

Heat stability of milk- Challenges and Opportunities

My Background

- Educated at Birmingham Univ. Chem.Eng.
- 38 years at Reading University
- Physical properties of foods
- Food processing operations
- Pilot plant activities (UHT pilot plant)
- Supervised over 35 PhD students and 150 BSc and MSc students
- Fascinated by milk, biological fluid
- **Website: www.dairy-solutions.com**

Summary

- Measurement of pH and ionic calcium
- Measurement of heat stability
- Factors affecting heat stability
- Centrifugation methods
- Comparison of heat stability for UHT and in-container sterilisation
- Is ethanol stability a good predictor of heat stability?

Some Milks available commercially

- Full-cream, skim and semi-skim
- Flavoured milk
- Lactose reduced
- Calcium enriched /vitamin fortified
- Goat milk, sheep milk, HTST/UHT (**Sterilised**)
- buffalo, horse milk
- Microfiltered milk
- Breakfast milk, sports nutrition and infant form.
- MWP (Upbeat)
- Melatonin milk eg Lullaby milk
- Omega –3 milk, CLA milk
- Benecol milks – plant sterol added to milk
- Carbohydrate free milk – for Atkins diet
- Milks exploiting bioactive peptides, A2 Milk
- Carbonated milk
- Milk for pets , such as cats and dogs.
- Soya, oat, almond and other plant drinks (not “milks”)

Different heat treatments

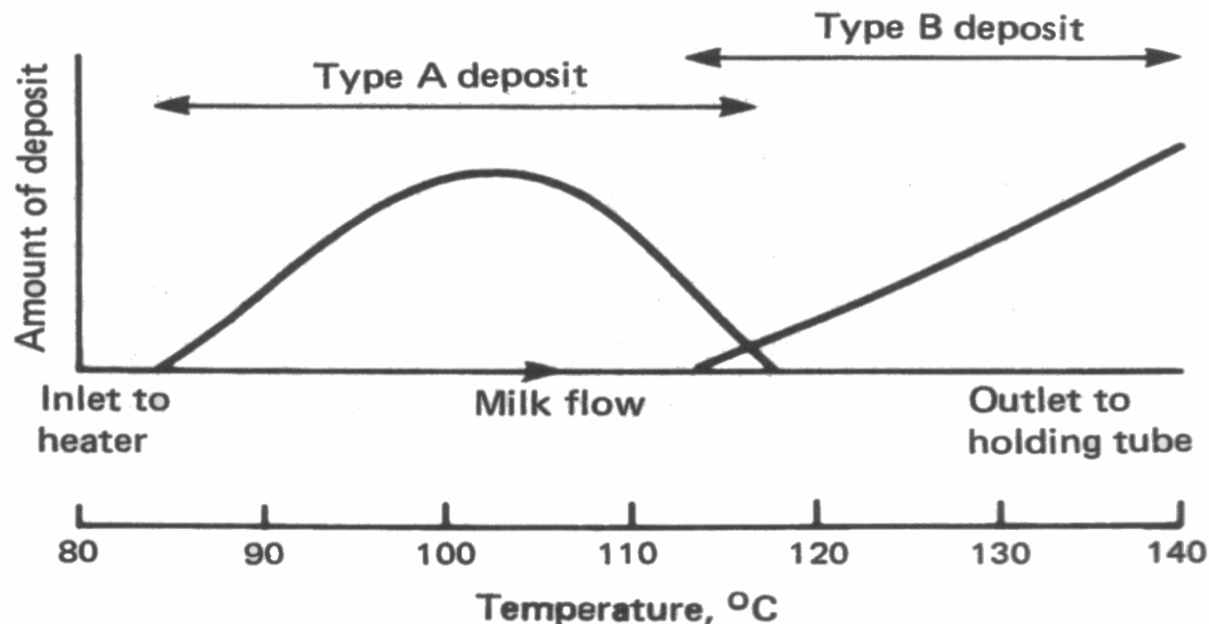
- Thermisation
- **Pasteurisation**
- **Extended shelf-life (ultrapasteurisation –US)**
- **UHT sterilisation**
- **In-container sterilisation**
- Tyndallisation (double heat treatment)
- **Question.** How does pH of milk change during heating and cooling?

Effects of poor heat stability

- Fouling of heat exchangers
- Sediment in products
- Increasing viscosity and coagulation

Fouling on hot surfaces or deposit formation

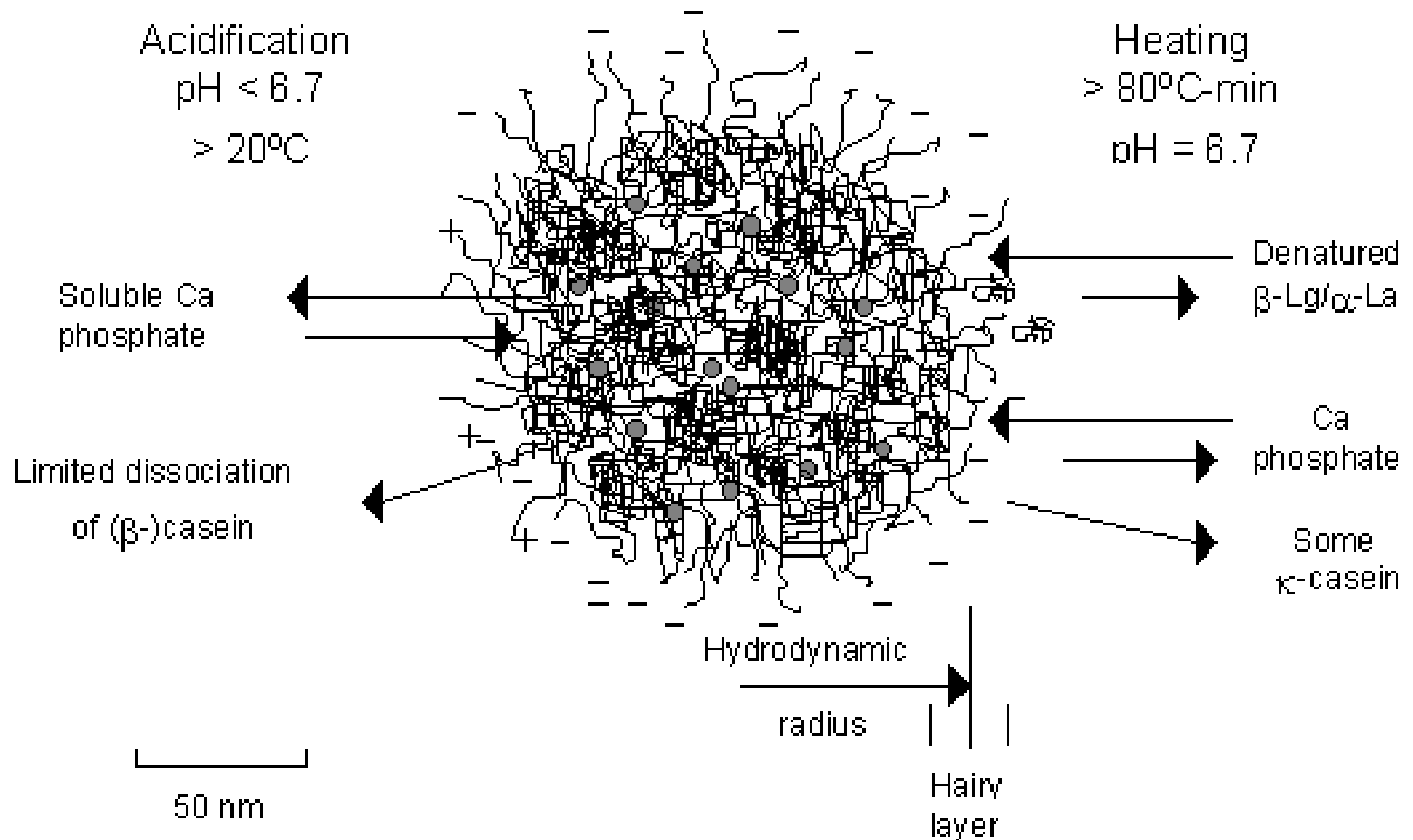
Two types: Type A and Type B



Some effects of poor heat stability



One model for the casein micelle



The soluble phase of milk



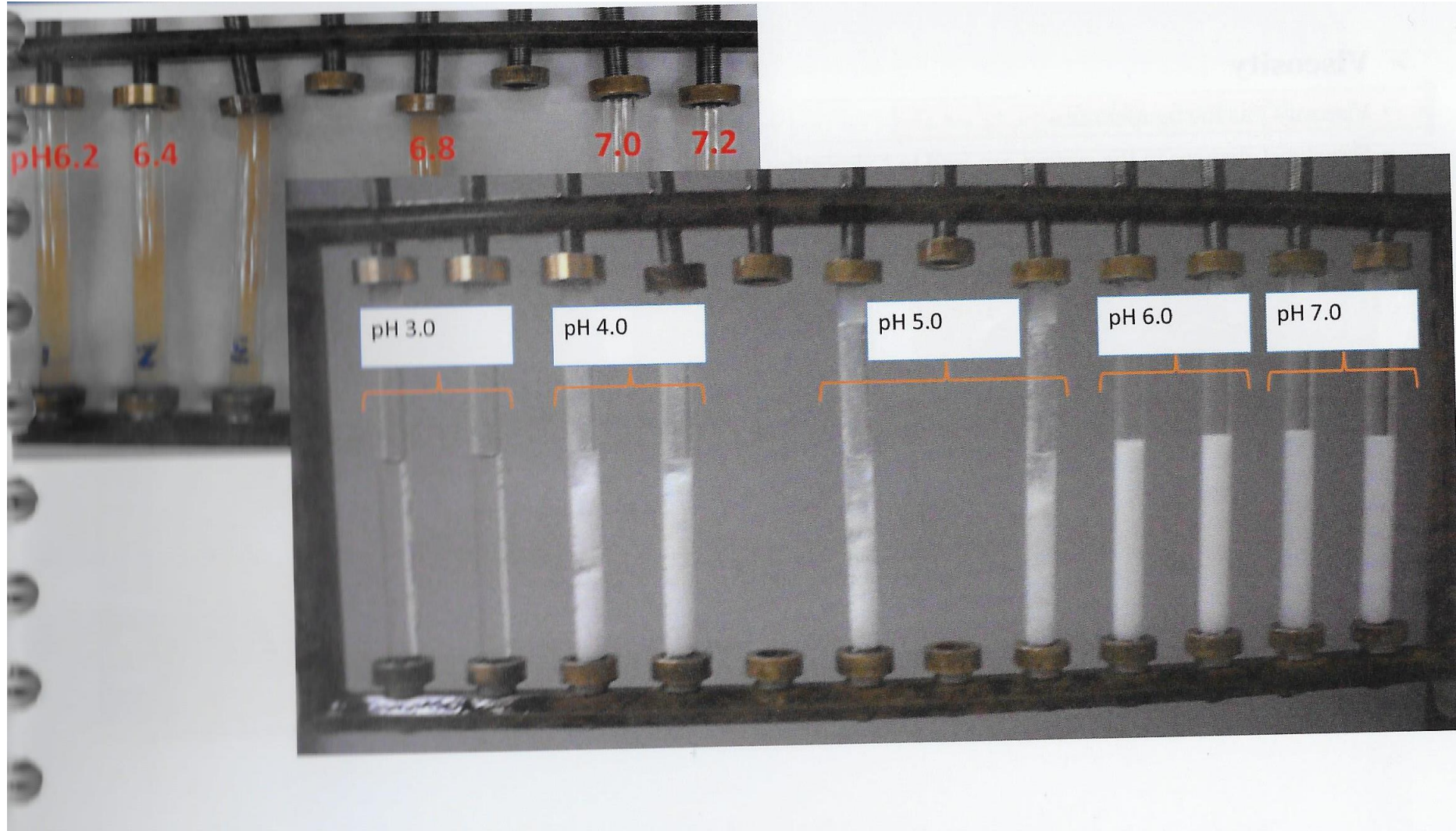
To coagulate or not to coagulate

- That is the question?
- What is the role of pH and ionic calcium in these processes.
- Need to prevent:
- Casein micelle aggregation in milk
- Whey protein aggregation in whey products

Methods for assessing heat stability

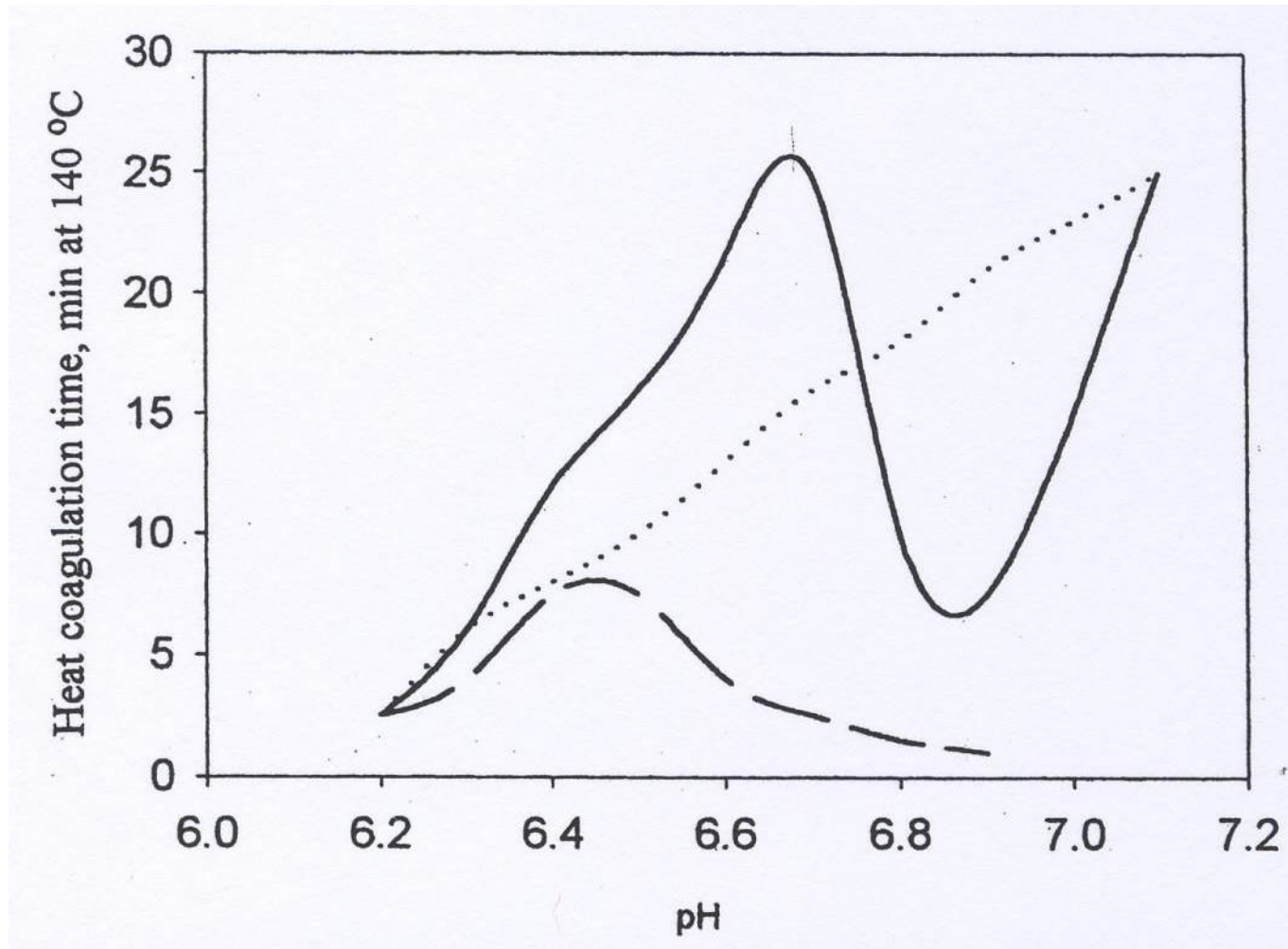
- Heat coagulation temperature
- **Heat coagulation time**
- Viscosity measurement
- **Heat exchanger fouling**
- **Sediment formation**
- **Coagulation**
- Casein micelle size
- **Alcohol (ethanol) stability**

HCT- The Oil Bath Method



Heat coagulation time-pH profile of unconcentrated type A milk, unconcentrated type B milk (····) and 3-fold concentrated type A milk (----).

Source: Fox and McSweeney (2003)



Some observation on this method

- Why does heat stability go through a maximum and minimum.
- As pH is increased, Ca^{2+} decreases, micelles less susceptible to coagulation.
- At pH maximum, K-casein dissociation occurs, this has a destabilising effect
- However at minimum, Ca^{2+} is further reduced and this becomes the dominating influence

Other 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.

Main cations in milk

K⁺

Na⁺

Ca²⁺

H⁺

31-43 mM

17-28 mM

1-3 mM

< 0.001 mM

These can be measured by selective ion electrodes

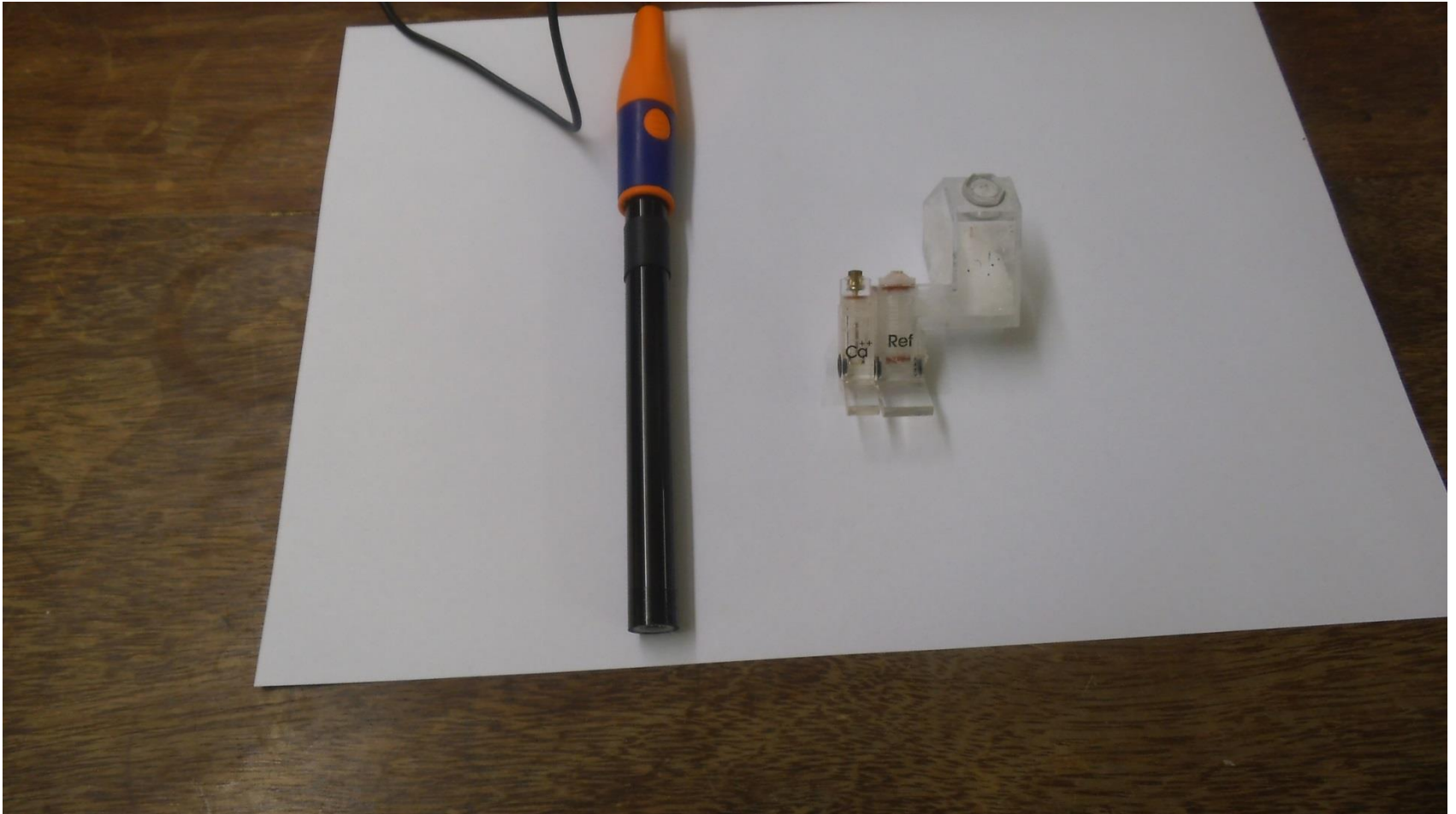
Total calcium and ionic calcium in milk of different species (average values)

| | 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).
- Use 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)
- **Lewis M J** (2011) The measurement and significance of ionic calcium in milk- A review. *International Journal of Dairy Technology*, **64**, 1-13

Immersion type and flow-through electrodes



Guidelines for reliable results

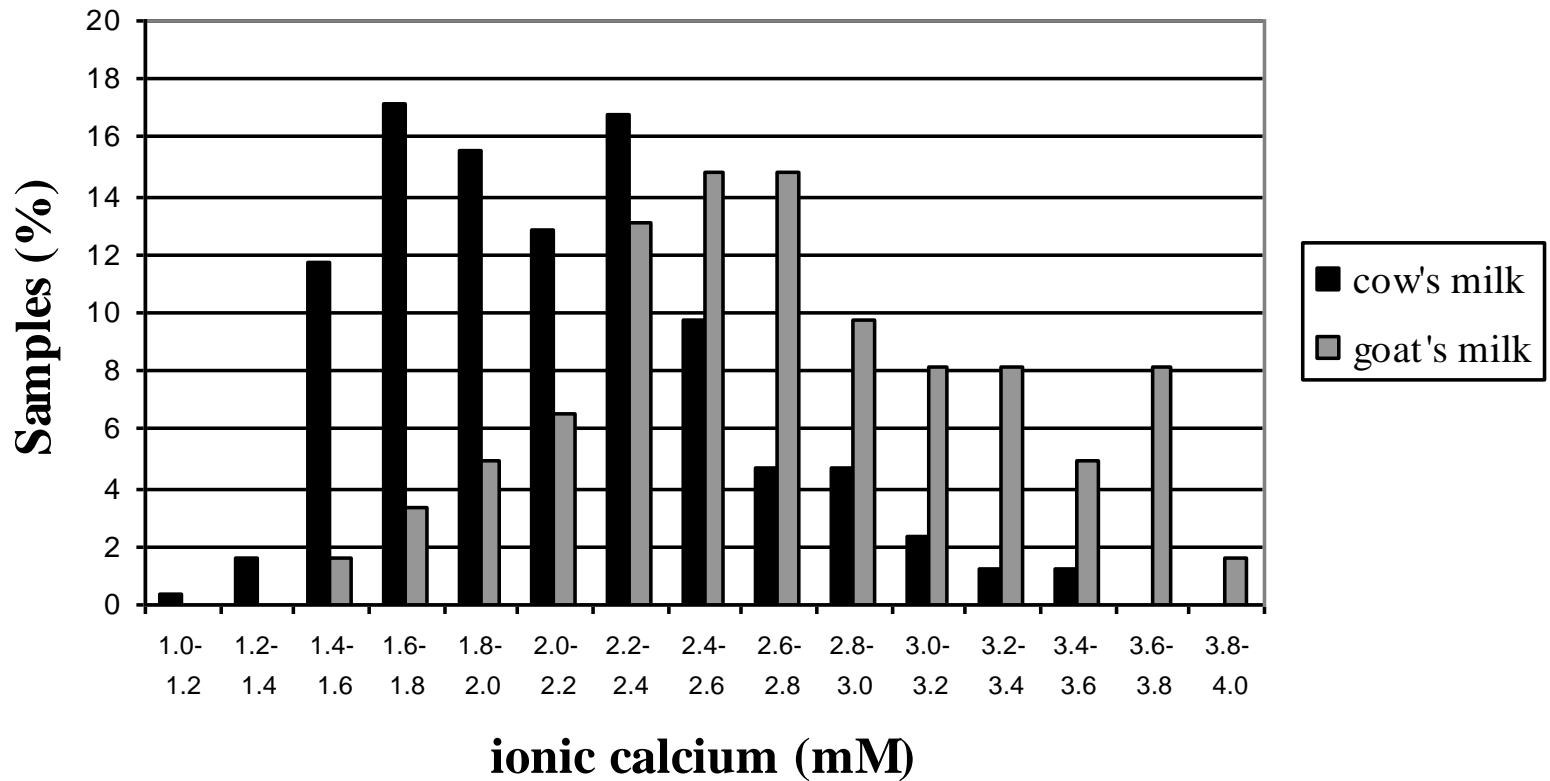
- Immersion probe or flow-through probes
- Divalent ions: ~ 29 mV change for 10 fold change in concentration
- 8 to 9 mV per doubling of concentration
- Important to check performance and reproducibility of the electrode
- Calibrate every day prior to use.

Note: ISEs measure activity- although concentration is much easier to understand

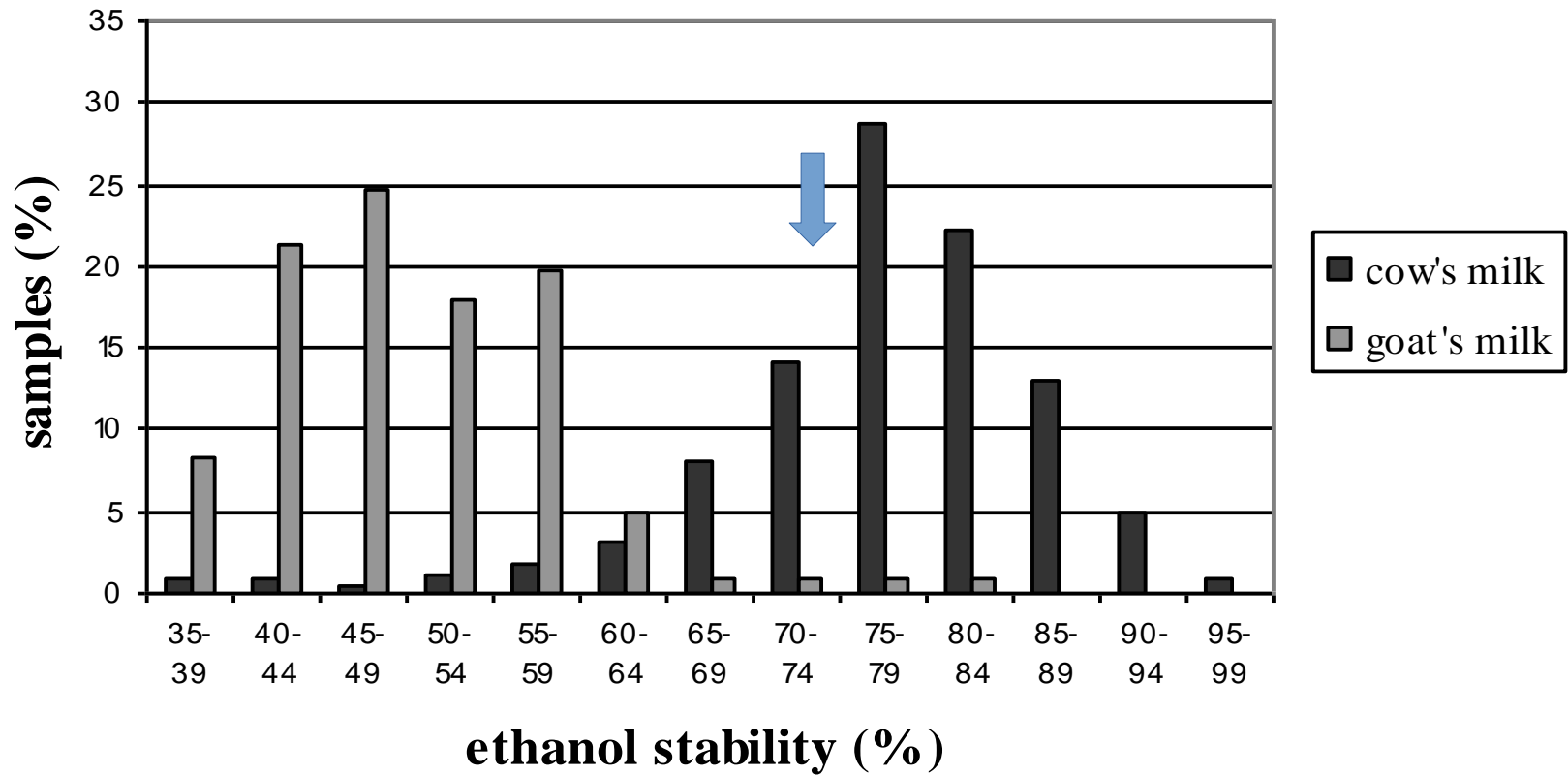
Ionic calcium and alcohol stability for 10 different cows over a complete lactation period

| 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% |
| 6506 | 2.67 | 0.57 | 68% | 7% |

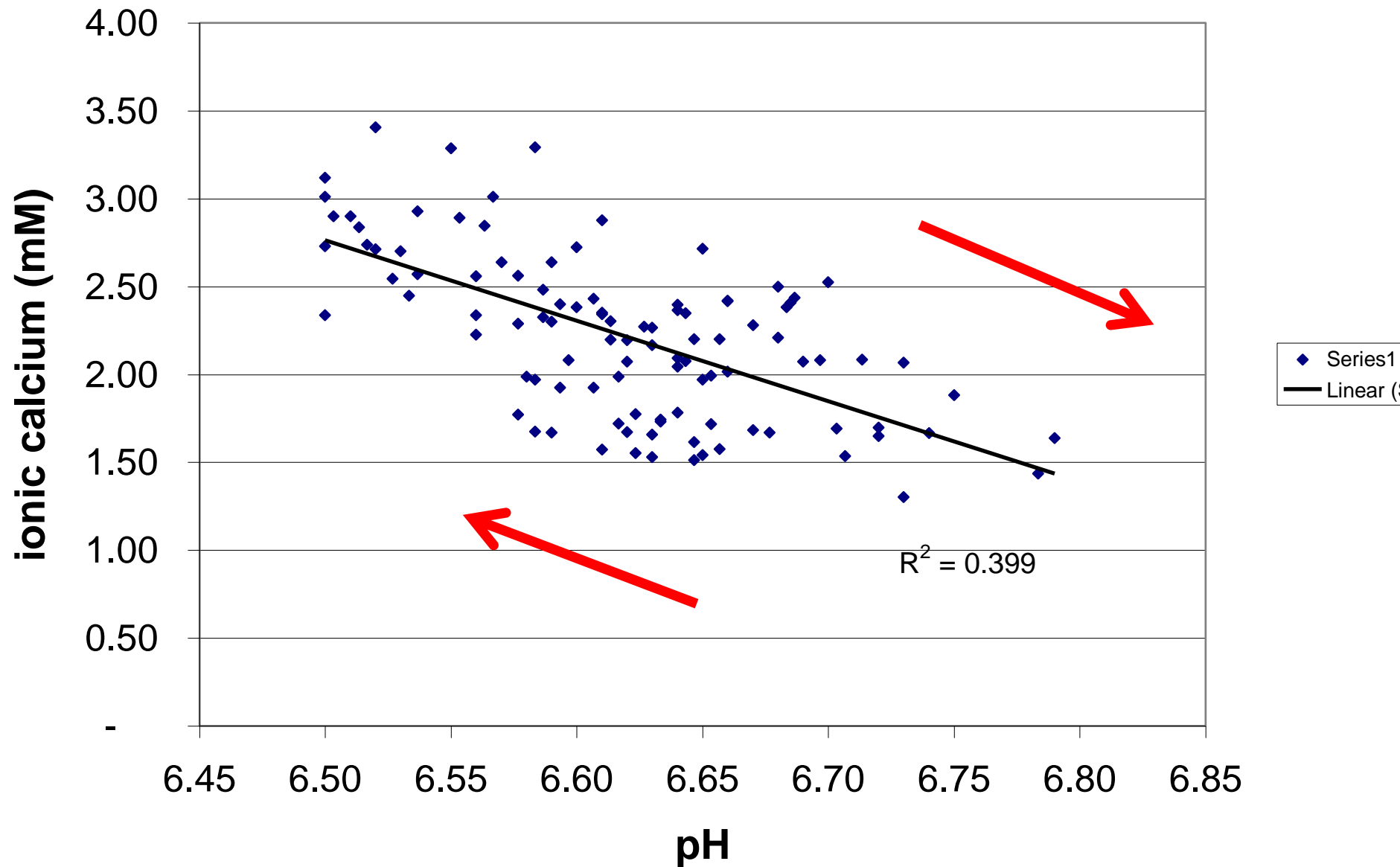
Distribution of ionic calcium in cow's and goat's milk



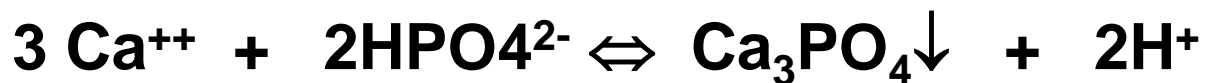
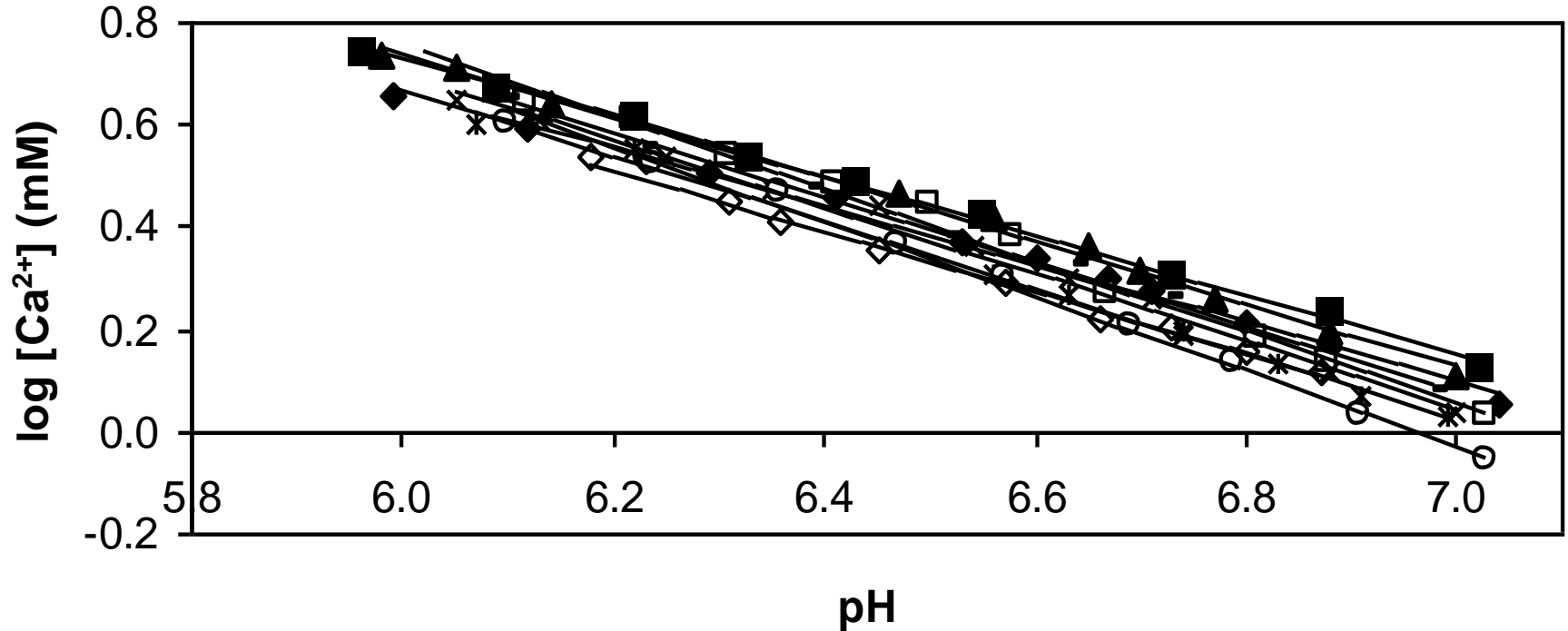
Distribution of ethanol stability in cow's and goat's milk



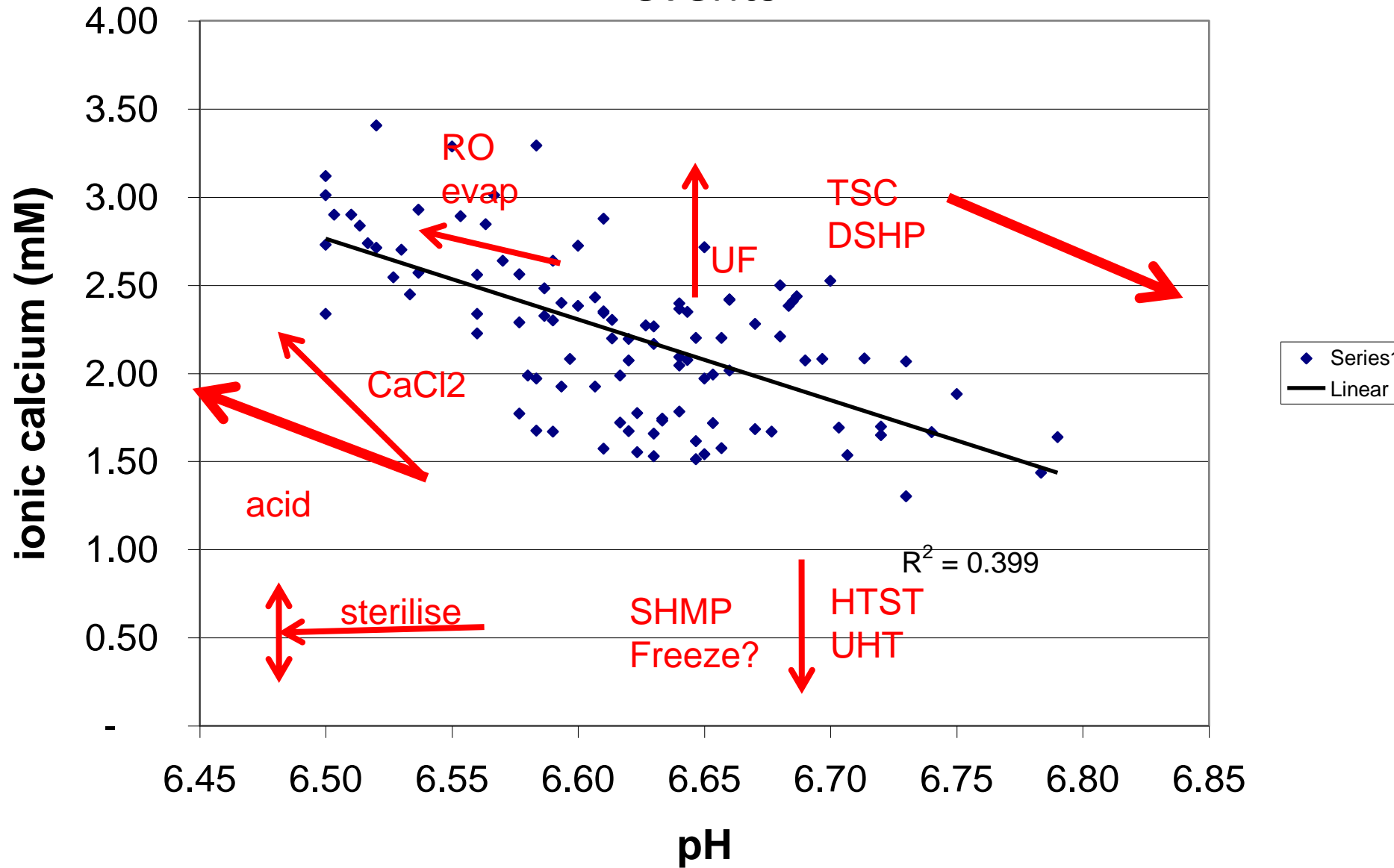
Relationship between pH and ionic calcium for milk samples from individual cows



Ionic calcium against adjusted pH for several cows



Changes in pH and ionic calcium caused by different events



Addition of different stabilisers, followed by in-can sterilisation at 120 C for 15 min

control



These differences arise from the relatively small changes in pH and ionic calcium resulting from stabiliser addition.

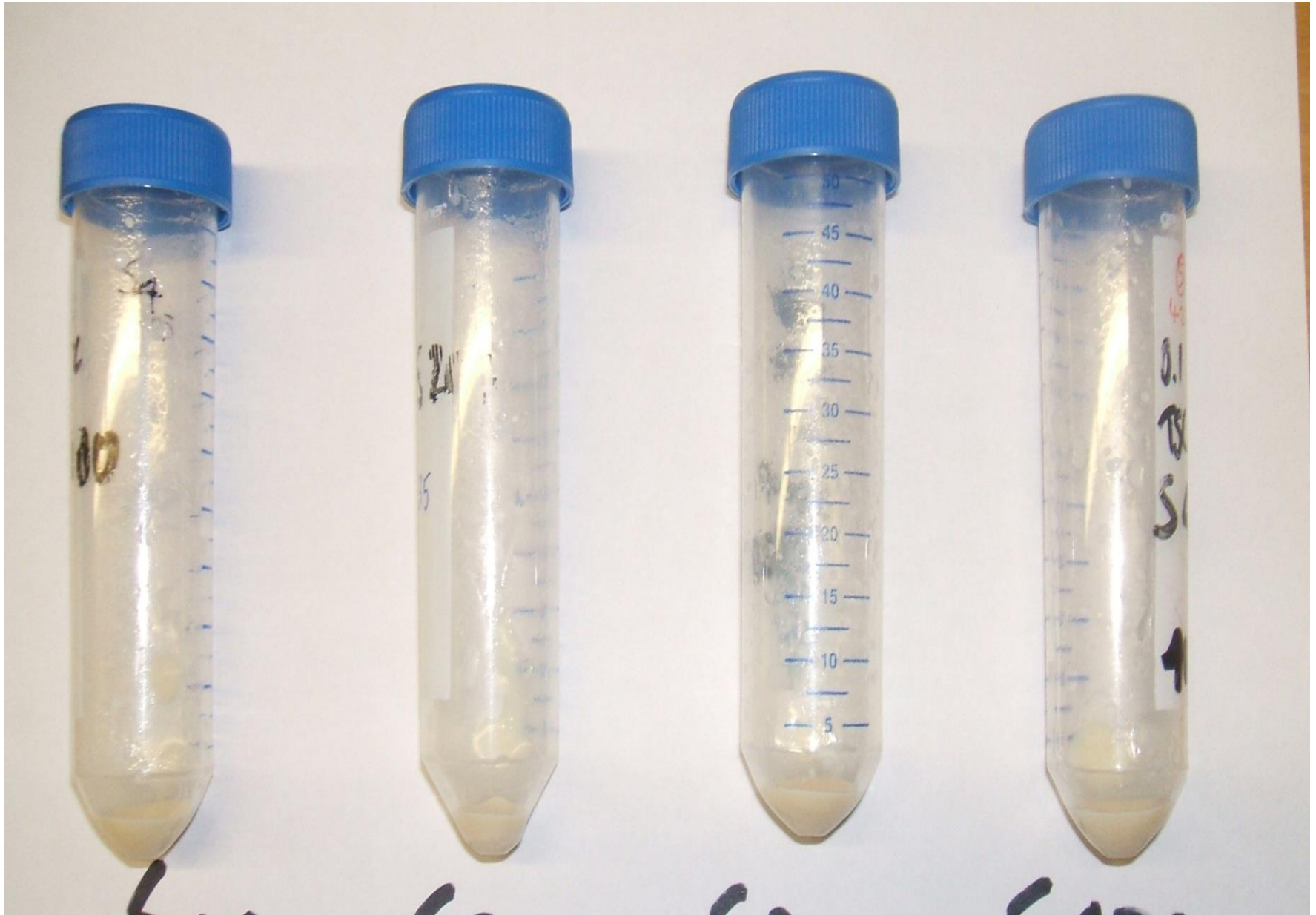
Measuring Stability of milk

- 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)

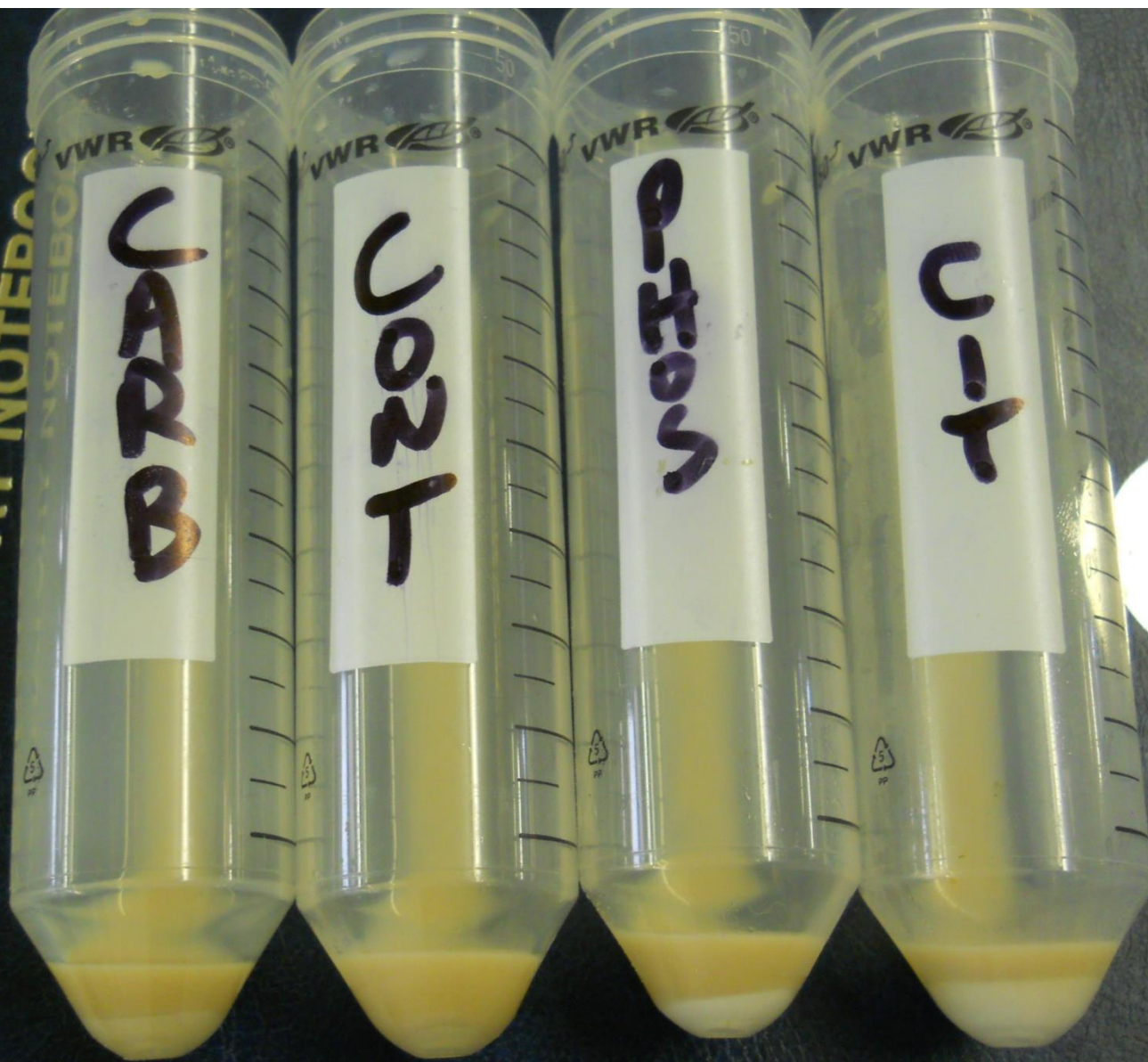
- Our experiences tasting milk samples lead to the following observations:
- Milk with sediment levels below 0.5% dwb are considered to be of good heat stability, as sediment cannot be detected by taste.
- Milk with sediment levels above 1.0% dwb is considered to be of poor heat stability as it can be detected by taste.

Heat Stability Measurement (our method)

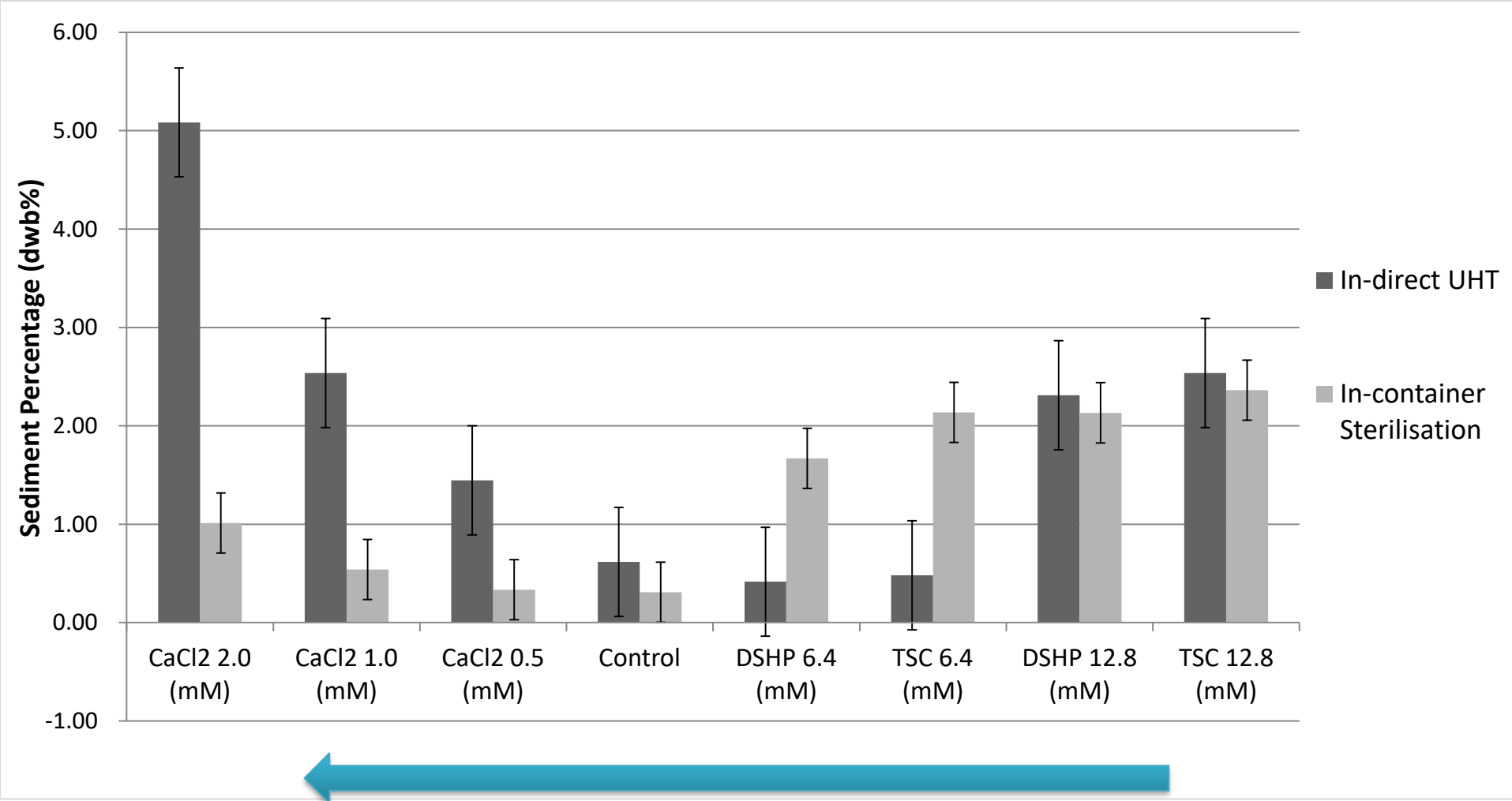




LABORATORY NOTEBOOK

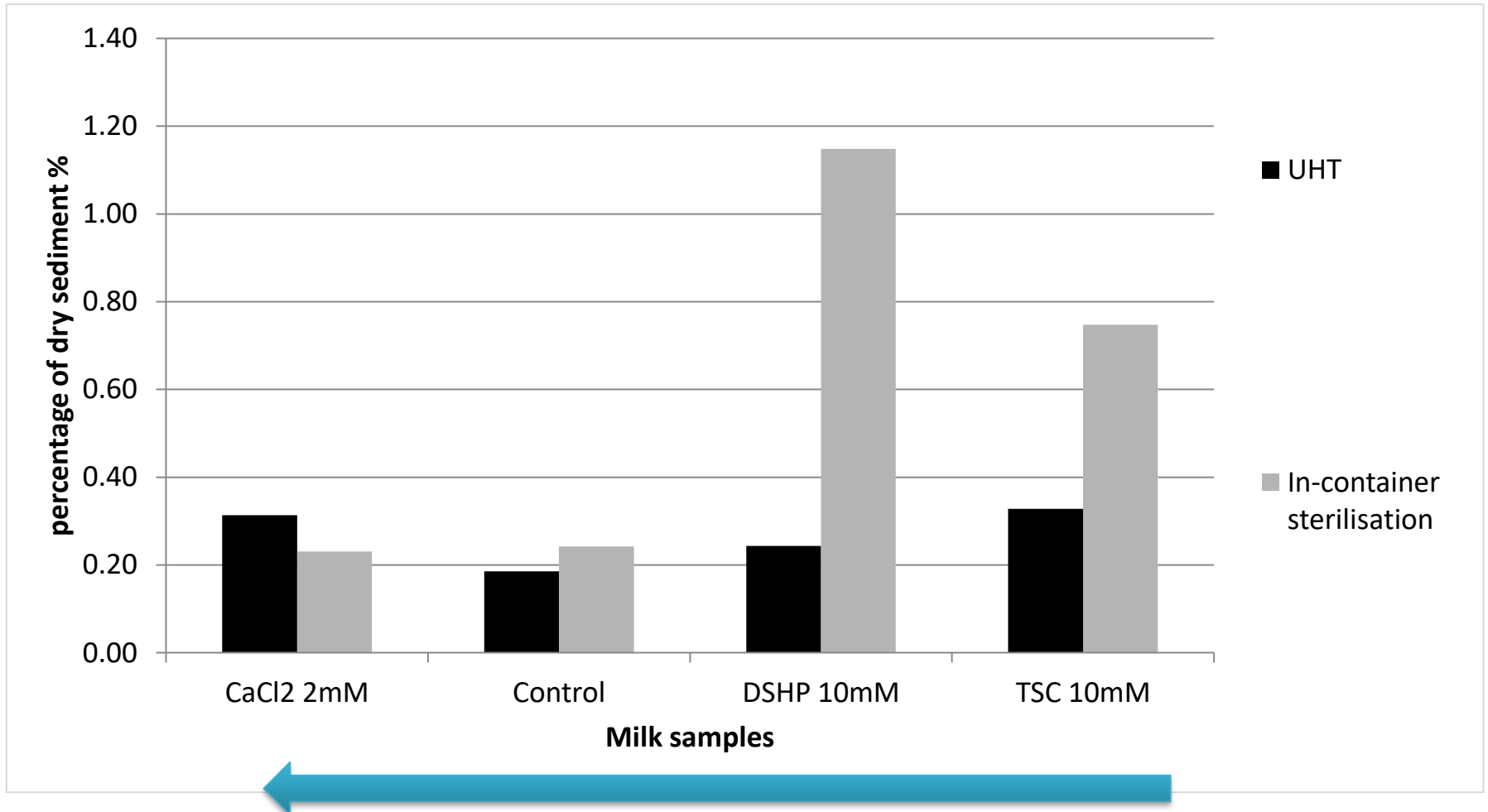


The effect of added DSHP, TSC and CaCl_2 on the sediment following UHT and in-container sterilisation for three fully replicated trials for **goat milk**



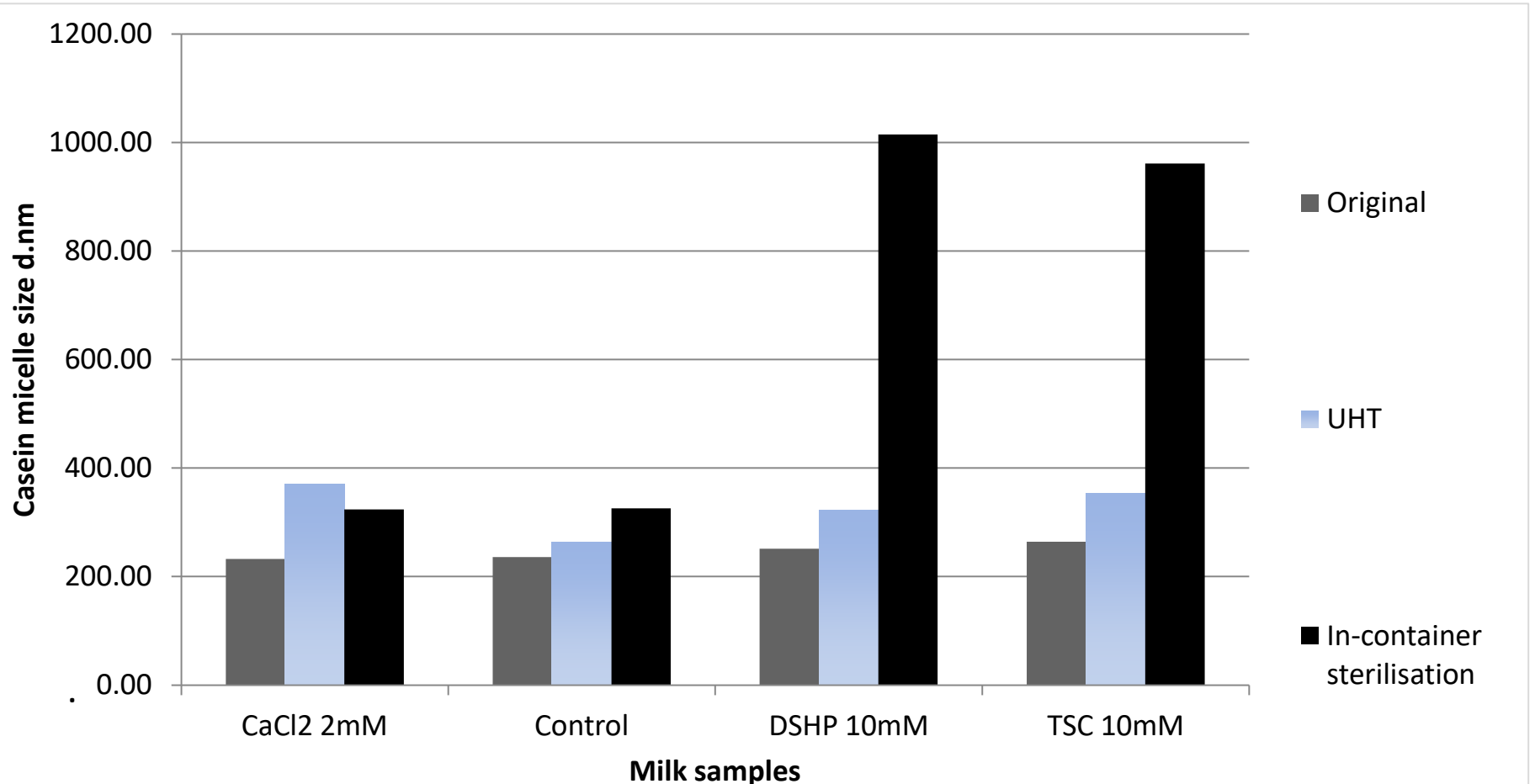
Bovine milk

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



Bovine milk

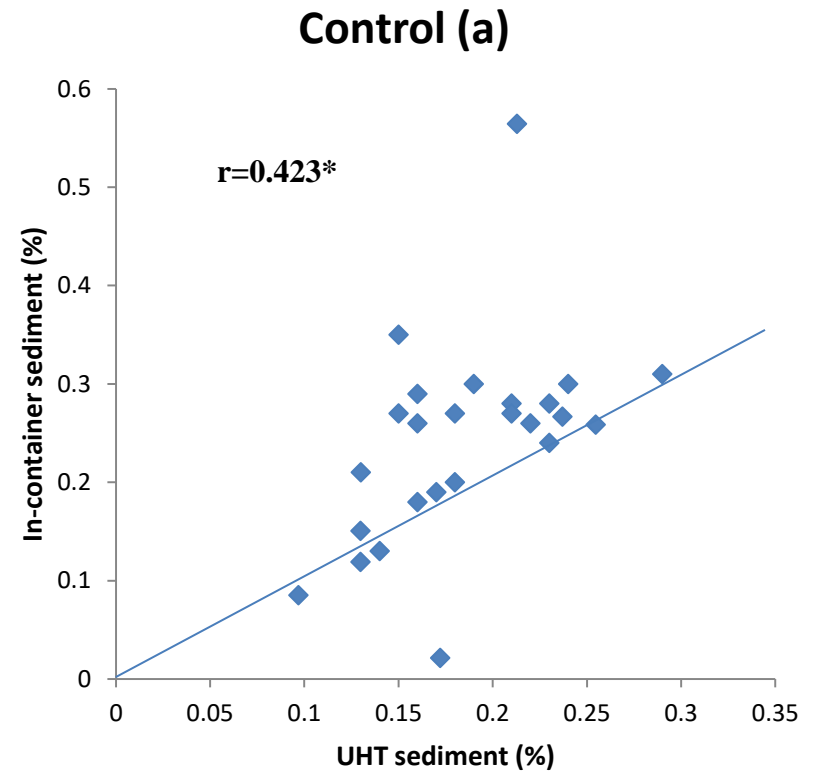
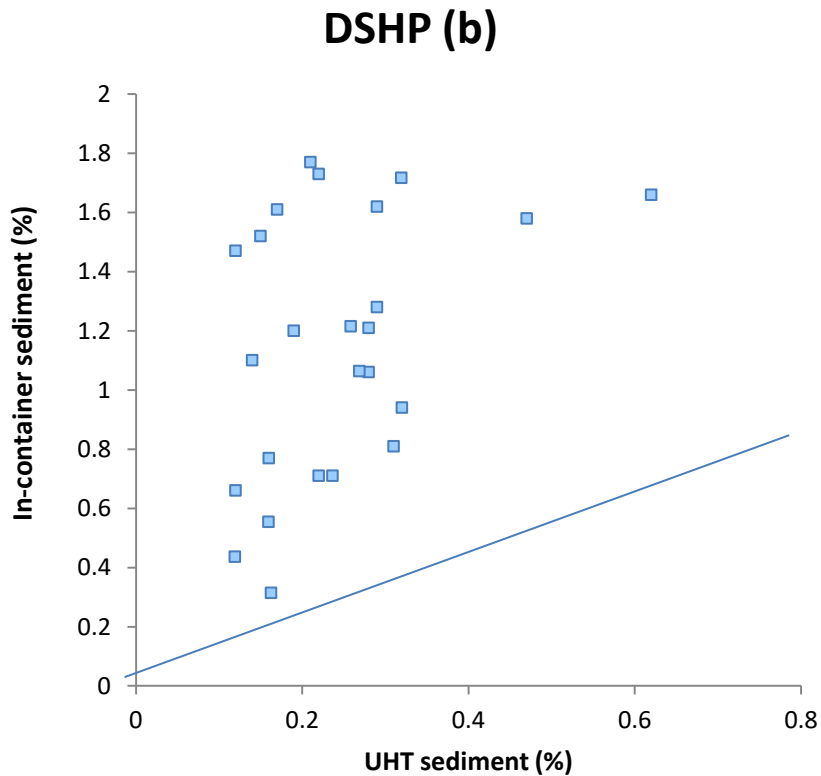
The effect of added DSHP, TSC and CaCl_2 on the casein micelle size following UHT and in-container sterilisation



Comparison of sediment produced for UHT and in-container sterilisation

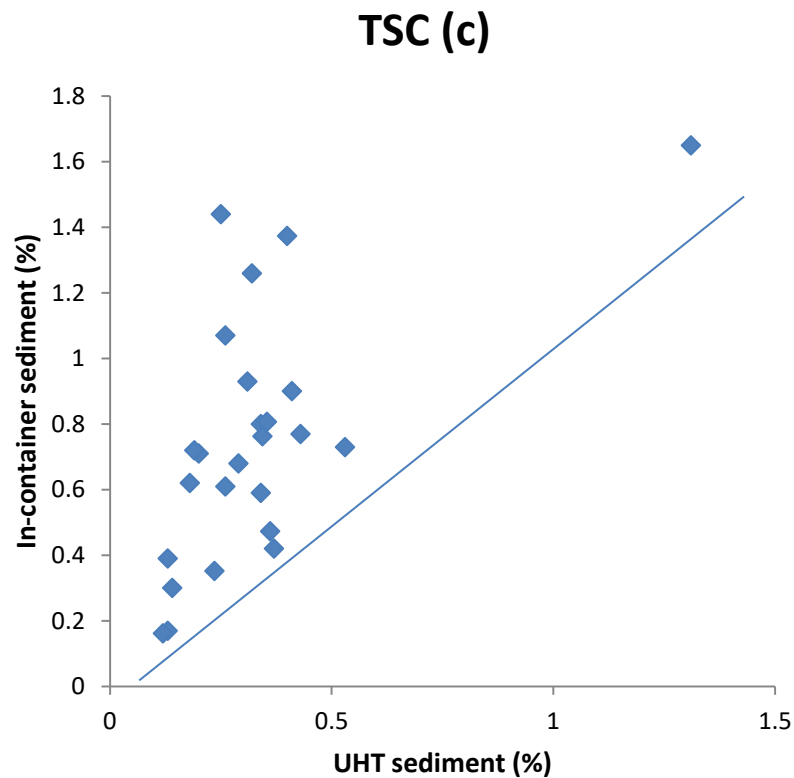
DSHP (10 mM)

Control

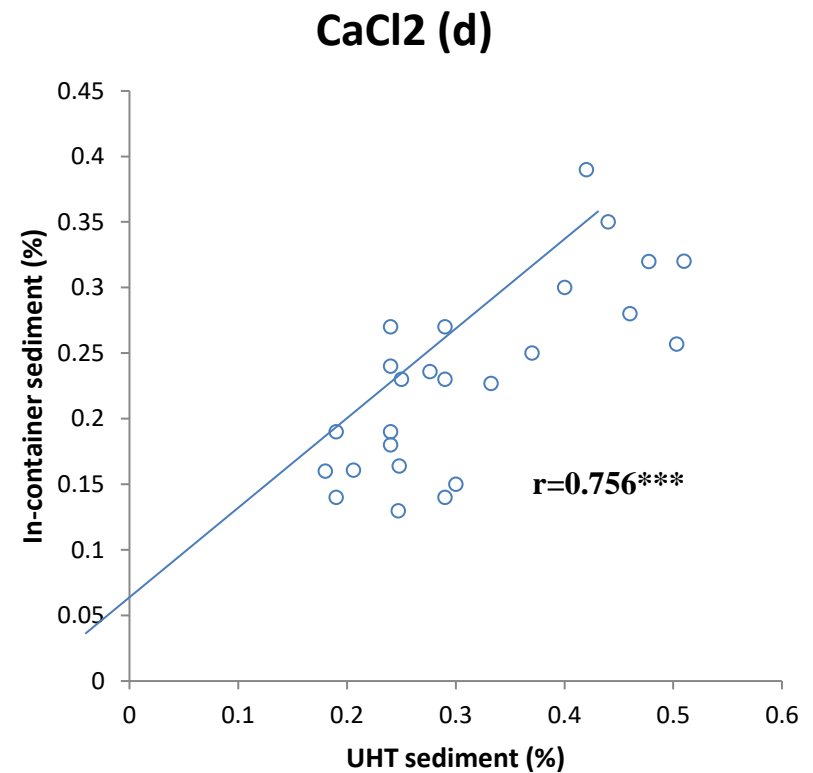


Comparison of sediment produced for UHT and in-container sterilisation

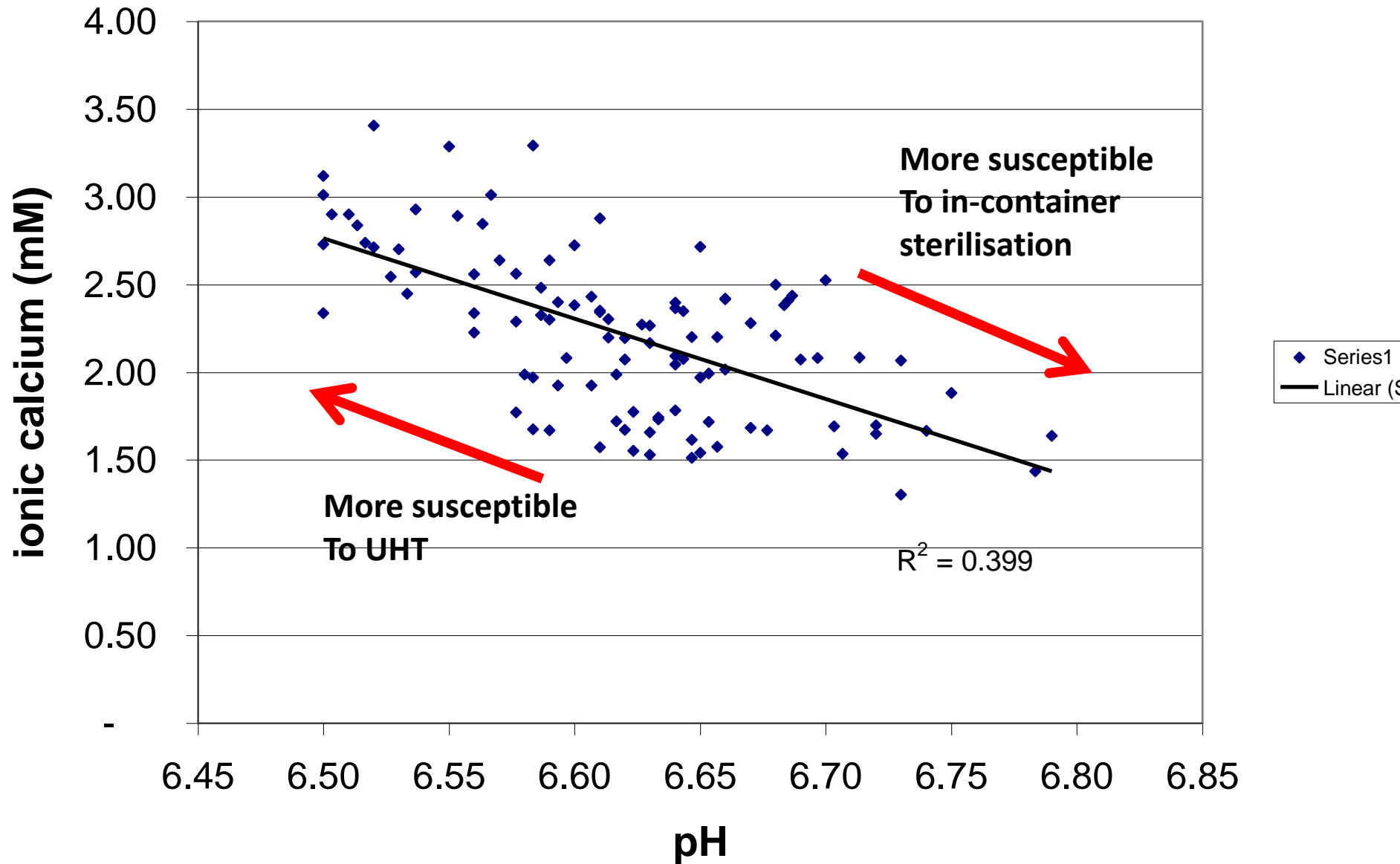
TSC (10 mM)



Calcium chloride (2 mM)



Summary



Discussion of Alcohol Stability

- It has some potential for UHT processing
- If alcohol stability is below 75%, show some caution
- If alcohol stability is above 75% but fouling or sediment is encountered, perhaps too much stabiliser has been added
- It is useful for formulating products for pilot plant trials

Is a preholding period worthwhile?

- Preholding between 75°C and 95°C for in excess of 30 s is used by some producers
- It is claimed that it preconditions the protein and improves its heat stability and reduces deposits in the high temperature section.
- It increases the heat load on the product.
- **UHT run times over 30 h are now claimed to be achievable**

Seasonal milk production(million L /day)

| | NZ | UK | Ireland |
|------|-------|------|---------|
| Jan | 76.9 | 40.3 | 5.7 |
| Feb | 62.8 | 40.7 | 11.8 |
| Mar | 52.6 | 42.2 | 23.4 |
| Apr | 43.9 | 44.3 | 32.8 |
| May | 28.4 | 44.6 | 36.0 |
| June | 7.5 | 42.7 | 34.4 |
| July | 9.0 | 40.7 | 31.8 |
| Aug | 46.0 | 38.7 | 28.0 |
| Sept | 87.7 | 38.7 | 24.2 |
| Oct | 101.5 | 38.9 | 20.8 |
| Nov | 94.8 | 39.7 | 15.0 |
| Dec | 85.9 | 40.4 | 8.2 |

USA is similar to UK; max Mar; Australia is similar to UK;- max Oct

Concluding remarks

- **Heat stability of UK bovine milk is good, but this can easily change in formulated milk products.**

Ionic calcium and pH are useful indicators of heat stability (together with buffering capacity)

- However for a better understanding of factors affecting heat stability, pH and ionic calcium should be measured at high temperatures.

Ethanol stability is useful for establishing levels of stabilisers required for optimising heat stability in UHT processing