Automated determination of sodium in milk with 859 Titrotherm and 814 USB Sample Processor

Of interest to: Food (dairy) industry

Summary

The sodium content of milk can be rapidly and easily titrated thermometrically using a standard solution of Al^{3+} as titrant. Sodium is quantitatively precipitated as NaK_2AlF_6 in the presence of an excess of fluoride and potassium ions. The determination is unique to thermometric titrimetry. The milk sample is first treated with a trichloroacetic acid solution to coagulate protein and fat and to ensure proper liberation of sodium ions. The serum containing the sodium is separated by filtration or centrifugation. An aliquot of clarified milk serum is treated with $NH_4F{\cdot}HF$ solution before titration to supply the excess of fluoride ions required to drive the formation of NaK_2AlF_6. Potassium ions required in the reaction are supplied in the titrant at a ratio of approximately K : Al 2.2 : 1.

This bulletin discusses the automated determination of sodium (using an 814 USB Sample Processor) in milk products available to the public. Results are reported as mg Na/100 mL.

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

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 Dosing Unit 10 mL included)
1 x 2.814.0030 814 USB Sample Processor
2 x 2.800.0010 800 Dosino
1 x 6.3032.150 Dosing Unit 5 mL
1 x 6.3032.210 Dosing Unit 10 mL with 6.1566.210 ETFE 10 mL cylinder unit with piston and valve disk (for $NH_4F.HF$ service).
1 x 6.1909.060 Stirring propeller
22x 6.1459.300 PP sample tube 120 mL
1 x 6.9914.159 Titration head
1 x 6.2041.470 Sample rack 22 x 120 mL
3 x 6.1805.030 FEP tubing M6 150 cm
1 x 6.2061.010 Reagent organizer
1 x 6.2065.000 Stacking frame

Reagents

Solvent:	deionized water
Standard:	$c(Na^+)$ = 0.25 mol/L NaCl
Titrant:	$c(Al^{3+}/K^+)$ = 0.5 mol/L $Al(NO_3)_3$, 1.1 mol/L KNO_3
Reagent/buffer:	30% w/v $NH_4F{\cdot}HF$ in water
Coagulant:	trichloroacetic acid 25% w/v in water

Samples

Full cream milk, pasteurized, homogenized low-fat milk, pasteurized, homogenized
Skim milk, pasteurized, with added milk solids and milk calcium

Calculations

Molarity Al^{3+}

The molarity of the titrant is computed from a regression analysis of titration results, where mmol of analyte (the standard) is plotted on the x-axis, and mL of titrant is plotted on the y-axis. This is computed automatically in ***tiamo***™ using the SLO command.

$c(Al(NO_3)_3)$ mol/L= c(NaCl) mol/L/slope

Calculations for molarity in tiamo™

Assignment	RS name	Formula
RS01	EP1 mL	'Al-K titration.EP{1}.VOL'
RS02	Slope	'RS.EP1 mL.SLO'
RS03	Intercept	'RS.EP1 mL.ITC'
RS04	Corr Coeff	'RS.EP1 mL.COR'*'RS.EP1 mL. COR'
RS05	Molarity	Std Na solution.CONC'/'RS.Slope'

The value for the molarity of the standard sodium solution is stored in Configuration>Titrants/ Solutions>Concentration against the relevant Dosino.

The method *"Automated Al-K Standardization"* is available to perform this determination.

Calculations for method blanks

The method blank is determined by titrating different amounts of a representative sample of the product and plotting the sample amount against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in titrant dose rate or filter factor will require a new determination of the method blank. While a change in the titrant dose rate will require a new set of titrations to be run, a change in the filter factor can be performed by editing the set of titration data stored in the database.

This parameter is stored along with the other method parameters. For all determinations, the method blank in mL is subtracted from the volume of titrant.

Before performing a blank determination, it is important to set up in Configuration>Common Variables, a CV "Na blank" as this CV is used in the calculation for the determination of Na in milk. The value for the CV can be entered automatically during the blank determination titration run by double-clicking on the line for "Intercept Na", selecting the "Options" tab, and checking the box "Save result as common variable", then selecting the correct CV title.

Calculation for method blank in tiamo™

Assignment	RS name	Formula
RS01	EP1 mL	'Al titration.EP{1}.VOL'
RS02	Slope Na	'RS.EP1 mL.SLO'
RS03	Intercept Na [1]	'RS.EP1 mL.ITC'
RS04	Corr Coeff Na	'RS.EP1 mL.COR'*'RS.EP1 mL.COR'

[1] *"Intercept Na" = Na blank*

The method *"Automated determination of Na in dairy – blanks detn"* is available to perform this determination.

Calculations for determination of sodium in tiamo™

Assignment	RS name	Formula
RS01	EP1 mL	'Al-K titration.EP{1}.VOL'
RS02	mg Na/100 mL	(('RS.EP1 mL'-'CV.Na blank')*'Al-K titration.CONC'*22.98977*100)/'MV.Sample size'
RS03	Mean mg Na/100 mL	'RS. mg Na/100 mL.MNV'
RS04	Std Dev mg Na/100 mL	'RS. mg Na/100 mL.ASD'

Note: Where only single titrations on a sample are to be performed, lines for mean and standard deviation values may be omitted.

Methods

Procedure for determination of titrant molarity

Use the method *"Automated Al-K Standardization"*. Set up a 10 mL Dosino to dispense the c(Na^+) = 0.25 mol/L standard. In Workplace>Run>Determination Series create a sample table with 8 sample positions. Enter the method *"Automated Al-K Standardization"* in each position. In sample positions 1-8, enter values of 9, 8, 7, 6, 5, 4, 3, 2 mL, respectively. Save the sample table as "Al-K titrant standardization". Check the statistics box, and set the number of samples to 8.

Place two tubes filled with approx. 100 mL of water in position 21 and 22 of the sample rack. These are intended for the "double dip" rinse of the titration assembly after each titration.

Set up sample tubes as follows in positions 1- 6 of the sample rack:

Sample rack position	~mL deion. water
1	16
2	17
3	18
4	19
5	20
6	21
7	22
8	23

NOTE: It is essential that the titration assembly must be adjusted that the propeller stirrer is ~1 mm above the bottom of the titration tube at the fully lowered position. The Thermoprobe and the fluid delivery tubes should be 1 mm above the tips of the propeller. It is recommended that the fluid delivery tubes are tied together with a plastic tie about 35 mm from the bottom and the group of delivery tips angled towards the Thermoprobe. The direction of rotation of the stirrer must be set to carry the fluid delivered away from the sensor of the Thermoprobe to minimize noise. This setup should be used for all automated determinations.

Procedure for method blank determination

A method blank for the type of sample under examination is determined by titrating a range of sample amounts and calculating the y-intercept (in mL) of a regression curve formed by plotting sample amount (x-axis) against mL of titrant delivery (y-axis). This can be done automatically in ***tiamo™***.

Prepare a quantity of milk serum by transferring 500 mL of milk product into a 1000 mL beaker equipped with a large magnetic stirring bar. Place on a magnetic stirrer, and while stirring, slowly add 50 mL 25% (w/v) trichloroacetic acid . Stir for 20 minutes and wait for another 10 minutes. Either filter the coagulated milk through a Whatman no. 4 filter paper (or similar), or separate the milk serum by centrifugation. Approximately 200 mL of milk serum is required.

Place two tubes filled with approx. 100 mL of deion. water in positions 21 and 22 of the sample rack. These are intended for the “double dip” rinse of the titration assembly after each titration.

Prepare a series of titration tubes as follows:

Rack position	[1] Milk serum aliquot, mL	Deion. water, mL
1	50	0
2	40	10
3	30	20
4	25	25
5	20	30

[1] Aliquots are to be dispensed by glass volumetric (bulb) pipettes.

Before titration with Al-K solution, 5 mL of $NH_4F{\cdot}HF$ reagent is added automatically by a Dosino.

In Workplace>Run>Determination Series, prepare a sample table for 5 sample positions with the method *“Automated determination of Na in dairy – blanks detn”* in each position, and the sample size varied to match the rack position in the above table. Check the „Statistics“ box, and nominate 5 samples to be titrated.

Procedure for automated determination of sodium in milk products

Prepare an aliquot of serum of the milk product by pipetting 100 mL of milk into a 250 mL beaker equipped with a large magnetic stirring bar. Set on a magnetic stirrer, and slowly add 10 mL 25% (w/v) trichloroacetic acid solution. Stir for 10 minutes and wait another 10 minutes. Separate the clarified milk serum either by filtration through a Whatman no. 4 filter paper or by centrifugation. Pipette 50 mL of milk serum into a titration tube. Before titration with Al-K solution, 5 mL of $NH_4F{\cdot}HF$ reagent is automatically added by a Dosino.

Place two tubes filled with approx. 100 mL of water in positions 21 and 22 of the sample rack. These are intended for the “double dip” rinse of the titration assembly after each titration.

In Workplace>Run>Determination Series, prepare a sample table for the appropriate number of sample positions, with the method “Automated determination of Na in dairy products” in each position. Nominate a sample size of 45.45 mL, and identify each milk product according to its sample position. Note that a 50 mL aliquot is equivalent to 45.45 mL of original milk sample, since the addition of trichloroacetic acid solution needs to be taken into account.

Results

Molarity of Al-K titrant

Slope	1.8582
Intercept, mL	0.1889
Correlation (R^2)	1.0000
Molarity, mol/L	0.5382
Titrant dose rate, mL/min	4
Filter factor	30

Blank determinations

	Full cream milk	Low fat milk
Na slope	0.0363	0.0411
Na intercept (blank), mL	0.1595	0.1971
Na Correlation (R^2)	0.9997	0.9994
Titrant dose rate, mL/min	4	4
Filter factor	30	30

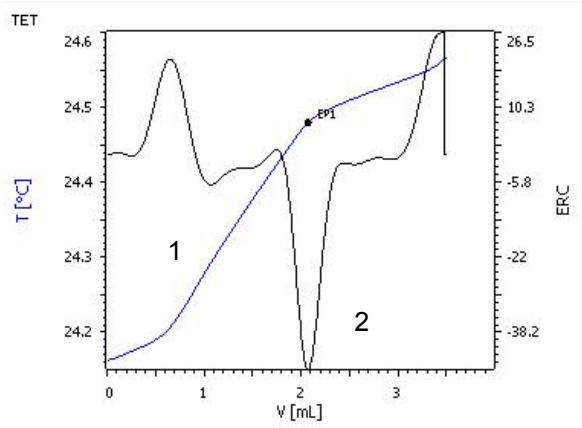
	Skim milk with milk solids and milk calcium
Na slope	0.0466
Na intercept (blank), mL	0.1295
Na Correlation (R^2)	0.9997
Titrant dose rate, mL/min	4
Filter factor	30

Results of sodium analysis

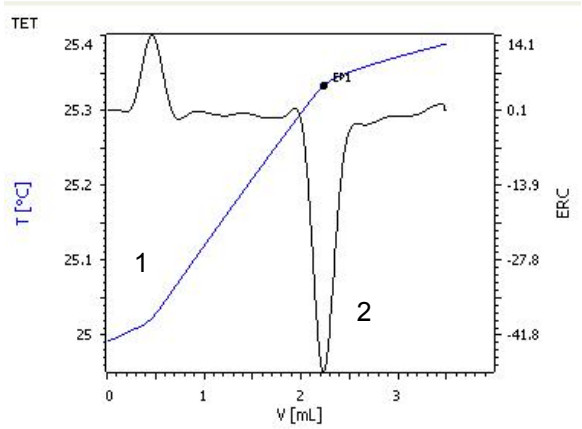
	Full cream milk	Low fat milk
Nutrition Information on label mg Na/100 mL	46	67
Titrotherm mg Na/100 mL	51.7±0.38 (n=8)	55.4±0.32 (n=9)

	Skim milk with milk solids and milk calcium
Nutrition Information on label mg Na/100 mL	69
Titrotherm mg Na/100 mL	62.7±0.26 (n=9)

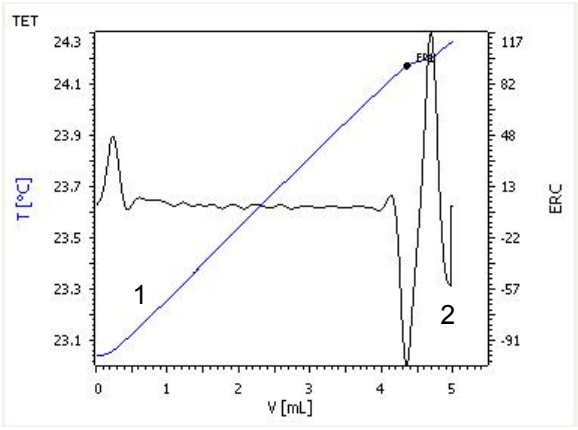
Titration plots



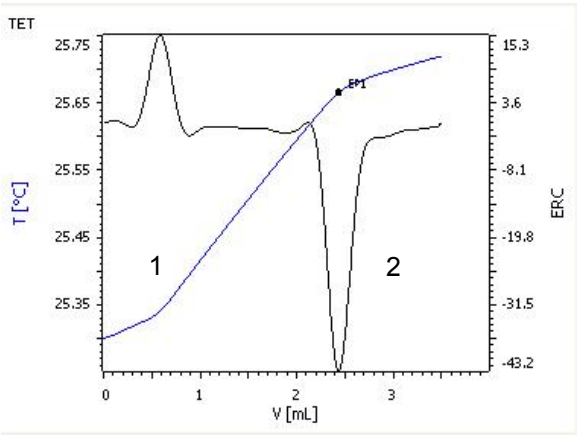
Na in full cream milk



Na in low fat milk



Na in skim milk with added milk solids and milk calcium



Standardization of Al-K titrant with NaCl solution

Notes

1 = solution temperature
2 = second derivative curve (for endpoints)

EP1 = sodium endpoint (exothermic reaction, negative endpoint "peak")

Notes on safe working and disposal of residues

$NH_4F{\cdot}HF$ ("ammonium bifluoride") and its solutions are toxic and corrosive. Adhere to recommendations in MSDS documentation. Wear appropriate protective clothing. $NH_4F{\cdot}HF$ may be decomposed by treating with H_3BO_3 (boric acid). Disposal of solutions and residues containing $NH_4F{\cdot}HF$ should be in accordance with local regulations. It is strongly recommended to automatically dispense $NH_4F{\cdot}HF$ solutions using a Dosino equipped with an ETFE dosing unit. The storage bottle should be of polypropylene.

CCl_3COOH (trichloroacetic acid) and its solutions are toxic and corrosive. Wear appropriate protective clothing. Adhere to recommendations in MSDS documentation. Disposal of CCl_3COOH solutions and residues containing CCl_3COOH should be in accordance with local regulations.

Residues containing both $NH_4F.HF$ and CCl_3COOH should be disposed of as for CCl_3COOH residues alone.