

## Titration

### **What is TITRATION?**

This is a wet chemistry technique for determining the concentration of an unknown reagent using a known concentration of another reagent (titrant) that chemically reacts completely with the unknown sample.

The point at which the reaction is completed is known as the end-point of the titration or the equivalence point. At the equivalence point the entire unknown sample has reacted with a quantity of the standard (known concentration) of titrant, this being determined by some kind of indicator e.g. a colour indicator like phenolphthalein or a potentiometric indication.

### **At the equivalence point equilibrium is set up whereby:**

Number of equivalent weights of titrant = Number of equivalent weights of the Unknown sample.

- or -

Normality of the titrant x volume of titrant required to reach the end point = normality of the unknown x volume of the unknown.

Generally we know the Normality of the titrant since it is a standard solution and we titrate this against a known volume of sample. Once the end point of the titration has been determined one can thus calculate the concentration of the unknown.

### **Typical titration reaction:**

ACID + BASE -> SALT + WATER

HCl + NaOH -> NaCl + H<sub>2</sub>O

- Or -

HCl + NH<sub>4</sub>OH -> NH<sub>4</sub>Cl + H<sub>2</sub>O

In the ideal case, titration reactions should meet the following requirements:

- The stoichiometry of the reaction must be known exactly and must not change during the course of the titration.
- The forward reaction to form the reaction products must be quantitative; i.e. the equilibrium constant of the reaction must be large.
- The equilibrium must be established quickly.
- No interfering parallel or consecutive reactions should occur.

## TITRANTS

These should be stable and the titer of these is determined with the aid of primary standards, and this should be checked on a regular basis. Examples of suitable primary standards are:

### **Primary Standard Application**

#### **Benzoic acid Alkalimetry**

#### **Calcium carbonate Acidimetry**

## TITRATION MEDIA

Most titrimetric determinations are performed in aqueous media, as the practical and theoretical aspects of such titrations are well known. Less clear however are titrations in non-aqueous media.

- The use of non-aqueous media should be considered for the following cases:
- The substance is poorly soluble in water.( e.g. acid or base numbers in mineral oils)
- The product formed in precipitation titration's is too soluble in water.(e.g. lowering of the solubility of silver Chloride by addition of dioxane)
- The substance to be determined is a very weak acid or base and can no longer be titrated in water.(e.g. phenol & urea derivatives)
- A mixture of substances cannot be determined selectively in water e.g. H<sub>2</sub>SO<sub>4</sub> HN0<sub>3</sub> in nitrating acid)
- The substance to be determined reacts chemically with water(e.g. acid chlorides , acid anhydrides)

A distinction is made between amphiprotic solvents, which exhibit a "water-like" self-dissociation and aprotic solvents with no noticeable self-dissociation.

In both groups a distinction is made between solvents with predominantly acidic, basic or neutral character. The weaker the 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.

**Amphiprotic solvents:** These have a limited working range but they possess good solubilising power and cause no potentiometric indication problems due to static charging.

**Aprotic solvents:** These have a wide working range but usually have a low solubilising power

## INDICATION OF THE END-POINT

Of the various indication methods available, potentiometric is the main and most suitable for automated titration's because of its versatility. In potentiometric titration the zero current potential changes during the titration and this is measured at the indicator electrode. Selection of the indicator electrode depends on the nature of the titration reaction and, in ideal situations, should only respond to the

ion being measured. In order to make measurements possible; a reference electrode is needed to supplement the indicator electrode. This reference electrode should not respond to changes in the titration solution. The measuring and reference electrode must both be well shielded from electrostatic and electromagnetic fields.

### **ACID/BASE TITRATION**

These are performed using a glass electrode to monitor the pH. The sample, which can be an acid or a base is titrated with a known concentration of acid or base (titrant) to a fixed pH End Point or alternatively to the equivalence point of the reaction. The latter is automatically evaluated by the autotitrator.

These types of titration are normally carried out in aqueous media and have applications in a variety of industries.

#### **Common examples of being:**

- P and m alkalinity of river, process and drinking water.
- Boric acid in cooling water.
- Acidity in soft "cola" type drinks.
- Acidity of Fruit Juices.

#### **Some Acid/Base titrations need to be carried out in non aqueous media. This is necessary when:**

- The sample is insoluble in water.
- The sample reacts with water.
- The sample is a mixture of acids that need to be differentiated.
- The acid or base is too weak to be titrated in water.

#### **Some examples of Non Aqueous Acid /Base titrations:**

- TAN (Total Acid Number) and TBN (Total Base Number) determinations on motor oil.
- Various weak base drug assays by titration with Perchloric acid in a Glacial Acetic acid media.
- Differentiation of Nitric and Sulphuric Acids in Nitrating Acid used in the explosives industry.

Although the above titrations utilise glass electrodes, non aqueous filling electrolytes are sometimes necessary and special electrode conditioning routines must be employed to obtain successful titrations.

### **REDOX TITRATIONS**

These are titrations which involve an oxidation/reduction reaction.

A redox system exists when a species can form a redox couple by gaining or losing electrons.



When the redox potential of two species differ by more than 300mv they can react with each other. This is called a conjugate redox system.

Redox titrations are monitored using a Platinum or Gold Electrode and common examples would be:

- COD (Chemical Oxygen Demand) determinations on river water, which conclude with a titration of Ferrous Ammonium Sulphate against Potassium Dichromate.
- Hydrogen Peroxide determinations using Potassium Permanganate as titrant.
- Free Chlorine in bleach determinations which, after an addition of excess Potassium Iodide, the liberated iodine is titrated with a Sodium Thiosulphate solution.

## **ARGENTOMETRIC TITRATIONS**

These are precipitation titrations based on the following simple reaction



Where X is halide (Chloride, Bromide or Iodide)

The reaction is monitored using a Silver Metal Electrode and titrations can be performed using Silver Nitrate solution as titrant for the determination of halides and Potassium chloride or bromide for the determination of Silver in solution. Common examples of these types of titrations are:

- Determination of salt in various foods and snacks.
- Determination of Chloride in drinking Water
- Simultaneous determination of Chloride, Bromide and Iodide in Seawater.
- Determination of 925 Silver in the jewellery Industry
- Determination of Silver in Photographic developing solutions.

## **WHY USE TITRATION AS AN ANALYTICAL TECHNIQUE?**

Titration is one of the oldest established analytical methods and as such is today's standard method for quantitative analysis due to:

- Absolute content determinations, i.e. the analytical results provide direct information regarding the amount of the analysed substance.
- It is an easily implemented and understood technique the rudiments of which are normally taught at school, if not it can be quickly learned.
- Titration determinations are rapid.

- Versatility ....titration methods are fully worked out for anything from inorganic ions to complex organic compounds and the concentration ranges for detection, ranges from pure to trace levels.
- Sample size: - up to several grams.
- Accuracy & Reproducibility , typical reproducibility's is better than 0.1%
- Moderate price, the price being very reasonable compared with other analytical techniques.

**Detection levels for titration: - 100% down to ppm levels**

## **METROHM'S AUTOMATIC POTENTIOMETRIC TITRATION METHODS**

Metrohm automatic potentiometric titrators have multipurpose application possibilities thanks to their ability to handle all basic methods important in practical titration:

### **DYNAMIC EQUIVALENCE POINT TITRATION (DET)**

This is the universally applicable dynamic equivalence point titrator with automatic evaluation of the equivalence point. Adaptation of the volume increments to the slope of the titration curve provides precise results in a minimum of time. Even very poorly defined equivalence points are reliably detected. The titration data can be used for automatic determination of pK value.

### **MONOTONIC EQUIVALENCE-POINT TITRATION (MET)**

Monotonic titration with automatic evaluation of the equivalence point. MET employs constant volume increments and is particularly suitable for kinetically inhibited titrations, e.g. acid number & base number in oils (TAB & TBN), determination of the Chemical Oxygen Demand etc. The titration data recorder can also be used for the automatic determination of the pK value

### **TITRATION TO PRE SELECTED END POINTS (SET)**

This method allows rapid routine determinations with or without polarisation of the indicator electrode. If desired, the titration vessel's content can be conditioned between determinations and the corresponding drift value displayed.

### **MEASUREMENT OF pH/mV/temperature (MEAS)**

This method is for the measurement of pH, voltage U in mV (potentiometrically or with polarised electrodes), temperature in °C.

- Maintaining a reaction at a constant pH , with temperature monitoring (STAT)
- pH/mV gradient control against time , with temperature control (DOC)
- Dispensing of liquids with pH or temperature monitoring (DOS)
- Linkage of up to nine single steps to form a procedure, (TIP) the individual steps of which can be methods, pauses, status conditions etc.

## TITRATION AUTOMATION

Metrohm have long been able to perform analyses automatically, however large sample throughput can only be achieved using an efficient sample changer system, which suits your throughput, sample size, collection vessel shape, sample preparation and budget.

### When should a sample changer system be used?

- For large numbers of samples.
- When a high level of automation is required.
- Where sample preparation must be rationalised.
- Where there is no time for sample preparation.
- Where the sample must be dissolved immediately before the titration
- Where the highest precision & reproducibility is demanded
- Lower cost analysis
- Greater sensitivity in the detection of end-points through mathematical evaluation
- Error-free documentation of analysis results on-line to LIMS systems

### The benefits of automating your titration system!

- High sample throughput.
- Reproducible results.
- Operator requires no special knowledge.
- Operational personnel are freed for the duration of the analysis.
- Contact with toxic chemical is reduced to a minimum.
- The system can operate seven days a week for twenty-four hours.

### **tiamo™ - the powerful partner for laboratory automation in the titration laboratory**

The innovative control and database software **tiamo™** offers numerous new functions for automated titration systems. Some of the most interesting features are outlined below.

#### **Your LIMS determines the course of action**

The management of samples and analytical procedures is usually carried out with the help of a laboratory information and management system (LIMS). All incoming samples are logged into the LIMS and classified for further processing. The LIMS draws up a working list for the samples to be processed that contains, among other things, the sample identification and the analytical method to be used.

**tiamo™** automatically takes over this working list and displays the samples to be processed in the sample table. In this way the manual input of the data into the sample table, which is both time-consuming



and error-prone, can be dispensed with. The user is immediately informed about which and how many samples are to be analyzed at the particular titration workplace.

### **Precise control of sample metering**

Pipetting is the most frequent sample preparation step for liquid samples. With the new graphical method editor, this liquid-handling operation can be programmed step by step in tiamo™. This gives you the possibility of adapting the pipetting procedure to suit the particular sample matrix. Sample volumes in the  $\mu\text{L}$  to mL range can be metered reliably and extremely precisely. In this way you can save valuable time and also improve the quality of your analytical results.

### **Automatic thermostating and homogenizing of samples**

Thermostatable water baths are used for keeping samples at a constant temperature, for example to dissolve a sample component. If the water bath has an RS 232 interface then it can be remotely controlled by tiamo™. The temperature is defined in the tiamo™ method and transmitted to the heating or cooling bath via the serial interface.

tiamo™ can also control dispersing tools used for sample preparation. This means that it is possible to reduce the particle size of the sample and homogenize it within a preset time and at a controlled speed.

### **Parallel preparation and analysis of samples**

In order to increase sample throughput at your automated titration system it is important that the processing time per sample is reduced. One way of doing this is to allow different method steps to take place at the same time.

The cleverly devised control system of tiamo™ is now able to reliably control several procedures taking place in parallel. For example, the next sample can be prepared while the current sample is still being titrated. The simultaneous determination of several parameters is also possible with tiamo™. This brings enormous savings in time and costs.

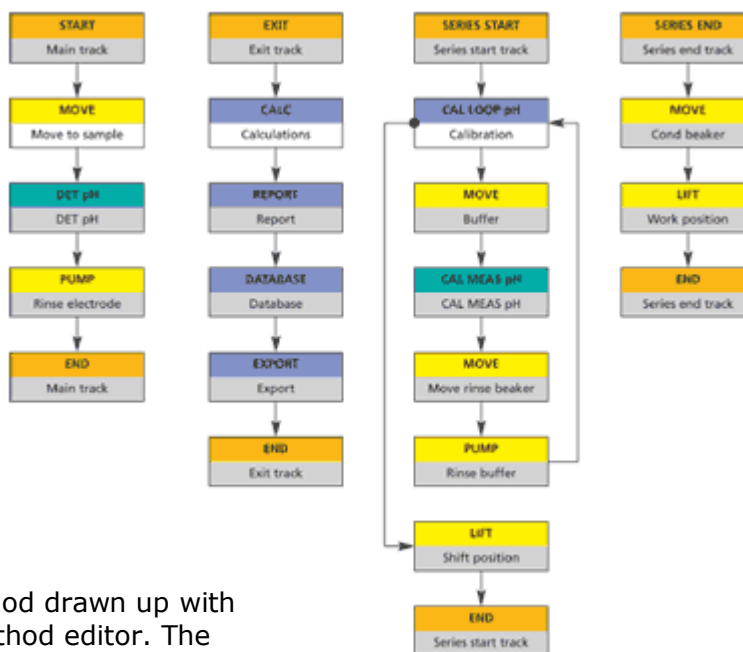
### **Result monitoring and appropriate action**

tiamo™ monitors the analytical results. If predetermined limits are infringed its control functions allow predefined actions to be triggered. Everything is possible from the simple display of a message on the screen up to the automatic dispatch of an E-Mail. You can also define whether the system is to continue to work or whether it is to be stopped until the arrival of the user to avoid the loss of valuable samples.

### **tiamo™ does part of the thinking**

Intelligent programming allows tiamo™ to take decisions. We will use an example to illustrate this. If the analysis result obtained lies within the limits then it will be stored in the sample database and automatically exported to the LIMS. However, if the result is outside the limits it will be stored in a second database and the user informed by E-Mail. In this case no export to the LIMS takes place. The user is immediately informed when a given sample is outside the defined limits and can

take appropriate action. In addition, tiamo™ automatically analyzes a control sample to check the proper functioning of the system.



Automation method drawn up with the graphical method editor. The overall procedure is divided up into four so-called tracks.

### Powerful report generator

The demands placed on an analytical report differ greatly – but are always high. tiamo™ has a powerful report generator that is unequalled on the market. You can generate your own report templates completely freely by graphical means. You can arrange database information, texts, graphics, titration and calibration curves as you require and group them together to form specific templates. By using these report templates the analytical results can then be printed out or generated as a PDF file. Even the automatic transmission of analytical reports by E-Mail is available to you.

### Flexible data export

If the sample table has been drawn up directly by the LIMS and then used by tiamo™ then it is now the turn of tiamo™ to send the analytical results back to the LIMS. Export flexibility is again decisive here. What information about the determination has to be sent where and in what format? No problem for tiamo™. The wide range of export formats and the integration of the export function in the method sequence allow any type of export that is required. From generating a simple Excel table up to export in the modern XML format, everything is possible.

### **Integration into the company network**

The rapid exchange of and direct access to analytical results are of crucial importance today. As a real client/server program tiamo™ utilizes the most modern network technology so that you can access your data anywhere and at any time. Analytical results, methods and system settings are stored centrally and are available to each tiamo™ client.

To sum it up:

**tiamo™** – titration and more

The full range of Metrohm Titration products can be viewed at

[www.metrohm.co.uk](http://www.metrohm.co.uk)