Thermometric titration with 859 Titrotherm

What is thermometric titration?

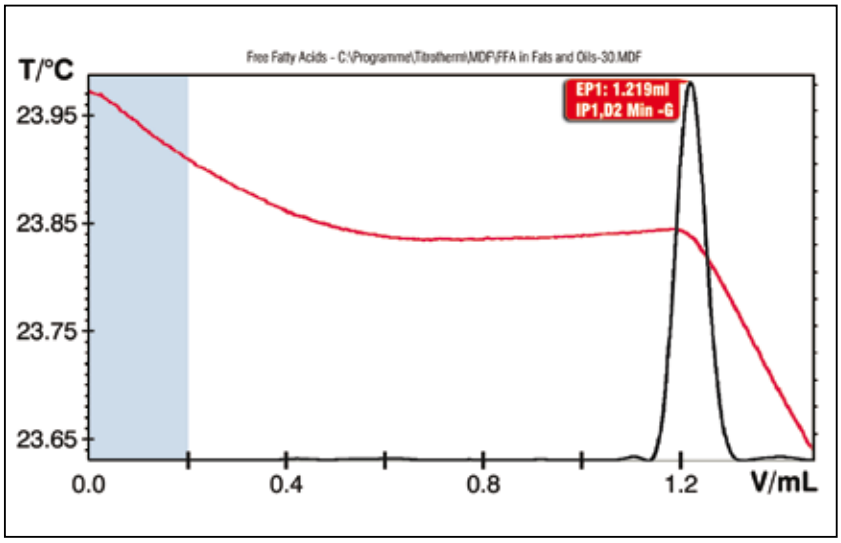
Each chemical reaction is associated with a change in enthalpy: heat is either released (exothermic reaction) or removed from the surroundings (endothermic reaction). This means that changes in enthalpy are a universal feature of all reactions. The course of the reaction can be followed by recording the change in temperature; in a thermometric titration this is used for determining the endpoint.

In a thermometric titration, the reagent solution (titrant) is added to the analyte at a constant rate until the endpoint is reached. The endpoint can be recognized by a break in the titration curve obtained by plotting the added amount of titrant against the temperature. The precise position of the endpoint is obtained by using the second derivative of the temperature curve. A thermistor is used as the sensor (Thermoprobe); it responds to very small temperature changes in the analyte solution. When recording very small temperature gradients in the stirred sample solution, the measured values are overlaid by slight instrumental noise. In order to minimize this noise, the sample solution must be stirred at high speed.

The applications described in this article show just how versatile thermometric titration is.

Determining the free fatty acid (FFA) content in olive oil

The acid content of oils – often only present in traces – is a quality criterion and can be determined by thermometric titration. For example, in mineral oils and lubricating oils the total acid number (TAN) is determined and in edible fats and oils the free fatty acids (FFA).



Determining the content of free fatty acids in olive oil. Titration curve (added volume of reagent vs. measuring temperature) in red and its second derivative in black.

Procedure

Dissolve the olive oil in a 1:1 mixture of toluene and 2-propanol and add a small amount of paraformaldehyde to achieve a better endpoint indication. Titrate with c(KOH) = 0.1 mol/L in 2-propanol to the endpoint; the reaction is slightly endothermic. At the endpoint, the excess hydroxyl ions catalyze the hydrolysis of paraformaldehyde. This strongly endothermic reaction can be seen from the sharp bend in the titration curve. No sample preparation is necessary. The samples can be weighed out directly into the titration vessel. The titrant delivery rate is set to 1 mL/min.

Ten successive measurements for determining free fatty acids in olive oil. The free fatty acid content is given as the percentage of the total weight.

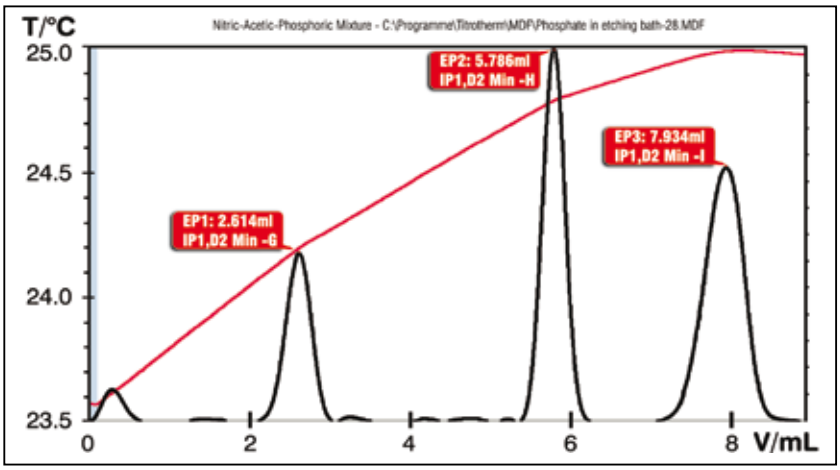
Weight [g]	Titrant [mL]	FFA content
12.0522	1.251	0.290%
14.3130	1.480	0.289%
9.9720	1.023	0.287%
16.5299	1.686	0.286%
17.9919	1.837	0.286%
18.3100	1.875	0.287%
15.9473	1.611	0.283%
14.1140	1.432	0.284%
12.0272	1.223	0.284%
9.9525	1.011	0.284%
Mean value		0.286%
Standard deviation		0.0024%
Relative standard deviation		0.86%

Determining the phosphate content in acidic etching baths

In addition to nitric acid, etching baths also contain acetic and phosphoric acid. The acids are titrated with sodium hydroxide solution. The phosphoric acid content is calculated with the help of the third endpoint of the titration and allows the content of the two other acids to be determined. As some of the five pK_A values are not far enough apart from each other, the titration curve shows only three endpoints (see Metrohm Monograph «Practical Titration»).

The pK_A values of nitric, acetic and phosphoric acid and their contribution to the three endpoints.

Endpoint 1	Endpoint 2	Endpoint 3
pK_A (HNO_3) = -1.3	pK_A (HOAc) = 4.75	
pK_A (H_3PO_4) = 2.12	pK_A ($H_2PO_4^-$) = 7.21	pK_A (HPO_4^{2-}) = 12.36



Determining the content of nitric, acetic and phosphoric acid in a single titration.

Procedure

The aqueous mixture of phosphoric, acetic and nitric acid is prepared as follows: add 41.389 g phosphoric acid, 10.735 g acetic acid and 6.600 g nitric acid to approx. 200 mL of ultrapure water in a 500 mL volumetric flask. After shaking the mixture, make it up to the mark with ultrapure water. Transfer an aliquot of this sample solution to the titration vessel and add aqueous sodium chloride solution (265 g/L) until the measuring head of the Thermoprobe is immersed in the solution. After stirring for 5 seconds, titrate the solution with c(NaOH) = 1.0 mol/L up to the third endpoint of the exothermic reaction. The titrant delivery rate is set to 6 mL/min.

Ten successive measurements for determining the content of the three acids in the sample.

Sample volume [mL]	HNO_3 [%w/v]	HOAc [%w/v]	H_3PO_4 [%w/v]
3.0	0.90	2.17	6.89
3.0	0.97	2.17	6.80
3.0	0.95	2.11	6.91
3.0	0.90	2.12	6.94
3.0	0.90	2.13	6.91
3.0	0.92	2.11	6.91
3.0	0.96	2.19	6.81
3.0	0.87	2.11	6.94
3.0	0.84	2.13	6.96
3.0	0.88	2.06	6.99
Mean value	0.91	2.13	6.91
Standard deviation	0.042	0.032	0.056
Relative standard deviation	4.67%	1.51%	0.80%

What sort of instrument do I need for a thermometric titration?

Thermometric titrations can be carried out conveniently using the 859 Titrotherm from Metrohm. This titrator can, of course, also be used for classically indicated titrations.

The 859 Titrotherm with the Thermoprobe, two 800 Dosinos and a PC with the thermometric titration software.

The Titrotherm system:

- 859 Titrotherm
- Thermistor-based temperature sensor (Thermoprobe)
- One 800 Dosino for adding the reagent
- Titration vessel
- Stirrer
- PC with thermometric titration software

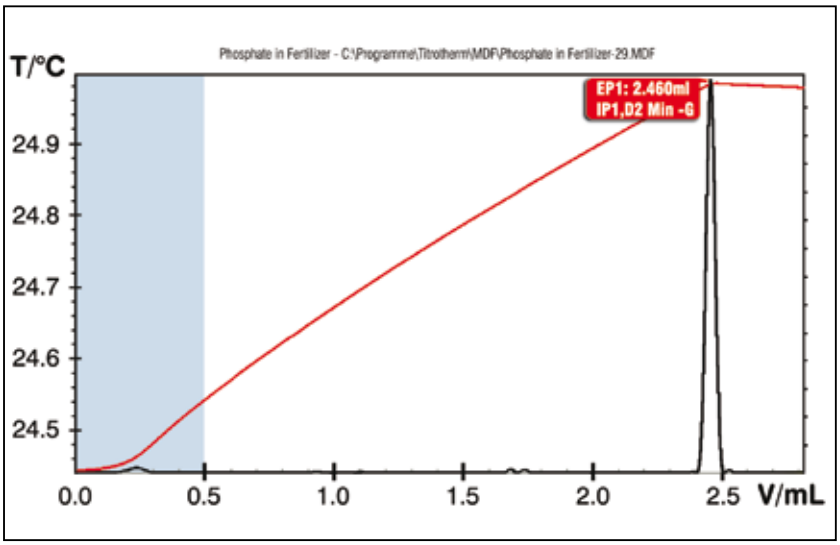
Thermometric titrations can be used for the following reaction types:

- Acid-base reactions
- Redox reactions
- Precipitation reactions
- Complexing reactions

The temperature sensor does not enter into electrical or electrochemical interaction with the analyte solution, whose conductivity has therfore no influence on the determination of the content. Titrations can also be carried out in non-conductive, apolar media. Titrations are also possible in turbid solutions or suspensions. As no diaphragm is present there are no diaphragm problems and even precipitation titrations can be carried out without any problems.

Determining 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.



Titration curve for the determination of phosphate in liquid fertilizers.

Procedure

A sample of a commercially available liquid fertilizer is titrated with a $Mg(NO_3)_2$ solution in the presence of excess ammonium ions. No sample preparation is necessary. The phosphate content is determined as follows: weigh out the liquid fertilizer directly into the titration vessel and then add approx. 25 mL ultrapure water shortly before starting the titration. After stirring for 5 seconds, titrate the solution with $c(Mg(NO_3)_2)$ = 1 mol/L up to the endpoint of the exothermic reaction. The titrant delivery rate is set to 1 mL/min.

Ten successive measurements for determining the content of phosphate in liquid fertilizer. The results are given as percent phosphorus referred to the weight of the sample.

Sample weight [g]	**% P**
7.8064	0.83
6.9810	0.83
8.6260	0.83
8.4610	0.83
7.8105	0.83
8.9244	0.84
7.9867	0.84
7.1572	0.84
7.9080	0.84
8.7764	0.83
Mean value	0.83
Standard deviation	0.004
Relative standard deviation	0.53%

Determining 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 contents of a nitrating solution are determined. Knowing the experimentally determined sulfate content, the nitric acid content can be calculated from the total acid content. The sulfate is determined by a precipitation titration with barium chloride as the reagent.

Titrotherm on the Internet:

Further information related to thermometric titrations and the 859 Titrotherm from Metrohm, together with numerous applications, can be found under www.titrotherm.com.

Procedure

The aqueous mixture of sulfuric and nitric acid is prepared as follows: add 20.817 g sulfuric acid and 19.478 g nitric acid to approx. 100 mL of ultrapure water in a 200 mL volumetric flask. Shake the mixture, then make it up to the mark with ultrapure water.

- Determining the sulfate content:

  Pipet 2 mL of the above sample solution into the vessel and add approx. 25 mL of ultrapure water. After stirring for 5 seconds, titrate the solution with c($BaCl_2$) = 1.0 mol/L up to the endpoint of the exothermic reaction. The titrant delivery rate is set to 2 mL/min.

- Determining the total acid content:

  The total acid content is determined after the sulfate determination using the reaction solution already present in the titration vessel. This solution is titrated with c(NaOH) = 1.0 mol/L up to the endpoint of the exothermic reaction. The titrant delivery rate is set to 3 mL/min.

Ten successive measurements for determining the sulfate content as well as sulfuric and nitric acid contents (sum corresponds to the total acid content) in a nitrating solution. The results are given as sulfate content in g/L nitrating solution as well as sulfuric and nitric acid contents in percent by weight referred to the sample volume.

Sample volume [mL]	SO_4 content [g/L]	H_2SO_4 [%w/v]	HNO_3 [%w/v]
2.0	107.35	10.96	4.82
2.0	108.54	11.08	4.83
2.0	109.39	11.17	4.65
2.0	108.34	11.06	4.84
2.0	108.88	11.12	4.82
2.0	108.07	11.03	4.82
2.0	109.56	11.19	4.94
2.0	110.68	11.30	4.92
2.0	110.11	11.24	4.88
2.0	108.17	11.04	4.95
Mean value	108.91	11.12	4.85
Standard deviation	1.02	0.10	0.09
Relative standard deviation	1.77%	0.94%	1.77%