TITRATION
THEORY AND PRACTICE

THEORY OF TITRATION

Introduction

The aim of this booklet is to explore titration from a historical, theoretical and practical point of view, dealing first with preset end point titration then with inflection point titration. We look at common applications and give useful advice on how to choose between techniques and get the best results.

Why titration?

In most manufacturing or processing industries, it is essential to know the exact concentration of a product, a species or a chemical function in order to ensure the efficiency of a process or the quality of a finished product.

This is achieved by:

Finding a characteristic of the product directly related to its concentration. The analyst uses either physical (colorimetry, UV IR spectrophotometry, flame spectrophotometry, atomic absorption, etc.) or electrochemical methods like polarography. These methods are often long and costly and require dedicated instruments and skilled operators.

Dissolving the analyte and making it react with another species in solution (titrant) of known concentration. This is what is known as titration and it can be performed manually or automatically. It remains to determine the point at which titrant amount is equivalent to the analyte amount. Once the operator has perfectly characterised the reaction between the analyte and the titrant, the concentration or the exact quantity of the analyte can be determined by simple calculation.

Determining the analyte / titrant equivalence

First of all, let's briefly look at the different types of reactions used in analytical chemistry and some of their applications.

Acid/base reactions

These involve the reaction of H^+ or H_3O^+ with OH^- to form H_2O. They are the most common in both aqueous and non-aqueous media and are used every day in a wide range of applications:

- alkalinity determination in water,
- acid content in wine or fruit juice,
- acid content in milk,
- TAN and TBN in petroleum products, edible or inedible oils and fats,
- determination of boric acid in cooling fluids of nuclear power stations,
- determination of free or total acidity in plating baths,
- determination of active ingredients in drugs or raw materials for the pharmaceutical industry,
- total nitrogen determination using the Kjeldahl technique.

Redox reactions

As their name implies, these reactions make use of the reactivity of the oxidising/reducing pair. During the reaction, the oxidising ion, whether it is the analyte or the titrant, is reduced by gaining one or more electrons as the reducing ion is oxidised, losing one or more electrons. These reactions are less common than acid/base reactions but involve a wider range of titrants including:

Oxidising agents
- Iodine, potassium dichromate, potassium permanganate solutions.
- Cerium IV salts, hydrogen peroxide, oxidised chlorine, for example ClO^-, ClO_2.

Reducing agents
- Sodium thiosulphate solutions, oxalic acid, ammonium iron (II) sulphate (Mohr's salt), hydrogen peroxide, phenylarsine oxide (PAO).

Fields of application
Environment
- COD of water
- Oxidation capacity of water by permanganate

Food and beverage
- Determination of free and total SO_2 in water, wine, alcohol,

dried fruit etc.

Pharmaceuticals
• Vitamin C determination

Surface treatment
• Titration of copper or tin using iodine
• Titration of chromium VI

Petrochemicals
• Determination of water in hydrocarbons

Complexometric reactions

These are mainly used to determine the concentration of divalent cations such as calcium, magnesium, copper, lead, zinc and cadmium as well as other cations such as aluminium. The most commonly used complexants are ethylenediaminetetraacetic acid (EDTA) and ethylenebis(oxyethylenenitrilo)tetracetic acid (EGTA).

Although these reactions are easy to perform, it is necessary to work within a well-defined pH interval.

Fields of application
Environment

• Total hardness of water (Ca^{2+} and Mg^{2+})

Surface treatment
• Determination of Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} in plating baths

Cement works
• Determination of Ca^{2+} and Mg^{2+}

Precipitation reactions

Insoluble salts are common in nature and the most frequent use of precipitation reactions in analytical chemistry is the titration of halides, in particular Cl^- by Ag^+.

Fields of application
The determination of the anions I^-, Br^- and Ag^+ is also common.

Environment

• Determination of chloride in water

Food and beverage
• Determination of chloride in finished products (cooked meats, preserves)
• Determination of chloride in dairy products

Precious metals
Determination of silver in various alloys (for jewellery)

Pharmaceuticals
• Titration of halides

Colour indicators

The electrochemical detection of the analyte/titrant equivalence is a relatively recent method dating from the beginning of the 20th Century. Before then, the only instrument available was the operator's eye which lead to the discovery and the use of colour indicators. The way these indicators work depends on the type of reaction but the quantity added is always much less than the species to be titrated.

pH measurement (acid/base reactions)
Many colour indicators are still used today (phenolphthalein, helianthine, methyl red etc.). They tend to be weak organic acids or bases with double bonds (-C=C-) in their formulas. The ionic formula of these indicators changes for a given pH zone and the new arrangement of the double bonds causes the colours to change.

Redox reactions
These colour indicators are systems capable of exchanging electrons. As they have different colours in their oxidised and reduced states, their colour changes according to the redox potential of the solution. As for those used in pH measurement, these indicators have specific colour change ranges expressed in mV.

Colour indicators in complexometric reactions
Complexometric reactions are used to determine many cations. The colour indicators used here are organic molecules capable of forming a coloured complex with the cation to be determined which is less stable than the complex formed by the cation with the corresponding titrant, e.g. EDTA. When the entire species has been titrated, the indicator will change colour. These indicators are still used, for example Murexide or Eriochrom Black T.

Precipitation reactions
These colour indicators are often systems which form highly coloured complexes with one of the constituents of the reagent. During a titration, the end of the precipitation reaction means excess titrant and a coloured complex appear immediately.

Limitations of colour indicators
Although easy to use, colour indicators have their limitations. It is not always easy to find a suitable indicator for a particular determination and some are complicated to use, expensive or highly toxic.

In **pH measurement**, it is sometimes difficult to find a colour indicator with a colour change range corresponding exactly to the pH of the analyte/titrant equivalence point.

In some cases, a significant difference between the colour change range of the indicator used previously and the "real" equivalence point may lead to systematic errors on the results. In order to be able to compare new and old results, you would have to choose as end point, a value which is electrochemically incorrect but corresponds to the method used, for example the average value of the colour change range of the indicator used.

Colour indicators tend to be organic dyes which are light sensitive and temperature sensitive. Colour changes are not always significant and depend on individual perception. Obviously, colour indicators cannot be used in coloured solutions or samples with high suspended matter.

Potentiometric determination of the equivalence point

pH measurement and zero current potentiometry
The discovery of the laws governing analytical electrochemistry, in particular those concerning the definition of the electrode potential (Nernst equation) and development of the instruments and sensors to implement them provided a new way of determining the analyte/titrant equivalence, i.e. the equivalence point.

Using a pH/millivoltmeter, a titration curve E or pH = f(volume) can be plotted by following the potential E of an indicator electrode (together with a reference electrode) as a function of the added volume of reagent.

In pH measurement and zero current potentiometry, this curve is S-shaped with the inflection point(s) of the curve representing the equivalence point(s).

Imposed current potentiometry (polarised electrodes)
This technique, which is more recent than zero current potentiometry, generally uses two identical electrodes as measuring electrodes. A low direct or alternating current passes through these two electrodes and the resulting difference in potential is measured.

This technique is mainly used in redox measurements, in particular in iodometry. The titration curves obtained are similar to those in zero current potentiometry with sharper changes in the potential near the equivalence point. Double platinum electrodes are ideal for this type of titration.

Irrespective of the detection technique used:
If the pH or potential reached at the equivalence point can be reproduced easily and the titration curve has a sufficiently sharp potential or pH change, you can add titrant to the analyte until the measuring electrode indicates the potential or pH of the equivalence point: this is known as **preset end point titration**.

You can perform an analysis by adding excess titrant then determine the inflection point graphically or mathematically. This is known as **automatic inflection point determination**.
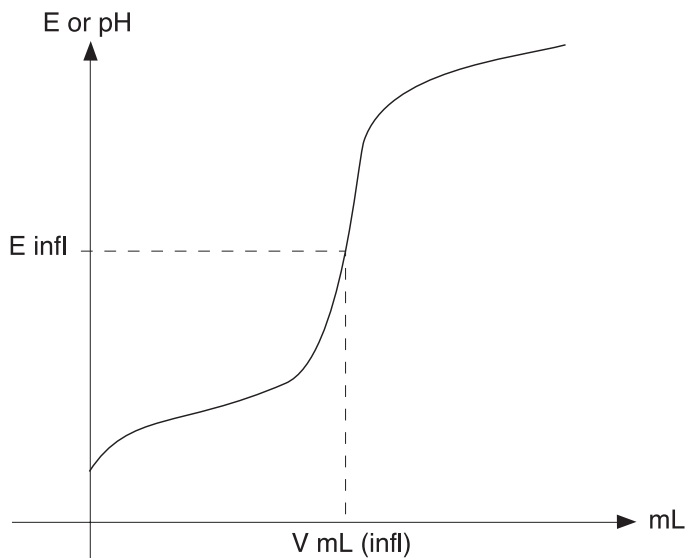

Diagram 1: General shape of a titration curve E infl = Analyte/titrant equivalence = Value of the preset end point

PRACTICAL CONSIDERATIONS FOR TITRATION

Setting up a titration

Choosing the right reagent and medium

The choice is made on the basis of laboratory conventions and standard methods. HACH's application notes are of great help here. The titration methods and calibration procedures of the main titrants used are described in the Appendix.

Acid/base reactions

These are usually fairly simple, as they tend to be fast and complete reactions using well-known reagents.
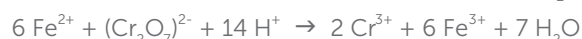
Redox reactions

These tend to take place in strongly acidic media and consume H^+ ions. A medium containing sulphuric acid (H_2SO_4) or phosphoric acid (H_3PO_4) is therefore required, as can be seen in the examples below:

$KMnO_4$ reduction (potassium permanganate) to Mn^{2+} by the oxalate ion $(COO^-)_2$

$$2\ MnO^{4-} + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 10\ CO_2 + 2\ Mn^{2+} + 8\ H_2O$$
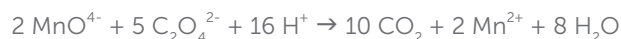
Fe(II) oxidation to Fe(III) by the dichromate ion $(Cr_2O_7)^{2-}$

$$6\ Fe^{2+} + (Cr_2O_7)^{2-} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

When dealing with an unknown reaction, we recommend writing the equation to discover the stoichiometric coefficients and obtain the analyte/titrant consumption.

Complexometric reactions

These reactions require a relatively well-defined working medium, in particular for pH.

The stability of the complexes formed between the cation to be titrated and the complexing agent used (commonly EDTA) during the titration depends on the pH of the medium and will be optimal in a given pH area.

An example is the titration of Ca^{2+} which takes place at pH 9 in a buffer medium whose composition takes into account the behaviour of the indicator electrode used. This is opposed to Zn^{2+}, which is titrated with the same reagent but at a pH of approximately 4.5.

In complexometric and redox reactions, the success of the titration depends to a large extent on the working conditions being respected THROUGHOUT THE TITRATION. In the event of poor results, check the pH in particular at the BEGINNING and at the END of the analysis.

As a general rule, inflection point titration is ideal for these reactions.

Precipitation reactions

These reactions, which are relatively easy to perform, use silver nitrate and involve the titration of halides (Cl^-, Br^-, I^-) or the cation Ag^+. They take place at a slightly acid pH (approx. pH 4.5), with organic solvents such as ethanol (C_2H_5OH) or acetone (CH_3COCH_3) sometimes being added to reduce the solubility of precipitate formed and improve the titration conditions.

However, when diluted reagents are used (concentration less than 0.02 M), the formation of the precipitate is not a fast reaction and the working conditions may need to be optimised (slower reagent addition speed for example).

The precipitation of hydroxides is more delicate as their solubility can vary according to the pH of the medium.

Choosing the right electrode

The indicator and reference electrodes should be chosen according to the following simple criteria:

- **Choose an indicator electrode** which measures an increasing or decreasing concentration of the analyte or titrant or both.
- **Choose a reference electrode** with a filling solution that does not interfere with the medium. Traces will enter the solution via the porous pin.
- **Choose a junction** for the reference electrode whose behaviour is compatible with the predefined criteria to perform a correct titration.

pH measurement

The choice between two separate or one combined electrode is made for practical rather than theoretical reasons. Glass electrodes are the most suitable for use as indicator electrodes for pH measurement. If the pH of the preset end point is greater than pH 9, it is preferable to use an electrode with a low alkaline error.

If a combined electrode is used, an Ag/AgCl reference element is suitable for most applications. An exception is an acid/base titration in the presence of TRIS (THAM) or Ag^+ ions. Here it is better to use a double junction reference element with a potassium nitrate bridge for example in order to avoid interference from Cl^- or Ag^+ ions.

The precipitation of AgCl during an acid/base titration leads to a modification in the reference electrode junction potential altering the pH of the solution compared to the initial calibration. This will cause an error in the result of the preset end point titration.

Redox measurement

The same type of indicator electrode always tends to be used: a platinum plate or wire electrode, either combined or separate usually in conjunction with an Ag/AgCl reference electrode or a calomel reference electrode. In concentrated sulphuric acid (chemical oxygen demand of water), a mercurous sulphate electrode should be used as reference electrode.

Imposed current potentiometry

This method provides titration curves which are ideal for preset end point titration. It is also known as the "Dead Stop End Point method" and is mainly used in iodo-metry. The most well-known application is Karl Fischer water content determination. A double platinum electrode is generally used.

Complexometry

By analogy with colour indicators for complexometry, the indicator electrode used in this type of reaction should be selective to the ion being titrated, for example Cu^{2+} or Ca^{2+}. If the selective electrode does not exist, the solution is to use an electrode made of the metal corresponding to the analysed cation.

It is possible to create a mercury electrode which responds to EDTA by amalgamating a silver electrode. Before starting the titration, several drops of diluted mercuric EDTA should be added.

The Silver rod electrode can be amalgamated easily by dipping it in clean mercury for 2 to 3 seconds after having cleaned the silver bar with fine-grained abrasive paper (BAO3 or BSC3 strips). When using this electrode, ensure the reactive medium does not have too high a concentration of Cl^- ions which might react with the mercury. If the method requires the use of a NH_4OH/NH_4Cl buffer, NH_4Cl can be replaced by NH_4NO_3.

Precipitation titrations

The most common case is argentimetry. Use a silver electrode in conjunction with a reference electrode which does not introduce any Cl^- ions in the solution. Choose a combined electrode. Use with mercurous sulphate reference electrode and K_2SO_4 filling solution) or a silver electrode together with a reference electrode with an electrolytic bridge which can be filled with a KNO_3 conductive solution, for example.

Junction of the reference electrode

A porous pin junction is perfectly adequate for most uses. However, for solutions which tend to clog or in the case of precipitation reactions leading to the formation of insoluble colloids, junctions with a large flow and large contact surface (sleeve or annular junction) are more suitable. The quality of this junction is to a large extent responsible for the reproducibility and sometimes the stability of the measurement.

HACH

Electrode maintenance

In preset end point titration, it is essential to be sure of the accuracy and reliability of the response of the electrodes used. The result of the titration is directly related to the quantity of reagent added to reach a preset pH or potential and not the shape of a titration curve as is the case in automatic inflection detection.

Before performing a series of pH measurements, it is essential to carefully calibrate the electrodes used in the end point area. During a series of identical analyses, check the reliability of the electrodes by adding a test sample (quality control) or systematically checking the potential indicated by the electrodes at the start of the titration.

Platinum electrodes cannot be calibrated but they can be checked using redox buffers with known characteristics or by using a quality control sample. The same applies to the other indicator electrodes.

Briefly checking the stability of the measurement and the time taken to reach a stable value will give you an idea of the condition of the junction of the reference electrode.

The basics

For complete information on maintenance, storage and use, refer to the operating instructions of your electrode.

Combined glass/reference electrodes
When not in use, store in the recommended solution. For combined pH electrodes with saturated KCl, the GK ANNEX Electrode Maintenance Kit can be used to keep electrodes in optimum condition.

Reference electrodes
Top up the filling solution regularly with the recommended solution. When not in use, store in the recommended solution.

Glass electrodes
Clean from time to time with RENOVO X or RENOVO N cleaning solution. When not in use, store in distilled water.

Metal electrodes
Silver electrodes only require rinsing in distilled water after titration. Platinum electrodes may need to be cleaned with a fine-grained 3 µ or 0.3 µ abrasive. Double platinum electrodes do not require any particular maintenance but should be kept clean.

WHY AUTOMATED TITRATION?

A titration made manually, even if using the possibilities of electrochemical methods to detect the equivalence points, pose a certain number of difficulties for the operator, which can be time consuming to solve.

Amongst the limitations of manual titration the most difficult to overcome are:

- the eventual difficulty in interpreting a curve made point by point that describes one or more poorly defined inflection points,
- irreproducibility of results that depend on factors that cannot be controlled,
- risk of human transcription errors.

An automated titrator is able to relieve the operator of all repetitive and fastidious tasks, in particular:

- control of the titrant perfectly adapted to the requirements of the operator and of the reaction being used during the titration,

- correct measurement of the electrode signal regardless of the method employed,

- reliable and reproducible mathematical treatment of the titration curves, stored in the memory of the titrator as couples of potential or current measured against volume of titrant, leads to the security of the result,

- secure transmission of the final results and raw data for future follow up as required.

A modern automated titrator is not just simply an instrument for realising any titration. It is an indispensable tool for analytical laboratories concerned with the quality of traceability and recording of results, that need to work according to the rules of Good Laboratory Practice (GLP).

TITRATION WITH PRESET END POINT DETERMINATION

Preset end point titration is a popular method but accurate and reproducible results will be obtained only if certain conditions are fulfilled.

When to select a preset end point titration method

This method consists of adding a titrant to the analyte until a preset potential or pH is measured by an indicator electrode. The volume of titrant added corresponds to the equivalence point between the analyte and the titrant.

The following conditions are important:

- fast and complete reaction between the analyte and the titrant,
- easy determination of the preset end point pH/potential,
- reliable indicator electrode,
- reproducibility of the potential (or pH) of the preset end point from one experiment to the next,
- well-defined titration curve around the equivalence point.

The influence of the shape of the titration curve on the reproducibility of preset end point titration results is illustrated in Diagrams 2A and 2B. It shows the two most common titration curves. **Diagram 2A** is a typical curve of the titration of a weak acid or base by a strong base or acid whereas **Diagram 2B** is a strong acid/strong base titration.

These diagrams show that, for a titration like the one shown in Diagram 2A, it is necessary to be much stricter on the value and the reproducibility of the preset end point in order to achieve the same acceptable uncertainty $\Delta(v)$.

If these conditions are fulfilled, preset end point titration is a useful technique because it is:

- easy to programme,
- quick to perform,
- economical, as it only uses the necessary amount of reagent.

The factors described above can be applied to all titrators in the TITRALAB family capable of performing preset end point titration.
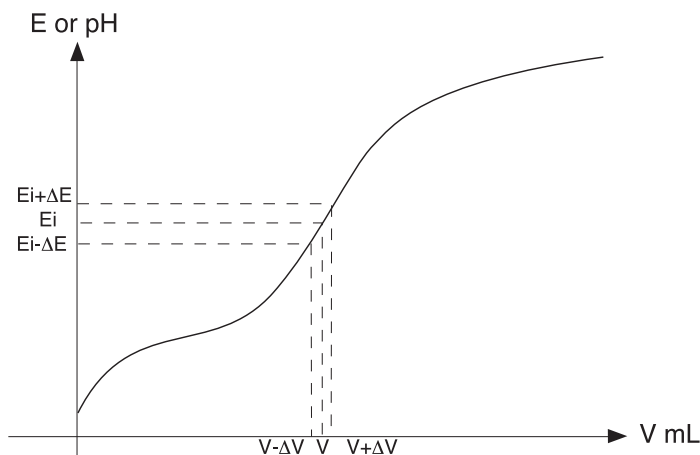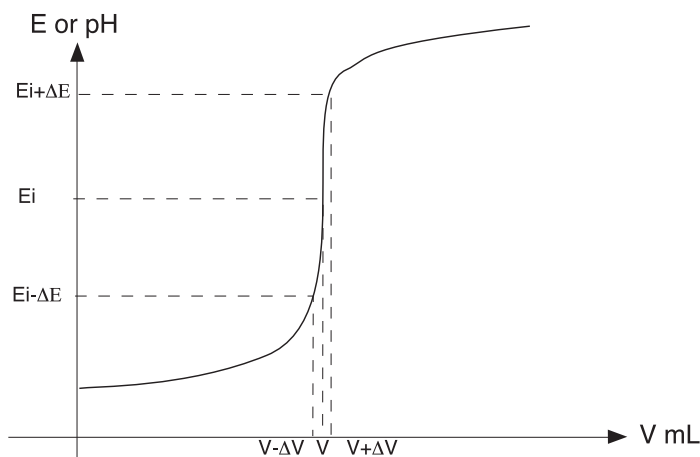

Diagram 2A

Diagram 2B

Determining titration parameters

In addition to the sample characteristics (weight or volume) and numerical data required to obtain the result (measuring unit and titrant concentration), the parameters to be determined are the actual value of the end point and titrant burette handling data (initial speed and slowing down near the end point).

Determining the preset end point value

You can consult scientific literature on the subject or use simple laboratory practice. In pH measurement, knowing the colour change range of the colour indicator used previously allows the pH of the equivalence point to be determined approximately.

Another way is to first perform a manual or automatic titration, plotting the corresponding curve or noting the acquired measuring points. By examining these points, you can easily determine the inflection point of the titration curve which corresponds to the greatest potential or pH change recorded for a given increment in the titration volume (Diagram 3).

If the increments added are small enough, you can write:

E or pH (end point) = E(i)+dEmax/2

If E(i) is the last potential (or pH) noted before the biggest change, this is equivalent to determining the potential or pH for which the derivative of the d(E or pH)/d(vol) titration curve is at its maximum.

The titrant burette

The way titrant is added during the titration must take into account the response of the indicator electrode, which in turn depends on the analyte/titrant reaction. In most cases, you need to find a compromise between the speed of the analysis and the accuracy and reliability of the result obtained. It is important to be familiar with the titration curve and the working of the titrator in order to determine burette parameters.

Depending on the functions available on the titrator, it is possible to start a titration with a fairly high addition speed and then to slow the speed as you near the end point where the variation in the measured potential is faster. This optimises the titrating time without "overtitrating" at the end point.
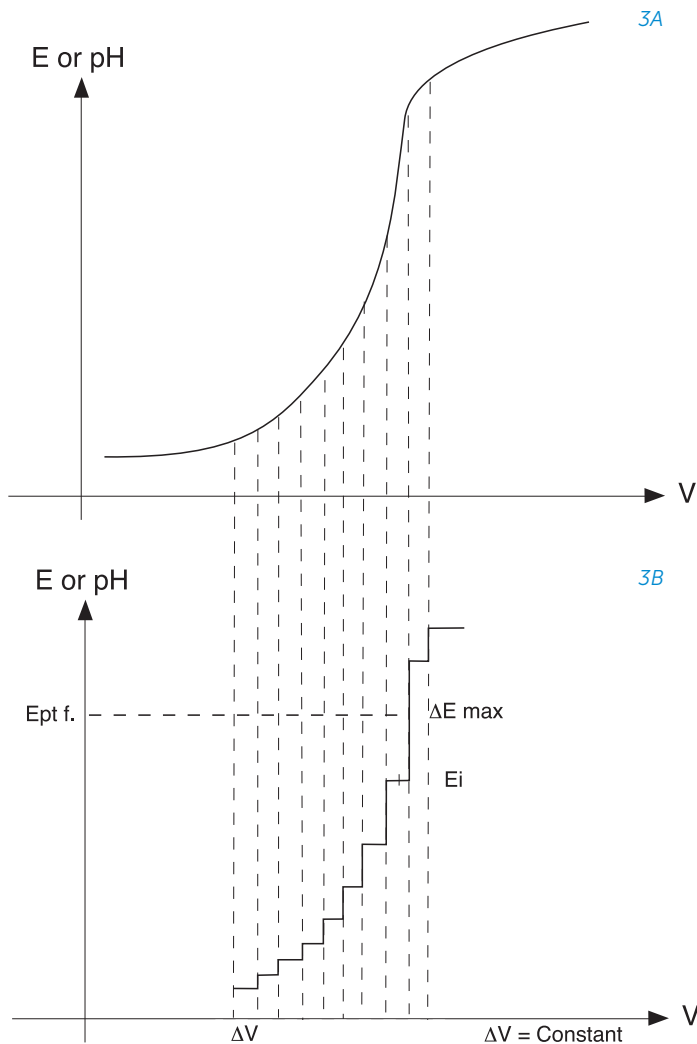

Diagram 3A: the tiration curve

Diagram 3B: the series of points noted (E or pH = f(vol) for constant titrant additions

Titrant addition mode

Incremental reagent addition

This addition mode reproduces the actions of an analyst working with a manual burette and a pH/millivoltmeter:

- measurement of the potential indicated by the measuring electrode/reference electrode,

- addition of an increment of the reagent volume,

- wait until the electrode potential stabilises or the maximum time delay set is reached,

- recording of the potential reading and volume delivered,

- addition of the next reagent volume increment etc.

Each titrant increment added generates a point on the titration curve.

Monotonic incremental mode

This is the easiest mode to use. All the increments are identical and the size does not depend on the variation in the measured potential, (Diagram 5). This mode limits the number of increments added, minimising titration time in some cases.

This reagent addition mode is suitable for:

- quick plotting of a new titration curve,

- performing titrations in which the reaction speed is not regular. Titrations using potassium permanganate ($KMnO_4$) are the most common example as their reaction speed is catalysed by the presence of Mn^{2+} ions. These "self-catalysing" titrations have a relatively slow reaction speed at the beginning of the titration which increases as the titration goes on,

- keeping complete control of the titration time. As the operator knows the number of increments required to obtain a given volume, the stabilisation criteria between two incre-

ments can be set to zero and successive increments then only take into account the maximum stabilisation time,

- simplifying the manual processing of a titration curve (as the variation in volume is monotonic, subsequent data processing is easier).

However, the equivalence point can be determined more accurately by the automatic titrator if the size of the increment is reduced, but this leads to an inevitable increase in the titration time.

Dynamic incremental mode

The size of the increments added depends on the shape of the curve. This mode allows the titration time and the accuracy of the equivalence point to be optimised. It is easy to use and is ideal for titrations with only one equivalence point or several equivalence points which are well separated.
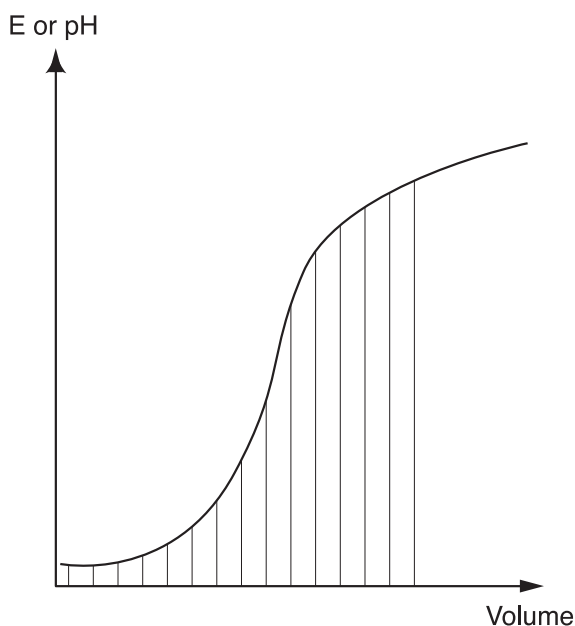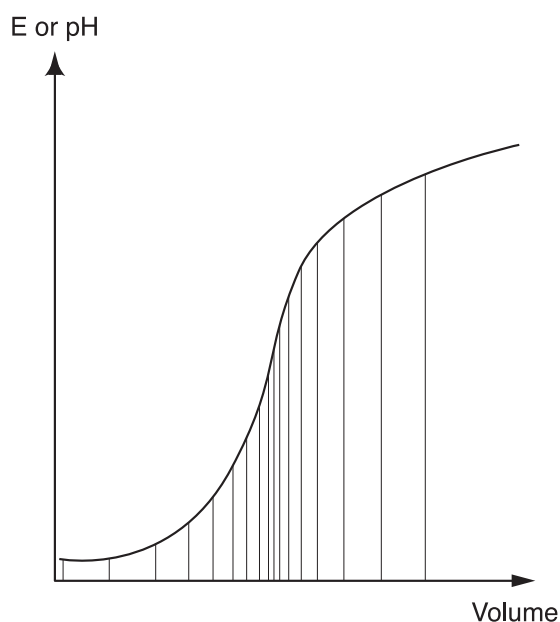

Diagram 5: Monotonic incremental addition

Diagram 6: Dynamic incremental addition

Performing calculations with TITRALAB AT1000 series

Whether preset end point or inflection point detection is used, it is necessary to know the volume of titrant used in order to obtain a final result, i.e. a concentration in the unit requested by the operator.

The AT1000 series is programmed with all the international units commonly used to express the concentration of the titrant, volumetric and gravimetric units plus the relevant calculation formulas.

Use of molar units

Today, titrant concentration is most commonly expressed as a molar unit (mol/L or mmol/L). The operator simply fills in the equation of the reaction in **the corresponding result coefficient line** so that the method programming knows the stoichiometry of the reaction.

A few examples make the process clearer:

Determination of the concentration of a monoacid titrated with NaOH (1 H^+ reacts with 1 OH^-)

- Coefficients: 1 sample and 1 titrant

Determination of the concentration of a diacid (2 acid functions titrated at the same time (H_2SO_4 with NaOH)).

- Coefficients: 1 sample and 2 titrants

Determination of the concentration of a divalent cation titrated with EDTA (Ca^{2+} titrated with EDTA).

- Coefficients: 1 sample and 1 titrant

Determination of a divalent cation by precipitating its hydroxide (Ni^{2+} titrated with NaOH).

- Coefficients: 1 sample and 2 titrants

It is then easy to obtain a result as a unit of volume or weight by entering the molar mass.

Use of normality units

The notion of normality based on the variation in the oxidation number of the species in question is becoming less popular.

According to this principle, a solution of $KMnO_4$ 0.1 M (or 0.1 mol/L) will be 0.5 N (or 0.5 eq/L) as in most redox equations it goes from an oxidation state of +7 to +2 .

In this case, the coefficients to be entered need to take into account the number of electrons exchanged in the reaction used. It is therefore not recommended to mix molar and equivalence units.

The above are simple guidelines. Application notes and technical support provide answers to more specific problems.

Use of equations

It is possible to obtain a result in a unit not belonging to the SI system or produced using a complex calculation by following special programming instructions.

Sample handling

Prior to analysis, the sample is frequently dissolved in a given volume of solvent in a graduated flask. An aliquot of this volume is then used for the titration. The automatic titrator calculates a result in relation to the sample unit once the sample amount have been entered.

CONCLUSION

Automatic titration remains one of the most popular analytical techniques in a wide variety of applications:

- acid analysis in aqueous or nonaqueous media,
- redox titration
- precipitation reactions,
- complexometry.

As this technique is relatively simple to use and cost-effective to set up and operate, it is found in most sectors of industry:

- food and beverage industry,
- water analysis,
- petrochemicals,
- pharmaceuticals,
- surface treatment and plating baths.

The new automatic titrators in the TITRALAB AT1000 series cover all these techniques. They come complete with dedicated application packages containing all the accessories and electrodes necessary to get started straight away. Full details and all the latest available information and updates can be found at our website.

TITRALAB AT1000 SERIES

The AT1000 model is a one touch, automatic titration system, with pre-set methods that can quickly deliver accurate and reliable results.

- Ready to use application kits for your parameters in water, food, beverage, and petrochemical
- Optimised analytical methods are already pre-programmed
- GLP features inside for results and calibration traceability
- Easy export of data and methods to USB (Excel format compatible)
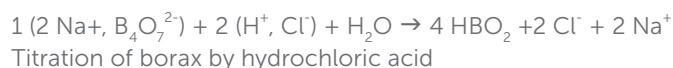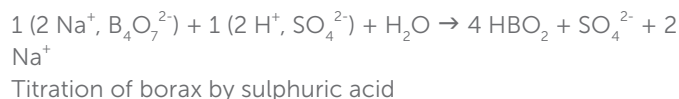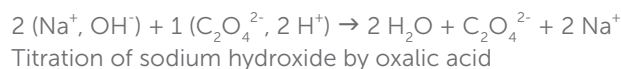- Dedicated KF1000 Karl Fischer model available

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APPENDIX TITRATION GUIDE

Colour changes of some colour indicators in pH measurement

Methyl orange (helianthine)	pH 3.1 to pH 4.4
Bromophenol blue	pH 3.0 to pH 4.0
Bromocresol green	pH 4.0 to pH 5.6
Methyl red	pH 4.2 to pH 6.2
Bromothymol blue	pH 6.2 to pH 7.6
Phenolphthalein	pH 8.0 to pH 10.0

Equations of some titration reactions

The syntax below is used to show the relationship between titrant and analyte during the reaction which helps explain the stoichiometry of the reactions.
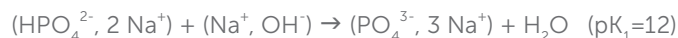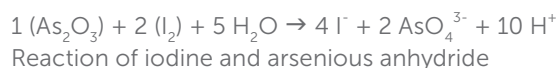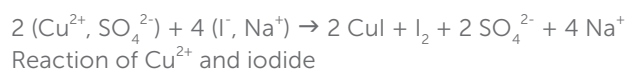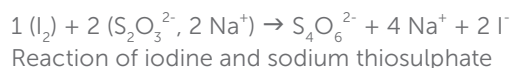
Acid/base reactions

$1 (Na^+, OH^-) + 1 (H^+, Cl^-) \rightarrow H_2O + Na^+ + Cl^-$
Reaction of sodium hydroxide with a monobasic acid

$2 (Na^+, OH^-) + 1 (SO_4^{2-}, 2H^+) \rightarrow 2 H_2O + 2 Na^+ + SO_4^{2-}$
Reaction of sodium hydroxide with a dibasic acid

$1 (2 Na^+, CO_3^{2-}) + 2 (H^+, Cl^-) \rightarrow CO_2 + H_2O + 2 Na^+ + 2 Cl^-$
Complete neutralisation of sodium carbonate by hydrochloric acid

$1 (2 Na^+, CO_3^{2-}) + 1 (2 H^+, SO_4^{2-}) \rightarrow CO_2 + H_2O + 2 Na^+ + SO_4^{2-}$
Complete neutralisation of sodium carbonate by sulphuric acid

$1 (Na^+, OH^-) + 1 (H^+, -OOC-C_6H_4-COO-, K^+) \rightarrow H_2O + (Na^+, -OOC-C_6H_4-COO-, K^+)$
Titration of sodium hydroxide by potassium hydrogen phthalate

$2 (Na^+, OH^-) + 1 (C_2O_4^{2-}, 2 H^+) \rightarrow 2 H_2O + C_2O_4^{2-} + 2 Na^+$
Titration of sodium hydroxide by oxalic acid

$1 (2 Na^+, B_4O_7^{2-}) + 1 (2 H^+, SO_4^{2-}) + H_2O \rightarrow 4 HBO_2 + SO_4^{2-} + 2 Na^+$
Titration of borax by sulphuric acid

$1 (2 Na+, B_4O_7^{2-}) + 2 (H^+, Cl^-) + H_2O \rightarrow 4 HBO_2 + 2 Cl^- + 2 Na^+$
Titration of borax by hydrochloric acid

Example of phosphoric acid H_3PO_4
This is a triacid with the following pKs:
pK_3=2.1, pK_2=7.2 and pK_1=12

In an aqueous medium, only the first two acids can be titrated. The reactions are as follows:
$H_3PO_4 + (Na^+, OH^-) \rightarrow (H_2PO_4^-, Na^+) + H_2O$ (pK_3=2.1)

$(H_2PO_4^-, Na^+) + (Na^+, OH^-) \rightarrow (HPO_4^{2-}, 2 Na^+) + H_2O$ (pK_2=7.2)

$(HPO_4^{2-}, 2 Na^+) + (Na^+, OH^-) \rightarrow (PO_4^{3-}, 3 Na^+) + H_2O$ (pK_1=12)

Redox reactions

$2 (MnO_4^-, K^+) + 5 (C_2O_4^{2-}, 2 Na^+) + 16 H^+ \rightarrow 10 CO_2 + 2 Mn^{2+} + 8 H_2O + 2 K^+ + 10 Na^+$
Reaction of potassium permanganate and sodium oxalate

$1 (MnO_4^-, K^+) + 5 (Fe^{2+}, SO_4^{2-}) + 8 H^+ \rightarrow Mn^{2+} + 5 Fe^{3+} + 5 SO_4^{2-} + 4 H_2O + K^+$
Reaction of potassium permanganate and iron sulphate

$1 (Cr_2O_7^{2-}, 2 K^+) + 6 (Fe^{2+}, SO_4^{2-}) + 14 H^+ \rightarrow 2 Cr^{3+} + 6 Fe^{3+} + 6 SO_4^{2-} + 2 K^+ + 7 H_2O$
Reaction of potassium dichromate and iron sulphate

$1 (I_2) + 2 (S_2O_3^{2-}, 2 Na^+) \rightarrow S_4O_6^{2-} + 4 Na^+ + 2 I^-$
Reaction of iodine and sodium thiosulphate

$2 (Cu^{2+}, SO_4^{2-}) + 4 (I^-, Na^+) \rightarrow 2 CuI + I_2 + 2 SO_4^{2-} + 4 Na^+$
Reaction of Cu^{2+} and iodide

$1 (As_2O_3) + 2 (I_2) + 5 H_2O \rightarrow 4 I^- + 2 AsO_4^{3-} + 10 H^+$
Reaction of iodine and arsenious anhydride

Complexometric reactions

The most common complexing agent used is disodium salt of

ethylenediaminetetraacetic acid, or EDTA, usually expressed in its simple form as H_2Y^{2-}.

As it is often used to complex divalent metals of the Me^{2+} type, the reaction is written as follows:
$$1\ Me^{2+} + 1\ H_2Y^{2-} \rightarrow 1\ (MeY^{2-}) + 2\ H^+$$

Precipitation reactions

The most important use of precipitation reactions is silver nitrate used to titrate halides (Cl^-, Br^-, I^-) and CN^- and SCN^- used to titrate Ag^+ ions.

For halides, the reaction is as follows:
$$1\ Ag^+ + 1\ X^- \rightarrow 1\ AgX$$

Some other reactions correspond to the precipitation of usually divalent metal hydroxides:
$$1\ Me^{2+} + 2\ OH^- \rightarrow Me(OH)_2$$

Characteristics of some standards

We consider a standard to be a commercially available substance of sufficient purity, delivered with a certificate. Such a standard can be weighed to make stable solutions.

pH standards

Oxalic acid $(COOH)_2$, $2\ H_2O$
MW=126.03 g/mol

Potassium hydrogen phthalate $KOOC\text{-}C_6H_4\text{-}COOH$
MW= 204.22 g/mol

Sodium carbonate Na_2CO_3
MW=105.99 g/mol

TRIS or THAM $H_2N\text{-}C(CH_2OH)_3$
MW=121.14 g/mol

Sodium borate (Borax) $Na_2B_4O_7$, $10\ H_2O$
MW=381.4 g/mol

Redox standards

Oxalic acid $(COOH)_2$, $2\ H_2O$

MW=126.03 g/mol

Potassium dichromate $K_2Cr_2O_7$
MW=294.19 g/mol

Ferrous ammonium sulphate
(Mohr's salt) $(NH_4)_2SO_4$, $FeSO_4$, $6\ H_2O$
MW=392.14 g/mol

Arsenious anhydride As_2O_3
MW=169.87 g/mol

Potassium iodate KIO_3
MW=213.97 g/mol

Complexometric standards

Disodium salt of EDTA Na_2H_2Y, $2\ H_2O$
MW=372.24 g/mol

Precipitation standards

Silver nitrate $AgNO_3$
MW=169.87 g/mol

Potassium chloride KCl
MW=74.56 g/mol

Sodium chloride $NaCl$
MW=58.44 g/mol

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