously reduced to iodide at the cathode.

Fig. 3 shows a typical titration curve of an iodometric Dead Stop titrations:

As long as reducing agents are still present in the sample, added iodine is consumed immediately, in solution there is only iodide, no current flows. When all the reducing components have been consumed, iodine and iodide are present next to each other as a reversible redox pair, a current flows between the electrodes.

In contrast to iodometry, the current is not plotted versus the titration volume with the Karl Fischer titration, but the titration volume versus time. More information about the course of the reaction, as e.g. secondary reactions, can be obtained (see Fig. 4).

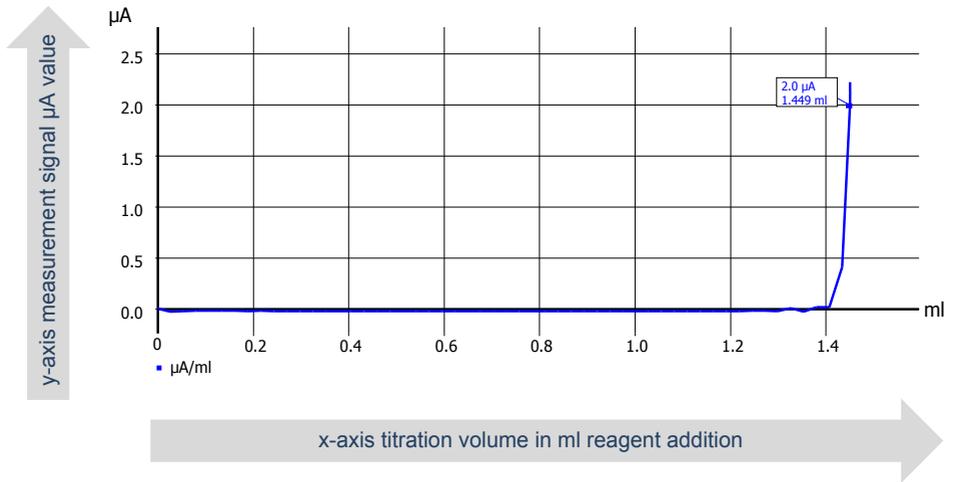


Fig. 3 Dead Stop titration curve

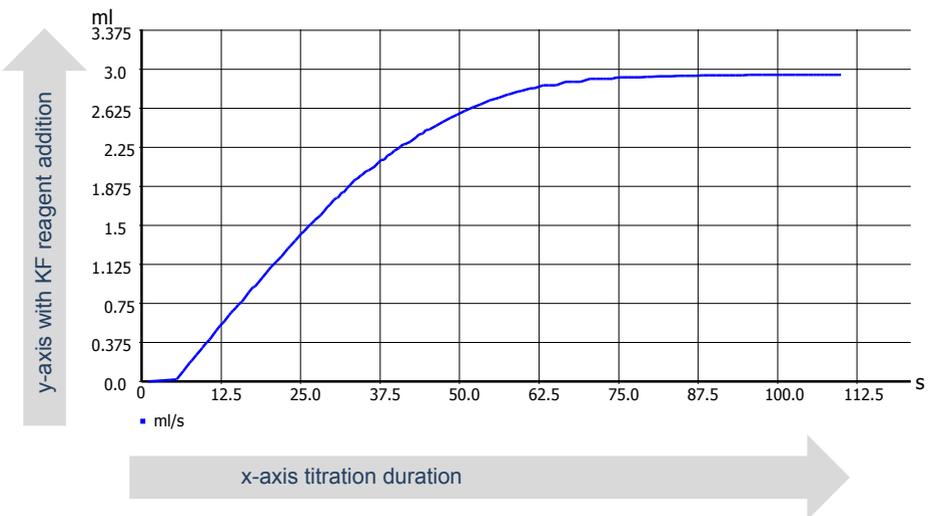


Fig. 4 Karl Fischer titration curve

Titration guide

Photometric

In a photometric titration, the colour change of an indicator is detected with an optical sensor (e.g., OptiLine 6). The basis for this is Lambert Beer's law, which describes the relationship between concentration, sample properties and absorption:

$$\lg \frac{I_0}{I_1} = \varepsilon * c * l$$

- I_0 : Intensity of the incident light beam
- I_1 : Intensity of the transmitted light beam
- ε : molar extinction coefficient (dependent on wavelength)
- c : Concentration
- l : Path of the light beam through the sample

At the EQ, the colour indicator reacts with the titrant; the colour and thus also the extinction coefficient of the titrated solution change. The intensity of the light arriving at the sensor changes.

Conductometric

In the conductometric titration, the determination of the EQ takes place via changing the conductivity of the sample solution during the titration. The conductivity K of a sample solution depends on the ion mobility u_i , the concentration c_i and the ion charge z_i :

$$\kappa = \text{Const} * \sum u_i z_i c_i$$

Thermometric

All voluntarily running chemical reactions release energy that leads to a temperature increase. This temperature of the reaction solution is exploited in the thermometric titration for the determination of the EQ. It is determined with a sensitive temperature sensor. Typically, the temperature increases up to the EQ, in order to fall thereafter by addition of further (colder) titrant solution.

1.3 Titration types

Titration can be carried out in different manners [1].

Direct titration

The best known is the direct titration, in which the sample is titrated directly with a suitable standard solution. The amount of reagent consumed to the equivalence point (or endpoint) is the amount of substance to be determined.

Direct titrations also include the inverse titration, in which the reagent solution is presented and titrated with the sample. Reasons for inverse titration may be e.g. a better recognizability of the equivalence point, the stability of the reactants, or a greater reaction speed.

Back titration

In the back titration, the sample is mixed with a defined amount of reagent A. Reagent A must be present in excess. After a reaction time, the excess is titrated with another reagent solution B. The difference between the added reagent solution A and reagent A still present after the reaction corresponds to the amount of the substance to be determined. Both reagent A and reagent B must be dosed exactly. Back titrations are e.g. used when the reaction speed between sample and reagent A is low, no suitable sensor is available, or the equivalence point can only be determined with difficulty.

Titration guide

Indirect titration

In the indirect titration, the substance to be determined, which is contained in the sample in a non-titratable form, is converted into a titratable compound by a chemical reaction. A known example of an indirect titration is the determination of nitrogen according to Kjeldahl; non-titratable nitrogen compounds are converted to readily titratable ammonium borate.

Substitution titration

In a substitution titration, a good titratable component is released from the substance to be determined by addition of suitable substances in excess, which can be titrated directly.

Phase transfer titration

In phase transfer titration, the detection of the EQ takes place in a different phase than the reaction. An application for this is e.g. the surfactant titration according to Epton.

11.4 Overview of the used methods

The past 200 years offered sufficient time for the development of new titration methods. Several thousand methods or modifications exist nowadays. Areas, in which titrations are carried out are:

- Water and environmental analysis
- Food industry
- Chemical industry
- Pharmaceutical industry
- Coating and metal processing, electroplating
- Oil industry

In *food analytics*, a number of products or contents are quantified in these products by means of titration according to § 64 LFGB (food requirement objects and feed code). The methods include the determination of acids in drinks and other foods, the determination of the salt content, content of proteins and nitrogen functions, bases, oxidation components or oxidation protection and much more.

An important area is the determination of humidity or water content in food. The Karl Fischer titration is the method of choice here, as it is also comparatively selective in addition to a high accuracy. The water content influences numerous properties, such as durability, processability, taste and much more.

In the *environmental field*, water analysis is of particular importance. Titrations for waste water, surface water and seawater are added to the methods of drinking water analysis [1], [10].

In the *chemical industry*, various methods are used, which mainly serve to determine key Figures for production raw materials or finished products. Wastewater must also be examined. Numerous methods are recorded in standards. The ISO standards and also the ASTM regulations are used worldwide.

Pharmacy uses strictly regulated, consistent methods that are defined in pharmacopoeias. These are often content determinations of the pharmaceutically active substances. The humidity content is also determined by Karl Fischer titration.

The samples in electroplating are very challenging. They often contain high concentrations of strong acids and various metals. Titration is the most important method here and is often used directly in the production area.

Oil can also be titrated. This works in suitable solvents. Often, acids are determined in the oil to give a measure of the aging of the oil by oxidation and realization with air. Base numbers and water content are also typically titrated.

Some of the most important methods are presented in the following.

Titration guide

Acid-base titrations are used widely. These are endpoint titrations to a fixed pH value. The endpoints are therefore often pH 7.0, pH 8.1 or pH 8.2. This depends on the type of acids and the comparative values determined in the past with colour indicators. A glass electrode is used for the pH measurement, which must be calibrated. For this, the buffers 4.01 pH and 6.87 pH are recommended. Due to possible problems with alkaline buffers (CO_2 absorption, low durability), a correct two-point calibration without alkaline buffers is often more accurate than the more elaborate three-point calibration.

Further information on calibrating the pH electrodes can be found in our pH guide.

A special method is the determination of alkalinity in seawater. A multiple of the CO_2 of the atmosphere is dissolved in seawater. The pH value of the sea drops, the temperature rises and thus less CO_2 can be dissolved in the seawater.

The accurate CO_2 content is determined by means of Gran titration, a method that can be easily automated with a sample changer.

With the frequent determination of chloride or "salt", a calibration of the electrode is not necessary. The titrant is silver nitrate and a silver or silver chloride electrode is used. However, the potentials may vary depending on the state of the electrode, concentration and sample matrix. This is why titration is performed here until an EQ is detected. It does not depend on the potential itself then, but on the potential change.

Another common titration type is iodometry. Here, a sample is usually mixed with an excess of iodine. The iodine oxidizes a part of a sample. The iodine which is not converted is then titrated with thiosulphate. This is a back titration, as both the reagent iodine (or a mixture of iodate with iodide) must be precisely dosed or weighed, as well as the back titration must be done with a well-defined concentration.

For drinking and mineral water, water hardness is an important parameter. Calcium and magnesium are relevant with respect to health and are titrated with EDTA (**E**thylene-**D**iamine-**T**etra-**A**cetic-acid). For the detection, either a calcium ion-sensitive electrode (ISE) is used for the determination of both parameters or a copper electrode for the determination of the total hardness. Instead of the usual combination electrodes, separate measuring chains (ISE indicator electrode with separate reference electrode) are often used, which are somewhat more robust. The calcium electrode can directly detect the signal of Ca and Mg, while the copper electrode is required for the indication of copper EDTA to detect the total hardness.

In electroplating, many metals in the sample are also determined complexometrically. One often titrates with EDTA as titrant and the Cu-ISE as electrode. The detection takes place as complex displacement reaction by the addition of Cu-EDTA.

In pharmacy, many complex bases are titrated. The most important method is the titration

with perchloric acid in glacial acetic acid, in which the nitrogen functions are determined. As many bases are present as hydrochloride, an indirect determination is also possible. Free hydrochloric acid is added and the free HCl is first titrated with sodium hydroxide solution, then the HCl bound to the nitrogen. Two equivalence points result whose difference corresponds to the number of amine groups.

With a glass electrode, acid-base titration is possible even in black oil. The most important titration parameters in oils are, apart from the Karl Fischer titration for water determination, the TAN (Total Acid Number) and TBN (Total Base Number) determinations. The TAN is titrated in toluene/isopropanol with KOH in isopropanol. A glass electrode and a reference electrode with ground-joint diaphragm, often as a combination electrode is used as the electrode.

The examples should briefly show the range of the extent to which titration methods are used for quantification. A number of completed application specifications can be found on our website.

SECTION 2

VOLUME MEASUREMENT DEVICES, MANUAL AND AUTOMATIC TITRATION

2.1 Volume measurement devices and standards

The volume has a special importance in titration. It is the measured value of the titration and most samples are measured volumetrically with pipettes.

The analysis scale continues to be the basic instrument. The volume is attributed to the weight. All volume measurement devices have their nominal volume at 20°C (attention: the electrochemistry relates to 25°C). At other temperatures corrections of the volume must be applied. It should be noted, however, that the density for different solutions with different temperatures does not always behave identically.

$$\text{Volume} = \frac{\text{weight}}{\text{density}}$$
$$\text{with the units [ml]} = \frac{[\text{g}]}{[\text{ml}]}$$

As a rule, volume vessels are checked with water. The water amount corresponding to the volume is weighed and divided by the density. (Motor piston) burettes are tested according to [ISO 8655 part 6](#) (Gravimetric test with water) [2]. A factor Z is used hereby, the reciprocal of the density, corrected by the following factors:

- Temperature
- Buoyancy corrections (scales weights, weighed sample)
- Correction of the cubic expansion coefficient of the glass
- Air humidity

The correct volume is then the weight of the water multiplied by the factor Z (Fig.5).

Temperature in °C	Air pressure in kPA (Z values in ml/g)					
	80.0	85.3	90.7	96.0	101.3	106.7
15.0	1.0018	1.0018	1.0019	1.0019	1.0020	1.0020
15.5	1.0018	1.0018	1.0019	1.0020	1.0020	1.0021
16.0	1.0019	1.0020	1.0020	1.0021	1.0021	1.0022
16.5	1.0020	1.0020	1.0021	1.0022	1.0022	1.0023
17.0	1.0021	1.0021	1.0022	1.0022	1.0023	1.0023
17.5	1.0022	1.0022	1.0023	1.0023	1.0024	1.0024
18.0	1.0022	1.0023	1.0024	1.0024	1.0025	1.0025
18.5	1.0023	1.0024	1.0025	1.0025	1.0026	1.0026
19.0	1.0024	1.0025	1.0025	1.0026	1.0027	1.0027
19.5	1.0025	1.0026	1.0026	1.0027	1.0028	1.0028
20.0	1.0026	1.0027	1.0027	1.0028	1.0029	1.0029
20.5	1.0027	1.0028	1.0028	1.0029	1.0030	1.0030
21.0	1.0028	1.0029	1.0030	1.0030	1.0031	1.0031
21.5	1.0030	1.0030	1.0031	1.0031	1.0032	1.0032
22.0	1.0031	1.0031	1.0032	1.0032	1.0033	1.0033
22.5	1.0032	1.0032	1.0033	1.0033	1.0034	1.0035
23.0	1.0033	1.0033	1.0034	1.0035	1.0035	1.0036
23.5	1.0034	1.0035	1.0035	1.0036	1.0036	1.0037
24.0	1.0035	1.0036	1.0036	1.0037	1.0038	1.0038
24.5	1.0037	1.0037	1.0038	1.0038	1.0039	1.0039
25.0	1.0038	1.0038	1.0039	1.0039	1.0040	1.0041
25.5	1.0039	1.0040	1.0040	1.0041	1.0041	1.0042
26.0	1.0040	1.0041	1.0042	1.0042	1.0043	1.0043
26.5	1.0042	1.0042	1.0043	1.0043	1.0044	1.0045
27.0	1.0043	1.0044	1.0044	1.0045	1.0045	1.0046
27.5	1.0046	1.0046	1.0047	1.0048	1.0048	1.0049
28.0	1.0046	1.0046	1.0047	1.0048	1.0048	1.0049
28.5	1.0047	1.0048	1.0048	1.0049	1.0050	1.0050
29.0	1.0049	1.0049	1.0050	1.0050	1.0051	1.0052
29.5	1.0050	1.0051	1.0051	1.0052	1.0052	1.0053
30.0	1.0052	1.0052	1.0053	1.0053	1.0054	1.0055

Fig. 5 Factor Z in dependence on temperature and air pressure

Titration guide

In the “Guideline for the volume determination in reference measurement procedures in medical reference laboratories” of the DAkkS (German accreditation body), the standards of the individual volume measurement vessels are listed [3]:

- Volumetric flasks
(DIN EN ISO 1042, DIN 12664-1, DIN 12664-2)
- Volumetric pipettes
(DIN 12687, DIN 12688, DIN 12691, DIN 12690)
- Graduated pipettes
(DIN 12689, DIN 12695, DIN 12696, DIN 12 697, DIN 12 699)
- Piston-stroke pipettes
(DIN EN ISO 8655-2, DIN EN ISO 8655-6)
- Piston burettes
(DIN EN ISO 8655-3, DIN EN ISO 8655-6)
- Diluters
(DIN EN ISO 8655-4, DIN EN ISO 8655-6)
- Dispensers
(DIN EN ISO 8655-5, DIN EN ISO 8655-6)

2.2 Volume measurement devices in the laboratory

Pipettes and graduated pipettes

Pipettes serve for measuring samples. One distinguishes between graduated pipettes and volumetric pipettes (Fig. 6). Preferably, volumetric pipettes with a volume greater than 5 ml are used due to the higher accuracy and easier handling. For smaller volumes, piston-stroke pipettes are preferably used. The size of the opening and the discharge time are optimized on water with its surface tension. If an organic solvent is used, this usually has a lower surface tension. However, this also effects a faster discharge in addition to smaller drops. If one drop is smaller than the opening and the surface tension is small, the solution will easily run out of the pipette without opening the Peleus ball.

Pipettes are filled up to the mark (using a pipetting aid such as the Peleus ball) and are read off at the lower meniscus (Fig. 7).

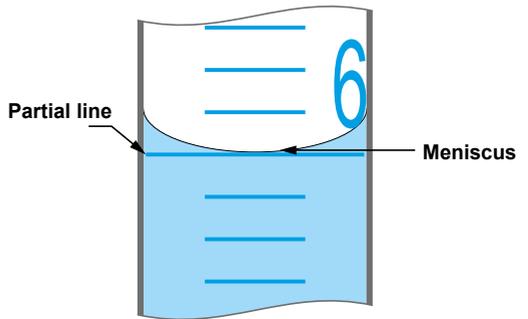
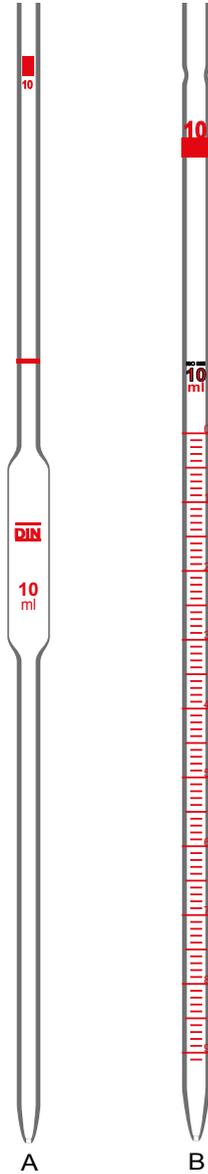


Fig. 6 Volumetric (A) and graduated pipette (B)

Fig. 7 Meniscus

Titration guide

All pipettes must always be held vertically. The liquid is discharged on an obliquely held beaker on the side wall. The follow-up time must be observed. Fig. 8 gives an overview of the accuracy of the measurement and volumetric pipettes.

Accordingly, graduated pipettes are used to measure liquids that are used as auxiliary reagents and that often require different volumes. For accurate volumetric measurements, that directly enter into a calculation, only volumetric pipettes are suitable.

Graduated pipette

Content ml	Error limit \pm ml	Division ml	Color coding DIN 12 621	Elapsed time s
1	0.006	0.01	yellow	2-8
2	0.01	0.02	black	2-8
5	0.03	0.05	red	5-11
10	0.05	0.1	orange	5-11
25	0.1	0.1	white	9-15

Content ml	Error limit \pm ml	Color coding DIN 12 621	Elapsed time s
1	0.007	blue	7-11
2	0.01	orange	7-11
5	0.015	white	9-13
10	0.02	red	11-15
20	0.03	yellow	12-16
25	0.03	blue	15-20
50	0.05	red	20-25
100	0.08	yellow	25-30

Fig. 8 Accuracy of a volumetric and of a graduated pipette

Piston-stroke pipettes

Piston-stroke pipettes up to 10 ml sample volume, preferably from 1 to 5 ml, are particularly safe and easy in its handling.

Piston-stroke pipettes (Fig. 9) can be equipped with a fixed or variable volume. Handling is usually easier than with volumetric pipettes. The pipettes must be checked regularly according to **ISO 8655 part 6** (such as also the motor piston burettes).

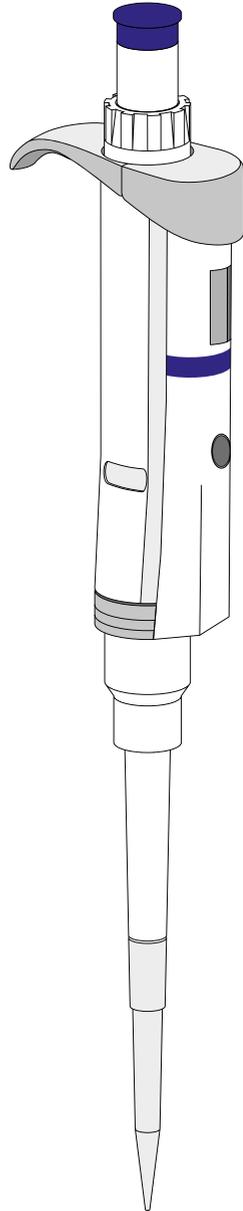


Fig. 9 Piston-stroke pipette

Titration guide

Volumetric flasks

Volumetric flasks are used to prepare solutions. A certain amount is weighed and transferred quantitatively into the volumetric flask. In the titration, the following work steps are often carried out with a volumetric flask:

- Preparation of comparison solutions and reagent additions. A defined amount of a substance is weighed into a weighing boat and transferred quantitatively (e.g. with distilled water) to the volumetric flask by means of a funnel or rinsed.

- Many solid samples are dissolved and transferred into the volumetric flask via a funnel. The unit of such samples is then weight/volume, e.g. mg/l or g/l.

It is filled up to the ring mark. As with the pipettes, the fill level is reached when the meniscus rests on the ring mark.

Measurement cylinders

Measuring cylinders are used to be able to add a defined amount of reagent quickly and accurately. They are not suitable for measuring a sample. In water analysis, 100 ml sample volumes are often used. But also for this, the volumetric pipette and not the measuring cylinder is recommended. As with the pipettes, the fill level is reached when the meniscus rests on the ring mark.

Burettes

Manual burettes (Fig.10) are still used for manual titration. In contrast to motor piston and bottle-top burettes, they have no digital display. Reading errors can easily lead to false results (Fig.11). The reagents must be protected more against disturbing influences, as e.g. CO_2 , which can falsify the content of alkaline titrants. Some titrations, such as the Karl Fischer titration are virtually impossible with glass burettes.

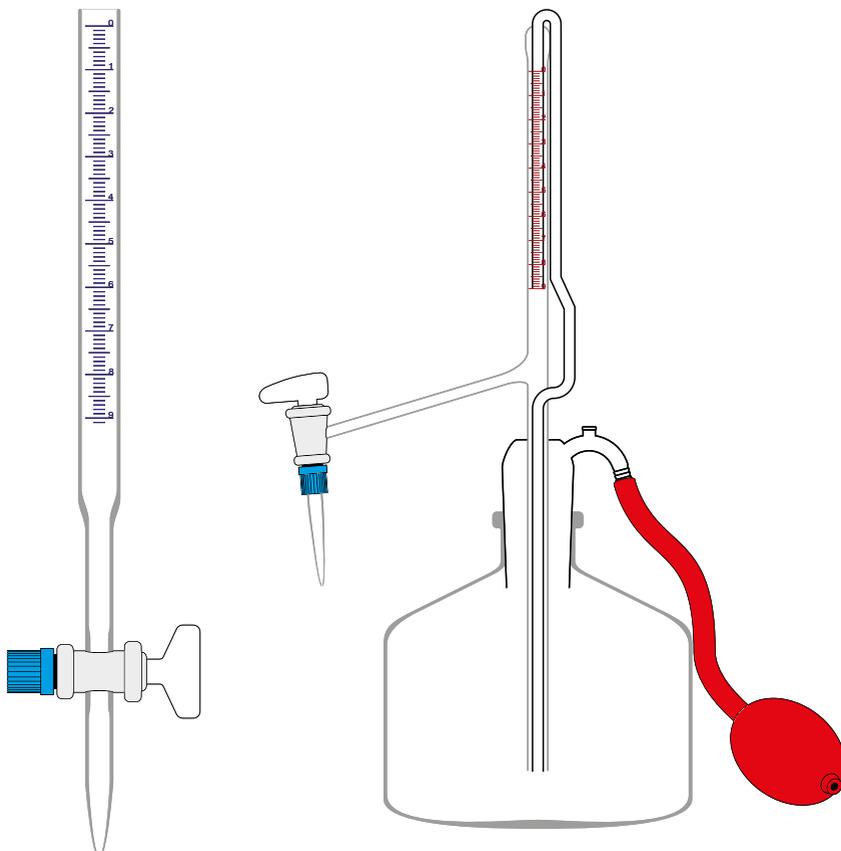


Fig. 10 Glass burette and pellet burette

Glass burette AS

Content ml	Error limit \pm ml	Division ml	Elapsed time s
10	0.02	0.02	35-45
25	0.03	0.05	35-45
50	0.05	0.1	35-45

Fig. 11 Accuracy of a glass burette AS

Titration guide

Piston burettes

Piston burettes offer the most accurate way to dose volumes from 1 to 100 ml. This can be done by means of a bottle-top burette (with or without motor) or as a motor piston burette. The accuracy depends on the cylinder volume, the length to diameter ratio, the motor and the transmission. Thus, accuracy specifications going beyond the specifications of the **ISO 8655** also exist (Fig. 12). The motor piston burette TITRONIC® 500 (Fig. 13) exceeds for example the required standard values.

Criteria for the selection of a motor piston burette could be the following:

- Accuracy
- Automatic filling
- Automation
- Interfaces
- Exchangeable units
- Handling

Table 1 - Maximum permissible errors for motor-driven piston burettes

Nominal volume ml	Maximum permissible systematic error		Maximum permissible random error	
	± %	± µl ^a	± % ^b	µl ^c
≤ 1	0.6	6.0	0.1	1.0
2	0.5	10	0.1	2.0
5	0.3	15	0.1	5.0
10	0.2	20	0.07	7.0
20	0.2	40	0.07	14
25	0.2	50	0.07	17.5
50	0.2	100	0.05	25
100	0.2	200	0.03	30

^a Expressed as the deviation of the mean of a tenfold measurement from the nominal volume or from the selected volume, (see ISO 8655-6:202, 8.4).

^b Expressed as the coefficient of variation of a measurement (see ISO 8655-6:202, 8.5).

^c Expressed as the repeatability standard deviation of a tenfold measurement (see ISO 8655-6:202, 8.5).

Fig. 12 Accuracy of motor piston burettes **ISO 8655 part 3** [2]



Fig. 13 Motor piston burette TITRONIC® 500 with exchangeable unit

Titration guide

2.3 Verification of the correct volume

The verification of the volume correctness usually takes place according to [ISO 8655 part 6](#) and is documented in a check table (Fig. 14).

10 doses each are carried out on an analytical balance at 10%, 50% and 100% of the cylinder volume with water (with defined purity). For these 30 dosages, the weighing results are multiplied by a numerical factor Z (see Fig. 5).

The difference of the average value is compared to the displayed volume. The systematic error is calculated from the difference. The "fluctuations" are calculated as the relative standard deviation and represent the random error.

The calculation formulas are:

$$V_i = m_i \cdot Z$$

$$\bar{V} = \frac{1}{10} * \sum_{i=1}^n V_i$$

$$e_s = 100(\bar{V} - V_s) / V_0$$

$$s_r = \sqrt{\frac{\sum_{i=1}^n (V_i - \bar{V})^2}{n-1}}$$

$$cv = 100 \frac{s_r}{\bar{V}} * \frac{V_s}{V_0}$$

- V_i Dosed individual volume
- m_i Weight in [g] of this individual volume
- \bar{V} Average value of the same 10 volumes
- e_s Relative systematic error of the individual measurement
- s_r Random error as the standard deviation
- cv Relative, random error
- V_s Target volume
- V_0 Nominal volume cylinder

No.	% Cylinder (Ex)	Displayed volume [ml]	Weight [g]	Calculated volume [ml]	Difference (target vol.- actual volume) [ml]	Systematic measurement deviation [%]	Variation coefficient [%]
1	10	2.0000	1.9870	1.9940	0.0060	0.0368	0.0056
2			1.9850	1.9919	0.0081		
3			1.9950	2.0020	-0.0020		
4			1.9820	1.9889	0.0111		
5			1.9790	1.9859	0.0141		
6			1.9850	1.9919	0.0081		
7			1.9780	1.9849	0.0151		
8			1.9940	2.0010	-0.0010		
9			1.9900	1.9970	0.0030		
10			1.9820	1.9889	0.0111		

Fig. 14 Test according to *ISO 8655 Teil 6*: here, the first 10 dosages of a 20 ml unit are given

Titration guide

2.4 Cleaning and care

All piston burettes require a small but careful care effort. This shall be shown in detail using the example of motor piston burettes (Fig. 15). The care naturally also depends on the type and frequency of its use (Fig. 16).

An important element is the seal between the piston and the glass wall of the cylinder. If the sealing lips are leaking, the piston and/or the cylinder must be replaced.

At the latest when the space between the two lower sealing lips (Fig. 17) is filled with liquid, a replacement is absolutely necessary. If the dosing system is not used for more than two weeks, we recommend that the dosing attachment be emptied and cleaned. This applies in particular to the operating conditions cited under "High demand". Failure to do so may cause the piston or valve to leak and the titrator is damaged.

We recommend the following test and maintenance work	High demand	Normal demand
Simple cleaning: • External wiping of chemical splashes	Always during use, when necessary	Always during use, when necessary
Visual check: • Check for untightness in the area of the dosing system? • Is the piston tight? • Is the valve tight? • Titrating tip free?	Weekly, and when restarting	Monthly, and when restarting
Basic cleaning of the dosing system: • Clean all parts of the dosing system individually.	Every three months	When necessary
Technical check: • Check for air bubbles in the dosing system. • Visual check • Check electrical connections	Half-yearly, and when restarting	Half-yearly, and when restarting
Check of the volume according to ISO 8655: • Carry out basic cleaning • Check according to ISO 8655 part 6 or part 7	Half-yearly	Yearly

Fig. 15 Maintenance and check plant at piston burettes

<p>High demand: Use of concentrated dissolutions, reagents and chemicals (> 0.5 mol/l); chemicals which attack glass such as fluorides, phosphates, alkaline solutions, solutions which tend to crystallize; FE(III) chloride solutions; oxidizing and corroding solutions such as iodine, potassium permanganate; Cerium(IV), Karl Fischer titrants, HCl; solutions with a viscosity > 5 mm²/s; use often, daily.</p> <p>Normal demand: Use of for example solutions which do not attack glass, do not crystallize or do not corrode, reagents and chemicals (< 0.5 mol/l).</p>
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Fig. 16 Usage of burettes

Titration guide

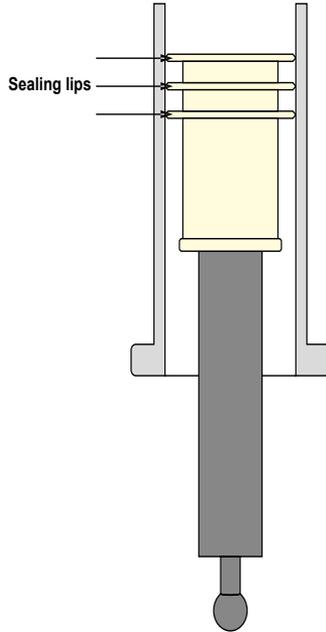


Fig. 17 There may not be any liquid between the sealing lips

2.5 Manual titration

The manual titration can be carried out with simple glass burettes or with piston burettes. It still has its legitimacy when it comes to carrying out very few individual content determinations with minimal effort.

Manual titration (Fig.18) is still included in many older standards as prescribed methods. However, the automated methods have prevailed today. They can be implemented analogously to the "old" methods, optimize and accelerate the processes.

In manual titration, an indicator is usually used that changes its colour at the EQ.

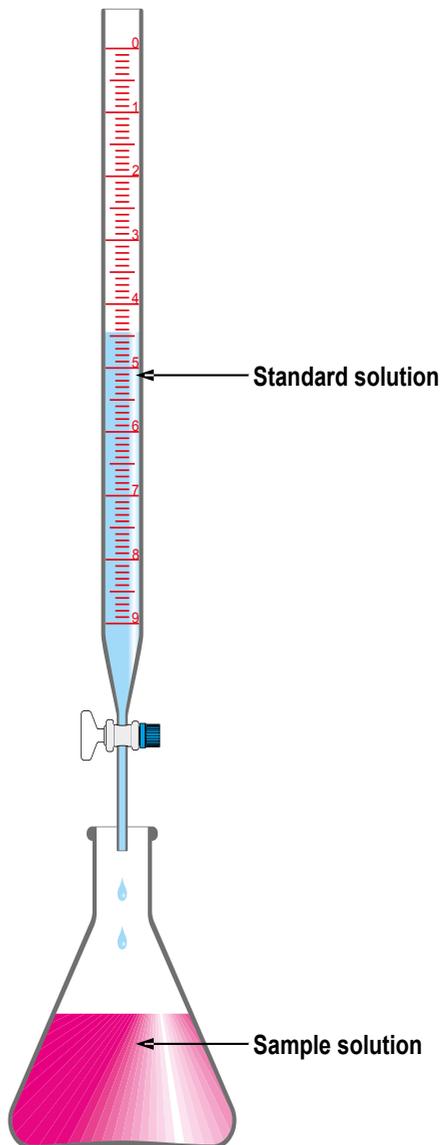


Fig. 18 Manual titration with the sample solution in an Erlenmeyer flask and the reagent in a glass burette

Titration guide

Indicators exist for nearly all titrations. Acid-base, redox and metal indicators are the most common (Fig. 19, general overview in [16]). In the acid titration with sodium hydroxide, phenolphthalein is often used, which turns from colourless to pink at the endpoint (Fig. 20). In some titrations, the colour also changes by the titrant itself, so that no indicator has to be added, e.g. with potassium permanganate.

Colour indicators have some considerable disadvantages:

- They are not suitable for heavily coloured samples
- The colour changes are perceived subjectively
- The colour changes are often only temporary or sluggish
- The indicators change colour in a larger transition area and participate in the reaction.

Indicator	Indicator range	Colour changeover	Manufacture
Bromophenol blue	3.0 – 4.6	yellow-violet	0.1 g, ethanol (20%)
Kongo red	3.0 – 5.2	blue-red	0.1 g, water
Bromocresol green	3.1 – 4.4	red-yellow orange	0.04 g, water
Bromocresol green	3.8 – 5.4	yellow-blue	0.1 g, ethanol (20%)
2.5 dinitrophenol	4.0 – 5.8	colorless yellow	0.05 – 1 g, ethanol (20%)
Alizarin S	4.3 – 6.3	yellow-violet	0.1 g, water
Methyl red	4.4 – 6.2	red-yellow	0.1 g, ethanol
Litmus	5.0 – 8.0	red-blue	0.2 g, ethanol
Bromocresol purple	5.2 – 6.8	yellow-purple	0.1 g, ethanol (20%)
Bromophenol red	5.2 – 6.8	yellow-purple	0.1 g, ethanol (20%)
Bromothymol blue	6.0 – 7.6	yellow-blue	0.1 g, ethanol (20%)
Phenol red	6.4 – 8.2	yellow-red	0.1 g, ethanol (20%)
Neutral red	6.8 – 8.0	red-yellow	0.1 g, ethanol (70%)
Phenolphthalein	8.2 – 9.8	colorless-red	0.1 g, ethanol
Thymolphthalein	9.3 – 10.5	colorless-blue	0.04 – 0.1 g, ethanol (50%)

Fig. 19 Some examples of acid base indicators with pH indicator ranges, colour changeover and manufacture [16]

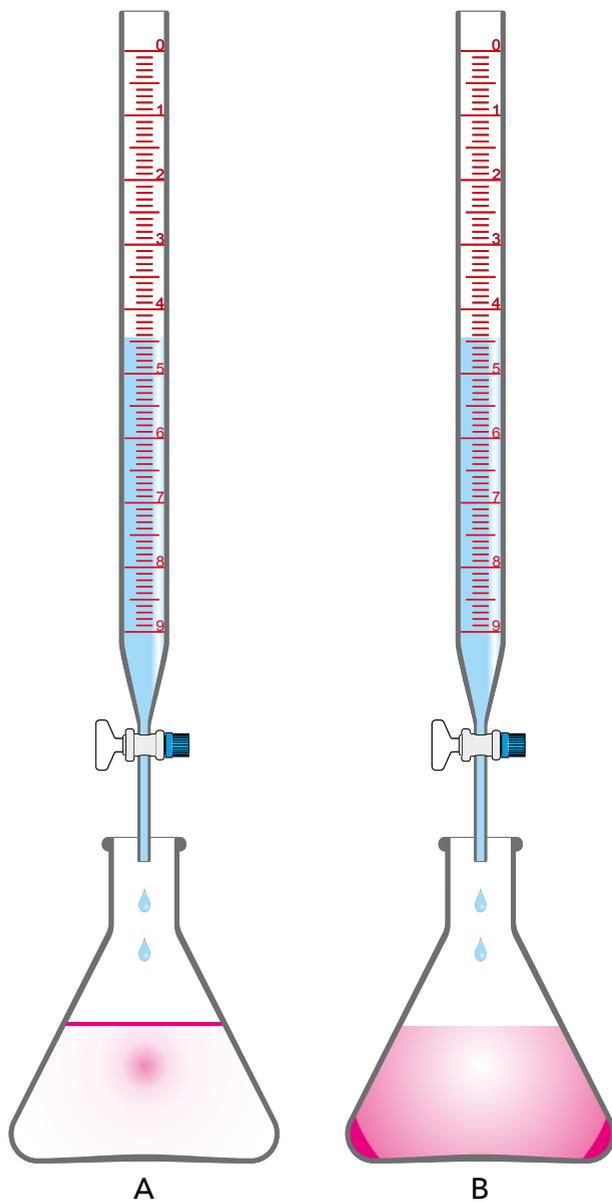


Fig. 20 Acid titration with sodium hydroxide, with phenolphthalein as indicator; close before the EQ (A), at the EQ (B)

Titration guide



Fig 21 Modern titrator TitroLine® with sample changer in use

2.6 Comparison of manual and automatic titration

Even if manual titrations are still carried out today, the many advantages speak in favor of using an automatic titrator (Fig. 21).

In Fig. 22, the two application forms are compared. Manual titration is often faster. The duration of the titration consists of the reaction duration and the setting of the sensor potential.

With manual titration, the sensor and thus its influence on the total titration time are eliminated. In slow reactions, too fast manual titration can lead to over- or under- findings. Thus, some redox reactions are so slow that they run at higher temperatures or that catalysts must be added. There is a risk here that the titration in manual determination is too fast and the chemical conversion cannot follow.

Manual titration	Automatic titration
<input checked="" type="checkbox"/> very fast	<input checked="" type="checkbox"/> fast
<input checked="" type="checkbox"/> exact	<input checked="" type="checkbox"/> very exact
<input checked="" type="checkbox"/> simple	<input checked="" type="checkbox"/> simple after implementation
<input checked="" type="checkbox"/> versatile	<input checked="" type="checkbox"/> versatile
<input checked="" type="checkbox"/> very many standards and regulations	<input checked="" type="checkbox"/> very many standards and regulations
<input checked="" type="checkbox"/> reproducibility	<input checked="" type="checkbox"/> reproducibility, documentation
<input checked="" type="checkbox"/> comparability	<input checked="" type="checkbox"/> correctness and comparability
<input checked="" type="checkbox"/> automation capacity	<input checked="" type="checkbox"/> automation capacity

Fig. 22 Comparison of manual and automatic titration

Titration guide

The automatic potentiometric titration works in a drift-controlled manner, that is, the progress of the reaction can be monitored by means of a sensor. With manual titration with indicator, one titrates until the colour changes. With the content calculation, exactly one point of the entire titration is thus used for the evaluation. There thus does not exist any possibility to get information about:

- Reaction process
- Signal/noise ratio
- Behavior directly before and after the endpoint
- Characteristics for an uncertainty consideration
- Are there several endpoints?

With the potentiometric titration, the entire titration curve is available and thus also evaluation criteria for the above points. In addition, several measurement points in the region of the equivalence point are used for an equivalence point calculation.

With the endpoint titration, one also titrates to one point. The direct potentiometric implementation of a manual titration is thus an endpoint titration to the point where the indicator changes colour. In contrast to manual titration, a complete titration curve is also available here for evaluation.

In Fig. 23, the equivalence point is at pH 7.42. The colour change starts at pH 6.80, an endpoint titration would be ended at pH 7.00. However, as the titration curve is very steep, differences in consumption, which is in effect the measurement unit of the titration, are very low. For flat titration curves, in contrast, significant differences can occur. The three different detections (optical manual, EP titration and EQ titration) must therefore be regarded as (slightly) different methods.

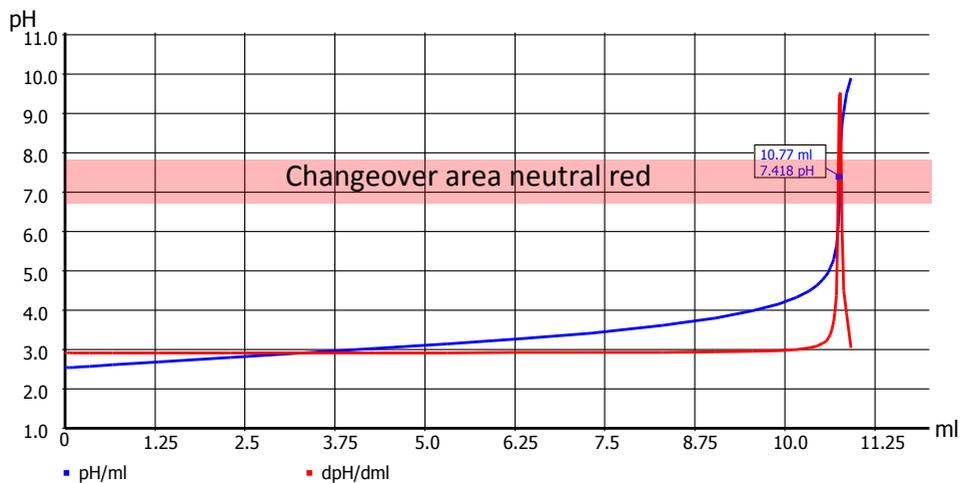


Fig. 23 Changeover area and equivalence point with a suitable indicator

SECTION 3

SAMPLE HANDLING

3.1 Basics

Sampling and homogenization are important prerequisites for achieving a "correct" result.

When transporting a sample, it cannot always be ensured that it will remain unchanged upon arrival. An example are samples that can absorb or release humidity. There are only a few packagings that are really absolutely impermeable to water vapor. Many plastic bottles are permeable to water vapor to a small extent. Temperature fluctuations and other influences of the transport should also be considered. For this reason, care must already be taken when sampling to see how it can be transported without changing.

In any case, a sample must first be brought into a homogeneous, dissolved form in order to be titrated. This happens according to the scheme in Fig. 24. For this, it is important to remove enough sample from the material, as it is not always ensured that the content of a sample is homogeneously distributed in a material. The following points should be observed:

- Is there a sediment for liquid samples?
- Is there a difference in concentration due to a temperature difference in the vessel?
- Is it natural samples, which e.g. have a shell and an inner part?
- Do the samples have a coating?
- Does the surface absorb humidity?

Another issue is the release of the parameter to be determined. For example, the chloride content in cheese is an important indicator of shelf life and taste. If there is not enough chloride in the cheese, it spoils. If there is too much salt in the cheese, it does not taste good. For the determination of the chloride content, a piece of cheese (about 0.5 to 1 g) may well be placed in a beaker and filled with water. But almost nothing happens. The cheese floats in the water and the salt stays in the cheese. Only with increased temperature and a homogenizer, the largely complete release of the salt succeeds.

A homogenizer can be used profitably in the sample preparation of many samples. It can shred many food samples faster and ensure a fine distribution. The analysis components to be determined are released from the samples of water or solvent and are well distributed at the same time.

Solid sample	<ul style="list-style-type: none">• crushing• homogenizing• dissolving
Liquid sample	<ul style="list-style-type: none">• dissolving• homogenizing
Gaseous sample	<ul style="list-style-type: none">• absorbing in a solvent

Fig. 24 Processing of samples

Titration guide

With special titrations, a strategy must be developed in advance to ensure that the quantity to be determined is also obtained in a quantitative manner. Fig. 25 illustrates the procedure. In the case of water determination, e.g. according to Karl Fischer, an attempt is made to dissolve the sample completely. If this is not possible, the water of the sample must be evaporated in an oven or only the adhering water is determined. An attempt is made to change the duration of the dissolution process and the polarity of the solvent, or to increase the temperature. In order to change the polarity, one works with different solvents or mixtures.

3.2 Direct volume

In most cases of general titration, a specific volume of the sample is pipetted directly into the titration vessel. For volumes up to 5 ml, the piston-stroke pipette has proven itself. For volumes above 5 ml to 100 ml, the volumetric pipette is the instrument of choice. Usually, 50 to 150 ml beakers are used as the titration vessel. The samples are then filled with solvent, usually water, until the titration tip and the electrode are immersed in the solution. At the electrode, the diaphragm must be covered with solvent.

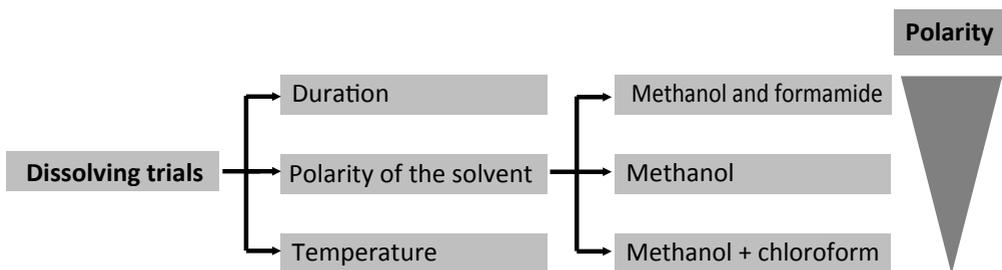


Fig. 25 Sample preparation for KF titration

3.3 Direct weighed sample

Soluble samples are weighed directly into the titration vessel. The direct weighed sample should be over 100 mg. Otherwise, the method as described in section 3.4 is recommended. The solid samples are also filled with solvent as described with the solutions.

3.4 Aliquoting

It is not always possible to use a sample as a solid or liquid sample directly for a titration. Thus, a high content in a sample may require titration with a high concentration of titrant or effect high consumption. This can lead to high costs (e.g. with silver nitrate), to long titration times or to unfavorable handling (e.g. due to large volumes). The size of the sample vessels are often predetermined by the degree of automation and thus also the sample amounts are limited. In addition, the high accuracy of the motor piston burettes no longer requires high consumption in order to obtain a safe result. Samples with a high content are therefore often filled

in a volumetric flask to a certain volume in order to use a specific aliquot for the titration.

Example:

5 ml of a highly concentrated sample are filled up to 100 ml in a volumetric flask. Of these, 20 ml are taken with a volumetric pipette for the determination.

The calculation formula for a result in [mol/l] without dilution step is:

$$\text{Result [mol/l]} = \frac{\text{consumption [ml]} \times \text{concentration of the titrant [mol/l]}}{\text{sample volume [ml]}}$$

As the 5 ml sample is diluted to 100 ml, each ml of this dilution contains 0.05 ml of original sample, thus 1.00 ml original sample for 20 ml dilution:

$$\text{Result [mol/l]} = \frac{\text{consumption [ml]} \times \text{concentration of the titrant [mol/l]}}{(\text{volume aliquot [ml]} \times 5/100)}$$

Titration guide

3.5 Weigh out small solid amounts

Solid samples are often weighed directly into a beaker, dissolved or homogenized and titrated. The 4-digit analytical balance is the right instrument for this. Nevertheless, handling weighed samples less than 100 mg is difficult and often involves large errors. This may be due to the scale or the handling of the sample, but also to the installation conditions of the balance in its place.

With many solid samples, the accuracy can be increased by one order of magnitude when operating with the procedure shown in (Fig. 26).

A larger amount of the sample (e.g., 5.8443 g NaCl) is weighed in, plus water in a larger amount (e.g. 95.000 g). A portion of this solution is removed and weighed again (e.g. 1.0000 g). The NaCl part can be calculated according to the following formula:

$$\text{sample part [g]} = \frac{T * E}{E + W}$$

Example sodium chloride (salt)

Symb.	Description	Example values	Unit
(E)	Weighted sample of the salt	5.8443	[g]
(W)	Water is weighed in	95.000	[g]
(G)	(G = E + W) total weight	100.844(3)	[g]
(T)	(T) weigh the partial amount to the titration	1.0000	[g]
PA	The partial amount contains sodium chloride sample part = T * E / (E + W)	= 5.8443 * 1.0000 / 100.8443 = 0.057953	[g]

Fig. 26 Calculation of a partial amount (PA) with gravimetric manufacture of the solution

In practice, the following procedure has been proven to be successful:

The solution is drawn into a syringe, placed on an analytical balance and is tared (Fig.27). An arbitrary partial amount is added to the titration vessel from the syringe and the syringe is weighed back.

The direct weighed sample of NaCl with 0.0580 g would already have an uncertainty of ± 0.0002 g through the balance. Handling errors and other influences are not yet included.

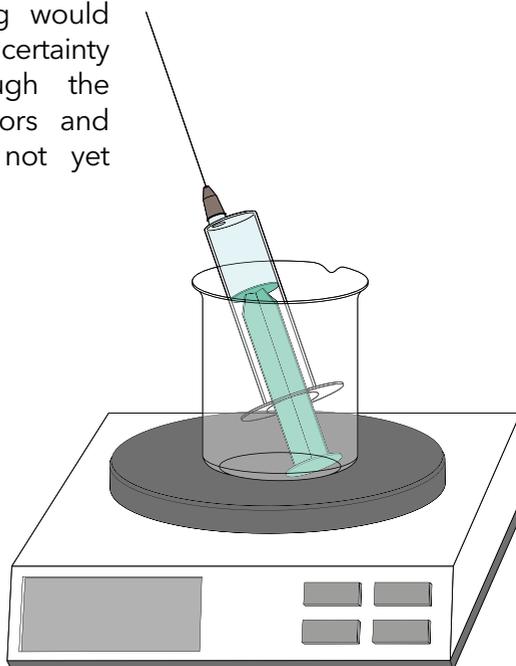


Fig. 27 Syringe with sample on analytical balance

Titration guide

SECTION 4

SENSORS AND REAGENTS

4.1 Overview of the sensors

The following electrodes are part of the standard equipment of a titration laboratory:

- pH combination electrode with platinum diaphragm (for all aqueous acid-base titrations)



- Silver combination electrode (for the determination of e.g. chloride...)



- Platinum combination electrode (for all redox reactions)



- Platinum double electrode
(for reversible redox reactions with dead stop detection)



- pH combination electrode with ground-joint diaphragm (with organic electrolyte solutions for titration in organic solutions)



- Ion-sensitive electrodes (ISE), such as Ca electrode, Cu electrode, fluoride electrode as combination electrode or with a separate reference electrode (depending on the task and type of the samples)



Titration guide

Individual electrode potentials cannot be measured directly, but only the difference between two electrode potentials. Therefore, a combination of indicator and reference electrode must always be used. The potential of the reference electrode must not change during the titration. Either a combined measuring chain or separate indicator and reference electrodes can be used (see Fig. 28).

Details regarding the measuring chains are represented in detail in our pH guide [\[5\]](#).

Combination electrodes, i.e. combined electrodes containing the indicator and reference electrodes, are usually used nowadays. In special cases, an indicator electrode is used together with a separate reference electrode. Separate measuring chains are often used with ISE electrodes, as their durability - depending on the application - of indicator and reference electrodes is different.

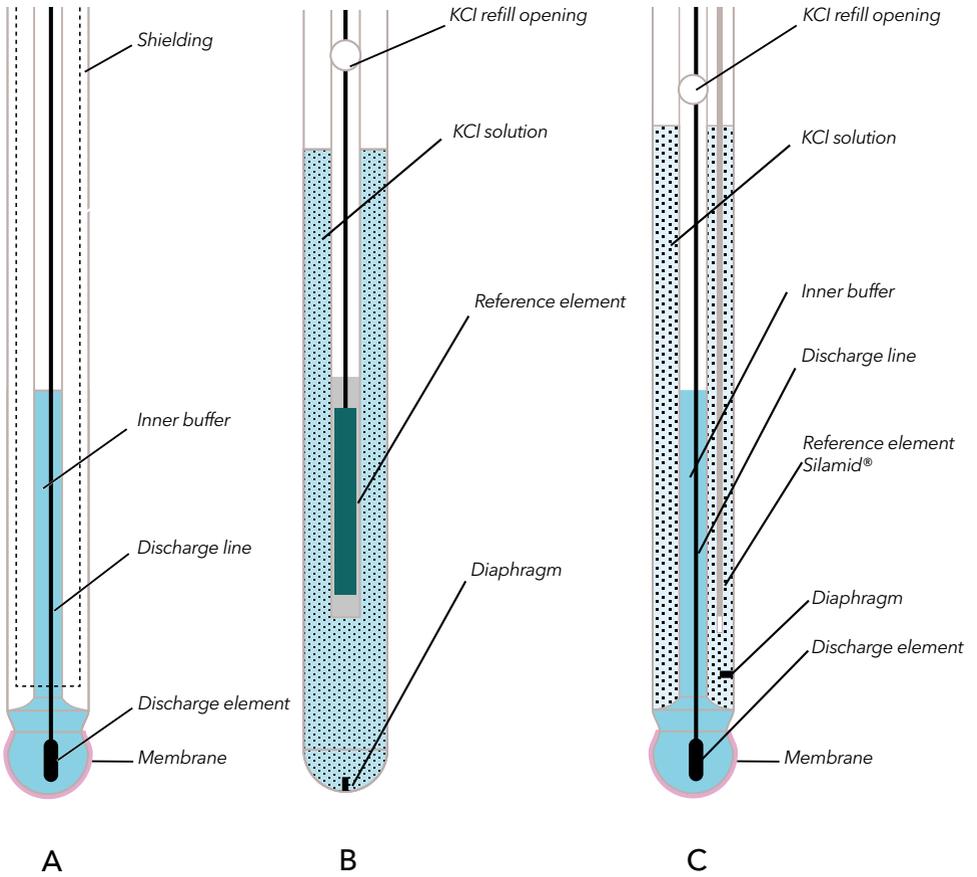


Fig. 28 pH indicator electrode (A) reference electrode (B) and combined measuring chain (C) [5]

Titration guide

The conductive connection of the reference electrode is made via the diaphragm. In the case of electrodes with liquid electrolyte, a small amount of the reference electrolyte must always flow out here. The used diaphragms are shown in Fig. 29.

For titrations, electrodes with platinum diaphragms are mainly used. For applications in organic solvents, electrodes with a ground-joint diaphragm are recommended, as they are less prone to clogging due to the higher discharge.

When using a glass electrode as a reference electrode, it must be noted that the glass electrode must be connected to the high-impedance measuring input due to its high resistance, and not to the measuring input for the reference electrode. The titration curves change their direction.

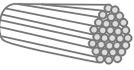
	Type	Resistance	Discharge	Application / Properties
	Ceramic	1 k Ω	0,2 ml/d	+ general application. robust, - juniversally, short response time, constant insensible against dirt and chemical reactions, tend to pollution/blockage
	Platinum	0,5 k Ω	1 ml/d	+ universal, fast setting, constant contamination-resistant, clean defined discharge channels, less diffusion tension - only clean chemically, not mechanically
	Ground joint	0,2 k Ω	3 ml/d	+ Emulsion, pastes, purest water, easy cleaning, - discharge deviations due to different placement of the ground joint; loosening of the ground joint difficult with internal overpressure, filigree
	Annular gap	0,1 k Ω	solid electrolyte	+ Annular gap symmetrical, easy handling, resistant to contamination - sample can reach the reference system, cleaning of the reference system not possible
	Fibre	1 k Ω	solid electrolyte	+ fast setting, easy handling, - sample can reach the reference system, cleaning of the reference system not possible

Fig. 29 Diaphragm types [5]

4.2 Electrolyte solutions

The reference electrodes can provide their ions in different ways:

- Solid electrolyte
- Thickened liquid electrolyte
- Liquid electrolyte with different concentration

KCl 3 mol/l is often used as electrolyte. KNO_3 2 mol/l with KCl 0.001 mol/l is inserted into silver combination electrodes, since as little chloride as possible should escape. In some surfactant titrations sodium chloride is recommended, in organic solvents LiCl in ethanol or glacial acetic acid is used depending on the solvent.

4.3 Calibration of electrodes

Only pH electrodes in aqueous solutions are calibrated. According to DIN 19268, the buffers contribute the highest uncertainty factor to the calibration. The most stable buffers are e.g. the buffers 4.00 pH, 4.01 pH, 6.87 pH, 7.00 pH. Alkaline buffers can absorb CO_2 , have a greater temperature dependence and, depending on the composition, are more affected by fungal growth and bacterial attack. As the electrodes behave in a very linear manner, there is no need to calibrate with more than 2 buffers, even if measured outside the range of pH 4 to 7. Calibration is only mandatory if an endpoint titration is carried out to a fixed pH. In a titration with EQ evaluation, it only depends on the change in the measured value, and not on the value itself. The maximum of the first derivation is consulted for the EQ calculation. The calibration values are however a quality criterion for the electrode.

Titration guide

The slope and the zero point are calculated. Their limits depend on their own requirements of the measurement uncertainty. The following limits are widely used, within which an electrode is still considered to be trustworthy:

- Slope > 95 % to 102 %
- Zero point pH 6.5 to pH 7.2

The slope of the electrode and the response time are often linked. A slow electrode also has a low slope. The response behavior is important for the titration. We recommend an exchange with a slope below 95%. Too slow electrodes can lead to errors: If the titration is carried out with an electrode which is too slow, a value that is too high is often found.

All other electrodes are checked by the titration of a standard and evaluation of the titration curve.

The criteria are:

- (1) Is the content found again?
- (2) Is the EQ in the expected potential range (Fig. 30 ①)?
- (3) Does the titration take longer than normal?
- (4) Are the start and stop potentials in the expected range (Fig. 30 ②and③)?
- (5) Does the first derivation have the usual height or the usual value at the maximum?
- (6) Is the titration free from noise?

If one or even more of the criteria is not met, the electrode should be exchanged after a thorough error analysis.

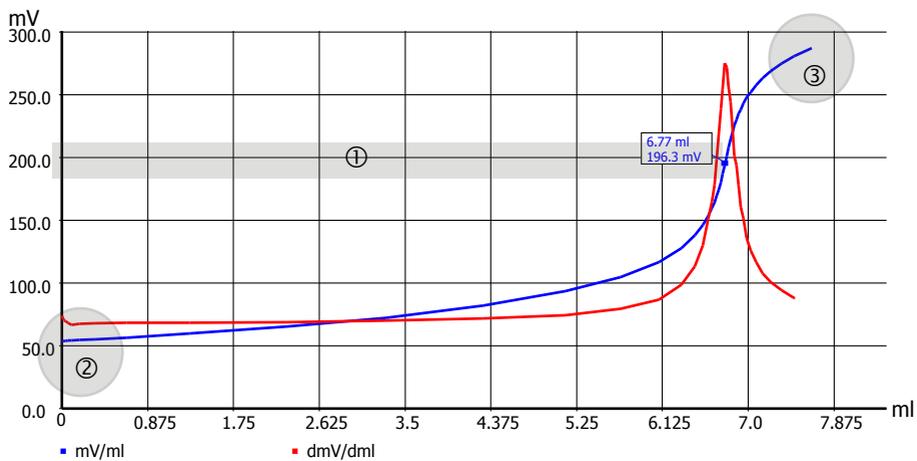


Fig. 30 Criteria for evaluating the electrode quality

Titration guide

4.4 Reagents

The most commonly used reagents are (sorted by the frequency of their applications):

- NaOH, sodium hydroxide (for the determination of acids in aqueous systems)
- HCl, hydrochloric acid (for the determination of bases, carbonates and bicarbonates in aqueous systems)
- Na₂EDTA (for complexometric determinations)
- HClO₄, perchloric acid in glacial acetic acid (determination of bases in organic solvents)

When using the reagents, in addition to the safety regulations, some matters must be observed:

Sodium hydroxide

Sodium hydroxide is used in a concentration of 0.01 mol/l to 1 mol/l. The highly diluted solutions can absorb CO₂ from the atmosphere and thus alter their content. They are used for very accurate titrations under inert gas. The reagent bottles with alkaline reagents are closed with CO₂ absorption tubes. These contain soda lime, a mixture of solid NaOH and Ca(OH)₂. This must be exchanged regularly. An indicator in soda lime indicates the exchange too late. Higher concentrations than 0.1 mol/l can attack the glass of the cylinder. Therefore, the tightness of the pistons must be specially observed.

Hydrochloric acid

Hydrochloric acid in concentrations up to 0.1 mol/l is easy to handle. It is corrosive in higher concentration and can cause damages in the titrator. It is recommended to remove the unit from the titrator when not in use.

Na₂EDTA

Na₂EDTA contains some NaOH. The same aspects apply as with sodium hydroxide. Concentrations of 0.01 mol/l to 0.1 mol/l are common.

AgNO₃

Silver nitrate can be used over a wide concentration range and is also very stable. Due to the high molecular weight and the easy solubility, a silver nitrate standard solution can be produced very accurately. Silver nitrate is sensitive to light and must be stored in dark bottles.

Na₂S₂O₃

Sodium thiosulphate is a reducing agent and is stabilized with commercially available titrants. If you make it yourself, the titer is only stable after some time.

Ce(SO₄)₂

Cerium sulphate is a strong oxidizer and must correspondingly be handled with care. It is corrosive.

(NH₄)₂Fe₂(SO₄)₂

Ammonium iron (II) sulphate is a reducing agent. It is often stabilized with sulfuric acid and therefore has a corrosive effect.

KOH in Ethanol or isopropanol

Potassium hydroxide in alcohol is a very strong base. The same aspects apply here as with sodium hydroxide.

HClO₄ in glacial acetic acid

Perchloric acid in glacial acetic acid is a very strong acid. Perchloric acid is usually used with 0.1 mol/l. Solutions which are more diluted lead to flatter titration curves.

Titration guide

4.5 Titer determination

The titration is an absolute method which is directly attributable to the chemical conversion. The measured value is the volume of titrant that is converted during the reaction. This assumes that the concentration of the titrant is actually correct. It is therefore always the first step of an application to determine its concentration accurately. If this is carried out with a certified standard, the concentration can be traced back to a national standard (original titer substance) and its concentration can be determined accurately at the same time. The certified standards must be treated carefully. They should be kept dry at 15 - 25 °C in their original sealed packaging. If necessary they must be dried before use (Fig. 31).

The titer is a dimensionless number for correcting the indicated concentration. The titer is about 1.0.

$$\text{Titer} = \frac{W}{EQ * c * M}$$

The real concentration of the titrant is often calculated during the titer determination:

$$\text{real concentration } T = \frac{W}{EQ * M}$$

In the software of the titration devices from SI Analytics®, the term "Titer" describes the real concentration and not the dimensionless factor. We also use this term in the examples of titration applications in this guide.

$$T[\text{mol/l}] = \frac{W * F2}{(EQ - B) * M * F1}$$

- T: Real concentration of the titrant
- W: Weighed sample standard / sample in [g]
- EQ: Consumption titrant
- M: molar mass of the standard
- B: Blank value of the solvent
- F1, F2: variable factors e.g. for the conversion of units, stoichiometry
- c: Target concentration of the titrant

Application	Standard titer substance	Formula	Molar mass [g/mol]	Drying
Acidimetry	sodium carbonate free of water	Na_2CO_3	105.99	180 °C
	Tris(hydroxyl-methyl-aminomethan (TRIS)	$\text{C}_4\text{H}_{11}\text{N}_3$	121.14	105 °C
Alkalimetry	Benzoic acid	$\text{C}_7\text{H}_6\text{O}_2$	122.12	-
	Potassium hydrogen phthalate	$\text{C}_8\text{H}_5\text{K}_2\text{O}_4$	204.23	105 °C /3h
Argentometry	Sodium chloride	NaCl	58.443	110 °C
Karl Fischer titration	Di-sodium tartrate Di-hydrate	$\text{C}_4\text{H}_4\text{Na}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$	230.08	-
Complexometry	Calcium carbonate	CaCO_3	100.09	105 °C
	Zinc	Zn	65.37	-
Oxidimetry Cerimetry	di-arsenic trioxide	As_2O_3	197.84	105 °C /3h
	di-sodium oxalate	$\text{C}_2\text{Na}_2\text{O}_4$	133.999	105 °C
	Iron(II) ethylene diammonium sulfate	$(\text{CH}_2\text{NH}_3)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	382.15	-
	potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	294.19	105°C
	potassium iodate	KIO_3	214.00	150 °C / 180 °C

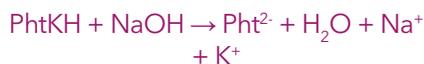
Fig. 31 Standard titer substances and reference materials for the titration

Titration guide

Titer determination of bases

Alkalis can be adjusted with acids. Suitable acids are potassium hydrogen phthalate, benzoic acid, oxalic acid dihydrate or amidosulfonic acid. In water or acetic acid as solvent, potassium hydrogen phthalate is recommended, in organic solutions, e.g. in the pharmaceutical sector, benzoic acid is usually used.

The reaction equation for the titer determination with potassium hydrogen phthalate is:



Potassium hydrogen phthalate (Fig. 32) is only weakly dissociated in aqueous solution. The titration curve therefore increases initially, similar to acetic acid, to show a steep jump after a plateau. The $\text{pK}_{\text{s}2}$ value is 5.41.

Instruction for the titer determination of a 0.1 mol/l NaOH

Approximately 200 mg of potassium hydrogen phthalate are weighed into a 150 ml beaker with an analytical balance to four digits after the decimal point and are filled up with deionized carbonate-free water to approx. 100 ml. After complete dissolution, the titration is started to a pH 11 or up to an equivalence point. The equivalence point is evaluated. The consumption is approximately 10 ml.

Handling of the standard

- Drying:
two hours at 120 °C
- Storage:
Tightly closed in the original packaging, protect from light and humidity, at room temperature (+15 - 25 °C)
- Observe the minimum usability

The following must be observed:

- The slope of the pH electrode is > 95 % for the aqueous titration
- The NaOH solution in the storage bottle must be protected against CO₂ influence with soda lime
- All crystals of the standard must be completely dissolved at the start of the titration

The following titration parameters are recommended:

- Dynamic titration
- Normal (average) titration speed
- Dynamics: steep
- No damping
- End criterion 1 EQ with slope value 700 mV/ml and pH 11

Calculation of the titer

$$T[\text{mol/l}] = \frac{W * F2}{(EQ - B) * M * F1}$$

- T: real concentration of the titrant
W: Weighed sample standard / sample in [g]
EQ: Consumption titrant in [ml]
B: Blank value of the solvent in [ml]
M: 204,22 g/mol (molar mass of potassium hydrogen phthalate)
F1: 1
F2: 1000 (conversion ml - L)

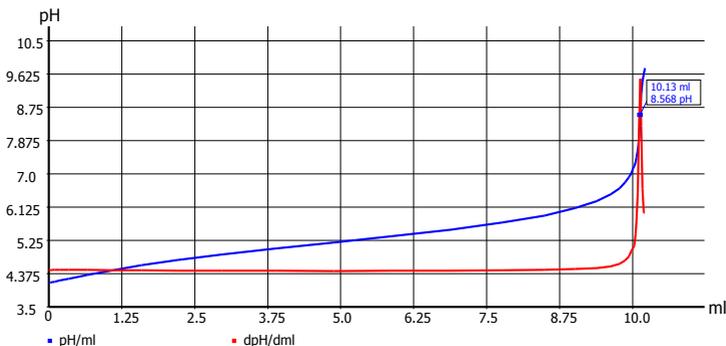


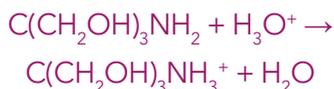
Fig. 32 Titer determination of an 0.1 mol/l NaOH with potassium hydrogen phthalate

Titration guide

Titer determination of acids

Acids can be adjusted with bases. As a base, e.g. sodium carbonate and TRIS (tris(hydroxymethyl)-aminomethane, or according to IUPAC 2-amino-2-hydroxymethyl-propane-1.3-diol) are suitable. TRIS is recommended, as the handling is simpler and more secure.

The reaction equation for titer determination with TRIS is:



A falling titration curve (Fig. 33) results, which can be interrupted at the EQ or which can be counted back after overtitration of the EQ. The latter method is recommended if carbonates are expected.

Instruction for the titer determination of a 0.1 mol/l HCl

Approx. 120 mg TRIS are weighed into a 150 ml beaker with an analytical balance to four digits after the decimal point, and filled with deionized, carbonate-free water to approx. 100 ml. After complete dissolution, the titration is started to a pH 2.5 or up to an equivalence point. The equivalence point is evaluated. The consumption is approximately 10 ml.

Handling of the standard

- **Drying:**
24 hours via desiccant in the desiccator
- **Storage:**
Tightly closed in the original packaging, protect from light and humidity, at room temperature (+15 - 25 ° C)
- Observe the minimum usability

The following must be observed:

- The slope of the pH electrode is > 95 % for the aqueous titration
- The added solvent must be free from CO₂
- All crystals of the standard must be completely dissolved at the start of the titration

The following titration parameters are recommended:

- Dynamic titration
- Normal (average) titration speed
- Dynamics: steep
- No damping
- End criterion 1 EQ with slope value 700 mV/ml and pH 2.5

Calculation of the titer

$$T[\text{mol/l}] = \frac{W * F2}{(EQ - B) * M * F1}$$

- T: Real concentration of the titrant
- W: Weighed sample standard / sample in [g]
- EQ: Consumption titrant in [ml]
- B: Blank value of the solvent in [ml]
- M: 121.14 g/mol (molar mass of TRIS)
- F1: 1
- F2: 1000 (conversion ml - l)

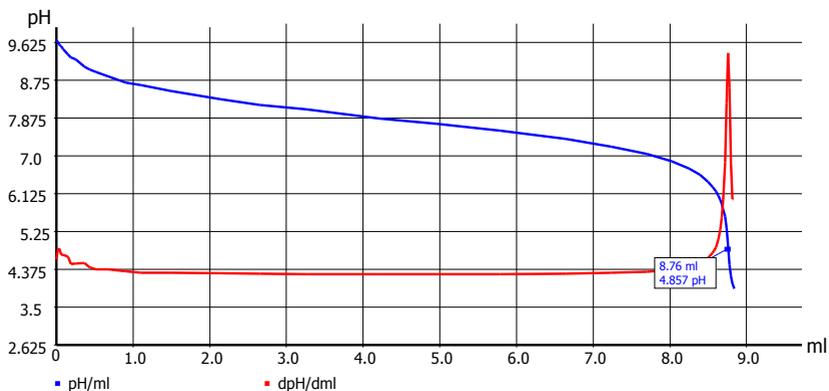


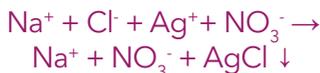
Fig. 33 Titer determination of an 0.1 mol/l HCl with TRIS

Titration guide

Titer determination of silver nitrate

Silver nitrate is often adjusted with NaCl. This is available as a secondary NIST standard. Although KCl would have a higher molecular weight, it is often not available in the necessary purity.

The reaction equation for the titer determination with NaCl is:



An increasing titration curve (Fig. 34) results, which can be interrupted at the EQ or which can be counted back after over-titration of the EQ. When a glass electrode is used as a reference, a falling titration curve results.

Instruction for the titer determination of a 0.1 mol/L AgNO₃

Approx. 58 mg of NaCl are accurately weighed into a 150 ml beaker to four digits after the decimal point using an analytical balance, filled with deionized water up to approx. 100 ml, and 2 ml of semi-concentrated HNO₃ or H₂SO₄ are added. The equivalence point is evaluated. The consumption is approximately 10 ml. A white precipitation forms during titration.

Handling of the standard

- Drying: at 110 °C 3 hours
- Storage: Tightly closed in the original packaging, protect from light and humidity, at room temperature (+15 - 25 °C).
- Observe the minimum usability

The following must be observed:

- The titration shall last between three and five minutes.

The following titration parameters are recommended:

- Dynamic titration
- Measuring speed:
 - Measurement time 3 s
 - Drift 10 mV/min
 - Min time 3 s
 - Max time 15 s
- Dynamics: steep
- No damping
- End criterion 1 EQ with slope value 400 mV/ml

Calculation of the titer

$$T[\text{mol/l}] = \frac{W * F2}{(EQ - B) * M * F1}$$

- T: Real concentration of the titrant
- W: Weighed sample standard / sample in [g]
- EQ: Consumption titrant in [ml]
- B: Blank value of the solvent in [ml]
- M: 58.433 g/mol (molar mass of NaCl)
- F1: 1
- F2: 1000 (conversion ml - l)

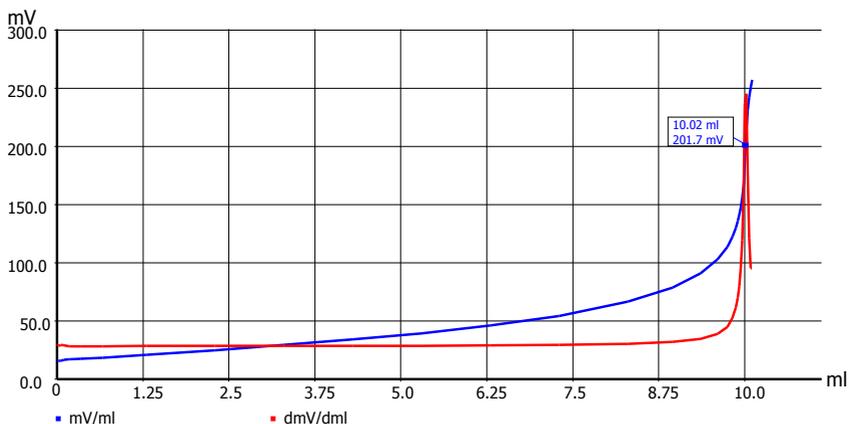


Fig. 34 Titer determination of a silver nitrate solution with sodium chloride

Titration guide

Titer determination of perchloric acid

Perchloric acid is a very strong acid that can be used to titrate potassium hydrogen phthalate as the base in acetic acid.

The reaction equation for the titer determination with potassium hydrogen phthalate is:



The titration is performed as mV titration. It therefore increases and does not fall, as would be the case with a titration with acid in the pH range.

Instruction for the titer determination of a 0.1 mol/l HClO_4

Approximately 200 mg of potassium hydrogen phthalate (Fig. 35) are weighed into a 150 ml beaker with an analytical balance to four digits after the decimal point and are filled up with glacial acetic acid to approx. 80 - 100 ml. After complete dissolution, the titration is started up to an equivalence point. The equivalence point is evaluated. The consumption is approximately 10 ml.

Handling of the standard

- Drying:
two hours at 120 °C
- Storage:
Tightly closed in the original packaging, protect from light and humidity, at room temperature (+15 - 25 °C).
- Observe the minimum usability

The following must be observed:

- All crystals of the standard must be completely dissolved at the start of the titration!
- LiCl in ethanol or in glacial acetic acid should be used as electrolyte.

The following titration parameters are recommended:

- Dynamic titration
- Measuring speed:
 - Measurement time 2 s
 - Drift 10 mV/min
 - Min time 3 s
 - Max time 15 s
- Dynamics: average
- average damping
- End criterion 1 EQ with slope value 300 mV/ml

Calculation of the titer

$$T[\text{mol/l}] = \frac{W * F2}{(EQ - B) * M * F1}$$

- T: Real concentration of the titrant
- W: Weighed sample standard / sample in [g]
- EQ: Consumption titrant in [ml]
- B: Blank value of the solvent in [ml]
- M: 20422 g/mol (molar mass of potassium hydrogen phthalate)
- F1: 1
- F2: 1000 (conversion ml - l)

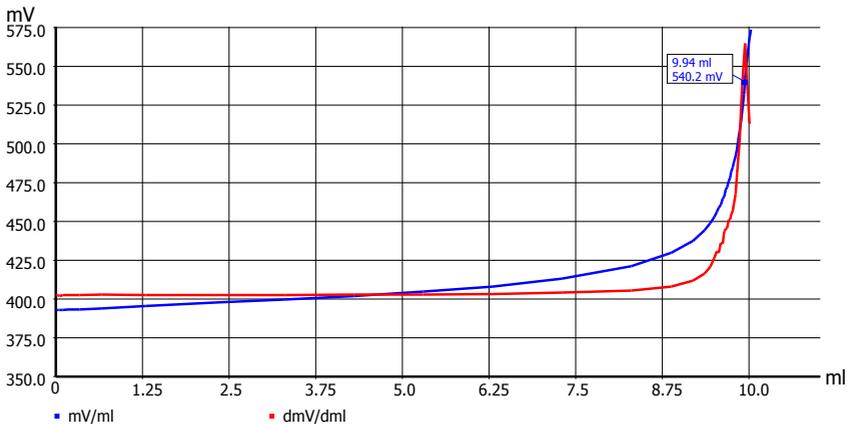


Fig. 35 Titer determination of a perchloric acid with potassium hydrogen phthalate

Titration guide

Titer determination of thiosulphate

Thiosulphate is usually adjusted with potassium iodate. This is available as a secondary NIST standard.

The reaction equation for the titer determination with KIO_3 is:



A falling titration curve results (Fig.36), which can be interrupted at the EQ or which can be counted back after overtitration of the EQ.

Instruction of a 0.1 mol/l thiosulphate solution

Approx. 50 mg KIO_3 are weighed into a 150 ml beaker with an analytical balance to four digits after the decimal point; approx. 1 g potassium iodide is added and filled with deionized water to approx. 100 ml. 5 ml of approx. 5% HCl is added. The equivalence point is evaluated. The consumption is approximately 14 ml.

Handling of the standard:

- Drying:
at 150 °C 3 hours
- Storage:
Tightly closed in the original packaging, protect from light and humidity, at room temperature (+15 - 25 °C)
- Observe the minimum usability

The following must be observed:

- A platinum combination electrode is used as electrode
- Potassium iodate and potassium iodide react iodine in acid, with their oxidizing properties
- Sufficient acid must be present in the solution
- The iodide must be present in a very high excess

The following titration parameters are recommended:

- Dynamic titration
- Measuring speed:
 - Measurement time 2 s
 - Drift 10 mV/min
 - Min time 3 s
 - Max time 15 s
- Dynamics: average
- No damping
- End criterion 1 EQ with slope value 300 mV/ml

Calculation of the titer

$$T[\text{mol/l}] = \frac{W * F2}{(EQ - B) * M * F1}$$

- T: Real concentration of the titrant
- W: Weighed sample standard / sample in [g]
- EQ: Consumption titrant in [ml]
- B: Blank value of the solvent in [ml]
- M: 214.00 g/mol (molar mass of potassium iodate)
- F1: 1 / 6 as stoichiometric factor from the reaction equation
- F2: 1000 (conversion ml - l)

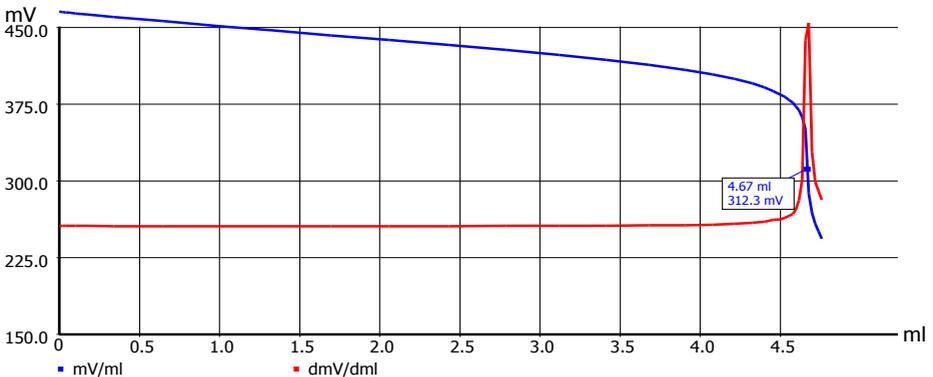


Fig. 36 Titer determination of a $\text{Na}_2\text{S}_2\text{O}_3$ solution

Titration guide

Titer determination of iodine

The titer of an iodine solution can be set directly with arsenic (III) oxide. However, this is not recommended due to the toxicity of arsenic. Nowadays it is best to use an adjusted sodium thiosulphate solution, which is titrated with the iodine solution.

The reaction equation for the titer determination is:



Instruction for the titer determination: a 0.05 mol/l iodine solution

5 ml of a 0.1 mol/l sodium thiosulphate solution is pipetted into a 150 ml beaker, filled with deionized water to approx. 100 ml and 5 ml of approx. 5% HCl is added. The titration can be carried out both as a potentiometric titration with a redox electrode and as a Dead Stop titration. The consumption is at approx. 5 ml (Fig. 37).

The following titration parameters are recommended:

- Dead Stop titration
- linear steps: 0.02 ml
- Pre-titration: none
- Dosing speed 20 %
- Titration direction: increasing
- Measuring speed:
- fixed waiting time 1s
- Polarization voltage: 100 mV
- Delta endpoint: 1.0 μA
- Titration end: 2.0 μA
- Endpoint delay: 5 s

Calculation of the titer

$$T[\text{mol/l}] = \frac{V * F2}{(EP - B) * M * F1}$$

- T: Real concentration of the titrant
- V: Volume of the $\text{Na}_2\text{S}_2\text{O}_3^-$ solution [ml]
- EP: Consumption titrant in [ml]
- B: Blank value of the solvent in [ml]
- M: 1
- F1: 2 as stoichiometric factor from the reaction equation
- F2: Concentration of the $\text{Na}_2\text{S}_2\text{O}_3^-$ solution [mol/L]

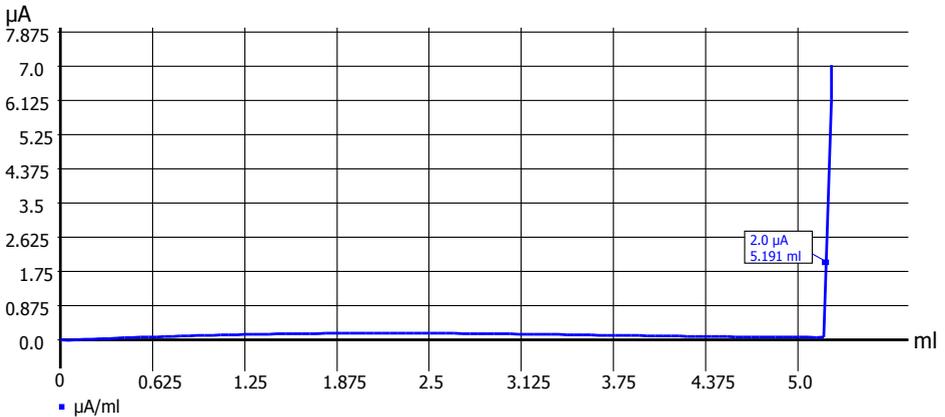


Fig. 37 Titer determination of an iodine solution (Dead Stop)

Titration guide

SECTION 5

TITRATION PARAMETERS AND CALCULATIONS

5.1 Overview

Titration methods have to be adapted to the type of application and partly to the type of samples.

This adjustment requires the selection of the measured variable (and the associated sensor), the appropriate titrator or attachment with the associated reagent and the correct parameters in the titration device or the software. The selection of the measurand and the reagent can be found in the application description. The settings in the methods and the theory behind them shall be briefly described here. A titration is parameterized by five elements:

- Control of the dosage
- Response behavior of the electrode and speed
- Definition of the titration end
- Calculation(s)
- Documentation of the result.

The titration takes place in many individual steps. It is true that part of the titration volume can be added in one step or continuously. However, the part of the titration curve that is used for the calculation is created in defined steps as a list of data with consumption, measured value, time and possibly additional information. From these data, the endpoint or equivalence point is calculated with appropriate functions.

An important requirement is that the measured values are also reliable. This is achieved by monitoring the measured values and only taking them into a titration curve when they are stable. From the calculated equivalence or endpoint, the result can then be calculated taking into account the weighed sample, titer and blank value in the correct unit.

Titration guide

5.2 Control of the dosage

Reagent addition can be done in titrators in three different ways:

- Continuous addition
- Equidistant steps (Linear titration)
- Step size dependent on the gradient of the titration curve (dynamic titration)

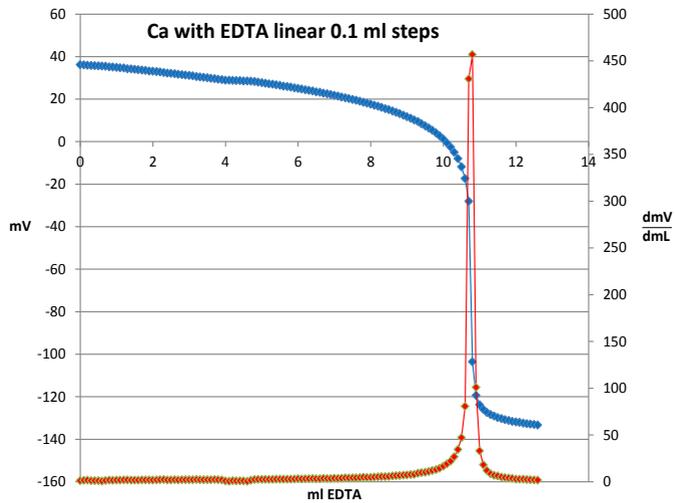
These can also be used in a combined manner. For example, it is possible to add continuously in order to then continue to titrate in a linear or dynamic manner.

The continuous addition has the advantage of a fast addition. Even if measurements can be generated during the addition, this does not mean that the reaction speed is set correctly or that the adjustment behavior of the sensor is taken into account. In practice, for most titrations, too much would clearly be found in this manner with fast continuous addition, but too little with a kinetically inhibited reaction.

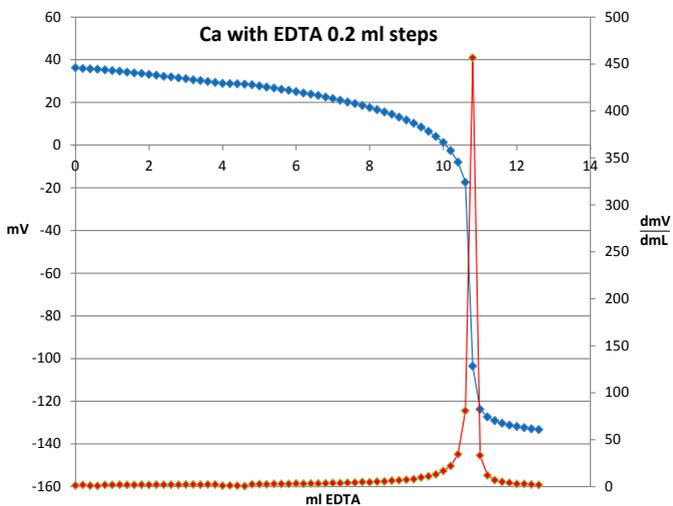
Linear Titration

In linear titration, the reagent is added in equal steps. Usually, it is waited after each step until the potential has adjusted or it can be assumed after a fixed waiting time that the potential is stable. A titration curve should not have too many but also not too few measuring points. Too few measurement points lead to a less accurate calculation, but also too many. This is due to the small potential change with small steps, resulting in less stable measured values and less accurate dosages. In addition, it is not always ensured that small volumes actually arrive at the titration tip. As a rule of thumb, a linear titration should have 20 to 50 measured values and only exceed 100 measured values in special cases.

In Fig. 38 a/b, the influence of the smaller number of titration steps is shown.



A

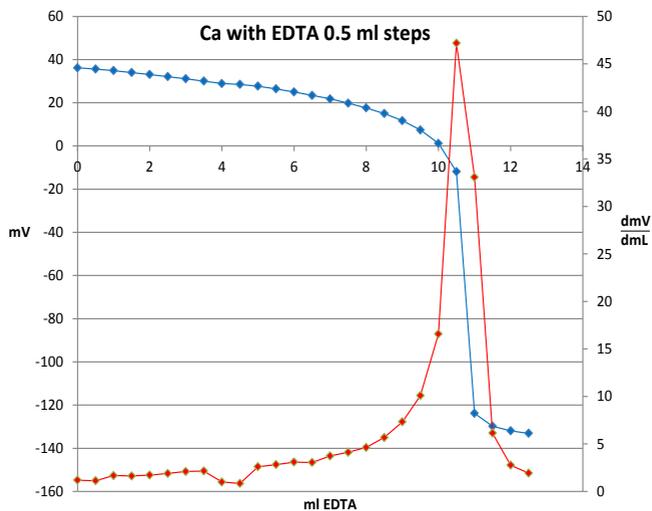


B

Fig. 38a Ca determination with EDTA linear with 126 (A) and 64 (B) measured values

Titration guide

C



D

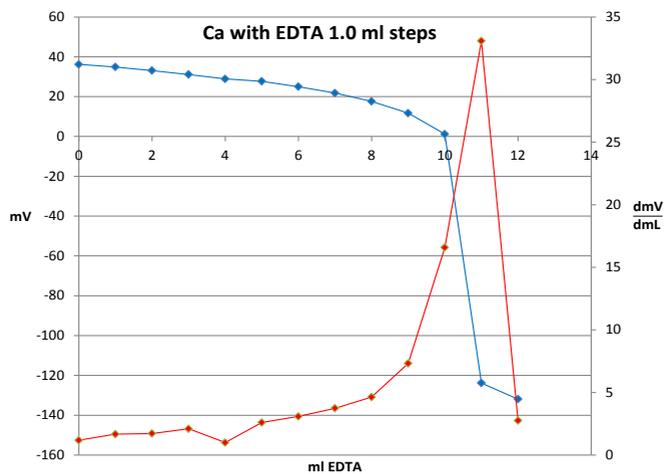


Fig. 38b Ca determination with EDTA linear with 26 (C) and 13 (D) measured values

A titration curve with 126 titration steps is clearly overloaded, 64 measuring points result in a perfect titration curve (with many measuring points in the low ml range). At 26 measuring points, small changes of the distributed first derivation can already be observed. At 13 measuring points, it may no longer be possible to carry out a correct evaluation, as measuring points may be missing for the EQ calculation. With such a titration curve, it is recommended to select smaller titration steps in order to obtain a larger number of measuring points and a titration curve that can be evaluated in a better manner.

Application areas of linear titration are e.g.:

- titrations in organic solvents,
- titration of very small contents,
- conductivity titrations,
- photometric titrations
- μA titrations

It has important advantages:

- more stable potentials result, as usually sufficient reagent is converted in order to achieve a significant potential change,
- disturbances of potentials only have a small influence on the titration curve.

The disadvantages can be seen clearly:

- too many measurement points in areas where little happens.
- only a few measurement points in the EQ area.

Titration guide

Dynamic Titration

Dynamic titration is the preferred form of reagent addition. It is used in most titrations according to the Nernst equation, for example:

- Acid-base titrations in aqueous and alcoholic solutions
- Chloride determinations
- Redox titrations

It has many advantages:

- High accuracy
- Fast titration
- Only the number of data points which is really necessary

It is not used when:

- A connection according to the Nernst equation does not exist
- Stable potentials do not exist
- With very small contents
- Organic solvents are used

With dynamic titration, the step is calculated as a function of the slope of the titration curve.

This means that in the flat part of the curve large volume steps are dosed and in the steep part small steps.

Fig. 39 clearly shows what matters: The titration shall be carried out quickly, but also very accurately with high resolution. Due to the high resolution, e.g. errors can be found in the titrant: The KOH in Fig. 40 is contaminated with carbonate. This is often not detected in a titration. For this, the titration in the steep part, but also only there, must be titrated with a particularly high resolution, so that both EQs are recognizable.

Fig. 39 shows the individual addition steps with dynamic titration. In the beginning, it is carefully started with small steps so that it is not over-titrated. Then a few large volume steps follow until just before the EQs. The EQ area is then titrated with small steps. Even if the distance of the steps in the jump area appears to be different, on the x-axis with the ml values, the volume steps are all equal to the smallest set step.

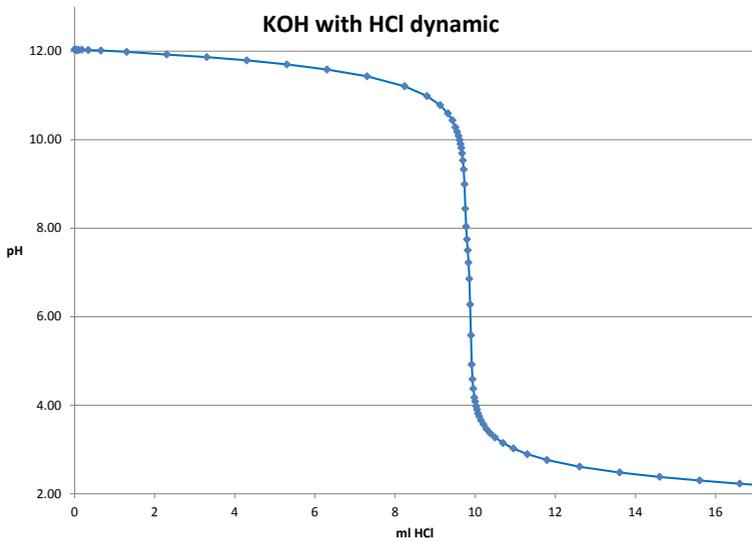


Fig. 39 Representation of the measure values on the titration curve

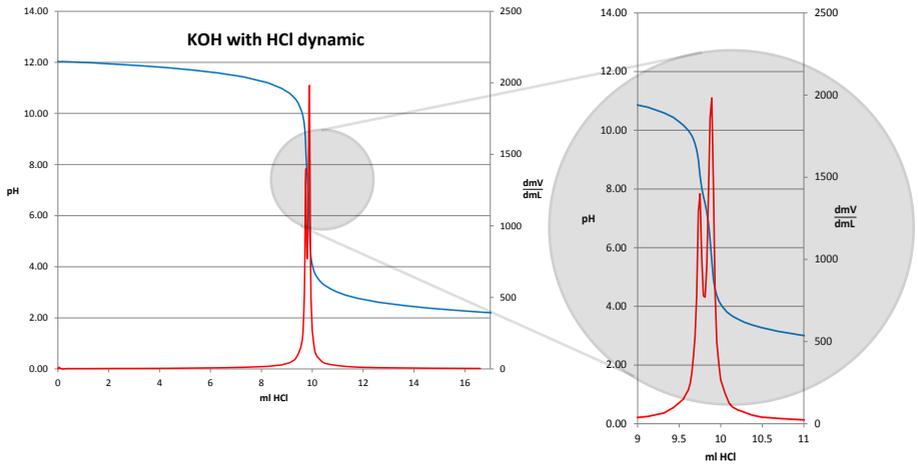


Fig. 40 Titration curve of a carbonate-containing KOH dynamically titrated with HCl

Titration guide

The calculation of the step takes place on the basis of a hyperbolic function:

$$\text{Step size [ml]} = \frac{a}{\text{Gradient}^b} + c$$

with "a", "b" and "c" as calculation factors, which are automatically determined from the titration curve.

This hyperbolic function is derived from the Nernst equation, which represents an "ln" function. The derivation of the ln(x)-function is 1/x, which is behind this formula.

Fig. 41 shows that large steps are titrated with a small slope value and small steps with a large slope.

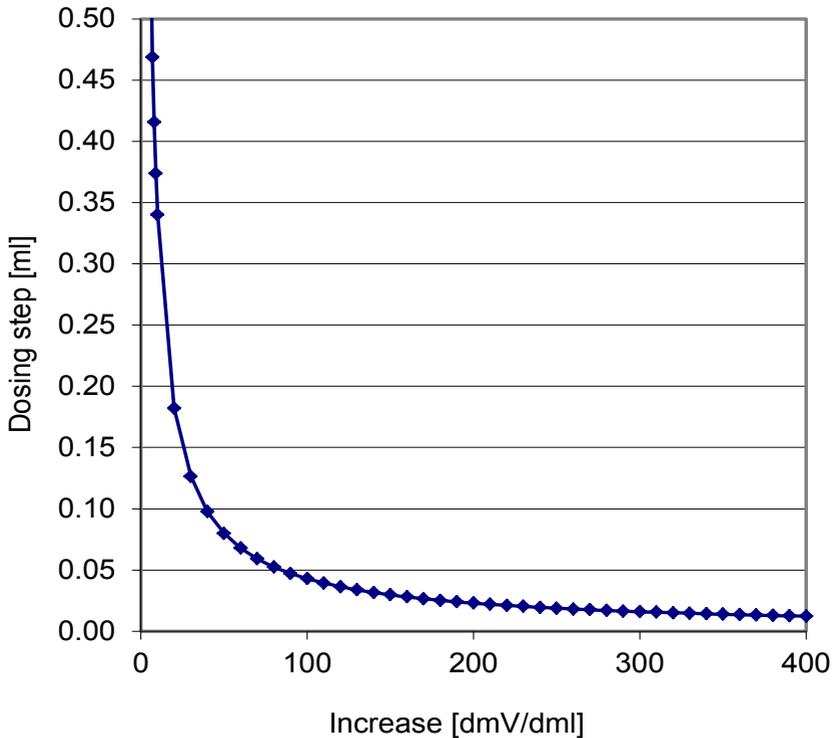


Fig. 41 Function for calculating the step of the titration curve

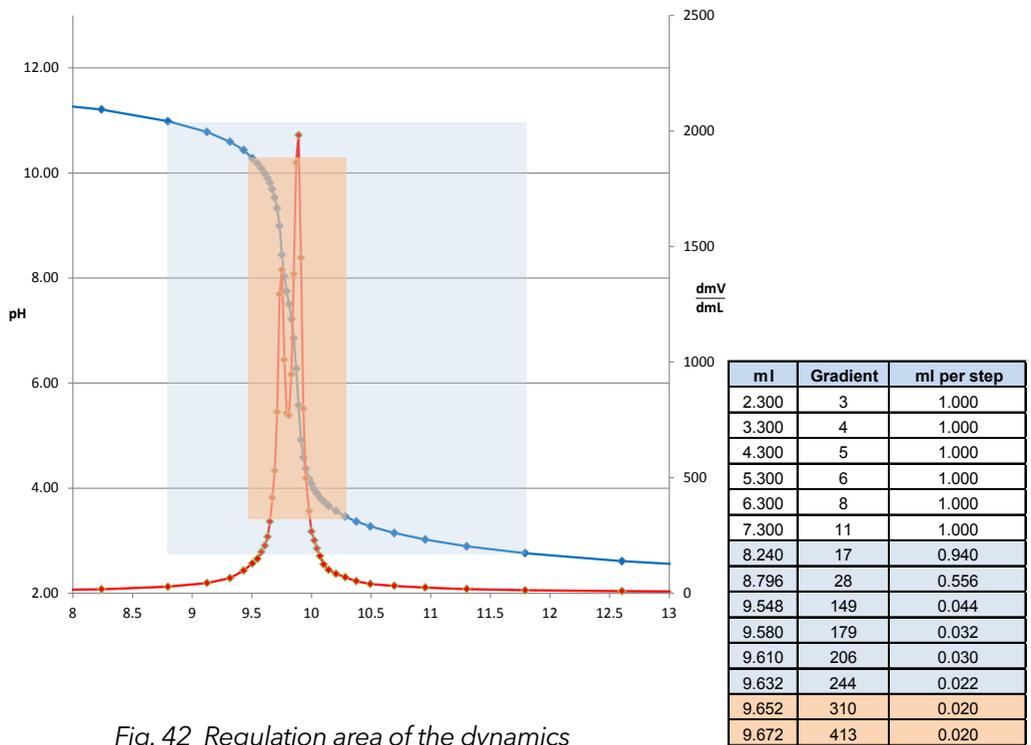


Fig. 42 Regulation area of the dynamics

Fig. 42 shows the regulation areas of the titration. Within the blue area, the step is reduced or increased again, in the orange area, the smallest step is dosed with a defined accuracy. The following entries are required for the parameterization:

- Largest step in [ml]
- Smallest step in [ml]
- Gradient, until which the largest step shall be dosed [dmV/dmL]
- Gradient, from which the smallest step shall be dosed [dmV/dmL]

In the above example these are:

- 1.000 ml
- 0.020 ml
- 15 mV/ml
- 250 mV/ml

Titration guide

In order to obtain meaningful results, the settings "steep, average or weak jump" are usually sufficient. Steps that are too large steps can lead to over-titration, too small lead to potential differences and thus to strong noise of the curve. This reduces the accuracy of the titration. As a rule of thumb, approx. 5-10 % of the total titration volume are suitable as the largest step, 2 % for the smallest step. Certain requirements for extra accuracy or speed may require different settings.

5.3 Response behavior of the electrode and speed

The adjustment of the step alone is not sufficient to control a titration curve. It must also be ensured that the "correct" stable measuring signal is applied to the electrode. In certain circumstances measuring signal needs some time until stable values are adjusted. This time depends on various factors, such as type, age and condition of the electrode and the concentration of the material to be measured. In practice, therefore, the setting behavior of the electrode is observed and evaluated the course of the measured value per unit time. The change in the measured value per time is called drift (Fig. 43). The measurement unit is [mV/min].

Fig. 44 clearly shows that most of the titration time is used for accurate drift control in the area of the equivalence points. The graph shows a linear titration with the same step size, in order to avoid effects due to several small volume additions instead of one large addition.

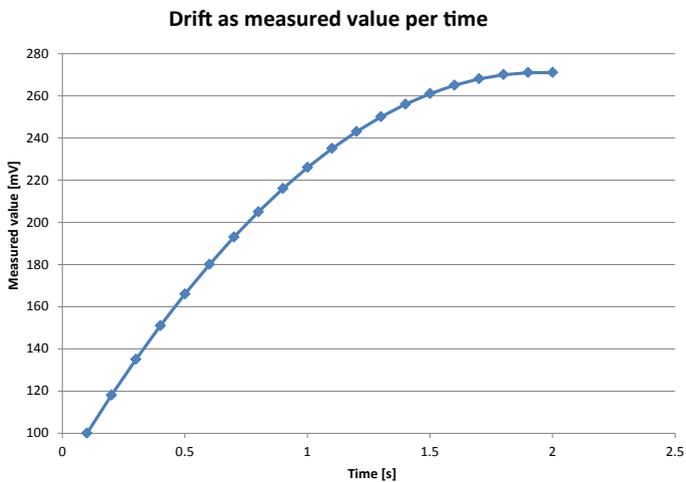


Fig. 43 Measured value change per time

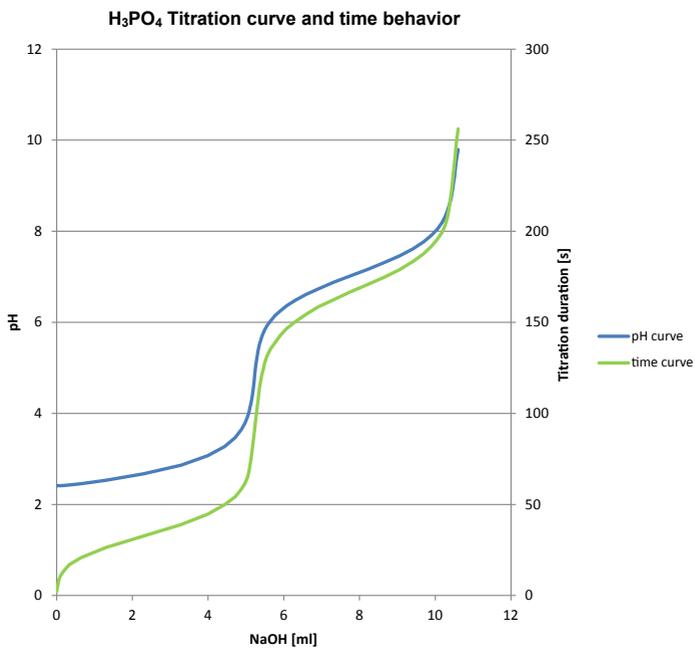


Fig. 44 Titration curve (blue) and titration duration (green)

Titration guide

As parameters,

- the minimum waiting time,
- the maximum waiting time,
- the window for the testing time,
- the drift value,

can be set (Fig. 45).

The minimum waiting time must be waited for in any case, even if the drift within the testing time is already monitored during this time.

A minimum waiting time of 10 seconds is waited for in Fig. 46. Within the last five seconds (testing time), however, the drift is already determined and compared with the target value (Fig. 47). The window for the testing time will continue to move until the maximum drift time or drift value is reached. The value represents the gradient of the drift curve.

It is recommended to select the minimum time not too short, as an alternating system can build up. The current value is accepted very quickly, but causes the next value to take longer to adjust.

In some cases, it may be sensible to work with fixed waiting times instead of a drift-controlled waiting time; especially for applications that provide only a few stable measured values, low potential changes, or do not provide mV or pH values according to the Nernst equation (e.g. μA values, mS values, or temperatures). Fixed waiting times are usually set in the range of 5 - 30 seconds.

Titration duration	Minimum waiting time t_{min} [s]	Maximum drift time t_{max} [s]	Measurement time t_{p} [s]	Drift value [mV/min]
Fast	1	5	1	50
Average	2	15	2	20
Exact	5	20	2	10

Fig. 45 Setting parameters for the drift (practical values)

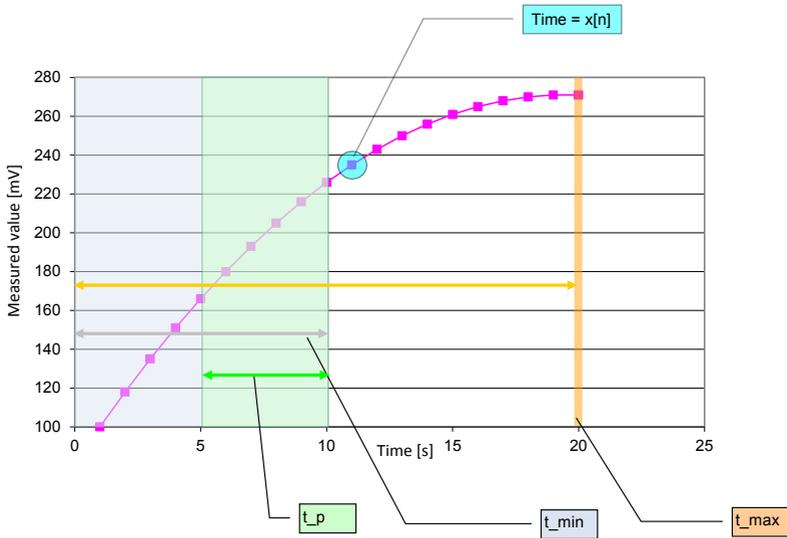


Fig. 46 Setting the drift and the necessary parameters (description of the parameters, see Fig. 45)

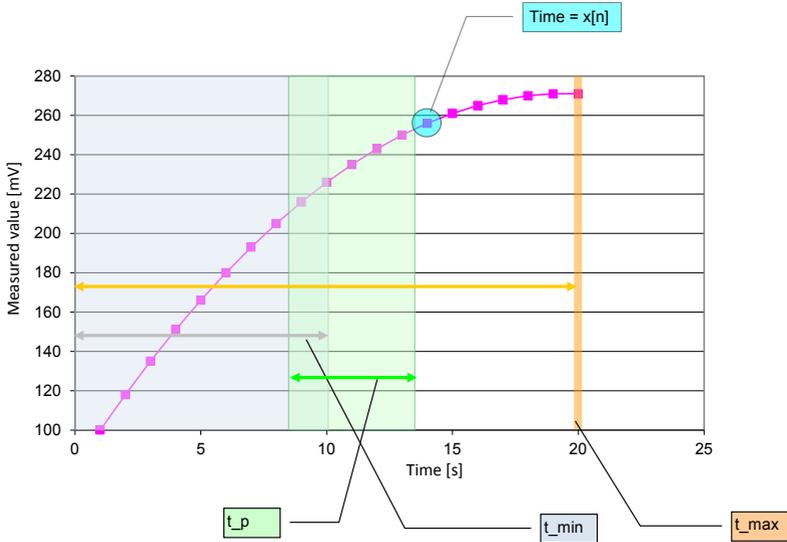


Fig. 47 Setting the drift with control time window (labeling see Fig. 45, parameter "Exact")

Titration guide

5.4 Definition of the titration end

With a manual titration, the titrator stops as soon as the "manual button" is released. What if the user cannot be present for the entire time? This is often the case during titration.

In order to terminate an automatic titration, several criteria exist:

Titration up to:

- a maximum volume of the titrant
- a certain endpoint (pH or mV, also μA or μS are possible)
- a certain duration (pH Stat, KF titration)
- one or several EQs
- a calculated result
- a manual interruption

The essential criteria for stopping a titration are listed in Fig. 48.

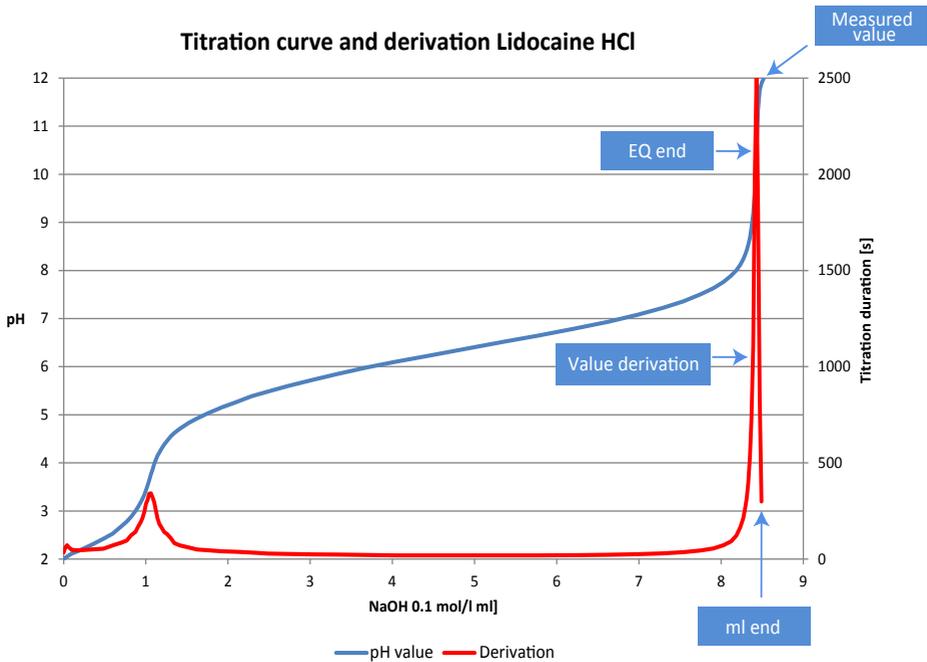


Fig. 48 Criteria for ending the titration

Titration interruption at maximum volume

This criterion should always be there, as beakers are limited in their volume. Usually 20 to 50 ml are used as an additional criterion. For some titrations with very small changes in potential (e.g. TAN) it can also be the only criterion.

Titration interruption at a certain measured value

If it is not known how many equivalence points can be calculated, this criterion will be used. E.g. a maximum pH value is defined at which the titration stops. Then it can be decided in the calculation whether one or more EQs should be calculated. For EP titrations to a defined endpoint, the interruption criterion is the desired endpoint. This endpoint must be exceeded for a defined time (endpoint delay) or by a certain value.

Titration interruption when recognizing an EQ

For titrations in which a clearly recognizable EQ is calculated, this is also the most sensible end criterion. An EQ is calculated as the maximum of the first and the zero point of the second derivation. It is therefore associated with the value of the first derivation. The first derivation must reach a certain (adjustable) value in order for the EQ to be accepted as such.

Titration guide

For some applications, other criteria exist for terminating the titration. During the pH Stat titration (the pH value is kept constant for a while), the duration of the titration is used as a criterion (Fig. 49). The total volume should always be a criterion, as the titration cell can also overflow.

With the Karl Fischer titration, one titrates to one endpoint. A voltage is applied to the indicator double platinum electrode. A current flows if a reversible redox couple is present in the solution (iodine and iodide). The titration is stopped if this reaches the set end value.

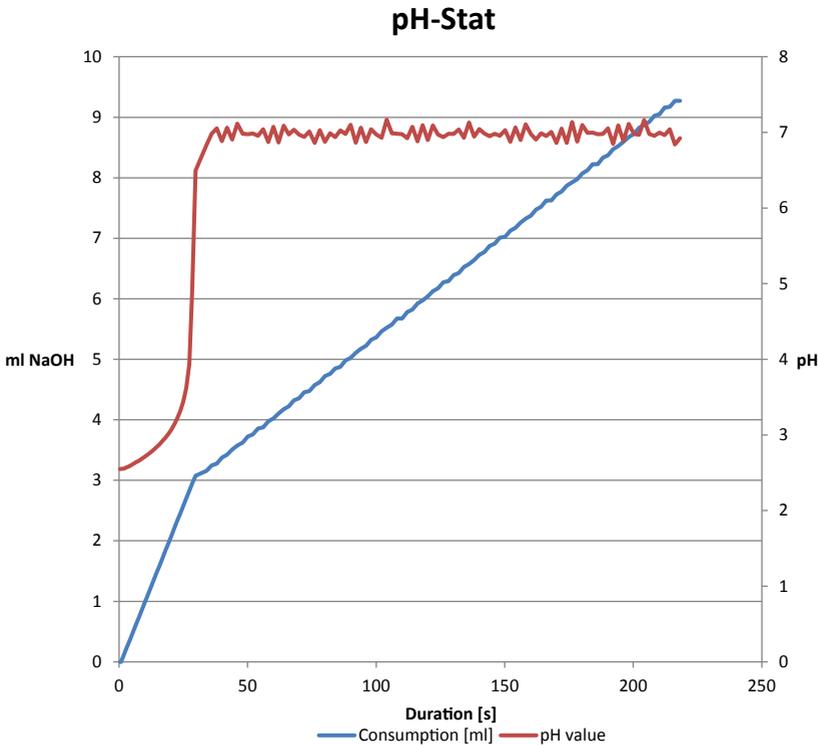


Fig. 49 pH stat titration with stat phase of 180 s

5.5 Evaluation of the titration

During the titration, endpoints (EP) or equivalence points (EQs) are evaluated.

In a titration to an endpoint (EP), the titration is typically interrupted at the point that would correspond to the colour change of an indicator. EP titrations are thus conventional methods that are primarily intended to provide good comparability. EPs are thus also the last point of a titration or partial titration. Titrations with several partial titrations with up to three endpoints exist.

An equivalence point (EQ) is determined based on a turning point of the titration curve. The maximum of the first derivation and the zero point of the second derivation are calculated for this. Typically, the turning point corresponds to the equivalent conversion of the reagent with the sample. With several turning points, however, it may happen that the actual equivalence point has not yet been reached when the curve "bends" for another EQ. In some cases corrections to the EQ are advantageous. Their complex calculation shall not be discussed here.

In practice, the EQs are almost always used to calculate the result. In order to calculate an EQ, it is over-titrated by a few titration points and interpolated from the titration points around the EQ. The result is the more accurate the smaller the titration steps. If measuring points are missing after the EQ, it may be possible that a calculation is not possible. It is therefore important to ensure that there are still enough measuring points for a calculation after an EQ (see Fig. 50). The calculated pH or mV value of the EQ is of minor importance for very steep curves. The slope of the titration curves can be very high, so that the changes of the pH value in the volume often have practically no effect. The volume is however used for the evaluation and calculation of the result.

Titration guide

If the correct EP or EQ is determined, the desired result can be calculated from this.

Basically, only 2 types of formulas are used hereby: on the one hand, the calculation of the titer or the concentration of the titrant, and on the other hand the calculation of the concentration of a sample.

Formula for the titer

$$\text{Titer} = \frac{W * F2}{EQ * C * M * F1}$$

Titer: Dimensionless number, for example 1.0

W: Weighed sample standard / sample [g]

EQ: Consumption titrant [ml]

C: specified concentration of the titrant [mol/l]

M: molar mass of the standard [g/mol]

F1: 1

F2: 1000 (conversion ml - l)

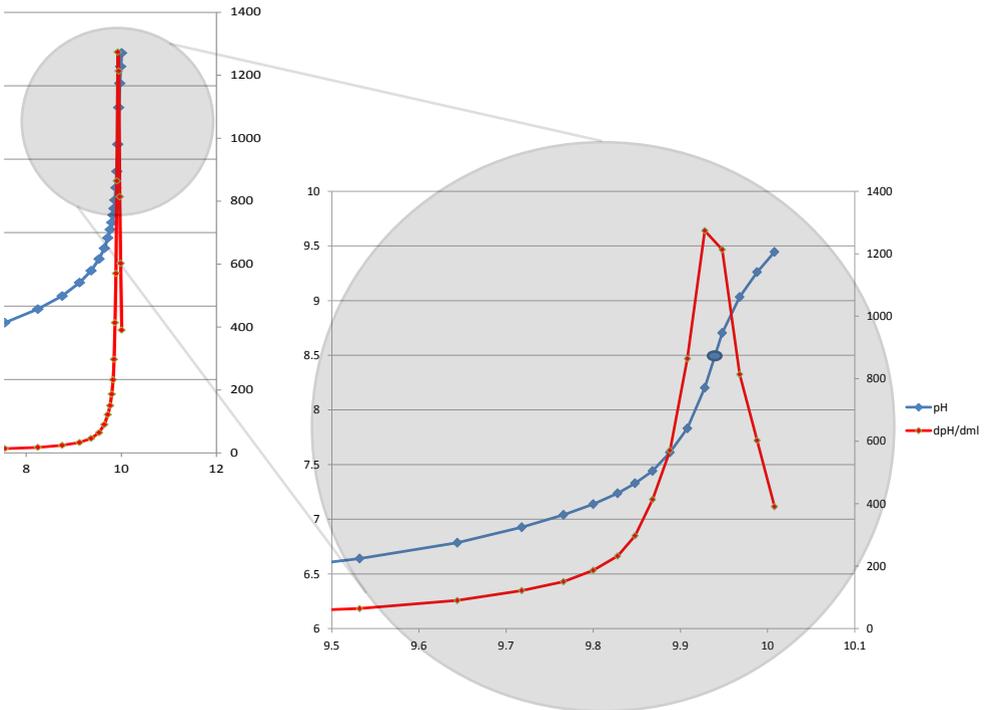


Fig. 50 Interpolation of an EQ

Sometimes a blank value has to be included in the calculation of the result. Some solvents have a (small) self-consumption of titrant. This self-consumption is deducted from the EQ or EP, so that only the consumption of the sample contributes to the result in the calculation. Another type of blank value can be found in the back titration: The blank value is the consumption of the used reagent without sample. Here the consumption of EP or EQ is deducted from the blank value.

Formula for the content in % with blank value in the solvent

$$\text{Content [\%]} = \frac{(EQ - B) * T * M * F1}{W * F2}$$

- EQ: Consumption titrant [ml]
- B: Blank value of the solvent [ml]
- T: Exact concentration of the titrant [mol/l]
- M: molar mass of the substance to be determined [g/mol]
- W: Weighed sample standard / sample [g]
- F1: 100 conversion in %
- F2: 1000 (conversion ml - l)

Formula for the content in % as back titration

$$\text{Content [\%]} = \frac{(B - EQ) * T * M * F1}{W * F2}$$

- B: Consumption during titration of the added reagent without sample [ml]
- EQ: Consumption titrant [ml]
- T: Exact concentration of the titrant [mol/l]
- M: molar mass of the substance to be determined [g/mol]
- W: Weighed sample standard / sample [g]
- F1: 100 conversion in %
- F2: 1000 (conversion ml - l)

The titration often has an "accuracy" of four significant digits in total (regardless of whether before or after the decimal separator). However, all the individual components in the formula must also be defined with this number of digits, starting with the weighed sample through the molar weights to the consumption. To achieve higher accuracy, all numbers in the formula must always be defined with a higher number of digits.

Titration guide

Examples:

Titer of silver nitrate with NaCl

The titer of a 0.1 mol/l silver nitrate solution shall be determined with NaCl:

- the molar mass of NaCl is 58.44 g/mol,
- the weighed sample W was 0.584 g,
- the consumption EQ was at 10.05 ml,
- with F1 = 1 and F2 = 1000 (conversion ml - l), the following results:

$$\begin{aligned} \text{Titer} &= \frac{0.0584 * 1000}{10.05 \left[\frac{\text{mol}}{\text{l}} \right] * 58.44 \left[\frac{\text{g}}{\text{mol}} \right] * 1} \\ &= 0.9943 \end{aligned}$$

or the exact concentration used for most calculations T:

$$\begin{aligned} T \left[\frac{\text{mol}}{\text{l}} \right] &= \text{Titer} * 0.1 \left[\frac{\text{mol}}{\text{l}} \right] \\ &= \frac{0.0584 * 1000}{10.05 [\text{ml}] * 58.44 \left[\frac{\text{g}}{\text{mol}} \right]} \\ &= 0.0994 \left[\frac{\text{mol}}{\text{l}} \right] \end{aligned}$$

The 0.1 mol/l AgNO₃ solution thus has a concentration of 0.0994 mol/l.

NaCl content in %

The NaCl content of a sample shall be determined with the above-mentioned standard solution:

- the exact concentration is 0.0994 mol/l
- the molar mass of NaCl is 58.44 g/mol
- the weighed sample W was 1.12 g
- the consumption EQ was at 10.05 ml,
- with F1 = 1 and F2 = 1000 (conversion ml - l), the following results:

$$\begin{aligned} \text{Content [\%]} &= \frac{10.05 [\text{ml}] * 0.0994 \left[\frac{\text{mol}}{\text{l}} \right] * 58.44 \left[\frac{\text{g}}{\text{mol}} \right] * 100\%}{1.12 [\text{g}] * 1000} \\ &= 5.21\% \end{aligned}$$

In the example, the sample would have a sodium chloride content of 5.21%.

SECTION 6

APPLICATIONS

Examples from the application database

For many applications, application documents can be downloaded from our homepage. Some applications shall be listed here as examples.

Titration guide

6.1 Acid-base titrations

Titration of citric acid in drinks

Almost all drinks contain acids that are usually already contained in the raw fruit materials. They improve the taste and the durability. Acids are still added to some soft drinks. Citric acid (Fig. 51) is a tribasic acid, whose pK_s values are very close together and therefore difficult to titrate individually. As drinks often also contain other acids, an endpoint titration to a pH of 8.2 (in some cases also 8.1, 8.3 or 8.5) is carried out in practice (Fig. 52). This corresponds to the change of phenolphthalein.

The manual titration with colour indicator is often difficult to carry out in contrast to the potentiometric titration due to the inherent colour of the drinks. The calculation is also carried out for other acids with the molecular weight of citric acid (192.13 g/mol).

One usually titrates with a NaOH 0.1 mol/l.

The following must be observed:

- A titer determination takes place with potassium hydrogen phthalate.
- The sodium hydroxide must be protected with a CO_2 absorption means. Soda lime is recommended.
- The electrode must be calibrated. The buffers pH 4.01 and pH 6.87 are recommended.

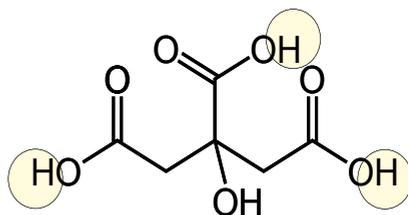


Fig. 51 Structural formula citric acid

The following titration parameters are recommended:

- Endpoint titration to pH 8.2
- Dosing speed 40 %
- Linear step: 0.04 ml normal (average) titration speed
- Delta value for the linear end part: 1.2
- Endpoint delay 5 s
- No damping

Formula for the acid value in g/l:

$$\text{acidity [g/l]} = \frac{\text{EP} * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

- EP: Consumption titrant [ml] to pH 8.2
 T: Exact concentration of the titrant
 M: Molar mass of citric acid 192.13 g/mol
 V: Volume sample [ml]
 F1: 1
 F2: 3 (stoichiometric factor, 3-basic acid)

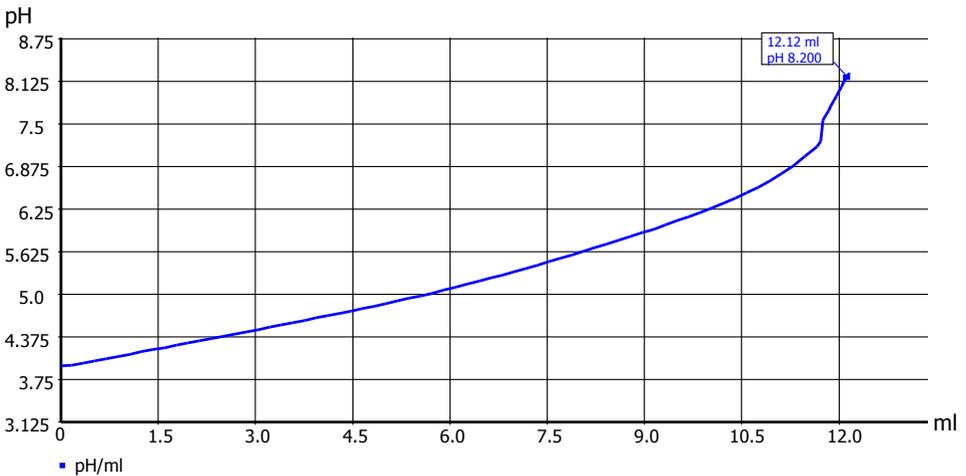


Abb. 52 Titration curve orange juice

Titration guide

Titration of a strong acid

Many applications contain strong, completely dissociated acids such as HCl, H₂SO₄ or HNO₃. These behave the same for the acid-base titration. Sulfuric acid e.g. behaves in aqueous solutions as a dibasic strong acid and it is thus difficult to distinguish it from "two" monobasic strong acids. Different organic acids as e.g. salicylic acid (Fig. 53), whose pK_s value is approximately in the area of the 1st protons of phosphoric acid, behave like a strong acid during titration. The titration usually takes place in a dynamic manner up to an EQ. With an endpoint titration, the indicator would depend on the type of acid.

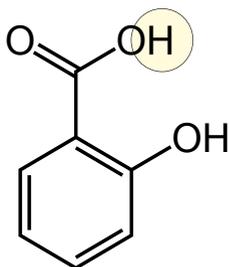


Fig. 53 Structural formula salicylic acid with proton of the carboxyl group

The calculation is different, depending on the type of application (Fig. 54) and the sample weight (volume vs. mass). The result can be calculated as acid concentration mol/l, acid content g/kg, mg/g or g/l or mg/ml. For some applications it is sensible to indicate the acid content as base consumption/g sample, thus mg (NaOH)/g or mg (KOH)/g. One usually titrates with a NaOH 0.1 mol/l.

The following must be observed:

- A titer determination takes place with potassium hydrogen phthalate.
- The sodium hydroxide must be protected with a CO₂ absorption means. Soda lime is recommended.
- The electrode can be calibrated. Buffers pH 4.01 and pH 6.87 are recommended. The calibration parameters serve as proof of the state of the pH electrode. The slope should be > 95 %.

The following titration parameters are recommended:

- Dynamic titration
- Normal (average) titration speed
- Dynamics: steep
- No damping
- End criterion 1 EQ with slope value 700 mV/ml and pH 12
- Dosing speed 100 %

Formula for the acid value in g/l:

$$\text{Content [\%]} = \frac{(\text{EQ} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ: Consumption titrant at the equivalence point
- B: Blank value of the solvent
- T: Exact concentration of the titrant
- M: Molar mass of salicylic acid 138.12 g/mol
- W: Weighed sample [g]
- F1: 100 (conversion %)
- F2: 1000 conversion ml - l)

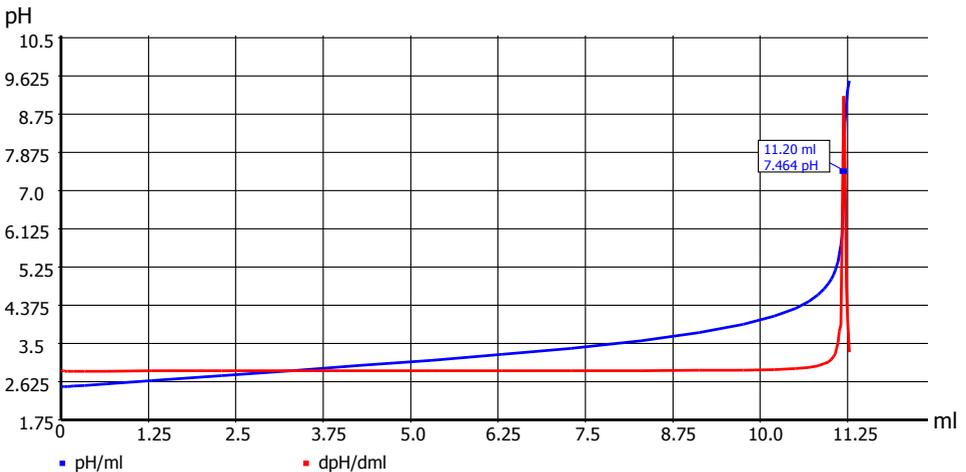


Fig. 54 Titration curve salicylic acid

Titration guide

Titration of phosphoric acid

The phosphoric acid is a tribasic acid, of which only the first two protons can be titrated in aqueous solutions. The third proton has such a high pK_s value that the aqueous sodium hydroxide solution is not basic enough. Some methods are based on the fact that phosphates form compounds with heavy metal ions, in which the protons are then released in an equivalent amount. The direct titration with sodium hydroxide and the calculation of the content is described here as difference of the two EQs (Fig. 55). Strong acids do not interfere, but weak or multibasic ones such as e.g. citric acid.

One usually titrates with a NaOH 0.1 mol/l.

The following must be observed:

- A titer determination takes place with potassium hydrogen phthalate.
- The sodium hydroxide must be protected with a CO_2 absorption means. Soda lime is recommended.
- The electrode can be calibrated. Buffers pH 4.01 and pH 6.87 are recommended. The calibration parameters serve as proof of the state of the pH electrode. The slope should be $> 95\%$.

The following titration parameters are recommended:

- Dynamic titration
- Normal (average) titration speed
- Dynamics: steep or average
- No damping
- End criterion 2 EQ with slope value > 200 mV/ml
- Dosing speed 65 %

Formula for the phosphoric acid in %:

$$\text{Content [\%]} = \frac{(\text{EQ2} - \text{EQ1}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

EQ1,

EQ2: Consumption of titrant at the respective equivalence point

T: Exact concentration of the titrant

M: Molar mass of phosphoric acid 98.00 g/mol

F1: 100 (conversion %)

W: Weighed sample [g]

F2: 1000 (conversion ml - l)

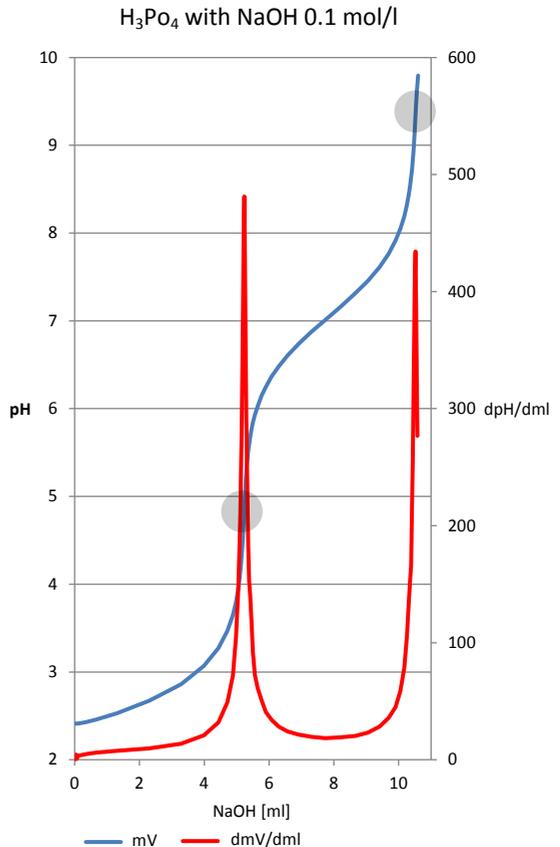


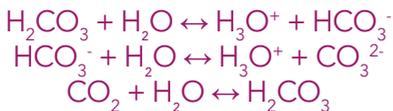
Fig. 55 Titration curve phosphorous acid with two EQs

Titration guide

Titration of Alk._{8.2} and Alk._{54.3}

The titration of the alkalinity (Alk.) is carried out with HCl and determines which proportions of carbonate and bicarbonate are contained in the water (Fig. 56). The alkalinity values are a measure of the temporary hardness of the water, which can be removed by boiling. Scale = lime precipitates during boiling, the CO₂ is boiled away. So that the results of manual titration can be compared with an indicator (phenolphthalein and methyl orange, often referred to as the p and m value), one titrates to endpoints (pH 8.2 and pH 4.3) [6]. The electrode must thus be calibrated.

The basis is the carbonate/hydrogen carbonate system in water:



The endpoint at pH 8.2 corresponds approximately to the carbonate content, the consumption between pH 8.2 and pH 4.3 to the hydrogen carbonate content. One usually titrates with a HCl 0.1 mol/l.

The following must be observed:

- A titer determination takes place with TRIS
- The electrode must be calibrated. Buffers pH 4.01 and 6.87 are recommended

The following titration parameters are recommended:

- Titration to two endpoints pH 8.2 and pH 4.3
- Normal (average) titration Speed
- No damping
- Dosing speed 15 %
- Delta value for the linear end part: 1.0
- Endpoint delay 10 s
- Linear steps 0.02 ml

Formula for the Alk_{8.2}:

$$\text{Alk}_{8.2}[\text{mmol/l}] = \frac{\text{EP1} * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

EP1: Consumption titrant [ml]
to pH 8.2
T: Exact concentration of the titrant
M: 1
V: Volume sample [ml]
F1: 1000 (conversion mol - mmol)
F2: 1

Formula for the Alk_{4.3}:

$$\text{Alk}_{4.3}[\text{mmol/l}] = \frac{\text{EP2} * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

EP2: Consumption titrant [ml]
to pH 4.3
T: Exact concentration of the titrant
M: 1
F1: 1000 (conversion mol - mmol)
V: Volume sample [ml]
F2: 1

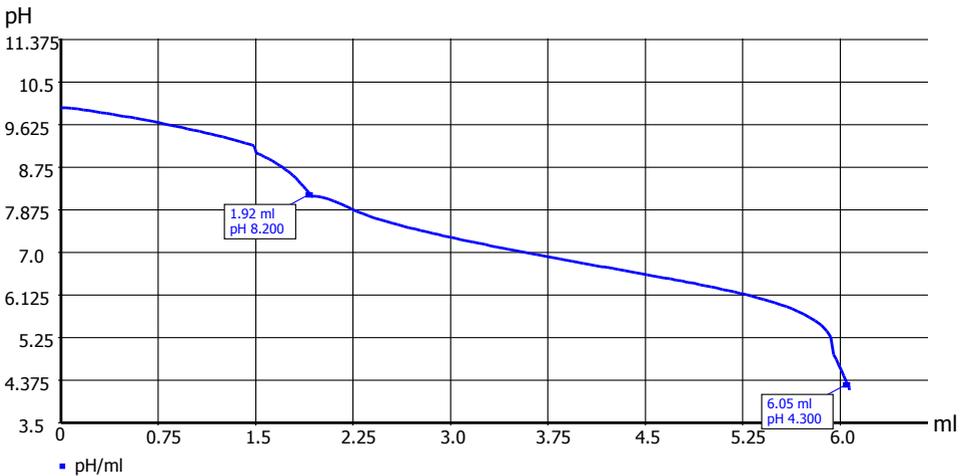
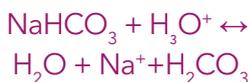
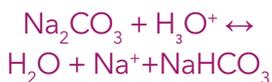


Fig. 56 Titration curve carbonate system with HCl on 2 EPs

Titration guide

Titration of sodium carbonate

Sodium carbonate is the sodium salt of carbon acid. It is titrated with hydrochloric acid. Sodium bicarbonate is formed in the first step, which is converted to carbonic acid in the second step (Fig. 57).



One usually titrates with a HCl 0.1 mol/l.

The following must be observed:

- A titer determination takes place with potassium hydrogen phthalate.
- The electrode can be calibrated. Buffers pH 4.01 and pH 6.87 are recommended. The calibration parameters serve as proof of the state of the pH electrode. The slope should be > 95%.

The following titration parameters are recommended:

- Dynamic titration to two EQs
- Dynamics: flat
- Dosing speed 100%
- Normal (average) titration speed
- No damping

With pure sodium carbonate it would be sufficient to calculate only one EQ. However, if free alkali is still present or more hydrogen carbonate through CO_2 intake, the difference of the two EQs is often evaluated.

Formula for the carbonate in g/l

$$\text{CO}_3^{2-}[\text{g/l}] = \frac{\text{EQ1} * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

EQ1: Consumption titrant [ml] until the first equivalence point

T: Exact concentration of the titrant

M: Molar weight of CO_3^{2-}
(60.01 g/mol)

V: Volume sample [ml]

F1: 1

F2: 1

Formula for the hydrogen carbonate in g/l

$$\text{HCO}_3^-[\text{g/l}] = \frac{(\text{EQ2} - \text{EQ1}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

EQ1: Consumption titrant [ml] until the first equivalence point

EQ2: Consumption titrant [ml] until the second equivalence point

T: Exact concentration of the titrant

M: Molar weight of HCO_3^-
(61.017 g/mol)

V: Volume sample [ml]

F1: 1

F2: 1

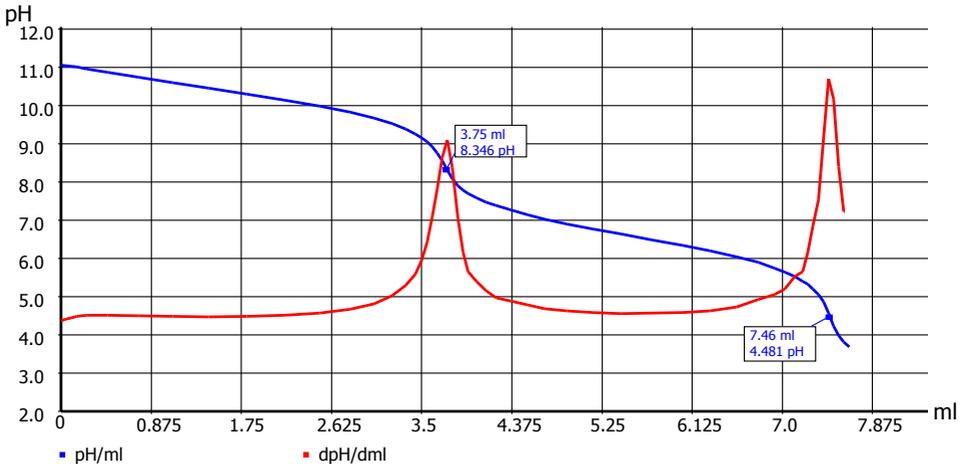


Fig. 57 Titration curve sodium carbonate with two EQs

Titration guide

Determination of pharmaceutical bases as hydrochlorides with NaOH

Pharmaceutical bases are usually titrated in acetic acid with perchloric acid.

Another method is the determination of the hydrochloride of the base. For this, the sample is mixed with an excess of HCl and titrated with NaOH. As the pKa values of free HCl and the hydrochloride differ significantly, one obtains two EQs whose difference corresponds to the hydrochloride of the base.

One example is the determination of lidocaine as hydrochloride. The titration is carried out in ethanol with aqueous NaOH (Fig. 58). The first jump corresponds to the excess amount of HCl (2 ml 0.1 mol/l). The difference between the two EQs corresponds to the hydrochloride of the nitrogen base. PharmEur describes the method with the addition of 5 ml of 0.01 molar HCl (or in an even lower concentration).

The following titration parameters are recommended:

- Dynamic titration to two equivalence points
- Normal (average) titration speed
- weak damping
- Dynamics: steep
- Titration end: 2 EQs, slope value flat

Formula for Lidocaine in %

$$\text{Lidocaine [\%]} = \frac{(\text{EQ2} - \text{EQ1}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the first equivalence point
EQ2: Consumption titrant [ml] until the second equivalence point
T: Exact concentration of the titrant
M: Molar weight of lidocaine (234.34 g/mol)
W: Weighed sample [g]
F1: 0.1 (conversion l - ml and %)
F2: 1

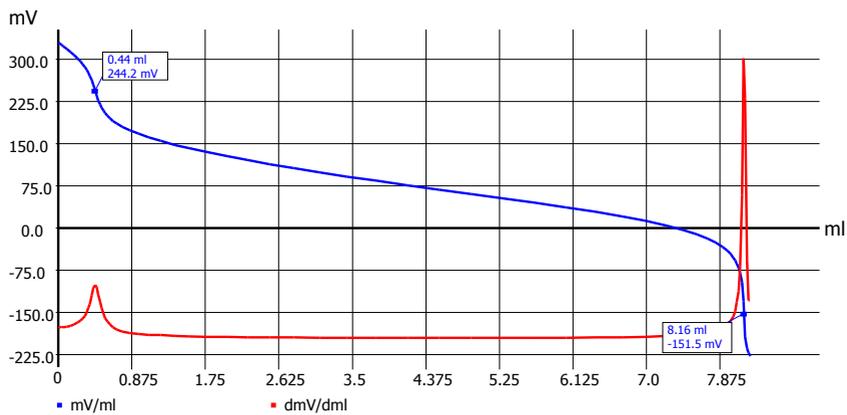


Fig. 58 Titration curve lidocaine hydrochloride

Titration guide

Determination of pharmaceutical bases with perchloric acid in glacial acetic acid

The most common method for the determination of pharmaceutical bases is the direct titration with perchloric acid in glacial acetic acid.

A titer determination of perchloric acid is carried out with potassium hydrogen phthalate. A blank value of the glacial acetic acid should be determined, even if the PharmEur does not require this. A pH electrode with a ground-joint diaphragm and a filling of LiCl in glacial acetic acid or ethanol is used as electrode. In our example, the titration of diclofenac sodium is shown. Approx. 0.250 g dichlophenac sodium are dissolved in approx. 30 ml glacial acetic acid (Fig. 59 and Fig. 60).

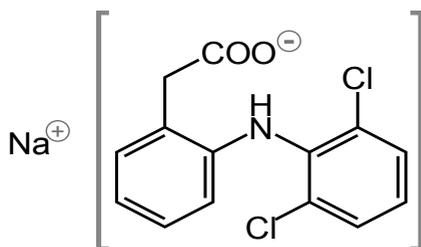


Fig. 59 Diclofenac sodium

The following must be observed:

- Determination of a blank value of the glacial acetic acid
- Consideration of the humidity of the molecule
- Humidity in glacial acetic acid or at the sample flattens the curve

As the jump is very clear, a dynamic titration can be performed up to an equivalence point. A ml end criterion ensures that an overflow of the titration vessel is impossible.

The following titration parameters are recommended:

- Dynamic titration, mV
- Dynamics: average
- Normal measurement speed
- average damping
- Titration end: 1 EQ, slope value 300 mV/ml

Formula for diclofenac sodium in %

$$\text{Lidocaine [\%]} = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
B: Blank value of the solvent
T: Exact concentration of the titrant
M: Molar weight of dichlorfenac sodium (318.1 g/mol)
W: Weighed sample [g]
F1: 0.1 (conversion l - ml and %)
F2: 1

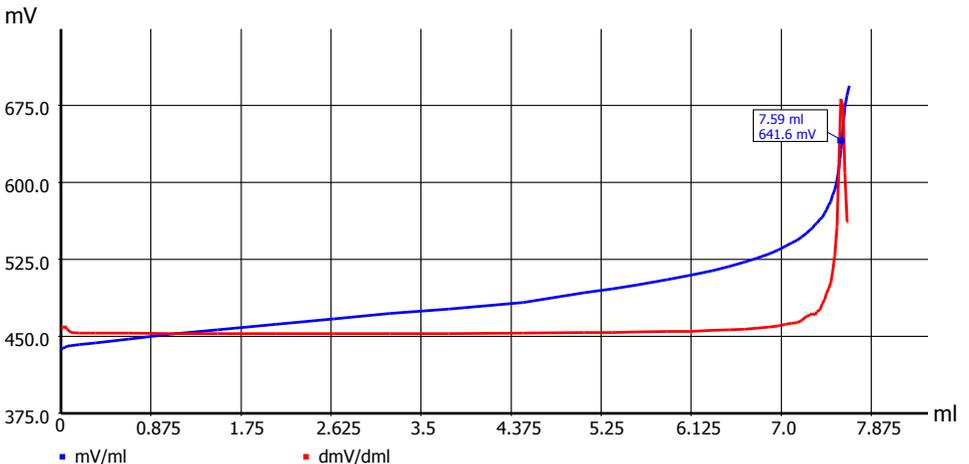


Fig. 60 Titration curve dichlorfenac sodium

Titration guide

Determination of the free fatty acids in vegetable oils (FFA)

The determination of free fatty acids in unsaturated oils and fats is a measure of their freshness. The lower the content, the fresher the oils.

The titration is carried out with KOH in isopropanol or ethanol. Ethanol/diethyl ether 1:1 is used as the solvent. The blank value of the solvent mixture must be determined (Fig. 61). Both the titration of the blank value and of the sample are carried out in a linear manner. The titration of the blank value takes place with an end consumption of 0.3 ml and an step size of 0.01 ml or 0.02 ml.

A fixed waiting period of 15 s is suitable for the blank value. A pH electrode with a ground-joint diaphragm and a filling of LiCl in ethanol is used as electrode.

The following titration parameters are recommended:

- Linear titration, mV
- Step size 0.05 ml
- Measuring speed:
 - Measurement time 4 s
 - Drift 10 mV/min
 - Min time 7 s
 - Max time 20 s
- strong damping
- Titration end: 1 EQ, slope value flat

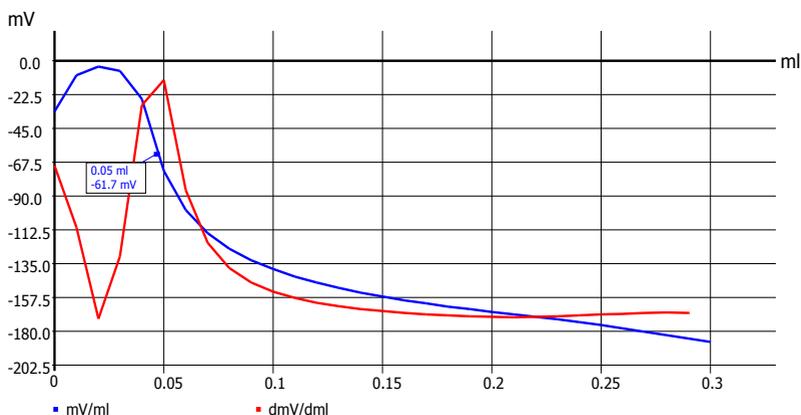


Fig. 61 Blank value solvent mixtures FFA

Formula for FFA in mg KOH / g

$$\text{FFA [mg KOH/g]} = \frac{(\text{EQ1}-\text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
- B: Blank value of the solvent
- T: Exact concentration of the titrant
- M: Molar weight KOH (56.1 g/mol)
- W: Weighed sample [g]
- F1: 1
- F2: 1

The sample for FFA should be in the range of 0.2 - 1 mg KOH/g at 10 - 20 g and in the range of 1 - 10 mg KOH/g at 1 - 3 g.

In the example, the FFA is given as mg KOH/g. In other cases, however, the reference magnitude is not the amount of KOH, but the molecular weight of the titrated oil, usually the oleic acid (molar weight 282 g/mol) is assumed:

Formula for FFA in % acid

$$\text{FFA [%]} = \frac{(\text{EQ1}-\text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
- B: Blank value of the solvent
- T: Exact concentration of the titrant
- M: Molar weight oleic acid (282.46 g/mol)
- W: Weighed sample [g]
- F1: 0.1 (conversion l - ml and %)
- F2: 1

The adaptation of the amplifier to the titration in organic media is important. The adaptation of the damping has been proven to be efficient, which can be adjusted in the method parameters. The strongest damping is adjusted here (Fig. 62).

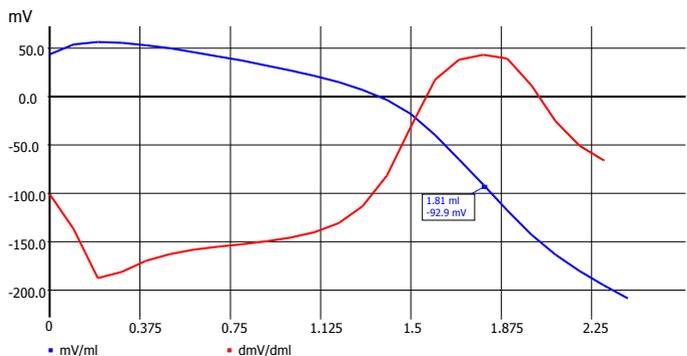


Fig. 62 Titration curves FFA in rapeseed oil

Titration guide

Determination of acids in oil (TAN, ASTM 664)

The titration of acids in oils is one of the most difficult applications. A mixture of toluene (50%), isopropanol (49.5%) and water (0.5%) is often used as solvent. Titrant is KOH in isopropanol. The challenge for the pH electrode is the titration in a medium that contains hardly any protons or ions at all. In addition, the glass membrane is occupied by the oil, which additionally complicates an exchange [5].

A pH electrode with ground-joint diaphragm is used, with LiCl in ethanol as electrolyte. The electrode must be cleaned, conditioned and be re-adapted to the solvent after each titration. For this, the electrode is rinsed successively in different solvents:

- 1 minute in toluene or toluene/ isopropanol
- 1 minute in water
- 1 minute in clean toluene/ isopropanol / water.

A titer determination is carried out with potassium hydrogen phthalate and the blank value of the solvent is determined. The blank value is performed as an EQ titration.

The titration of the blank value is carried out as a linear titration with steps size of 0.01 ml up to an EQ or a consumption of about 0.3 ml. One preferably titrates with a fixed waiting time of 10 to 20 s. At a higher consumption, the solvent mixture should be exchanged.

In some cases it is so small that no EQ can be detected. Then, one titrates with very small steps, e.g. 0.004 ml to the potential at which the EQ of the sample is found.

Fig. 63 shows a typical titration curve for the blank value of the solvent mixture. Here the BW is high enough to detect an EQ.

The TAN titration is carried out in a linear manner. The titration end is set to 4 to 6 ml or until an EQ is detected. The drift is often parameterized with a fixed waiting time of 15 s. This waiting time is adapted to the sample until a titration curve results, which enables a clear evaluation of the EQ.

Fig. 64 shows the titration curve of a used transformer oil. The EQ can be evaluated very well here. For different oils, the titration curve may be too shallow or too restless to detect an EQ. In this case, one has to titrate to an end potential. The potential which adjusts at the electrode in an aqueous buffer of pH 11 is used as the end potential.

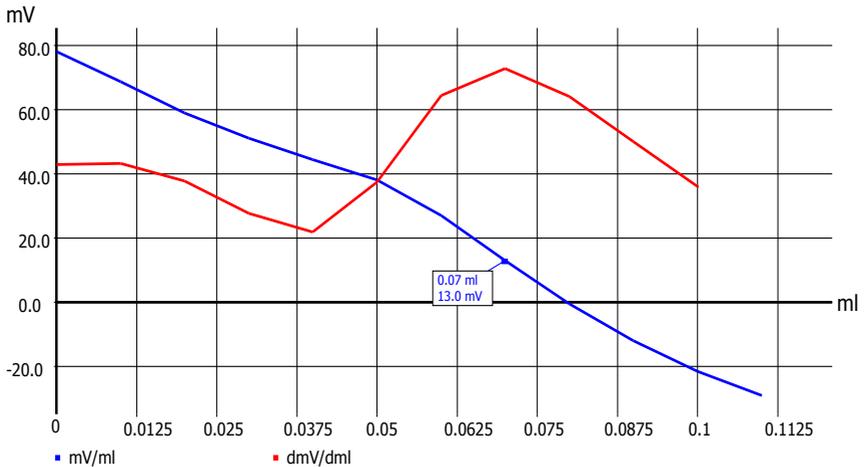


Fig. 63 Blank value titration TAN

Titration guide

The following titration parameters are recommended:

- Linear titration, mV
- Step size 0.05 ml
- Measuring speed:
fixed waiting time 15 s or
measurement time 4 s
Drift 10 mV/min
Min time 7 s
Max time 20 s
- strong damping
- Titration end:
1 EQ, slope value flat

Formula for TAN in mg KOH / g

$$\text{TAN [mg KOH/g]} = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

EQ1: Consumption titrant [ml] until the equivalence point

B: Blank value of the solvent

T: Exact concentration of the titrant

M: Molar weight KOH (56.1 g/mol)

W: Weighed sample [g]

F1: 1

F2: 1

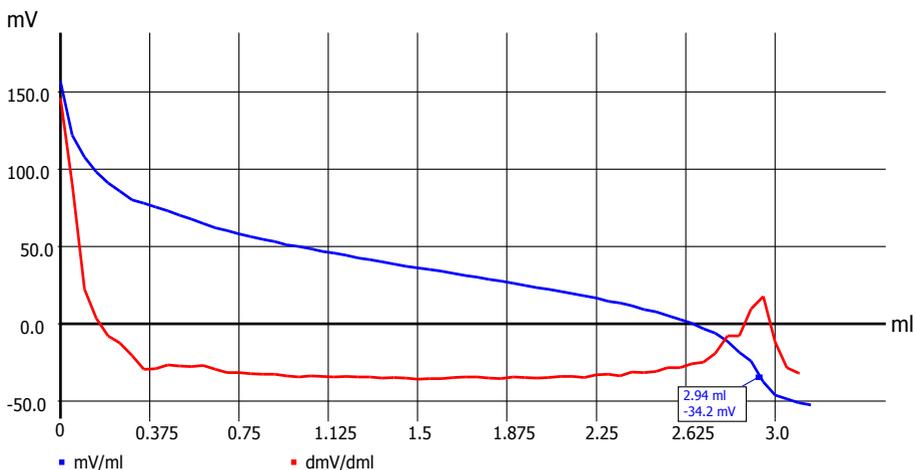


Fig. 64 Titration curve TAN of an oil sample

Determination of bases in oil (TBN, ISO 3771)

The base number in oils, like TAN, is a sum parameter and is determined according to [ASTM 2896 / ISO 3771](#).

A pH electrode with a ground-joint diaphragm and LiCl in glacial acetic acid is used as the electrolyte. If the base number of the sample is not too low, it is also possible to work with LiCl/ethanol. Many electrode adhesives are not resistant to acetic acid. The electrolyte LiCl in glacial acetic acid should therefore only be filled into electrodes that are intended for this purpose.

The solvent for the titration is acetic acid/chlorobenzene, the titrant is perchloric acid in glacial acetic acid. Potassium hydrogen phthalate is used for the titer determination. The blank value of the solvent must be determined. The result is calculated as mg KOH needed to neutralize 1 g of sample. The consumption should not exceed 4-6 ml, the sample amount must be adjusted accordingly.

A rule of thumb for the sample amount is: $\text{g sample} = 28 / \text{expected TBN}$. The TBN titration is carried out as a linear titration. The titration end is set to 4 to 6 ml or until an EQ is detected (Fig. 65). The step size should not be too small, e.g. 0.1 ml.

The titration is carried out as a mV titration either drift-controlled or with a fixed waiting time of 15 - 20 s.

Titration guide

The following titration parameters are recommended:

- Linear titration, mV
- Step size 0.1 ml
- Measuring speed:
 - Measurement time 4s
 - Drift 10mV/min
 - Min time 7s
 - Max time 20s
 - or fixed waiting time 15-20 s
- strong damping
- Titration end: 1 EQ,
- Slope value flat

Formula for TBN in mg KOH / g

$$\text{TBN [mg KOH/g]} = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

EQ1: Consumption titrant [ml] until the equivalence point

B: Blank value of the solvent

T: Exact concentration of the titrant

M: Molar weight KOH (56.1 g/mol)

W: Weighed sample [g]

F1: 1

F2: 1

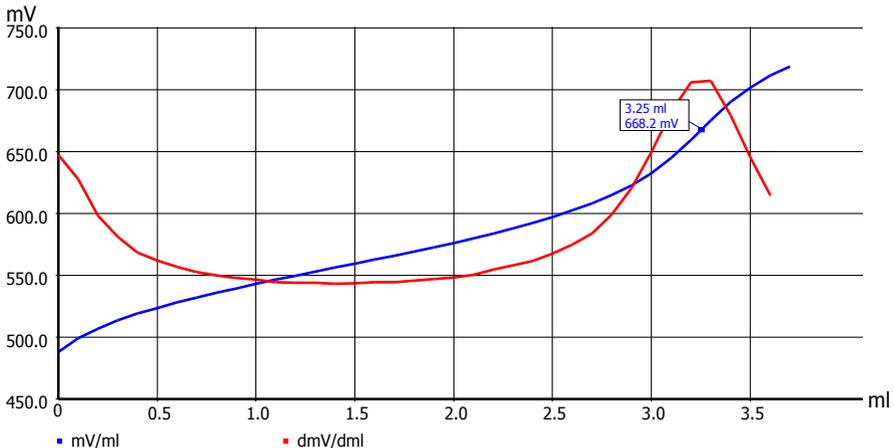
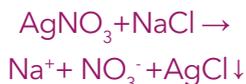


Fig. 65 Titration curve TBN

6.2 Argentometric titrations

Argentometric titrations are carried out with silver nitrate as titrant and silver electrodes. A combination electrode with silver indicator electrode and Ag/AgCl reference electrode is usually used. The reference electrolyte should contain as few chloride ions as possible: KNO_3 2 mol/l with little KCl (0.001 mol/l) is recommended.

The reaction equation is as follows:



For samples in which the pH is constant or also in organic solvents, a silver electrode can be used which has a glass electrode as the reference electrode. Due to its resistance, the glass electrode is connected to the indicator measuring input and the silver indicator electrode to the reference measuring input.

AgNO_3 is used as titration solution. The concentration can be 0.001 to 0.1 mol/l. The potential jump is more pronounced, the higher the concentration (Nernst law). As it is a precipitation titration, the formed precipitate can contaminate the electrode and disrupt the titration. This can be prevented by the addition of polyvinyl alcohol (1 ml of a 0.5% PVA solution). Such an addition is not necessary with very low contents. The titration must take place in an acid environment so that no silver hydroxide is formed. Diluted HNO_3 is suitable for acidification.

The titration can be carried out with samples with chloride contents of a few ppm - 100%. Depending on the chloride content, the amount of sample should be adjusted:

Chloride content [%]	weighed sample [g]
< 0.1	> 10
0.1 - 1	1 - 10
1 - 10	0.1 - 2
10 - 50	0.05 - 0.1
50 - 100	0.05

Titration guide

Titration of salt in butter

For food, sample preparation is important to capture all the chloride. Often the sample is crushed (also automatically with a homogenizer) or stirred in hot water.

Approximately 2-3 g of butter are weighed in, 100 ml of boiling water is added, 1 ml of HNO_3 1 mol/l is added, the electrode and the titration tip are dipped into the solution and the titration is started. The titration is carried out up to an EQ (Fig. 66). It can be seen from the increasing titration curve that an Ag indicator electrode and an Ag/AgCl reference electrode were used here. The result is calculated as % NaCl.

The following titration parameters are recommended:

- Dynamic titration to an equivalence point
- Dynamics: steep
- Measuring speed:
 - Measurement time 3 s
 - Drift 10 mV/min
 - Min time 3 s
 - Max time 15 s
- no damping
- Titration end:
 - 1 EQ, Slope value 400

Formula for sodium chloride in %

$$\text{NaCl} [\%] = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
B: Blank value of the solvent
T: Exact concentration of the titrant
M: Molar weight NaCl (58.443 g/mol)
W: Weighed sample [g]
F1: 0.1 (conversion l - ml and %)
F2: 1

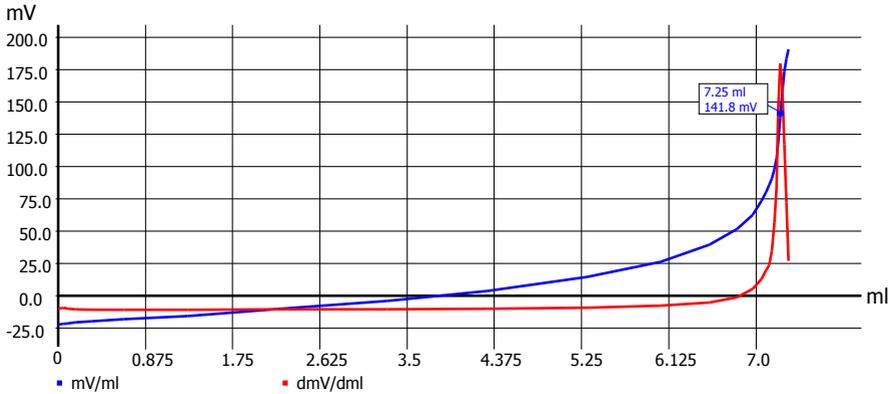


Fig. 66 Titration curve chloride in butter

Titration of chloride in drinking water

Up to 250 mg/l of chloride may be contained in drinking water, thus significantly less than e.g. in butter. The titration is analogous to the titration of salt in butter, only the slope of the EQ has to be adjusted due to the flatter jump.

100 ml water is mixed with 1 ml HNO_3 1 mol/l and the titration is started. The curve in Fig. 67 shows a falling titration, typical for a silver electrode with a glass reference electrode. The calculation takes place as mg Cl/l.

The following titration parameters are recommended:

- Dynamic titration to an equivalence point
- Dynamics: steep
- Measuring speed:

Measurement time	3 s
Drift	10 mV/min
Min time	3 s
Max time	15 s
- no damping
- Titration end: 1 EQ, gradient value 150 mV/ml

Titration guide

Formula for chloride in mg/l

$$\text{Cl}^- [\text{mg/l}] = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

EQ1: Consumption titrant [ml] until the equivalence point

B: Blank value of the solvent

T: Exact concentration of the titrant

M: Molar weight Cl⁻ (35,45 g/mol)

V: Volume sample [ml]

F1: 1000 (conversion g - mg)

F2: 1

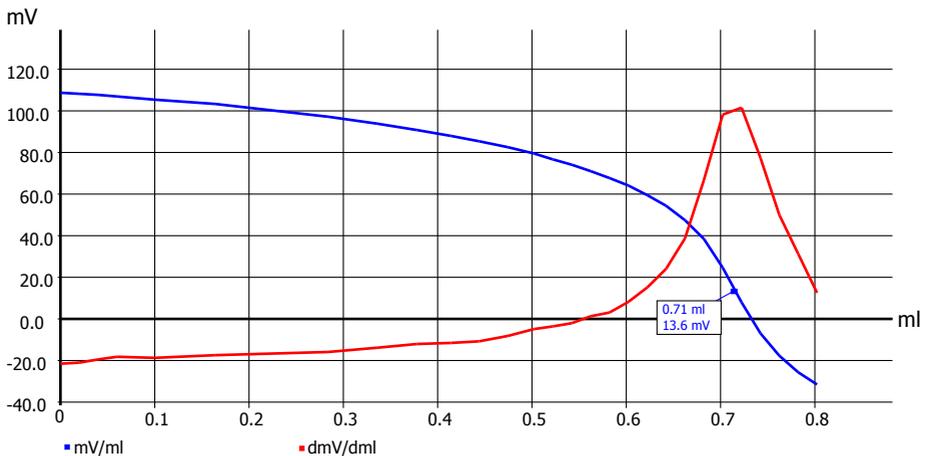


Fig. 67 Titration curve chloride in drinking water

6.3 Potentiometric redox titrations

In redox titrations, oxidizable or reducible samples are titrated with oxidizing or reducing agents.

Titrations with oxidizing agents generally show increasing titration curves falling with reducing agents. A titer determination of the titrant is recommended. The detection is performed with a combined platinum indicator electrode with an Ag/AgCl reference electrode.

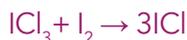
The titrations can be carried out as direct titration or as back titration.

In the back titration, e.g. an excess of oxidant is added and the reagent which is not converted is back titrated with a reducing agent. Even if back titration shows the errors of back and forth titration, benefits such as faster response and better detection are clearly in the foreground.

Iodine number for characterizing fats and oils

In the determination of the iodine number of an oil or fat, the oxidizable components and double bonds are determined. The more double bonds an oil contains, the higher the iodine number. The iodine number is defined as the amount of iodine that can be added to 100 grams of fat or oil.

One form of the determination takes place according to **DIN 53241-1:1995-05** with Wijs reagent (organic solvent, acetic acid, iodine, iodine trichloride). In an upstream reaction, the iodine trichloride and iodine react to iodine monochloride. The reaction mixture must be anhydrous, otherwise the formed iodine monochloride will decompose to HCl, I₂ and HI.



However, iodine monochloride in pure form is also available, so that one can also use a solution of iodine monochloride in glacial acetic acid (16.2 g / l).

Titration guide

The iodine monochloride reacts in an electrophilic addition to the double bond of the oil:



The excess iodine monochloride is converted with KI to I_2 :



The resulting I_2 is then titrated with sodium thiosulphate in a 1:1 reaction:



The iodine monochloride is dissolved in glacial acetic acid (16.2 g/l), the KI solution is aqueous (25 g/250 ml), magnesium acetate (45 g/l glacial acetic acid) is used as catalyst.

The sample is weighed into a 200 ml Erlenmeyer flask, 20 ml of glacial acetic acid, 25 ml of iodine monochloride solution and 20 ml of magnesium acetate solution are added. The flask is closed, shaken, allowed to stand in the dark for 5 minutes and titrated after addition of 15 ml of KI solution and 50 ml of distilled water (Fig. 68).

A blank value titration is carried out under the same conditions. As it is a back titration, the consumption of the sample is subtracted from the blank value (Fig. 69).

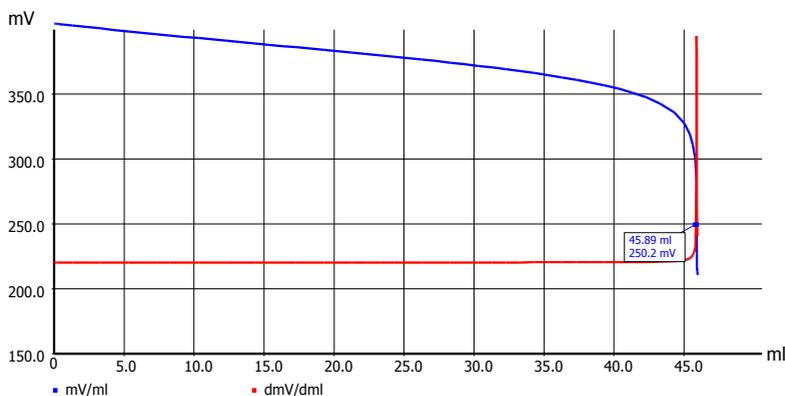


Fig. 68 Titration curve blank value iodine number

The following titration parameters are recommended for the titration and blank value determination:

- Dynamic titration to an equivalence point
- Dynamics: average
- Measuring speed:
 - Measurement time 3 s
 - Drift 10 mV/min
 - Min time 3 s
 - Max time 15 s
- no damping
- Titration end:
 - 1 EQ, slope value 350

Formula for iodine number in $\text{g}_{(\text{iodine})}/100\text{g}_{(\text{sample})}$

$$IZ = \frac{(B - EQ1) * T * M * F1}{W * F2}$$

- B: Consumption without sample
- EQ1: Consumption titrant [ml] until the equivalence point
- T: Exact concentration of the titrant
- M: Molar weight I (126.9 g/mol)
- W: Weighed sample [g]
- F1: 0.1 (conversion l - ml and reference to 100 g)
- F2: 1

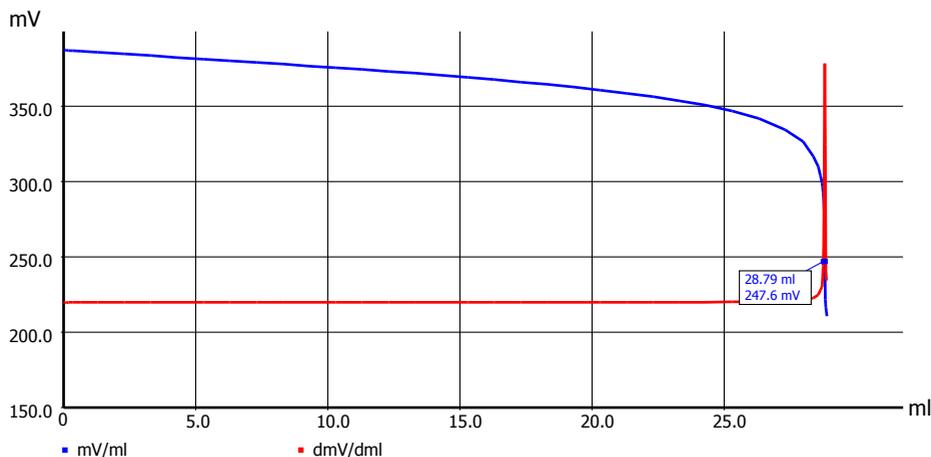


Fig. 69 Titration curve iodine number of olive oil

Titration guide

Determination of the vitamin C content with DCPIP

Vitamin C is added to many drinks as an antioxidant and also specified with its content. Lots of natural vitamin C contain citrus fruits and their juices.

The titration of ascorbic acid = vitamin C is possible as a redox titration with DCPIP (di-chlorophenol-indo-phenol) (Fig. 70). The ascorbic acid reduces the disodium DCPIP (Tillmann's reagent), a 1:1 reaction. As the redox potential drops during the titration and then increases again, a large step is initially dosed before the titration is continued in a linear manner. The blue DCPIP is decolourized during the titration.

As the DCPIP is not very stable, the titer is determined with freshly dissolved ascorbic acid in a first titration. Fig. 71 and 72 show the titration curve with calculations for the titer determination and sample titration.

For the preparation of the DCPIP solution, 163.1 mg of DCPIP is added to 250 ml water and stirred at 50° C for 20 minutes. The solution is then filtered, transferred to a 500 ml volumetric flask, 50 mg KHCO_3 (for stabilization) added and filled up to 500 ml. For the titer determination, freshly prepared ascorbic acid solution is used: 50 mg of ascorbic acid is dissolved in water in a 100 ml volumetric flask, 10-20 ml of oxalic acid solution (100 g/l) is added and filled up to 100 ml.

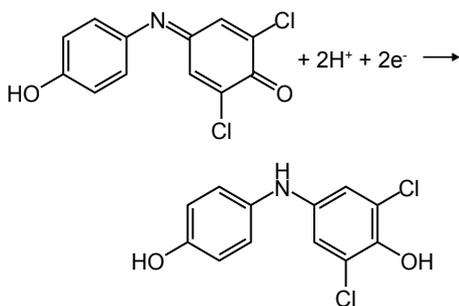


Fig. 70 Redox reaction DCPIP

For the titer determination, 10 ml of oxalic acid solution (100 g/l), 15 ml of distilled water and 1 ml of sodium acetate solution (100 g/l) are placed in a beaker, 1 ml of the ascorbic acid solution is added and is titrated with the DCPIP solution.

The following titration parameters are recommended:

- Linear titration to an equivalence point
- Step size: 0.05 ml
- Measuring speed:
 - Measurement time 2 s
 - Drift 40 mV/min
 - Min time 5 s
 - Max time 10 s
- Pre-titration 1.2 ml, 10s waiting time
- no damping
- Titration end: 1 EQ, slope value 80

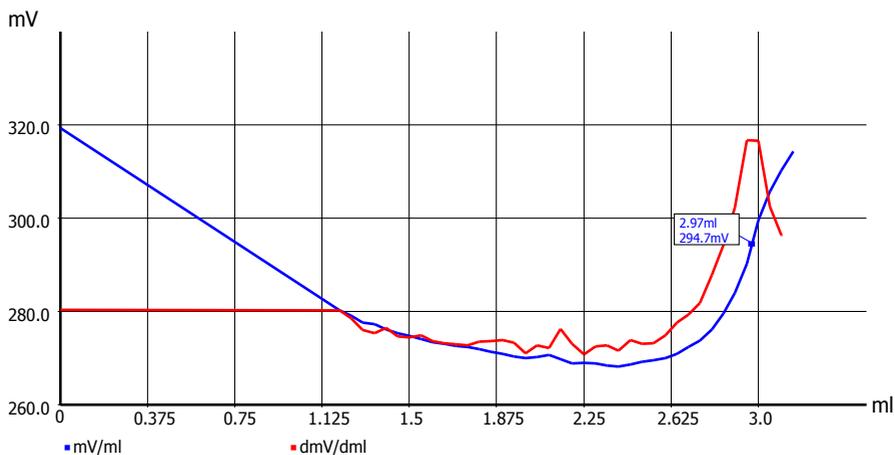


Fig. 71 Titer determination of DCPIP with ascorbic acid

Titration guide

For the titration of a juice sample, 0.5 - 5 g of sample are mixed with 40 ml of oxalic acid solution (100 g/l) and 1 ml of sodium acetate solution (100 g/l). 40 ml water is added after 5 minutes and titrated with DCPIP (Fig. 72).

The following titration parameters are recommended:

- Linear titration to an equivalence point
- Step size: 0.05 ml
- Measuring speed: fixed waiting time 7 s
- no damping
- Titration end: 1 EQ, slope value 80

Formula for ascorbic acid mg/100g

$$\text{Ascorbic acid [mg/100g]} = \frac{(EQ1-B) * T * M * F1}{W * F2}$$

- EQ1: Consumption titrant [ml] until the equivalence point
B: Blank value of the solvent
T: Exact concentration of the titrant
M: Molar mass of ascorbic acid (176.12 g/mol)
W: Weighed sample standard/sample
F1: 100 (conversion l - ml, g - mg, reference to 100 g)
F2: 1

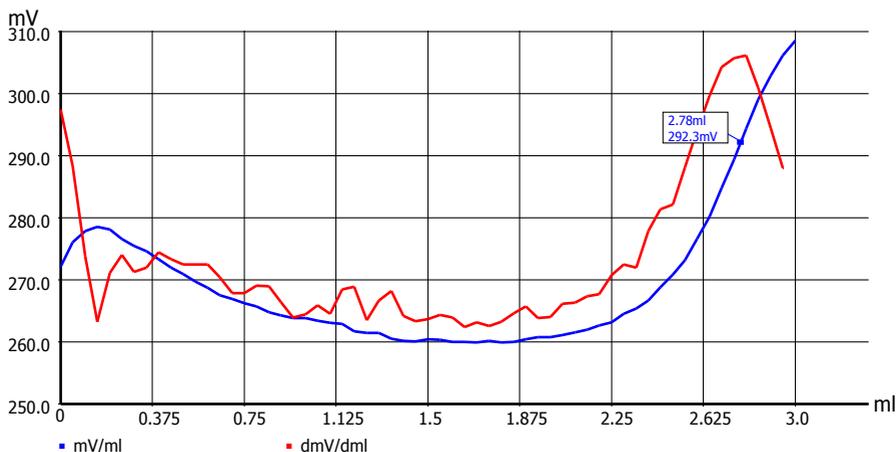


Fig. 72 Titration ascorbic acid in a drink

6.4 Dead Stop Titrations

The Dead Stop titration can be used when reversible redox pairs occur. An important example is the titration with iodine. The detection with a double platinum electrode proceeds much faster than the potentiometric detection with a platinum redox electrode. At the endpoint of the titration, both iodine and iodide ions are present in the solution. Two anions of iodide migrate to the anode and release two electrons there. At the cathode, the iodine absorbs two electrons and reacts to form two iodide ions. With an applied (low) voltage (approx. 100 mV) a current flows, which is detected (Fig. 73).

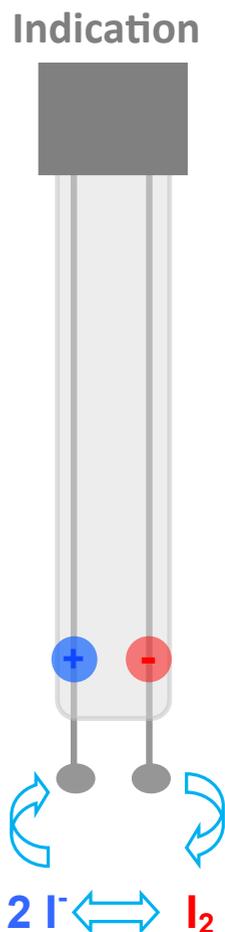


Fig. 73 Reversible redox reaction of iodine

Titration guide

Direct iodometric determination of vitamin C

The iodometric titration of ascorbic acid is usually performed as a Dead Stop titration. It is the usual titration for many drinks. As sulfite ions can also be present in drinks, they must be converted with glyoxal.

50 ml of sample and 2 ml of glyoxal solution (40% in water, adjusted to pH 7 with NaOH) are placed into a beaker. After 5 minutes, 5 ml of 25% sulfuric acid are added and titrated with 0.01 mol/l iodine solution. The content is calculated as ascorbic acid mg/l.

In our example (Fig. 74), the ascorbic acid content of a fruit juice was determined. The iodometric determination offers - despite the lower selectivity - some advantages over the titration with DCPIP:

Iodine solutions are significantly more titer-stable than DCPIP solutions, additionally iodine standard solutions are available in various concentrations.

The following titration parameters are recommended:

- Dead Stop Titration
- linear step: 0.02 ml
- Pre-titration: 0.1 ml
- Dosing speed: 20 %
- Titration direction: increasing
- Measuring speed: fixed waiting time 1 s
- Polarization voltage 100 mV
- Delta endpoint: 2.0 μ A
- Titration end: 2.5 μ A
- Endpoint delay: 5 s

Formula for ascorbic acid mg/l

$$\text{Ascorbic acid [mg/l]} = \frac{(EP1 - B) * T * M * F1}{V * F2}$$

- EP1: Consumption titrant [ml] until the endpoint
B: Blank value of the solvent
T: Exact concentration of the titrant
M: Molar weight ascorbic acid (176.12 g/mol)
V: Volume sample [ml]
F1: 1000 (conversion g - mg)
F2: 1

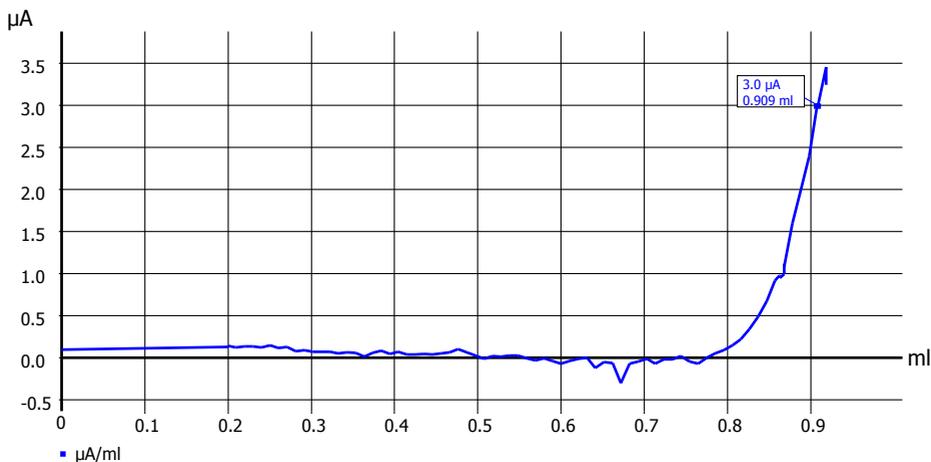


Fig. 74 Titration curve ascorbic acid with iodine

Determination of the SO_2 content in wine

Wine is protected from oxidation by adding SO_2 . Free and bound SO_2 are therefore differentiated.

The free SO_2 is determined by adding 3 ml sulfuric acid 10%, 30 mg Na_2EDTA and 10 ml KI solution (5%) to the 50 ml sample in a beaker and titrating immediately with iodine. The total SO_2 is determined by adding 8 ml 4 mol/l NaOH to a 50 ml sample and waiting 5 minutes. Then 10 ml of 10% sulfuric acid are added and titrated immediately with iodine.

The titre of the iodine solution can be determined with thio-sulphate solution (Fig. 75). If additionally ascorbic acid is present in the sample, the sum of all reductones is titrated in this application. The ascorbic acid can be determined after the addition as described in the section "Direct iodometric determination of vitamin C" according to the reaction of SO_2 with glyoxal.

Titration guide

The following titration parameters are recommended:

- Linear step: 0.02 ml
- Pre-titration: none
- Dosing speed: 20 %
- Titration direction: increasing
- Measuring speed: fixed waiting time 1s
- Polarization voltage 100 mV
- Delta endpoint: 1.0 μA
- Titration end: 2.0 μA
- Endpoint delay: 5 s

Formula for SO_2 in mg/l

$$\text{SO}_2[\text{mg/l}] = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

- EP1: Consumption titrant [ml] until the endpoint
B: Blank value of the solvent
T: Exact concentration of the titrant
M: Molar weight SO_2 (64.06 g/mol)
V: Volume sample [ml]
F1: 1000 (conversion g - mg)
F2: 1

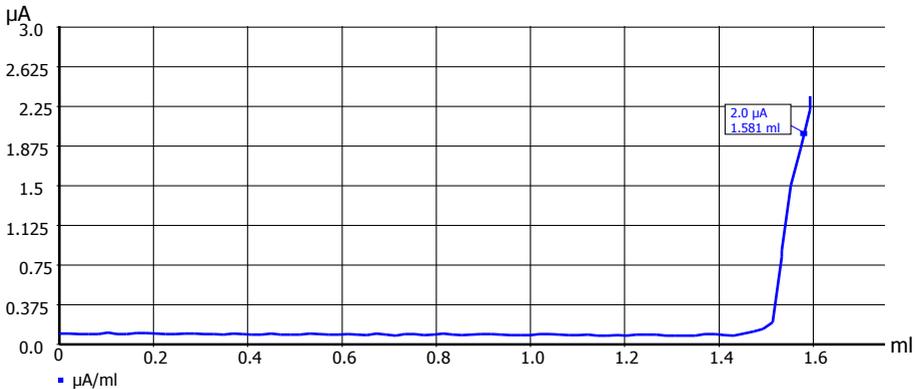


Fig. 75 Titration curve SO_2 in wine

6.5 Complexometric titration

Complexometry enables the determination of numerous metal ions. Chelate complexes have higher stability than complexes with several smaller ligands for two reasons:

- One molecule instead of several small ligands reacts with a central atom (entropy effect)
- If a bond is free, the metal central atom still remains bonded

Na_2EDTA , di-sodium-ethylenediamine-tetra acetic acid is often used. The stability of the complexes there depends on the pH. The higher the pH value, the more stable the complex. In acidic solution, the less dissociated acid provides less complexation possibilities. The pH dependence of the complex stability can be exploited during the titration. Stable complexes can still be titrated in acid, while less stable complexes require a high pH value.

At high pH values, the hydroxide formation is a competitive reaction. Work is often done in ammoniacal solutions.

The detection of the titration is carried out with ion-sensitive indicator electrodes (ISE) and a (usually separate) Ag/AgCl reference electrode, preferably with a platinum diaphragm.

Titration guide

Calcium and magnesium in drinking water

In drinking water, calcium and magnesium form the permanent hardness of the water as cations. The determination of water hardness is an important parameter of water chemistry. Calcium and magnesium can be determined next to each other with Na_2EDTA and a calcium-sensitive electrode.

Two potential jumps occur during titration (Fig. 76). Their form can be influenced by the pH value and the addition of auxiliary complexing agents. At a very high pH value, the weaker Mg complex is also stable and the difference between the Ca and Mg complex in the potential is very low. This means that first the stronger Ca complex forms, but that the Mg jump follows soon.

The first derivation therefore shows only a flat first jump for the calcium. Only after the magnesium, if no other metals are present, comes a strong jump.

If the pH value decreases, the Mg complex becomes less stable and the Ca jump more pronounced. The first derivation shows to peaks of an approximately same height. If the pH value is too low, Mg can no longer be detected, but the Ca complex also becomes less stable, the potential jump will be flatter.

In practice, one titrates at a pH value of about pH 8-9. Acetylacetone and TRIS are added as auxiliary complexing agents.

In the titration of tap water, 100.00 ml of the sample are pipetted into a 150 ml beaker. 15 ml TRIS/acetylacetone buffer (20.4 g TRIS and 12 ml acetylacetone to 1000 ml) are added and titrated with 0.05 mol/l EDTA.

A Ca-ISE indicator electrode and an Ag/AgCl reference electrode with a platinum diaphragm are used as electrodes.

The following titration parameters are recommended:

- Dynamic titration
- Dynamics: flat
- Dosing speed 100%
- Measuring speed:
 - Measurement time 4 s
 - Drift 5 mV/min
 - Min time 5 s
 - Max time 12 s
- no damping
- Titration end: 2 EQ,
- slope value 120

Formula for calcium oxide [mg/l]

$$\text{CaO [mg/l]} = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
 B: Blank value of the solvent
 T: Exact concentration of the titrant

- M: Molar mass of CaO (56.08 g/mol)
 V: Volume sample [ml]
 F1: 1000 (conversion g - mg)
 F2: 1

Formula for magnesium oxide [mg/l]

$$\text{MgO [mg/l]} = \frac{(\text{EQ1} - \text{EQ2}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the first equivalence point
 EQ2: Consumption titrant [ml] until the second equivalence point
 B: Blank value of the solvent
 T: Exact concentration of the titrant
 M: Molar mass of MgO (40.32 g/mol)
 V: Volume sample [ml]
 F1: 1000 (conversion g - mg)
 F2: 1

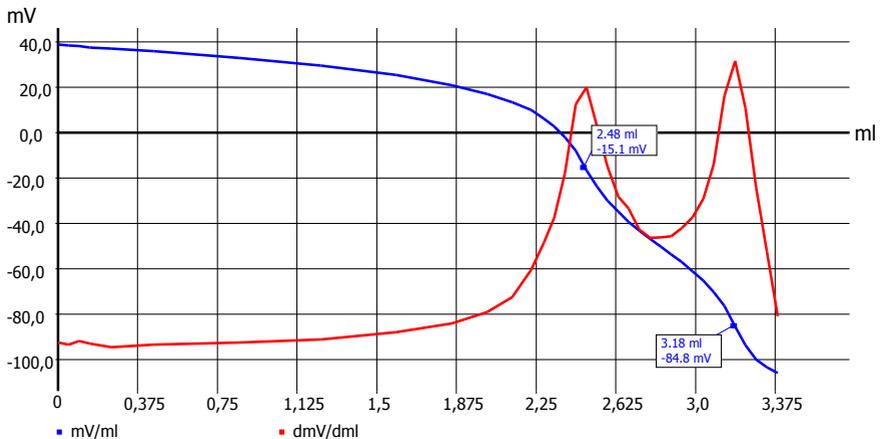


Fig. 76 Titration curve drinking water

Titration guide

Total hardness in drinking water

If the total hardness is to be determined, it often makes sense to have only one jump in the titration curve (Fig. 77). In this case, the sum of all metals is determined. A Cu-ISE indicator electrode (solid-state electrode) and an Ag/AgCl reference electrode with a platinum diaphragm is used as indicator electrode. So that all metals can be detected, $\text{Cu}(\text{NH}_4)_2\text{EDTA}$ 0.1 mol/l is added as indicator. With very small contents (< 0.1 °dH), a blank value must be determined.

Almost all divalent metal ions can be titrated in the same manner. The water hardness is nowadays given mainly in mmol/l alkaline earth ions. From this it is easy to calculate the water hardness in other units such as °dH or °fH.

5 ml of ammonium chloride/ammonia buffer pH 10 are added to a 100 ml sample and 1 ml of indicator $\text{Cu}(\text{NH}_4)_2\text{EDTA}$ 0.1 mol/l is added, then one titrates with Na_2EDTA 0.05 mol/l.

The following titration parameters are recommended:

- Dynamic titration
- Dynamics: flat
- Dosing speed 100%
- Measuring speed:
 - Measurement time 4 s
 - Drift 3 mV/min
 - Min time 5 s
 - Max time 12 s
- no damping
- Titration end: 1 EQ, slope value 120 mV/ml

Formula for water hardness [mmol/l]

$$\text{Water hardness [mmol/l]} = \frac{(\text{EQ1} - \text{EQ2}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
B: Blank value of the solvent
T: Exact concentration of the titrant [mol/l]
M: 1
V: Volume sample [ml]
F1: 1000 conversion g - mg
F2: 1

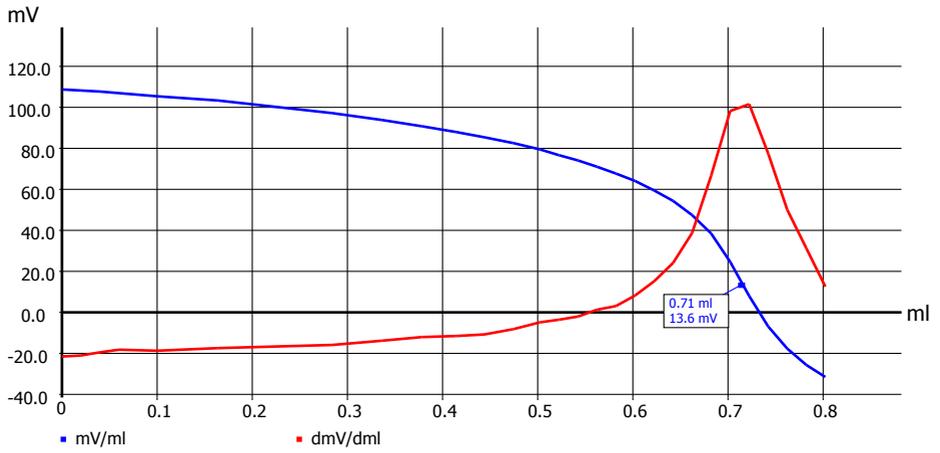


Fig. 77 Titration curve drinking water

Titration guide

6.6 Determination of molecular weights by titration

Titration is usually a method for the quantitative determination of known samples. The method can also be used for the determination of substance sizes if the content of a sample is clearly and precisely known.

The simplest case is a reversal of the calculation formula for the determination of salicylic acid:

$$\text{Salicylic acid [\%]} = \frac{\text{EQ} * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

EQ: Consumption titrant [ml] until the equivalence point

T: Exact concentration of the titrant [mol/l]

M: Molar weight [g/mol]

W: Volume

F1: 0.1 (conversion l-ml and %)

F2: 1

The formula indicates the acidity in % of a salicylic acid solution having a molecular weight of 138.12. However, if the content is known very accurately (because a pure compound is present), the molecular weight can be calculated from the consumption:

$$\text{Molar mass [g/mol]} = \frac{\text{W} * \text{F2} * [\%]}{\text{EQ} * \text{T} * \text{F1}}$$

W: Volume

[%]: Content in %

EQ: Consumption titrant [ml] until the equivalence point

T: Exact concentration of the titrant [mol/l]

F1: 0.1 (conversion l-ml and %)

F2: 1

If a compound is thus prepared in pure form, its molecular weight can be determined in this manner. The most common application is certainly the determination of the crystal water of a molecule, as the molecular weight changes significantly with crystal water.

6.7 Determination of pK_s values

Further substance-specific parameters can be determined from the titration curve: pK_s value (acid strength), pK_b value (base strength), complex stability constants, solubility products, stability constants and extraction equilibria.

As an example, a simple possibility serves for the determination of the pK_s value:



Here, the HAc acetic acid is an example of a monobasic acid which dissociates in water to a hydronium ion and acetate anion to a small extent. The concentration of water is considered constant in diluted solutions and is included in the equilibrium constant.

$$K_s = \frac{[\text{H}_3\text{O}^+] \cdot [\text{Ac}^-]}{[\text{HAc}]}$$

The negative logarithm of the equation is:

$$pK_s = \text{pH} - \log \frac{[\text{Ac}^-]}{[\text{HAc}]}$$

At the point on the titration curve where HAc and acetate ions have the same concentration, the pH is equal to the pK_s value:

$$\text{pH} = pK_s$$

This point, the half neutralization point (HNP), can be read from the titration curve (Fig. 78).

In methods for determining the pK_s value, the equivalence point is thus determined first. The pK_s value is then determined from the titration curve during the consumption $EQ/2$ ("y at x"). This is also possible with several jumps and EQs in a first approximation.

Titration guide

However, the pK_s values thus obtained are still subject to small errors. In order to accurately determine the pK_s value of an acid, other factors must be considered, for example:

- Electrode properties
(Slope, zero point, deviation from the theoretic behavior in acid and alkaline)
- The ion activities instead of the concentrations
- Evaluation of a larger curve area instead of an individual data point

Special software (for example Hyperquad) is used for the evaluation.

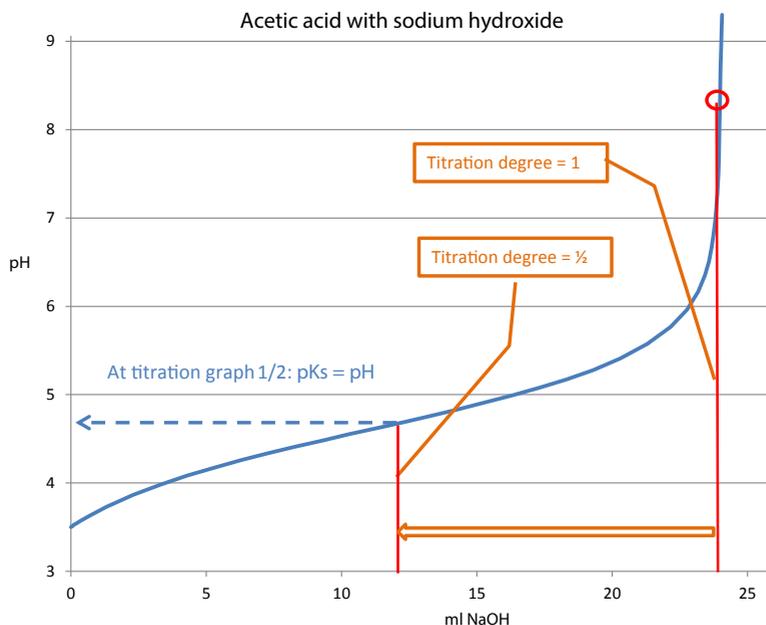


Fig. 78 Graphic representation of the pK_s value from the HNP point

An interesting variant is the representation of an acid profile. The pH value of a titration curve is plotted on the x-axis and the quotient dml/dpH on the y-axis, similar to the gradient of the titration curve, only transferred to the normal pH-y axis. The pK_s value can be recognized as the maximum (Fig. 79).

The advantage of this representation is evident in applications where several acids or acid centers are present in a molecule. In all cases, it is sensible to have more data points in the flat part of the titration. Dynamic titration is therefore unsuitable and linear titration is the method of choice.

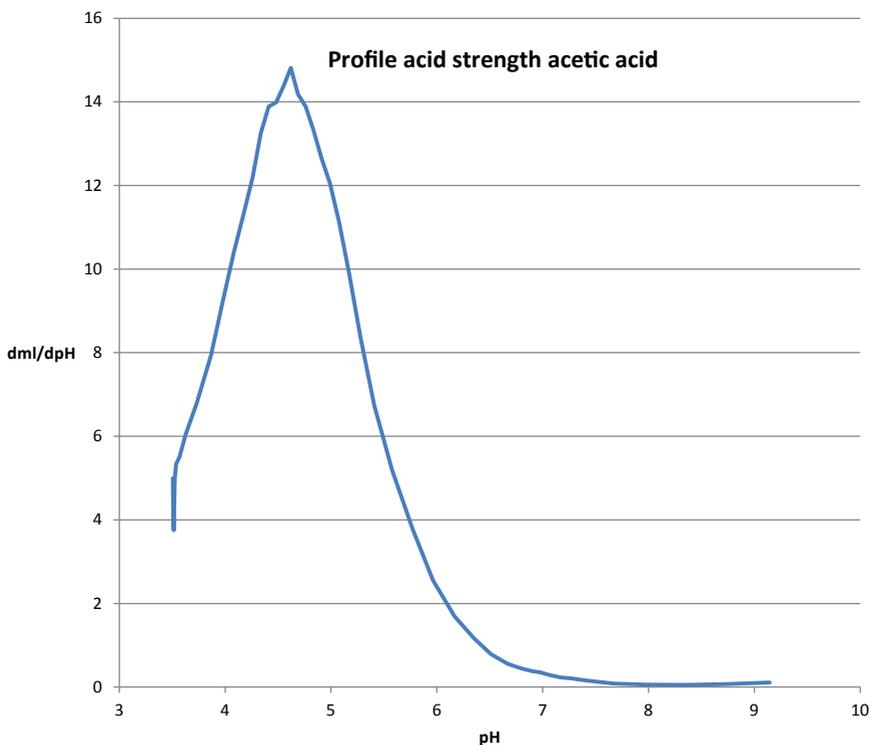


Fig. 79 Graphic representation of the acid strength with pK_s value as maximum

Titration guide

6.8 pH Stat titrations

pH Stat titrations can cover very different applications. Even analog potentials of other sensors can be kept constant.

Typical applications are:

- Enzymatic titrations in which protons are released.
- Extraction reactions, e.g. of soil samples from which alkaline acid components are released for 24 hours by an acid.
- Stability studies of e.g. concrete at very low pH values, in order to get an idea of the corrosion behavior.
- Crystal growth, in which the ions, which are removed by crystallization from the solution, are supplied continuously in order to always obtain the same concentration.
- Neutrality reactions over a longer period of time.

In the pH Stat titration, one often works under nitrogen at an accurately set temperature to prevent the influence of CO₂ from the air.

The titration is divided into phases; an setting phase in which the starting pH must first be reached, at which the reaction proceeds optimally and a Stat phase in which a defined pH value or measured value must be maintained (Fig. 81).

The following can be consulted as the result:

- The total consumption [ml]
- The consumption of the Stat phase without setting phase [ml]
- The gradient of the Stat phase consumption per time [ml/s] or [mmol/s]

The duration of the stat phase starts when the pH value of the reaction is reached. Two different times can be set as time variable; the total duration of the titration and the interval for the documentation. The total duration is the period during which the pH value is kept constant. The time interval defines the number of measurement points for the documentation. One also titrates between these intervals and the pH is kept constant.

If a titration takes 24 hours, that are recorded every five minutes. 288 value triplets with consumption [ml], time [s] and pH value [pH] are obtained.

Fig. 80 shows a data section of the pH Stat titration from Fig. 81 with a recording frequency of two seconds. A pH value around pH 7.00 is kept constant.

The pH value is kept very constant on average between the documented time and volume values.

Time [s]	NaOH [ml]	pH value [pH]
...
44.013	3.509	6.905
46.014	3.574	7.116
48.016	3.624	6.984
50.018	3.724	6.977
52.02	3.759	6.987
54.021	3.857	6.957
56.023	3.874	7.043
58.024	3.974	6.874
60.025	4.024	7.073
62.026	4.106	6.867
64.028	4.174	7.089
...

Fig. 80 pH-Stat table with an interval of 2 s

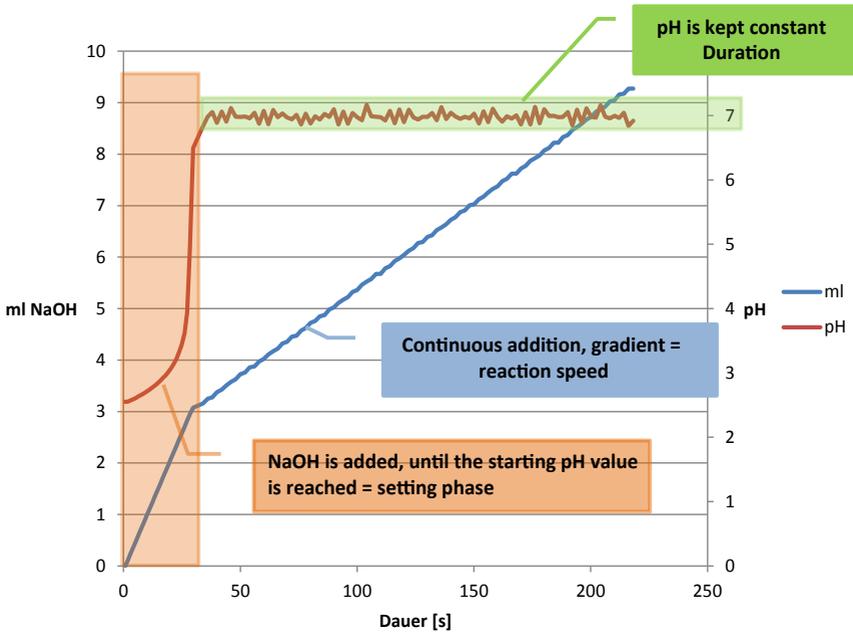


Fig. 81 pH-Stat titration curve with the phases of the pH Stat titration

Titration guide

6.9 Gran titrations

The Gran titration is led back to two publications by Gunnar Gran [7], [8]. It is based on a linearization of titration curves.

The basis is the Nernst equation:

$$E = E^0 + \frac{R \cdot T}{z_e \cdot F} \cdot \ln \frac{a_{\text{ox}}}{a_{\text{red}}}$$

E	Electrode potential
E ⁰	Standard electrode potential
R	Universal or molar gas constant R = 8.314 J mol ⁻¹ K ⁻¹
T	absolute temperature (=Temperature in Kelvin)
z _e	Number of electrons transferred (also equivalence number)
F	Faraday constant, F = 96485.34 C mol ⁻¹
a	Activity of the respective redox partner

The acid/base equilibrium is contained in the equation in a logarithmic form. An exponential notation thus leads to a linearization of the titration curve. Thus if, taking into account the volume correction, a titration of a base with a strong acid is calculated according to the formula

$$(\text{Start volume} + \text{titration volume}) \cdot 10^{\text{pH}}$$

(and the highest value is scaled to 1), the green straight line in Fig. 82 is obtained. The "Gran" values do not reach the value "0", but they become very small. If a straight line is now placed through the Gran function until just before the equivalence point, the Gran line will intersect the x-axis exactly at the equivalence point. The values can also be extrapolated linearly, the titration does not have to reach this point then. The advantage is of course that "later" disturbances are not included.

Analogously, the excess of hydrochloric acid can be calculated back to the last equivalence point with the Gran function, in that the pH value is used as a negative exponent in the Gran equation:

$$(\text{Start volume} + \text{titration volume}) \cdot 10^{-\text{pH}}$$

This Gran function can be seen as an orange function in Fig. 82. In order to detect no further bases or acids, the straight line area must not be placed too close to the equivalence point.

This opens up the possibility of a number of applications. Whenever the endpoint or equivalence point is disturbed by other effects, Gran titration is an alternative. Examples are:

- Determination of the acid capacity in waters where other acids (humic acids, phosphates) than carbonic acid interfere with the usual endpoints.

- Acid samples in which acid/base titrations falsify metals by hydroxide formation at the equivalence point.
- The pH value of the equivalence point must not be reached because a subsequent reaction is then no longer possible.

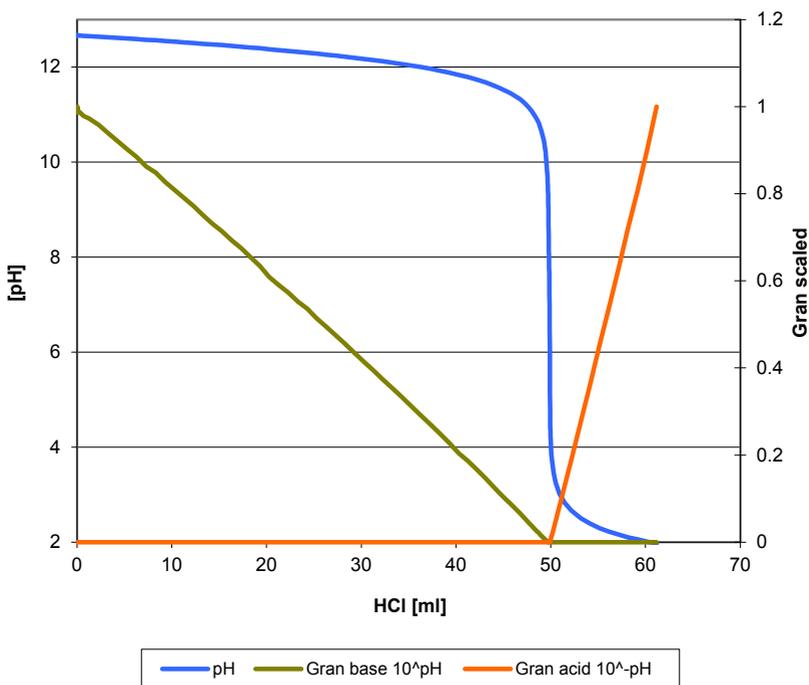


Fig. 82 Gran function at a titration of NaOH with HCl

Titration guide

A widely used application is the determination of alkalinity in seawater [9].

The standards

ISO 22719:2008 [9] ASTM D3875 - 08 [10] ASTM D1067 - 06 [11] ASTM D513 - 06 [12]

describe methods for determining the hydrogen carbonate or the alkalinity for various waters. Even in wooded areas, a simple endpoint titration is often not possible due to humic acids [13].

The determination of the alkalinity should be picked out here. The CO_2 equilibrium has a large influence on our climate. A multiple of the CO_2 content of the atmosphere is dissolved in seawater. If the pH value decreases and/or the temperature increases, less CO_2 dissolves in the seawater. The change of the pH value is called acidification. Instead of a pH value of 8.3, nowadays only a pH 8.1 is usually reached.

The titration is carried with HCl up to a value of pH 3.0. For a range of pH 4.0 to 3.0, a Gran evaluation takes place.

In Fig. 83, the classic titration curve is shown in dark blue. The evaluation range of the Gran titration is marked with dark blue dots. The light blue first derivation shows how difficult it would be to calculate an equivalence point or endpoint. The Gran function is represented in red and orange. For the evaluation range between pH 4 and 3, the Gran straight line is marked with red dots. The extrapolation of the Gran straight line with the x-axis gives the alkalinity.

The excess of hydrochloric acid is calculated back to the last EQ by means of the Gran evaluation. As a result, disturbances in the area of the EQ have no influence on the result.

Alkalinty

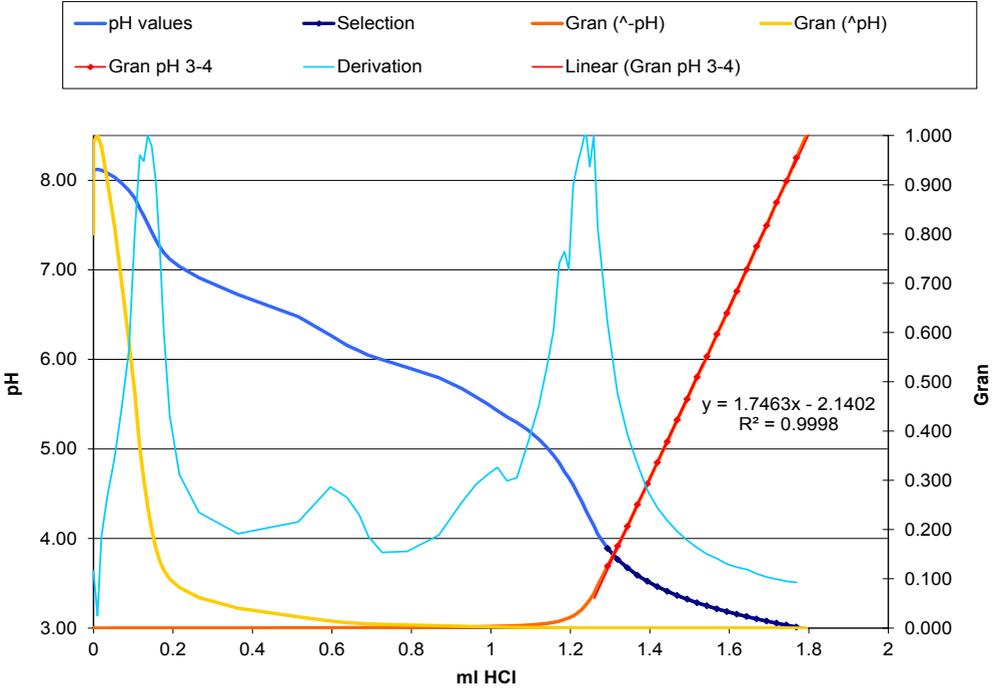


Fig. 83 Gran titration of sea water

SECTION 7

PHOTOMETRIC TITRATIONS

Classic titrations usually work with an optical indicator, in order to display the end of a titration (also see section 2.5 “Manual titration”). Many standards therefore still require the use of optical indicators nowadays. The use of a photometric sensor to detect the endpoint offers several advantages:

- Objective evaluation of the colour change
- Possibility of method automation
- Low-maintenance sensor
- Inert against most solvents
- Simple operation
- Long lifetime

As optical indicators exist for almost all titration applications, a photometric sensor also has a correspondingly broad application range for:

- Acid / base titrations in aqueous and organic solvents
- Complexometric titrations
- Redox titrations
- Precipitation titrations

Typical application examples for photometric sensors are:

- Determination of chondroitin sulphate sodium according to Ph.Eur. and USP.
- Determination of carboxyl end groups in PET according to [ASTM D7409](#)
- TAN/TBN according to [ASTM D974](#)
- Titration of sulphate (indicator thorin)
- Complexometric determination of the total hardness

7.1 The OptiLine 6

The OptiLine 6 electrode offers the possibility to select between six different wavelengths (Fig. 84). The shaft material consists of titanium, whereby a maximum compatibility with the different solvents is ensured. Power is supplied through a USB interface, via which the measured values are also transmitted to the TitroLine titrator (digital sensor). The setting of the titration parameters, such as wavelength and intensity, is performed directly in the titration software. In addition, the sensor has an analog DIN/BNC interface, which allows you to connect the OptiLine to any titrator with a corresponding input.



Shaft diameter	12 mm
Shaft length	132 mm
Minimum immersion depth	25 mm
Shaft material	Titanium
Cable	Fixed cable
Connections	USB interface A, BNC interface, with BNC-DIN adapter
Current supply	via USB
Measurement range	0 – 2000 mV
Temperature range	0 – 50 °C
pH range	0 – 14
Adjustable wavelengths	470, 520, 570, 590, 605, 625

Fig. 84 OptiLine 6 electrode, technical data

Titration guide

7.2 Measurement principle

During a photometric determination, the change in intensity is measured, which is caused by the colour change of the indicator used. Due to the colour of the solution, the light emitted by the sensor is absorbed. The change in absorption that is caused by the colour change of the indicator, is measured as a change in intensity on the detector is used as a regulating parameter for the titration.

During a precipitation titration, either turbidity is generated during the titration, which reaches its maximum at the end of the reaction or the occurrence of turbidity indicates the end of the reaction. In both cases, the turbidity causes a dispersion of the light emitted by the sensor, which in turn causes the change in intensity on the detector.

The wavelength should be selected so that the absorption difference between the start and the end of the titration is greatest. In order to determine the correct wavelength, you could use a photometer to record a spectrum at the start and at the end of the reaction. The maximum or minimum of the difference spectrum shows the optimal wavelength for this determination. The wavelength closest to this wavelength can now be selected for the determination.

7.3 Error sources

Air bubbles

In particular in aqueous media, air bubbles may form on the OptiLine. These lead to refractions of light, whereby no stable signal can be measured. Therefore, one should work with degassed water if possible. The degassing of the water can take place via a vacuum or boiling. Furthermore, the sensor should be aligned in such a manner that the optical range of the sensor points against the flow direction so that any air bubbles in the sample are removed.

Ambient light

As optical electrodes are light dependent, in certain circumstances, strong ambient light may interfere with the measurement leading to erroneous readings. As such, it is important to consider the location when performing photometric titrations.

7.4 Applications

Determination of the alkalinity $K_{S4,3}$

A general description of the alkalinity can be found in the section "Titration of $K_{S8,2}$ and $K_{S4,3}$ ". The indication takes place by means of methyl orange (0.2 % in H_2O).

Titration guide

a) Titer determination

Approx. 120 mg TRIS (Tris-(hydroxymethyl)aminomethane) are weighed in for the determination of the titer. The determination takes place at 520 nm (Fig. 85).

- Waiting time: 10 s
- Pre-titration: 8.5 ml
- Wavelength: 520 nm
- Titration end: 1 EQ
- slope value: steep
- Intensity: 30 %
- Smoothing: average

The following titration parameters are recommended:

- Measured value: mV (E)
- Linear titration to an equivalence point
- Linear step: 0.05 ml
- Measuring speed:
Measurement time 3 s
Drift 10 mV/min
Min time 5 s
Max time 12 s

Formula for titer in mol/l

$$c_{\text{HCl}} [\text{mol/l}] = \frac{W \cdot F2}{(EQ1 - B) \cdot M \cdot F1}$$

EQ1: Consumption titrant [ml] until the equivalence point

B: Blank value = 0

M: Molar weight of TRIS (121.14 g/mol)

W: Weighed sample TRIS [g]

F1: 1

F2: 1000 (conversion g - mg)

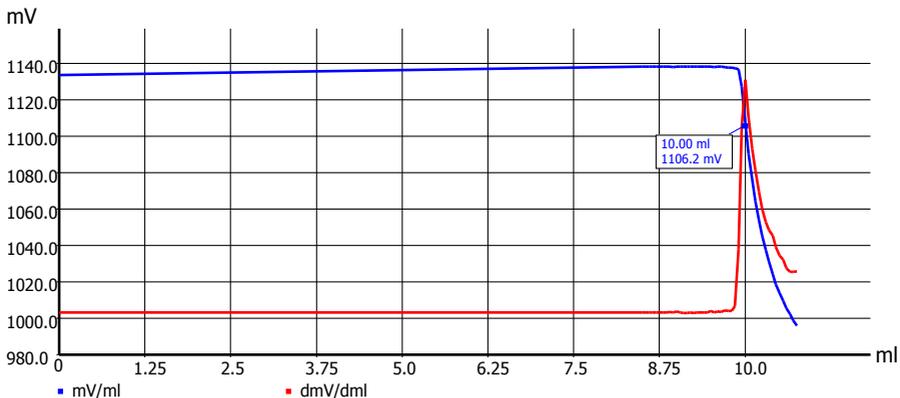


Fig. 85 Titration curve of a photometric titer determination with 0.1 molar HCl

b) Sample measurement

To determine the alkalinity of drinking water, 100 ml of sample are placed in a 150 ml beaker. Depending on the alkalinity, the sample amount must be adjusted (Fig. 86).

- Pre-titration: none
- Wavelength: 520 nm
- no damping
- Titration end: 1EQ
- slope value: steep
- Intensity: 30 %
- Smoothing: average

The following titration parameters are recommended:

- Measured value: mV (E)
- Linear titration to an equivalence point
- Linear step: 0.05 ml
- Measuring speed:
 - Measurement time 3 s
 - Drift 10 mV/min
 - Min time 5 s
 - Max time 15 s

Formula for $K_{s4,3}$ mmol/l

$$K_{s4,3} [\text{mmol/l}] = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{V} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
- B: Blank value = 0
- T: Exact concentration of the titrant [mol/l]
- M: Molar weight = 1
- V: ml presentation
- F1: 10
- F2: 0.01

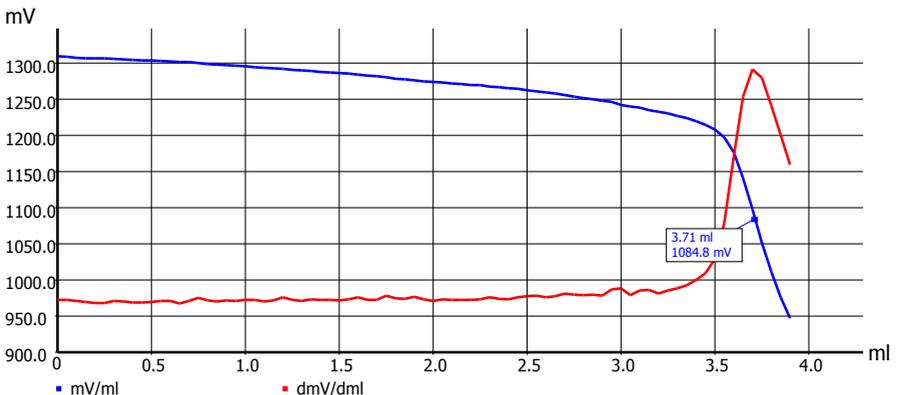


Fig. 86 Titration curve of a photometric $\text{Alk}_{4,3}$ determination of drinking water

Titration guide

Photometric determination of acids in oils (TAN)

A description of the optical indication of the acid titration in oils can be found in the **ASTM D974**. 0.05 mol/l KOH in ethanol is used as titrant. The solvent consists of a mixture of 500 ml of toluene, 495 ml of isopropanol and 5 ml of dist. water. Indicator is p-naphtholbenzein (1% solution, dissolved in the solvent).

a) Titer determination

The determination of the titer is carried out in the aqueous at a wavelength of 520 nm by means of potassium hydrogen phthalate and phenolphthalein as an indicator. Approx. 50 mg of potassium hydrogen phthalate are weighed in and after the dissolving, 50 µl is added (Fig. 87).

The following titration parameters are recommended:

- Measured value: mV (E)
- Linear titration to an equivalence point
- No damping
- Linear step: 0.05 ml
- Measuring speed:
 - Measurement time 3 s
 - Drift 10 mV/min
 - Min time 5 s
 - Max time 12 s
- Waiting time: 10 s
- Pre-titration: 4 ml
- Wavelength: 520 nm
- Titration end: 1 EQ
- Slope value: steep
- Intensity: 30 %
- Smoothing: average

Formula for titer in mol/l

$$c_{\text{KOH}} [\text{mol/l}] = \frac{W * F2}{(EQ1 - B) * M * F1}$$

EQ1: Consumption titrant [ml] until the equivalence point

B: Blank value = 0

M: Molar weight of potassium hydrogen phthalate (204.22 g/mol)

W: Weighed sample potassium hydrogen phthalate [g]

F1: 1

F2: 1000 (conversion g - mg)

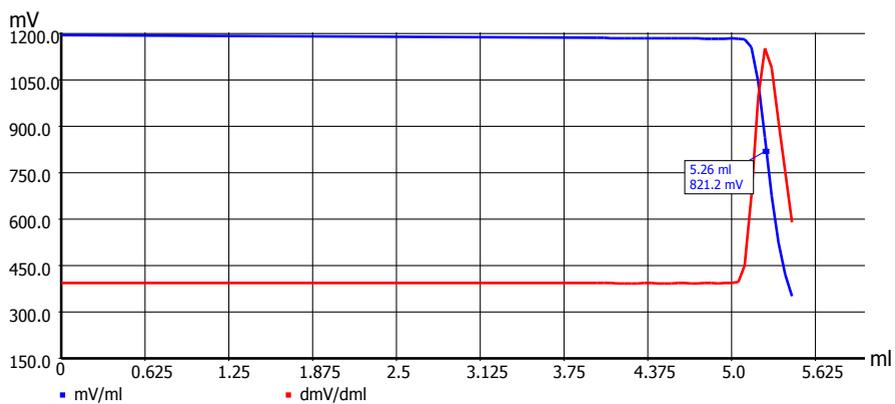


Fig. 87 Titration curve photometric titer determination 0.05 molar KOH

Titration guide

b) Blank value of the solvent

To 100 ml of the solvent, 0.05 ml of indicator is added and the titration is carried out. The measurement is carried out at 625 nm (Fig. 88).

- Wavelength: 625 nm
- No damping
- Titration end: 0.3 ml max. dosing volume
- Intensity: average
- Smoothing: average

The following titration parameters are recommended:

- Measured value: mV (E)
- Linear titration to an equivalence point
- Linear step: 0.02 ml
- Measuring speed:
Measurement time 4 s
Drift 20 mV/min
Min time 10 s
Max time 40 s

Formula for blank value

$$\text{Blank value [ml]} = \text{EQ1}$$

EQ1: Consumption titrant [ml] until the equivalence point

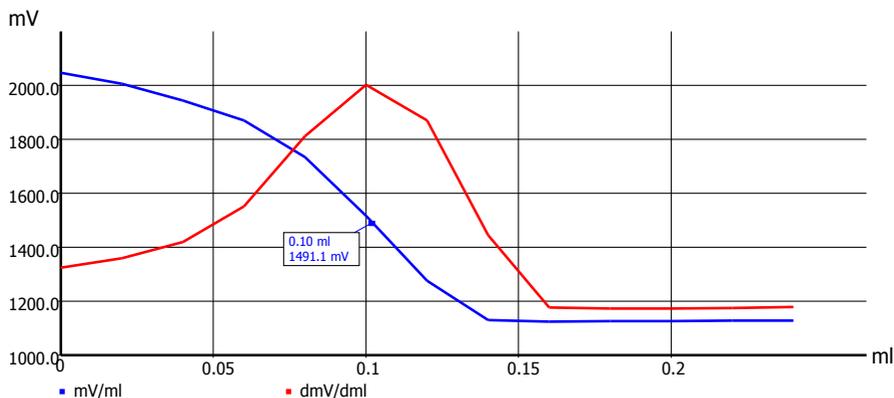


Fig. 88 Titration curve of a photometric blank value determination of a solvent mixture (toluene/IPA/water)

c) Sample measurement

The weighing in of the sample depends on the acid number of the oil. The sample is dissolved in 100 ml of the solvent (Fig. 89).

- Wavelength: 625 nm
- Titration end: 1 EQ
- Slope value: steep
- Intensity: average
- Smoothing: average

The following titration parameters are recommended:

- Measured value: mV (E)
- Linear titration to an equivalence point
- No damping
- Linear step: 0.04 ml
- Measuring speed:
 - Measurement time 4 s
 - Drift 20 mV/min
 - Min time 10 s
 - Max time 40 s

Formula for FFA in mg KOH

$$\text{TAN [mg KOH / g]} = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

- EQ1: Consumption titrant [ml] until the equivalence point
- B: Blank value of the solvent
- T: exact concentration of the titrant [mol/l]
- M: Molar weight KOH (56.1 g/mol)
- W: Weighing in the sample [g]
- F1: 1
- F2: 1

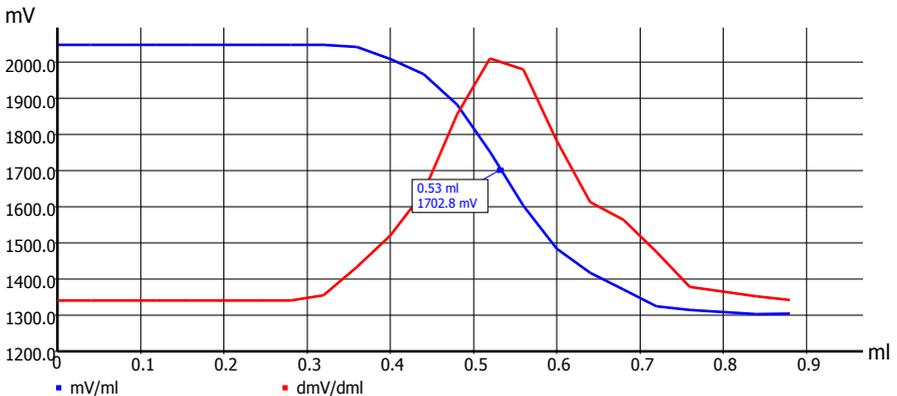


Fig. 89 Titration curve of a photometric TAN determination of an insulating oil

Titration guide

Determination of carboxyl end groups in PET

The determination of carboxyl end groups in PET pellets (polyethyleneterephthalate) is described in the [ASTM D 7409](#). Bromophenol blue (0.5% in ethanol) is used as indicator, 0.05 molar ethanolic KOH as titrant. A blank value determination of the solvent is carried out (Fig. 90).

Approx. 1 g of the pellets are weighed in for the determination. 20 g o-cresol is added to the sample. The sample is boiled under reflux until it has completely dissolved. An adjustment of the sample and solvent amount is necessary if e.g. precipitations result. After cooling, the mixture is mixed with 35 ml of chloroform. For the indication 0.04 ml bromophenol blue are added (Fig. 91).

a) Titer determination

The titer determination can be determined photometrically, as described in the part "Determination of the alkalinity $K_{S4,3}$ ".

b) Blank value of the solvent

For the determination of the blank value, the solvent is treated as described above, but no sample is added. The blank value is boiled under reflux just as long as the sample needed to dissolve. The titration is carried out after adding the indicator (0.04 ml).

The following titration parameters are recommended:

- Measured value: mV (E)
- Linear titration to an equivalence point
- Linear step: 0.004 ml
- Measuring speed:
fixed waiting time: 20 s
- Wavelength: 605 nm
- Titration end: 0.1 ml max. dosing volume
- Intensity: 50 %
- Smoothing: high

Formula for blank value

$$\text{Blank value [ml]} = \text{EQ1}$$

EQ1: Consumption titrant [ml] until the equivalence point

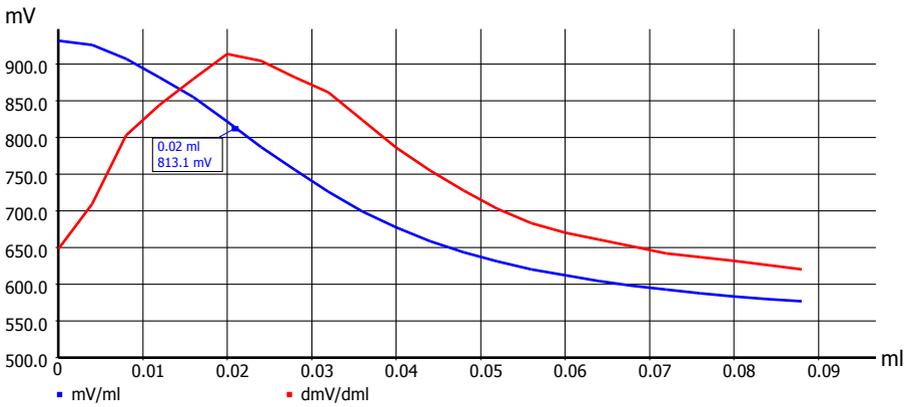


Fig. 90 Titration curve of a photometric blank value determination of a solvent mixture (o cresol/chloroform)

Titration guide

c) Sample measurement

The implementation of the measurement is described in the general method part.

The following titration parameters are recommended:

- Measured value mV (E)
- Linear titration to an equivalence point
- no damping
- Linear step: 0.1 ml
- Measuring speed: fixed waiting time: 20 s
- Wavelength: 605 nm
- Titration end: 1 EQ
- Slope value flat
- Intensity: 50 %
- Smoothing: high

Formula for R-COOH in mmol/kg

$$\text{R-COOH [mmol/kg]} = \frac{(\text{EQ1} - \text{B}) * \text{T} * \text{M} * \text{F1}}{\text{W} * \text{F2}}$$

EQ1: Consumption titrant [ml] until the equivalence point

B: Blank value of the solvent

T: exact concentration of the titrant [mol/l]

M: Molar weight = 1

W: Weighing in the sample [g]

F1: 1

F2: 1000 (conversion g - mg)

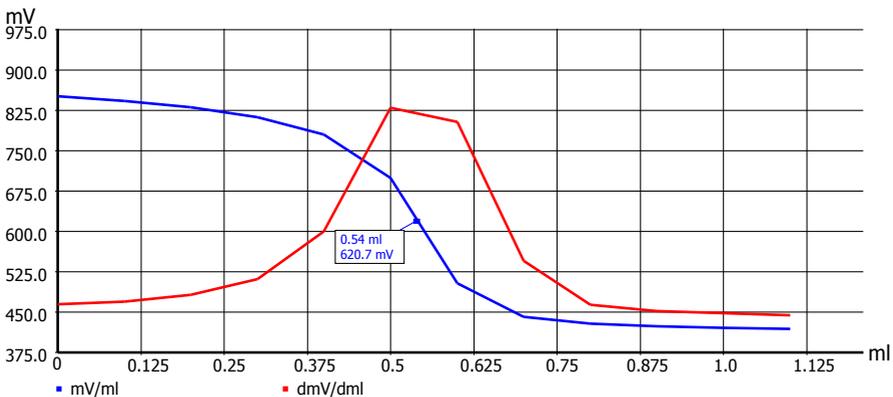


Fig. 91 Titration curve of a photometric carboxyl end group determination of PET pellets

SECTION 8

KARL FISCHER TITRATION

8.1 The Karl Fischer reaction and reagents

The Karl Fischer titration serves to determine the water content of a sample. It has the advantage of faster determination compared to the drying method and is also more selective. The exact mechanism of the Karl Fischer reaction has been controversial for a long time. Even the stoichiometry of the reaction was not clear for a long time. In principle, a titration would not be possible therewith. In more recent times, there have been some investigations of the mechanism, which have resulted in the following reaction equation:



Wherein:

ROH An alcohol, e.g. methanol, ethanol, ethylene glycol monoethyl ether

R'N A base, e.g. imidazole (previously often pyridine)

The oxygen of the sulphate ester comes from the water molecule. The examinations of the mechanism show a change of the stoichiometry when working in other solvents. The addition of other solvents should therefore not exceed 50 % by volume. In addition to water, four components (an alcohol, sulfur dioxide, a base, iodine) participate in the reaction; these must be present so that the reaction takes place.

With the classic KF titration, all components are offered as a combined reagent and are available in sufficient stability with suitable bases and alcohols. In addition, 2-component reagents are also offered nowadays, in which the solvent component contains an alcohol, a base and SO_2 .

Titration guide

The titration solution then consists of an iodine solution in an alcohol. This reagent has the advantage of pH buffering and a higher concentration of all components on the left side of the reaction equation. The reaction is clearly faster and the reagents last clearly longer.

With the one-component reagent (Fig. 92), it is possible to adapt the solvent to the solubility of the sample.

The KF titration is largely selective for water under the given circumstances. However, there are of course limitations for a number of secondary reactions. These can be divided into the following types:

- Reactions which generate water
- Reactions which require water
- Redox secondary reactions of iodine
- External water

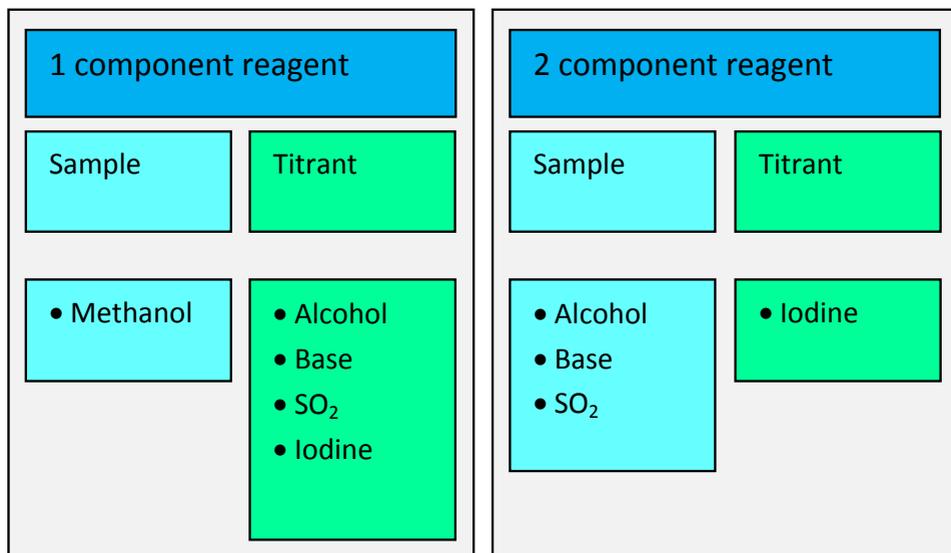


Fig. 92 Schematic of 1 and 2 component reagents

The best known water-producing reaction is the formation of acetals or ketals. The alcohol necessary for the reaction and used as a solvent reacts with carbonyl groups ($C=O$) while forming water. This water is also detected by the titration. The titration does not seem to stop. A high permanent "drift" results.

However, acetal or ketal formation can be avoided by using special reagents for aldehydes and ketones. A second possibility is the mode of operation with reduced temperature. One works at temperatures below 0°C . The ionic KF reaction proceeds in a virtually unaffected manner, while the acetal and ketal formation is significantly slowed down. The lower temperature limit is determined by the viscosity of the solvent and the crystallization of secondary components.

Aldehydes can also form a bisulfate addition with SO_2 under certain conditions. This reaction should be largely suppressed with a correctly set pH value. This reaction also requires water and could pretend in this way a water content that is too low.

Further reactions with water formation are the reaction of carbonyls with amines to form Schiff's bases, the formation of enamines and the esterification of acids with the alcohol of the solvent. The risk is reduced when using methanol-free solvents.

External water is the most common error source in KF titration. It can reach the titration cell through various possibilities. First, the solvent or the presentation component must of course be dry-titrated. This procedure is called conditioning. If External water still gets into the titration cell, this is assigned to the sample as External water. External water reaches the titration cell in the following manners:

Titration guide

The titration cell is not tight. Foreign particles can for example hang between the ground joints. Another possibility is defective O-rings on the screw connections of the titration cell.

- While the titration cell is opened to add the sample, air humidity enters.
- The septum for the addition of liquid samples is leaking and worn.
- The molecular sieve in the drying tube for pressure equalization is used up and must be dried.
- Humid air is present in the pump system. The air for adding the solvent must also be dried with the molecular sieve.

The KF titration is strongly pH-dependent (Fig. 93). At values below 5.5 pH, the reaction speed slows by up to a factor of 1000.

Secondary reactions can occur in the alkaline range. But this also implies that in the KF titration of acids, bases must be added and in the titration of bases (e.g., amines), acids must be added.

- Acidic samples: add imidazole or methyl imidazole
- Alkaline samples: add benzoic acid oder salicylic acid

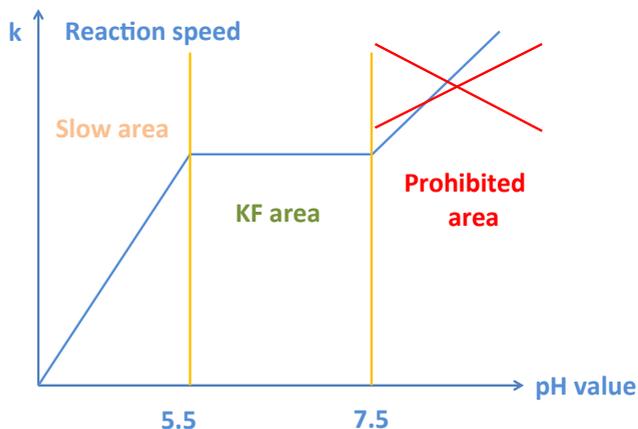


Fig. 93 Dependence of the reaction speed from the pH value

8.2 The detection of the KF titration and titration curves

The KF titration uses a double platinum electrode for detection, to which a voltage of 20-200 mV is applied. The titration is titrated with an iodine solution. The iodine reacts directly to iodide in the KF reaction. No current can flow at the double platinum electrode of the detection system. However, as soon as the first drop of an iodine solution is present in excess, a reversible redox system of iodine and iodide is present. A current flows, which is measured and indicates the end of the titration.

However, the current curve does not give any information about the course of the reaction. Therefore, a representation is usually chosen in which the time is plotted on the x-axis and the consumption on the y-axis. First, the reagent is added quickly and a steep increase results. Then, one titrates slower and more carefully, because the titrator detects the approaching endpoint. The smaller reagent additions make the titration curve increasingly flatter until no more reagent is added and the titration runs parallel to the x-axis (Fig. 94).

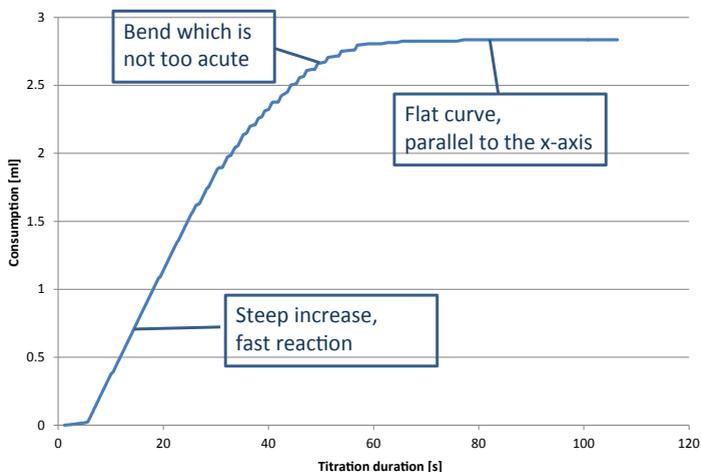


Fig. 94 KF titration curve

Titration guide

If a secondary reaction is present during the titration, e.g. because ketones are present and two moles of water are formed per mole of ketal, a continuous increase can be seen, the drift does not go down and the titration does not stop when there is no time limit. Fig. 95 shows an example for a titration with secondary titrations.

8.3 Sample handling

The samples must be completely dissolved for the safe total determination of the water content. Not all samples dissolve in methanol or the solvent component of the 2-component reagent. In these cases, the one-component reagent is preferred and the methanol is treated with a solubility enhancer. For polar samples, formamide is often used. For non-polar samples chloroform, xylene or long-chain alcohols are used.

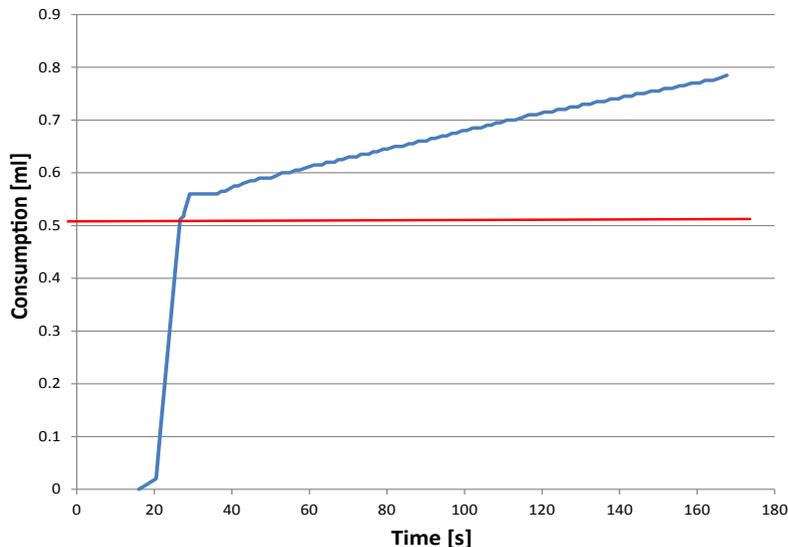


Fig. 95 Titration curve with secondary reaction

Even a sample that does not release the water immediately would show a continuous increase. Different ways exist to optimize the water release:

- Adaptation of the solvent, where possible (Fig. 96)
- Heating of the solution (to approx. 50 °C) by means of a heatable magnetic stirrer, or a double jacket vessel and a water bath
- External sample preparation/ extraction
- Use of a homogenizer
- Use of a KF oven

The possibilities are often limited by the water content and the type of the sample. Thus, external extraction is unsuitable if the water content of the sample is significantly lower than the water content of the solvent.

For some samples, however, a drying oven is required for sample preparation. An example are plastic samples that are virtually insoluble, at least not in a solvent that is suitable for KF titration. However, the oven can only be used to a limited extent if the samples decompose before they release the water or if volatile components outgas and condense in the colder part of the oven.

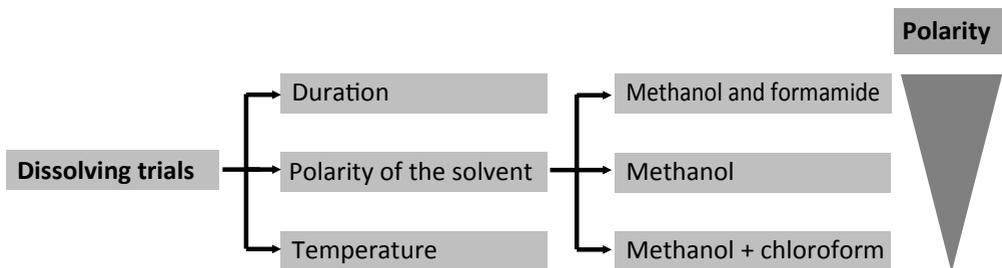


Fig. 96 Dissolving trials with the KF titration

Titration guide

8.4 The coulometry

The volumetric reagent addition is preferably replaced by coulometrically generated iodine with low water contents.

Coulometry is based on the same chemical reaction, but the iodine is not dosed by a burette but generated in situ at the anode of a generator electrode by oxidation of iodide (Fig. 97).

At the cathode, hydrogen is generated by reduction. The amount of iodine generated is calculated from the titrator according to Coulomb's law:

$$m = \frac{M \cdot Q}{z \cdot F}$$

- | | |
|---|--|
| m | mass of the water to be determined |
| M | molar mass |
| Q | measured charge amount |
| z | valency |
| F | Faraday constant
(96,485.3 Coulomb/Mol) |

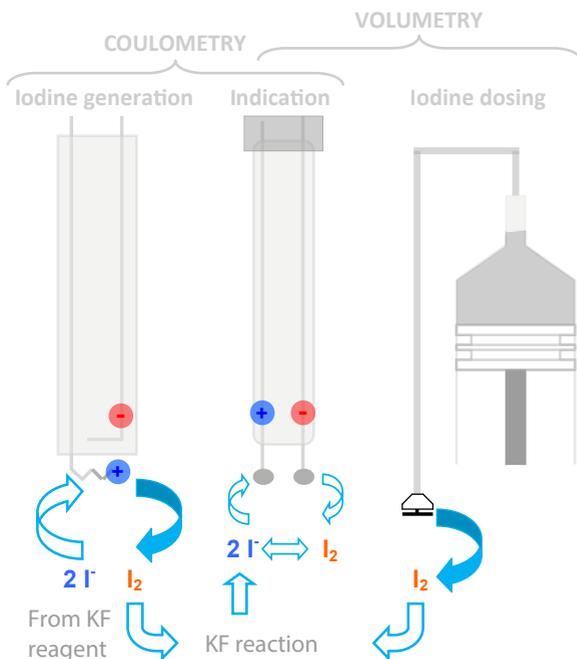


Fig. 97 Comparison KF coulometry and volumetry

Coulometry is an absolute method; a titer determination is not necessary and also not possible. KF volumetry and coulometry are the same except for the iodine addition (Fig. 98). Nowadays, a generator electrode is mostly used, which dispenses with a diaphragm.

Only with very small amounts of water, difficult samples and very high demands of the accuracy, electrodes with diaphragms are used. Then suitable reagents are available for the cathode chamber.

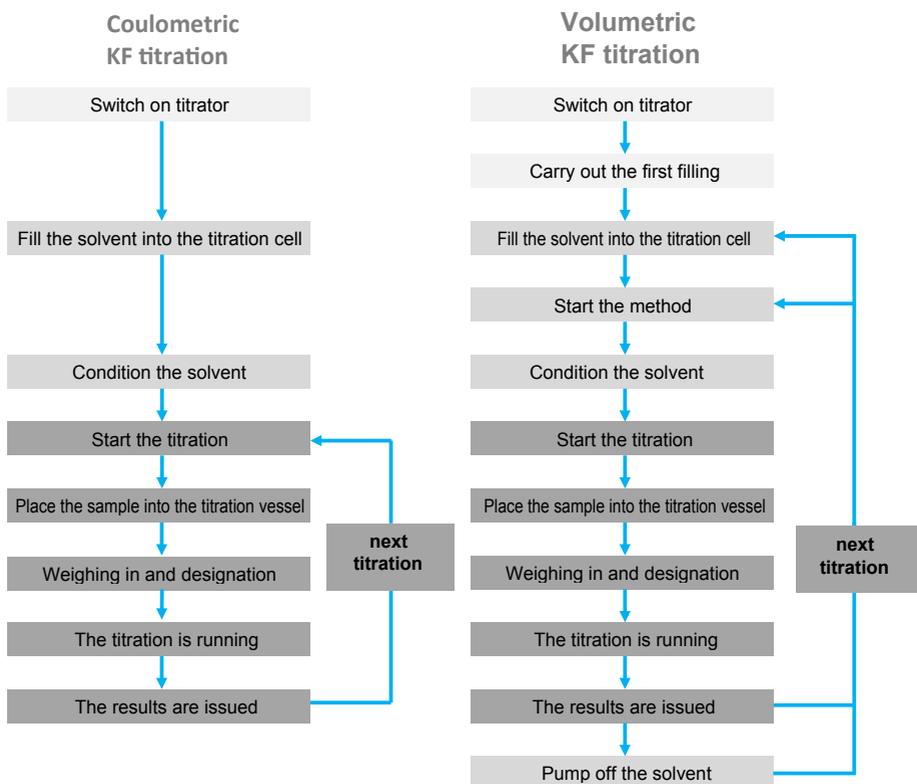


Fig. 98 Workflows for the coulometric/volumetric KF titration

Titration guide

In a direct comparison, the coulometric KF titration is simpler, as there is automatically conditioned in the background, so the titration cell is kept dry. With volumetric titration, conditioning is added, which is necessary for each sample prior to titration (Fig. 98 and 99).

Both methods complement each other and one can rarely be completely replaced by the other. Coulometry has its advantages in the ease of operation and the determination of very small amounts of water, while volumetry can be used far more flexibly.

Property	Coulometry	Volumetry
Water content and sample amount	<ul style="list-style-type: none"> • small water contents • small sample amounts 	<ul style="list-style-type: none"> • medium and large water contents • adapted sample amounts
Sample types	<ul style="list-style-type: none"> • liquid • gaseous (e.g. oven) • fixed samples with oven 	<ul style="list-style-type: none"> • solid • liquid
Sample addition	<ul style="list-style-type: none"> • direct with the syringe • gas introduction with oven • external extraction • heat out solid samples in the oven 	<ul style="list-style-type: none"> • solids direct • sample crushing with homogenizer • work with increased temperature • with syringe directly
Operation	<ul style="list-style-type: none"> • very fast • very simple 	<ul style="list-style-type: none"> • fast • simple
Working range	<ul style="list-style-type: none"> • µg range • 10 µg to 5 mg water 	<ul style="list-style-type: none"> • mg range • 200 µg to 50 mg water
Correctness	<ul style="list-style-type: none"> • very good for small water amounts > 400 µg water (+/- 0.5%) 	<ul style="list-style-type: none"> • very good for water amounts > 5 mg water (+/- 0.5% current titer determination necessary)
Reproducibility	<ul style="list-style-type: none"> > 400 µg water, typical RSA approx. 1% 	<ul style="list-style-type: none"> > 5 mg water, typical RSA approx. 1%

Fig. 99 Comparison use of coulometric and volumetric KF titration

SECTION 9

VERIFICATION OF THE TITRATION

9.1 Overview

An important prerequisite for the correctness of titrations is the correctness of the concentration of the titrant. The titration is an absolute method, that is, the consumption is directly attributable to the chemical conversion.

As many titrants cannot be weighed in directly or their concentration does not always remain the same, the current content must be checked and documented again and again. This happens by means of the titer determination of the titrant.

Usually secondary reference materials according to NIST are used nowadays. These are provided by the manufacturer with a certificate of the exact content, uncertainty and durability. All titrations whose titers have been set with such a standard can be traced back to NIST. Titer determinations are described in detail in section 4.

In principle, all devices and methods must be validated in the laboratory so that traceability can be guaranteed.

Definition of the validation according to (DIN EN ISO 8402, 1994):

"Confirmation by examining and providing an objective evidence that the special requirements for a special, intended use are fulfilled..."

Verifiable information based on facts obtained by observation, measurement, test or in another manner."

For the validation, a comparison between the requirements and their fulfillment must always underlie according to ISO 8402. This is verified with the execution of a validation process.

9.2 Qualifications

The qualification of a titrator happens essentially by checking its correct volume (the measurement unit of the titration) according to [ISO 8655](#). For use in the laboratory, however, the device additionally has to be qualified by a series of processes (Fig. 100). IQ and OQ can usually be carried out by the manufacturer.

After the qualification, the device can be used in the laboratory for the routine. An additional validation is necessary for the methods. This takes place with the same scheme for all analysis methods and is described in detail in the literature [\[14, 15\]](#) for many methods.

Qualification	Description	What has to be done?	Aids/documentation
Design qualification (DQ)	The DQ specifies the functional and operational qualifications of an instrument.	<ul style="list-style-type: none"> • Describe the usage purpose • Select the instrument • Evaluate the manufacturer 	<ul style="list-style-type: none"> • Manuals, operating instructions • Standards and quality guidelines • Conformity guidelines • Manufacturer documents
Installation qualification (IQ)	The IQ ensures that an instrument in the delivery state corresponds to the specifications of the order. It also documents the installation of the selected work environment.	<ul style="list-style-type: none"> • Check delivery scope • Set up • Start up • Carry out a test 	<ul style="list-style-type: none"> • Operating instructions • Device support • Support of the manufacturer • IQ document
Operational qualification (OQ)	Within the scope of the OQ, it is verified that an instrument in the selected work environment functions in correspondence with the operational specifications.	<ul style="list-style-type: none"> • System suitability test • e.g. linearity with standard • Determination of the standard deviation • Calibration • Training 	<ul style="list-style-type: none"> • OQ forms • Standards • Certificates • Training certificates
Performance qualification (PQ)	The PQ verifies that an instrument continuously delivers the performance according to the specifications during normal use.	<ul style="list-style-type: none"> • Adapt analysis methods • Validate the methods 	<ul style="list-style-type: none"> • Log book • Application support • Seminars • Standards • SOPs
Maintenance qualification (MQ)	The MQ describes and documents the necessary maintenance.	<ul style="list-style-type: none"> • Cleaning and care • Re-qualifying • Maintenance • Titer checks 	<ul style="list-style-type: none"> • Maintenance contracts • Technical customer service • Test means monitoring

Fig. 100 Qualifications of a titration measurement place

Titration guide

9.3 Validation

The extent of the validation depends on how much of a product is contained in a sample and how the influence of the sample matrix is. Fig. 101 reproduces the validation scheme according to USP (United States Pharmacopoeia). In practice, the focus is on precision and linearity, as they give characteristics such as area, determination and detection limit.

Characteristic	Category I (Content determination)	Category II (Limit check)	Category II (Quant. determination)	Category III (Quant. determination)
Precision	+	-	+	+
Correctness	+	(+)	+	+
Verification limit	-	+	-	+
Determination limit	-	-	+	+
Selectivity	+	+	+	+
Range	+	(+)	+	+
Linearity	+	-	+	+
Robustness	+	+	+	+
Regulations of the USP XXII for validation:				
• Category I:	Main components			
• Category II:	Secondary products			
• Category III:	Performance parameters (substance release)			

Fig. 101 Validation elements according to USP

9.4 Check of the correctness of a titration

It shall be shown at an example that the small additional effort of a linearity test compared to a simple multiple determination provides a great number of information.

A relative standard deviation (RSD) of almost 12% is the result (Fig. 102, a). The linearity now shows that a negative consumption of 0.3 ml results from a 0.00 ml sample. This indicates a defective sample amount.

The used pipette was examined according to [ISO 8655](#) and the found volume error was inserted into the data as correction. At 0.2%, the RSD is in the expected order of magnitude after the correction. The linearity shows a correlation coefficient of 1,000. The straight line passes (almost) through the zero point (Fig. 103).

Titration guide

ml sample	ml result	"content"
0.2	0.8558	4.279
0.4	2.0596	5.149
0.6	3.2748	5.458
0.8	4.4574	5.572
Mean		5.114
SD		0.585
RSD		11.436

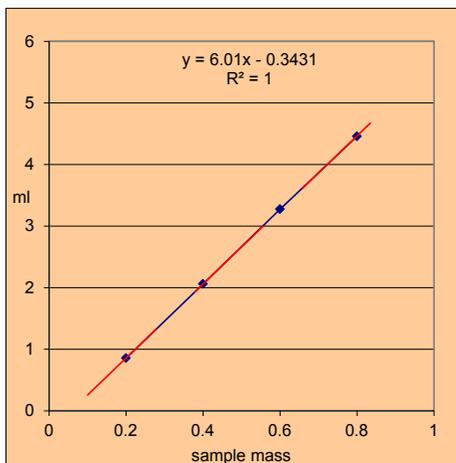


Fig. 102 Linearity of the titration results shows a serious error

ml sample	ml result	"content"
0.142	0.8558	6.027
0.342	2.0596	6.022
0.542	3.2748	6.042
0.742	4.4574	6.007
Mean		6.025
SD		0.014
RSD		0.238

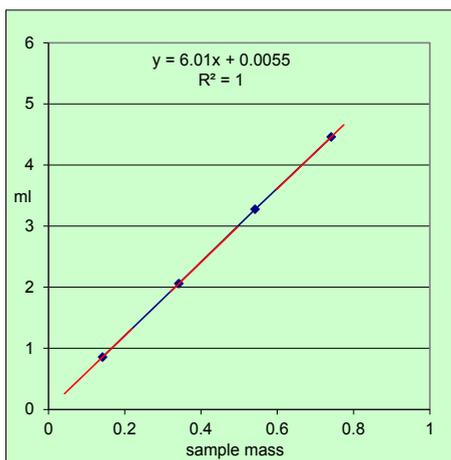


Fig. 103 Linearity after the correction of the volume error

For a simplified validation, only a few characteristics have to be checked and only a few titrations are required. In the example (Fig. 104 and 105), five titrations are performed, the average value and the relative standard deviation RSD are calculated.

The curves are analysed and the results are represented in a graph:

- x-axis = sample amount
- y-axis = consumption.

The RSD is very low at 0.02%. For a titer determination, values up to approx. 0.5% would be routinely accepted. The average value is also exactly where you expect it.

Titer determination NaOH 0.1 mol/l			
No.	Weighted sample [g]	Consumption [ml]	Titer NaOH
1	0.1189	5.8445	1.0060
2	0.1576	7.7489	1.0057
3	0.2090	10.2722	1.0061
4	0.2578	12.6710	1.0061
5	0.3045	14.9631	1.0063
MW titer			1.0060
SD titer			0.0002
RSD titer			0.0218

Fig. 104 Result of a titer determination

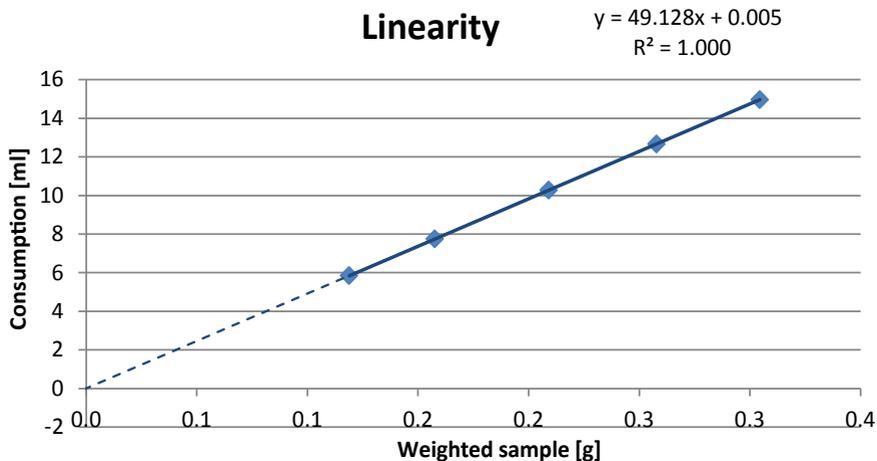


Fig. 105 Linearity representation of the titer determination

Titration guide

The titration curve is a very important element for the evaluation of the titration result (Fig. 106).

The criteria are as follows:

- Calm titration curve without “dents” and “fluctuations”
- Steep 1st derivation
- Even form of the derivation
- Only one peak, no secondary peaks

If the titration curves are correct, the linearity is examined.

The characteristics are as follows:

- Correlation coefficient better than 0.99(9)
- Interface with the y-axis ($x = 0$) smaller than a drop of titrant (0.05 ml)
- The factor of the slope is examined if necessary

Some parameters such as the correctness have not been examined. This could be checked by adding a standard that can be recovered at 100%.

It is important that sample preparation is taken into account in the various titrations. It is not permissible to take several partial amounts of a prepared sample.

Fig. 107 shows an example of a validation of a KF coulometer. A volume test is not possible due to a lack of burette, but the linearity test can also prove the correct function of the device here. By means of the linearity test and a reference substance, the correctness of the water determination is verified according to specified criteria.

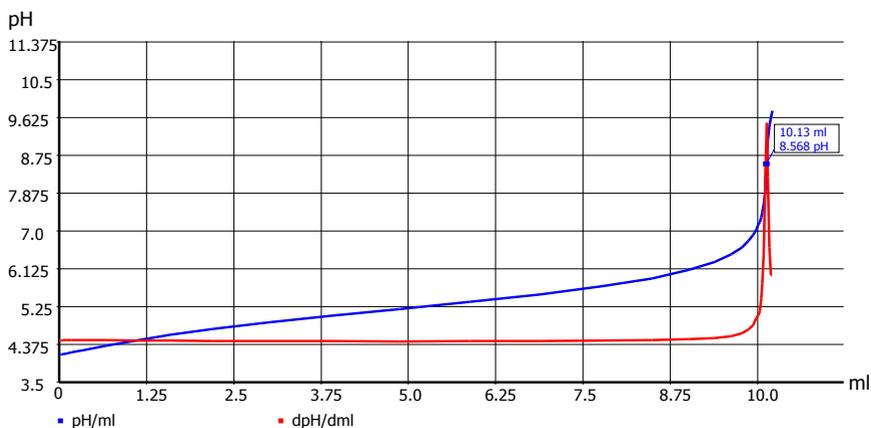


Fig. 106 Exemplary curve of a titer determination

Test protocol of manufacturer test TL KF Trace

KF Reagent:

Hydranal Coulomat AD, Fluka Analytical No. 34810
 LOT SZ BA 0760, Date of Prod. Mar.2010, Exp. Date Feb. 2015

Hydranal Coulomat CG, Fluka Analytical No. 34840
 LOT SZ BA 014 A, Date of Prod. Jan.2011, Exp. Date Dez. 2015

Reference Material:

Hydranal Water Standard 1.0 , Fluka Analytical No. 34849
 LOT SZ E 93380, Date of Prod. Mar. 2010, Exp. Date Nov. 2014

Temperature: 22.7°C

Specified value	1.000	[mg/g]
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No. Sample	Weight [g]	Result [μ g]	Found [%]
1	0.2153	214.9	99.8
2	0.2879	288.8	100.3
3	0.3684	371.0	100.7
4	0.4269	427.1	100.0
Mean			100.220
RSD			0.241

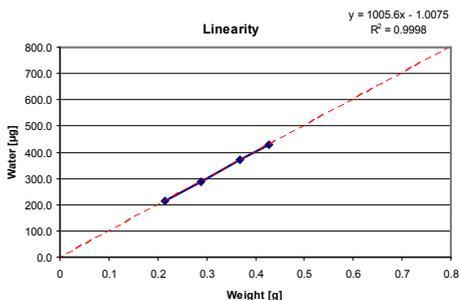


Fig. 107 Check of a KF titrator with the help of a linearity test

Titration guide

9.5 Measurement uncertainty

Today, the accuracy of a method is no longer specified, but the uncertainty "u" is estimated. For this, a method is examined by means of a cause-effect diagram (Fig. 108) for all parameters that have an influence on the calculated result. In the titration, all factors are evaluated that are directly or indirectly contained in the calculation formula.

The variables are quantified and converted into equal measuring units. Then the relative errors can be plotted as shown in Fig. 109. The uncertainty "u" of a titer determination then essentially depends on the correctness of the volume.

The uncertainty is multiplied by a factor $k = 2$ and added as an expanded uncertainty to an analysis value, such as e.g. can be seen on the certificates of the reference materials.

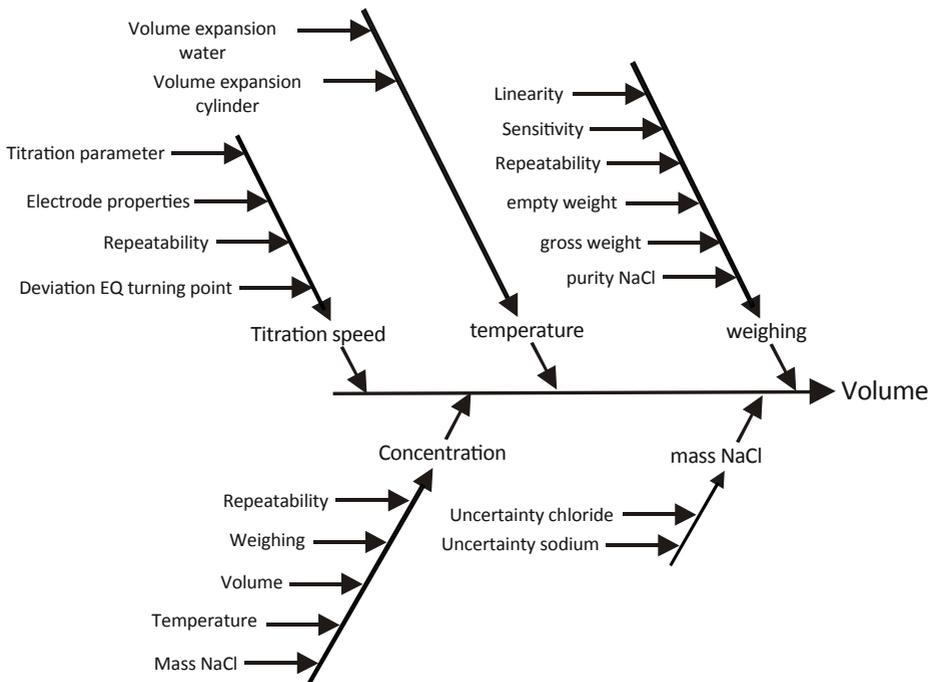


Fig. 108 Cause-effect diagram of a titration

	Description	Value	Standard uncertainty	Relative standard Uncertainty $u(x)/x$
rep	Repeatability	1	0.0005	0.0005
m_{KHP}	Weight of KHP	0.3888 g	0.00013 g	0.00033
P_{KHP}	Purity of KHPs	1	0.00029	0.00029
M_{KHP}	Molar mass of KHP	204.2212 g mol ⁻¹	0.0038 g mol ⁻¹	0.000019
V_T	Volume of the NaOH during KHP titration	18.64 ml	0.013 ml	0.0007

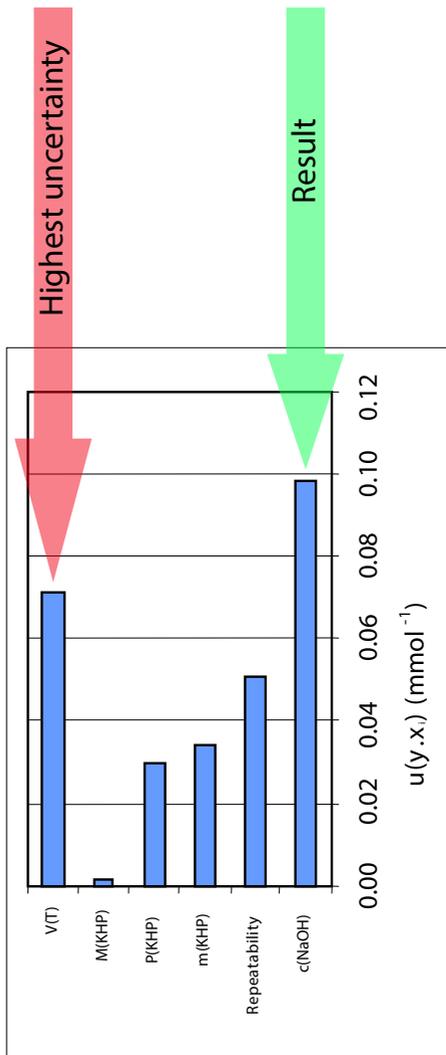


Fig. 109 The uncertainties of a titration in comparison according to GUM [15]

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