Heat stability of milk

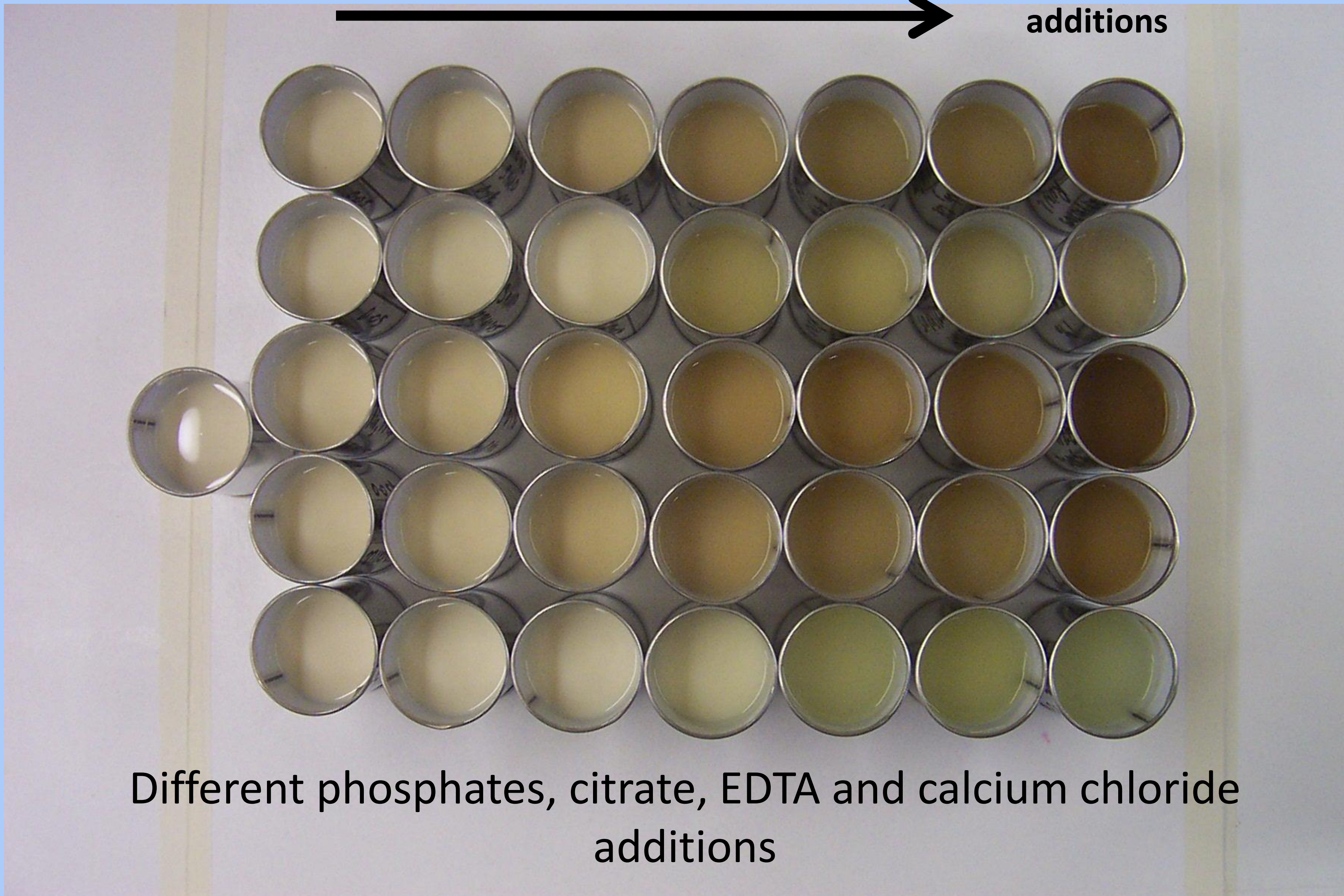
Mike Lewis

Heat Stability

- Poor heat stability may influence the following operations:

- Pasteurisation
- Sterilisation
- UHT
- In-container (especially concentrates)
- Evaporation

Milk sterilised at 120 C for 15 min



Different phosphates, citrate, EDTA and calcium chloride additions

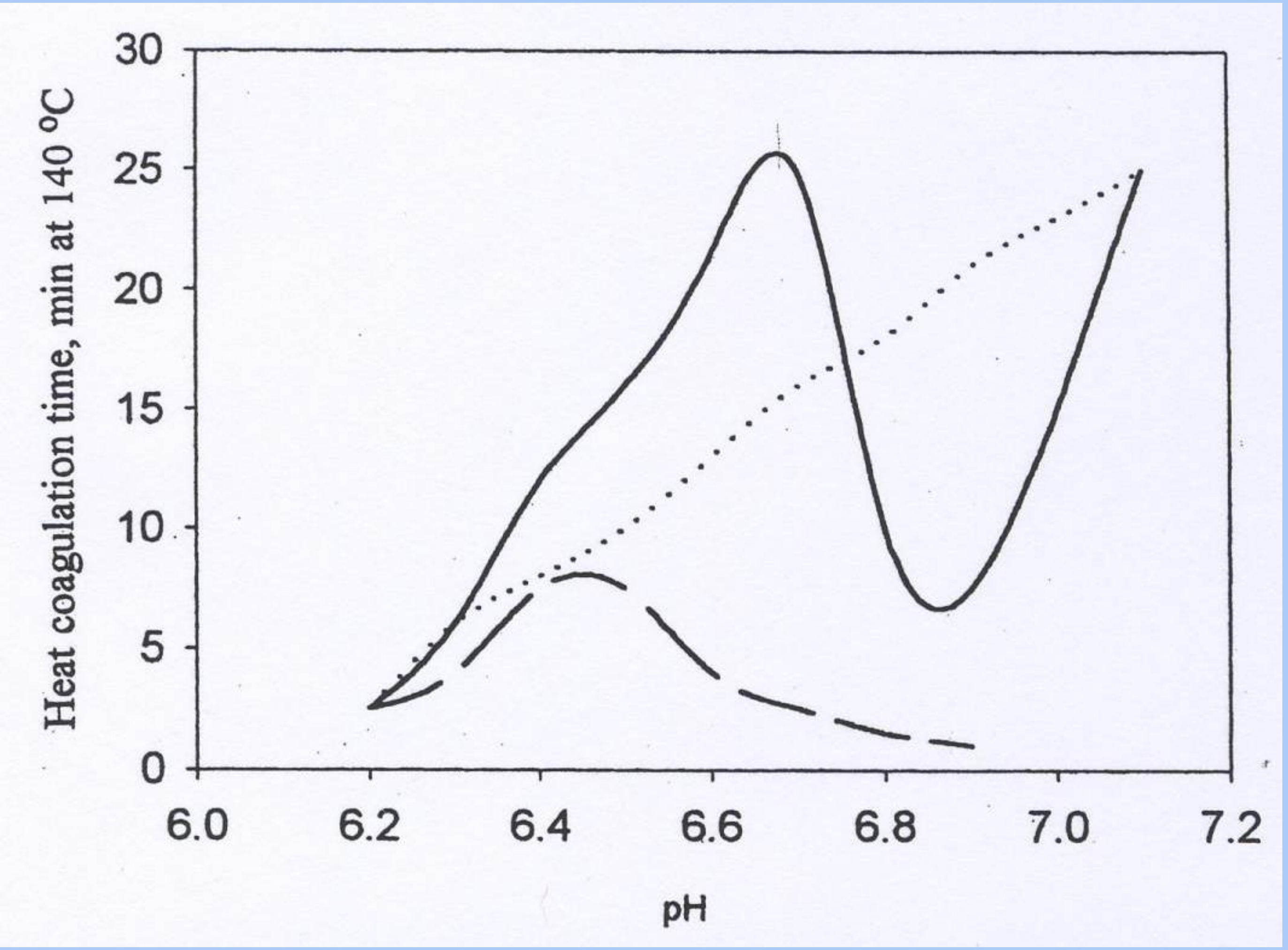
Effects of poor heat stability

- In UHT treatment, milk having poor heat stability can give rise to fouling of heat exchangers and sediment formation. It is best to avoid UHT treating such milk.
- These problems may be encountered to a lesser extent in pasteurisation and ESL milks
- Evaporators may also be susceptible to fouling and hence to longer cleaning regimes
- Fouling of membranes also occurs

Methods for assessing heat stability

- Heat coagulation temperature
- Heat coagulation time
- Viscosity measurement
- Heat exchanger fouling
- Sediment formation
- Coagulation
- Casein micelle size
- **Two main determinants of heat stability are pH and ionic calcium**

Heat coagulation time-pH profiles



Some observations on this method

- Why does heat stability go through a maximum and minimum.
- As pH is increased, Ca2+ decreases, micelles are less susceptible to coagulation.
- At pH maximum, K-casein dissociation occurs, this has a destabilising effect
- However at minimum, Ca2+ is further educed and this becomes the dominating influence

- There is an element of subjectivity in determining the point at which coagulation first takes place.
- However, it is claimed that it is possible to obtain reproducible results with practice.
- A variant on this procedure is to determine the heat coagulation temperature, which is the temperature required to coagulate milk in a given time period (Rose, 1962; Horne and Muir, 1990).

Noteworthy Observations

- However, despite all the research work, problems related to poor heat stability of milk are still encountered in commercial processes.
- Singh (2004) stated that the heat coagulation time (heat stability) often correlates very poorly with the stability of milk on commercial sterilization.
- He also pointed out that from an industry point of view, the use of a pilot scale or laboratory scale sterilizer which simulates sterilization conditions used in practice provides more reliable results and prediction of behaviour of milk in commercial plants, although this is not possible without access to pilot plant facilities.

Some studies on pH and ionic calcium relationships in cow's and goat's milk

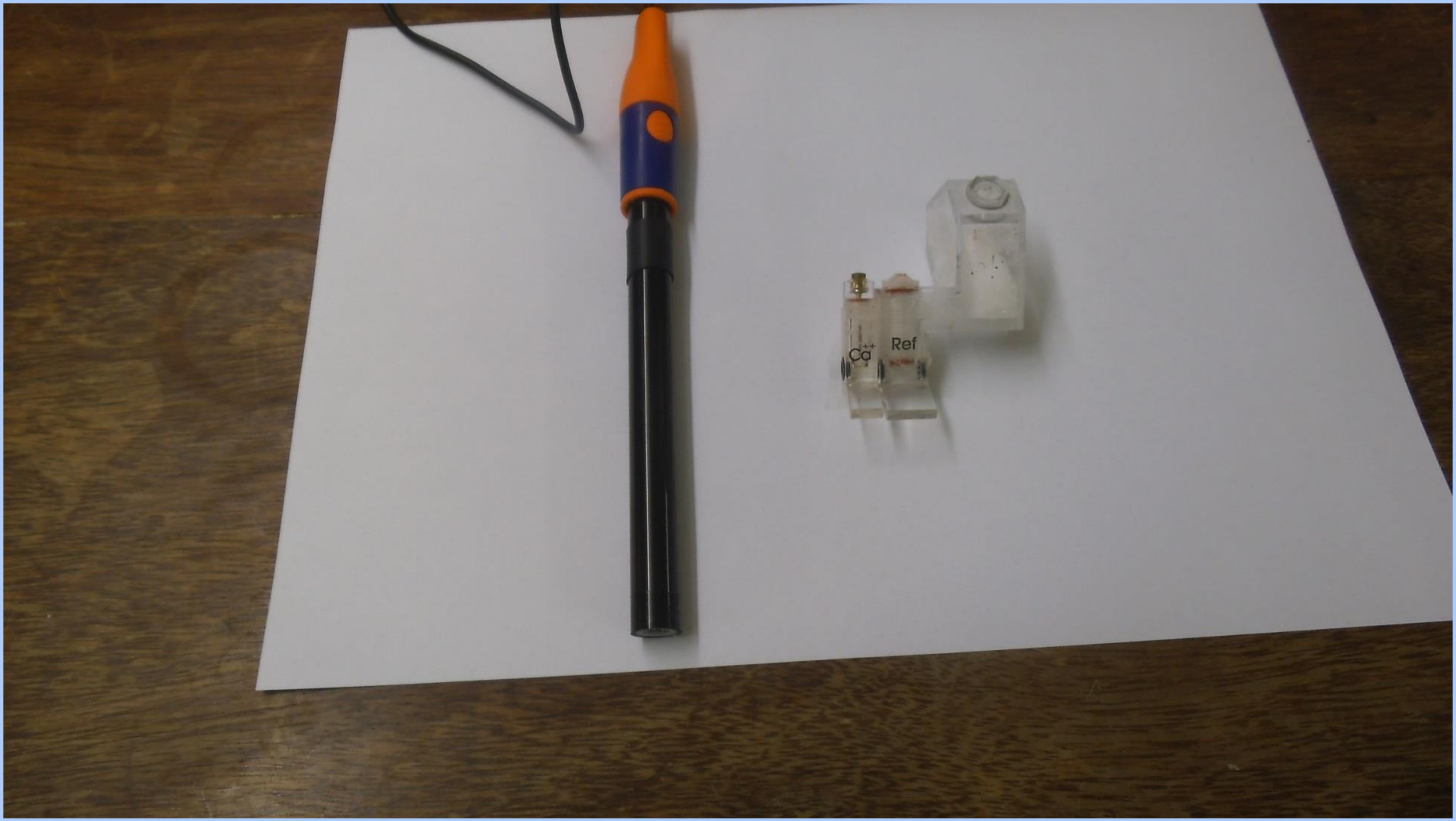
Total calcium and ionic calcium in milk of different species (average values)

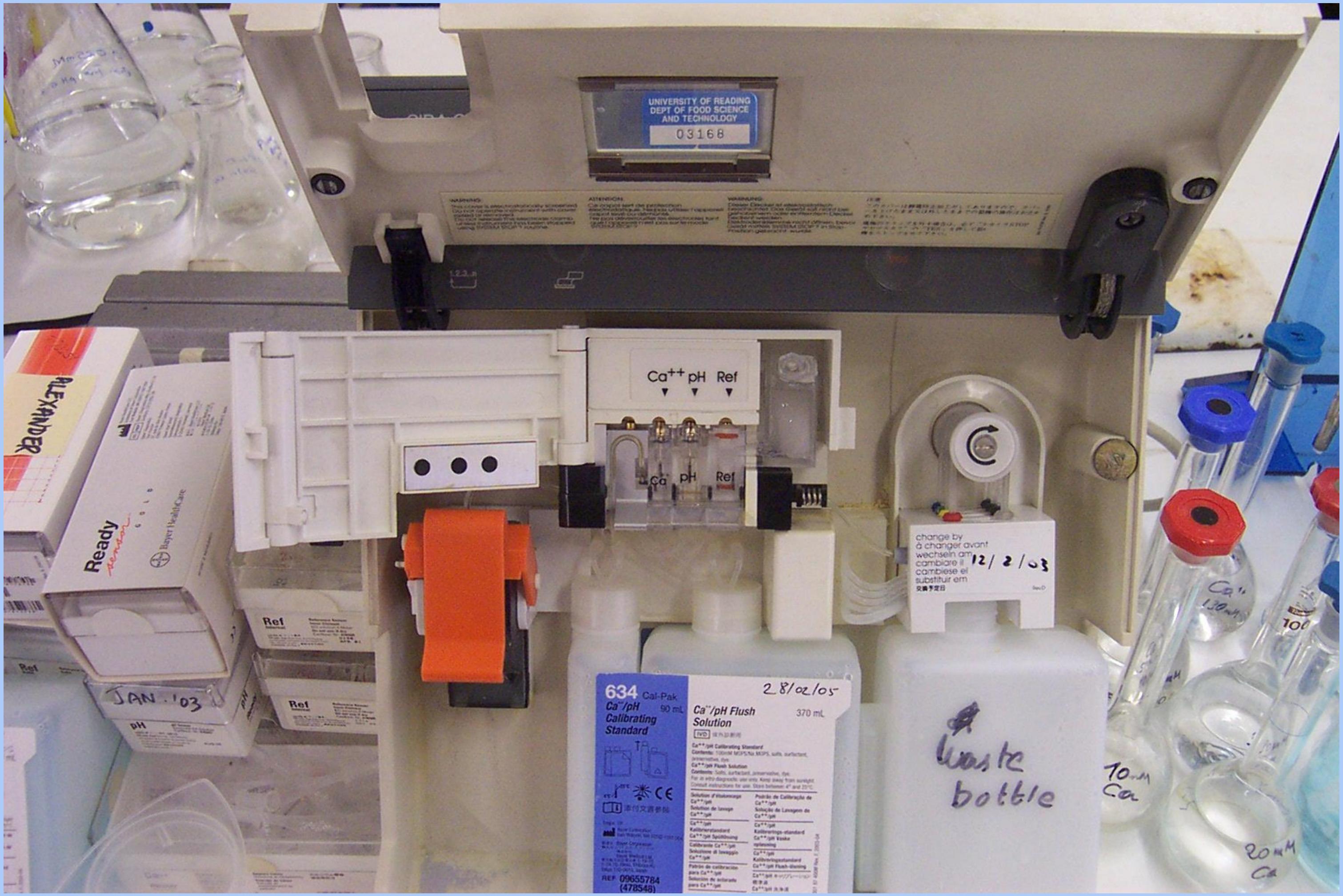
	Total Calcium (mM)	Ionic calcium (mM)
Human	7.5	3.0
Cow	30	1.80
Goat	34	2.67
Sheep	55	2.01
Mouse	71	?
Human Blood	**2.05-2.5**	**1.1 – 1.32**

Measuring ionic calcium in milk

- **Ion-exchange** equilibration, Christianson et al. (1954).
- **Murexide** complexing agent, Tessier and Rose (1958); White and Davis (1958).
- Use of an **ion selective electrode** designed for measuring calcium in blood (measures activity).
- Development of **standards** with pH (6.7) and ionic strength (81mM) similar to milk
- **Calibration** of the system prior to use daily: (with five standards, over range 0.25 to 3.00 mM)

Immersion type and flow-though electrodes

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12/2/03
634 Cal-Pak
Ca++/pH Calibrating Standard
90 mL
Ca++/pH Flush Solution
370 mL
28/02/05
Waste bottle
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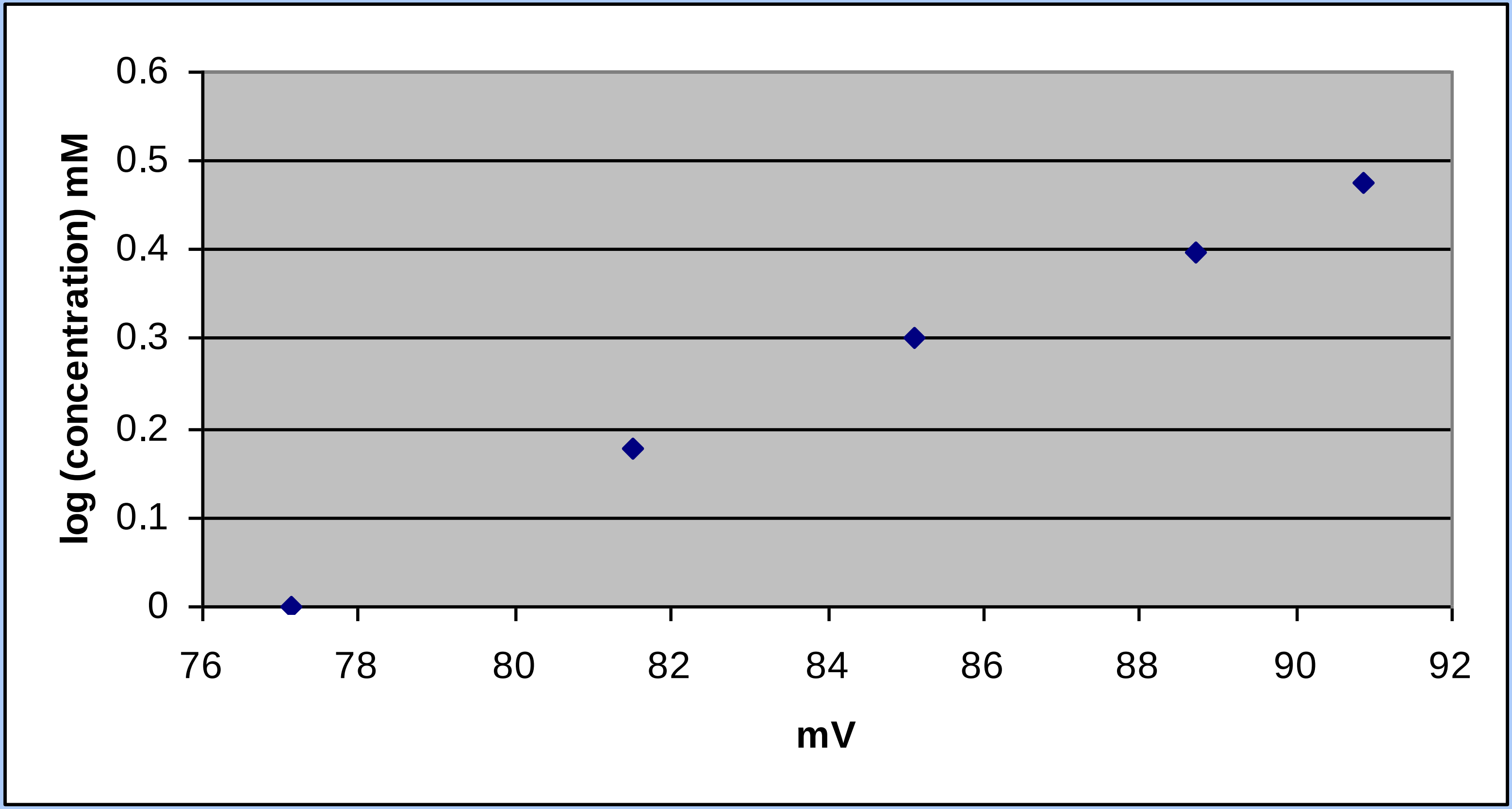
JAN. '03
Ready
Bayer HealthCare
Ref
pH
10 mM Ca
20 mM Ca

Calibration for ionic calcium meter



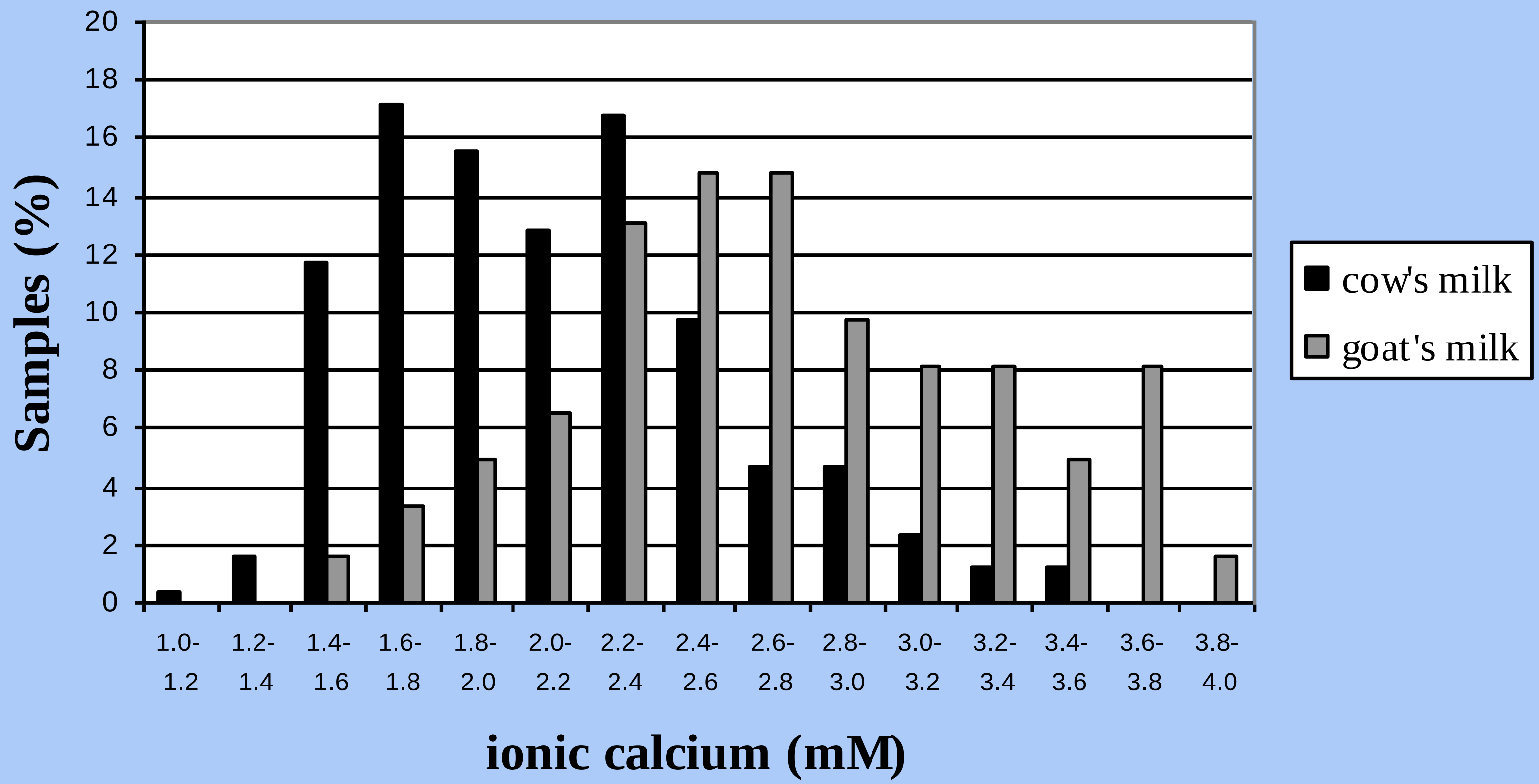
Guidelines for reliable results

- Immersion probe or flow-through probes
- Divalent ions: ~ 29 mV change for 10 fold change in concentration
- 8 to 9 mV per doubling of concentration
- Important to check performance and reproducibility of the electrode
- Calibrate every day prior to use.

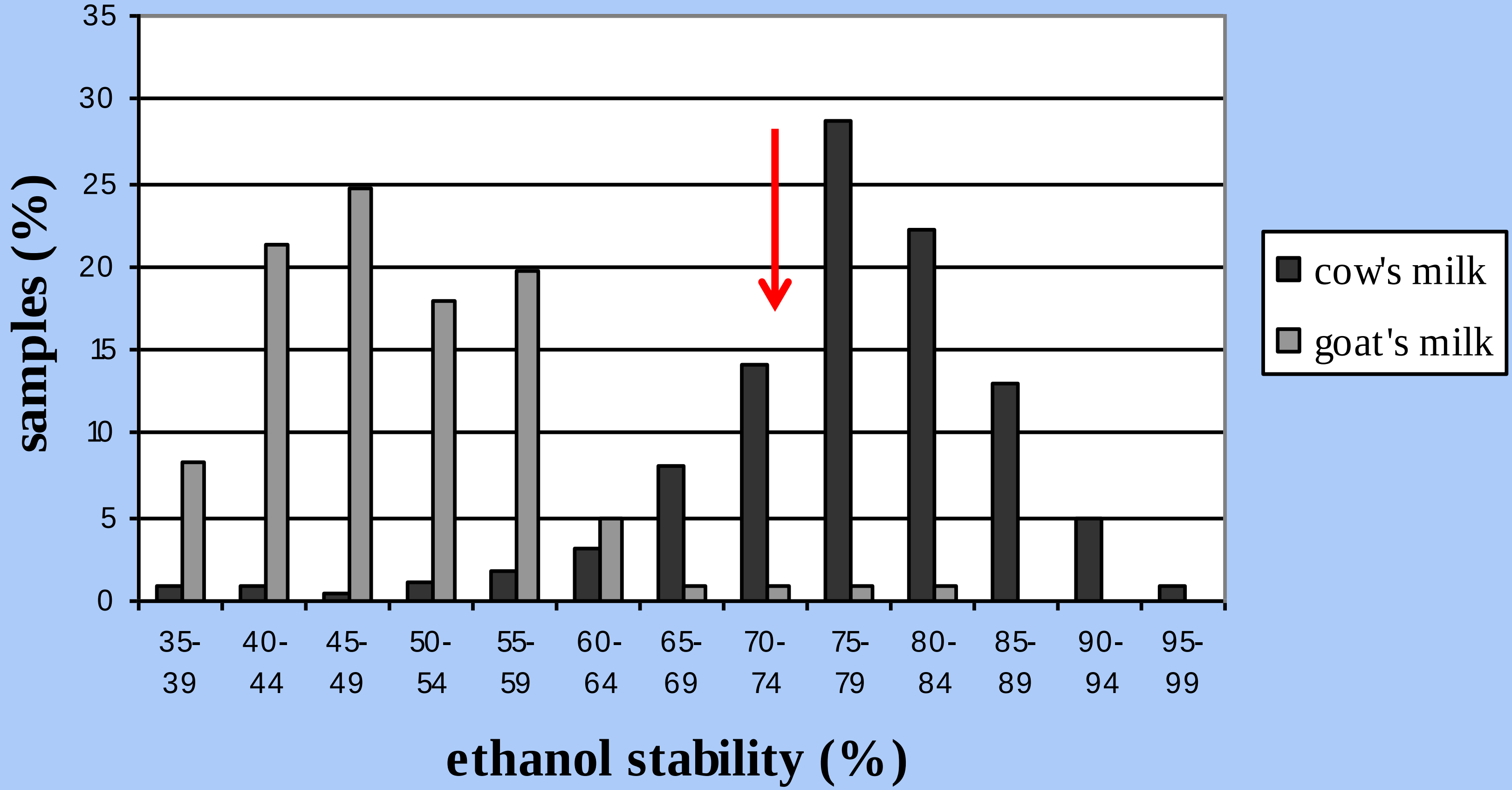
Ionic calcium and alcohol stability for 10 different cows over a complete lactation period

Cow No	Ionic Calcium (mM)		Alcohol stability (%)	
	Mean	sd	Mean	sd
6848	1.53	0.22	84%	5%
227	1.87	0.19	87%	7%
6737	1.92	0.29	79%	7%
6789	1.97	0.41	79%	7%
6653	2.14	0.44	75%	10%
6930	2.23	0.65	78%	12%
36	2.30	0.53	79%	6%
6790	2.38	0.56	72%	11%
6747	2.40	0.38	76%	5%
6596	2.67	0.57	68%	7%

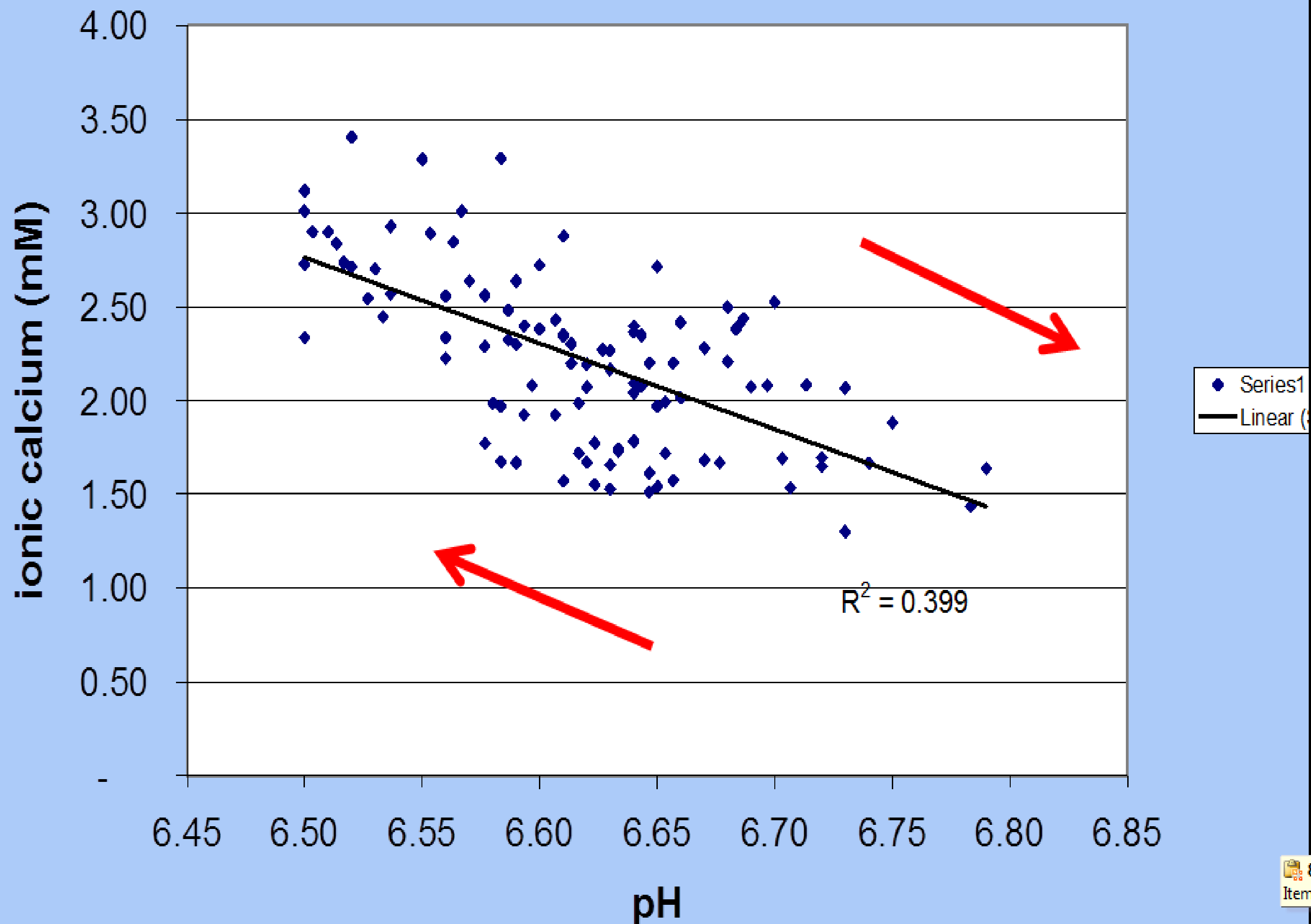
Distribution of ionic calcium in cow’s and goat’s milk



Distribution of ethanol stability in cow's and goat's milk



Relationship between pH and ionic calcium for milk samples from individual cows



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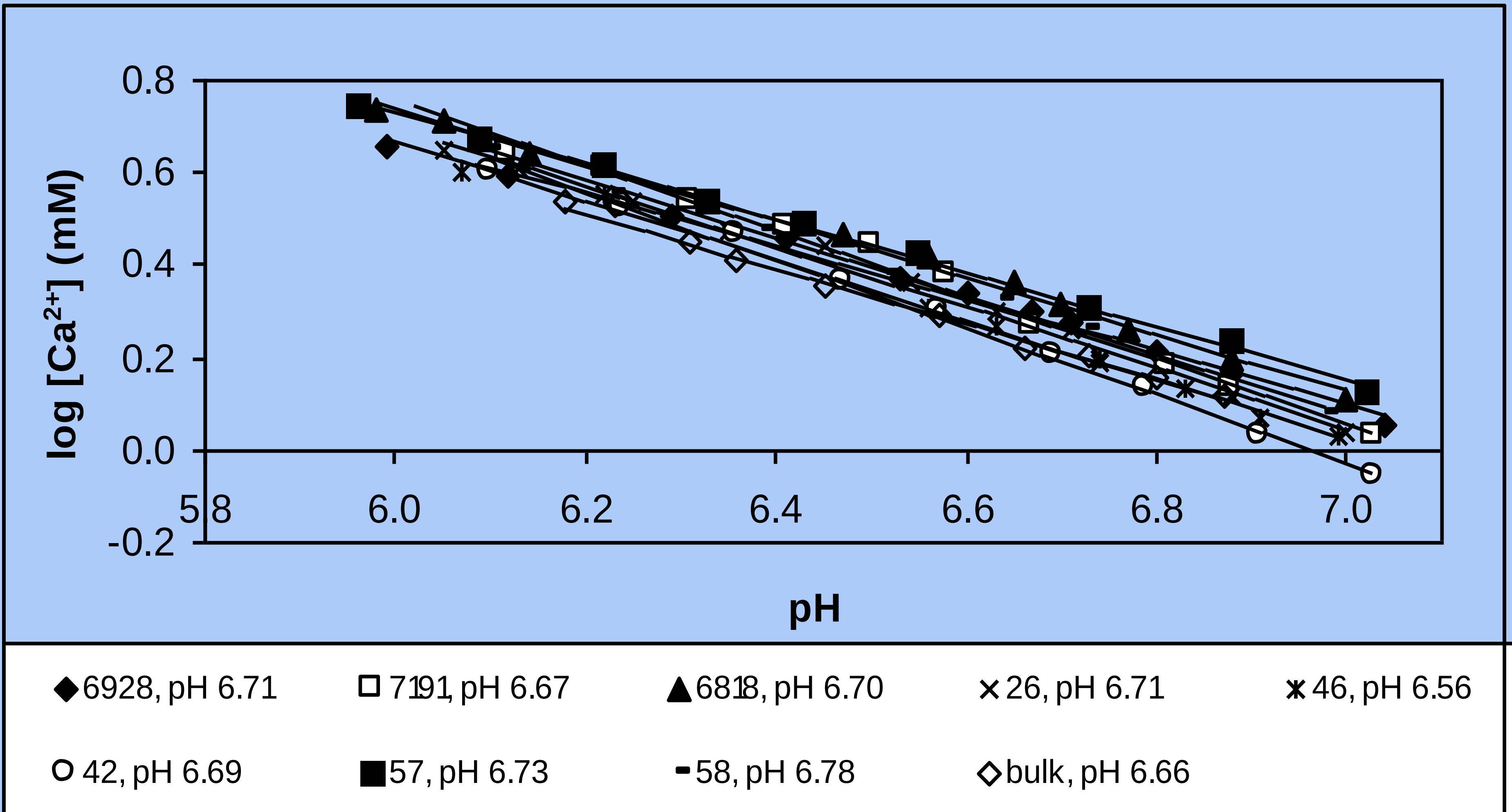
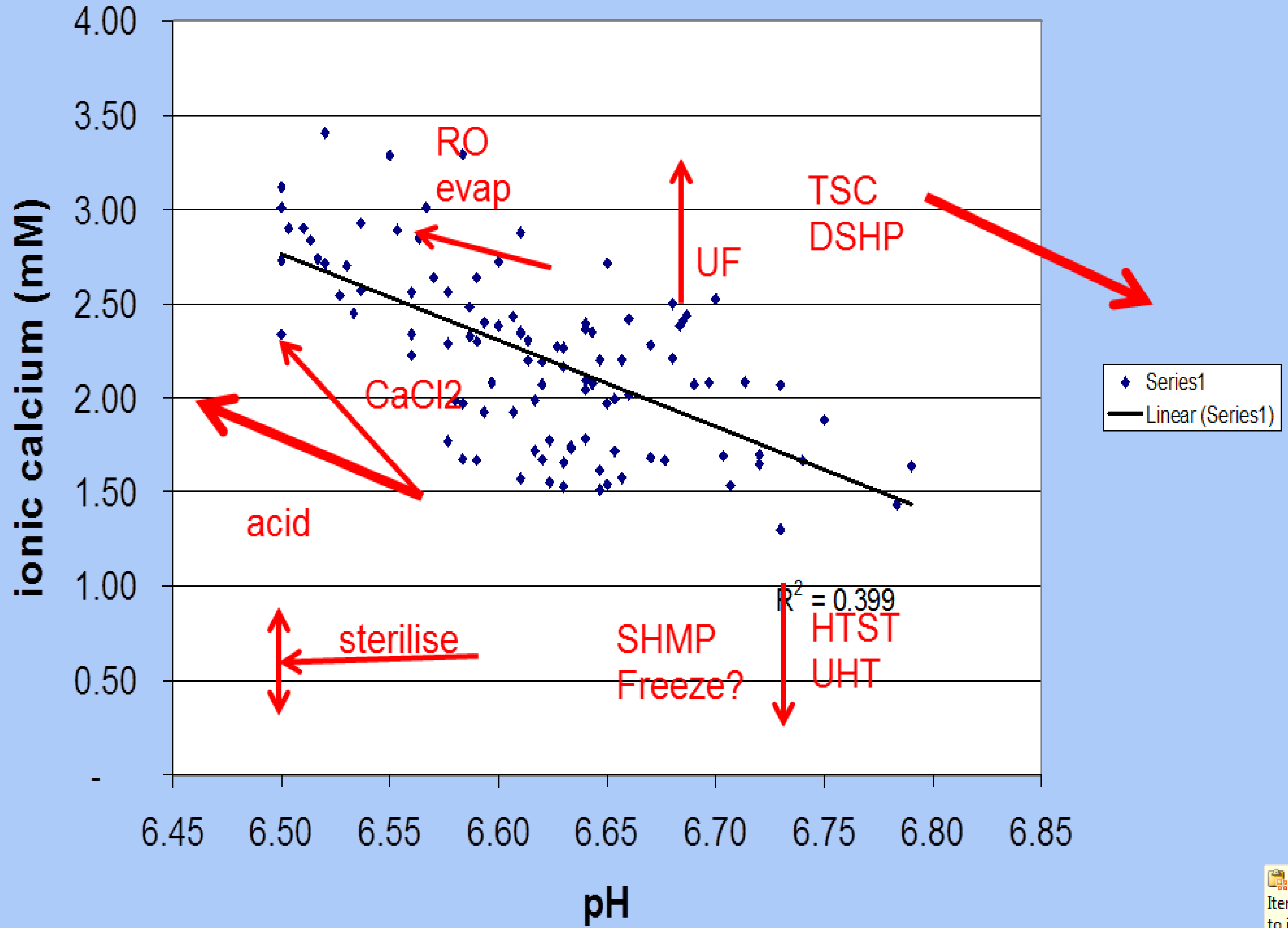
Item collected.

Ionic calcium against adjusted pH for several cows

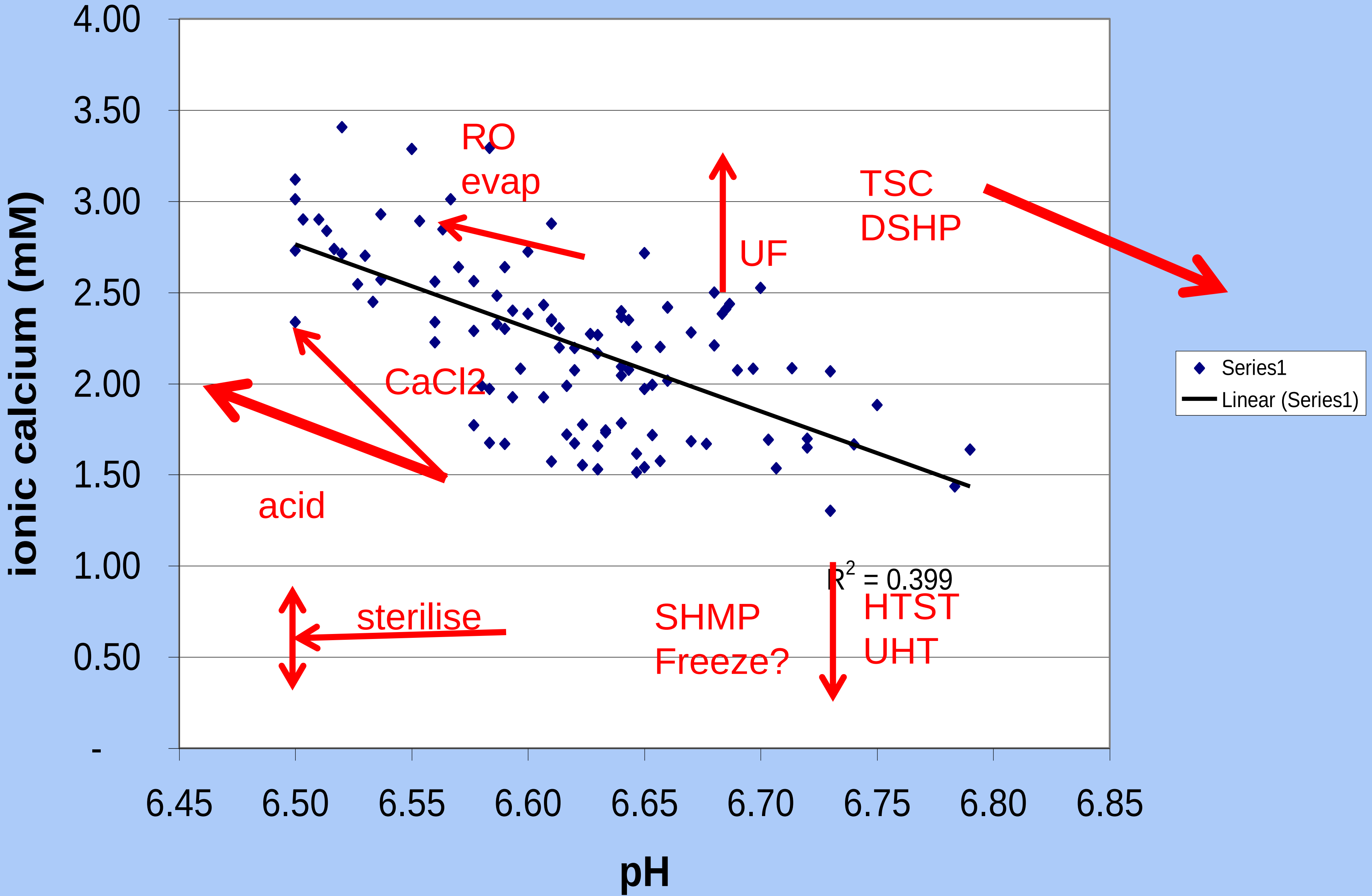


$$3\ Ca^{++} + 2HPO4^{2-} \Leftrightarrow Ca_3PO_4\downarrow + 2H^+$$

Changes in pH and ionic calcium caused by different events



Changes in pH and ionic calcium caused by different events



Salts that could be used

- Trisodium citrate (TSC)
- Dihydrogen sodium phosphate (DHSP)
- Disodium hydrogen phosphate (DHSP)
- Sodium hexametaphosphate (SHMP)
- EDTA (disodium salt)
- EDTA (tetrasodium salt)
- EDTA (disodium,calcium salt)
- Calcium chloride

Some calcium salts

- Calcium carbonates: E170
- Calcium lactate: E327
- Calcium citrates E333
- Calcium phosphates E341
- Calcium chloride E509
- Calcium hydroxide E526
- Calcium gluconate E578
-
- Calcium acetate (E263); calcium tartrate (E354); calcium sulphate (E516); calcium oxide (E529), calcium ferrocyanide (E538), Calcium silicate (E552), calcium diglutamate (E623), calcium guanylate (E628), Calcium Inosinate (E362); calcium 5’-ribonucleotides (E634)
- Calcium DISODIUM ethylene diamine tetra acetate (E385)

Measuring sediment in milk

- Centrifuge milk at ~ 3000 G for 30 min to 1 h
- Useful for assessing heat stability
- Emulsion stability during storage
- All milk contains sediment
- One important question is how much sediment is required before it can be detected by taste?

Heat Stability Measurement (our method)


LABORATORY NOTEBO
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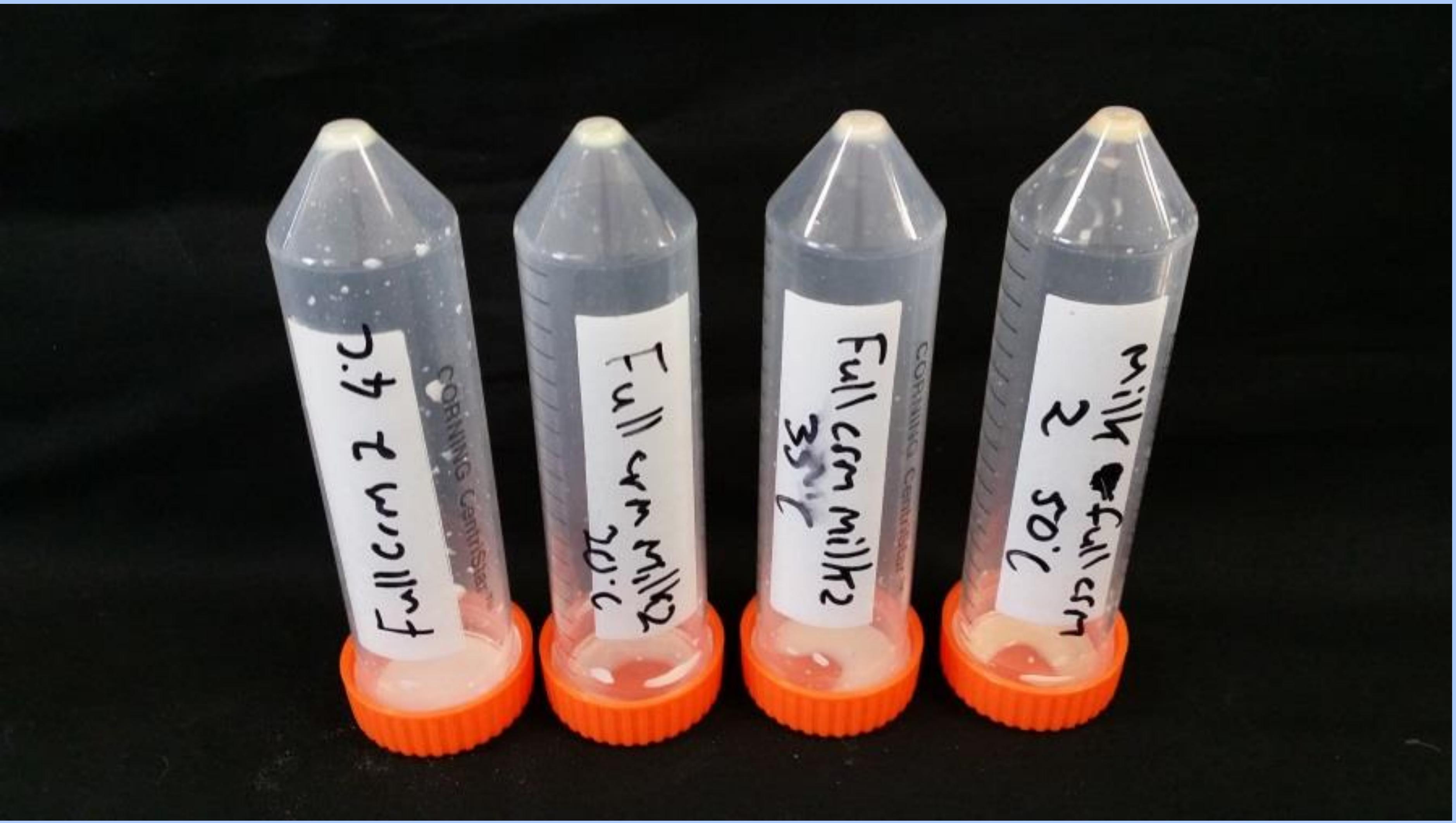
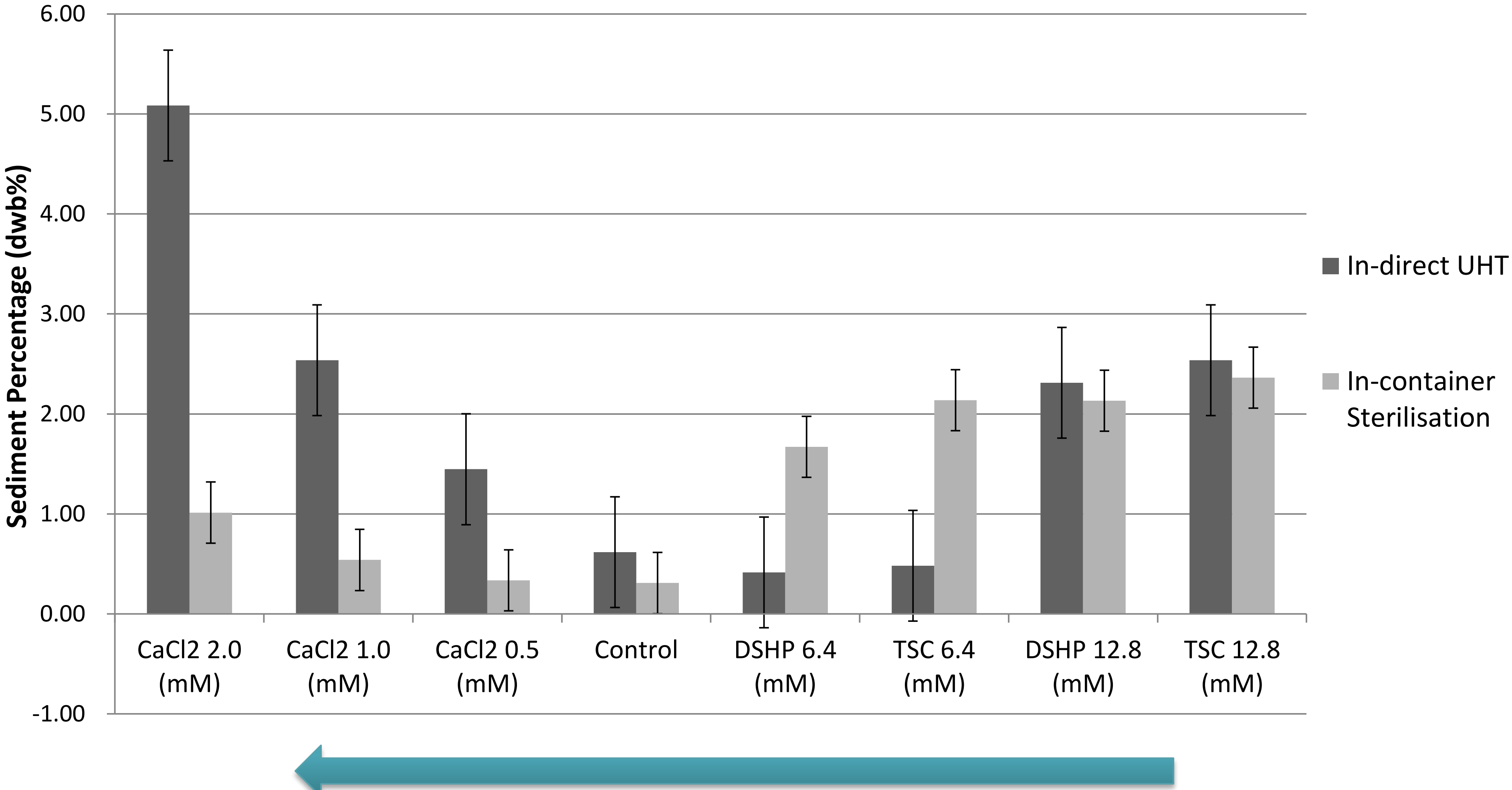
Sediment from whole milk stored for 4 months at different temperatures



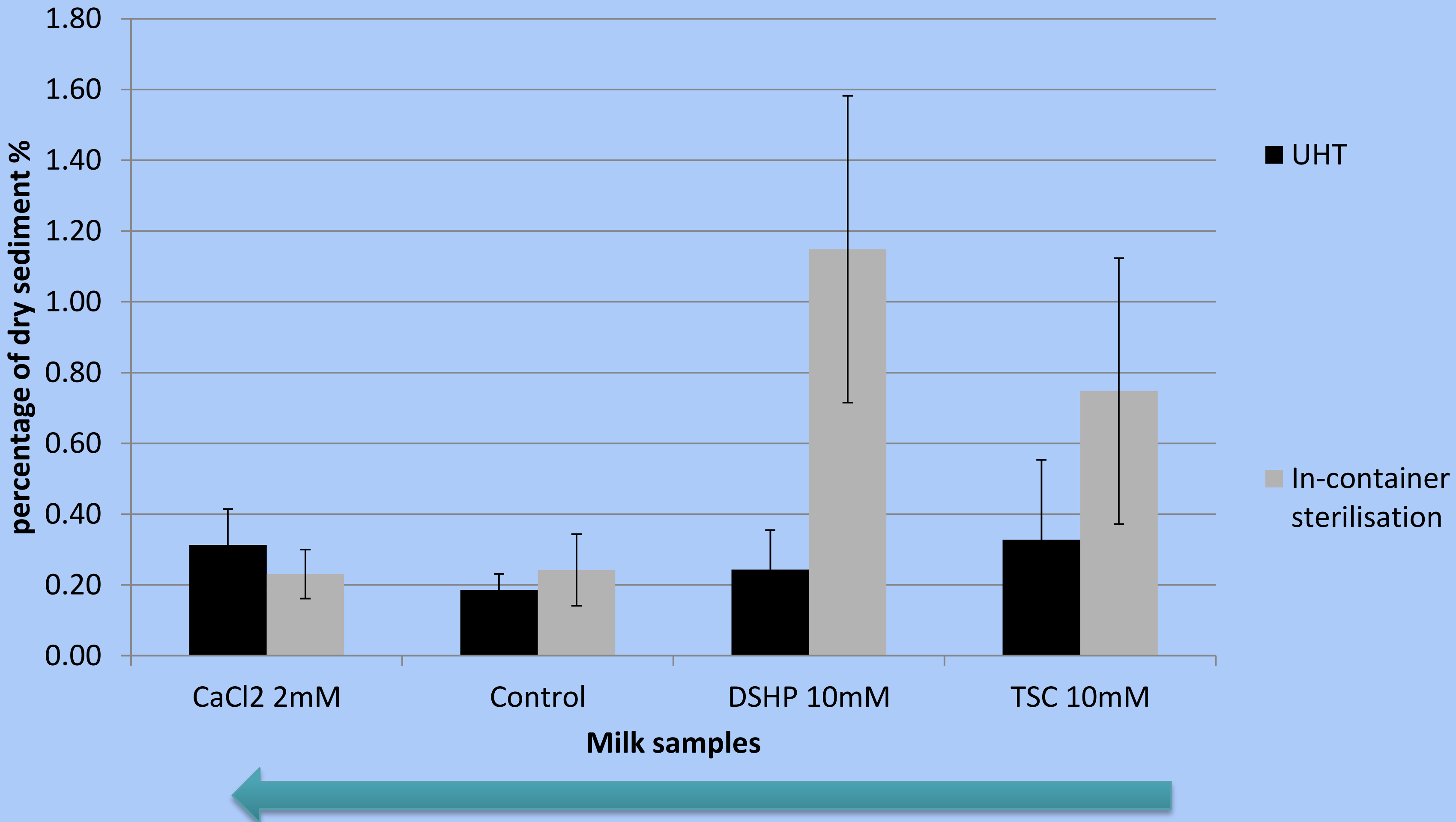
In-container and UHT products

- Comparison studies for goat's milk and cow's milk
- Measuring sediment and casein micelle size
- Making goat milk behave like cow milk and vice versa.
- **One conclusion is that on some occasions there are quite big differences between in-container and UHT sterilisation.**

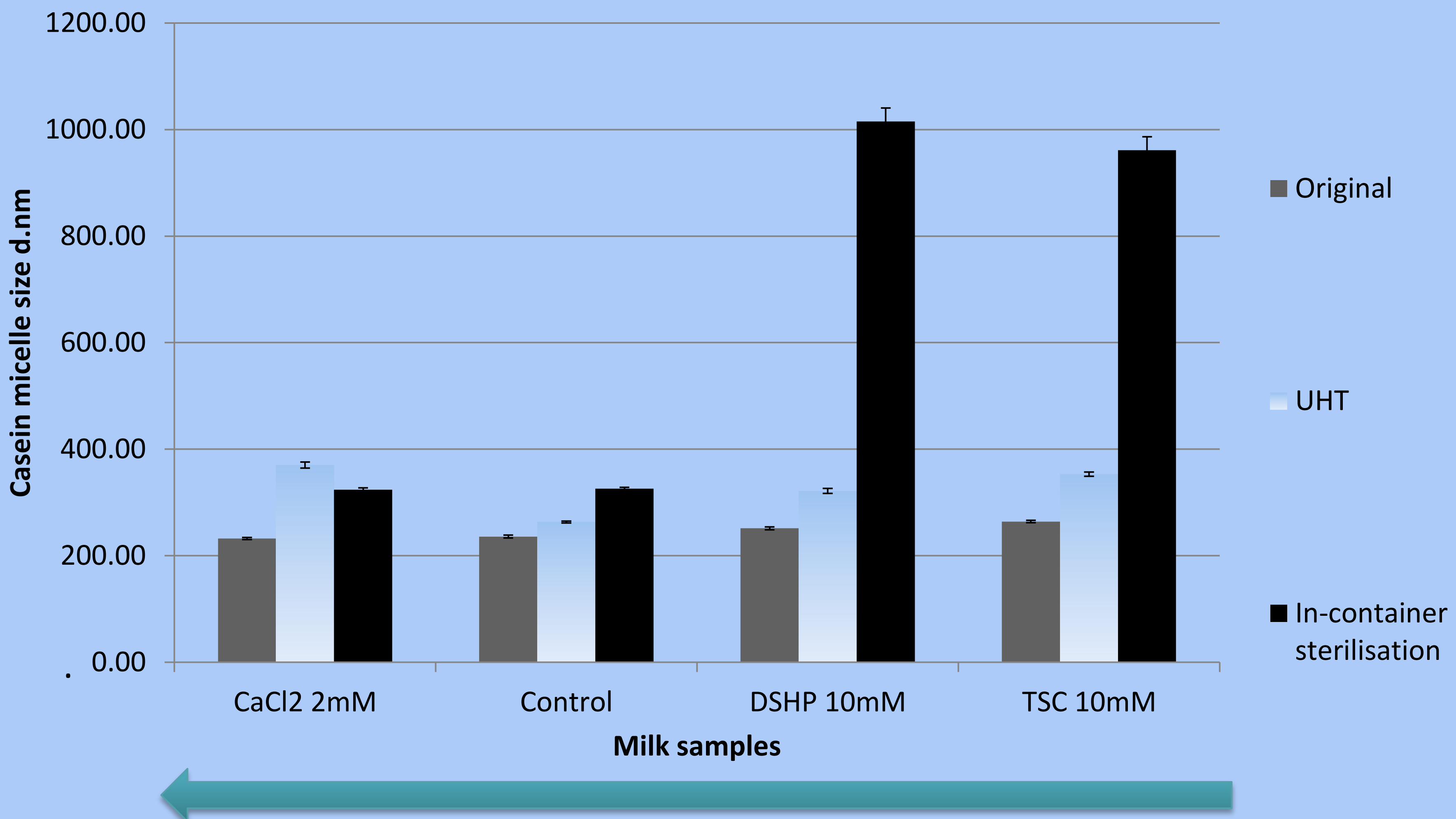
The effect of added DSHP, TSC and $CaCl_2$ on the sediment following UHT and in-container sterilisation for three fully replicated trials for **goat milk**



Bovine milk
The effect of added DSHP, TSC and $CaCl_2$ on the sediment following UHT and in-container sterilisation.



Bovine milk
The effect of added DSHP, TSC and $CaCl_2$ on the casein micelle size following UHT and in-container sterilisation



Thee Effect of added DSHP, TSC and $CaCl_2$ on pH and Ca^{2+} before and after UHT treatment

		Before heat treatment		Indirect UHT	
Properties	**Milk samples**	**Mean±SD**	**Range**	**Mean±SD**	**Range**
pH	*Control*	6.78±0.03[b]	6.70 - 6.85	6.77±0.03[b]	6.71 - 6.83
	10 mM DSHP	6.96±0.03[c]	6.89 - 7.01	6.93±0.03[c]	6.86 - 6.99
	10 mM TSC	7.05±0.03[d]	6.99 - 7.11	7.03±0.03[d]	6.97 - 7.10
	2 mM $CaCl_2$	6.71±0.03[a]	6.65 - 6.78	6.70±0.03[a]	6.64 - 6.76
Ca^{2+} (mM)	*Control*	1.91±0.23[b]	1.38 - 2.29	1.81±0.24[b]	1.43 - 2.44
	10 mM DSHP	0.87±0.10[a]	0.65 - 1.06	0.84±0.13[a]	0.63 - 1.10
	10 mM TSC	0.93±0.13[a]	0.68 - 1.14	0.92±0.13[a]	0.68 - 1.24
	2 mM $CaCl_2$	2.34±0.27[c]	1.81 - 2.84	2.14±0.26[c]	1.75 - 2.63

Table 3. Effect of added DSHP, TSC and $CaCl_2$ on the dry sediment percentage after UHT treatment

PS: SP=Spring; SM=Summer; A=Autumn; W=Winter; NS=Non-significant difference

	Indirect UHT			
Properties	**Milk samples**	**Mean±SD**	**Range**	**Seasonal variation**
Heat stability (Dry sediment %)	*Control*	0.19±0.05[a]	0.10 - 0.29	SM > A and W
	10 mM DSHP	0.24±0.11[ab]	0.12 - 0.62	SP > A and W SM > A
	10 mM TSC	0.33±0.23[b]	0.12 - 1.31	SP > A and W
	2 mM $CaCl_2$	0.31±0.10[b]	0.18 - 0.51	SM > SP, A and W

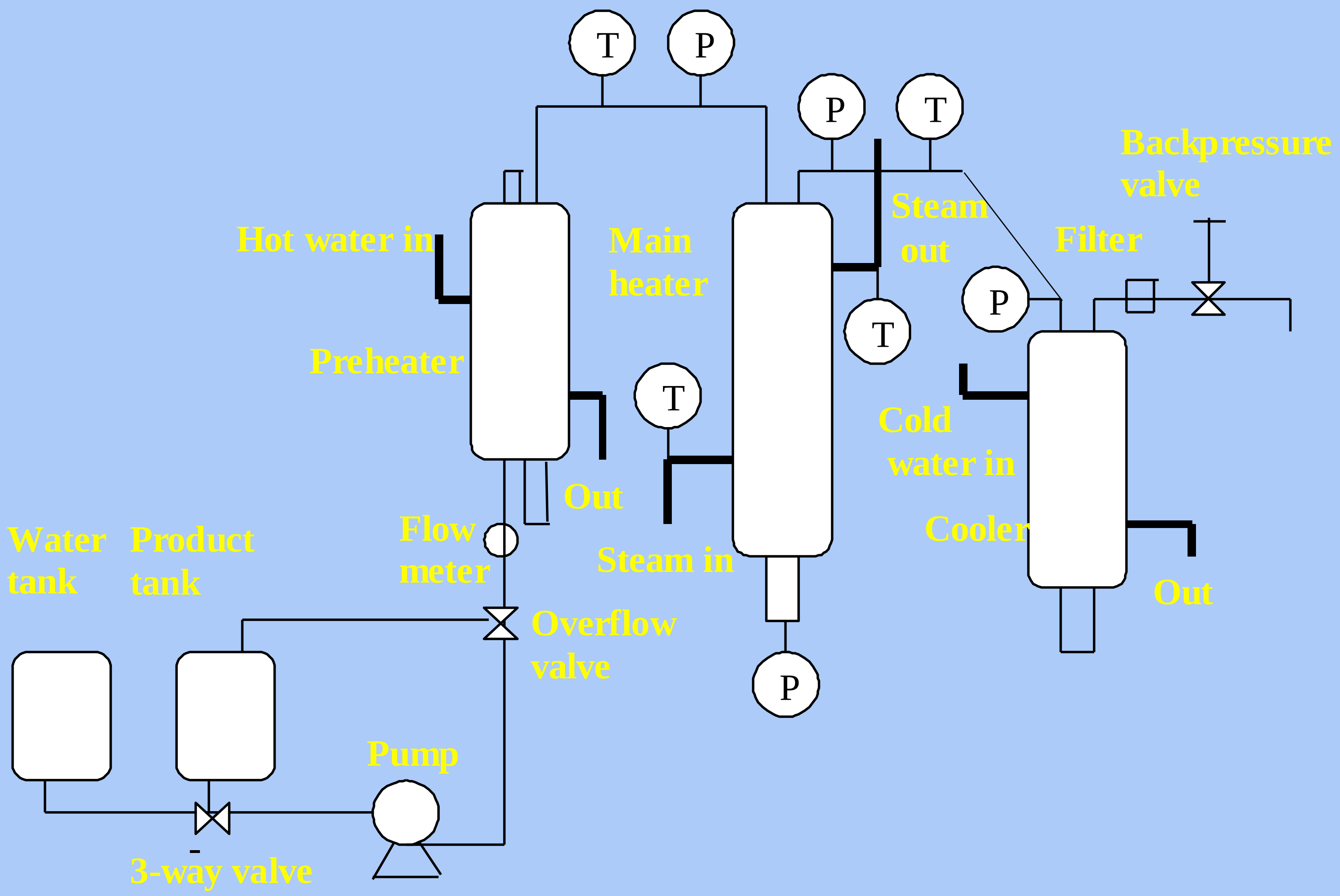
Table 4. Effect of added DSHP, TSC and $CaCl_2$ on pH and Ca^{2+} before and after in-container sterilisation.

		Before heat treatment		In-container sterilisation	
Properties	**Milk samples**	**Mean±SD**	**Range**	**Mean±SD**	**Range**
pH	*Control*	6.78±0.03[b]	6.70 - 6.85	6.62±0.03[c]	6.57 - 6.70
	10 mM DSHP	6.96±0.03[c]	6.89 - 7.01	6.59±0.03[b]	6.52 - 6.65
	10 mM TSC	7.05±0.03[d]	6.99 - 7.11	6.80±0.03[d]	6.70 - 6.86
	2 mM $CaCl_2$	6.71±0.03[a]	6.65 - 6.78	6.55±0.03[a]	6.49 - 6.62
Ca^{2+} (mM)	*Control*	1.91±0.23[b]	1.38 - 2.29	1.85±0.24[c]	1.35 - 2.20
	10 mM DSHP	0.87±0.10[a]	0.65 - 1.06	0.64±0.15[a]	0.36 - 1.13
	10 mM TSC	0.93±0.13[a]	0.68 - 1.14	1.01±0.18[b]	0.72 - 1.44
	2 mM $CaCl_2$	2.34±0.27[c]	1.81 - 2.84	2.23±0.30[d]	1.60 - 2.64

Table 5. Effect of added DSHP, TSC and $CaCl_2$ on the dry sediment percentage after in-container sterilisation
PS: SP=Spring; SM=Summer; A=Autumn; W=Winter; NS=Non-significant difference

In-container sterilisation				
Properties	**Milk samples**	**Mean±SD**	**Range**	**Seasonal variation**
Heat stability (Dry sediment %)	*Control*	0.24±0.10[a]	0.02 - 0.56	NS
	10 mM DSHP	1.15±0.44[c]	0.31 - 1.77	W > A
	10 mM TSC	0.75±0.38[b]	0.16 - 1.65	W > SM and A; SP > A
	2 mM $CaCl_2$	0.23±0.07[a]	0.13 - 0.39	SM > SP

Miniature UHT plant



Monitoring Fouling

- Monitoring temperature, pressure and flow rate and overall heat transfer coefficient.
- OHTC = $U = \dfrac{GC_p\Delta\theta}{A\Delta T_{lm}}$

Where U = overall heat transfer coefficient in kcal/hr-m2

G = mass flow rate in kg/h

Cp = specific heat of milk in kcal/kg -°C

Δθ = Temperature difference in °C

A = surface area of the tubings in m^2

ΔT_{lm} = log mean temperature difference in °C =

[(steam in – milk out)-(steam out – milk in)]/ log [(steam in –milk out)/(steam out – milk in)]

Comparison of cows' and goats' milk

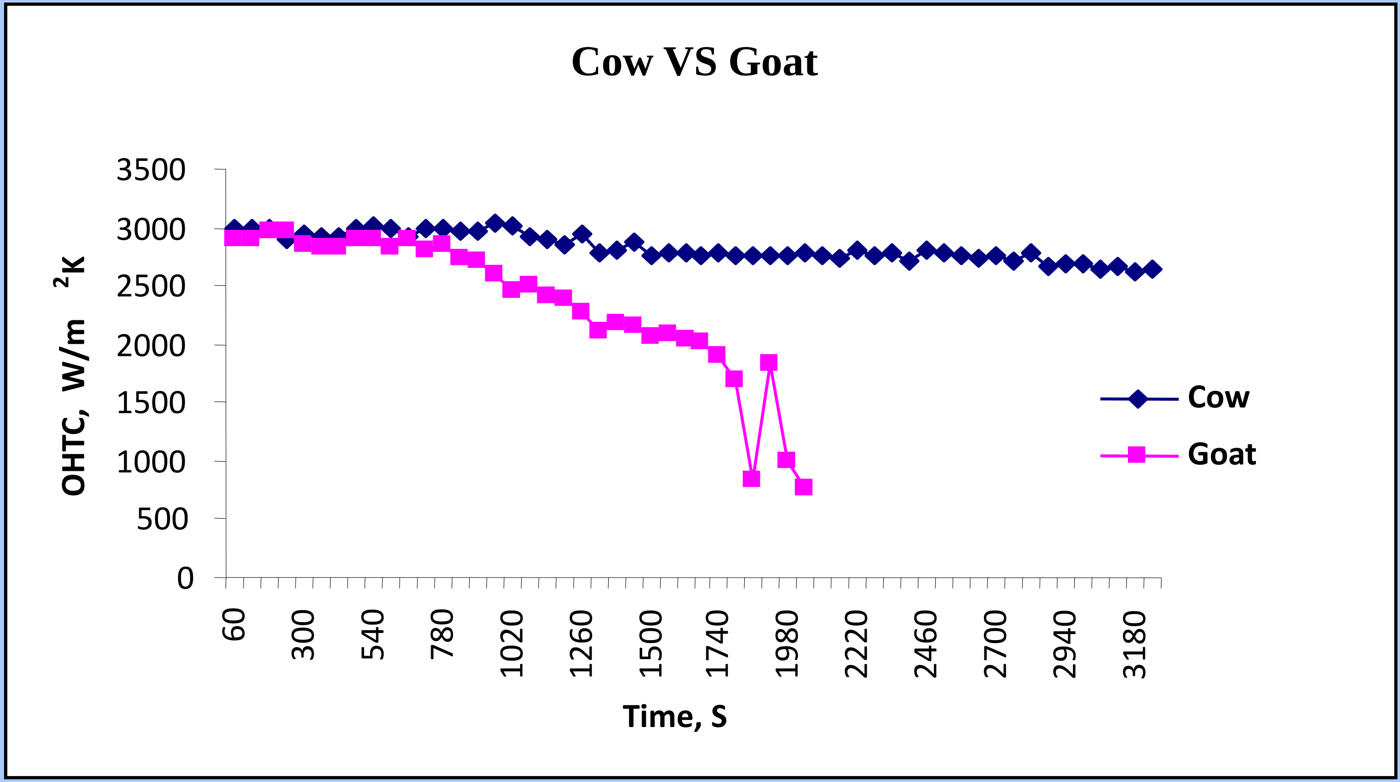


Table showing the effect of additives on pH, ethanol stability and ionic calcium for goat's milk

	pH	Ionic Calcium (mMol)	Ethanol stability (%)
Fresh goat milk	6.63	2.55	54
Fresh goat milk with 0.2% tri-sodium citrate	6.76	1.24	76
Fresh goat milk with 0.2% sodium hexa metaphosphate	6.73	0.83	98
Fresh goat milk with resins (0.3%)	6.62	1.72	68

Comparison of ionic calcium reduced milk with raw goats' milk

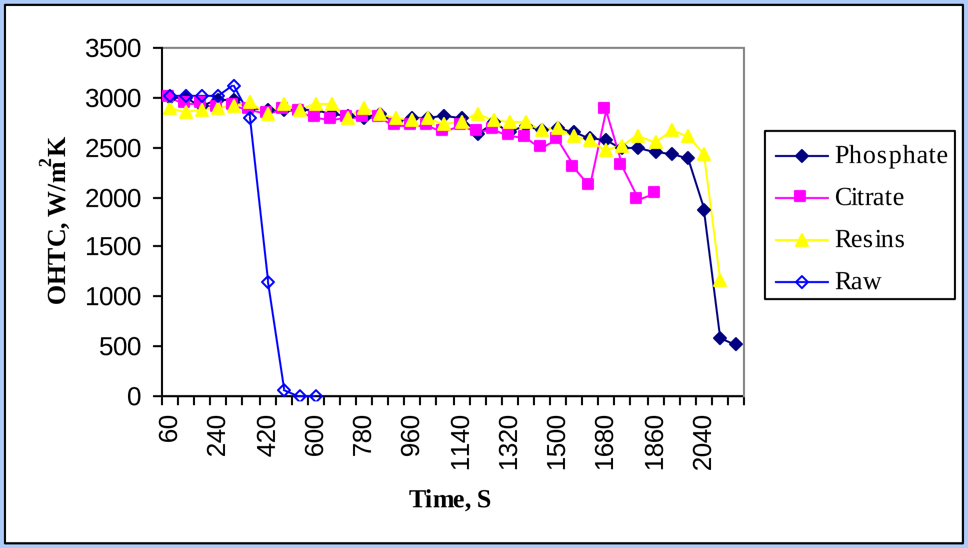
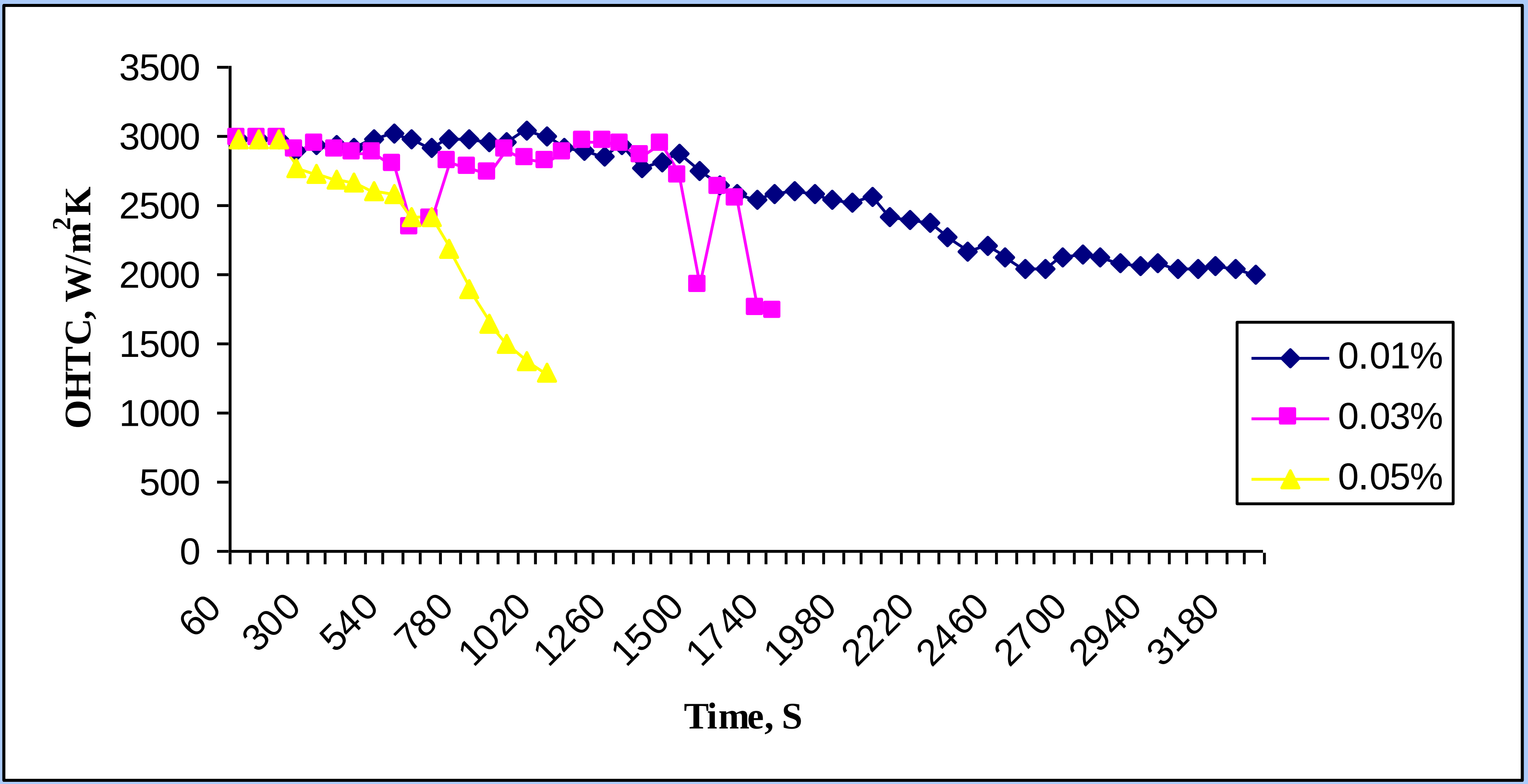


Table showing the effect of $CaCl_2$ on pH, ethanol stability and ionic calcium in cows' milk

	pH	Ionic Calcium (mMol)	Ethanol stability (%)
Fresh cow milk	6.76	1.75	86
Fresh cow milk with 0.01% $CaCl_2$	6.73	1.99	80
Fresh cow milk with 0.03% $CaCl_2$	6.70	2.36	78
Fresh cow milk with 0.05% $CaCl_2$	6.64	2.97	58

Effect of increased ionic calcium level in Cows' milk



Effects of heat on whey

- **whey easily coagulates on heat treatment**
- **eg production of ricotta (whey cheese)**
- **coagulation can be prevented by heating and controlled shear**
- **controlled aggregation/ microparticulation**
- **effects of pH on whey protein denaturation!!**

Upbeat(whey protein (8%) drink)

Some challenges

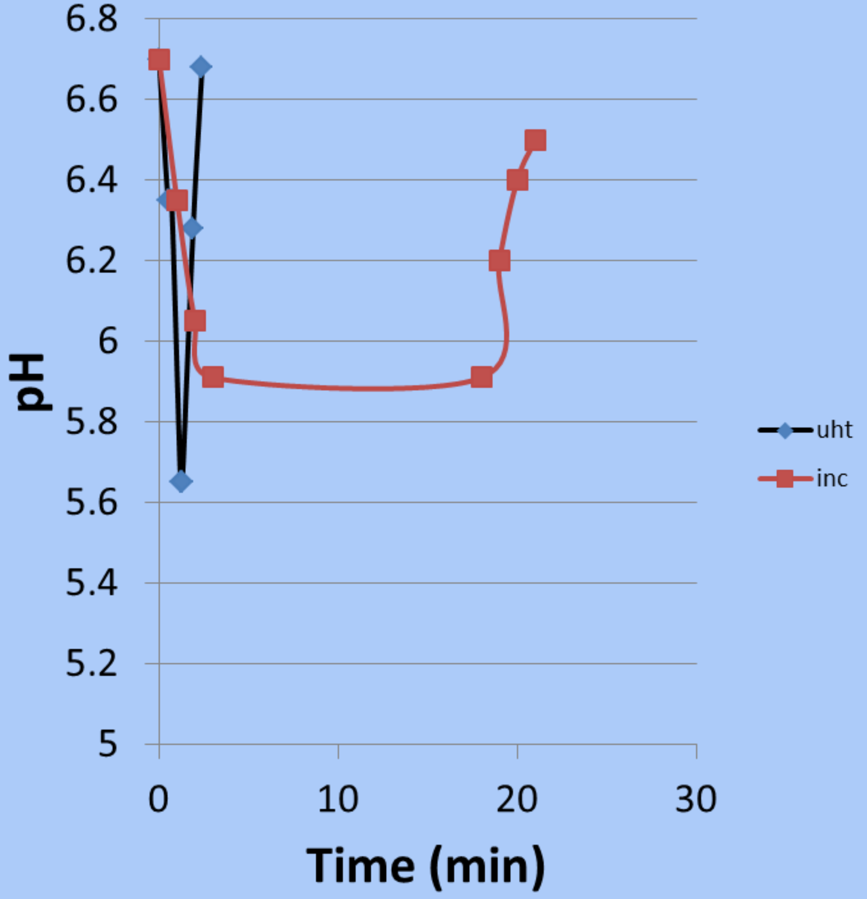
- Fouling of evaporators has been little researched.
- Microparticulation improves the hea stability of whey protein. However, there is scope for further improvements
- Heat stability of milk will be better understood when pH and ionic calcium can be measured at sterilisation temperatures

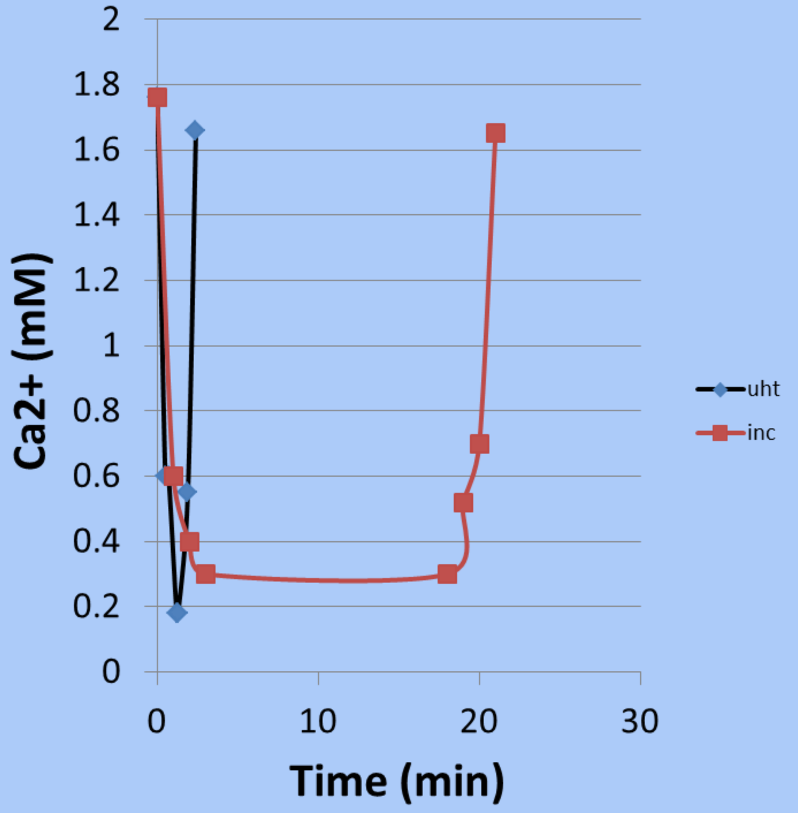
Sterilised evaporated milk samples with different stabilisers

pH and ionic calcium in UF permeates at different temperatures

Samples	pH	Ca^{2+} (mM)
Milk	6.70±0.04	1.76±0.55
Permeate at 80°C	6.41±0.04	0.57±0.19
Permeate at 120°C	5.91±0.03	0.29±0.03
Permeate at 140°C	5.65±0.04	0.19±0.04

Changes in pH and ionic calcium during UHT and in-container sterilisation





Questions?

- Please type your questions into the chat box