Zeitschrift: Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene = Travaux de chimie alimentaire et d'hygiène

Herausgeber: Bundesamt für Gesundheit

Band: 65 (1974)

Heft: 1

Artikel: Screening method for the determination of the freezing point of milk

Autor: Welboren, J.Th. / Velden, H. van der / Jäger, A.J.

DOI: https://doi.org/10.5169/seals-983684

Mitt. Gebiete Lebensm. Hyg. **65**, 151—156 (1974)
Received 13 November 1973. Accepted 7 December 1973

Screening Method for the Determination of the Freezing Point of Milk

J. Th. Welboren and *H. van der Velden*
Keuringsdienst van Waren (Food Inspection Service), Haarlem
(Director: Drs. *A. J. Jäger*)

Introduction

Among the routinary tests used in the laboratories of the Food Inspection Service for the control of milk, the test for the detection of added water is important. For this purpose the measurement of the freezing point depression is almost universally chosen. It is known that the osmotic pressure of body fluids, which is determined by the number of dissolved molecules, is almost a constant. The same dependance with the number of dissolved molecules exists for the freezing point depression, hence the freezing point depression of milk is also almost a constant. The Dutch Food Act uses a freezing point depression of 0,530 ° C for a minimum quality standard for milk (1).

As great care has to be taken to get accurate results, the determination of the freezing point depression is a rather cumbersome method (2). Therefore the method cannot be used to test all samples of milk that are brought to the laboratory and so samples suspected of having too low a freezing point depression have to be selected.

Until recently this selection was made by determining the solids-not-fat content of each sample of milk. This parameter can easily be calculated from density and fat content (2), which can both be quickly and accurately determined. Those samples were selected which showed a solids-not-fat content below 8,5 %. This percentage was chosen because it is also a minimum quality standard. That this selection is not very accurate can be seen from table 1, where some cases are summarized of milk in which an addition of water is likely, while the solids-not-fat content is still over 8,5 %.

It is true that the percentages of added water are not excessive in most of these samples, but on the other hand it would be possible to add some more water to some of these samples without lowering the solids-not-fat content below 8,5 %. The cause of this uncertainty can be found in the natural range of the solids-not-fat content, 7,7 till 9,8 % (4). Therefore it is worthwile looking for other parameters which will give a more precise estimate of the freezing point depression.

Table 1

Added water in samples of milk with a relatively high solids-not-fat content, calculated according to (3)

Solids-not-fat (%)	Freezing point depression (°C)	Added water %
8,60	0,506	4,0
8,60	0,517	2,0
8,66	0,522	1,5
8,67	0,521	1,5
8,77	0,526	0,5
8,80	0,520	1,5
8,87	0,526	0,5
8,94	0,524	1,0

Theoretical calculation of the freezing point depression

The freezing point depression is caused by dissolved compounds; in milk these comprise minerals, organic acids and lactose. The fat in milk forms an emulsion while the proteins form a colloidal solution; in both cases there is no measurable contribution to the freezing point depression.

A calculation shows this to be true. In table 2 the compounds are tabulated that make a contribution to the freezing point depression of milk (5). These figures refer to fresh cow's milk.

Calcium, magnesium and phosphorus are partly dissolved (about 33 %); the rest is assumed to be bound to casein (6). In the table one finds in parentheses

Table 2. Dissolved compounds in 100 g of milk (mean value and range)

Compound	Content (mgs/100 g)		Content (moles/100 g)	
	Mean	Range	Mean	Range
Lactose	4840	4760—4920	14,1	13,9 —14,3
Citrate	265	250— 280	1,26	1,19— 1,33
Sodium	47	32— 54	2,02	1,39— 2,24
Potassium	155	147— 160	3,96	3,76— 4,09
Chloride	90	87— 93	2,53	2,45— 2,61
Calcium	(128)	(126— 130)	1,06	1,05— 1,08
Magnesium	(15)	(9— 24)	0,20	0,12— 0,33
Phosphorus	(87)	(80— 95)	0,93	0,86— 1,02
Total dissolved compounds			26,06	24,72—27,00

the total content of these elements in milligrams. All other figures represent contents in dissolved compounds.

Now the theoretical mean of the freezing point depression can be calculated from the mean total content of dissolved compounds: Mean value is

$$\frac{26{,}06}{1000} \times \frac{100}{87{,}5} \times 18{,}6 = 0{,}554\ ^\circ\mathrm{C}.$$

In this formula means:

87,5 — the mean water content of 100 g of milk (range 87,0—88,0)
18,6 — the molar freezing point depression of water (1 mole of a compound dissolved in 100 g of water).

In the same way the theoretical range of the freezing point depression can be calculated to be 0,525 till 0,574 ° C. This concurs reasonably with the range as found in literature: 0,532—0,580 (7), $>$ 0,525 (8). The calculated mean also gives a good estimate of the experimental mean; in 25 samples of pooled milk from several factories this Service determined a mean freezing point depression of 0,548 ° C with a standard deviation of 0,003 ° C.

Calculation of the freezing point depression from experimental parameters

As shown in the last paragraph it is possible to calculate the freezing point depression from the contents of all dissolved compounds in milk. Of course if one had to test a large number of samples by first determining these contents and therefrom calculating the freezing point depression, this would be a very cumbersome procedure. For this reason we looked for a simple set of parameters that would make possible a good estimate of the number of dissolved molecules and so allow to compute the freezing point depression.
Throughout the rest of the article we will use following symbols:

X: freezing point depression, expressed in degrees centigrade; the freezing point itself is then represented by minus X in the case of solutions in water. In this way X is defined as a positive number.
F: fat content of milk, in % ($^w/_w$)
D: density of milk at 20 ° C
S: solids-not-fat content in % ($^w/_w$), calculated from F and D by the equation

$$S = 0{,}23\ F + \frac{260\,(D - 0{,}9982)}{D} \qquad \text{(equation 1)}$$

A very good approximation is given by

$$S = 0{,}23\ F + 245{,}8\ D - 245{,}15 \qquad \text{(equation 2)}$$

C: conductivity, expressed in milli Siemens

In about 250 samples of milk X, F, D and C were measured, while S was then computed from F and D. S is supposed to be proportional to the sum of minerals and lactose and therefore also to X. This relation will be negatively influenced by variations in the protein content. C is proportional to the amount of dissolved minerals and organic (mainly citrate).

S and C were chosen as parameters because of the ease and quickness they can be measured in large series of samples. The three parameters (X, S, C) were checked against each other for possible correlations. It was assumed that a relation would exist of the type $Y = aX + b$, where a and b are constants. Table 3 gives the results.

Table 3

Relations between freezing point depression X, solids-not-fat content S and conductivity C in milk

Correlation coefficient	Partial correlation coefficient	Equation	Equation number
0,67	0,77	$X = 0{,}0400\,S + 0{,}1904$	3
0,32	0,58	$X = 0{,}0231\,C + 0{,}4302$	4
— 0,15	— 0,53	$S = -\,0{,}1864\,C + 9{,}4037$	5

It appears that the three parameters are all related to each other. The correlation coefficient, which can vary from ± 1 (exact linear relation) till 0 (no relation), is a measure for a relation between two parameters (Table 3, column 1).

As is in the case here, if two correlated parameters are both influenced by a third parameter the calculated correlation coefficient is not representative for the relation between the first two parameters, but has to be corrected for the influence of the third parameter. This correction is made by keeping the third parameter constant and then calculating the so-called partial correlation coefficient (9). Results are shown in Table 3, column 2.

It is clear that X is positively correlated to either parameters; correlation between S and C is negative, which means that a high solids-not-fat content generally corresponds with a low conductivity. As both S and C are positively correlated to X, it might be expected that a combination of S and C gives still better results. Therefore, assuming a relation of the type $X = b_1S + b_2C + a$ holds true, the multiple correlation coefficient and the regression coefficients were calculated by the method of least squares.

This resulted in a multiple correlation coefficient $R = 0{,}80$ and an equation:

$X = 0{,}0440\,S + 0{,}0312\,C + 0{,}0172$ (equation 6)

Discussion

In table 4 a comparison is made between equation 6 and equation 3 from table 3. The samples were selected in such a way that they represent the whole range of X.

Table 4

Comparison of values of the freezing point depression, computed from equations 3 and 6, experimentally determined values

S	C	X (determined)	X_3 (equation 3)	X_6 (equation 6)
7,97	3,70	0,471	0,509	0,483
7,39	4,54	0,481	0,486	0,484
8,04	4,10	0,497	0,512	0,499
8,44	4,21	0,511	0,528	0,520
8,69	3,98	0,520	0,538	0,524
8,65	4,20	0,530	0,536	0,529
8,76	4,35	0,540	0,541	0,538
8,94	4,32	0,550	0,548	0,545
8,79	5,00	0,560	0,542	0,560

The mean deviation between X and X_3 is 0,013 °C and between X and X_6 0,004 °C. It is obvious then that X_6 is a better estimate of X than X_3 and it can be seen that approximation of X by equation 6 is very reasonable.

If we now substitute equation 2 into equation 6 we obtain, after rearrangement:

$$X = 0{,}0101\ F + 10{,}8152\ D + 0{,}0312\ C - 10{,}7694 \qquad \text{(equation 7)}$$

Conclusion

By measuring fat content F, density D and conductivity C of samples of milk a good approximation of the freezing point depression X can be obtained from the equation

$$X = 0{,}0101\ F + 10{,}8152\ D + 0{,}0312\ C - 10{,}7694$$

In this way a simple detection of added water to milk is possible.

Summary

Determination of the freezing point of milk is commonly used in food control as a means for detection of added water in milk. This method ist not very suited to examine large numbers of samples, therefore the use of other parameters was tested for this purpose.

By statistical evaluation of the values of fat, density and conductivity determined in about 250 samples of milk, an equation was derived which makes it possible to calculate the freezing point from these parameters. As fat content, density and conductivity can be determined quickly and accurately in many samples, this equation allows a fast insight into the possibility of wateraddition.

Résumé

La détermination du point de congélation du lait est utilisée pour détecter un mouillage éventuel. La méthode ne se prête pas à l'examen d'un grand nombre d'échantillons. L'examen statistique de valeurs analytiques concernant la teneur en lipides, la densité et la conductivité a été effectué sur 250 échantillons de lait. Une équation en a été dérivée qui permet de calculer le point de congélation à partir de ces paramètres analytiques. La teneur en lipides, la densité et la conductimétrie sont des grandeurs que l'on peut déterminer rapidement avec une certaine précision. L'équation proposée permet donc de déterminer rapidement un mouillage éventuel.

Literature

1. Nederlandse Warenwet, Melkbesluit, art. 3. Vermande Zonen, Ijmuiden.
2. *Nuijten. A.:* Tabellen. Joh. Boevink, Enschede 1951.
3. Dutch Standard NEN 3460, Determination of the freezing point of milk. Nederlands Normalisatie Instituut, Rijswijk 1971.
4. Jaarboek voor de Zuivelbereiding, 13 th ed., p. XI—2. Rijks Middelbare Zuivelschool, Bolsward 1957/1958.
5. *Souci, S. W., Fachmann, W.* und *Kraut, H.:* Die Zusammensetzung der Lebensmittel, p. A—II—1. Wissenschaftliche Verlagsgesellschaft MBH, Stuttgart 1962—1973.
6. *Kirchmeier, O.:* Handbuch der Lebensmittelchemie, Band III/I, p. 57. Springer Verlag, Berlin 1968.
7. *Oijen, C. F. van:* Voedingsmiddelen van dierlijken oorsprong (Melk) p. 60. J. van Boekhoven, Utrecht 1941.
8. Official Methods of Analysis of the A.O.A.C., 11th ed., p. 257. Washington 1970.
9. *Renner, E.:* Mathematisch-statistische Methoden in der Praktischen Anwendung, p. 70. Verlag Paul Parey, Berlin 1970.

J. Th. Welboren
Drs. H. van der Velden
Keuringsdienst van Waren
Nieuwe Gracht 3

Haarlem
Netherlands