# Thermometric Titration with OMNIS – fast, simple, and reliable

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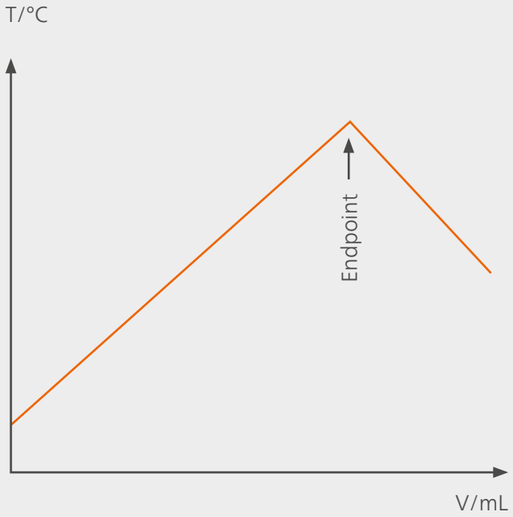
Metrohm

# What is thermometric titration?

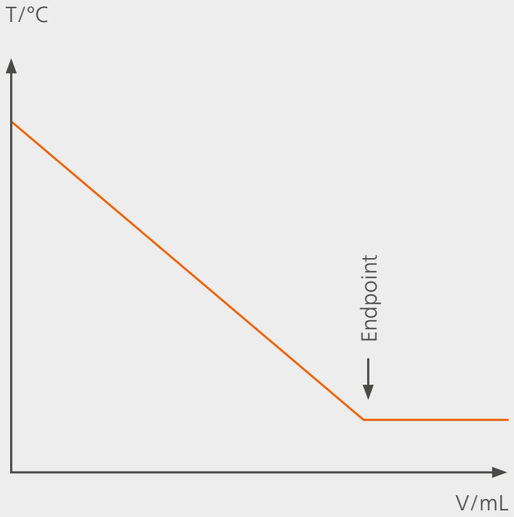
Titration is one of the oldest and most common chemical analysis techniques in the world. However, a suitable potentiometric sensor is not always available for every application challenge. Fortunately, observing the changes in the potential of these sensors is not the only way to follow a chemical reaction. Another option is monitoring the reaction enthalpy, i.e. thermometric titration. In fact, every chemical reaction is accompanied by a change in enthalpy (ΔH):

ΔH = ΔG + TΔS, where
ΔG = change in free reaction energy
T = absolute temperature
ΔS = change in reaction entropy

As the chemical reaction takes place, either an increase (exothermic reaction) or decrease (endothermic reaction) can be registered in the sample solution. This increase or decrease of the temperature is related to the converted amount of sample. In summary, this means that in thermometric titration a change in the temperature is observed as long as the added titrant reacts with the analyte in the sample solution.




Exothermic titration




Endothermic titration



**WHY THERMOMETRIC TITRATION?**

- A problem solver for difficult samples that cannot be titrated potentiometrically
- Fast – results within a minute
- No additional hardware needed – thermometric titration is available in OMNIS
- Robust method for high-throughput routine analysis
- Well suited for aggressive media
- One sensor for all applications
- No sensor calibration needed
- Maintenance-free sensor (no diaphragm, no membrane, no electrolyte)

# Application overview TET

**Thermometric titration is a highly versatile technique. In principle any chemical reaction with a sufficiently large temperature change can be monitored.**

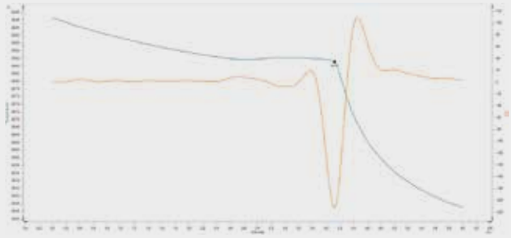
| Analyte | Matrix | Titrant |
|---|---|---|
| Total acid number (TAN) | Mineral oils, biodiesel, edible oils… | KOH in isopropanol |
| Total base number (TBN) | Mineral oils, biodiesel, edible oils… | $HClO_4$ in acetic acid |
| Acid mixtures (HF, $HNO_3$, $H_2SO_4$…) | Electroplating baths | NaOH |
| Phosphate | Liquid/solid NPK fertilizer | $Mg(NO_3)_2$ |
| Sulfate | Liquid/solid NPK fertilizer | $BaCl_2$ |
| Sodium | Salts, foodstuff | $Al(NO_3)_3$ / $KNO_3$ solutions |
| Magnesium & Calcium | Milk | $Na_4EDTA$ |

# Application examples

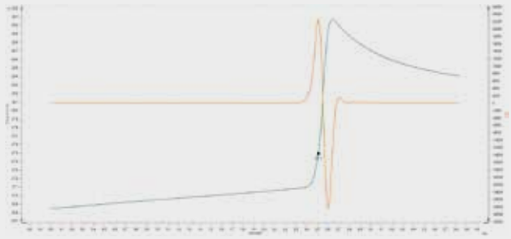
## CATALYTICALLY ENHANCED THERMOMETRIC TITRATION FOR DETERMINATION OF ACID NUMBER (AS PER ASTM D8045)

ASTM D8045 describes the simple, fast, and robust determination of total acid number (TAN) by thermometric titration in petroleum prodcuts. The chemical reaction is catalytically enhanced with paraformaldehyde to obtain a pronounced change of the temperature of the sample solution. Catalytic enhancement is needed, if the target analyte is present in the sample in only low concentrations or if the chemical reaction is characterized by a low enthalpy. The same principle can be applied for the determination of total base number (TBN) where isobutyl-vinyl-ether is used as catalyst.

The same method as for TAN can also be used to determine free fatty acids in edible oils, which then allows conclusions to be drawn on the oxidation stability/quality of the oil or fat.



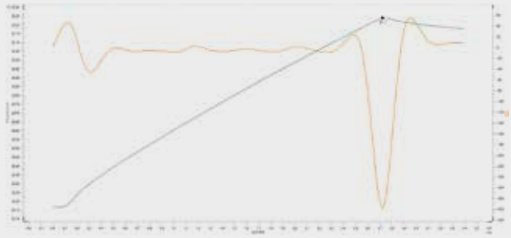
Titration curve of TAN analysis by thermometric titration



Titration curve of TBN analysis by thermometric titration

## ANALYSIS OF FERTILIZERS

In liquid or solid fertilizers, the phosphate or sulfate content can be analyzed fast by thermometric titration. Traditionally, these parameters have been determined gravimetrically, which is a rather time consuming and complex procedure. Both, phosphate and sulfate, are determined in a precipitation titration with magnesium and barium, respectively.



Titration curve of phosphate analysis by thermometric titration



## ANALYSIS OF ELECTROPLATING BATHS

Electroplating baths are complex matrices and often contain mixtures of several acids. When used in such environments, potentiometric sensors need careful cleaning and maintenance.

As the sensor for thermometric titration is highly robust and maintenance-free, this method is ideal for measuring such matrices. Moreover, with thermometric titration, it is easier to determine the third endpoint of phosphoric acid. In potentiometric titration this is only possible upon addition of sodium chloride, while with thermometric titration the third endpoint is visible without spiking the sample.

## SODIUM DETERMINATION

Sodium is present in many different foodstuffs such as potato chips, (soy) milk, instant noodles, cheese, and many more. Often it is present as sodium chloride, i.e., plain table salt.

Excessive consumption of sodium chloride is known to be detrimental to human health, which is why the world health organization (WHO) recommends a limit of no more than 5 grams table salt per day. With thermometric titration you can determine the sodium content (and therefore also the salt content) in your sample reliably and accurately in less than three minutes.

# Thermometric titration and the OMNIS Titrator

## THE OMNIS THERMOMETRIC TITRATOR

With the «Functional license Thermometric Titrator», the OMNIS Titrator becomes a dedicated instrument for thermometric titration. It also includes pH and temperature measurement to support further routine laboratory measurements. For maximum stirring efficiency and precise titrations, a rod stirrer is recommended.

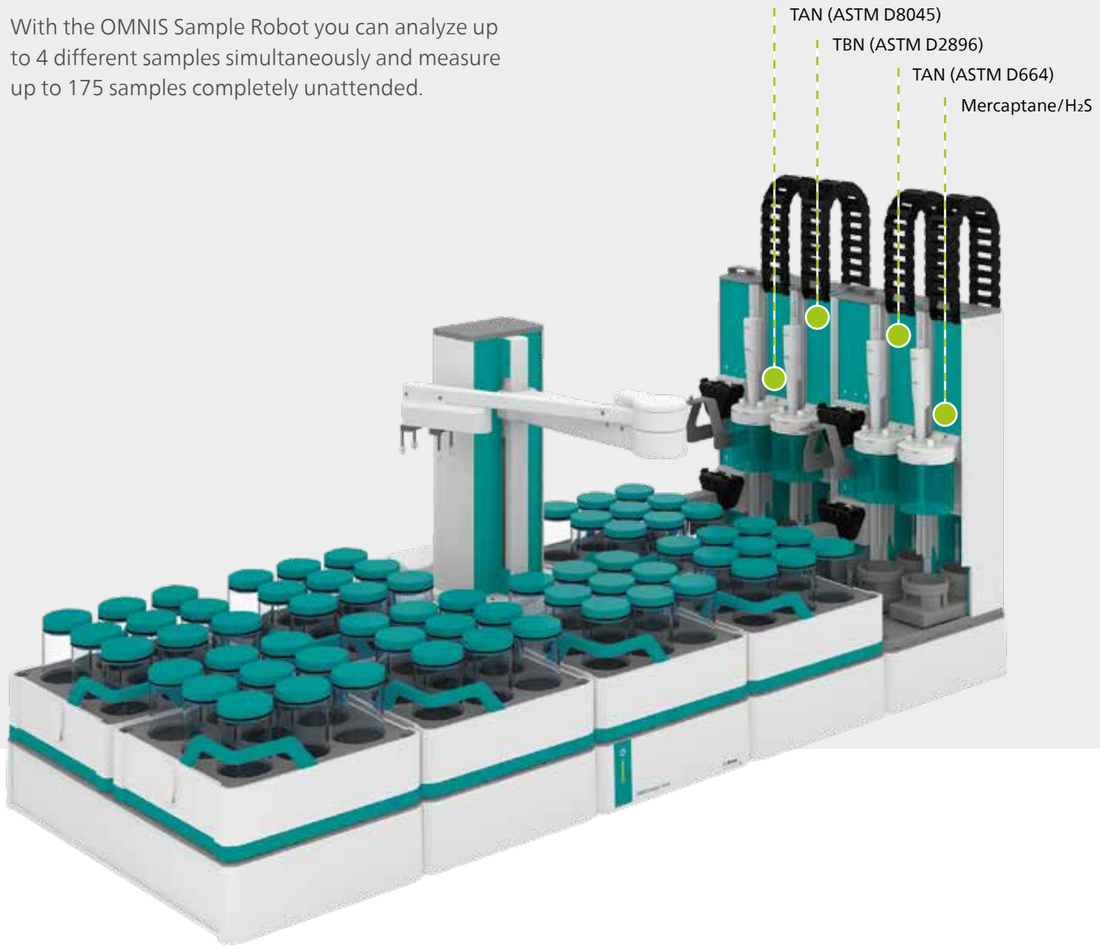
## MODULARITY AND SCALEABILITY

Expand your stand-alone OMNIS Titrator with up to four additional OMNIS Dosing Modules or OMNIS Titration Modules and you can perform up to five applications in parallel.

You can consolidate all your potentiometric and thermometric standard titration applications, e.g., for petrochemical analysis, on one fully automated OMNIS titration system.

## HIGHER SAMPLE THROUGHPUT NEEDED?

With the OMNIS Sample Robot you can analyze up to 4 different samples simultaneously and measure up to 175 samples completely unattended.




## ROBUST YET HIGHLY SENSITIVE – THE DIGITAL THERMOPROBE

The heart of thermometric titration is clearly the sensor – the digital Thermoprobe. The dThermoprobe includes a highly sensitive thermistor, which measures the enthalpy changes during the titration reactions. The dThermoprobe has a short response time of just 0.3 seconds and a high resolution of $10^{-5}$ K which makes it highly suited for thermometric titration.

The dThermoprobe is available in two versions: dThermopobe which is suitable for (non)-aqueous titrations and the dThermoprobe HF, which tolerates aqueous solutions containing HF.

## ORDERING INFORMATION

| Instrument | |
|---|---|
| 2.1001.0020 | OMNIS Titrator with magnetic stirrer, without function license |
| 2.1002.0010 | OMNIS Titration Module without stirrer |
| 2.1002.0110 | OMNIS Titration Module with magnetic stirrer |
| 2.1003.0110 | OMNIS Dosing Module with magnetic stirrer |
| 2.1006.0020 | OMNIS Rod Stirrer Titration |
| 6.02100.010 | Measuring module digital |
| 6.06001.130 | Function license TET<br>(for upgrading an existing OMNIS Titrator) |
| 6.06001.930 | Function license Thermometric Titrator<br>(dedicated OMNIS Titrator for thermometric titration) |
| 6.03001.120 | OMNIS 2 mL cylinder unit |
| 6.03001.150 | OMNIS 5 mL cylinder unit |
| 6.03001.210 | OMNIS 10 mL cylinder unit |
| 6.03001.220 | OMNIS 20 mL cyliner unit |
| 6.03001.250 | OMNIS 50 mL cylinder unit |
| 6.01117.300 | dThermoprobe |
| 6.01118.300 | dThermoprobe HF |
| 6.01405.000 | 5 x SGJ 14 titration vessel lid OMNIS |
| 6.01406.220 | 20 – 90 mL titration vessel |



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