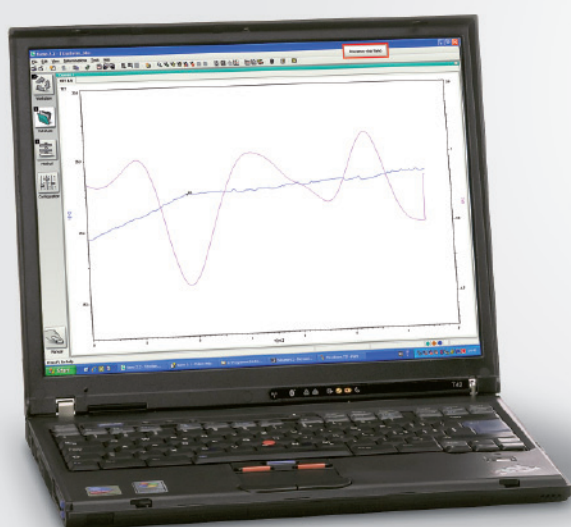


# 859 Titrotherm

**tiamo**<sup>™</sup>  
titration and more



Thermometric titration – the ideal complement to potentiometric titration

## What is thermometric titration?

02

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 ( $\Delta H$ ). The following equation applies.

$\Delta H = \Delta G + T\Delta S$ , where

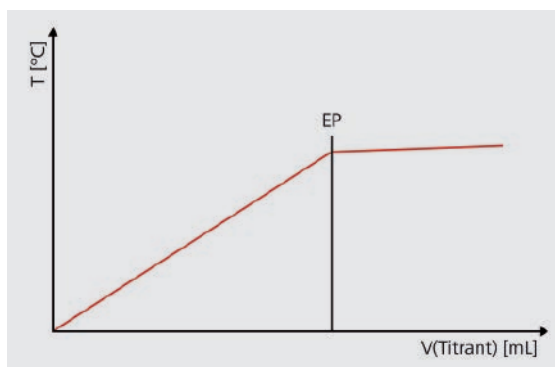
$\Delta G$  = change in free reaction energy

$T$  = absolute temperature

$\Delta S$  = 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.

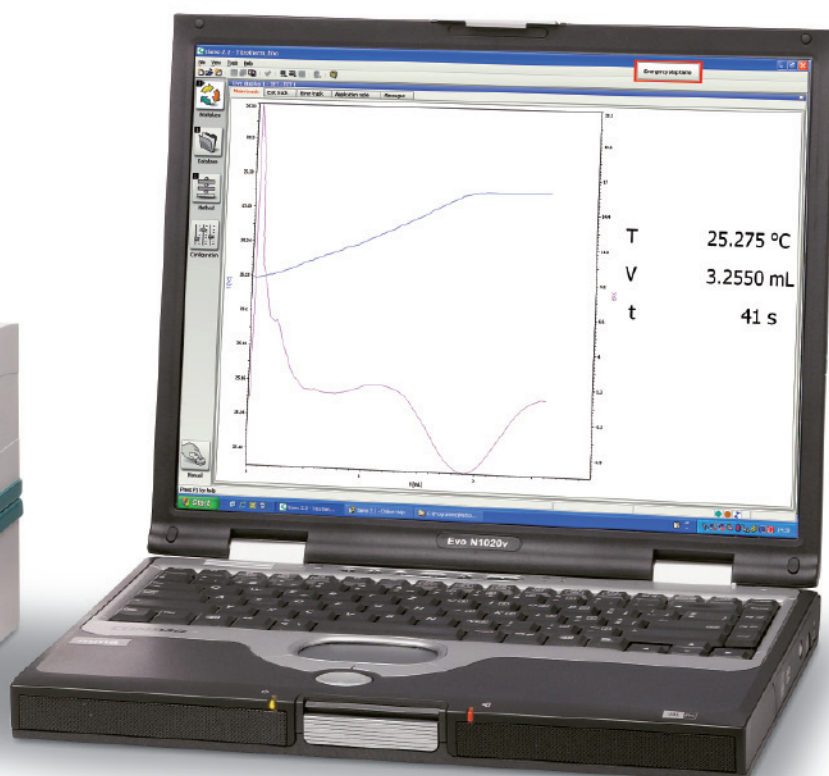


## Advantages of thermometric titration

03

- Proven method
- Easy learning and easy carrying-out of thermometric titration through incorporation of the method in the **tiamo**<sup>TM</sup> 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**<sup>TM</sup>  
titration and more



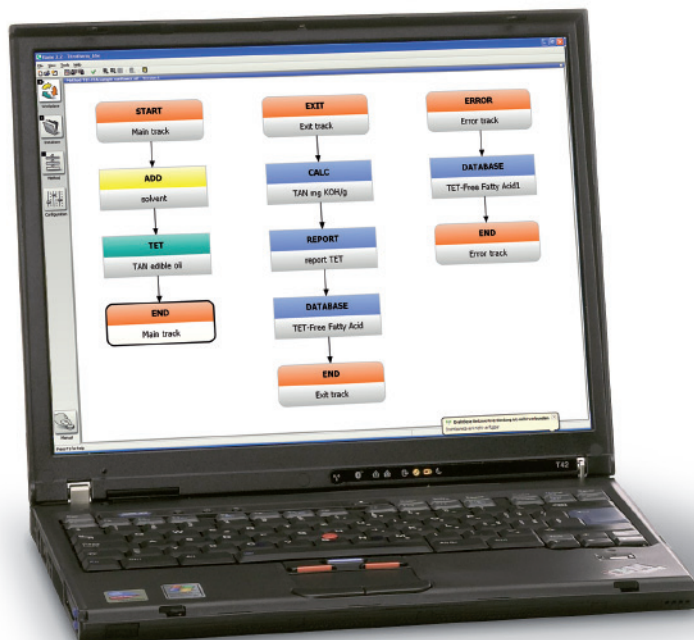
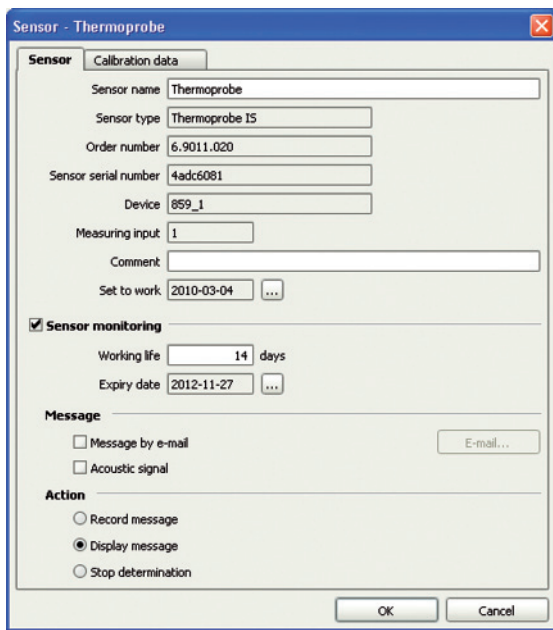
# Titrotherm 859 – can you feel the heat?

04

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*<sup>TM</sup> – everything at a glance, everything under control

The universal, clearly laid-out *tiamo*<sup>TM</sup> 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.

05

The image displays the TET software interface for 'sample sulfate fertilizer' across five overlapping windows, each showing a different configuration tab:

- General/Hardware:** Device name: 859\_1, Device type: 859 Titrotherm, Dosing device: 1, Solution: BaCl2, Measuring input: 1, Sensor: Thermoprobe, Stirrer: 2, Stirring rate: 8, Switch off automatically:
- Start conditions:** Start volume: 0 mL, Dosing rate: maximum mL/min, Pause: 20 s
- Titration parameters:** Dosing rate: 7 mL/min, Filter factor: 50, Damping until: 0.5 mL
- Stop conditions:** Stop volume: 3.0 mL, Stop measured value: off °C, Stop time: off s, Stop slope: < off °C/mL, Additional volume after stop: 0.5 mL, Filling rate: maximum mL/min
- Thermometric evaluation:** Evaluation start: 0.5 mL, End points: Sort by volume (ascending) selected, Table with 1 exothermic reaction and EP criterion -20.

| Reaction type | EP criterion |
|---------------|--------------|
| 1 exothermic  | -20          |

**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.



07

## 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 <sub>3</sub> ) <sub>3</sub> / KNO <sub>3</sub> -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 <sub>2</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O, KF |
| Acid mixtures (HF, H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> ...) | Electroplating baths (containing HF)         | NaOH  |

An overview of other applications can be found at [www.titrotherm.com](http://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.

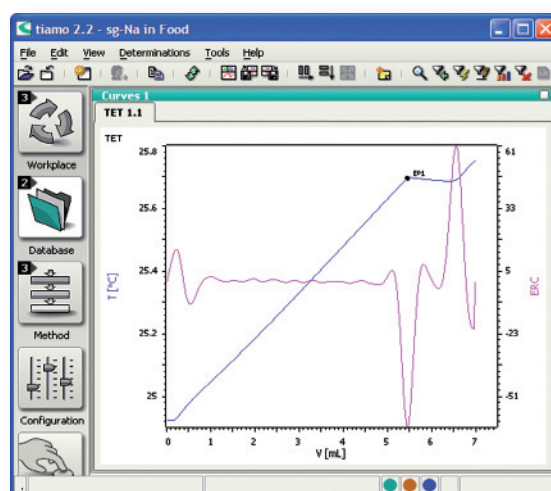
This application shows how sodium can be determined directly, at relatively low cost in terms of time and money, using thermometric titration. Here, the homogenized sample is titrated thermometrically in the presence of ammonium hydrogen difluoride at  $\sim$ pH 3 with a standardized, aluminum-containing solution, which contains a stoichiometric excess of potassium ions. This produces an exothermic reaction with the formation of insoluble  $\text{NaK}_2\text{AlF}_6$  (elpasolite):

**Reagents:**

Titratant: mixture of 0.5 mol/L  $\text{Al}(\text{NO}_3)_3$ ,  
1.1 mol/L  $\text{KNO}_3$  solution  
Complexing reagent: 300 g/L  $\text{NH}_4\text{F}\cdot\text{HF}$

**Procedure:**

Add 5 mL complexing reagent ( $\text{NH}_4\text{F}\cdot\text{HF}$  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.

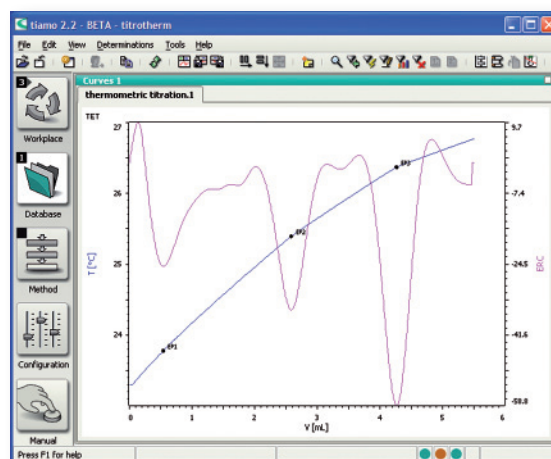
Thermometric titration, in contrast, allows the determination of the third endpoint very easily – and above all very rapidly. The individual acid concentrations can then be calculated from the separations between the endpoints.

**Reagents:**

Titratant:  $c(\text{NaOH}) = 2$  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  $c(\text{NaOH}) = 2$  mol/L.

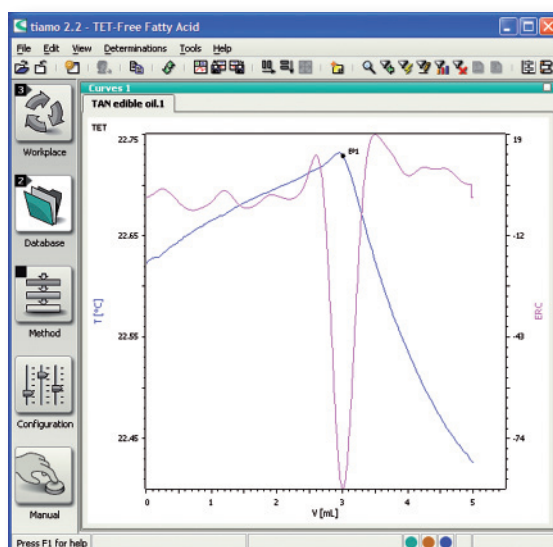




## Catalytically enhanced thermometric titration

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  $c(\text{KOH}) = 0.1 \text{ mol/L}$  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

**2.859.1010 Titrotherm 859** 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     Program: 500 MB  
memory            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](http://www.metrohm.com)