859 Titrotherm

Thermometric titration – the ideal complement to potentiometric titration

Metrohm

What is 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 titrimetric applications. 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.

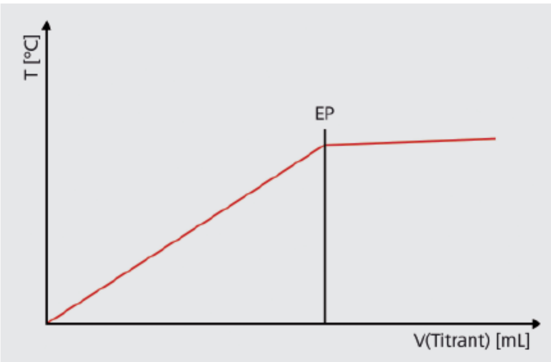
However, the electrochemical potential is only one of the possible ways of following a chemical reaction. A far more universal parameter is the reaction enthalpy.

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 (exothermic reaction) or decrease (endothermic 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.

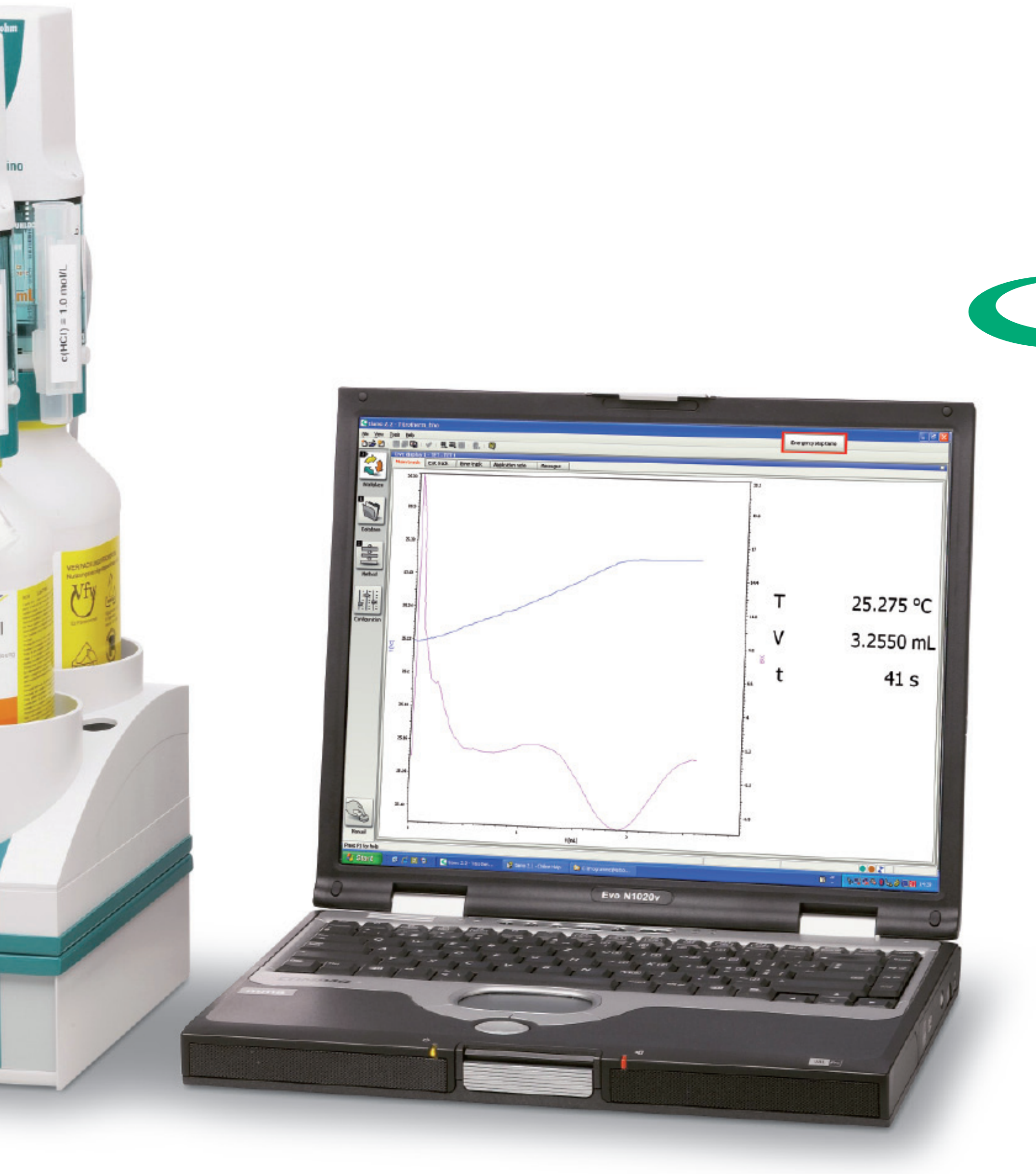
The result is that in a thermometric titration a change in temperature can only be observed as long as the added titrant reacts with the analyte in the sample solution.



Schematic of a thermometric titration curve.

Advantages of thermometric titration

- Proven method
- Easy learning and easy carrying-out of thermometric titration through incorporation of the method in the ***tiamo***™ titration software
- 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



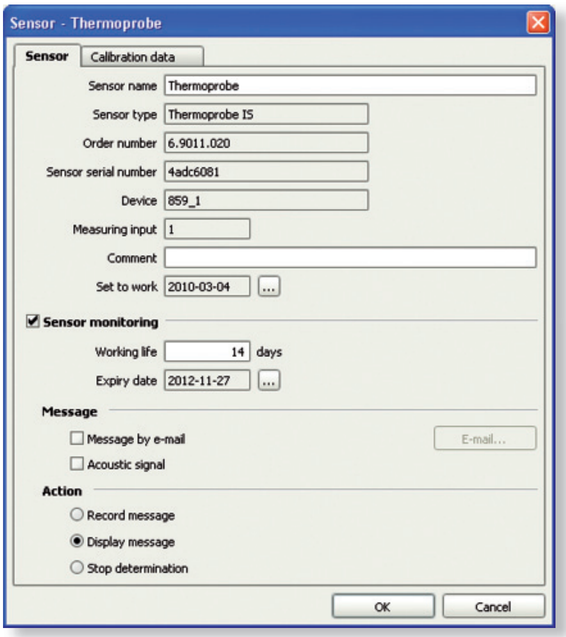
tiamo™ titration and more

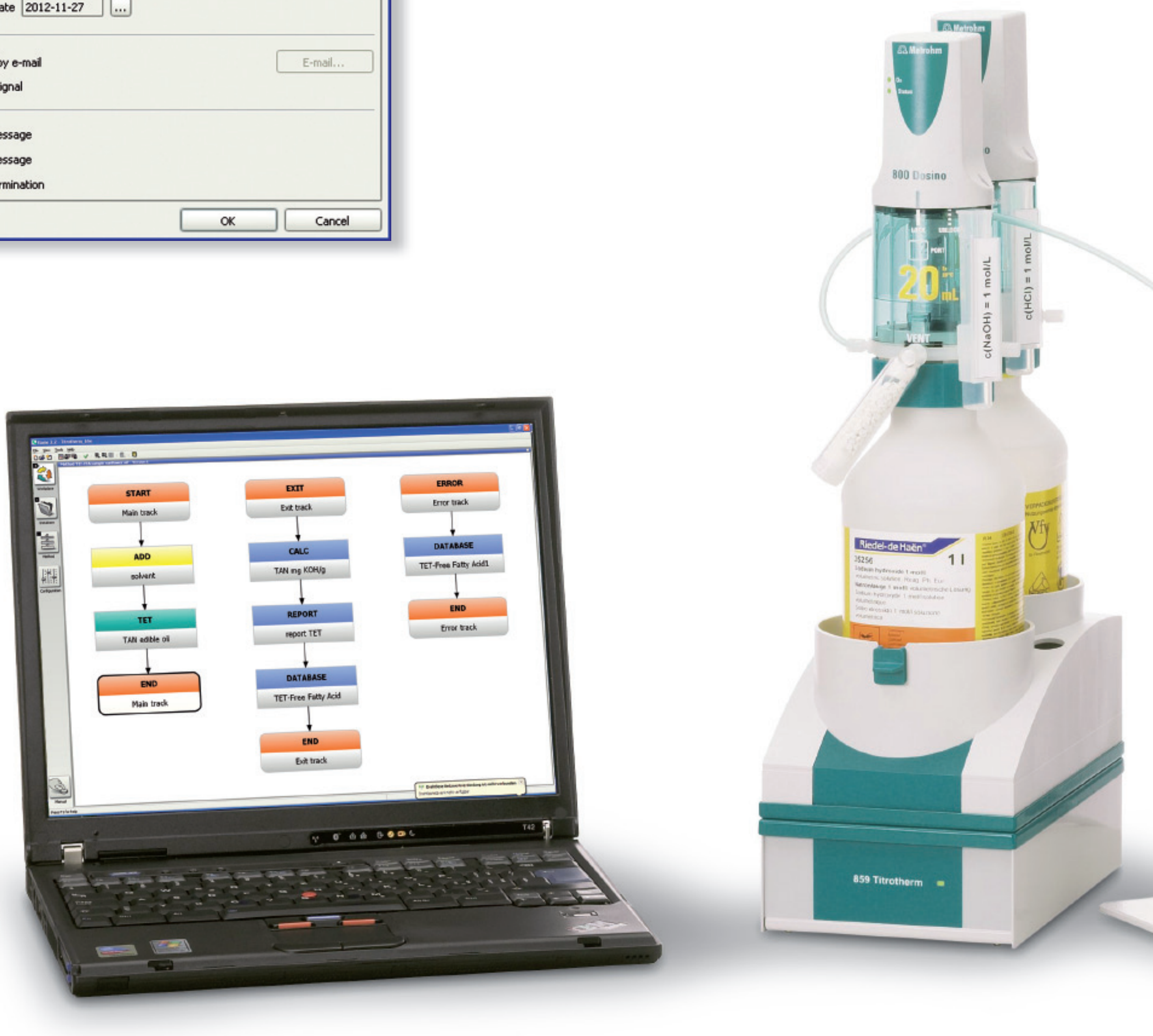
Titrotherm 859 – can you feel the heat?

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

859 Titrotherm – latest USB technology for perfect ease of use

The 859 Titrotherm's easy operation becomes apparent even during installation. Thanks to advanced USB technology the instrument is recognized automatically by the ***tiamo***™ titration software 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 Titrotherm.

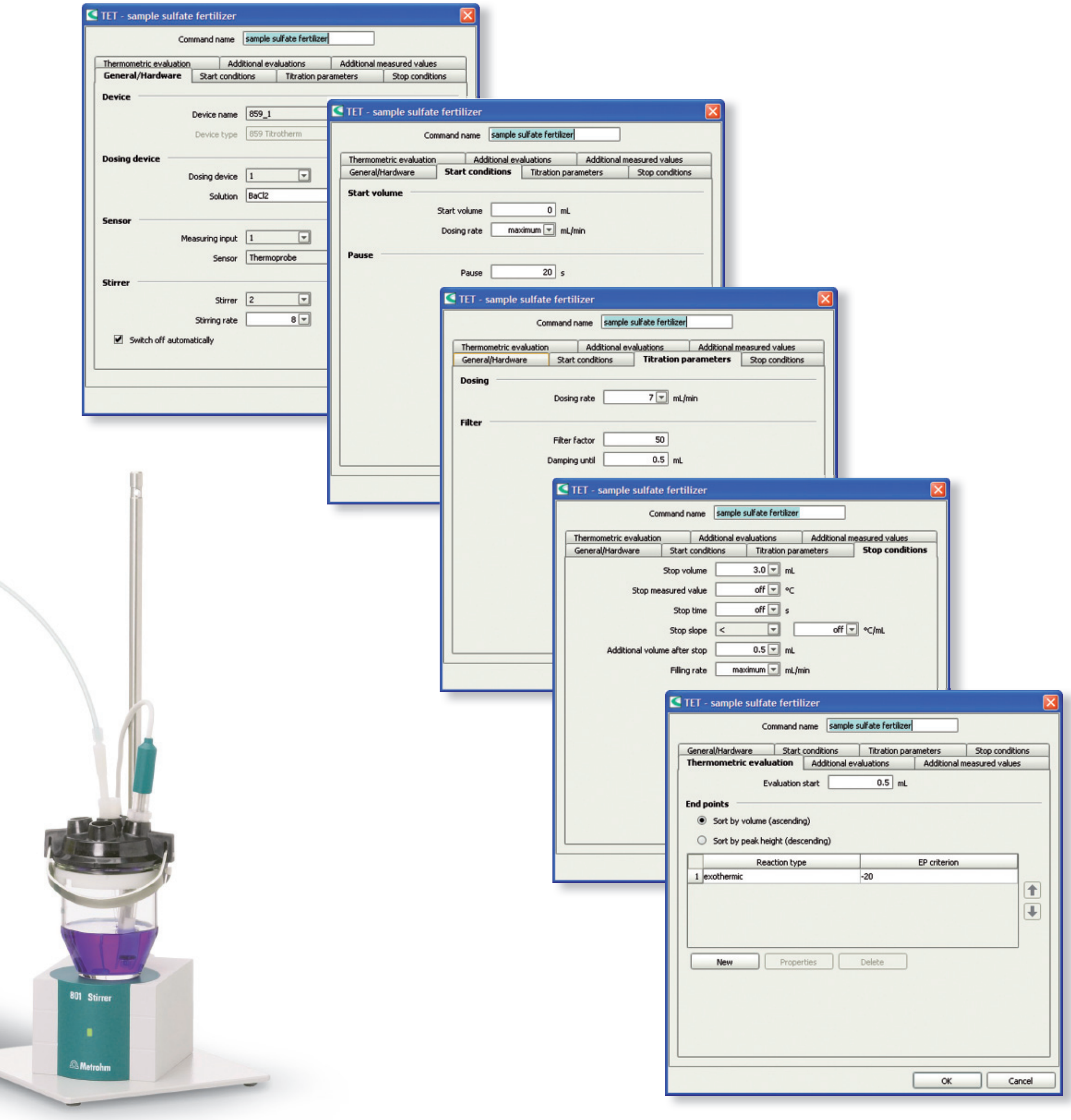




tiamo™ – everything at a glance, everything under control

The universal, clearly laid-out ***tiamo***™ software allows the titration parameters to be adapted quickly to the particular method and thus provides rapid, effective method development and also fast and easy generation of results.

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 template.



Automation pays dividends!

Increasing sample numbers, time-consuming sample preparation steps and unattended overnight operation are good reasons for using sample changers. The 859 Titrotherm comes with the necessary intelligence to control sample processors. Together with the 814 USB Sample Processor and 815 Robotic USB Sample Processor XL, the 859 Titrotherm offers a high degree of automation at low investment costs.

It's amazing: You simply connect the sample changer to the Titrotherm's USB port and the world of automation opens up to you.

Thermoprobe – quick, precise and robust

Thermoprobe, a temperature sensor based on semiconductor technology (thermistor), has a response time of only 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 glass 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
Sodium	Salts, process solutions, foodstuffs	$Al(NO_3)_3$ / KNO_3-solution
FFA (free fatty acids)	Edible oils and edible fats	KOH in isopropanol (2-propanol)
TAN (Total Acid Number)	Mineral oil products, edible oils, biodiesel	KOH in isopropanol (2-propanol)
Caustic, aluminum, carbonate	Bayer Liquor (aluminum production)	HCl, $KNaC_4H_4O_6 \cdot 4H_2O$, KF
Acid mixtures (HF, H_2SO_4, HNO_3 ...)	Electroplating baths (containing HF)	NaOH

An overview of other applications can be found at **www.titrotherm.com**

Application example 1:

Direct determination of sodium in foodstuffs, using ketchup as an example

Because direct determination of sodium by means of atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectroscopy (ICP-MS) is a very expensive and time-consuming process, also requiring a large amount of investment in the infrastructure, the method frequently adopted is indirect determination by way of quantitative analysis of chloride. However, this can lead to very inaccurate results, since the sodium in foodstuffs can also be present in the form of sodium benzoate or monosodium glutamate. The chloride can also be present in large quantities as potassium iodide, so a molar 1:1 ratio of chloride ions to sodium ions cannot be assumed.

This application shows how sodium can be determined directly, at relatively low cost in terms of time and money, using thermometric titration. Here, the homogenized sample is titrated thermometrically in the presence of ammonium hydrogen difluoride at ~pH 3 with a standardized, aluminum-containing solution, which contains a stoichiometric excess of potassium ions. This produces an exothermic reaction with the formation of insoluble NaK_2AlF_6 (elpasolite):

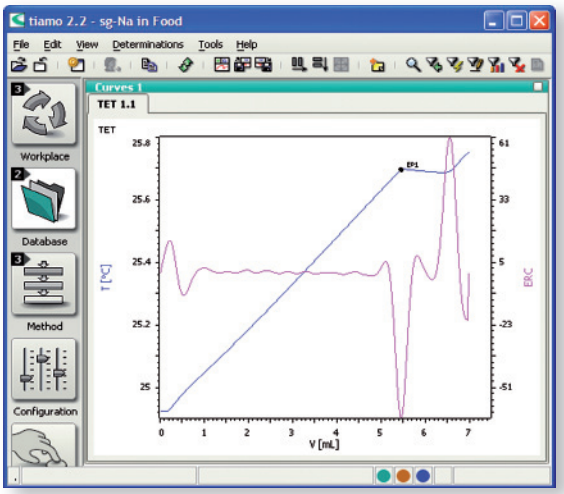
$$Al^{3+} + Na^{+} + 2K^{+} + 6F^{-} \longleftrightarrow NaK_2AlF_6 \downarrow$$

Reagents:

Titrant: mixture of 0.5 mol/L $Al(NO_3)_3$,
1.1 mol/L KNO_3 solution
Complexing reagent: 300 g/L $NH_4F \cdot HF$

Procedure:

Add 5 mL complexing reagent ($NH_4F \cdot HF$ solution) to 5 - 10 g ketchup (depending on sodium content), make up to 35 - 40 mL with deionized water, stir for approx. 60 seconds, and then titrate thermometrically to the EP.



Application example 2:

Analysis of an acid mixture comprising phosphoric acid and nitric acid

This acid mixture from the production process for artificial fertilizers 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.

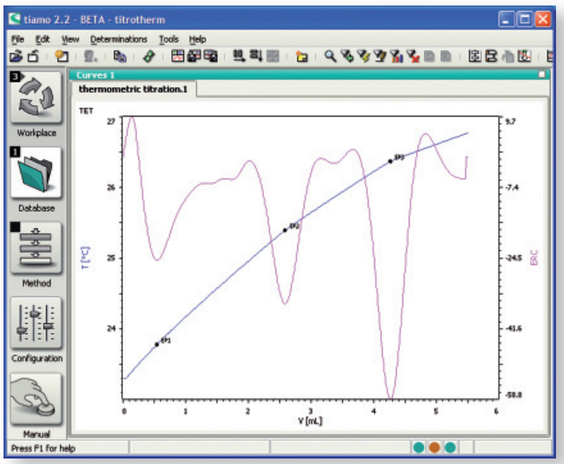
Thermometric titration, in contrast, allows the determination of the third endpoint very easily – and above all very rapidly. The individual acid concentrations can then be calculated from the separations between the endpoints.

Reagents:

Titrant: c(NaOH) = 2 mol/L
Solvent/conditioning solution: 180 g/L NaCl solution
(to hydrolyze the hexafluorosilicic acid)
Titration rate: 5 mL/min

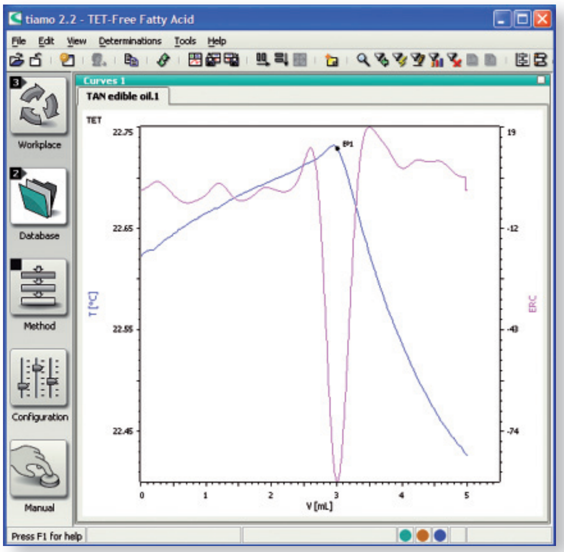
Application:

Measure 0.7 mL (about 1 g) of the acid mixture from the fertilizer production process exactly into a clean, dry titration vessel. Add 30 mL of the 180 g/L NaCl solution and allow to stand for about 30 min, so the whole of the hexafluorosilicic acid contained in it is hydrolyzed. Titrate with c(NaOH) = 2 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 endothermic reaction now provides a well marked endpoint.



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

Ordering information

	Titrotherm 859
2.859.1010	USB-enabled thermometric titrator with two measuring inputs for Thermoprobe. Four MSB connections for 800 Dosinos and stirrer.
	Including
6.9011.020	Thermoprobe
2.800.0010	Dosino
2.802.0010	Rod stirrer
2.804.0010	804 Titration stand without stand rod
6.3032.210	Dosing Unit 10 mL
6.2151.000	Cable USB A – mini-DIN 8 pins
6.1414.010	Titration vessel lid SGJ
6.1415.210	Titration vessel 10 - 90 mL
6.2026.010	Stand rod with base plate
6.2013.010	Clamping ring
6.2021.020	Electrode holder
6.6056.231	***tiamo***™ 2.3 light CD: 1 license
	Optional accessories
6.9011.040	HF-resistant Thermoprobe
6.2061.010	Bottle holder for 800 Dosino
6.2065.000	Rack for 846 Dosing Interface
6.1450.210	PFA titration vessel 10 - 90 mL
6.3032.120	Dosing Unit 2 mL
6.3032.150	Dosing Unit 5 mL
6.3032.220	Dosing Unit 20 mL
6.3032.250	Dosing Unit 50 mL

System requirements for titration software *tiamo*™ 2.3 or higher

Processor	Pentium 4; clock frequency 1 GHz
RAM	1 GB (Windows™ 2000 / Windows™ XP) 2 GB (Windows™ Vista)
Free hard disk memory	Program: 500 MB Data: 2 GB (for approx. 5’000 determinations)
Operating system	Windows™ 2000 SP4 Windows™ XP Professional SP2 Windows™ Vista Windows™ 7
Connections	free USB connection

www.metrohm.com

Subject to modifications
Layout by Ecknauer+Schoch ASW, printed in Switzerland by Metrohm Ltd., CH-9100 Herisau
8.859.5004EN – 2012-07

Metrohm