Metrohm International Headquarters

Automated sodium determination in various foods with 859 Titrotherm

Keywords

total sodium / bouillon / gravy / tomato ketchup / corn chips / pretzel sticks / crackers / 859 Titrotherm / automated / 815 Robotic USB Sample Processor

Summary

In an acidic solution (containing NH_4F * HF, $Al(NO_3)_3$ / KNO_3), sodium forms NaK_2AlF_6 which precipitates in an exothermic solution.

Several foods were analysed, namely bouillon, gravy, tomato ketchup, corn chips, pretzel sticks as well as crackers. The reproducibility of the results was good.

After weighing in and adding solutions, the samples were crushed again with a polytron to ensure homogeneity in the measuring solution.

Relative standard deviations between 0.08% and 3.75% were obtained.

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.

The amount of analyte determined is not related to the change in temperature of the solution. Therefore, it is not necessary to use insulated titration vessels.

Theory

IN GENERAL

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.

TITER DETERMINATION

If a liquid standard is used, pipette it 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 $y = a \cdot x + b$, where the molarity of the titrant is calculated from the slope with the following formula: $a \cdot c(\text{Titrant})$.

BLANK DETERMINATION

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.

Solutions

- *Titrant: $c(Al(NO_3)_3) = 0.5$ mol/L and $c(KNO_3) = 1.1$ mol/L*

  187.57 g $Al(NO_3)_3$ and 111.22 g KNO_3 were weighed into a 1000 mL volumetric flask, dissolved in approx. 800 mL deion. water and filled up to the mark.

- *Complexing agent : $\beta(NH_4F \cdot HF) = 300$ g/L*

  300 g $NH_4F \cdot HF$ were weighed into a 1000 mL volumetric flask and filled up to the mark with deion. water.

- *Standard : $c(Na_2SO_4) = 0.4$ mol/L*

  28.408 g Na_2SO_4 (dried for 2 h at 105 °C) were weighed into a 500 mL volumetric flask and filled up to the mark with deion. water.

- *Deion. water*

Materials

1×	859 Titrotherm (containing 1 × 800 Dosino and dosing unit 20 mL)	2.856.1010
1×	HF resistant Thermoprobe	6.9011.040
1×	815 USB Robotic Sample Processor XL	2.815.0130
1×	Dispersing aggregate for Polytron, 157 mm	6.9012.010
1×	Swing arm for Polytron and 786 swing head, left swinging	6.1461.250
1×	Robotic arm with holder for titration head, right swinging	6.1462.070
1×	Titration head, 3 × SGJ14	6.1458.040
1×	External Polytron washing station	6.2841.000
1×	Sample Rack 59 × 120 mL	6.2041.850
3×	800 Dosino	2.800.0010
2×	843 Pump Station	2.843.0150
1×	Polytron PT 1300 D	2.136.0100
2×	Dosing unit 5 mL	6.3032.150
1×	Dosing unit 5 mL ETFE	6.1575.150
1×	Dosing unit 50 mL	6.3032.250
1×	Sample beaker 100 × 120 mL	6.1459.300

Samples

- Tomato ketchup
- Bouillon as solution
- Bouillon as powder
- Gravy as powder
- Corn chips
- Pretzel sticks
- Crackers

Procedures

TITER DETERMINATION

1 to 2.5 mL Na_2SO_4 solution, 5 mL complexing agent as well as 40 mL deion. water were dosed into the titration beaker and titrated with $Al(NO_3)_3$ / KNO_3 – solution up to the first end point. The consumption of the titrant was regressed against the sample size. For formula see Calculation section.

BLANK DETERMINATION

Table 1: Sample Sizes for Blank Determination

Sample	*Sample size [g] for 1st blank determination*	*Sample size [g] for 2nd blank determination*	*Sample size [g] for 3rd blank determination*
Ketchup	1.35	2.21	3.65
Bouillon as solution	0.11 = 5 mL	0.18 = 8 mL	0.21 = 10 mL
Bouillon	0.17	0.21	0.24
Gravy	0.32	0.43	0.50
Cracker	1.65	2.30	3.17
Corn chips	3.06	6.32	9.58
Pretzel sticks	0.91	1.57	2.02

The Sample sizes for the blank determination were chosen depending on the sodium content. A few examples were shown in table 1. The consumption of titrant was regressed against the sample size. The intercept was taken as blank value and was saved automatically as Common variable. This blank value has to be subtracted from each further analyzed sample.

SAMPLE DETERMINATION

Table 2: Sample Sizes for Sample Determination

Sample	*Sample size*
Ketchup	3.5 g
Bouillon as solution	10 mL = 0.2 g
Bouillon	0.3g
Gravy	0.7 g
Cracker	2.7 g
Corn chips	5 g
Pretzel sticks	2 g

Before beginning the determination crush the samples with the mortar. Afterward weigh for each sample type approximately the sample sizes mentioned in Table 2, add 5 mL complexing agent, 40 mL water and titrate with $Al(NO_3)_3$ / KNO_3 solution up to the first end point. For the calculation of the sodium content the blank value has to be subtracted. The whole

measurement including homogenization with the Polyton takes about 8.5 minutes. The content was calculated in % as well as in mg/100g.

Titration Parameters

	Titer determination	*Blank and Sample determination*
Stirring rate	10	Depending on sample[1]
Start volume [mL]	0.5	0.5
Pause [s]	30	30
Switch off autom.	no	no
Dosing rate [mL/min]	4	4
Filter factor	45	Depending on sample[2]
Damping until [mL]	0.5	0.5
Stop volume [mL]	5.0	5.0
Stop slope	off	off
Add. volume after stop [mL]	2	2
End points [Reaction type]	ex*	ex*
EP criterion [ERC]	-50	Depending on sample[3]

* nicht erklärt. Bei end points.

1	*Sample*	*Stir rate*
	- Ketchup	10
	- Bouillon	11
	- All others	12

2	*Sample*	*Filter factor*
	- Ketchup - Bouillon as solution	45
	- Gravy - Pretzel sticks	50
	- Cracker - Corn chips	60
	- Bouillon	65

3	*Sample*	*EP criterion*
	- Ketchup - Bouillon as solution	- 45
	- Gravy - Cracker - Corn chips - Pretzel sticks	-40
	- Bouillon	-20

Calculations

TITER DETERMINATION

Assignment	***RS name***	***formula***
2	EP	'TET.EP{1}.VOL'
RS02	Slope	'RS.EP1.SLO'
RS03	Intercept	'RS.EP1.ITC'
RS04	Correlation (R^2)	'RS.EP.COR' · 'RS.EP.COR'
RS05	Molarity[mol/L]	'TET.CONC' · 'RS.EP.SLO'
RS06	titer	('RS.EP1.SLO' · 'TET.CONC') / ('Add.CONC' · 2)

BLANK DETERMINATION

Assignment	***RS name***	***Formula***
RS01	EP	'TET.EP{1}.VOL'
RS02	Slope	'RS.EP1.SLO'
RS03	Intercept	'RS.EP1.ITC'
RS04	Correlation (R^2)	'RS.EP.COR' · 'RS.EP.COR'

SAMPLE DETERMINATION

Assignment	***RS name***	***Formula***
RS01	EP	'TET.EP{1}.VOL'
RS02	Content [%]	('TET.TITER' · 'TET.CONC' · ('TET.EP{1}.VOL' – 'CV.Blank') ·M(Na) · 100) / (1000 · 'MV.Sample Size')
RS03	Content [mg/100g]	('TET.TITER' · 'TET.CONC' · ('TET.EP{1}.VOL' – 'CV.Blank') ·M(Na) · 100) / 'MV:Sample Size'

Legend formula

TET.EP1.VOL	= thermometric end point [mL]
.SLO	= slope of the linear regression
.ITC	= intercept of the linear regression
.COR	= correlation factor
Add.CONC	= Concentration of Na_2SO_4 solution = 0.4 mol/L
TET.CONC	= Concentration of $Al(NO_3)_3$ / KNO_3 - solution = 0.5 mol/L
TET.TITER	= Titer of the $Al(NO_3)_3$ / KNO_3 - solution
Blank	= intercept of the linear regression at the blank determination
M(Na)	= 22.990 g/mol
MV.Sample Size	= Sample size in g
2	= two Na^+-Ions in Na_2SO_4
100	= for % and for mg/100g
1000	= conversion factor from g to mg

Results

TITER DETERMINATION

	Values
Slope	1.5819 mL/mL
Intercept	0.1976 mL
Molarity	0.7909 mol/L
Titer	0.9887
Corr. coefficient	1.0000

BLANK DETERMINATION

Sample	*Slope [g/mL]*	*Intercept [mL]*	*Corr. Coefficient*
Ketchup	1.0968	0.2143	0.99997
Bouillon as Solution	13.8983	0.2181	0.99986
Bouillon	16.3180	-0.2337	0.99975
Gravy	5.6772	0.2847	0.99813
Cracker	1.0288	0.1948	1.00000
Corn Chips	0.4203	0.0410	0.99945
Pretzel sticks	1.5793	0.2577	0.99827

SAMPLE DETERMINATION

Ketchup

	Calculation in [%]	*Calculation in [mg/100g]*
Mean	1.257	1256.8
abs. standard deviation	0.0024	2.427
rel. standard deviation	0.19 %	0.19 %
n =	6	6

Bouillon as solution

	Calculation in [%]	*Calculation in [mg/100g]*
Mean	16.04	16041.4
abs. standard deviation	0.013	14.101
rel. standard deviation	0.08 %	0.09 %
n =	6	6

Bouillon weighed in directly

	Calculation in [%]	*Calculation in [mg/100g]*
Mean	18.02	18019.9
abs. standard deviation	0.34	336.6
rel. standard deviation	1.89 %	1.87 %
n =	6	6

Gravy

	Calculation in [%]	*Calculation in [mg/100g]*
Mean	6.34	6335.8
abs. standard deviation	0.06	57.45
rel. standard deviation	0.95 %	0.91 %
n =	6	6

Crackers

	Calculation in [%]	*Calculation in [mg/100g]*
Mean	1.169	1168.9
abs. standard deviation	0.0058	5.777
rel. standard deviation	0.5 %	0.49 %
n =	6	6

Corn chips

	Calculation in [%]	*Calculation in [mg/100g]*
Mean	0.507	506.6
abs. standard deviation	0.019	18.76
rel. standard deviation	3.75 %	3.7 %
n =	6	6

Pretzel sticks

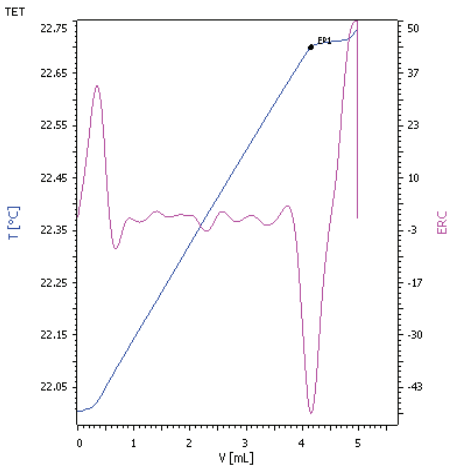
	Calculation in [%]	*Calculation in [mg/100g]*
Mean	1.809	1809.4
abs. standard deviation	0.0185	18.726
rel. standard deviation	1.02 %	1.03 %
n =	6	6

Comparison labeled / found results

Sample	*Labeled [g/100g]*	*Found [g/100g]*	*Difference [%]*
Ketchup	3.1 g NaCl = 1.22 g Na^+	1.257 g Na^+	+ 2.94%
Bouillon as solution	41 g NaCl =16.13 g Na^+	16.04 g Na^+	- 0.56 %
Bouillon	41 g NaCl =16.13 g Na^+	18.02 Na^+	+ 10.49 %
Gravy	6.67 g Na^+	6.34 g Na^+	- 5.21 %
Crackers	2.5 g NaCl =0.984 g Na^+	1.169 g Na^+	+ 15.83 %
Corn chips	0.5 g Na^+	0.507 g Na^+	+ 1.38 %
Pretzel sticks	4.6 g NaCl =1.810 g Na^+	1.809 g Na^+	- 0.055 %

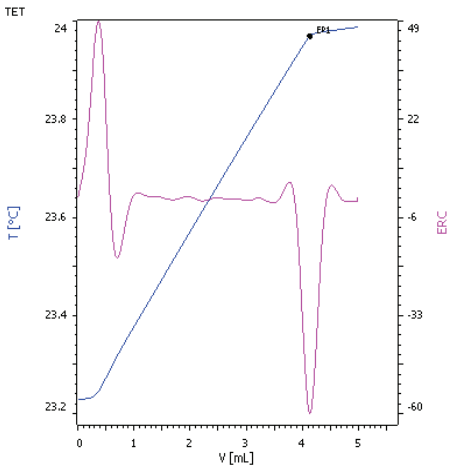
Curves

TITER DETERMINATION

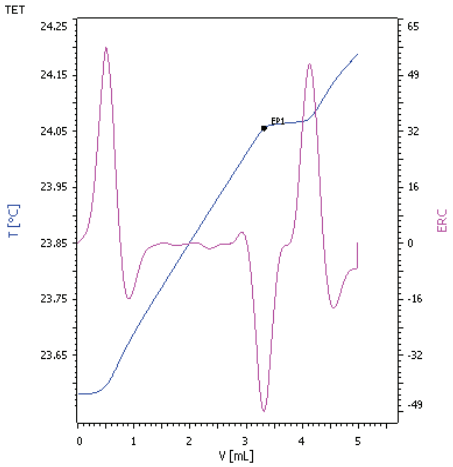


SAMPLE DETERMINATION

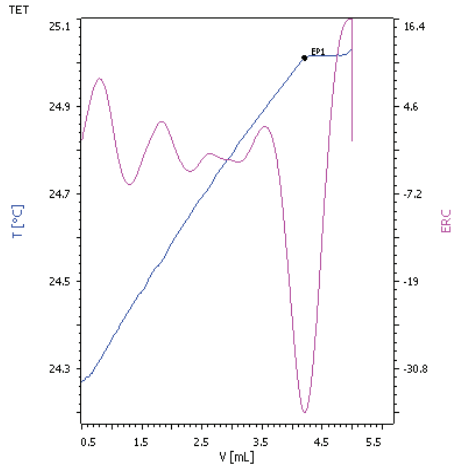
Ketchup



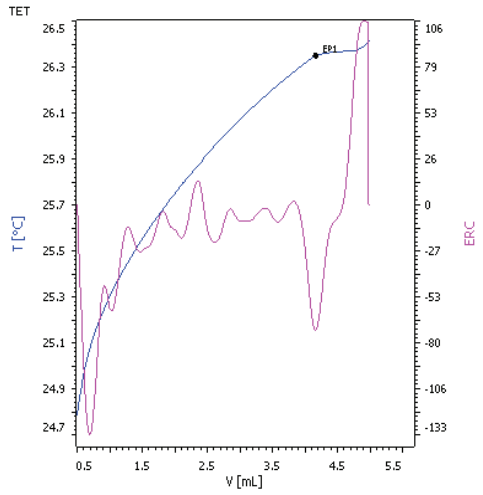
Bouillon as solution



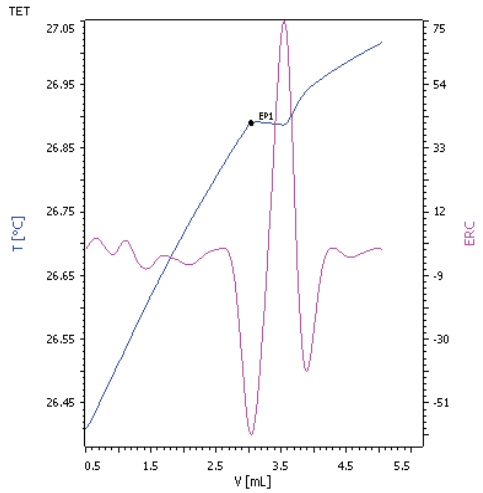
Bouillon weighed in directly



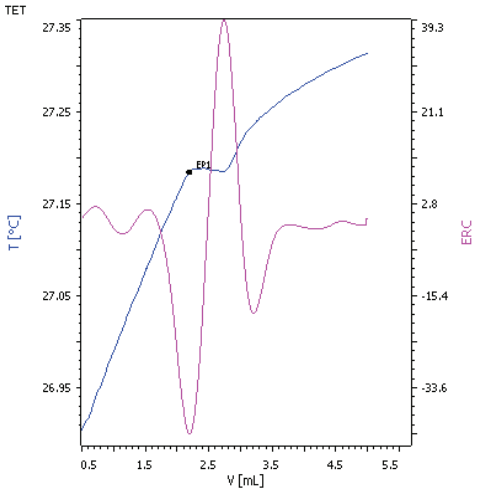
Gravy



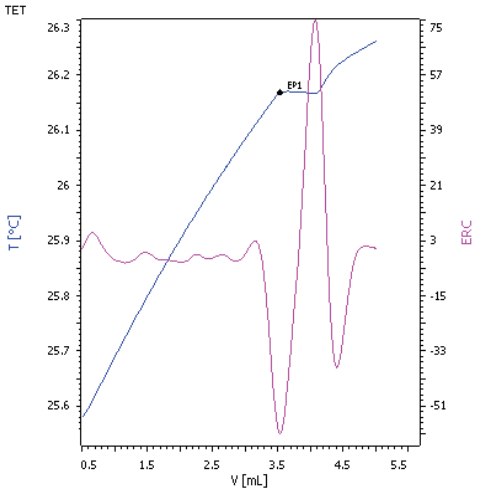
Crackers



Corn chips



Pretzel sticks



Comments

- For the cleaning of the Polytron and the electrodes, a dip rinsing was done in a beaker filled up with hexane. The further cleaning was carried out with deion. water.
- The speed of the Polytron was set to 20000 rpm.
- After crushing with the Polytron a milky suspension was obtained.
- For the dosing of the $NH_4F \cdot HF$ – solution an ETFE dosing unit was used.

Date

16.2.2010

Name

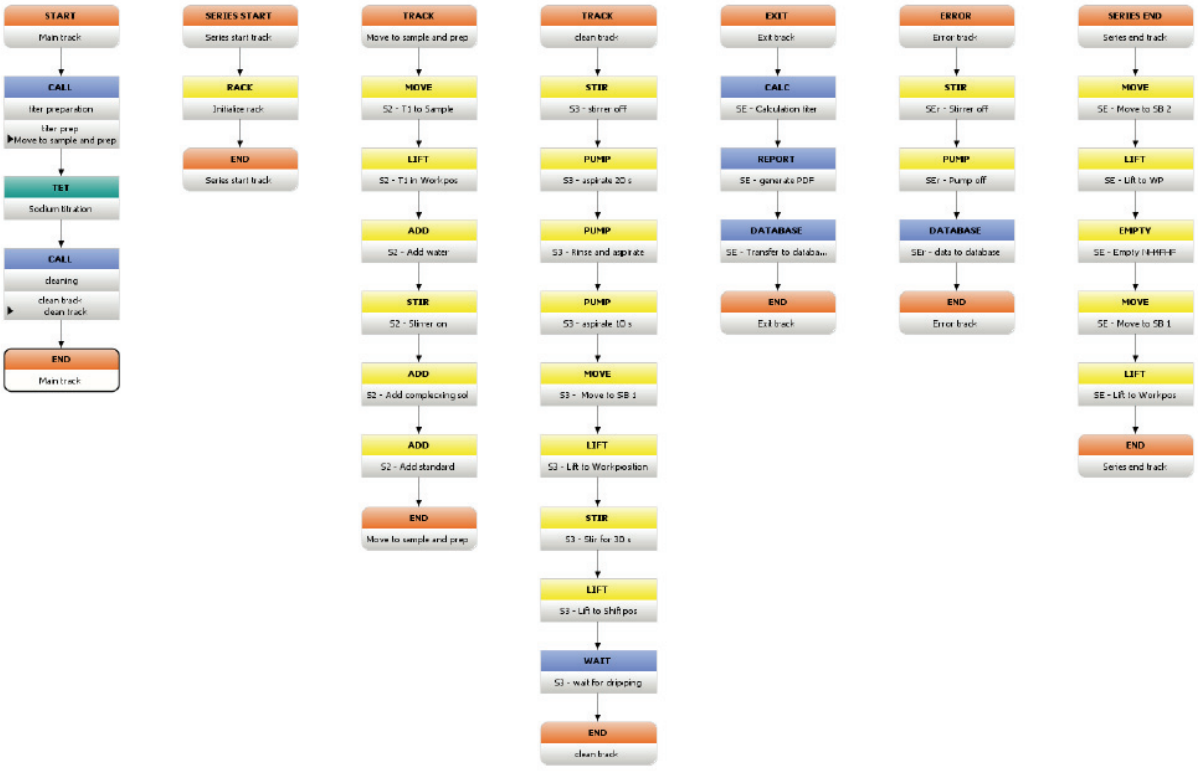
Metrohm AG, CH-9100 Herisau

Iris Kalkman, CC Titration

Appendix

METHODS

Titer Determination



Blank / Sample Determination