International Conference on Science and Technique in the Agri-Food Business

ICoSTAF2008

UNIVERSITY OF SZEGED
FACULTY OF ENGINEERING

FOOD AGRICULTURE ORGANIZATION OF THE UN

HUNGARIAN ACADEMY OF SCIENCES
REGIONAL COMMITTEE IN SZEGED

HUNGARIAN SCIENTIFIC SOCIETY FOR FOOD INDUSTRY

November 5-6, 2008
SZEGED

PUBLISHER:

Dr. Antal Véha
Dean
UNIVERSITY OF SZEGED
FACULTY OF ENGINEERING

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ISBN 978-963-482-908-9
UNIVERSITY OF SZEGED
FACULTY OF ENGINEERING
H-6724 SZEGED , Mars tér 7.

CONTENTS

THE PROBLEM OF THE DETERMINATION OF ADDED WATER AND COW MILK IN GOAT MILK

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ABSTRACT

The demonstrability of the adulteration of goat milk with added water and cow milk was investigated by measurement of the freezing point of the milk. Milk samples collected from a Saanen goat flock were mixed with water in the ranges 0-90% and 1-10% and with cow milk in the ranges 0-90%. The freezing points of the samples were determined by a standard cryoscopic method.
Our results suggested that the freezing point prescribed as a reference value by the Codex Alimentarius Hungaricus and the EU directives for fresh and unadulterated goat milk (-0.52 °C) is too liberal, and this opens the door for the adulteration of goat milk. Only extraneous water in excess of 6% could be detected reliably in goat milk and therefore the measured freezing points at lower extraneous water contents appear falsely as good results. Accordingly, revision of the reference freezing point value of goat milk seems reasonable. Similarly, demonstrated that the adulteration of goat milk with cow milk can not be proved by measurement of the freezing point unless the goat milk contains cow milk in excess of 50%.

Keywords: Goat milk, freezing point, adulteration

INTRODUCTION

During the past ten years has been a perceptible change in the outlook of goat breeding worldwide. The goat sector seems to be waking up from a century-long dream and to be showing the signs of a slow development. Increasing attention is being paid to the production of milk and meat products from goat.
Goat milk contains nutrients with high physiological value and goat milk as a drink has advantages over cow milk in many ways. Goat milk is the most digestible milk for humans, it has a full set of amino acids and it is especially healthy in consequence of properties according to most references. It is most important therefore that available goat milk should not be adulterated.

In Hungary, section 2-51-180 of the Codex Alimentarius Hungaricus relates to the quality standard of raw goat milk. Adulteration (with water) is investigated via measurement of the freezing point of the milk. The Codex gives -0.52 °C as the reference freezing point for both goat milk and cow milk.
However, in many references the average freezing point of goat milk is given as markedly lower (more negative) than for cow milk. The average freezing point of raw goat milk is given by Hermann (1940) -0.5848 °C; Princivalle (1948) -0.582 °C; Dharmarjan et al. (1954) -0.579 ° C; Szíjarto & van de Voort (1983) -0.5527 °C; Mayer et al. (1995) -0.548 °C; Sanchez et al. (2005) -0.564 °C; El-Gadir et al. (2005) -0.561 °C; Whitney (2006) -0.553 °C; Sánchez et al. – 0.553 °C and Janštová et al. (2007) -0.5513 °C.

The range of freezing point was reported by Hermann (1940) to be between -0.537 and -0.646 °C; James (1976) to be between -0.550 °C and -0.578 °C; by Juarez & Ramos (1986) to be between -0.540 ° and -0.573 °C; by Rattray & Jelen (1996) to be between -0.553 °C and -0.574 °C; by Haenlein (2001) to be between -0.53 °C and -0.55 °C; by Kukovics et al. (2004) to be between -0.542 °C and -0.565°C; by Sanchez et al. (2005) to be between -0.545 °C and -0.657 °C; by Janštová et al. (2007) to be between -0.5466°C and -0.5567°C,. In contrast, Barbano (2006) concluded that the freezing point of goat milk is the same as that of cow milk (- 0.519 °C).

Some authors draw attention to the importance of the circumstances of the milking, the sampling and the measurement in the interest of achieving the correct result. A common mistake in the cleaning of the milking machines is the retention of a small quantity of rinsing water. Some water will be present in the milk samples if the milking machine or/and the holding tank was not properly dried after cleaning and sterilization.
Other circumstances of the measurement that affect the results are added preservatives (Sanchez et. al. 2005), the temperature of the sample and the settings of the cryoscope.

Our aim in the present work was to investigate the demonstrability of extraneous water in goat milk considering the current official reference freezing point. We also investigated whether the addition of cow milk, as the most obvious method for the adulteration of goat milk, is demonstrable. Our investigation of fresh goat milk samples furnished information especially about the freezing point of milk from Saanen goats.

METHODS

Samples collection

The samples for the investigation were collected from the goat farm of the "MKF Company's (Szarvas, Hungary). One litre bulk milk samples were made by mixing the morning and the evening milk from 20 Saanen goats registered in the National Registration System and stored at 5 °C until the measurement. The goats were milked by hand in milking boxes during feeding. Samples were collected in 10 occasions in the period from February until the end of April in 2007.

Cow milk samples for investigations of the mixing of cow milk with goat milk were also collected also from the farm of the MKF Company. The bulk milk samples were collected from regularly milked Holstein Friesian cows, and stored similarly to the goat milk samples.

Freezing point determination

88 goat milk samples were mixed with water, and 44 goat milk samples were mixed with cow milk in duplicate for determination of the freezing points.
The freezing point measurements and the making of the calibration solutions were carried out by the IDF method as detailed in the 2nd Appendix of Section 3-1-91/180 of the Codex Alimentarius Hungaricus. The instrument was calibrated with NaCl solutions with freezing points of -0.408 °C and -0.600 °C.
Original cells supplied by the producers of the Cryoscope I (Gerber-Funke GMBH) were used in the measurements. The cells were first cleaned then rinsed with distilled water,

dried at 105 °C and cooled in a desiccator over anhydrous silica gel before use. 2.5 ml samples were added to the cells with a BIOHIT Proline automatic pipette.

Instrument settings

Measuring method: Plateau
Temperature of cooling liquid: -6.5 °C
Cooling back temperature: 2.0 °C
Frequency of agitator: 91.5 Hz
Amplitude of agitator: 42%
Stirred beat: 46

The measurements were carried out on the basis of the current reference freezing point (-0.52 °C) and also on the basis of the mean freezing point that were determined (-0.56 °C) similar to that reported by Szijártó & Van de Voort (1983).
The compositions of the original milk samples were determined with a Bentley B150 Infrared Instrument (Bently Instruments, Inc. Chaska, Minnesota 55318, USA).
MS Excel was used to evaluate the results and to draw the diagrams.

RESULTS AND DISCUSSION

The mean composition of Saanen goat milk samples was close to that of cow milk (3.12% protein; 3.40% fat; 4.39% lactose; 12.07% total solid). We did not observe any indicative of mastitis, and the low fat content of the goat milk samples was therefore somewhat unusual. The lactose content in the goat milk samples was lower than that in the cow milk confiring published results of Posati & Orr (1976); Jennes (1980); Fenyvessy & Csanádi (1999); and Park & Haenlein (2006) but in contrast with those of Irvine (1974) and Balatoni & Ketting (1981).

Evaluation of the freezing points of the milk samples

The values of the freezing points of the collected cow milk samples varied between -0.5247 °C and -0.5317 °C with a mean of -0.5285 °C (SD=0.0029; CV%=0.548). These data correspond to those in recent references: Boor et al. (1998) -0.517 °C; IDF BS3095 (1988) -0.5233°C, ADAS (1999) -0.517 °C (range: -0.486 - -0.532 °C); Slaghuis & Klungel (2008) -0.530 °C (range: -0.463 - -0.584 C°); Unger (2001) range: -0.510 - -0.53 °C; Henno et al. (2008) range: -0.527 - -0.5249 °C.

The freezing points of the goat milk samples varied from -0.5526 °C to -0.5825 °C, with a mean of -0.5616 °C (SD=0.101, CV%=1.798). These data correspond to those in publications which reported a lower freezing point of goat milk as compared with the freezing point of cow milk.
Adulteration of goat milk with cow milk

In our preliminary research we found that the freezing point of goat milk changes to an appreciable extent only when is added in a considerable quantity; we therefore report now only results on samples to which cow milk was added 10% steps up to 90%.

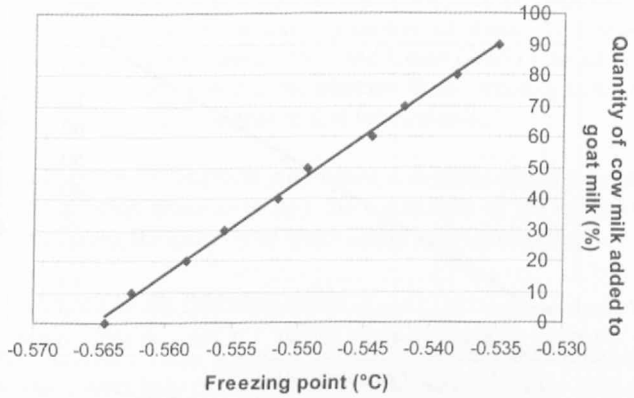

Figure 1. Influence of added cow milk on the freezing point of goat milk

As we expected, we observed a close linear correlation (R^2=0.997) between the quantity of cow milk added and the change in the freezing point. The freezing point of the milk increased in parallel with the increase of the amount of added cow milk.
If the average freezing point value cited in the literature (-0.56° C) as the basic freezing point of the unadulterated goat milk was used as a reference value, the adulteration with cow milk could demonstrate only in the samples that contained more than 17-18% cow milk.
Thus, we proved that only large-scale adulteration with cow milk is demonstrable with this method, but even then only if we have a correct reference freezing point. Accordingly, other methods were devised for the demonstration of the adulteration of goat milk with cow milk, based on determination of the protein fractions in the milk.

Adulteration of goat milk with water

Inasmuch as the freezing point of water is markedly higher than that of goat milk, the addition of water in 10% steps up to 90% gave freezing points which unequivocally indicated the added water in the goat milk. As expected, the freezing point of goat milk was to a noteworthy extent by the added water, and the current reference value (-0.52 °C) was exceeded even when only 10% of water was added.

The close linear correlation between the freezing point and the quantity of added water *(Fig. 2.)* indicated a 0.01 °C increase in freezing point for every 1.78% of water added to the goat milk. Alternatively, every 1.0% of added water increases the freezing point of goat milk by 0.0047%.

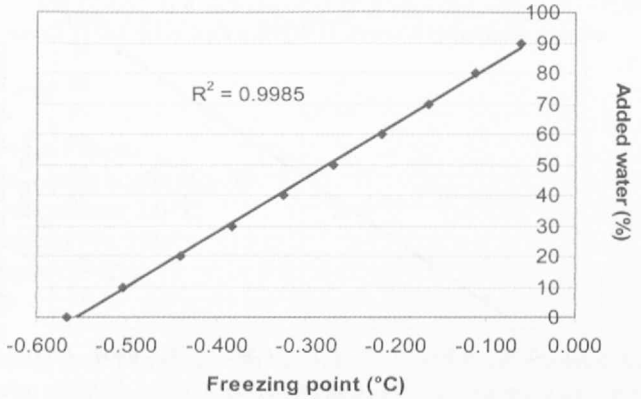

Figure 2. Effect of adulteration with water on freezing point of goat milk

Our data closely resemble those reported by Balatoni (1978) and Advanced Instruments (1995): every 0.01 °C freezing point increase corresponds to 1.82-1.90% added water, i.e. each 1.0% of added water increases the freezing point by 0.005 °C.

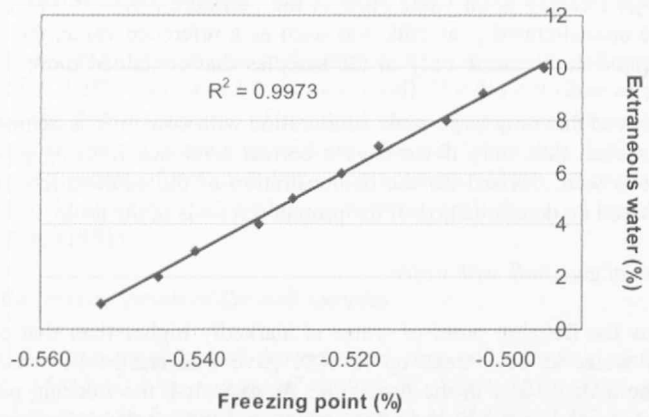

Figure 3. The effect of added water on the freezing point of goat milk (Range of the added water: 0-10%)

Our data parallel results of Unger (2001), who suggested that a 0.01°C freezing point increase corresponds to 2.0% added water in the milk.
Such a wide range of adulteration is not probable in practice and we therefore repeated the investigations within the range from 0.0 to 10.0%. These results are demonstrated in *Fig. 3.*

A close linear correlation was again found between the level of adulteration and the freezing point of the milk samples containing these lower quantities of water. According to expectations, the regression coefficient was slightly better than in the previous experiment and 1.71% of added water was found to change the freezing point by 0.01 °C in this experiment.
It should be noted that the samples containing less than 6.0% of would have been classified as "unadulterated" if the current reference value (-0.52 °C) had been used.

There were differences between our and the literature data as concerns the changes in freezing point caused by addition of fixed quantities of water. The results reported by Balatoni (1976), Advanced Instruments (1995) and Unger (2001) refer to cow milk, but the good level of accordance indicates that the increase in the freezing point of goat milk in consequence of the addition of is similar to that for cow milk.

Insofar as the adulteration of goat milk with water is demonstrable by measurement of the freezing point, the question arises as to how the correctness of the reference value affects the conclusion concerning the quantity of water added to the goat milk.

Dependence of accuracy on the reference value

When the current reference value was used, we found that the determination of the extent of adulteration was correct only if the goat milk contained more than 40% of added water *(Table 1.)* The imprecision of the results in the low ranges did not allow determination of the real quantity of added water.

Table 1. Accuracy of determination of water added to goat milk (n: 5; reference value: -0.52°C)

Quantity of added water %	Mean of measured values	SD	CV%
0	0.00	0.00	0.00
10	6.04	1.13	18.64
20	17.82	1.05	5.88
30	28.64	0.91	3.17
40	39.37	0.76	1.94
50	49.69	0.67	1.35
60	59.72	0.56	0.93
70	69.53	0.55	0.79
80	79.13	0.81	1.03
90	88.3	0.90	1.02

A high quantity of added water in goat milk can easily be demonstrated by other means (sensory analysis, composition, density, or Ld°), and we therefore investigated adulteration with smaller quantities of added water.

The results proved that, when the current reference value is used, determine of the degree of adulteration with less than 7.0% added water is impossible *(Fig. 4.)*. We found an imprecision of ~ 6-7% relative to data when the correct freezing point was used.

Because the classification requirements do not prescribe other examinations for the determination of such adulteration, the criterion "corresponds to the natural composition" is not sufficient for verification of the lack of adulteration.

As the quantities of the milk components decrease in a similar ratio (%) as the added quantity of water increased, possible changes in composition of these components do not prove adulteration. For instance, 10% added water decreases the fat content from 4.0% only to ~3.6%. Thus the current reference value can not be regarded as trustworthy, and this gives a possibility for adulteration even 6-7% water without the danger of detection.

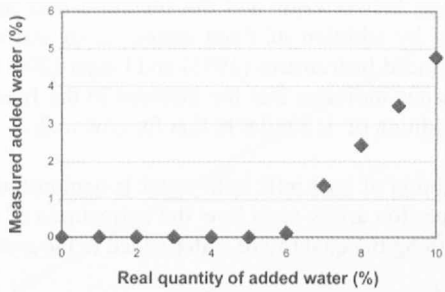

Figure 4. Relationship between real and measured quantities of added water in goat milk (Reference value: -0.52 °C)

We presumed that precise demonstration of the level of adulteration would become possible only trough use of a well-chosen reference value. Accordingly, we repeated the examinations, but with the mean freezing point of the original goat milk samples as reference value. These experiments led to very interesting results (*Fig. 5.*).

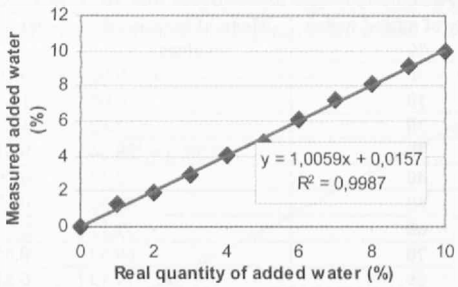

Figure 5. Relationship between real and measured quantities of added water (Reference value: -0.56 °C)

The mean of the differences of the measured values from the real quantities of water added was 0.049%, while the range of the difference was 0.0-0.25%; this imprecision is negligible. The results prove that real quantity of water added to goat milk can be determined with good accuracy by using a well-chosen reference value.

It is important, that at the moment we can not specify a precise and correct reference value relating to the freezing point of Hungarian goat milk. However, the results to date clearly show that the current reference value is not sufficiently precise for quality control and particularly not for the improvement of the quality of goat milk.

CONCLUSIONS

Most of the published reports and also our own investigations confirm that the freezing point of goat milk is lower than that of cow milk. Despite this fact, the reference value for the freezing point of goat milk in the European Union is -0.52 °C. The present results demonstrate that the current reference value gives a possibility for the adulteration of goat milk in marked amount of water (up to 7%). This does not facilitate efforts to improve the quality of goat milk.

The mean freezing point that we found, -0.561 °C, corresponds with the published data. We confirmed the effect of the adulteration on the freezing point for goat milk samples

mixed with either cow milk or water. As there was a close linear correlation between the extent of adulteration and the freezing point of milk.

On the basis of our preliminary and present results and keeping the principle of graduation, we suggest a reference freezing point of -0.545 °C for determination of the adulteration of goat milk.

It is not possible to demonstrate the adulteration of goat milk with cow milk in any range by using the current reference value. When the instrument was adjusted to the measured mean freezing point of goat milk, only more than 16% cow milk was demonstrable. Hence, other methods must be used for this purpose, e.g. the method described by Szíjarto & Van de Vort (1983).

The selection of a correct freezing point reference value is very important in the determination of the adulteration of goat milk because an incorrect reference can lead to marked differences from the true determination of the quantity of extraneous water. When the EU-recommended reference value is used, only more than ~ 6% added water is demonstrable in goat milk. Accordingly, there is a current need for the determination of the correct reference value of the freezing point of goat milk, which may even vary from country to country. So the revision of the reference freezing point value of goat milk seems reasonable and will demand a huge numbers of investigations.

REFERENCES

1. Advanced Instruments (1995): Brochure: Added water and the freezing point of milk.
2. Balatoni (1976): Tejipari táblázatok. Mezőgazdasági Kiadó Budapest ISBN: 963 230 335
3. Balatoni M, Ketting F. (1981): Tejipari kézikönyv (Dairy Handbook), Agricultural Publishing Hungary
4. Barbano C. A. (2006): DPC2: Animal Products (Dairy) Approved Criteria for Farm Dairies New Zeeland. Food Safety Authority. http://www.nzfsa.govt.nz/dairy/publications/approved-criteria/dpc2approvedcriteriaforfarmdairies_1.pdf
5. Boor K. J., Brown D. P., Murphy S. C., Kozlowski S. M., and Bandler D. K. (1998): Microbiological and Chemical Quality of Raw Milk in New York State. Journal of Dairy Science Vol. 81, No. 6, p. 1743-1748.
6. Codex Alimentarius Hungaricus 2-51. 1.4.3. Nyers kecsketej. Fizikai és kémiai követelmények. p. 15.
7. Council directive 92/46/EEC of 16 July 1992. Laying down the health rules for the production and placing on the market of raw milk, heat-treated milk and milk based products.
8. Dharmarjan, C.S., Rao, R.V., Dastur, N. N. (1954): Composition of Milk of Indian Animals. V. Freezing Point, Lactose, Chloride and Acidity in Goat and Sheep Milk. Indian J. Vet. Sci., 24. (51) p. 2954. In: W. F. Shipe (1959): The Freezing Point of Milk. A Review J. of Dairy Sci. 42. pp. 1745-1762.
9. El-Gadir, M. E. A., El-Zubeir, I. E. M. (2005): Production performance of crossbred (Saanen and Nubian) goats in the second kidding under Sudan conditions. Pakistan Journal of Biological Sciences, (Vol. 8), No. 5. p. 734-739.
10. Fenyvessy J., Csanádi J. (1999): Nutritional evaluation of components of small ruminants (ewe's, goat) milk. Hungarian Dairy Journal – Science and Practice. 59. (2) p. 23-27.

11. Haenlein G.F.W. (2001): The concept of milk quality in the USA, Int. J. Anim. Sci. 16, p. 5–8.
12. Henno M., Ots M., Jõudu I., Kaart T. and Kärt O. (2008): Factors affecting the freezing point stability of milk from individual cows. International Dairy Journal, Volume 18, Issue 2, February 2008, p. 210-215.
13. Hermann C. Lythgoe (1938): Composition of goat milk of known purity. Journal of Dairy Science 23. (11) pp. 1097-1108.
14. IDF BS3095; Part 2:1988. Recommendations for the Interpretation of the Freezing Point
15. Irvine M. D. (1974): The composition of milk as its effect the yield of cheese. Proceeding of 11th Annual Marshall Invitational Cheese Seminar, Marshall Div. Miles Lab. Madison WI., USA in: Park & Haenlein Handbook of milks and non-bovine mammals. Blackwell Publishing 2006.
16. James, G. V. (1976): A note on the freezing point of goat milk. J. Assoc. Publ. Anal. 14, (3) p. 111-115.
17. Janštová, B., Dračková, M., Navrátilová, P., Hadra, L., Vorlová, L. (2007): Freezing point of raw and heat-treated goat milk. Czech J. Anim. Sci., 52, 2007 (11) pp. 394–398
18. Jennes R. (1980): Composition and characteristics of goat milk. Rewiew J. Dairy Sci. 63. 1605 p. 1968-1979.
19. Juàrez, M. and Ramos, M. (1986): Physico-chemical characteristics of goat milk as distinct from those of cow milk. In: Proceedings of the IDF Seminar in Production and Utilization of Ewe's and Goat's Milk, Bulletin No. 202 Athens, Greece (1986), p. 54–67.
20. Kukovics, S., Ábrahám, M., Németh, T (2004): Hygienic characteristics and classification of Hungarian sheep and goat milk. Tejgazdaság, 64:2. p. 35-40.
21. Mayer H. K., Schober D., Ulberth F., Kneifel W. (1995): Physico-chemical characteristics of goat milk in Austria – seasonal variations and differences between breeds. Production and Utilization of Ewe and Goat Milk IDF and CIRVAL Conference in Crete (Greece) 19-21. October 1995. Proceeding of the IDF/CIRVAl Seminar p. 278.
22. Park Y. W., & Haenlein G. F. W. Handbook of milks and non-bovine mammals. Blackwell Publishing 2006.
23. Posati L. P. & Orr M. L. (1976): Composition of Foods. Agric Handbook No. 8-1. ARS USDA, Washington, DC.
24. Princivalle, E. (1948): Richerche sul latte di capra. Nota I. Ann. Chim. Appl. Roma 8: (10/11) p. 617.
25. Rattray W. & Jelen P. (1996): Freezing Point and Sensory Quality of Skim Milk as Affected by Addition of Ultrafiltration Permeates for Protein Standardization, International Dairy Journal Vol. 6. No. 6. pp.569-579.
26. Sánchez A., Sierra D.; Luengo C.; Corrales J. C.; Morales C. T.; Contreras A.; Gonzalo C. (2005): Influence of storage and preservation on fossomatic cell count and composition of goat milk. Journal of Dairy Science (Vol. 88), No. 9. p.3095-3100.
27. Sánchez, A., Sierra, D. Luengo, C. Corrales, J. C. Fe, C. de la Morales, C. T. Contreras, A.and Gonzalo C. (2007): Evaluation of the MilkoScan FT 6000 Milk Analyzer for Determining the Freezing Point of Goat's Milk Under Different Analytical Conditions J. Dairy Sci. 2007 90: 3153-3161.
28. Slaghuis B. A. and Klungel G.H. (2008):Variation of freezing point of cows' milk free from extraneous water during lactation Research Station for Cattle, Sheep and

Horse Husbandry, PO Box 2176, 8203 AD Lelystad, NL. http://bsas.org.uk/downloads/milkcomp/28.pdf (23.01.2008.)
29. Szijarto, L., van de Voort F. R. (1983): Determination of added water and bovine milk to caprine milk. Journal of Dairy Science, (Vol. 66), No. 3. p. 620-623.
30. Unger A. (2001): A fagyáspont. In: Szakály S. Tejgazdaságtan, Mezőgazda Kiadó Budapest 2001. ISBN: 963 657 3333 6
31. Zee, B., Drogt, J. and Giessen, T.J.J, 1982. The freezing point of authentic farm tank milk in The Netherlands. Netherlands Milk and Dairy Journal 36, pp. 291–303.
32. Whitney H. (2006): Raw Milk Quality Testing Animal Production Factsheet Publication: AP017. Government of Newfoundland and Labrador, Department of Natural Resources.

Készült az Európa Terv (GVOP 3.2.1. 2004-04-0252/3.0) támogatásával