Determination of free fatty acids (FFA) in edible oils with 859 Titrotherm

Of interest to: food industry

Summary

Edible oils are dissolved in a mixture of toluene and 2-propanol (1:1) and titrated with standardized c(TBAOH) = 0.01 mol/L in 2-propanol to a catalytically enhanced thermometric endpoint.

Introduction

In a titration, the titrant reacts with the analyte in the sample either exothermically (gives out heat) or endothermically (takes in heat). The Thermoprobe measures the temperature of the titrating solution. When all of the analyte in the sample has reacted with the titrant, the temperature of the solution will change, and the endpoint of the titration is revealed by an inflection in the temperature curve.
Catalytically enhanced titrations using paraformaldehyde as catalyst are based on the endothermic hydrolysis of the paraformaldehyde in the presence of excess hydroxide ions.
The amount of analyte determined is not related to the change in temperature of the solution. Therefore, it is not necessary to use isulated titration vessels.

Theory

Thermometric titrations are conducted under conditions of constant titrant addition rate. In this respect they differ from potentiometric titrations, where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being given out or consumed, and hence a more or less constant temperature change up to the endpoint.

Apparatus and accessories

1 x 2.859.1010	859 Titrotherm (1 Dosino and 1 10 mL Dosing unit included)
2 x 2.800.0010	800 Dosino
1 x 6.3032.150	Dosing unit 5 mL
1 x 6.3032.250	Dosing unit 50 mL
1 x 6.1543.210	3-way stopper with antidiffusion tip
1 x 6.1446.000	3 x SGJ stoppers
1 x 6.2061.010	Reagent organizer
1 x 6.2065.000	Stacking frame

Reagents

Titrant:	c(TBAOH) = 0.01 mol/L 1:10 diluted with 2-propanol from 0.1 mol/L TBAOH in 2- propanol/ methanol (Merck)
Solvent mixture:	Toluene 99% (Fluka)/2-propanol purum (Fluka) 1:1 (v/v)
Catalyst:	Paraformaldehyde, 95% (Fluka)
Standard solution:	0.01 mol/L benzoic acid puriss. p.a. (Fluka) in 2-propanol

Samples

Olive oil, swiss rape oil, sunflower oil (Suprema, Migros)

Calculations

Titer TBAOH with 0.01 mol/L benzoic acid solution

If a liquid primary standard is used, dose aliquots directly into the titration vessel. Set up a regression plot with the sample size in mL (see appendix) on the x-axis and mL of titrant consumed on the y-axis. The plot will be a linear curve of the form y = a * x + b, where the molarity of the titrant is calculated from the slope (a) with the following formula:
$(slope)^{-1}$ * c(standard solution)

Calculation of titer in *tiamo*™

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept	'RS.EP.ITC'
RS04	Correlation (R^2)	'RS.EP.COR*'RS.EP.COR'
RS05	Molarity[mol/L] of titrant	('1/RS.EP.SLO')'*'benzoic acid.CONC'
RS06	Titer of titrant	('1/RS.EP.SLO')*benzoic acid. CONC/'TET1'.CONC
RS07	Filter factor	'MV.filter factor'

method blank

The method blank is determined by titrating a number of analyte solutions of different concentrations and plotting the analyte concentration against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in method parameters will require a new determination of method blank.
This parameter is stored along with the other method parameters. For all determinations it is subtracted from the volume of titrant.

Calculation of method blank in *tiamo*™

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept [mL]	'RS.EP.ITC'
RS04	Correlation (R^2)	'RS.EP.COR*'RS.EP.COR'
RS07	Filter factor	'MV.filter factor'

Calculation of TAN determination in *tiamo*™

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS07	filter factor	'MV.filter factor'
RS08	TAN mg KOH/g	('TET1.EP(1).VOL'-'CV.blank')* 'TET1.CONC'*TET1.Titer'* MW.KOH'/'MV.sample size
RS09	FFA %	('TET1.EP(1).VOL'-'CV.blank')* 'TET1.COC'*'TET1.Titer'*MW. oleic acid'*100/'MV.sample size/1000
RS10	Blank [mL]	'CV.blank'

Legend formula

'TET1.EP(1).VOL'	= Thermometric titration endpoint volume
'RS.EP.SLO'	= slope for linear regression
'RS.EP.ITC'	= Intercept for linear regression
'RS.EP.COR*'RS.EP.COR'	= correlation coefficient (R^2)
'MV.filter factor'	= Titration parameter (smoothing factor)
CV.blank'	= method blank in mL
'bencoic acid'.CONC'	= Concentration of standard solution (0.01 mol/L)
'TET1.CONC'	= Concentration of the titrant (0.01 mol/L)
'TET1.TITER'	= titer of the titrant
'MV.sample size'	= sample size in g
TAN mg KOH/g	= total acid number in mg KOH/g
FFA %	= free fatty acid in %
'MW.KOH'	= 56.10564 g/mol
'MW.oleic acid'	= 282.46 g/mol
100	= factor for conversion in %
1000	= factor for conversion mg

Sample preparation for titer, blank and sample

	Titer determination	Blank determination	Sample determination
Benzoic acid 0.01 mol/L [mL]	1 - 5	-	-
Toluene/2-propanol 1:1 (v/v) [mL]	30	30	30
olive oil [g]	-	1 – 2.6*	1.2 – 1.4
rape oil [g]	-	6.7 – 10.6*	9.4 – 9.9
sunflower oil [g]	-	3.5 – 7.2*	6.0 – 6.8
number of determination (n =)	3 - 5	3 - 5	3 - 5

*depends on sample type

Method

Procedure for titer determination

Give approx. 0.5 g paraformaldehyde into the titration vessel, add an aliquote of standardized benzoic acid solution and 30 mL solvent mixture. Stir thoroughly for 10 seconds before titration. Titrate at least 3 different values of benzoic acid in an ascending order to the first exothermic endpoint. With the formula "Calculation of titer in ***tiamo***™" the titer is automatically calculated.

Procedure for method blank determination

The method blank is determined by titrating a range of aliquot sizes, and calculating the y-intercept (in mL) of a regression curve formed by plotting aliquote size (x-axis) against mL of titrant delivery (y-axis). This can be done automatically in ***tiamo***™.
Pipette an aliquote of oil (see "Sample preparation for titer, blank and sample") directly into the titration vessel, add approximately 0.5 - 0.7 g paraformaldehyde and 30 mL solvent mixture. Stir thoroughly for 20 seconds and titrate to a single thermometric endpoint. The method blank is automatically calculated with the formula "Calculation of method blank in ***tiamo***™". The intercept in mL, which represents the method blank, will be saved as a common variable. This blank has to be subtracted from each further analyzed sample

Titration Parameters for olive oil

	Titer determination	Blank determination	TAN olive oil
Stirring rate	8	8	8
Start volume [mL]	0	0	0
Pause [s]	10	20	20
Switch off autom.	yes	yes	yes
Dosing rate [mL/min]	5	5	5
Filter factor	50	50	50
Damping until [mL]	0.2	0.8	0.8
Stop volume [mL]	5.0	5.0	2.5
Stop slope	off	off	off
Add. volume after stop [mL]	off	off	0.5
Evaluation start [mL]	0.2	1.0	0.0
End points [Reaction type]	ex*	ex*	ex*
EP criterion [ERC]	-20	-20	-20

* exothermic

Titration Parameters for rape oil

	Titer determination	Blank determination	TAN rape oil
Stirring rate	8	8	8
Start volume [mL]	0	0	0
Pause [s]	10	20	20
Switch off autom.	Yes	yes	yes
Dosing rate [mL/min]	5	5	5
Filter factor	50	50	50
Damping until [mL]	0.2	0.5	0.5
Stop volume [mL]	5.0	5.0	5.0
Stop slope	off	off	off
Add. Volume after stop [mL]	off	off	off
Evaluation start [mL]	0.2	0.0	0.0
End points [Reaction type]	ex*	ex*	ex*
EP criterion [ERC]	-20	-20	-20

* exothermic

Titration Parameters for sunflower oil

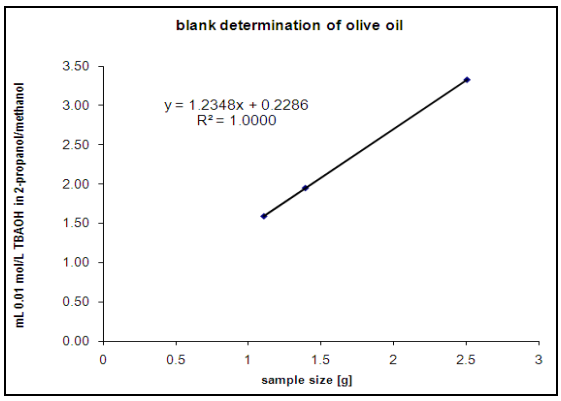
	Titer determination	Blank determination	TAN sunflower oil
Stirring rate	8	8	8
Start volume [mL]	0	0	0
Pause [s]	10	20	20
Switch off autom.	Yes	yes	yes
Dosing rate [mL/min]	5	5	5
Filter factor	50	50	50
Damping until [mL]	0.2	0.5	0.5
Stop volume [mL]	5.0	5.0	5.0
Stop slope	off	off	off
Add. Volume after stop [mL]	off	off	off
Evaluation start [mL]	0.2	0.5	0.5
End points [Reaction type]	ex*	ex*	ex*
EP criterion [ERC]	-20	-20	-20

* exothermic

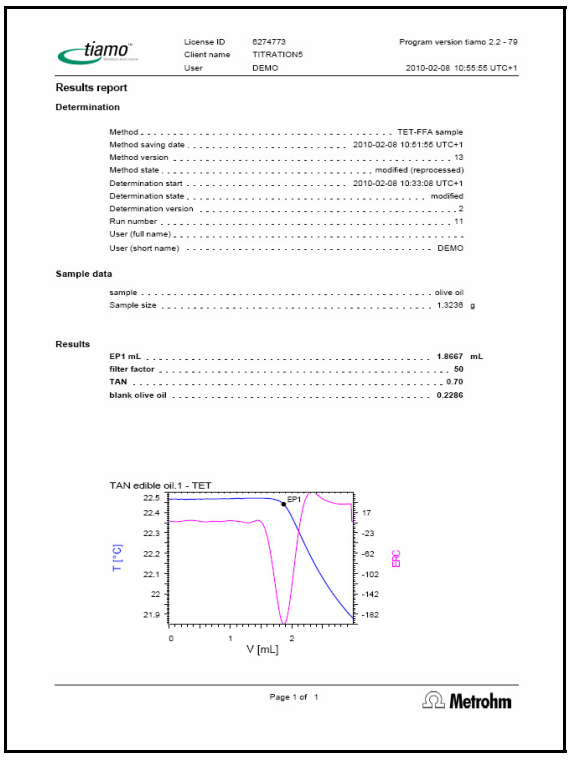
Procedure for sample preparation

Pipette an aliquote of oil (see “Sample preparation for titer, blank and sample”) directly into the titration vessel, add approximately 0.5 - 0.7 g paraformaldehyde and 30 mL solvent mixture. Stir thoroughly for 20 seconds and titrate to a single thermometric endpoint. The TAN value in mg KOH/g is automatically calculated with the formula “Calculation of TAN determination in ***tiamo***™”

Linear regression of blank olive oil (method blank = 0.2286 mL)



Tiamo™ *2.2 Result report of blank determination in olive oil*


tiamo

License ID 6274773
Client name TITRATION5
User DEMO
Program version tiamo 2.2 - 79
2010-02-08 10:55:55 UTC+1

Results report

Determination

Method . . . . . TET-FFA sample
Method saving date . . . . . 2010-02-08 10:51:55 UTC+1
Method version 13
Method state . . . . . modified (reprocessed)
Determination start . . . . . 2010-02-08 10:33:08 UTC+1
Determination state . . . . . modified
Determination version 2
Run number 11
User (full name) . . . . .
User (short name) . . . . . DEMO

Sample data

sample . . . . . olive oil
Sample size . . . . . 1.3236 g

Results

EP1 mL . . . . . 1.8667 mL
filter factor 50
TAN 0.70
blank olive oil 0.2286

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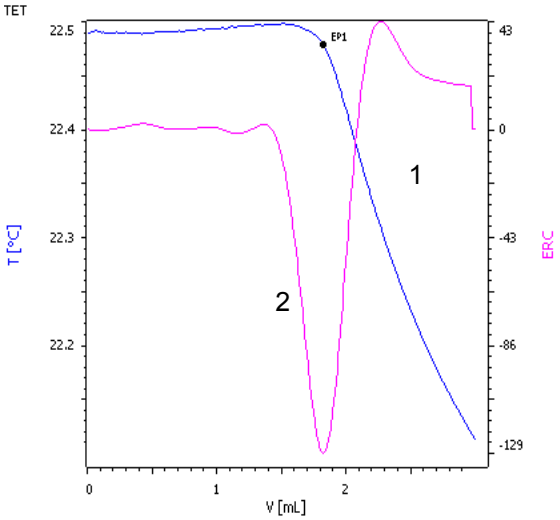
Metrohm

Thermometric Titration Plot (olive oil)



Legend:

1 = solution temperature curve

2 = second derivative curve (for endpoints)

Results (titer and blank)

	Titer	Blank olive oil	Blank rape oil	Blank sunflower oil
endpoint [mL]	3.3167	1.9500	1.2000	1.1500
slope	1.0084	1.2348	0.0832	0.1125
intercept [mL]	0.3028	0.2286	0.3151	0.3391
Correlation (R^2)	0.9996	1.0000	0.9932	0.9997
molarity [mol/L]	0.00992	-	-	-
Filter factor	50	50	50	50
titer	0.9917	-	-	-

Results of oil samples

	Olive oil	**Rape oil**	**sunflower oil**
TAN mg KOH/g	0.70	0.05	0.0651
s(abs) TAN mg KOH/g	0.0	0.0	0.0027
s(rel) %	0.0	0.0	4.15
n =	3	3	3