Metrohm
Ion analysis

859 Titrotherm

Thermometric titrator –
the ideal complement to
potentiometric titration

What is a thermometric titration?

Titration is the oldest and most widespread method used in analytical chemistry. For a long time now, potentiometric sensors (indicator electrodes) have been used to cover a wide range of applications in the titration field. As a result, potentiometric titration has become firmly established and features in many standards.

However, a suitable indicator electrode is not always available for an existing problem. There may be no suitable sensor for the analyte at hand or the sample matrix can either interfere with the indicator electrode or even render it unusable.

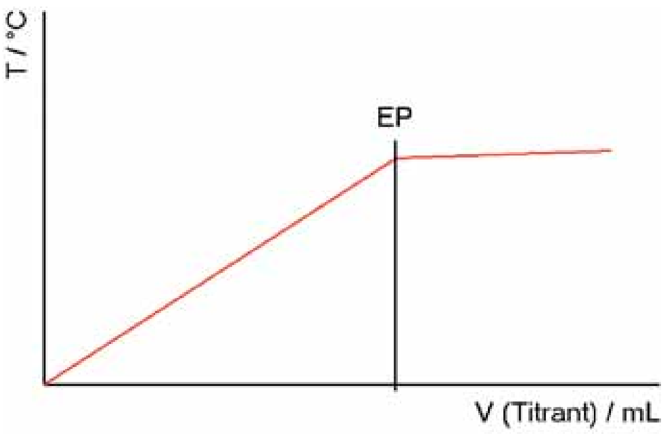
The electrochemical potential is only one of the possible ways of following a chemical reaction. A far more universal parameter is the reaction enthalpy.

Every chemical reaction is accompanied by a change in enthalpy (ΔH). The following equation applies:

$\Delta H = \Delta G + T\Delta S$, where
ΔG = change in free reaction energy
T = absolute temperature
ΔS = change in reaction entropy

As long as the reaction takes place, this results in either an increase (exothermal reaction) or decrease (endothermal reaction) in the temperature of the sample solution. For a simple reaction this means that the increase or reduction in temperature depends on the converted amount of substance.

The result is that in a thermometric titration a change in temperature can only be observed as long as the added titrant reacts with the analyte in the sample solution.



Schematic of a thermometric titration curve.

Advantages of thermometric titration

- Proven method
- Problem solver for difficult samples that cannot be titrated potentiometrically
- Rapid results
- No sensor calibration required
- Maintenance-free sensor
- Robust method for routine work
- Well suited for aggressive media
- One sensor for all applications
- No membrane or diaphragm problems

Titrotherm

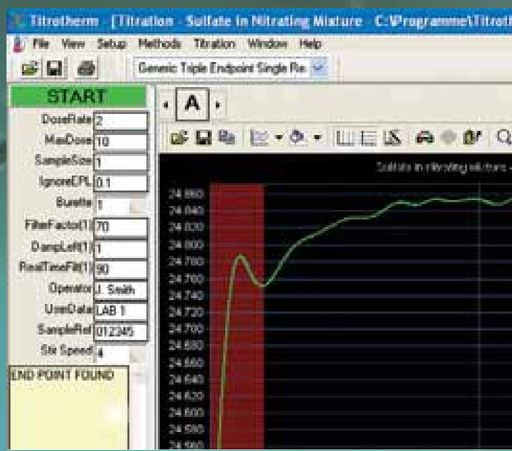
859 Titrotherm –
can you feel the heat?

The 859 Titrotherm combines innovative sensor technology with Metrohm's titration know-how.

859 Titrotherm – most modern USB technology
The 859 Titrotherm's easy operation becomes apparent even during installation. Thanks to advanced USB technology the instrument is recognized when it is connected to the PC and does not have to be manually configured. The same applies to the Dosing Units, stirrers and sensors connected to the 859 Titrotherm.

The software – everything at a glance, everything under control

The clearly laid out Titrotherm software allows adaptation of the screen view to the particular method parameters and thus provides rapid access to important commands or parameters. The endpoints are determined by calculating the first and second derivatives of the titration curve; by means of additional optimization parameters, the reproducibility can be improved even further. For report generation, the titration data can be exported manually or automatically into a freely arranged, method-specific report form.



Titrotherm

Semiconductor Acid Etch Mixture	
Titrant	NaOH
Analyte 1	HNO_3
Analyte 2	HOAc
Analyte 3	H_3PO_4
FW Analyte 1	63.013
FW Analyte 2	60.052
FW Analyte 3	97.995

Titration date	Time Sampled	Sample I.D.	Sample Size, g	Titrant mol/L	Titration blank, mL	Titer, Endpoint #1 mL	Titer, Endpoint #2 mL	Titer, Endpoint #3 mL	HNO_3 % w/v	HOAc% w/v	H_3PO_4% w/v
08.02.2006 11:09	5mL/min	filter=80	2.5000	1.0000	0.025	2.182	4.908	6.717	0.88	2.21	7.09
08.02.2006 11:13	5mL/min	filter=80	2.5000	1.0000	0.025	2.218	4.918	6.717	1.00	2.17	7.05
08.02.2006 14:30	5mL/min	filter=80	2.5000	1.0000	0.025	2.210	4.902	6.683	1.02	2.19	6.98
08.02.2006 15:03	5mL/min	filter=80	2.5000	1.0000	0.025	2.218	4.923	6.723	0.99	2.17	7.06
08.02.2006 16:20	5mL/min	filter=80	2.5000	1.0000	0.025	2.232	4.938	6.725	1.06	2.21	7.00
08.02.2006 17:06	5mL/min	filter=80	2.5000	1.0000	0.025	2.248	4.977	6.782	1.05	2.22	7.08
							Mean value		1.00	2.19	7.04
							Std. dev		0.07	0.02	0.04
							rel. Std. dev [%]		6.59	0.96	0.58

Thermoprobe – quick, precise and robust

Thermoprobe, a temperature sensor based on semiconductor technology (thermistor), has a response time of 0.3 s and a resolution of 10^{-5} K. This makes the Thermoprobe the ideal sensor for thermometric titration, as it can follow any change in temperature quickly and accurately.

The housing made of polypropylene (PP) and epoxy resin provides the sensor with outstanding resistance to many organic solvents and aggressive media.

Dosino technology – precise and simple dosing

Metrohm's Dosino technology has defined a new standard for volumetric titration. The Dosing Unit with its drive motor is mounted on the reagent bottle and thus guarantees maximum precision with minimum space requirements. The titrator and two burets require hardly more bench space than a sheet of DIN A5 paper.

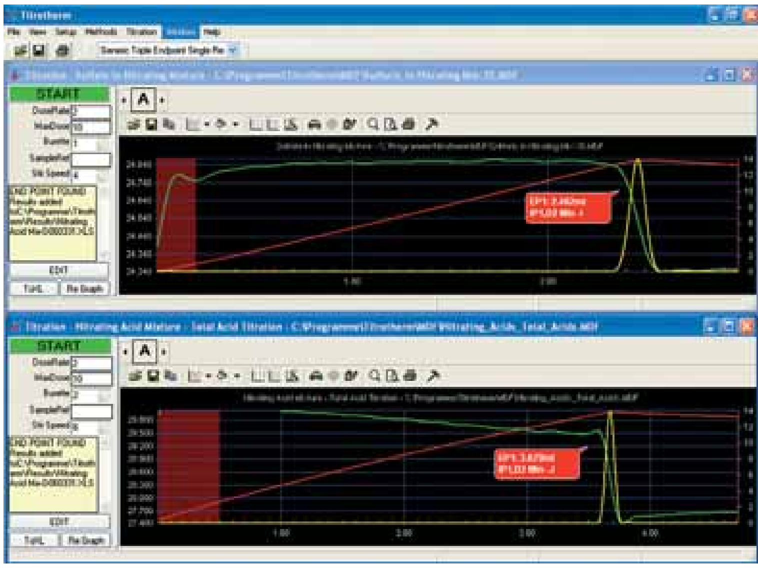
Scope of thermometric titration

Thermometric titration is a very versatile determination method and an ideal complement to potentiometric titration. In principle it is suitable for any reaction that produces a sufficiently large temperature change in the sample solution. It is particularly suitable for applications

- for which no suitable potentiometric sensor is available
- for which no suitable reference electrode is available
- in which the sample affects the indicator electrode or destroys it
- for which no solvent is available that is suitable for potentiometry

Typical applications for thermometric titration:

Analyte	Matrix	Titrant
Sulfate	Phosphate-containing solutions	Ba^{2+}
Phosphate	Buffer pH 10 (NH_3/NH_4Cl)	Mg^{2+}
Nickel	Ore leachates	Dimethylglyoxime
Acid mixtures	Electroplating baths (containing HF)	NaOH



Application example 1:
Determination of sulfate and total acid in a nitrating acid mixture (nitric acid/sulfuric acid)

This application demonstrates the flexibility of thermometric titration. By performing two sequential titrations («chained titrations») and using just one sensor, the contents of sulfuric and nitric acid can be rapidly determined. The first titration determines the sulfate content by a precipitation titration with barium chloride, the second titration the total acid content with NaOH. From these two results, the ratio of the two acid contents is calculated.

Reagents:
Titrant 1: c($BaCl_2$) = 1 mol/L (sulfate determination)
Titrant 2: c(NaOH) = 1 mol/L (total acid)
Solvent: deionized water
Titration rate: 2 mL/min

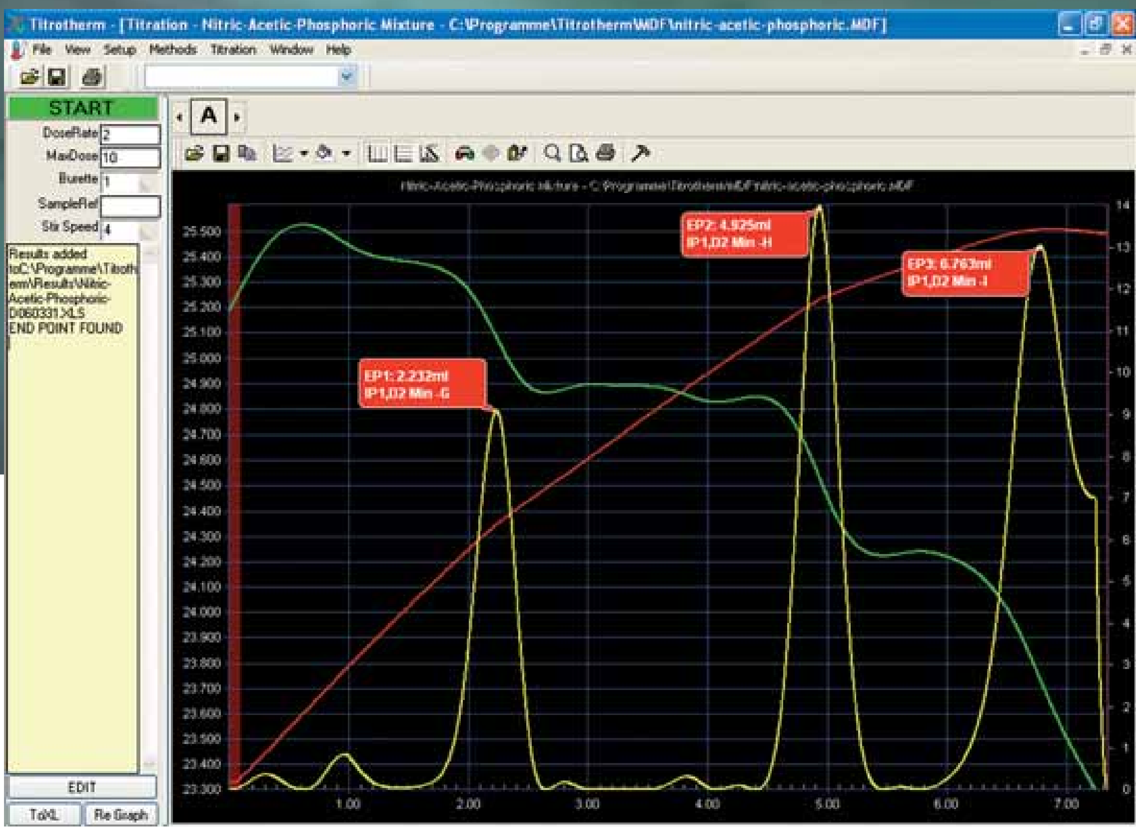
Procedure:
Transfer 40 mL deionized water into the titration vessel, add 2.5 mL nitrating acid mixture and titrate first with c($BaCl_2$) = 1 mol/L and then with c(NaOH) = 1 mol/L.

Application example 2:
Analysis of an acid mixture comprising acetic, nitric and phosphoric acid

This acid mixture used in the semiconductor industry can only be analyzed if the third endpoint – which is entirely due to the third proton of the phosphoric acid – can be unequivocally determined. Using a normal pH electrode in aqueous solution this would be impossible as the electrochemical dissociation potential is too low. Thermometric titration, however, allows the determination of the third endpoint very easily – and above all very rapidly. The individual acid concentrations can then be calculated from the separations between the endpoints.

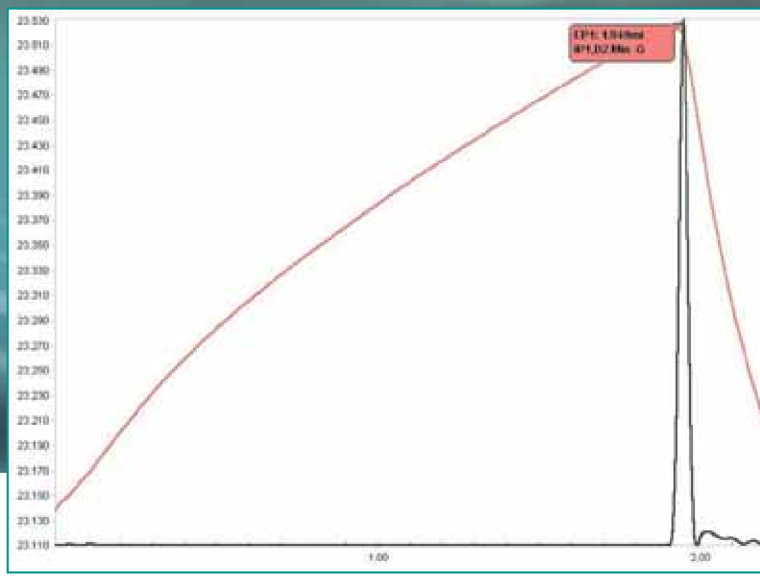
Reagents
Titrant: c(NaOH) = 1 mol/L
Solvent: deionized water
Titration rate: 2 mL/min

Procedure
Transfer 40 mL deionized water into the titration vessel, add 2.5 mL acid mixture and titrate with c(NaOH) = 1 mol/L.

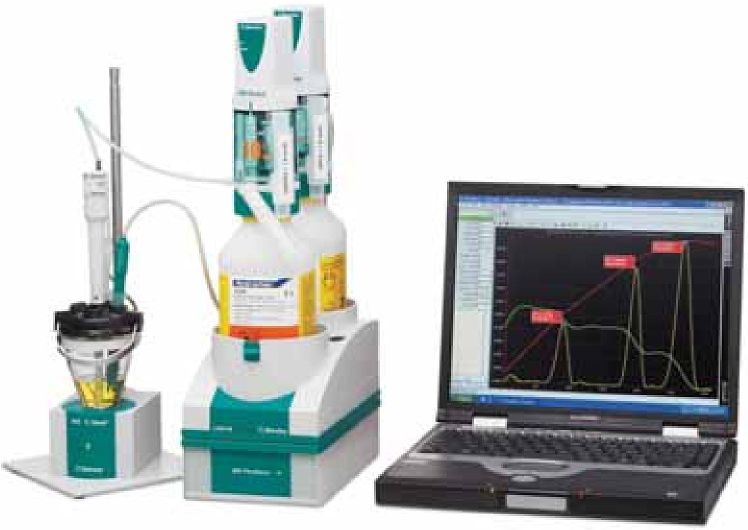


Catalytically enhanced thermometric titration

At very low sample concentrations or with low molar reaction enthalpies, the temperature change during the reaction is often inadequate for the reliable determination of the endpoint. With a clever trick it is possible to obtain a proper «jump» in such reactions. An example is the determination of very small amounts of organic acids with the titrant c(KOH) = 0.1 mol/L in isopropanol: In this case the addition of a small amount of paraformaldehyde makes it easier to detect the endpoint, for as soon as the endpoint is reached (i.e. as soon as excess hydroxide ions are present) the base-catalyzed hydrolysis of the paraformaldehyde starts. This strongly endothermal reaction now provides a well-marked endpoint.



Catalytically enhanced thermometric titration: after the endpoint has been reached, the excess hydroxide ions catalyze the endothermal hydrolysis of the added paraformaldehyde.



Ordering information

	859 Titrotherm
2.136.0010	USB-enabled thermometric titrator with two measuring inputs for Thermoprobe (an adapter allows to connect a combined pH glass electrode). Four MSB connections for 800 Dosinos and stirrer.
	Including:
6.9011.020	Thermoprobe
6.9011.030	Adapter for combined pH or metal electrodes with plug F
6.2151.000	Cable USB A – mini-DIN 8 pins
A.712.0001	859 Titrotherm CD-ROM Rel. 1
	Optional accessories:
2.800.0010	Dosino
2.804.0010	804 Titration stand without stand rod
2.802.0010	Rod stirrer
6.3032.220	Dosing Unit 20 mL
6.2026.010	Stand rod with base plate
6.2013.010	Clamping ring
6.2021.020	Electrode holder
	System requirements for Titrotherm software:
Processor	Pentium 4; clock frequency 1 GHz
RAM	512 MB
Free hard-disk memory	150 MB for program
Operating system	Windows® 2000 SP1, Windows® XP Professional
Connections	free USB connection

Metrohm
Ion analysis

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

Subject to modifications
Layout by Ecknauer+Schoch ASW, printed in Switzerland by Metrohm Ltd., Herisau
8.859.6003 – 2007-01