pH and Acidity in Milk

DOC316.52.93099

Endpoint potentiometric titration
Scope and application: Milk

1. Introduction

This working procedure refers to the determination of titratable acidity in milk.

2. Principle

The protocol rests on a weak acid titration by a strong base.

The equivalent volume is determined from the pH jump in endpoint mode. By default, the endpoint pH value is set to 8.4.

Acidity is given in dg of lactic acid per L of milk (also called Dornic degree), in mL of 0.1N NaOH per L of milk and in Soxhlet-Henkel degree (i.e. in mL of 0.25N NaOH per 100 mL of milk).

3. Electrode and reagents

Electrodes: Intellical combined pH electrode with integrated temperature sensor, PHC725

Titrant: NaOH 0.1 eq/L. Use a commercial solution or dissolve 4.00 g of sodium hydroxide in 1 L of CO_2-free boiled water

Standard for titrant calibration: Dihydrate oxalic acid**,** molar weight = 126.07 g/mol

pH standards: Colored 4.01, 7.00, 10.01 (part numbers 2283449, 2283549, 2283649)

Deionized water

4. Ranges and settings

4.1. Default parameters

The working procedure is described using the following parameters:

- V sample = 30 mL
- Syringe volume = 10 mL

4.2. Working range

For most samples, 1 syringe (10 mL) of titrant should be sufficient to reach the equivalent point. It provides the following range:

Veq (mL)	1.5	9.5
Acidity in dg/L of lactic acid	4.5	28.5
Acidity in mL of 0.1N NaOH/L	50	315
Acidity in °S-H	2	13

The syringe is allowed to refill once during titration, so the range is widened:

Veq (mL)	1.5	19
Acidity in dg/L of lactic acid	4.5	57.0
Acidity in mL of 0.1N NaOH/L	50	630
Acidity in °S-H	2	25

4.3. Settings

4.3.1. pH in milk

Name	Default parameter	Unit
Probe		
Recommended probe	PHC725	
Stirring		
Stirring speed	15	[%]
Stirring time	15	[s]
pH measurement		
Stirring speed	0	[%]
Measured parameter		[pH]
Stability criteria	0.05	[pH/min]
Stability max time	120	[s]

4.3.2. Acidity in milk

Name	Default parameter	Unit
Sample		
Name	Milk	
Amount	30	[mL]
Amount min	0	[mL]
Amount max	35	[mL]
Titrant		
Name	NaOH	
Titrant concentration	0.1000	[eq/L]
Syringe	Syringe 1	
Probe		
Recommended probe	PHC725	
Leveling		
Active	no	
Time	30	[s]
EP titration		
Stirring speed	20	[%]
Measured parameter		[pH]
Predose	0	[mL]
Max volume stop point	20	[mL]
Stop on last EQP	True	
Delay	0	[s]
Min increment size	0.2	[mL]
Max increment size	1.5	[mL]
EP Ordinates	8.4	[pH]
Result 1 name	Veq	
R1 hide	Yes	
Result 2 name	Acidity (g/L lactic acid)	
R2 hide	Yes	
Result 3 name	Acidity (dg/L lactic acid)	
R3 hide	No	
R3 resolution	2 decimals	
R3 min	0	[dg/L]
R3 max	60	[dg/L]
R3 QC min	0	[dg/L]
R3 QC max	60	[dg/L]
Result 4 name	Acidity (mL of 0.1N NaOH /L)	
R4 hide	No	
R4 resolution	2 decimals	
R4 min	0	[mL/L]
R4 max	670	[mL/L]
R4 QC min	0	[mL/L]

R4 QC max	670	[mL/L]
Result 5 name	Soxlet-Henkel acidity	
R5 hide	No	
R5 resolution	2 decimals	
R5 min	0	[°S-H]
R5 max	27	[°S-H]
R5 QC min	0	[°S-H]
R5 QC max	27	[°S-H]

4.4. Modification of the settings

The parameters are defined in order to have the best compromise between accuracy and titration time.

For higher concentration with a high titrant volume, titration time can be reduced with an addition of titrant (predose) at the beginning of the titration. Enter the predose volume (in mL) and the stirring time after the addition in the application edit window.

5. Titration procedure

5.1. Leveling

To use this method, an external pump is required. All elements (probes, tubes from the titrator and the tube from the external pump) have to be well installed on the probe holder. The beaker has to contain a level of sample higher than the position of the tube of the external pump. When the beaker is attached to the probe holder, this method allows the system to automatically remove the excess sample by a defined pump working time, and always keep the same sample volume before launching the analysis.

In order to define this volume, autoleveling calibration sequence has to be previously executed (see section **9.3 Autoleveling calibration**).

When this option is active, the working time of the external pump must be set (default 30 s). The minimum working time must allow the pump to be removing air during the last few seconds of the external pump activation.

Note: *Do not forget to re-edit the sample amount with the expected value when deactivating the leveling method.*

5.2. Titration

Rinse the pH probe with deionized water. If leveling is disabled, use a pipette to collect precisely 30 mL of sample.

Pour the sample into the 50 mL polypropylene beaker. Put in a magnetic stir bar, dip the probe and the delivery tip in the solution. Start the application.

At the end of the titration, a first window displays the result. A second window displays the titration curve and the equivalent point coordinates.

After the titration, there are two possibilities:

- Replicate the sample. This is used to study the repeatability by analyzing several samples successively. At the end of each titration, a window displays the average value, the standard deviation (SD) and the relative standard deviation (RSD in %).
- Analyze a new sample. Another titration can be started but no Standard Deviation and RSD value will be made.

6. Results

6.1. Result calculation

The calculations used are:

$$\text{Acidity (dg/L)} = \frac{C_{\text{titrant}}\,(\text{eq/L}) \times V_{\text{titrant}}\,(\text{mL})}{n_{\text{e- lactic acid}} \times n_{\text{e- titrant}} \times V_{\text{sample}}\,(\text{mL})} \times M_{\text{lactic acid}}\,(\text{g/mol}) \times 10$$

$$= \frac{0.1\,(\text{eq/L}) \times V_{\text{titrant}}\,(\text{mL})}{1 \times 1 \times 30\,(\text{mL})} \times 90.08\,(\text{g/mol}) \times 10$$

$$\text{Acidity (mL 0.1N NaOH/L)} = \frac{V_{titrant}\ (mL)}{V_{sample}\ (mL)} \times \frac{1000}{0.1} \times C_{titrant}\ (eq/L) \times FX$$

$$\text{Acidity (°S-H)} = \frac{V_{titrant}\ (mL)}{V_{sample}\ (mL)} \times \frac{100}{0.25} \times C_{titrant}\ (eq/L) \times FX$$

The factor FX (1 by default) has to be changed if the titrant unit is changed, for example:

Titrant titer unit	eq/L	meq/L
Factor FX	1	0.001

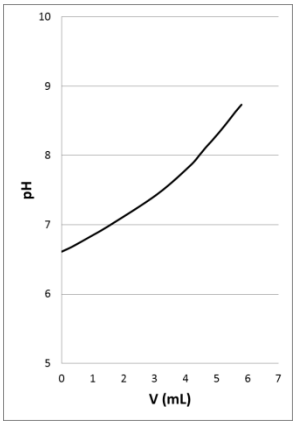
6.2. Experimental results

These results are indicative and have been obtained for a given sample of milk for ten successive determinations.

Measurement	**Parameter**	**Unit**
Mean concentration	15.60	[dg/L of lactic acid]
Standard deviation	0.08	[dg/L of lactic acid]
Relative standard deviation	0.5	[%]
Mean titration duration	43	[s]
Mean analysis duration (pH + acidity)	75	[s]

6.3. Example of a titration curve

This curve has been obtained during the analysis of one of the 10 samples.



7. Recommendations

Always rinse the pH probe and the delivery tip between measurements.

Refill the electrode regularly with KCl saturated solution to maintain the level of internal solution around 1 cm (0.4 inches) below the refill hole.

8. Bibliography

- *Standard ISO 6091:2010*

9. Appendices

9.1. Electrode calibration

For the precision of the titration, it is recommended to calibrate the probe with pH standards at the same temperature as the samples. For calibration, the pH is compensated at 25 °C.

Pour a sufficient amount of the first buffer into a 50 mL beaker and add a magnetic stir bar. Place it on the titrator under the probe holder and dip the probe into the beaker. Start the electrode calibration sequence. Rinse the probe between each buffer. Repeat this operation for each buffer (at least two buffers are recommended).

At the end of the calibration, the results of the slope and offset are displayed and the user can accept or reject this result.

Default settings for electrode calibration

Name	Setting	Unit
Stirring speed	25	[%]
Stability criteria	0.05	[pH/min]
Stability max time	300	[s]
Slope limit min	97	[%]
Slope limit max	102	[%]
Offset limit min	29	[mV]
Offset limit max	89	[mV]

9.2. Titrant calibration

The sodium hydroxide solution can be calibrated. The exact concentration can be determined from an acid-base titration using oxalic acid.

Weigh 30 mg of dihydrate oxalic acid in a 50 mL beaker and use a graduated cylinder to add 25 mL of deionized water. Put in a stir bar, dip the probe and the delivery tip into the solution and launch the titrant calibration sequence. When prompted, type in the exact weighed amount (three digits). At the end of the titrant calibration, titer (eq/L) is displayed and the user can reject, replicate, or save the result.

Default settings for titrant calibration

Name	Default parameter	Unit
Titrant		
Name	NaOH	
Titrant concentration	0.1000	[eq/L]
Syringe	Syringe 1	
Standard		
Name	Oxalic acid	
Amount	30	[mg]
Amount min	25	[mg]
Amount max	40	[mg]
Molar weight	126.07	[g/mol]
EP titration		
Stirring speed	25	[%]
Measured parameter		[pH]
Predose	2	[mL]
Max volume stop point	8	[mL]
Stop on last EQP	True	
Delay	0	[s]
Min increment size	0.08	[mL]
Max increment size	0.8	[mL]
EP Ordinates	8.55	[pH]
Result name	Titer	
Result resolution	4 decimals	
Result min	0.09	[eq/L]
Result max	0.11	[eq/L]

9.3. Autoleveling calibration

The aim of this method is to calibrate the volume of sample by leveling. The result of this calibration will be used as sample volume for the following titrations.

This option is **ONLY** available from the calibration menu if **Method Leveling** is set to Active (**Yes**). Refer to the documentation delivered with the external pump for a correct installation, paying particular attention to the suction tube from the pump.

Prepare a 0.007 mol/L oxalic acid solution: dissolve 0.882 g of dihydrate oxalic acid in 1 L of deionized water. Pour a sufficient amount of the solution into a beaker allowing the external pump tube to be immersed in the liquid. In the calibration menu select **Autoleveling calibration** and then **pH acidity in milk**.

The result in mL is compared to minimum and maximum amounts defined for the sample volume. The calculation used is:

$$V_{sample} = \frac{V_{titrant}(mL) \times C_{titrant}\ (eq/L)}{n_{e-\ oxalic\ acid} \times C_{oxalic\ acid\ solution}\ (mol/L)}$$

$$= \frac{V_{titrant}(mL) \times 0.1\ (eq/L)}{2 \times 0.007\ (mol/L)}$$

Autoleveling calibration uses the same settings as for a titrant calibration (see section **9.2 Titrant calibration**).

Default settings for autoleveling calibration

Name	Default parameter	Unit
Sample		
Amount min	0	[mL]
Amount max	35	[mL]
Autoleveling calibration		
Solution name	Oxalic Acid	
Concentration	0.007	[mol/L]
Resolution	3 decimals	

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