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APPLICATION OF CRYOSCOPY FOR DETECTION OF MILK ADULTERATION BY AMMONIA

The results of researches of freezing temperature and titratable acidity of milk forcibly adulterated by ammonia are given in the article. Samples of the sterilized milk are used for researches. To reconstruct the origin of the phenomena the conditions of high acidity milk production are considered in details. The process of natural souring of sterilized milk is analyzed. Buffer properties of milk are described. Much attention is paid to the description and discussion of occurring processesat introduction of additives of water solution of ammonia.

Introduction. One of the most often adulterated products because of its exclusive nutrition value and prevalence is milk. Most often adulteration of natural milk is carried out by addition of water, skimmed milk, neutralizers, skimming [1]. As the substances neutralizing the excess of acidity soda and ammonia are applied.

The milk adulterated by ammonia has soapy smack, spoils quickly because of the putrefactive microflora which is freely developing in milk in the absence of the lactic environment, and milk becomes unsuitable for processing in dairy products. The existence of ammonia and other neutralizers is defined at milk acceptance in the case of suspicion on their presence [2].

Crude milk at addition of neutralizers in small amounts is capable to support some time a constant of active acidity at slow increase of titratable acidity. This is explained by the fact that milk represents the buffer system, being characterized by the ability to support a constant value of *pH*. Buffer systems in biological liquids to which milk belongs, play a great role in protection of live organisms against sharp changes of *pH* that can lead to their death or create the adverse conditions for them [3].

Buffer properties of milk depend on the existence of proteins, hydrophosphates, citrates and carbon dioxide in it. So at increase of titratable acidity with development of lactic microflora the level of *pH* remains without changes some time.

Proteins of milk possess buffer properties thanks to carboxylic and amines groups. Comulative at souring lactic acid reacts with aminines groups of proteins, while addition alkali – with the carboxylic ones. The dissociation of proteins is insignificant therefore the concentration of hydrogen ions remains invariable, and titratable acidity increases as at its definition active and fixed ions of hydrogen react with alkali. The change of *pH* at accumulation of lactic acid in milk will happen only when all amines groups of proteins are used [3].

Buffer properties the salts phosphates are shown by gradual transition of twosubstituted phosphates into the monosubstituted ones with the growth of concentration of acid, and as $H_2PO_4^-$ anion is poorly dissociated this process practically doesn't change *pH* of environment, though titratable acidity will increase. And *pH* won't rise until twosubstituted phosphates transit into the monosubstituted ones. Bicarbonates and milk citrates possess the same buffer properties.

Buffer ability is characterized by buffer capacity – number of 0.1 N of solution of acid or alkali that is necessary to add to change the level of *pH* by one. Buffer capacity of milk on acid at *pH* 4.5–5.5 is 2.34–2.70 ml; on alkali it is 1.2–1.4 ml. I. e., in relation to acid milk possesses considerably larger buffer capacity than it is in relation to alkali [3].

At present, the acidity of dairy raw materials is controlled when purchasing. However, it isn't enough data about influence of adulterated additives on freezing temperature of subquality milk. Therefore, the aim of our work was investigating adulterated milk properties in actual storages conditions and studying of the possibility to apply the cryoscopic method, which is very sensitive to various additives (1% of water addition in milk increases the average freezing temperature of milk on 0.006°C that is surely determined by modern measuring means [4] for quality control of crude milk).

Main part. Two samples of 1.5% fat sterilized milk from two domestic producers in the consumer containers were chosen as the objects of our research. The choice of the sterilized milk is caused by slow changes of its physical and chemical parameters during the initial stages of souring as it was described by us earlier [5, 6], and during the working day.

The opened milk container was stored in consumer packing at room temperature during two days. Further, we closed a container and continued keeping of the samples during 2–23 days. Because it is accepted in dairy industry to define the milk sweetness by titratable acidity, milk souring was also defined by standard methods of titratable acidity as well as by freezing point measurement [7, 8].

Milk keeping at room temperature was continued as far as acidity level run to the required one by the National Standard [8].

Conditions of carrying out experiment and recieved average values of controlled parametres

Conditions of carrying out experiment	Sample number	
	I	II
Storage of the closed samples, days	9	23
Titratable acidity, °T	20	45
Freezing temperature, °C	–0.500	–0.572

Earlier, the changing of freezing temperature in the keeping process and after souring was described in details [5, 9]. At the first stage fast multiplication of microorganisms, which penetrated in the samples with atmospheric air, was the most probable reason of souring. At the second stage acidic coagulation of milk protein was more possible, whereas earlier point-like blobs were observed only. Totally soured milk consisted of not stable blobs of high dispersity of particles.

Measurement of freezing temperature was conducted by a milliosmometre-cryoscope thermoelectric MT-5-01 (Burevestnik, St. Petersburg). Accuracy of measurement was ±0.004°C for determination of freezing temperature, and ±0.5°T for determination of titratable acidity. The average arithmetic values of 2–5 parallel measurements of the given indicators and the conditions of carrying out experiment are shown in the table below.

Then, we extracted 7 hundred-gram tests from the prepared samples. Their compulsory adulteration for decreasing of titratable acidity was carried out by introduction of 5% water solution of ammonia in the quantity of 0.1–0.7 g. Accuracy of weight measurements was below 1 mg. The received deoxidated tests were vigorously stirred up in the closed flasks and left in quiescence not less than for 15 min. The rest of milk was used for control.

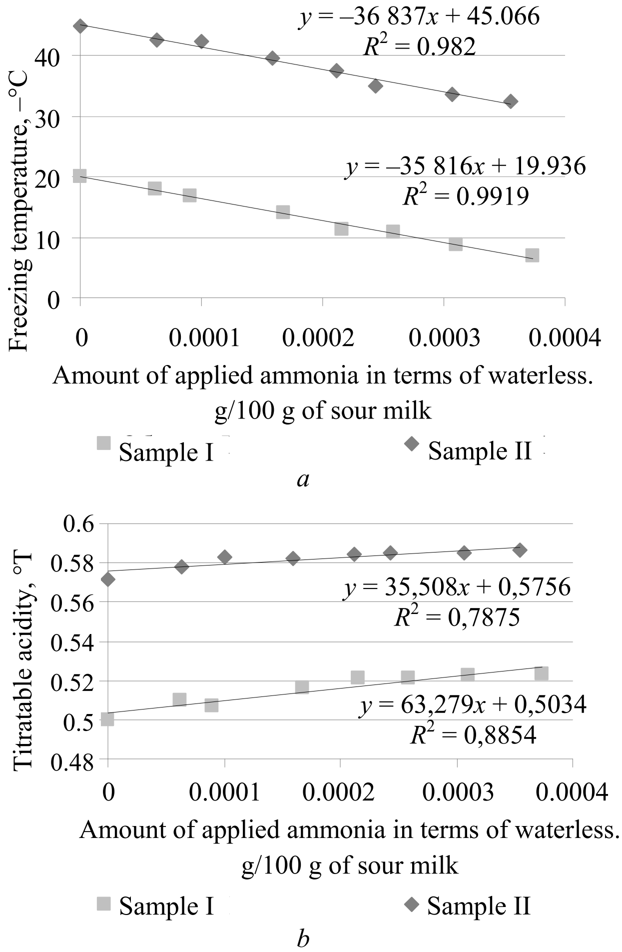
It is necessary to note that the prepared adulterated tests hadn't ammonia smell when titratable acidity measurement was available still.

The results, which are illustrated by the draw below, show a tendency of decreasing of freezing temperature and titratable acidity versa ammonia concentration growth.

Linear dependence of the measured parameters from the concentration was clearly observed for the products of the both manufacturers.

Evidently, buffer properties of the sour milk are shown quite poorly as linear nature of dependences remains up to zero concentration of the additive, and the sufficient masking effect is observed already after adding of 20 mg of ammonia in 100 g of the initial product.

It should be noted that when entering water solutions into milk, it decreases its density, fat content, milk solids, the nonfat milk solids [2, 3]. Besides, water brought with solution is the adulterator itself. However, in our case because of various mechanisms of water and ammonia interaction with milk their influence is somewhat compensated. Therefore, the use of very strongly diluted solutions will be found as watering, and determination of ammonia additives will be disguised.



Dependence of titratable acidity (*a*) and freezing temperature (*b*) of sour milk from the quantity of applied ammonia, (in waterless basis)

Thus, the obtained data reflect the effect compensated by additive components.

The mechanism of souring of the sterilized milk and its interaction with ammonia water solution includes the following processes:

1) accumulation of milk acid in the process of fermentation, which, in turn, promotes reactions with hydrophosphates and proteins, dissolves colloidal phosphate of calcium and in a consequence of it raises the content of titratable hydrophosphates [3];

2) acidic coagulation of milk proteins runs due to milk acid affection; probably, that is the reason of lack of buffer capacity for alkali;

3) ammonia water solution could be neutralized by lactic acid, which appears as a result of fermentation, as well as by different volatile acids;

4) obviously, additional water appears in the samples from solutions tests and as a product of reaction of neutralization;

5) influence of additional water on the level of titratable acidity and freezing temperature compensates the influence of ammonia.

Conclusion. An attempt of a reconstruction of conditions of the sterilized milk souring, which is storing in open consumer containers, and some subsequent study of influence of additive of ammonia water solution on freezing temperature and titratable acidity of a product is made.

Linear dependence of titratable acidity and freezing temperature of the sterilized milk from concentration of added ammonia is established.

The sterilized sour milk has no buffer properties on alkali.

The cryoscopic method is a perspective one for detection of milk adulteration by ammonia, and it allows to carry out the control of titratable acidity 3–5 times faster, than the classical method does.

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