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Added Water and the Freezing Point of Milk

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Theory and Results

A. The basic relationship

Milk freezes at a lower temperature than water. The average milk cryoscope freezing point reading on raw milk in most areas is about 540 (-0.540°). The average reading for your area is what is called your "base" freezing point.

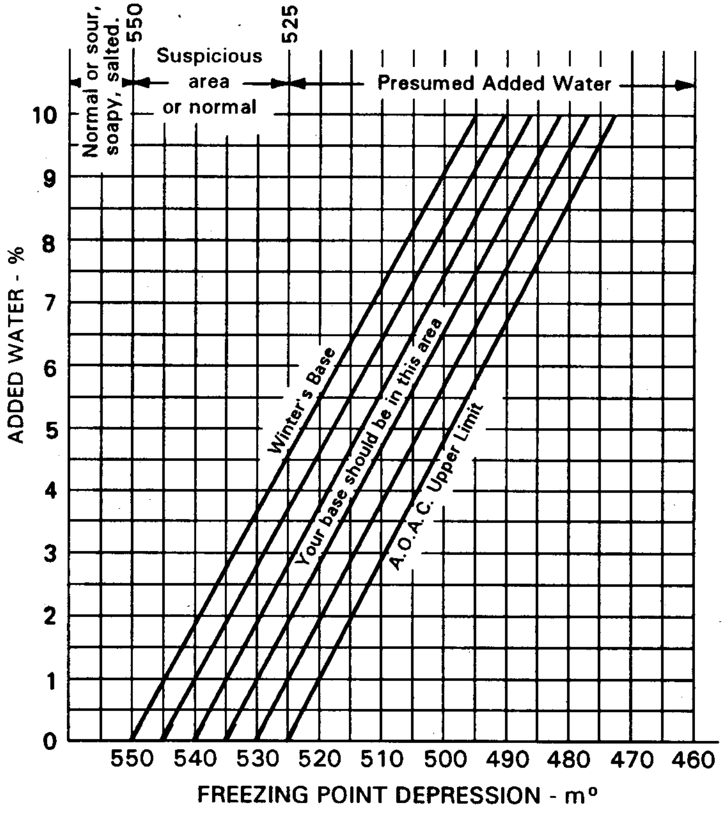
Pure water should have a freezing point of 000. The addition of water to milk changes its freezing point toward the freezing point of water. The difference between 0% and 100% added water is the difference between your base and 000. 1% added water is 1% of this difference.

Therefore, for a 540 base, 1% added water should decrease the milk cryoscope reading 0.01 x 540 = 5.4 digits to about 535. Conversely, a milk cryoscope reading of 539 would indicate (540-539)/5.4 = 0.19% added water.

With this information, we can construct a table and/or chart showing the relationship between added water and milk cryoscope reading for a given base.

F.P. Reading	Percent Added Water	F.P. Reading	Percent Added Water	F.P. Reading	Percent Added Water
540	0.0	518	4.1	496	8.2
539	0.2	517	4.3	495	8.3
538	0.4	516	4.4	494	8.5
537	0.6	515	4.6	493	8.7
536	0.7	514	4.8	492	8.9
535	0.9	513	5.0	491	9.1
534	1.1	512	5.2	490	9.3
533	1.3	511	5.4	489	9.4
532	1.5	510	5.6	488	9.6
531	1.7	509	5.7	487	9.8
530	1.9	508	5.9	486	10.0
529	2.0	507	6.1	481	11.0
528	2.2	506	6.3	475	12.0
527	2.4	505	6.5	470	13.0
526	2.6	504	6.7	464	14.0
525	2.8	503	6.9	459	15.0
524	3.0	502	7.0	454	16.0
523	3.2	501	7.2	448	17.0
522	3.3	500	7.4	443	18.0
521	3.5	499	7.6	437	19.0
520	3.7	498	7.8	432	20.0
519	3.9	497	8.0		

Freezing Point vs Added Water for a Base of 540



Freezing Point vs Added Water for Bases of 550, 545, 540, 535, 530, and 525

B. What is base freezing point?

The freezing point of milk is a "physiological constant." However, this *does not mean* that it will not vary. As a matter of fact, feed ... breed ... season ... time of lactation ... climate ... whether sample was taken at the beginning, middle, or end of lactation ... all are factors that will have an effect on the freezing point of an *individual* sample. It *does mean*, though, that there is an average or mean value to all these numbers. The more samples used in obtaining this average, the more reliable it is as a base.

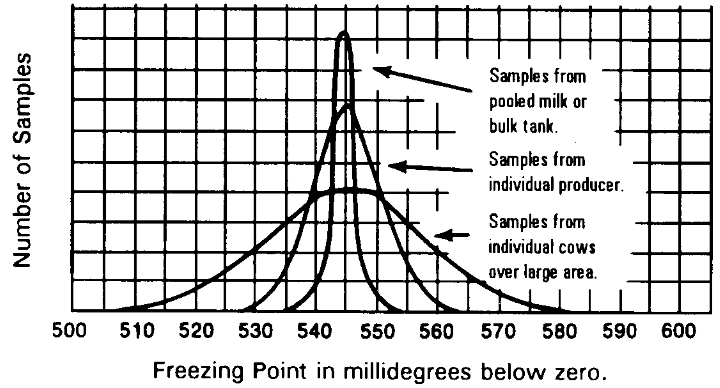
Consider the following table of test results and averages:

Number of Samples Averaged	Sample Values				Range of Variation
1	531 542 550 540 530 532 532 531 539	526 548 546 536 537 547 554 543 524	533 532 543 542 546 530 527 540 537	523 530 540 536 540 543 535 534 545	554-523=31
3	534 534 540	539 543 539	534 539 537	531 535 543	543-531=12
9	536	540	537	536	540-536= 4

The effect of averaging on range of variation

Note how the *range* decreases as the samples are averaged. The last line represents only 36 samples, or less than the number of cows represented in an average bulk tank!

The following graph illustrates this point even more clearly:



The effect of averaging on range of variation

One can obtain an average by taking the mean of many individual samples or by pooling many milk samples and making only one measurement.

A *base freezing point*, then is an *average* of many individual cows. When a laboratory checks a producer, it is simply comparing the average of the producer's cows against a larger area average. It does not make sense to talk about added water in relation to a single cow.

C. Who establishes base freezing points?

Base freezing points are established by health authorities in some areas, agriculture departments in others, and sometimes, by universities, individual dairies or producers' associations. Frequently, tolerances have been established on top of a base freezing point to allow for some variation in natural milk as well as instrument or operator variations.

D. Legal action

Without mentioning base freezing point, the Association of Official Analytical Chemists now recommends an upper limit freezing point at -0.525° (2.326 standard deviations above the most recently determined North American mean of -0.5404°), below which there will be a 95% confidence that 99% of all freezing point determinations on unwatered milk will fall:

> "If fp is -0.525° or below, milk *may* be presumed to be H_2O free or *may* be confirmed as H_2O free by tests specified below. If fp is above -0.525°, milk *will* be designated 'presumptive added H_2O' and *will* be confirmed as added H_2O or 'H_2O free' by tests specified below. Evaluate extreme daily fluctuations in fp of herd, pooled herd, or processed milk for presence of added H_2O."
>
> "Presumed added H_2O," as described above, must be "confirmed" by means of tests on authentic milk samples obtained as specified in the *AOAC METHODS*.

E. Explanations for odd results

Other factors than the intentional or accidental addition of water to milk can greatly alter the freezing point. Some of the conditions which may cause freezing points to be warmer and therefore falsely indicate added water are:

1. A predominance of Guernseys or Jerseys in the herd.
2. Use of commercial grain type feed in place of home grown or home-mixed feeds.
3. Poor pasture conditions.
4. Type of hay, and % pf total roughage used, if under 30% clover.
5. Drought area (precipitation under 2" for a 30-day period). This condition should be considered only when it causes poor pasture conditions and a greater dependence upon commercial feeds.
6. Poor herd condition: mastitis, udder infections, etc.
7. If daily amount of milk per cow is under 20 lbs.
8. Low specific gravity.
9. Herd individuality.

Please note, however, that despite probable vehement contentions to the contrary by the party concerned, in most instances you will find that altered or higher freezing point is due to the intentional or accidental addition of water to milk.

Freezing points can also be "colder" than the base ... 560, 570, etc. These do not mean "negative" added water. They could be:

1. Sample tubes not clean.
2. Cryoscope out of calibration.
3. Sour milk.
4. Chlorine sanitizer in milk.
5. Normal variation from average (for individual cow).
6. "Sharp" farmer salting his added water.

F. Sources of added water

In addition to the most obvious source — between the cow and the pail — there are several other possible places adulteration might occur. These include:

1. Pipeline milkers where water used in cleaning and flushing may collect in cups, drain lines, elbows and bellies in the milk line.
2. Bulk tanks where frost might collect on compressor units near the tank lid; milking heads dipped with the vacuum left on; or in the drain line where flush water can collect in low spots.
3. Truck tanks where water might be present due to inadequate draining.
4. At the bottling plant where water occasionally collects in HTST Pasteurizers and drains.

There are literally hundreds of possibilities for watering problems — many due to honest error. A little thought will reveal many. One frequently cited, however, is never a cause of watered milk ... and that is condensation. Since milk is 86% water to begin with, beads of condensation in a tank represent water which has evaporated and recondensed. Condensation from moist air is almost nil.

Reference for some of the previous material:

1. "The Freezing Point of Milk. A Review." Shipe, W.F., JOURNAL OF DAIRY SCIENCE, XLII, 11, 1745-1762, Nov. 1959.

2. "Cryoscopy and the Freezing Point of Milk," Levowitz, D., TRAINING COURSE MANUAL - CHEMICAL AND PHYSICAL ANALYSIS OF DAIRY PRODUCTS, American Public Health Service, 1962.

3. "Milk Cryoscopy News," Abele, J.E., ADVANCED INSTRUMENTS, INC., selected issues from volumes 1-3, 1962-1965.

4. "The Freezing Point of Milk Produced in North America," Henningson, R.W., JAOAC, 52, 142-151, 1969.

5. *AOAC METHODS,* Twelfth Edition, 264-267, 1975.

Standards and Accuracy

"Repeatability is a function of the instrument; accuracy is a function of the standards." This statement is applicable to most laboratory tests, and cryoscopy is no exception. All measurements must be referred to some highly repeatable master standard.

Freezing-point standards are simply solutions of known concentration and freezing point. The actual solute used is not critical but ideally should possess several characteristics. It should be relatively easy to purify, as well as to weigh and store. It should not contaminate easily, or break down in solution. It should be stable over a wide range of temperatures and it would be helpful if it were available as a primary standard. Values should be chosen which bracket the range of the unknown.

The dairy industry initially chose 7% and 10% sucrose solutions in the early 1920s because they were in the right range and the sugar industry had recently improved their refinement technique, and consequent studies had provided quite accurate freezing-point values. Due to its tendency to ferment and decompose with age, however, sucrose has largely been supplanted by sodium chloride in freezing-point standards.

Although sodium chloride is much more stable than sucrose, it is difficult to purify. And, because it is hygroscopic, it is somewhat difficult to handle in making up solutions. Most cryoscope users, consequently, prefer to purchase ready-to-use standards from the cryoscope manufacturer.

Sodium chloride standards are available from Advanced Instruments. Call for details.

A. Using standards

Unsureness about the accuracy of one's standards destroys confidence in the test. We take every precaution at the plant to insure reliable standards. Each lot is numbered and spot-checked. Errors can occur, however. The purpose of the following steps is to avoid being caught without a "yardstick."

1. Order more than one bottle of the same standard at the same time. If you make your own, put the quantity in several small containers rather than one large one.
2. Open at least two, and preferably all bottles of an order or lot at once and test them on the spot. Compare with previous lot.
3. Write on the bottle, date opened and test results.
4. Reseal tightly and store at room temperature. The difference between dissolved nitrogen and oxygen in water at room temperature and at freezing temperature accounts for about 1 millidegree.
5. Use one bottle at a time.
6. When the bottle used is 1/4 full, reopen a new bottle and compare it with the old one.

The use of a third standard at the mid-point is recommended, since it serves as an extra check on the high and low values, as well as simplifying the calibration.

B. One Standard Calibration

It is possible to calibrate using only one standard, 530 for example, if the span between your readings at 621 and 422 is reasonably close to 199.

The procedure is to adjust the "A" Calibrator at 530 and ignore the "B" Calibrator.

This will *not* correct the span, but the *effect of span error will* *be greatly reduced.* The readout span, or difference, between the high and low standards would be 621-422=199. If a cryoscope were to be exactly calibrated at 530, with the span incorrect by 10 millidegrees, the error at the readout of 535 would be only 0.25 millidegrees:

This error would be greater for unknowns reading further away from 530. At 540, for instance, if the span was incorrect by 10 milidegrees, the error would be 0.5 milidegree. Greater, admittedly, but still not very alarming.

C. Preparation of standards

If you would like to try making your own standards, the procedure and suggestions detailed below may be helpful. *AOAC METHODS* gives gravimetric quantities for sodium chloride and volumetric quantities for sucrose at the 422 and 621 bracketing points. For your convenience, those values are repeated here, along with values for two other useful calibration points, as well as sodium volumetric quantities.

1. Solute concentrations for specific freezing points:

Cryoscope Values	Grams of NaCl per		Grams of Sucrose per Liter of Solution
	Kilogram of H_2O	Liter of Solution	
27	0.406	0.406	—
422	6.892	6.861	70 (7%)
530	8.692	8.650	—
621	10.206	10.152	100(10%)

2. Significance of various factors in standards preparation

In preparation of standards, it is worthwhile considering the magnitude of error due to various factors.

a. *Weight of Water.* One liter of water at 20°C weighs 998.23 grams. A liter of water at 4°C weighs 1,000 grams. If a user were to make the error of using one liter of water, rather than 1,000 grams, his error would be 0.18%, or about 1 millidegree at 550.

b. *Purity of Water.* For a particular weight of contaminant the amount of error introduced will depend upon the molecular weight of that contaminant. The smaller it is, the greater the error. 1 millimole of sodium chloride in a kilogram of water, for example, will affect the freezing point by approximately 3.7 millidegrees.

c. *Weight of Solute.* This again depends upon which specific solute is being used. For sodium chloride, an error of 15 milligrams (per 1,000 grams of water) will change the freezing point by 1 millidegree.

d. *Purity of Solute.* This depends not only upon the solute, but the nature of the contamination. Some solutes form hydrates and as a result will actually give less freezing point depression than calculated. The magnitude of this error is proportional to the extent of this hydration. It is important to make sure a good reagent grade of solute is used. In the percentage of reagent-grade NaCl used in cryoscope standards, the contaminants listed on the reagent bottle will change the freezing point by less than 1/2 millidegree.

3. Equipment

The following equipment is needed to prepare standards:

Dry atmosphere or oven.
Analytical balance, 100-gram capacity, 0.1-milligram sensitivity.
Two 1000-ml volumetric flasks with stoppers and funnels.
Distilled water.
Room-temperature thermometer.
NaCl, granular reagent grade.

4. Proceed as follows, either method a or b:

a. Gravimetric method

1. Dry NaCl to constant weight in dry atmosphere or oven.
2. Boil distilled water to kill bacteria. Cool to room temperature.
3. Fill flask to within 1/2" of graduation mark with the boiled distilled water.
4. Adjust temperature of water to 20°C. Stir thoroughly.
5. Fill flask to graduation mark with more distilled water.
6. Weigh out NaCl from the grams per kilogram of H2O column (see table on page 8).
7. Use funnel to transfer NaCl to full flask so no crystals will stick to the walls.