

Thermometric Titration – The missing piece of the titration puzzle

M. Margreth¹, C. Haider¹, T. Smith²

Summary

Thermometric Titration is a very versatile titration method, because one sensor can be used for various kinds of applications. The temperature sensors (Thermoprobes) neither are specific to any ion type nor does their performance depend on the electrochemical properties of the sample solution. They require virtually no maintenance and can be used immediately without any conditioning.

Therefore Thermometric Titration can solve applications problems, potentiometry cannot or at least not with satisfying reproducibility:

- Free Fatty Acids (FFA) in edible oils or phosphate in fertilizers can be determined even at low levels with high reproducibility and without cross interference of other ions.
- Etching acids mixtures containing phosphoric acid can be titrated in aqueous media
- Two different analytes (e.g. sulfate and total acid) can be determined in two consecutive titrations without changing the sensor and sample solution.

In all cases the titration can be carried out without any special sample preparation and the results are usually obtained very fast.

Introduction

Each chemical reaction is associated with a change in enthalpy that causes a temperature change which, when plotted versus volume of titrant, can be used to monitor the course of the reaction and thus to detect the titration endpoint. For a simple reaction this means that the increase (exothermic reaction) or reduction (endothermic reaction) in temperature depends on the amount of substance converted.

In a thermometric titration, reagent solution (titrant) is added to the sample at a constant rate until the endpoint is reached. The latter can be recognized by a break in the titration curve obtained by plotting the amount of titrant added to the sample versus the temperature. The **second derivative (black)** of the **temperature curve (red)** yields the endpoint. Since the temperature sensor has a response time of 0.3 s and a resolution of 10^{-5} K, even small enthalpy changes are reliably monitored. The following applications demonstrate how versatile thermometric titration is.

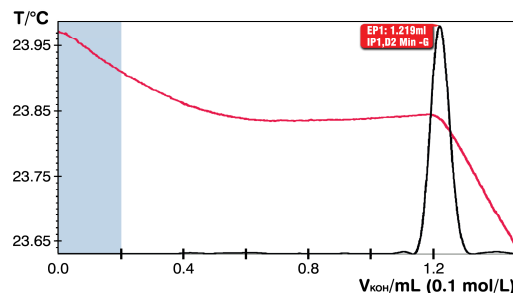
System setup



- 859 Titrotherm
- 800 Dosinos
- 804 Ti Stand and 802 Stirrer
- Laptop PC

Non-aqueous titration of free fatty acids (FFA) in olive oil

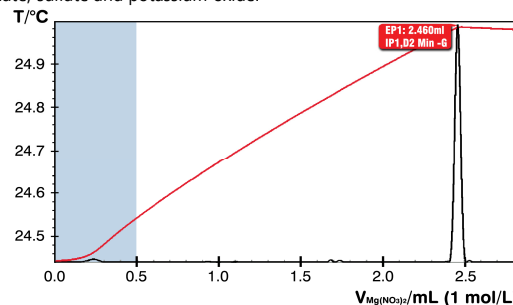
Unsuitable conditions of treatment and preservation of fats and olive oil favor the hydrolytic decomposition of triglycerides forming free fatty acids. The content of the latter – often only present in traces – is an important quality criterion and can be assessed by thermometric titration.



	FFA (%)
Mean value (N=10)	0.286
Standard deviation	0.002
Relative standard deviation	0.860

Determination of the phosphate content in liquid fertilizers

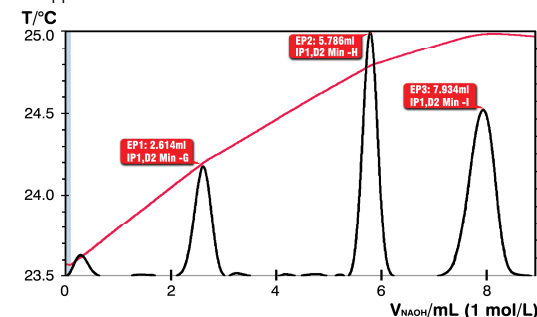
The most important constituents of liquid fertilizers are nitrogen, phosphorus, sulfur and potassium. In liquid fertilizers these constituents are given as nitrate, phosphate, sulfate and potassium oxide.



	Phosphorus content (%)
Mean value (N=10)	0.830
Standard deviation	0.004
Relative standard deviation	0.530

Determination of the phosphate content in acidic etching baths

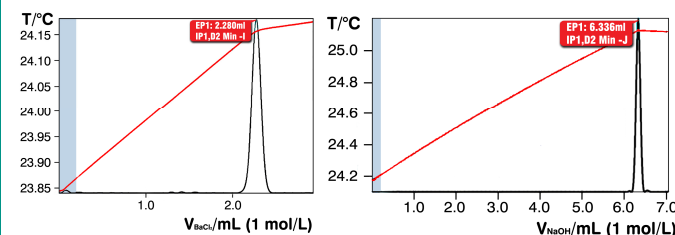
Etching baths contain nitric, acetic and phosphoric acid. The acids are titrated with aqueous sodium hydroxide. Due to the fact that two pairs of pK_A values lie within 5 units (see Metrohm monograph «titration tutorial»), only three from five endpoints appear in the titration curve.



	HNO ₃	HOAc	H ₃ PO ₄
	(% w/v)		
Mean value (N=10)	0.910	2.130	6.910
Standard deviation	0.042	0.032	0.056
Relative standard deviation	4.670	1.510	0.800

Determination of the sulfate and total acid content of a nitrating solution

The acid content of complex acid mixtures can be determined easily with aqueous sodium hydroxide in a thermometric titration. In this experiment the sulfate and total acid content of a nitrating solution are determined. The sulfate is quantified by precipitation titration with barium chloride. Both titrations can be carried out in sequence using the same sensor and the same sample.



	Sulfate content	H ₂ SO ₄	HNO ₃
	(% w/v)		
Mean value (N=10)	108.91 g/L	11.12	4.85
Standard deviation	1.02 g/L	0.10	0.09
Relative standard deviation	1.77 %	0.94	1.77