Monograph

Practical thermometric titrimetry
Thomas Smith

Ω Metrohm

Metrohm

Ion analysis

Practical thermometric titrimetry

Thomas Smith

Metrohm Ltd.
CH-9101 Herisau/Switzerland
Phone +41 71 353 85 85
Fax +41 71 353 89 01
www.metrohm.com

Contents

1.　Foreword

This monograph is intended primarily for practicing industrial analytical chemists as an introduction to the technique of thermometric titrimetry. The main purpose is to describe the basics of the technique as well as a range of applications that are suitable for use with the 859 Titrotherm thermometric titration system. Theoretical aspects are discussed only briefly, and readers seeking a more detailed exposition are encouraged to seek out the references listed in the bibliography as well as conducting searches in the academic literature. Examples chosen to illustrate various thermometric titration applications are from the author's own experiments.

2.   Introduction

Titration is a technique in analytical chemistry with a history dating to the mid-18th century. It may be defined as the reaction of a known volume of a reactant with a known concentration (the titrant) with another reactant contained in a sample (the analyte or titrand) to determine the amount of the analyte in the sample. The point at which stoichiometric amounts of titrant have been added to the sample is known as the equivalence point. The volume of titrant measured at this point is used to compute the amount of analyte present in the sample. The classical titration methods employ color change due to chemical indicators to determine the endpoint. The practical problems in the correct, unequivocal determination of endpoints based on the subjective interpretation of color change by the analyst have been recognized for many years, and analysts have sought alternative methods of precisely determining endpoints.

Thermometric titrimetry is one of a number of instrumental titration techniques where endpoints can be located accurately and precisely without a subjective interpretation on the part of the analyst. Enthalpy change is a universal property of chemical reactions. Accordingly, the observation of temperature change is a valid possibility for monitoring their progress.

This monograph commences with a brief discussion of some theoretical aspects of thermometric titrimetry followed by some practical considerations and finally by an introduction to some of the many applications.

3.   Theory and background to thermometric titrimetry

3.1.   Comparison between potentiometric and thermometric titrations

Potentiometric titrimetry has been the predominant automated titrimetric technique for the past half-century, so it is worthwhile considering the basic differences between it and thermometric titrimetry.

Potentiometric (and conductometric) titrations rely on a free energy change in the reaction system. Measurement of a free energy dependent term is necessary.

$$\Delta G^0 = -R\,T\ln K$$

Where: ΔG^0 = change in free energy
              R = universal gas constant
              T = temperature in K
              K = equilibrium constant at temperature T

In order for a reaction to be amenable to potentiometric titrimetry, the free energy change must be sufficient for an appropriate sensor to respond with a significant inflection in the curve where sensor response is plotted against the amount of titrant delivered.

However, free energy is just one of three related parameters in describing any chemical reaction:


Where: ΔH^0 = change in enthalpy
ΔG^0 = change in free energy
ΔS^0 = change in entropy
T = temperature in K

For any reaction where the free energy is not opposed by the entropy change, the enthalpy change will be significantly greater than the free energy. Thus a titration based on a change in temperature (which permits observation of the enthalpy change) will show a greater inflection than will curves obtained from sensors reacting to free energy changes alone.

3.2. Thermometric titrations

In a thermometric titration, titrant is added at a known constant rate to an analyte until the completion of the reaction is indicated by a change in temperature. The endpoint is determined by an inflection in the curve generated by the output of a temperature measuring device.

Consider the titration reaction:

$$aA + bB \rightleftharpoons pP$$
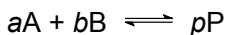
Where: A = titrant a = corresponding number of moles reacting
B = analyte b = corresponding number of moles reacting
P = product p = corresponding number of moles produced

At completion, the reaction produces a molar heat of reaction ΔH_r, which is shown as a measurable temperature change ΔT. In an ideal system, where no losses or gains of heat due to environmental influences* are involved, the progress of the reaction is observed as a constant increase or decrease of temperature depending respectively on whether ΔH_r is negative (indicating an exothermic reaction) or positive (indicating an endothermic reaction).

* Among «environmental influences» may be categorized:
  – Heat losses or gains from outside the system via the vessel walls and cover
  – Differences in the temperature between the titrant and the analyte
  – Evaporative losses from the surface of the rapidly mixed fluid
  – Heat of solution when the titrant solvent is mixed with the analyte solvent
  – Heat introduced by the mechanical action of stirring (minor influence)
  – Heat produced by the thermistor itself (very minor influence)

If the equilibrium for the reaction lies far to the right (i.e. a stoichiometric equilibrium has been achieved), then when all analyte has been reacted by the titrant continuing addition of titrant will be revealed by a sharp break in the temperature/volume curve. Figures 1a and 1b illustrate idealized examples.
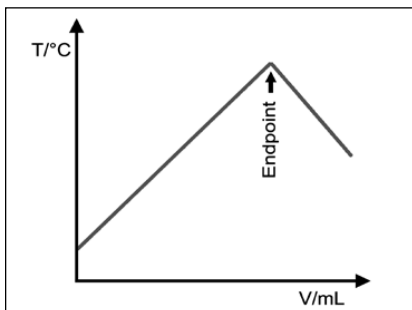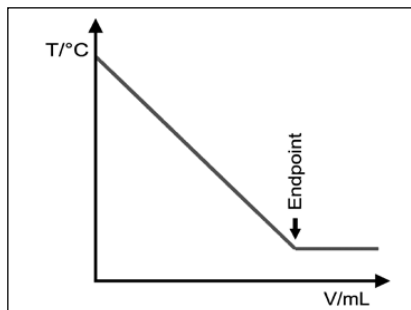

Fig. 1a: Exothermic reaction

Fig. 1b: Endothermic reaction

Fig. 1: Idealized thermometric titration curves for stoichiometric reaction equilibria.
Volume of titrant added plotted versus temperature of the solution.

The shape of experimentally obtained thermometric titration plots will vary from such idealized examples, and some of the environmental influences listed above may have impacts. Curvature at the endpoint might be observed. This can be due to insensitivity of the sensor or slow adjustment of the thermal equilibrium at the endpoint. There are also cases where the reaction between titrant and analyte does not proceed to stoichiometric completion. The determinant of the degree to which a reaction will proceed to completion is the free energy change. If this is favorable, then the reaction will proceed to completion and be essentially stoichiometric. In this case, the sharpness of the curve at the endpoint is dependent on the magnitude of the enthalpy change. If the free energy change is unfavorable, the curve at the endpoint will be rounded regardless of the magnitude of the enthalpy change.

Reactions where non-stoichiometric equilibria are evident can be used to obtain satisfactory results using a thermometric titration approach. If the portions of the titration curve both prior to and after the endpoint are reasonably linear, then the intersection of tangents to these lines will accurately locate the endpoint. This is illustrated in Figure 2.
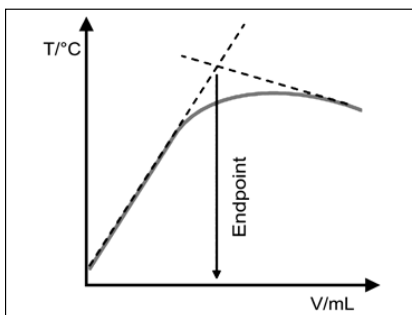

Fig. 2: Representation of a thermometric titration curve for a reaction with a non-stoichiometric equilibrium.

Consider the reaction for the equation $aA + bB \rightleftharpoons pP$, which is non-stoichiometric at equilibrium. Let A represent the titrant, and B the analyte. At the beginning of the titration, the analyte B is strongly in excess and the reaction is pushed towards completion. Under these conditions, for a constant rate of titrant addition the temperature increase is constant and the curve is essentially linear until the endpoint is approached. In a similar manner, when the titrant is in excess past the endpoint, a linear temperature response can also be anticipated. Thus intersection of tangents will reveal the true endpoint.

An actual thermometric titration plot for the determination of a strong base with a strong acid is illustrated in Figure 3.
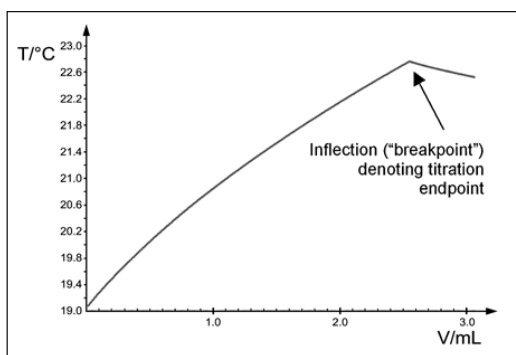

Fig. 3: Typical thermometric titration plot of an exothermic reaction. The volume of titrant added is plotted on the x-axis and the temperature of the solution on the y-axis.

The most practical sensor for measuring temperature changes in titration solutions has been found to be the thermistor. Thermistors are small solid-state devices manufactured from sintered mixed-metal oxides that exhibit relatively large changes in electrical resistance for small changes in temperature. The thermistor is encapsulated in a suitable electrically insulating medium with satisfactory heat transfer characteristics and acceptable chemical resistance. Typically for thermistors used for chemical analysis the encapsulating medium is glass, although thermistors encapsulated in epoxy resin may be used in circumstances where either chemical attack (e.g. by acidic fluoride-containing solutions) or severe mechanical stress is anticipated (see Figure 4). The thermistor is supported by a suitable electronic circuit to maximize the sensitivity to minute changes in the solution temperature. The circuitry in the 859 Titrotherm is capable of resolving temperature changes as low as 10^{-5} K.
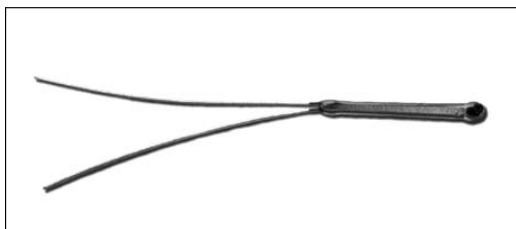

Fig. 4: Glass-encapsulated thermistor of the Thermoprobe.

A critical element in modern automated thermometric titrimetry is the ability to locate the endpoint with a high degree of reproducibility. The endpoint is determined by derivatization of the temperature curve. The second derivative essentially locates the intersection of tangents to the temperature curve immediately before and after the breakpoint.

Thermistors respond quickly to small changes in temperature such as temperature gradients in the mixed titration solution. The signal can therefore exhibit a small amount of noise. Prior to derivatization it is therefore necessary to digitally smooth (or «filter») the temperature curve in order to obtain sharp, symmetrical second derivative «peaks» that will accurately locate the correct inflection point. This is illustrated in Figure 5.
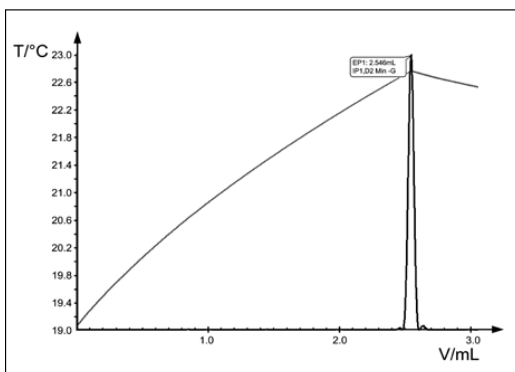

Fig. 5: Location of a thermometric titration endpoint using the second derivative of a digitally smoothed temperature curve.

The degree of digital smoothing is optimized for each determination and is stored as a method parameter for application every time a titration for that particular analysis is run.

Thermometric titrations generally demand rapid reaction kinetics in order to obtain sharp reproducible endpoints. Where reaction kinetics are slow, and direct titrations between titrant and analyte are not possible, indirect or back-titrations often can be used to solve the problem.

Catalytically enhanced endpoints can be helpful in some instances where the temperature change at the endpoint is very small and endpoints would not be detected satisfactorily by the titration software.

The suitability of a particular chemical reaction as a candidate for a thermometric titration procedure can generally be predicted on the basis of the estimated amount of analyte present in the sample and the enthalpy of the reaction. However, other parameters such as the kinetics of the reaction, the sample matrix itself, heats of dilution and losses of heat to the environment can affect the outcome. A properly designed experimental program is the most reliable way of determining the viability of a thermometric titration approach. Successful applications for thermometric titrations are generally where titrant-analyte reaction kinetics are fast and chemical equilibria are stoichiometric or nearly so.

Thermometric titration may be recommended where:

- *The titration environment is considered unsuitable for conventional titration sensors.* For example, glass membrane pH electrodes must be kept adequately hydrated for proper operation. The use of such electrodes in substantially non-aqueous media as in the determination of trace acids in lipids and lubricating oils can lead to loss of performance as the membrane fouls and dehydrates, and/or if the reference junction is partly or completely blocked. It is often necessary to keep a number of electrodes cycling through a rejuvenation program in order to keep up with an analytical workload. Thermometric sensors have no electrochemical interaction with the titration solution and therefore can be used (also for titrations in non-conducting media) on a continuous basis with essentially no maintenance.

- *No suitable reference electrode or diaphragm can be found.* This can be either because there is no suitable reference electrolyte available or the diaphragm of the reference electrode is blocked by the sample matrix.

- *A thermometric titration methodology that cannot be emulated using other types of titration sensors delivers superior or otherwise unobtainable results.* Examples are the determination of fluoride by titration with boric acid, the analysis of orthophosphate by titration with magnesium ions, and the direct titration of aluminum with fluoride ions.

The applications described in this monograph may serve as a guide to the analyst in determining whether automated thermometric titrations may be profitably employed in his or her laboratory.

4. Apparatus and setup for automated thermometric titrimetry

A suitable setup for automated thermometric titrimetry comprises the following:

• Precision fluid dispensing devices – burets – for adding titrants and dosing of other
  reagents
• Thermistor-based thermometric sensor
• Titration vessel
• Stirring device, capable of highly efficient stirring of vessel contents without splashing
• Computer with thermometric titration operating system
• Thermometric titration interface module – this regulates the data flow between the
  burets, sensors and the computer

Figure 6 illustrates an automated thermometric titration system based on the 859 Titro-
therm interface module with Thermoprobe sensor, 800 Dosino dispensing devices and a
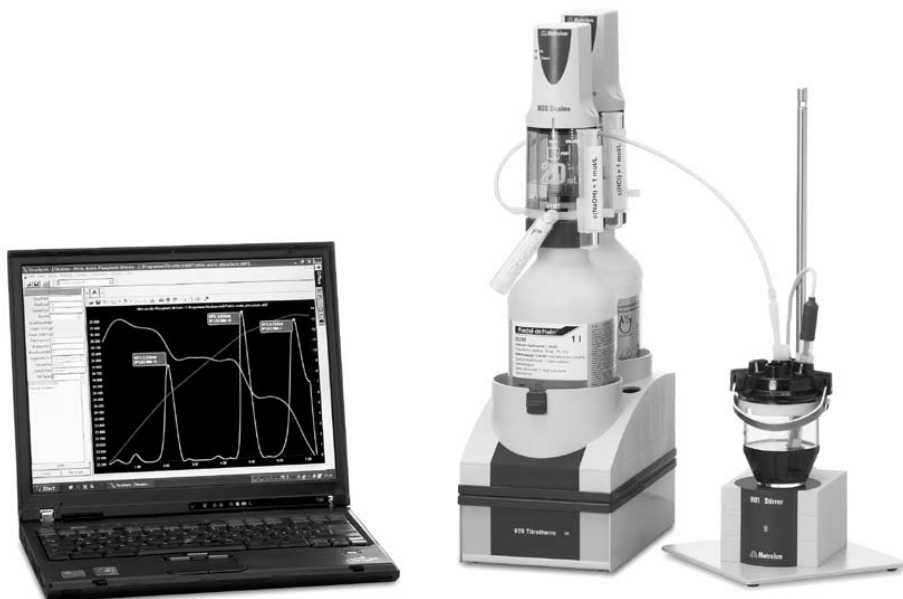computer running the operational software.

Fig. 6: Basic thermometric titration system featuring 859 Titrotherm interface module and 800 Dosino dispensing
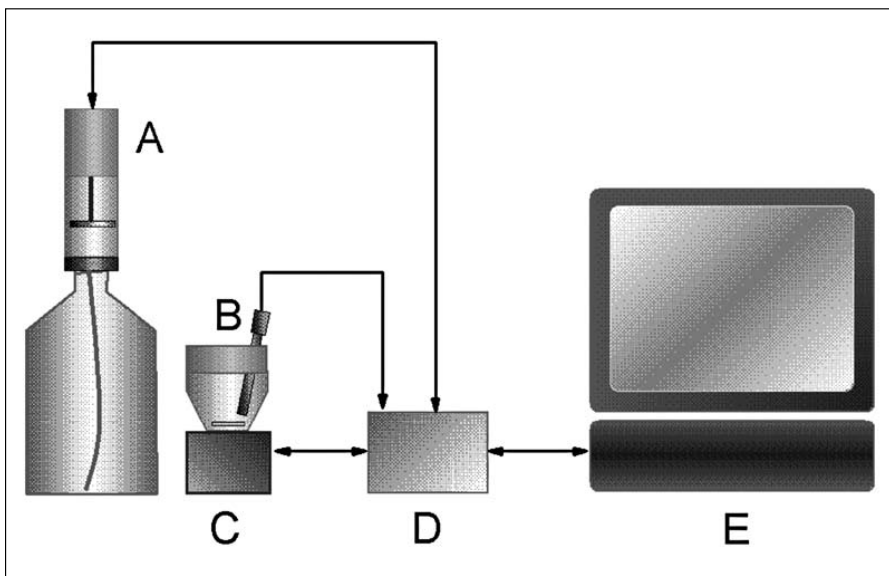devices.

Fig. 7: Schematic of the relationship between the components in an automated thermometric titration system.

A = dosing device
B = thermometric sensor
C = stirring device
D = thermometric titration interface module
E = computer

5. Optimization of thermometric titration parameters

5.1. Physical titration conditions

5.1.1. Mixing

The thermistors used in the Thermoprobe thermometric probes employed with Titrotherm have a response time of approximately 0.3 seconds. Most of the instrumental noise evident in thermometric titrations is thus due to the detection of temperature gradients in the stirred titration solution. Minimization of instrumental noise can therefore be obtained by using stirring speeds as high as possible consistent with the avoidance of splashing. Some compromise to stirring speed might be necessary when working with determinations where very little heat is evolved or absorbed, and where environmental influences such as solvent evaporation might have a deleterious impact.

5.1.2. Probe orientation

It has been observed by a number of workers in the field of thermometric titration that there is an optimum placement of the thermistor probe and the buret delivery tip in the titration vessel. This is at the periphery of the titration vessel, with the thermistor upstream of the delivery tip when referred to the direction of flow in the vessel.
This relative placement permits the thorough mixing and thus most efficient reaction of titrant and analyte.

5.1.3. Data density

Richter and Tinner (2001) have emphasized the importance of data density around titration breakpoints in order to define endpoints precisely. It has been stated previously that thermometric titrations are conducted at constant titrant addition rates, and so the practice of slowing down the titrant addition rates in potentiometric «dynamic titrations» to obtain higher data densities around breakpoints is not an option. Instead, the Titrotherm thermometric titration software permits data density to be preset before the start of the titration. The data density stays constant over the entire titration. With Titrotherm software, the analyst has the option of altering the sampling rate of the output from the thermometric sensor in the range of 5 to 25 times per second. The maximum permissible number of data points that can be collected during the course of a titration is 32'000. The data sampling rate is matched to the anticipated titrant consumption and to the titrant addition rate of the determination. Table 1 indicates the relationship between titrant consumption, data sampling rate and titrant addition rate. Higher titrant addition rates demand concomitantly higher data sampling rates with the converse applying for lower titrant addition rates.

Table 1: Relationship between anticipated titrant consumption and sensor data sampling rate.

Anticipated titrant consumption, mL	Data sampling rate, 1/sec	Titrant addition rate, mL/min	Data points collected
0…3	25	1	0…4500
3…7.5	10	1.5	1200…3000
7.5…10	10	2	2250…3000

5.1.4. Optimizing titration results with software

The Titrotherm software employs a powerful data-smoothing algorithm that exhibits a minimum endpoint shift as a function of the degree of filtering applied. However, it is inevitable that some shift will occur. For highest accuracy and precision this shift should be taken into consideration. For thermometric titrations, endpoint shift appears to be less pronounced in titration reactions involving large enthalpy changes with fast reaction kinetics. For example, redox and strong acid/strong base titrations usually exhibit a minimal endpoint shift. Apart from these, some reactions may require more careful optimization.

Figure 8 and Table 2 illustrate the effect of the filter factor on the endpoint peak shape and the endpoint shift. The titration illustrated was the determination of nickel using sodium dimethylglyoximate as titrant.
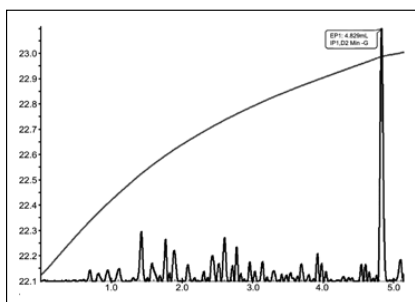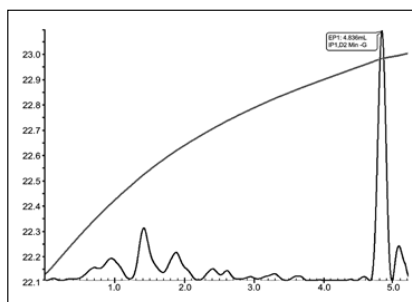

Fig. 8 a: Filter factor = 20
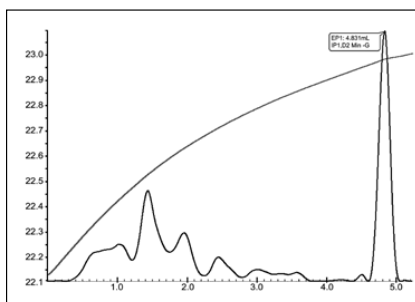

Fig. 8 b: Filter factor = 50

Fig. 8 c: Filter factor = 80
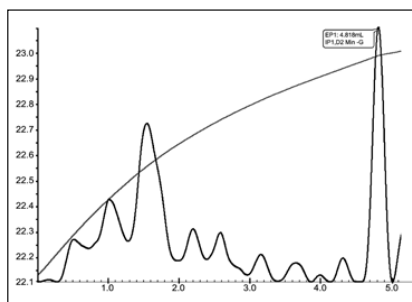
Fig. 8 d: Filter factor = 100

Figures 8 a – d: Effect of filter factor on endpoint derivative peak.

For a rigorous optimization, an examination of the effect of filter factor on the titrant consumption of the determination should be undertaken. Table 2 and Figure 9 illustrate this process.

Table 2: Titrant consumption determined at the endpoint as a function of the filter factor.

Filter Factor	Titrant consumed, mL	Filter Factor	Titrant consumed, mL
20	4.829	70	4.843
30	4.836	80	4.831
40	4.837	90	4.832
50	4.836	100	4.818
60	4.837	110	4.814

By plotting the filter factor (x-axis) against the titrant consumption determined (y-axis), it can be seen in the example illustrated in Figure 9 that stable endpoint values are obtained over a filter factor range of 30…60. An optimal filter factor could thus be found in the range 40…50.

Fig. 9: Determination of the optimal filter factor.

6. Titrant calibration and determination of the method blank

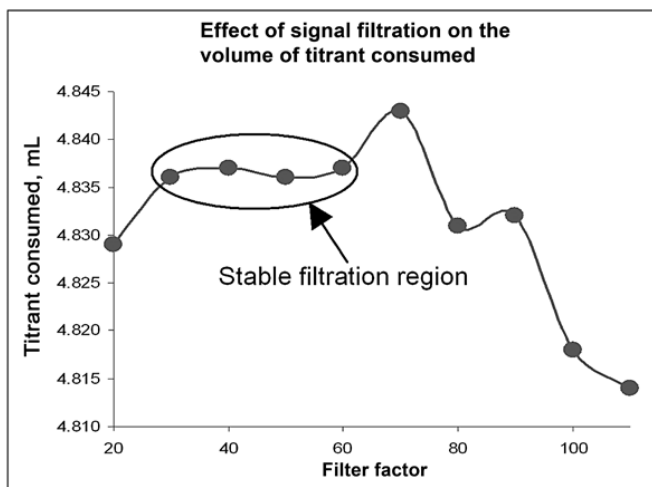This chapter deals with the optimum determination of the accuracy of the volume of titrant delivered to the endpoint and the concentration of the titrant.

As has been discussed previously, thermometric titrations are conducted under conditions of a constant titrant addition rate. In this respect they differ from potentiometric titrations, where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being given out or consumed, and hence a more or less constant temperature change up to the endpoint. Ideally, the temperature of the solution should be transmitted to the computer and processed instantaneously throughout the titration. Practically this is not the case and it takes a finite time before a change in temperature of the solution is received, computed and recorded. Since titrant is added at a constant rate, this time delay in the passage and processing of temperature information is expressed as a volume of titrant. Delays from various sources including the ones cited below affect the exact volume of titrant needed and hence the exact location of the endpoint:

- Inefficiencies in the mixing of the titration solution
- Reaction kinetics (in the case of non-ionic titrations)
- Heat transfer delays across the thermistor cladding and in the thermistor bead itself
- Electronic and software processing delays.

Furthermore, the shape of the inflection or breakpoint at the endpoint of the titration and the slopes of the temperature curve prior to and post the endpoint all have an impact on the optimum location of the endpoint as determined by the second derivative curve, and this has to be considered along with time delays in determining the actual amount of titrant consumed to the endpoint.

For given sets of titration conditions, these errors are constant and can be quantified as a single parameter – the titration method blank. This parameter is stored along with the other method parameters and is subtracted from all determinations of the volume of titrant needed in these particular titrations.

6.1.   Determination of method blank

The method blank is determined by titrating under previously optimized conditions a number of analyte solutions of different concentrations and plotting the analyte concentration against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in method parameters will require a new determination of the method blank.

6.2.   Determination of titrant concentration

The titrant concentration is conveniently determined at the same time as the method blank using a standard solution of analyte titrated under the same conditions considered optimum for titration of actual samples. Where the analyte is not a primary standard, it should be substituted by an appropriate primary standard.

The procedure of the determination of the titrant concentration may be summarized as follows:

- Write the chemical equation describing the reaction of the standard analyte with the titrant.

- Determine the number of moles of analyte reacting with one mole of titrant.

- Starting from an appropriate solution of a primary standard, prepare a range of amounts of analyte either by direct weighing or by serial dilution. The amounts of analyte present in this series of secondary standard solutions should encompass at least the normal range anticipated to be found in actual samples. Moreover, reasonable amounts of titrant have to be needed for titration.
  For example, during initial experimentation and optimization it may be found that aliquots of sample solution give titrant volumes needed in the range 2…4 mL. The range of standards chosen should therefore span at least say 1…5 mL. Generally for thermometric titrations, a maximum titrant consumption of 5…6 mL is suitable, but with some chemistries whose reaction enthalpies are modest, a maximum titrant consumption of only 2.5…5 mL may be advisable. Conversely, redox titrations exhibiting very high reaction enthalpies can tolerate higher maximum volumes of titrant consumed, say 10…12 mL. Overall, there is little to be gained in terms of analytical precision by employing large volumes of titrant required. Usually any gains made in using a high titrant volume to be added, are offset by decreases in the replication of the results. At least four standards should be used in the calibration process.

- If the primary standard is a liquid, use a series of high quality bulb pipets to deliver the aliquots. A suitable series may be 2, 3, 4, 5 and 10 mL or 5, 10, 15, 20 and 25 mL. The pipets should be freshly cleaned with a suitable laboratory glass cleaning agent and rinsed with deionized water prior to use. The choice of a set of pipets and the corresponding concentration of the standard analyte solution will be influenced by the volume of any reagent solutions that need to be added.
  For example, if you have to prepare buffered standard solutions of 25 mL each, then choose a pipet set of 2, 3, 4, 5 and 10 mL for transferring the required aliquots of primary standard to the flasks, add the necessary buffer solution volume (e.g. 10 mL) and make up to the mark with ultrapure water.

- If a solid primary standard is used, weigh it in on an analytical balance to ±0.1 mg.

- Set up the regression plot with the millimoles of analyte (contained in each prepared standard solution) plotted on the x-axis and milliliters of titrant consumed plotted on the y-axis.

- The plot will be a linear curve of the form $y = ax + b$, where the method blank is represented by the intercept b, and the molarity of the titrant is calculated from the gradient a. Table 3 gives some examples of how the molarity of the analyte may be calculated.

Table 3: Examples of the calculation of the molarity of the titrant from the determination of titrant concentration by regression analysis.

Analyte	Titrant	Reaction	Molarity
NaOH	HCl	$NaOH + HCl \rightleftharpoons NaCl + H_2O$	1 divided by gradient
H_2SO_4	NaOH	$H_2SO_4 + 2NaOH \rightleftharpoons Na_2SO_4 + 2\ H_2O$	2 divided by gradient
Al^{3+}	F^-	$Al^{3+} + Na^+ + 2K^+ + 6F^- \rightleftharpoons NaK_2AlF_6$	6 divided by gradient

An example of this approach to the determination of both method blank and titrant molarity is the thermometric titration of aluminum with fluoride ions. A primary standard solution of aluminum is made by dissolution of high-purity aluminum metal. Aliquots of this solution have been taken to prepare the diluted standard solutions. By plotting the aluminum ion concentration of these standards against the required volume of fluoride ion titrant, Figure 10 is obtained. The regression was carried out using the linear regression function in Microsoft Excel.

Fig. 10: Example of a calibration curve.
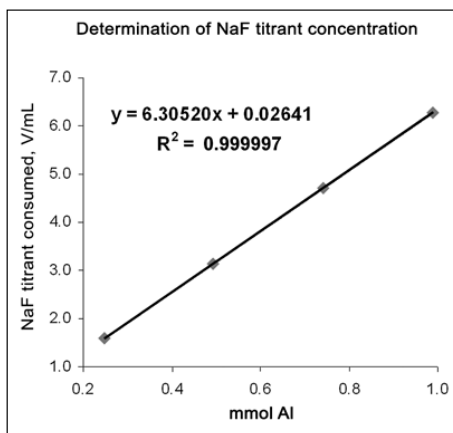
Results of regression analysis:
Gradient = 6.30520 mL/mmol
Y-intercept (method blank) = 0.0264 mL
Correlation coefficient (R^2) = 0.999997

Calculation of NaF molarity:
Molarity = 6 divided by gradient
(because 6 moles fluoride ion react with 1 mole aluminum ion).
Molarity = 6 / 6.30520 = **0.9516 mol/L NaF**

Therefore the diluted NaF standard solutions have a titer of:

$$\text{titer} = \frac{\text{concentration}_{measured}}{\text{concentration}_{nominal}} = 0.9516$$

An advantage of this approach is that not only two critical parameters can be determined at the same time, but also the analyst has the opportunity to check the linearity of response over the measurement range in question.

7.   Types of thermometric titration

Thermometric titrimetry can be used for the following reaction types:

• Acid-base (acidimetry and alkalimetry)
• Redox
• Precipitation
• Complexometric

Because the sensor does not interact electrically or electrochemically with the solution, electrical conductance of the titrating medium is not a prerequisite for a successful determination. Titrations may be carried out in completely non-conducting, non-polar media if required. Further, titrations may be carried out in turbid solutions or even suspensions of solids. Titrations where precipitates are formed can also be carried out.

7.1.   Acid-base titrations

7.1.1   Determination of fully dissociated acids and bases

The heat of neutralization of a fully dissociated acid with a fully dissociated base (see Figure 11) is approximately -56 kJ/mol and can be calculated as a standard enthalpy of reaction using standard enthalpies of formation.

$$H^+ \quad + \quad OH^- \quad \rightleftharpoons \quad H_2O$$

ΔH^0_f (kJ/mol)   0 -230.0 -285.8 $\Delta H^0_r = -55.8$ kJ/mol
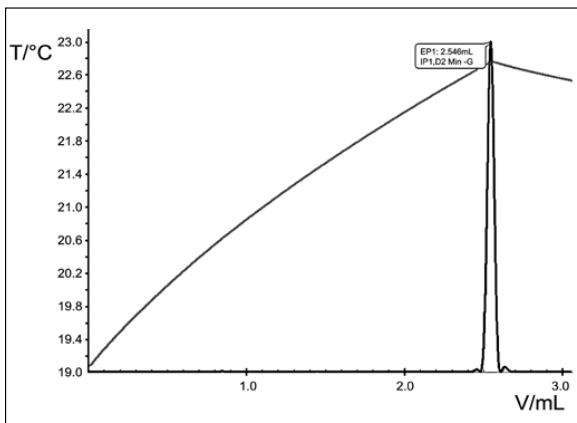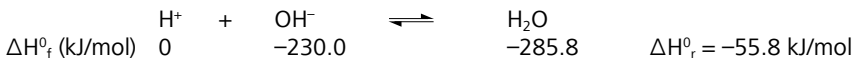

Fig. 11: Titration of NaOH with 1 mol/L HCl.

The reaction is strongly exothermic and thus provides an excellent basis for a wide range of analyses in industry. An advantage for the industrial analyst is that the use of stronger titrants (1…2 mol/L) permits a reduction of the sample preparation effort. Samples can often be directly and accurately dispensed into the titration vessel prior to titration.

Hydrogen carbonate can be unequivocally determined in the presence of carbonate by titration with hydroxyl ions (see Figure 12). The standard enthalpy of reaction is approximately −41 kJ/mol.
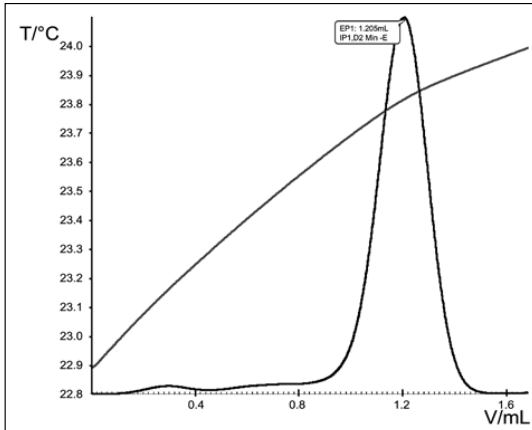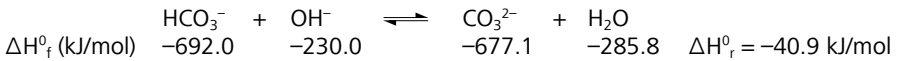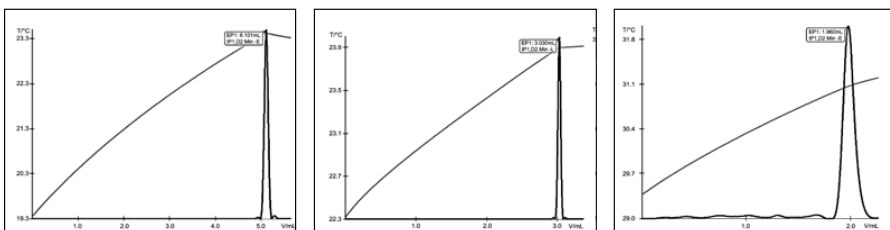
$$HCO_3^- \quad + \quad OH^- \quad \rightleftharpoons \quad CO_3^{2-} \quad + \quad H_2O$$

ΔH^0_f (kJ/mol) −692.0   −230.0   −677.1   −285.8 $\Delta H^0_r = -40.9$ kJ/mol

Fig. 12: Titration of HCO_3^- in company with CO_3^{2-} by 1 mol/L NaOH.

7.1.2. Titration of weak acids

Weakly dissociated acids yield sharp endpoints when titrated with a strong base (see Figure 13).

Formic acid   **Citric acid**   **Total acids in apple juice**
Fig. 13: Titration of weak acids with 1 mol/L NaOH.

7.1.3. Titration of acid mixtures

Mixtures of complex acids can be resolved by thermometric titration with standard NaOH in aqueous solution (see Figure 14 and Table 4). In a mixture of nitric, acetic and phosphoric acids used in the fabrication of semiconductors, three endpoints could be predicted on the basis of the dissociation constants of the acids:

Endpoint 1	Endpoint 2	Endpoint 3
HNO_3 ($pK_a = -1.3$)	HOAc ($pK_a = 4.75$)	
H_3PO_4 ($pK_{a1} = 2.12$)	H_3PO_4 ($pK_{a2} = 7.21$)	H_3PO_4 ($pK_{a3} = 12.36$)

Table 4: pK_a values in a mixture of nitric, acetic and phosphoric acids.

The key to determine the amount of each acid present in the mixture is the ability to obtain an accurate value for the amount of phosphoric acid present, as revealed by titration of the third proton of H_3PO_4.

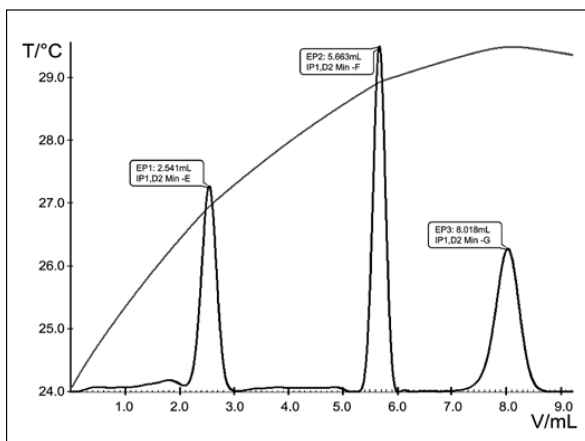Figure 14 illustrates a titration plot of this mixture, showing 3 sharp endpoints.

Fig. 14: Titration of a mixture of nitric, acetic and phosphoric acid with 2 mol/L NaOH.

7.1.4. Titration of complex alkaline solutions

The thermometric titration of sodium aluminate liquor (Bayer liquor) in the production of alumina from bauxite is accomplished in an automated two titration sequence. This is an adaptation of a classic thermometric titration application (VanDalen and Ward, 1973). In the first titration, tartrate solution is added to an aliquot of liquor to complex the aluminate, releasing one mole of hydroxyl ions for each mole of aluminate present. The carbonate ions along with the released and «free» hydroxyl ions are titrated acidimetrically in a second titration (see Part 1 of Figure 15). The second titration is preceded by the automatic addition of fluoride solution. The alumina-tartrate complex is broken in favor of the formation of an aluminum fluoride complex and the concomitant release of three moles of hydroxyl ions for each mole of aluminum ions present, which are then titrated acidimetrically (see Part 2 of Figure 15). The whole determination can be completed in less than 5 minutes.
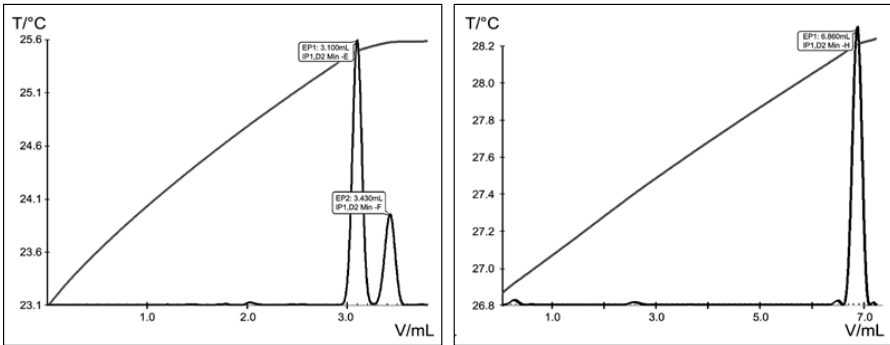
Part 1: Titration of the total hydroxyl and   Part 2: Titration of the hydroxyl ions equivalent
         carbonate content.   to the aluminum content.

Fig. 15: Titration plots for the determination of «total caustic», «total soda» and «alumina» in alumina refinery liquors.

7.1.5. Non-aqueous acid-base titrations

Non-aqueous acid-base titrations can be carried out advantageously by thermometric means.

Acid leach solutions from some copper mines can contain large quantities of Fe(III) as well as Cu(II). The «free acid» (sulfuric acid) content of these leach solutions is a critical process parameter. While thermometric titrimetry can determine the free acid content with modest amounts of Fe(III), in some solutions the Fe(III) content is so high as to cause serious interference. Complexation with necessarily large amounts of oxalate is undesirable due to the toxicity of the reagent. A thermometric titration was devised by diluting the aliquot with 2-propanol (isopropyl alcohol, propan-2-ol) followed by titration with standard KOH in 2-propanol. As a result, most of the metal content precipitated prior to the start of the titration, and a clear, sharp endpoint indicating the sulfuric acid content was obtained (see Figure 16).
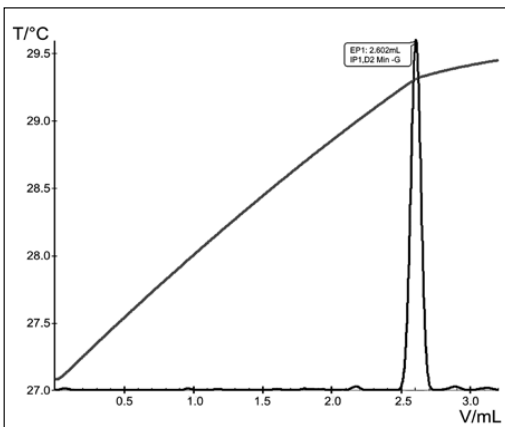

Fig. 16: Determination of free H_2SO_4 in copper leach solution by titration in 2-propanol with 1 mol/L KOH in 2-propanol.

7.1.6. Catalyzed endpoint thermometric acid-base titrations

The determination of trace acids in organic matrices is a common analytical task assigned to titrimetry. Examples are Total Acid Number (TAN) in mineral and lubricating oils and Free Fatty Acids (FFA) in edible fats and oils. Automated potentiometric titration procedures have been granted standard method status, for example by ASTM for TAN and AOAC for FFA. The methodology is similar in both instances. The sample is dissolved in a suitable solvent mixture and the trace acids are titrated with standard base dissolved in an alcohol.

A recent thermometric titrimetric procedure for the determination of FFA developed by Cameiro et al (2002) has been shown to be particularly amenable to automation. It is not only fast and highly precise but also the results agree very well with those obtained by the official AOAC method. In Cameiro's procedure, a small amount of paraformaldehyde is added as a fine powder to the sample solution before the titration. Without this addition, the temperature change for the titration of very weak acids such as oleic acid by 0.1 mol/L KOH in 2-propanol would be too small to yield an accurate endpoint. At the endpoint, the first excess of hydroxyl ions catalyzes the hydrolysis of paraformaldehyde. The reaction is strongly endothermic and yields a sharp inflection. The titration plot is illustrated in Figure 17.
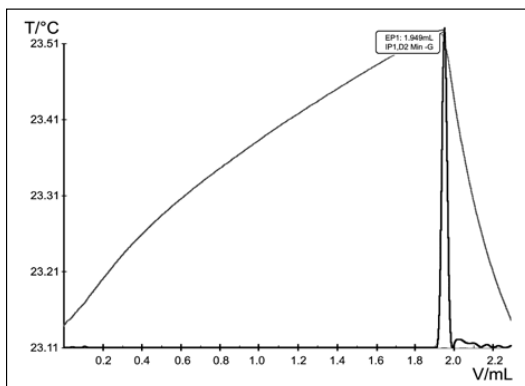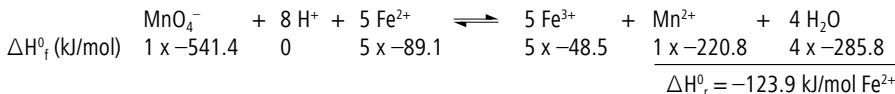

Fig. 17: Catalyzed endpoint thermometric titration of free fatty acids in tallow – hydroxyl-catalyzed endothermic hydrolysis of paraformaldehyde.

7.2. Redox titrations

7.2.1. Titrations with permanganate and dichromate

Redox reactions are normally strongly exothermic and can make excellent candidates for thermometric titrations. Consider the classical determination of ferrous ions with permanganate:

$$MnO_4^- \; + \; 8\,H^+ \; + \; 5\,Fe^{2+} \; \rightleftharpoons \; 5\,Fe^{3+} \; + \; Mn^{2+} \; + \; 4\,H_2O$$

ΔH^0_f (kJ/mol)   1 x −541.4   0   5 x −89.1   5 x −48.5   1 x −220.8   4 x −285.8

$$\Delta H^0_r = -123.9 \text{ kJ/mol Fe}^{2+}$$

The determination of hydrogen peroxide by permanganate titration is even more strongly exothermic:

$$2\ MnO_4^- \ +\ 6\ H^+ \ +\ 5\ H_2O_2 \ \rightleftharpoons \ 5\ O_2 \ +\ 2\ Mn^{2+} \ +\ 8\ H_2O$$

$\triangle H^0_f$ (kJ/mol)   2 x −541.4   0   5 x −89.1   5 x −11.7   2 x −220.8   8 x −285.8

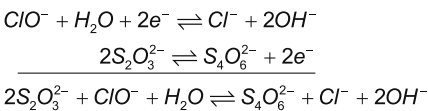$$\triangle H^0_r = -149.6 \text{ kJ/mol } H_2O_2$$
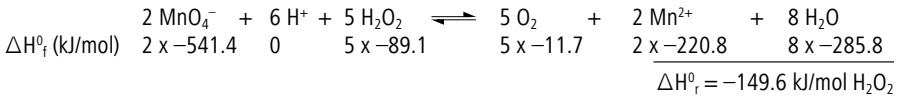
This reaction is catalyzed by the presence of Mn^{2+}. To avoid a sudden surge of temperature shortly after commencement of the titration, it is necessary to add a minute amount of Mn^{2+} prior to the start.

Other common titrants used in redox titrimetry can be employed. Due to its purity and stability, potassium dichromate has been used successfully as a titrant in the determination of Fe(II) and ascorbic acid (vitamin C).

### 7.2.2. Titrations with thiosulfate

In the determination of hypochlorite (for example in commercial bleach formulations), a direct titration with thiosulfate can be employed without recourse to an iodometric finish.

$$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$$
$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$$
$$2S_2O_3^{2-} + ClO^- + H_2O \rightleftharpoons S_4O_6^{2-} + Cl^- + 2OH^-$$

Thermometric iodometric titrations employing thiosulfate as a titrant are also practical, for example in the determination of Cu(II). In this instance, it has been found advantageous to incorporate the potassium iodide reagent with the thiosulfate titrant in such proportions that iodine is released into solution just prior to its reduction by thiosulfate. This minimizes iodine losses during the course of the titration.

7.2.3. Hypochlorite as a titrant

While relatively unstable and requiring frequent determinations of the titer, sodium hypochlorite has been used in a very rapid thermometric titration method for the determination of ammonium. This is an alternative to the classical approach of ammonia distillation from basic solution and consequent acid-base titration. The thermometric titration is carried out in hydrogen carbonate solution containing bromide (Brown et al, 1969).

$$3\ OCl^- + 2\ NH_4^+ \ \rightleftharpoons \ 2\ H^+ + 3\ Cl^- + N_2 + 3\ H_2O$$
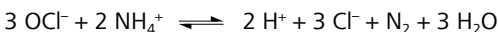
7.3. Complexometric (EDTA) titrations

Thermometric titrations employing sodium salts of ethylenediaminetetra-acetic acid (EDTA) have been demonstrated for the determination of a range of metal ions. Reaction enthalpies are modest, so titrations are normally carried out with titrant concentra-

tions of 1 mol/L. This necessitates the use of the tetrasodium salt of EDTA rather than the more common disodium salt, which is saturated at a concentration of only approximately 0.25 mol/L.

An excellent application is the sequential determination of calcium and magnesium. Although calcium reacts exothermically with EDTA (heat of chelation approximately −23.4 kJ/mol), magnesium reacts endothermically with a heat of chelation of approximately +20.1 kJ/mol. This is illustrated in the titration plot of EDTA with calcium and magnesium in sea water (Figure 18). Following the solution temperature curve, the breakpoint for the calcium content (endpoint on the left in Figure 18) is followed by a region of modest temperature rise due to competition between the heats of dilution of the titrant with the solution, and the endothermic reaction of Mg^{2+} and EDTA. The breakpoint for the consumption of Mg^{2+} (endpoint on the right in Figure 18) by EDTA is revealed by an upswing in temperature purely caused by heat of dilution.
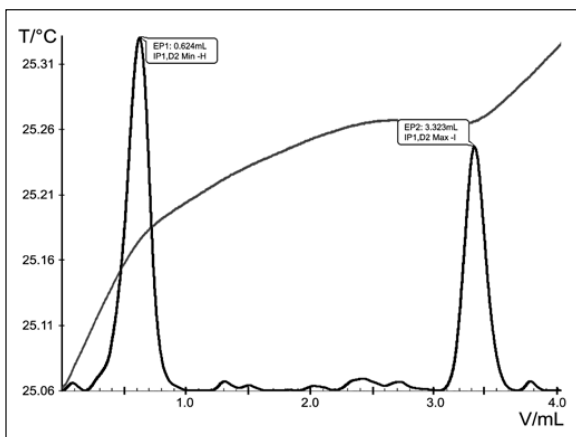

Fig. 18: EDTA titration of calcium and magnesium in sea water.

Direct EDTA titrations with metal ions are possible when reaction kinetics is fast as is the case with zinc, copper, calcium and magnesium. However, with slower reaction kinetics such as those exhibited by cobalt and nickel, back-titrations are used. Titrations for cobalt and nickel are carried out in an ammoniacal environment; buffered with ammonia/ammonium chloride solution. An excess of EDTA is added and back-titrated with Cu(II) solution (see Figure 19). It is postulated that the breakpoint is revealed by the difference in reaction enthalpies between the formation of the Cu-EDTA complex, and that for the formation of the Cu-ammine complex.
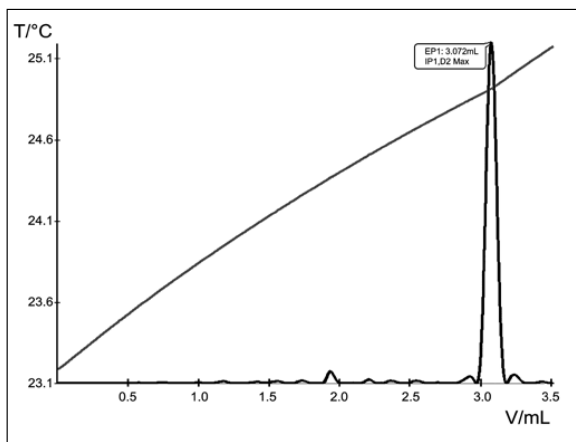
Fig. 19: Titration plot of back-titration of excess EDTA with Cu(II) in NH_3/NH_4Cl-buffered solution.

A catalyzed endpoint procedure to determine trace amounts of metal ions in solution (down to approximately 10 mg/L) employs 0.01 mol/L EDTA. This has been applied to the determination of low level Cu(II) in specialized plating baths and to the determination of total hardness in water. The reaction enthalpies of EDTA with most metal ions are often quite low. Therefore titrant concentrations typically around 1 mol/L are employed with correspondingly high amounts of analyte in order to obtain sharp, reproducible endpoints. Using a catalytically indicated endpoint in combination with a back-titration, very low EDTA titrant concentrations can be used. An excess of EDTA solution is added. The excess of EDTA is back-titrated with a suitable metal ion such as Mn^{2+} or Cu^{2+}. At the endpoint, the first excess of metal ion catalyzes a strongly exothermic reaction between a polyhydric phenol (such as resorcinol) and hydrogen peroxide (see Figure 20).
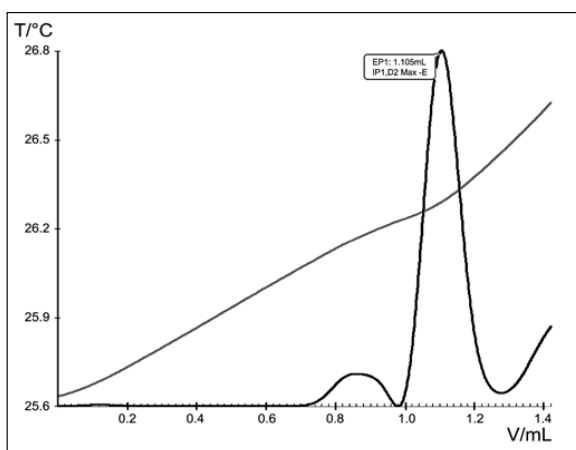

Fig. 20: Thermometric EDTA titration of trace Cu(II) by back-titration with Mn(II), in combination with catalytically enhanced endpoint detection using the exothermic reaction between hydrogen peroxide and a polyhydric phenol.

7.4.   Precipitation titrations

Thermometric titrimetry is particularly suited to the determination of a range of analytes where a precipitate is formed by reaction with the titrant. It may be employed for applications that cannot be satisfactorily analyzed by potentiometric titrimetry.

7.4.1. Titration of sulfate

Sulfate may be rapidly and easily titrated thermometrically using standard solutions of Ba^{2+} as titrant. Industrially, the procedure has been applied to the determination of sulfate in brine (including electrolysis brines), in nickel refining solutions and particularly for sulfate in wet process phosphoric acid, where it has proven to be quite popular. The procedure can also be used to assist in the analysis of complex acid mixtures containing sulfuric acid where resorting to titration in non-aqueous media is not feasible.

The reaction enthalpy for the formation of barium sulfate is a modest -18.8 kJ/mol. This can place a restriction on the lower limit of sulfate in a sample that can be analyzed.

7.4.2. Titration of aluminum with fluoride

Thermometric titrimetry offers a rapid, highly precise method for the determination of aluminum in solution. A solution of aluminum is conditioned with acetate buffer and an excess of sodium and potassium ions. Titration with sodium or potassium fluoride yields the exothermic precipitation of an insoluble alumino-fluoride salt.

$$Al^{3+} + Na^+ + 2\ K^+ + 6\ F^- \rightleftharpoons K_2NaAlF_6\downarrow$$
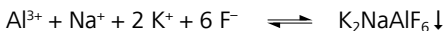
Because 6 mol of fluoride react with one mol of aluminum, the titration is particularly precise, and a coefficient of variance (CV) of 0.03 has been achieved in the analysis of alum.

When aluminum ions (say as aluminum nitrate) are employed as the titrant, fluoride can be determined using the same chemistry. This titration is useful in the determination of fluoride in complex acid mixtures used as etchants in the semiconductor industry.

7.4.3. Titration of total orthophosphate

Orthophosphate ions can be conveniently thermometrically titrated with magnesium ions in the presence of ammonium ions. An aliquot of sample is buffered to approximately pH 10 with an NH_3/NH_4Cl solution.

The reaction:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightleftharpoons MgNH_4PO_4\downarrow$$
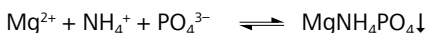
is exothermic. CV's of under 0.1 have been achieved in test applications. The procedure is suitable for the determination of orthophosphate in fertilizers and other products.

7.4.4. Titration of nickel

Nickel can be titrated thermometrically using disodium dimethylglyoximate as titrant. The chemistry is analogous to the classic gravimetric procedure, but the time taken for a determination can be reduced from many hours to a few minutes. Potential interferences need to be considered.

7.4.5. Titration of anionic and cationic surfactants

Anionic and cationic surfactants can be determined thermometrically by titrating one type against the other. For instance, benzalkonium chloride (a quaternary type cationic surfactant) may be determined in cleaners and algaecides for swimming pools and spas by titrating with a standard solution of sodium dodecyl sulfate (see Figure 21a). Alternatively, anionic surfactants such as sodium lauryl sulfate can be titrated with cetyl pyridinium chloride (see Figure 21b).
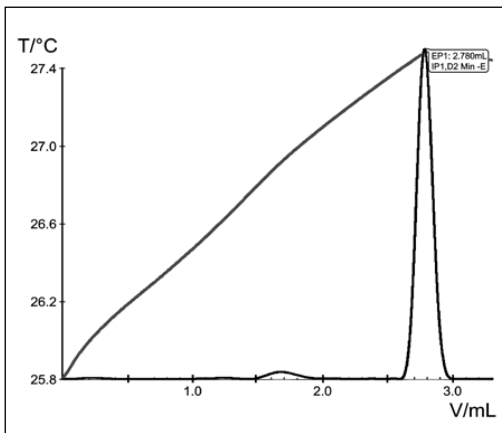

Fig. 21 a: Titration of benzalkonium chloride with sodium dodecyl sulfate
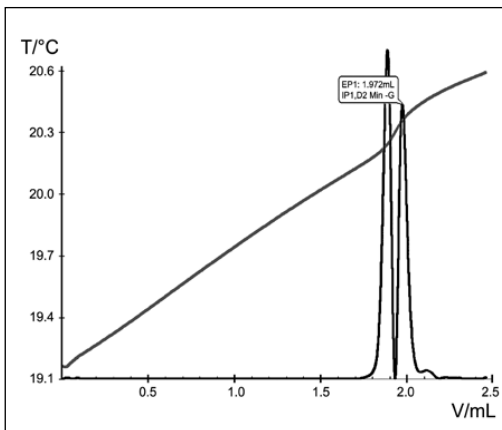

Fig. 21 b: Titration of sodium lauryl sulfate in shampoo by titration with cetyl pyridinium chloride. Acetonitrile added to repress micelle-related phenomena. Note sudden rise in temperature immediately prior to the endpoint.

Thermometric titrimetry offers an opportunity to observe the influence of micelles on the conduct of the determination. To avoid the influence of micelle-related phenomena on the outcome of the titration, it is sometimes necessary to add a suitable solvent such as acetonitrile.

7.4.6. Titration of non-ionic surfactants

When an excess of Ba^{2+} is added to a non-ionic surfactant of the alkyl propylene oxide derivative type, a pseudo-cationic complex is formed. This may be titrated with standard sodium tetraphenylborate (see Figure 22). Two moles tetraphenylborate react with one mole of the Ba^{2+}/ non-ionic surfactant complex.
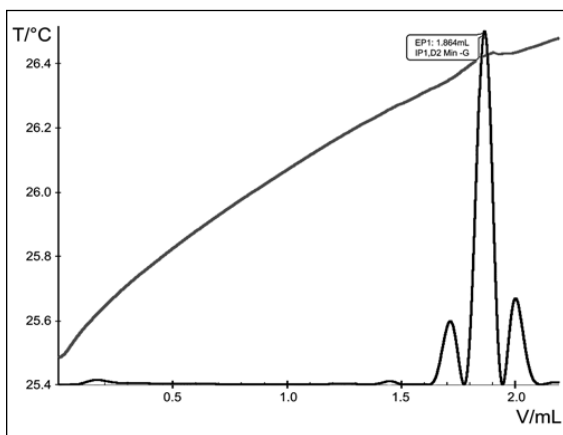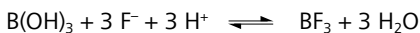

Fig. 22: Thermometric titration of a non-ionic surfactant in a formulation containing an anionic surfactant.

7.5. Miscellaneous aqueous titrations

7.5.1. Titration of fluoride with boric acid

Acidic solutions of fluoride (including hydrofluoric acid) can be determined by a simple thermometric titration with boric acid.

$$B(OH)_3 + 3\ F^- + 3\ H^+ \rightleftharpoons BF_3 + 3\ H_2O$$

The titration plot illustrated in Figure 23 shows that the endpoint is quite rounded, suggesting that the reaction might not proceed to stoichiometric equilibrium. However, since the regions of the temperature curve immediately before and after the endpoint are quite linear, the second derivative of this curve (representing the intersection of tangents) will accurately locate the endpoint. Indeed, excellent precision can be obtained with this titration, with a CV of less than 0.1.
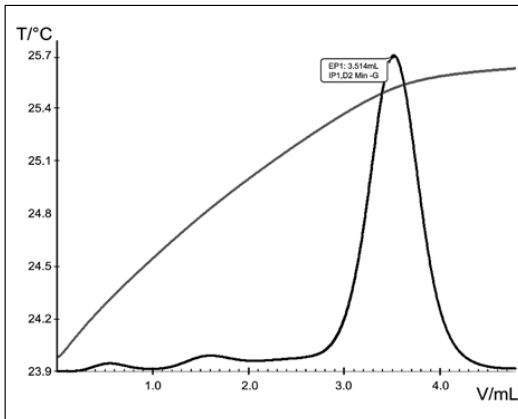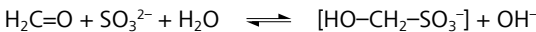
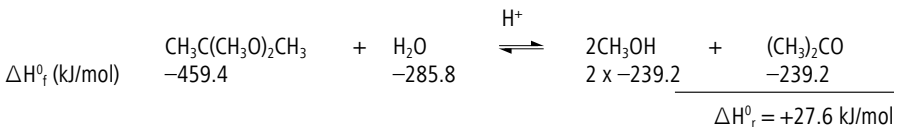Fig. 23: Titration plot of the determination of fluoride with boric acid.

7.5.2. Determination of formaldehyde

Formaldehyde can be determined in electroless copper plating solutions by the addition of an excess of sodium sulfite solution and titrating the liberated hydroxyl ion with standard acid.

$$H_2C=O + SO_3^{2-} + H_2O \rightleftharpoons [HO-CH_2-SO_3^-] + OH^-$$

7.6. Thermometric titration of water

The thermometric titration of water using Karl Fischer (KF) reagent is feasible due to the large reaction enthalpy involved (approx. −67 kJ/mol). However, other workers have sought to avoid some of the disadvantages and limitations inherent in the use of the KF reagent. Sadtler and Wilson (ca. 1980) developed a thermometric titration technique relying on the endothermic acid-catalyzed reaction of 2,2-dimethoxypropane (DMP) with water.

	$CH_3C(CH_3O)_2CH_3$	+	H_2O	$\overset{H^+}{\rightleftharpoons}$	$2CH_3OH$	+	$(CH_3)_2CO$
$\triangle H^0_f$ (kJ/mol)	−459.4		−285.8		$2 \times −239.2$		−239.2

$$\triangle H^0_r = +27.6 \text{ kJ/mol}$$

The reagent had seen prior use in the dehydration of histological specimens, and in infrared and gas chromatographic methods for the determination of water. DMP is of low toxicity, quite stable, not hygroscopic and only reacts with water in the presence of an acid. The reaction products (acetone and methanol) are relatively benign. Many applications have been demonstrated, including the determination of water in concentrated acids (where the acid itself provides the catalyst for the reaction) (see Figures 24 a and 24 b). Methane sulfonic acid may be used as a catalyst in many applications.
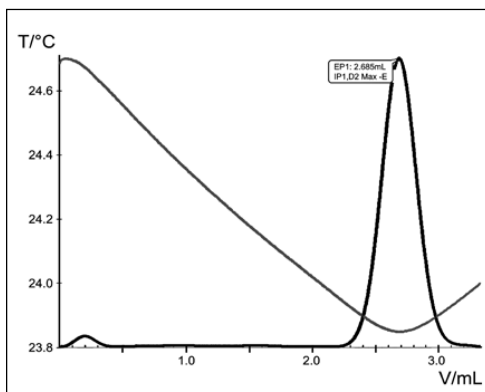
Fig. 24 a: Plot of thermometric titration of water in concentrated hydrochloric acid using DMP as titrant.
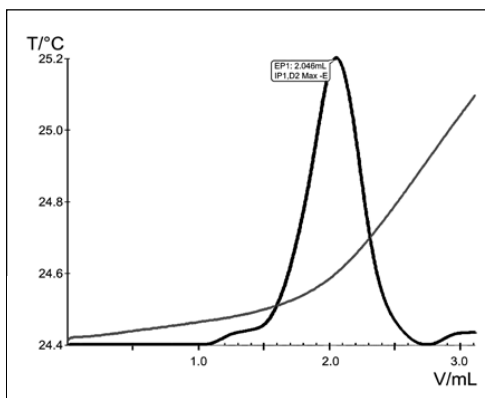

Fig. 24 b: Thermometric determination of moisture in commercial (ultrafine) cobalt oxyhydroxide. An excess of added DMP is back-titrated with a standard solution of water in 2-propanol.

Rounding of the endpoint suggests that the reaction might not proceed to stoichiometric equilibrium. Inspection of titration curves shows that, as expected, the reaction is driven closer to stoichiometric equilibrium when water is determined in strong acids.

### 7.6.1. Advantages of the DMP thermometric method:

- DMP is stable and essentially non-hygroscopic, does not react with water until catalyzed with acid. Does not require special conditions in storage
- DMP is of low toxicity, reaction products are relatively benign
- Analysis can be integrated with other thermometric titration procedures simply by adding an additional buret to the system
- Solvent system can be adjusted to suit the sample – a range of anhydrous organic solvents and mixtures thereof can be used
- Applicable to a wide range of sample types, particularly those that are acidic or neutral in character. Samples analyzed have ranged from plant oils with moistures in the range of 0.02…0.04% to concentrated HCl with a water content of 67%
- Can be useful for analysis of samples where Karl Fischer or other methods have not proven suitable

7.6.2. Limitations of the DMP thermometric method:

- High titration blanks may limit precision of procedure. Contributing factors to high blanks might be non-stoichiometry at equilibrium and/or residual moisture in solvents.
- Less well suited to analysis of moisture in basic samples
- Best results usually obtained with short titrations and a volume of titrant added generally less than 2 mL and frequently even less than 1 mL. This can affect the precision of the method.

7.6.3. Moisture determinations with triethyl orthoformate

Ortho esters such as triethyl orthoformate (TEOF) have been shown to be superior to DMP in the gas chromatographic determination of water (Chen & Fritz, 1991). The authors confirmed the non-stoichiometric equilibrium of the reaction of DMP with water. Ortho esters react with water in a similar manner to DMP, yielding a carboxylic ester and an alcohol.

$$HC(OCH_2CH_3)_3 + H_2O \xrightleftharpoons{H^+} HCOOCH_2CH_3 + 2CH_3CH_2OH$$
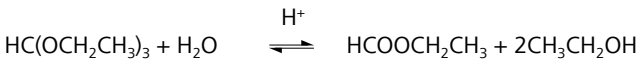
TEOF has been tested as a possible alternative to DMP in a number of applications, notably the determination of moisture in automotive engine oils. A typical thermometric titration plot of this application is shown in Figure 25. While the endpoint is subjectively sharper than that obtained with a DMP titration, the level of signal noise is clearly higher. This is undoubtedly due to the very modest changes in solution temperature experienced during the titration and the magnification of temperature variations in the stirred vessel.
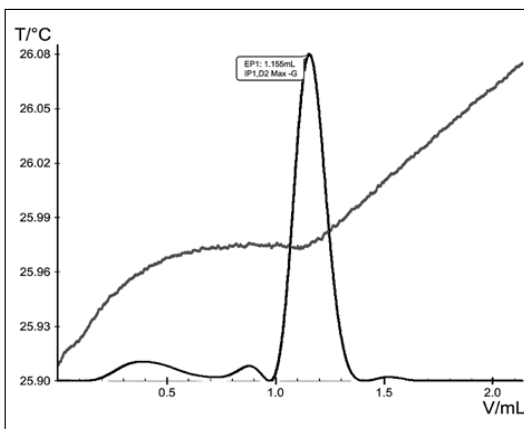

Fig. 25: Thermometric titration plot of the determination of water in automotive engine oil with triethyl orthoformate.

REFERENCES:

1. M. W. Brown, K. Issa, G. Sinclair. Precise manual enthalpimetric titrations. *Analyst,* **94,** 234–235 (1969)

2. J. Chen and J. S. Fritz. Gas chromatographic determination of water after reaction with triethyl orthoformate. *Anal. Chem.* **63** (18), 2016–2020 (1991)

3. W. Richter and U. Tinner. Practical aspects of modern titration *Metrohm Monograph* 8.016.5003 (2001)

4. E. VanDalen and L. G. Ward. Thermometric titration determination of hydroxide and alumina in Bayer process solutions. *Anal. Chem.* **45** (13), 2248–2251 (1973)

5. M. J. D. Carneiro, M. A. Feres Júnior, and O. E. S. Godinho. Determination of the acidity of oils using paraformaldehyde as a thermometric endpoint indicator. *J. Braz. Chem. Soc*. **13** (5), 692–694 (2002)

6. T. K. Smith. Analysis of FFA in edible oils by catalyzed endpoint thermometric titrimetry. *JAOCS* **80**, 21–24 (2003)

7. G. A. Vaughan and J. J. Swithenbank. Exothermic condensation of acetone to diacetone alcohol. *Analyst* **90,** 594–599 (1965)

BIBLIOGRAPHY:

(All of the following books are out of print, but might be available from academic libraries or through second-hand book sellers such as Amazon.com)

1. G. A. Vaughan (1973) *Thermometric and enthalpimetric titrimetry.* Van Nostrand Reinhold Company (London) ISBN 0-442-78385-X; Library of Congress Catalog Card No. 79-186764

2. L. S. Bark and S. M. Bark (1969). *Thermometric titrimetry. International Series of Monographs in Analytical Chemistry* vol. 33, Pergamon Press (Oxford); Library of Congress Catalog Card No. 68-57883

3. J. Barthel (1975) *Thermometric titrations*. John Wiley & Sons, New York. ISBN 0-471-05448-8; Library of Congress Catalog Card No. 75-17503

4. J. K. Grime (1985) *Analytical solution calorimetry*. John Wiley & Sons, New York. ISBN 0-471-86942-2; Library of Congress Catalog Card No. 84-28424

5. D. J. Eatough, J. J. Christensen, R. M. Izatt (1974) *Experiments in thermometric titrimetry and titration calorimetry*. Brigham Young University Press, Provo, Utah. ISBN 0-8425-0145-2; Library of Congress Catalog Card 74-13074