Monograph

Practical aspects of modern titration

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Metrohm

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1. Introduction

Titrimetry - one of the oldest analytical methods - has lost none of its relevance despite the introduction of many analytical methods. This is due not only to the unique advantages offered by the method but also to the advanced development in instrumental titrimetry.

New developments in sensor technology and the systematic utilization of the technical possibilities offered by digital electronics and microprocessor technology have led to considerable progress in the methodology and automation of titrimetric determinations.

A titrimetric analysis can be compared to a weighing (Fig. 1). The substance to be determined is in one weighing pan and successive "weights" in the form of the titrant are loaded on the other pan. Just like the weights, the titrant must be "calibrated" by determining its titer through titration against a primary standard. The ration of the two arms of the scale beam describes the stoichiometry of the titration reaction; the pointer on the scale, the display, is replaced in a titrimetric determination by the indicator system. In other words: in a titration an amount of substance is determined quantitatively by reaction with a calibrated standard substance.

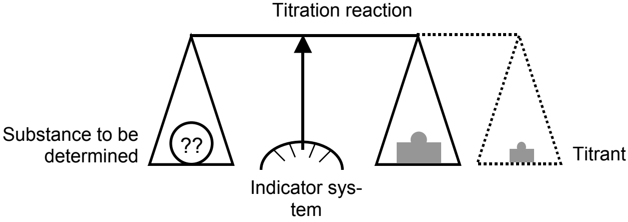


Fig. 1: Titrations can be compared to a weighing

Along with gravimetry, titration is one of the oldest analytical methods. Despite the advent of many newer, predominately physical methods of analysis, titrimetry is still used today as a standard method of quantitative analysis. This is due to the following unique advantages offered by the titrimetric method:

- Absolute content determinations, i.e. the analytical result provides direct information regarding the amount of analyzed substance without need to determine calibration factors specific to the instrument or method, as is usually the case in relative procedures.
- Easy implementation, easily understood method, i.e. the equipment and the operations to be performed are simple. The principles of the titrimetric methods are usually already well known; if not, they can quickly be learned.
- Rapidity: If the time needed for all operations from the setting up of the analytical instruments to the attainment of the final result is considered, titrimetric methods are rapid.

- Versatility: There are numerous fully worked out titration methods that extend from the determination of inorganic ions up to that of complex organic compounds. The possible content range of the analyzed substance spans the analysis of pure substances down to trace analyses in the ppm or even ppb range. The amount of sample can vary from a few µg up to several grams.
- Accuracy and reproducibility: Titrimetric determinations have typical reproducibility's of <1%. In high-precision titrimetry values of 0.1% and better are demanded and attained. This requires an accuracy that is within the limits of the standard deviation.
- Automation: Titrimetric determinations can run highly automized.
- Moderately priced: The costs are very reasonable compared to those of other analytical methods.

For the performance of titrations, the analyst has a wide range of auxiliaries available: From calibrated glass tubes with stopcock, e.g. the Schellbach buret, up to the microprocessor-controlled, automatic titration system with high-resolution motorized burets.

2. Sample preparation

Before a titration can be performed, the substance to be analyzed must be in solution. In the simplest case, the sample itself is a homogenous solution which can be titrated directly or the substance to be analyzed can easily be dissolved. In most cases, no special sample preparation is necessary for titrimetric methods.

If sample preparation is needed, its nature depends on the type of sample and the substance to be analyzed. Considering first the state of aggregation of the sample, the following systematic approach emerges:

Gaseous samples are generally introduced in an appropriate solvent. If with ***liquid samples***, the substance to be analyzed is in a chemical form that is unsuitable for the titrimetric determination, the following sample preparation steps can be employed to obtain a form which can be titrated:

- Oxidation
- Reduction
- Complex formation
- Decomposition (see below).

If the sample is ***solid,*** the following sample preparation steps are principally used:

- Dissolution of the sample and if necessary subsequent filtration or centrifuging
- Extraction of the substance to be analyzed
- Digestion and decomposition (see below).

2.1 Digestion and decomposition methods

If necessary, the sample is crushed and homogenized and can then be solubilised chemically or physically using one of the following methods:

- ***Exposure to heat (warming)***
- ***Combustion***
  The sample is combusted in a closed vessel and the products formed are dissolved. A method which is frequently used is the Schöniger combustion for the determination of sulphur in organic compounds. After combustion and subsequent oxidation with H_2O_2 the sulphur is present as SO_4^{2-}.
- ***Acidic digestions***
  The sample is heated to boiling in acid.
  The following acids and mixed acids are commonly used:
  - conc. HCl, e.g. for alkaline substances
  - conc. H_2SO_4 + K_2SO_4 + ($CuSeO_4$ + HgO as catalyst), known as the Kjeldahl digestion agent for the determination of nitrogen in organic compounds. After digestion nitrogen, is present in the form of NH_4^+ and can be separated from other compounds by distilling it off as NH_3.
  - conc. H_2SO_4 and conc. HNO_3. The H_2SO_4 is poured over the sample and the mixture heated until the organic substance carbonizes; this is followed by a further oxidation through addition of aliquots of HNO_3.

- ***Dry ashing***
  The powdered sample material is heated and ashed. This can be performed either in air or in a stream of O_2.
- ***Decompositions at high temperature and high pressure*** (sealed tube)
- ***Decompositions in molten salts***
  The sample is blended with a large excess of melting salt and heated in an inert crucible.
  The following salt mixtures are frequently used for decompositions:
  - Na_2O_2/Na_2CO_3 (oxidizing melts)
  - $KHSO_4$ (acidic melts)
  - Na_2CO_3/K_2CO_3 (alkaline melts)
- ***Irradiation with UV light***
  to destroy small quantities of organic compounds (e.g. in water) or as follow-up treatment after digestions (removing of nitrous gases)

After decomposition or digestion, often the digestion reagents have to be removed and the residue dissolved, e.g.:

- HCl and HNO_3 from the digestion can be evaporated.
- Excess peroxide from an oxidation can be destroyed by boiling.
- Addition of urea removes interfering nitrous gases present after digestions with HNO_3.
- Metals can often be brought into solution with a complexing agent, e.g. Cl^- as complexing agent (dissolution in hot HCl)

2.2 Sample pretreatment to increase selectivity

The selectivity of a titrimetric determination can be increased by various measures. This is important in cases where components of the sample matrix interfere with the determination of substance to analyze or if one titration should be used for selective determination of several substances.
The selectivity can be increased by auxiliary chemical reactions, physical separations or by a change in the titration conditions.

Auxiliary chemical reactions:

- Complexation
  e.g. determination of Pb^{2+}, Co^{2+} and Ca^{2+} in drying agents.
  1. Determination of the sum of Pb^{2+}, Co^{2+} and Ca^{2+} by an EDTA titration.
  2. Addition of CN^- to the titrated sample, formation of $CoCN_4^{2-}$ and back titration of the EDTA released.
  3. Addition of Dimercaptopropanol to break up the Pb^{2+}-EDTA complex and back titration of the EDTA released.

  Back titration of EDTA with Mg^{2+} in each case.
- Precipitation
  e.g. determination of Cu^{2+} and Zn^{2+} in brass baths.
  1. Iodometric determination of Cu^{2+} in one sample.
  2. In a second sample, CuS is precipitated and Zn^{2+} titrated with $K_4[Fe(CN)_6]$.
- Chemical elimination of a substance
  e.g. determination of Cl^-, Br^- and CN^- selectively.
  1. Titration of the sum Cl^-, Br^- and CN^- with Ag^+.
  2. In a second sample elimination of CN^- by oxidizing it with H_2O_2 and titration of

Cl^- and Br^- with Ag^+ (produces two separate breaks).

Physical separation operations:

- Filtration
- Extraction
  e.g. extraction of fatty acids from serum or blood
- Distillation
  e.g. distillation of NH_3 after a Kjeldahl digestion

Change of the titration conditions (see page 6ff)***:***

- Titration reaction
- Titration medium
- Indication method

The choice of suitable titration conditions concern the basic principles of titrimetry. They are therefore described separately in the following chapter.

3. Basic principles of titrimetric analyses

3.1 Titration reactions

In addition to the sample preparation, selection of a suitable chemical reaction, the titration reaction, is an important task of the analytical chemist. Titration reactions should meet the following requirements:

- The stoichiometry of the reaction must be known exactly and must not change in the course of the titration
- The forward reaction to form the reaction products must be virtually quantitative, i.e. the equilibrium constant of the reaction must be large
- The equilibrium must be quickly established
- No interfering parallel or consecutive reactions should occur
- Errors in detection of the endpoint must be kept to a minimum by selection of a suitable indication method

Let us have a brief look at the theoretical aspect of titration reactions. For the general reaction

$$rR + tT \rightleftharpoons aA + bB$$

the equation for the equilibrium constant K is

$$K = \frac{[A]^a \cdot [B]^b}{[R]^r \cdot [T]^t}$$

Before titration, the concentration of the reactant is $[R]_0$ and the volume of the sample solution V_0. Titrant of concentration $[T]_0$ is added. The volume of the added titrant solution is V_t. The concentration of the reactant R between the start of the titration and the equivalence point is given by the following equation

$$[R] = \frac{V_0[R]_0 - r/t \cdot V_t[T]_0}{V_0 + V_t} + [R]_{\text{from the back reaction}}$$

$$= \frac{V_0[R]_0 - r/t \cdot V_t[T]_0}{V_0 + V_t} + r/t \sqrt[t]{\frac{[A]^a \cdot [B]^b}{K \cdot [R]^r}} .$$

If the equilibrium constant is sufficiently large, the back reaction can be neglected and the following equation holds

$$[R] \approx \frac{V_0[R]_0 - r/t \cdot V_t[T]_0}{V_0 + V_t}$$

At the equivalence point, the system is in "equilibrium", i.e. $r[R]=t[T]$, and the following holds

$$[R]_{eq} = \sqrt[r+t]{(r/t)^t \cdot \frac{[A]^a \cdot [B]^b}{K}}$$

Titration reactions are analytically useful if the concentration of the reactant at the equivalence point $[R]_{eq}$ is less than 1/1000 $[R]_0$.

As an example, let us take the most well-known titration reaction, the neutralization reaction, where the following equilibrium holds

$$H_3O^+ + OH^- \rightleftharpoons 2\ H_2O$$

At the equivalence point, the concentration of the free acid is given by the equation above

$$[H_3O^+]_{eq} = \sqrt{\frac{[H_2O]^2}{K}} = \sqrt{\frac{1}{10^{14}}} = 10^{-7}\,\text{mol/L}$$

The neutralization reaction is thus suitable for use as titration reaction for determinations of strong acids or bases with initial concentrations $[R]_0 \geq 10^{-4}$ mol/L.

Several examples of titration reactions commonly used are listed in Table 1 together with their possible titrants.

Titration reaction	**Titrant**
Neutralization reactions	
Acidimetry	Acids
in aqueous medium	HCl
in non-aqueous medium	$HClO_4$ in CH_3COOH
Alkalimetry	Bases
in aqueous medium	NaOH
in non-aqueous medium	Tetrabutylammoniumhydroxid in isopropanol
Redox reactions	
Cerimetry $Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$	Ce^{4+}
Manganometry $5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightleftharpoons 5\ Fe^{3+} + Mn^{2+} + 4\ H_2O$	MnO_4^-
Dichromatometry $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightleftharpoons 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$	$Cr_2O_7^{2-}$
Diazotizations $Ar\text{-}NH_2 + NO_2^- + 2HCl \rightleftharpoons Ar\text{-}N = N\text{-}Cl + Cl^- + 2\ H_2O$	$NaNO_2$
Precipitation reactions	
Argentometry $Cl^- + Ag^+ \rightleftharpoons AgCl\ (s)$	Ag^+
Complexation reactions	
Complexometry $Ca^{2+} + H_2EDTA^{2-} \rightleftharpoons CaEDTA^{2-} + 2H^+$	Chelate ligand, e.g. EDTA

Table 1: Examples of various titration reactions and the associated titrants

A titrimetric determination can comprise several titration reactions if several substances have to be determined in one sample. Auxiliary reaction are frequently necessary to increase the selectivity of the individual determination (see also page 4).

For example, both Au^{3+} and Cu^{2+} can be titrated with Fe^{2+}: Au^{3+} is reduced by Fe^{2+} directly to the metal. Cu^{2+} is first reduced with I^-. The J_2 formed does not react until F^- has been added to form the FeF_6^{4-} complex, which is a more powerful reducing agent than $Fe(H_2O)_6^{2+}$:

$$Cu^{2+} + 2I^- \rightarrow CuI + \tfrac{1}{2} I_2$$

$$\tfrac{1}{2} I_2 + FeF_6^{4-} \rightarrow FeF_6^{3-} + I^-$$

$$Au^{3+} + 3\,Fe(H_2O)_6^{2-} \rightarrow Au + 3\,Fe(H_2O)_6^{3+} \qquad Cu^{2+} + 2\,I^- + FeF_6^{4-} \rightarrow CuI + I^- + FeF_6^{3-}$$

The practical execution of such complex titration routines is easy to achieve using modern titrators and therefore pose no problems for routine analysis.

3.2 Titrants

The titrant should be selected such that the conditions mentioned in chapter 3.1 for the titration reaction are fulfilled as far as possible. This concerns not only the reagent itself but also the solvent used.

The exact concentration of the titrant is determined periodically and indicated as its titer. The titer should be stable. It is determined with the aid of primary standards. Primary standards are analytically pure substances of clearly defined composition. Their content doesn't change and they can be dried. A list of such suitable primary standards is given in Table 2 together with their Merck order number as an example of a commercial source.

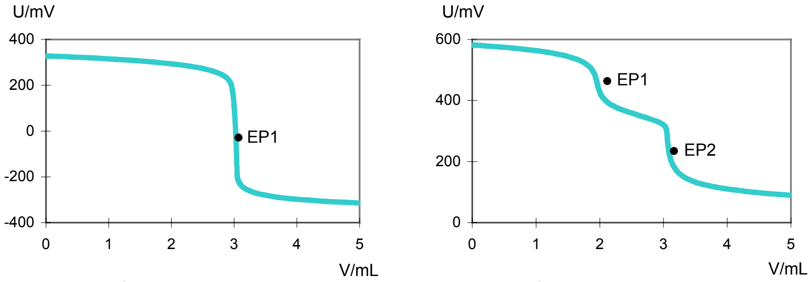
Primary standard	**Molar mass (g/mol)**	**Merck No.**	**Application**
Benzoic acid, $C_7H_6O_2$	122.12	102 401	Alkalimetry
Calcium carbonate, $CaCO_3$	100.09	-	Complexometry
Potassium dichromate, $K_2Cr_2O_7$	294.19	102 403	Oxidimetry, Cerimetry
Potassium hydrogen phthalate, $KC_8H_5O_4$	204.23	102 400	Alkalimetry
Potassium iodate, KIO_3	214.00	102 404	Oxidimetry, Cerimetry
Sodium carbonate, Na_2CO_3	105.99	102 405	Acidimetry
Sodium chloride, NaCl	58.44	102 406	Argentometry
Sodium oxalate, $Na_2C_2O_4$	134.00	102 407	Oxidimetry, Cerimetry
Sodium tartrate, $Na_2C_4H_4O_6 \cdot 2H_2O$	230.08	106 664	Karl Fischer titration
TRIS, Tris-(hydroxymethyl)-aminomethane, $C_4H_{11}NO_3$	121.14	102 408	Acidimetry

Table 2: Primary standards and their applications

3.3 Titration media

Most titrimetric determinations are performed in ***aqueous media***. The practical and theoretical aspects of such titrations are well known. Less clear, however, are the circumstances for titrations in non-aqueous media. The influence of the titration medium on the course of the titration is great. Titrations in non-aqueous solvents allow determinations that pose difficulties in water to be performed in a selective and optimal manner as well as the determination of many substances where the determination becomes only possible by changing from water to a non-aqueous solvent. The use of ***non-aqueous media*** is advisable or necessary in the following cases:

- The substance to be determined is poorly soluble in water (e.g. acid and base numbers in mineral oils)
- The product formed in precipitation titrations is too soluble in water (e.g. lowering the solubility of AgCl by addition of acetone)
- The substance to be determined is a very weak acid or base and can no longer be titrated in water (e.g. phenol derivatives, imines)
- A mixture of substances can not be determined selectively in water (leveling; e.g. H_2SO_4 and HNO_3 in nitrating acid, Fig. 2).
- The substance to be determined reacts chemically with water (e.g. acid chlorides, acid anhydrides)
- Water itself has to be determined (water determination by the Karl Fischer method)



Solvent: Water
Titrant: NaOH

Leveling of the two acids

Solvent: Methanol
Titrant: Cyclohexyl amine in methanol

Differentiation of the two acids

Fig. 2: Titration of nitrating acid (sulphuric acid/nitric acid, ca. 1:1)

A distinction is made between amphiprotic solvents, which exhibit a "water-like" self-dissociation, and aprotic solvents without any noticeable self-dissociation.

In both groups a distinction is made between solvents with predominantly acidic, basic or neutral character. The weaker an acid to be determined, the more alkaline the solvent should be selected. This increases the acid strength and allows a better titrimetric determination of the acid. The opposite is true for bases. Thus, for example, the weak base m-Bromoaniline (pK_B = 10.42) can easily be titrated in the acidic solvent glacial acetic acid.

Amphiprotic solvents have a limited working range due to their leveling effect and their self-dissociation. The smaller the self-dissociation of the solvent (the greater pK_{auto}), the broader its working range. On the other hand, amphiprotic solvents have usually a good solubilising power and no problems arise in potentiometric indication due to static charging.

Aprotic solvents have a wide working range but usually a low solubilising power and owing to poor conductivity require special measures for potentiometric indication (see page 12).

The noticeably lower dielectric constant of non-aqueous solvents compared with that of water also contributes to the differentiation of various acidic or basic functions: The lower the dielectric constant and the greater the charge of the reaction products, the stronger the coulombic attraction responsible for repressing the dissociation, i.e. the weaker the titrated acid or base appears.

Owing to the wide range of interactions that occur, a comprehensive overview lies outside the scope of this article. The reader is referred to the monograph on non-aqueous titrations.
Table 3 shows a few solvents in widespread use and their typical applications. In addition to pure solvents, solvent mixtures are also often used to obtain optimum working conditions.

Solvent type	Solvent	DC	pK_{auto}	Typical application
Amphiprotic, mostly neutral	Water Methanol Ethanol Isopropanol	80.4 32.6 24.3 18.3	14.0 16.7 19.5 20.8	For acids and bases, good differentiation
Amphiprotic, mostly acidic	Glacial acetic acid	6.2	14.5	For very weak bases (up to pK_B 12), leveling
Amphiprotic, mostly basic	Ethylendiamine	12.5	15.3	For acids (pK 2...12), levels strong acids
Aprotic, neutral	Acetic anhydride	20.7	-	For very weak bases (up to pK_B 12)
	Acetonitrile	36	ca.33	For bases (up to pK_B 9), good differentiation
	Acetone	21.2	-	For acids and bases, good differentiation
Aprotic, basic	Dimethylformamide	36.7	27.0	For strong acids (up to pK 0), good differentiation

Table 3: Solvents and their uses for titrimetric determinations
DC: Dielectric constant

3.4 Indication methods

By definition, the ***equivalence point*** of a titration corresponds to the exact stoichiometric reaction of the titration. The indication system, however, detects only ***titration endpoints.*** These should therefore be as close as possible to the equivalence point so that the error in the titration remains as small as possible. For the indication of the endpoint, an observation or measurement of a physical quantity that is proportional to the concentration of one of the reaction partners in the titration reac-

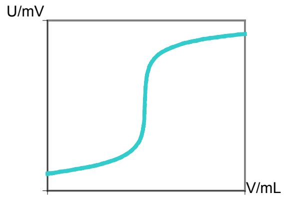
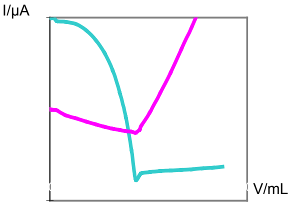
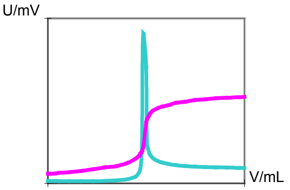
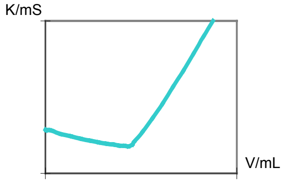
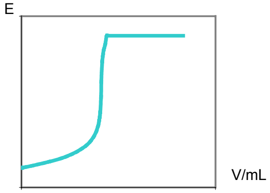
Indication method	**Measurement principle, equations**	**Possible curve**
Potentiometric indication	Zero-current measurement of potential U $U = U_0 + (RT/zF)\cdot\ln(a_{ox}/a_{red})$ $U = U_0 + (RT/zF)\cdot\ln a$ $pH = -\log a_{H^+}$ R: Gas constant T: Temperature in K z: Charge of ion F: Faraday constant a: Activity	
Amperometric indication	Measurement of current I at a fixed applied direct or alternating voltage $I = f(V)$ — amperometric — biamperometric	
Voltametric indication	Measurement of potential U at a fixed applied direct or alternating current $U = f(V)$ — voltametric — bivoltametric	
Conductometric indication	Measurement of electrical conductivity κ with electrodes carrying alternating current $\kappa = \text{constant}\ \Sigma(u_i\cdot z_i\cdot c_i)$ u_i: Mobility of ion i z_i: Charge of ion i c_i: Concentration of ion i	
Photometric indication	Measurement of extinction E or transmission T $E = c\cdot d\cdot\varepsilon$ $T = 10^{-c\cdot d\cdot\varepsilon}$ c: Concentration d: Path length ε: Extinction coefficient	

Table 4: Overview of different indication methods and their characteristic curve shapes

tion. If the reaction partners are not directly amenable to measurement, a suitable "indicator" can be used which reacts with one of the reaction partners and produces an observable signal.

Of the various indication methods available, electrometric and optical indication methods are the most suitable for the performance of automated titrations. Table 4 gives an overview of different indication methods.

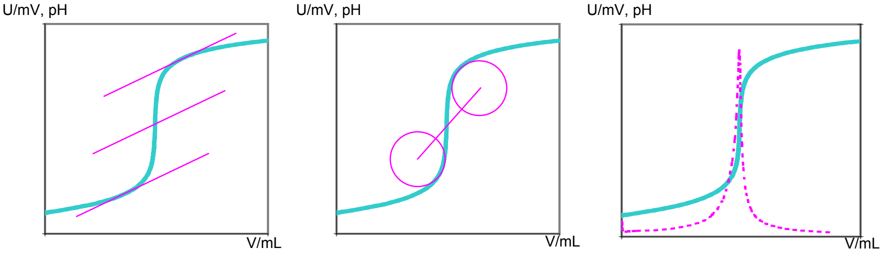
3.4.1 Potentiometric indication

Potentiometric indication is by far the most versatile and hence also the most widespread. In potentiometric indication the zero-current potential changes that occur during a titration at the indicator electrode are measured. Selection of the indicator electrode depends on the nature of the titration reaction. If possible, the indicator electrode should respond solely to the ion being indicated. In order to make measurement possible, a reference electrode is needed to supplement the indicator electrode. This reference electrode should not respond to the changes in the titration solution.

The endpoint of the titration lies in the inflection point of the titration curve. The evaluation of potentiometric titrations is carried out automatically by modern titrators. Other evalutions methods for potentiometric titrations are discussed below.

Graphical endpoint evaluation

As an aid for graphical evaluation, special evaluation rulers are available. Their use is illustrated in Fig. 3.



Tangent method
The tangents are drawn at the bends of the curve. The intersection point of the median line with the titration curve gives the endpoint of the titration.
Easy application, good results with symmetric titration curves.

Circle method according to Tubbs
The circles are drawn in the bends of the titration curve. The intersection point of the line connecting the centers of the two circles with the titration curve defines the endpoint of the titration.
Good results even for asymmetric curves.

Derivative titration curves
The first derivative of the titration curve shows a peak whose maximum represents the endpoint of the titration.
Time-consuming if performed manually.

Fig. 3: Graphical evaluation methods for potentiometric titrations

Numerical endpoint evaluation

Below, some widespread numerical methods for endpoint evaluation are described. For all three methods titrant dispensing must be performed with constant volume increments.

1. *Evaluation according to Kolthoff/Hahn*

   Note the greatest potential difference ΔU_{max} as well as the potential difference before and after ΔU_{max}, ΔU_{before} and $\Delta U_{after.}$ The endpoint volume is calculated using the volume V' before ΔU_{max} and the volume increment ΔV according to

$$V_{EP} = V' + \Delta V \frac{\Delta U_{max} - \Delta U_{before}}{2\Delta U_{max} - (\Delta U_{before} + \Delta U_{after})}$$

2. *Fortuin approximation*

   Note the three greatest potential differences $\Delta U_{max} > \Delta U_1 > \Delta U_2$ and calculate the quotients $R_1 = \Delta U_1/\Delta U_{max}$ and $R_2 = \Delta U_2/\Delta U_{max}$. Determine the factor ρ from the Fortuin nomogram. The endpoint volume is calculated using the volume V' before ΔU_{max} and the volume increment ΔV according to

   $V_{EP} = V' + \rho \cdot \Delta V$

3. *Gran evaluation*

   Linearisation of the potentiometric titration equation

   $U = U_0 + s/z \cdot \log c$

   gives

   $10^{z \cdot U/s} = \underbrace{10^{z \cdot Uo/s}}_{\text{constant}} c$

Potentiometric titrations in non-aqueous solvents

Problems may arise in pH titrations in organic solvents with low conductivity, particularly aprotic solvents. In these solvents, interfering voltages may disturb the recording or evaluation of the titration curve or even render it impossible. The interfering voltages originate from coupled electrostatic and electromagnetic fields. Such interference fields can arise through friction on synthetic material or floors.

The use of specially designed electrodes (e.g. Solvotrodes) may solve this problem. The glass membrane of the Solvotrode has a rather large surface area and is made of low-impedance pH glass. The ground joint diaphragm maintains a constant electrolyte flow.

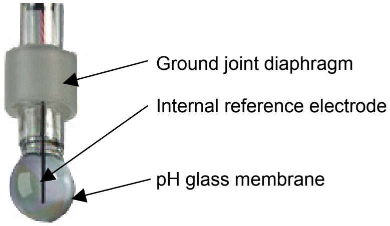


Fig. 4: Solvotrode
Specially designed for pH titrations non-aqueous titration

A practical example is the determination of the total base number (TBN) in mineral oil. The pH titration has to be carried out in a non-aqueous solvent because the oil is insoluble in water. A mixture of toluene and glacial acetic acid is used as solvent.

Fig. 5 shows the titration curves as well as the first derivatives. The potentiometric titration has been indicated with various electrodes. The use of a Solvotrode shows already an improvement (curve Fig. 5B): The endpoint can be evaluated and the titration curve has less noise which is obvious in the first derivative. The first derivative in Fig. 5C is even smoother. For this indication, a differential amplifier (see Fig. 6) has been used together with a symmetrical measuring assembly, i.e. a measuring assembly with an identical shielding of the indicator and reference electrode. Both electrodes are connected to a high impedance measuring input. An inactive auxiliary electrode produces a galvanically conducting connection between the titration solution and the reference point of the amplifier circuit. With this measuring setup, coupled stray interference fields are recorded by the indicator and reference electrode to the same extent and therefore compensated. Specially shielded reference electrodes are commercially available at Metrohm (Ag/AgCl double junction electrode).

The pH glass electrode should frequently be immersed in water between titrations, in order to preserve the H^+ ions active gel layer in good condition.

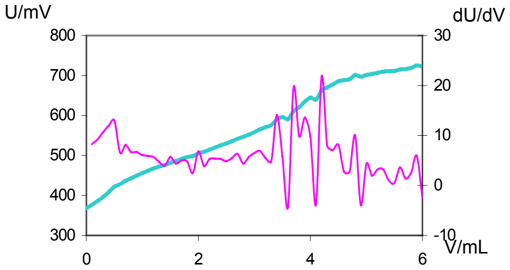


Fig. 5A:
Indication:
Separate pH glass electrode + double junction reference electrode

Potentiometric measuring input

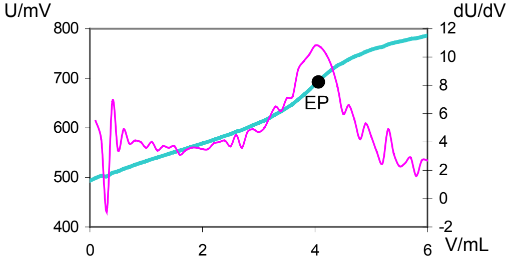


Fig. 5B:
Indication:
Solvotrode

Potentiometric measuring input

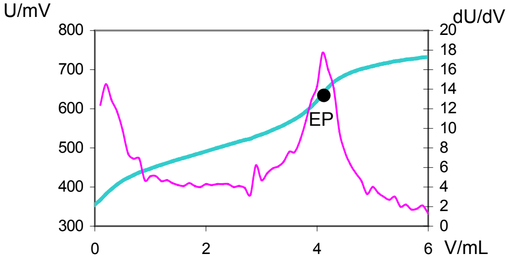


Fig. 5C:
Indication:
pH glass electrode with Pt auxiliary electrode (Pt Titrode) + shielded double junction reference electrode

Differential amplifier

Fig. 5: Determination of total base number in mineral oil: Titration with $HClO_4$ in glacial acetic acid; solvent: Toluene/glacial acetic acid. Representation of titration curves and their first derivatives

1, 3:	High impedance measuring inputs for indicator and reference electrodes
2:	Low impedance measuring input as reference point for an auxiliary electrode

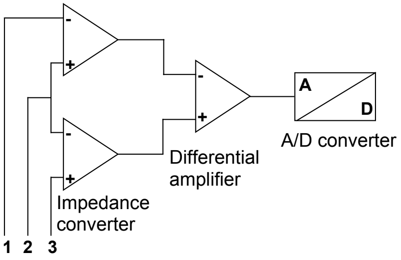


Fig. 6: Schematic representation of a differential amplifier

Indication with ion selective electrodes

Ion selective electrodes (ISE) are frequently used to indicate potentiometric titrations, they are specially suitable in complexometry (e.g. titrations with EDTA). The sensor element of ion selective electrodes responds selectively to a particular ion. The Ca selective electrode for example responds to hydrated Ca^{2+} ions. EDTA complexes of Ca^{2+} don't contribute to the potential. Ca^{2+} can therefore be titrated with EDTA using a Ca selective electrode as indicator electrode.

Surfactant titrations

The potentiometric surfactant titration is an alternative to the classical titration with colored indicators and visual or photometric indication. For potentiometric titrations, special surfactant electrodes with a sensor element which responds to surfactants are used.

In surfactant titrations, precipitations are normally formed, i.e. the surfactant builds a sparingly soluble compound with the oppositely charged molecule of the titrant. Nonionic surfactants are usually converted to pseudoionic compounds before titration by adding an auxiliary solution.

Surfactant electrode	**Application**	**Titrant**
Ionic Surfactant or High Sense electrode	Titration of anionic surfactants, aqueous	TEGO® trant A100
	Titration of cationic surfactants, aqueous	Na dodecylsulphate (laurylsulphate)
NIO electrode	Titration of non-ionic surfactants, aqueous. Use electrode for one type of non-ionic surfactant only!	Na tetraphenylborate (Use NaCl instead of KCl as reference electrolyte; K tetraphenylborate is sparingly soluble in water!)
Surfactrode Refill	2 phase titration without $CHCl_3$	*For anionic surfactants:* TEGO® trant A100 Hyamine 1622 *For cationic surfactants:* Na dodecylsulphate (laurylsulphate) Addition of TEGO add ensures an efficient blending of the two phases during titration
Surfactrode Resistant	2 phase titration with $CHCl_3$	

Table 5: Overview of surfactant titrations and frequently used titrants

3.4.2 (Bi)amperometric and (bi)voltametric indication

Irreversible redox reactions or inhibited electrode reactions that can not develop a definite potential are usually not suitable for potentiometric indication. In these cases, current-carrying electrodes frequently represent an alternative indication possibility.

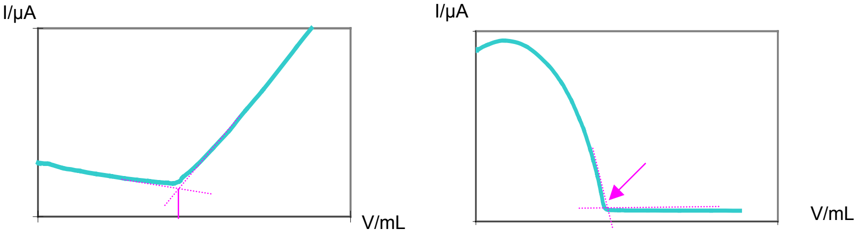
The following methods can be used:

	1 polarized electrode	**2 polarized electrodes**
Applied potential, measurement of the current	Amperometry	Biamperometry
Applied current, measurement of the potential	Voltametry	Bivoltametry

Table 6: Indication possibilities with polarized electrodes

Indication methods with polarized electrodes show sharper and steeper signal changes in the vicinity of the endpoint than potentiometric indications. They are therefore often used for micro-titrations. However, the titration reaction, the type of electrode pretreatment, the size of the electrode surface und the applied polarization current or voltage have a great influence on the signal; a widespread use of this indication method and its automation is therefore difficult.

Titration curves indicated with polarized electrodes can often be evaluated with the break point evaluation which is shown graphically in Fig. 7 for amperometric and biamperometric indicated curves.



Amperometric indication
Titration of Pb^{2+} with $Cr_2O_7^-$.
The endpoint is the intersection point of the extrapolated curve branches → break point evaluation.

Biamperometric indication
Titration of Fe^{2+} with $Cr_2O_7^{2-}$.
The endpoint is the discontinuity of the curve → break point evaluation.

Fig. 7: Evaluation of amperometrically and biamperometrically indicated titration curves

Voltametric titration curves often resemble potentiometric titration curves. The shape of such voltametric curves is greatly dependent on the titration conditions (magnitude of I_{pol}, anodic or cathodic polarization of the indicator electrode, type of titration reaction etc.). The endpoint evaluation of samples should therefore be performed using the same procedure as for titer determinations with standard substances.

Bivoltametric curves often show a peak, see page 11. The endpoint of these curves is determined by the intersection point of the extrapolated curve branches (as for amperometric curves).

A standard procedure where polarized electrodes are used is the water determination according to ***Karl Fischer***. This titration is performed as an endpoint titration (see page 22) and indicated bivoltametrically or amperometrically. It can readily be automated since not only is the titration reaction always the same but also the media are invariably similar:

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

3.4.3 Conductometric indication

Conductometric indication utilizes the change in the electrical conductivity during the titration. It should be noted that all ions in the solution contribute to the conductivity, irrespective of whether or not they participate in the titration reaction. Compensation of the background conductivity allows work to be performed in a more sensitive measurement range. This results in improved detection of conductivity changes.

Usually double Pt foil electrodes with or without platinization (Pt black) are used as current carrying electrodes. The endpoint of the titration is given by the intersection point of the extrapolated curve branches. The most important practical application of titrations with conductometric indication is the determination of alpha acids in hop extracts and the titration of SO_4^{2-} with $Ba(ClO_4)_2$ after the Schöniger combustion.

3.4.4 Optical indication

Optical indication can be used if the "color" (absorption at a specific wavelength), the turbidity or the fluorescence change in the course of the titration. If the actual titration reaction does not produce a change in one of these properties (self indication), a suitable indicator can be added that, for example, changes the color (external indication).

Indicators usually are colored organic compounds which react with the substance to be determined. The color of this reaction product changes at the endpoint. Well-known indicators are

- pH indicators for acid/base titrations
- fluorescent indicators for titrations in turbid or highly colored solutions
- adsorption indicators for precipitation titrations
- redox indicators
- metal indicators for complexometric titrations

pH indicators have to be selected in such a manner that their pK value is as close as possible to the pH value of the equivalence point of the titration in question (Fig. 8).

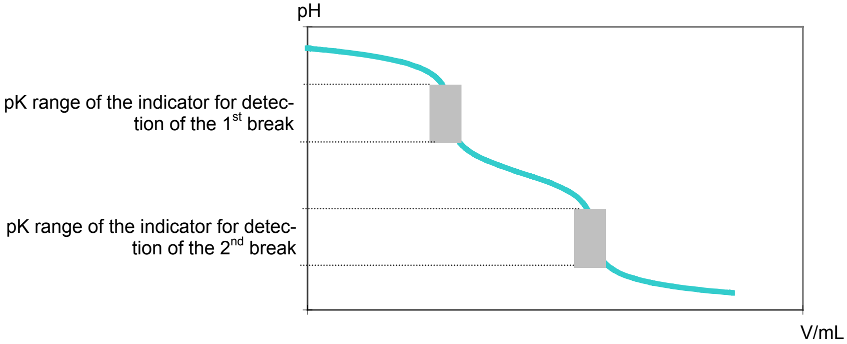


Fig. 8: Correct selection of the indicator with the aid of the titration curve. The pK value of the indicator should lie in the region of the break in the titration curve.

Table 7 shows the most common pH indicators with their pK values and color changes:

pH indicator	pK	Color change	pH value
Methyl orange	3.46	Red to orange-yellow	3.1... 4.4
Bromophenol blue	4.10	Yellow to purple	3.0... 4.6
Bromocresol green	4.90	Yellow to blue-violet	3.8... 5.4
Bromophenol blue	7.30	Yellow to blue	6.0... 7.6
Thymol blue	9.20	Yellow to blue	8.0... 9.6
Phenolphthalein	9.70	Colorless to red-violet	8.2... 9.8

Table 7: pH indicators with their pK values, the color changes and the pH values of their transition intervals

If mixed indicators are used, the pH range of the transition can be reduced which allows a sharper endpoint detection which is specially important for flat curves.

Titration curves with optical indication can take very different forms, depending on:

- the measured quantity: Transmission or extinction
- the indication of the titration: Self indication or external indication
- the stability constants of the indicator with the educt or the product of the titration reaction

For externally indicated curves, the basic curve shapes are shown in Fig. 9.

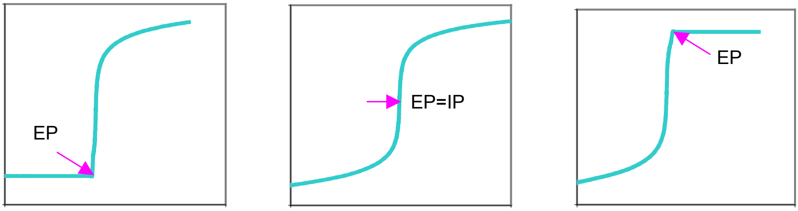


Fig. 9A:
The indicator changes its color after the endpoint of the titration reaction → break point evaluation

Fig. 9B:
The indicator changes its color in the range of the EP of the titration reaction (IP = Inflection point) → "Potentiometric" inflection point evaluation

Fig. 9C:
The indicator doesn't change its color after the endpoint anymore → break point evaluation

Fig. 9: Evaluation of photometrically indicated titrations

For curves of type as represented in Fig. 9B, a potentiometric inflection point evaluation is correct. This evaluation is possible with most commercially available titrators and can be applied to photometric titrations.
Curves of type 9A and 9C, however, should be evaluated by the break point method. This method is also often possible with modern automatic titrators.

4. Performing titrations

The classical method of titrating comprises manual addition of metered aliquots of the titrant and visual determination of the "endpoint". The endpoint of a titration is reached when the concentration of the substance to be determined is less than 1/1000 of its initial concentration. This must be ensured by appropriate selection of the titration reaction and indication, see page 6.

4.1 Addition of titrant

The traditional aid for the addition of titrant is a calibrated glass tube with stopcock that allows the addition of exactly metered volume increments. With development of the piston buret, it became possible to titrate appreciably more rapidly and precisely since the buret lag could be eliminated. The resolution of motorized piston burets is today 1/10000 of the cylinder volume or better, i.e. 5 µL (or less) with a cylinder volume of 50 mL. A 50 mL Schellbach buret with graduation marks 1mm apart would have to be app. 10 m long to give the same resolution! Compared with glass burets, piston burets have considerably greater accuracy, precision and volume resolution, a fundamental requirement for high performance titrimetry.

Automatic titrators use only motorized piston burets for volumetric addition of the titrant, see Fig. 10.

Coulometry

In addition to the volumetric addition of titrant, the reagent can also be added coulometrically. Here, the reagent is usually generated directly in the titration vessel from an intermediate reagent (I). The amount n (in mol) of titrant (T) generated by the reaction

$$I + z \cdot e^- \rightarrow T$$

is calculated from Faraday's law of electrolysis:

$$n = \frac{Q}{z \cdot F}$$

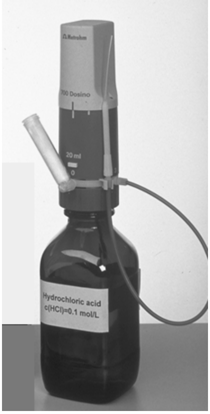
Q: Quantity of electricity in Coulomb (1C = 1 A·s)
z: Number of electrons participating in the reaction
F: Faraday constant, 96484.56 C/mol

The coulometric reagent generation is particularly suitable for use in the titrimetric determination of very small quantities since small currents can be measured exactly. A current of 1 µA applied during 1 s generates an amount of substance of 10 pmol (for $z = 1$).

The direct proportionality between current and generated reagent is responsible for another advantage of coulometric reagent generation: a titer determination, which is specially crucial with very dilute titrants, is unnecessary.

First piston buret (Metrohm 1955)
PTFE piston in a calibrated glass tube. Highly accurate volume resolution according to the micrometer principle.

Microprocessor-controlled piston buret
Used for automatic titrators and as buret with multiple dosing programs.



Dosino
The buret motor is directly placed onto the reagent bottle. Used for automatic titrators.

Titrino
Complete automatic titrator. The buret is part of the titrator.

Fig. 10: Development of the piston buret principle for automatic titrators

The coulometric reagent generation also allows work with "unstable" titrants since these can react immediately with the substance to be determined.

A prerequisite for the coulometric reagent generation is that a 100% current yield of the electrode reaction has been checked and ensured. Interferences can arise due to foreign ions or the sample matrix, which under certain conditions can be much more easily reduced or oxidized at the working electrode than the intermediate reagent. Additional interference is possible when products formed at the counter elec-

trode can react with the reagent. Such interferences must be kept at a minimum by suitable construction of the cell.
This leads to the conclusion that the coulometric reagent generation is sufficiently rapid and efficient for use in routine analysis only for well known and fully developed determinations. Dedicated coulometric titrators are used. Typical examples for coulometric routine titrations are the water determination according to Karl Fischer, the determination of chloride in blood, serum, and urine as well as the determination of SO_2 in air (SO_2 monitor).

4.2 Endpoint titrations

A basic requirement for an endpoint titration is a stable and reproducible indication signal. Titration is performed to a preselected set value, the "endpoint". The titrant consumption is used to calculate the content of the substance or of a class of compound.

In addition to manual endpoint titrations, these endpoint titrations are rapidly and precisely performed with automatic titrators. An endpoint titrator is in principle a controller which converts a preset/actual signal deviation into control signals for a device which adds the titrant.

There are two regions of feedback control:

- If the control deviation is grater than a preset threshold, titrant addition is relatively rapid and continuous.
- If the control deviation is less than this threshold, the titrant is added discontinuously.

Microprocessor-controlled titrators can accomplish this control rapidly and accurately through preassessment of the titration profile:

- During the continuous dispensing, the rate is gradually lowered when the threshold is approached. The slope of the titration curve is also taken into account.
- Within the discontinuous control range, dispensing is performed with precalculated volume increments at an increasingly slower rate as the endpoint is approached. In addition to the current measured value, the dynamic behavior of the system is taken into account since the measured value drift is included in the preassessment.

Owing to their simple operation, endpoint titrations find their principal use in routine analysis. Many standard methods are performed as endpoint titrations, e.g. acid and base capacity in water, chloride determinations, determinations of acid in wine and fruit juices.

Kinetic measurements are a special application of the endpoint titration methodology. The set value is kept constant during a preselected time interval (***pH stat function***) and the reagent consumption during this interval is recorded against time. The kinetic data are calculated $\Delta V/\Delta t$.

4.3 Recording the entire titration curve

If the indication signal is not sufficiently stable for an endpoint titration or if more information regarding the sample is desired, recording of the titration curve is necessary. The titration curve is the graphical representation of the change in the indication signal as a function of titrant consumption. Whereas the endpoint titration provides information only about the content of a substance or about the total amount of substances, additional information can be made available thanks to recording of the entire titration curve - particularly in cases of potentiometric indication:

- Several substances can be determined simultaneously in the same sample, e.g. different halogens in an argentometric titration
- The presence of impurities that also react with the titrant can be established, e.g. carbonate in acid-base titrations
- Any irregularities in the course of a titration, which could lead to spurious results, are apparent, e.g. disturbed establishment of equilibrium due to kinetic inhibitions of the titration reaction or the indication system
- From the data of the titration curve obtained with neutralization reactions, acid or base strength (pK values) can be determined.

Depending on the nature of the titration conditions (titration reaction, titration medium and the indication), different shapes of titration curves result. Fig. 2, page 9 shows the influence of the titration medium and Table 4, page 11 that of the indication system.

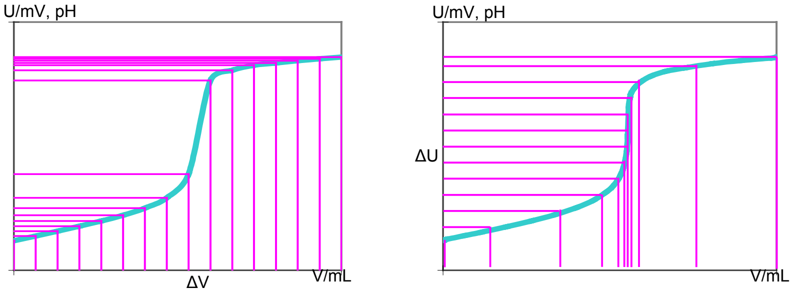
4.3.1 Dispensing principles

In order to record the titration curve as rapidly and as accurately as possible, optimum selection of the reagent dispensing is necessary.

A possibility for reagent addition is the dispensing of distinct volume increments as it is done in manual dispensing. The advantage of such ***incremental titrations*** lies in the possibility to wait for the establishment of the equilibrium of the measured signal after each increment. The size of the volume increments can be constant or variable.

If constant volume increments are added (known as monotonic reagent dispensing), 100 µL is usually a good value for the choice of the size of the increments. For low titrant consumptions or for sudden, steep breaks in the titration curve ("angular" curves), you may need a smaller value, e.g. 50 µL. For flat curves or with high titrant consumptions, you better use greater volume increments, e.g. 200 µL. In any case, you should have about 20 measured points before the endpoint.
The advantage of the monotonic dispensing principle is that even titration reactions with inhibited kinetics and/or indication signal can be performed satisfactorily. Such titrations include diazotizations or the determination of total acid/base number (TAN/-TBN) in mineral oil where other types of dispensing can lead to problems.
The disadvantage of the ***monotonic titration*** is the low data density around the equivalence point which means a loss of information in potentiometric titrations. This is especially evident for steep breaks (Fig. 11). Since this type of volume dispensing is simple to implement, the first "digital titrator" with monotonic titration was in operation as early as 1968.

Optimum distribution of the measurement point density for titrations with potentiometric indication is attained when the addition of volume increments is made dynamically, i.e. made to vary as a function of the slope of the titration curve $\Delta U/\Delta V$. Fig. 11 shows the change in volume increment size if constant measured value differences are to be attained. This method requires the calculation of successive volume steps from the available data of the titration curve. This dispensing principle was thus not implemented until the advent of microprocessor-controlled instruments. The shape of the titration curve enters the formula used to calculate the volume increment size. The ***dynamic titration*** is thus limited to potentiometric or approximately S-shaped titration curves. Thanks to the optimum distribution of the data density, a very sensitive detection of equivalence points is possible. On the one hand, acids can be distinguished whose pK_A values differ by only 1.5; on the other hand, minor impurities can still be determined.
A kinetically inhibited measured value acquisition or a non-S-shaped titration curve leads, however, to wrong calculations of the volume steps and hence to distorted curves. For such cases, it is necessary to fall back on the dispensing principle with constant volume steps.



Monotonic titration
Addition of constant volume increments ΔV

Dynamic titration
Addition of variable volume increments to acquire approximately constant potential differences ΔU

Fig. 11: Potentiometric titrations with different types of reagent addition

4.3.2 Measured value acquisition

In titrations with incremental dispensing, the measured value can be acquired either after a fixed waiting time or if it remains below a preselected drift value ("equilibrium titration"). Such an equilibrium titration allows titrations to be performed with extremely high precision. Table 9 gives an overview of the different types of measured value acquisition and possible associated dispensing principles with their range of application.

Type of measured value acquisition	Dosing principle	Application
After elapse of a fixed waiting time or drift controlled	Monotonic titration with constant volume increments	Precise titration mode suitable for all indication methods; specially for kinetic inhibited reactions or indications, e.g. diazotizations
After elapse of a fixed waiting time or drift controlled	Dynamic titration with variable volume increments	Highly precise titration mode with excellent selectivity for potentiometric and other S-shaped curves without kinetic inhibition

Table 9: Type of measured value acquisition and corresponding dosing principle

4.4 Automation of titrations

The tasks performed by means of manual titration are increasingly being taken over by partially or fully automated titrators. The reason for this are:

- Lower costs per analysis.
- More rapid and more reliable performance.
- Greater precision of the analytical results.
- Greater sensitivity in the detection of endpoints.
- Automatic evaluation of endpoints and calculation of results.
- Error-free, GLP-proof documentation of the analysis on a printer, PC or in a laboratory information system (LIMS).
- Multiple use of identical, validated titration methods in different labs of a company.
- Possibility to run analysis series without supervision with the aid of sample transport systems, with the option of including several or all sample preparation steps.

A first step for automation is a reagent addition which is controlled by the titrator as well as the recording of the indication signal. Some modern titrator systems offer several more functions which can be used for automation:

- Storing of sample data for serial analysis. This allows to process fully automatically different samples in any order.
- Possibility to send results to an external data system and receive external commands.
- Performing titrations with complex operations, e.g. with decisions (IF) in the course of the titration.
- Control of auxiliary functions for sample preparation before titration, e.g. addition of auxiliary reagents, elapse of waiting times etc.

- Possibility to control additional peripheral instruments such as Sample Changers, additional dosing elements etc.

Sample Changers are generally used to automate the sample feed thus allowing to stack a large number of samples. The sample data (weighings, sample identifications) are often stored directly in the automatic titrator. The samples are then conveyed automatically to the titration station, provided with the correct sample data, titrated and the results evaluated. Sample Changers can also usually be used to perform simple sample preparation steps, e.g. dissolution, dilution, or pipetting of samples.
If, however, sample preparation involves time-consuming operations, laboratory robots that allow sample transfer from one processing station to another can be used for the automation.

A high degree of automation is attained with ***on-line titrators*** in process analysis. The basic functions of the titrimetric determinations are the same as with laboratory titrators. In addition, a sampling pretreatment and metering system is needed. The sample is removed from the process operation with the aid of a bypass line; if need be, sample preparation steps such as dilution, filtration, cooling, warming etc. are performed, and the sample then led to the titration vessel via a metering loop.

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