COUNTERFEITING DETECTION OF MILK AND DERIVATIVE PRODUCTS

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Abstract: About the appearance on the market of unqualified milk products, within Practical Scientific Institute of Horticulture and Food Technology (Food Technology Directorate) were initiated research and development works to establish counterfeit milk products and detection methods of them. Physico-chemical quality indices of milk were determined with the use of modern instrumental methods: Milco-Scan device (9 indices), gas-liquid chromatography Chrom-5 (7 fatty acids) and analytical ones. In result of the investigation was established the existence of the Republic Moldova market – nonconforming drinking milk and counterfeit, both water dilution method and substitution of lactic fat with vegetable fat (falsification of content). The absence of respective information on the product label is assigned to the category of informational falsification.

Key words: milk, product counterfeiting, methods, monitoring

Introduction

The volume of counterfeit dairy products in many countries in recent years was 30-50% and it is assumed that in Republic of Moldova has created a similar situation so that the absence of a state system of dairy products quality control, as well as deficiency of qualified specialists, able to capitalize the materials and quality standards of EU countries. [1]

This problem, unfortunately, not had an approach in some state programs involving scientific institutions in developing quality standards and methods for identifying counterfeit food, so the elaboration of authenticity/deceleration criteria of falsified food and representative index determination, specific besides those who are established in the standards for dairy products, is a vital issue at the moment with a significant economic and social impact, including on health.

Actually, in manufacturing of drinking milk the enterprises use whole milk produced in private farms or bought directly from producers, as well as dry milk powder to reconstitute it, and the product placed on the market needs to be conformed under the respective normative documentation [2-4]. In many cases there is the replacement of dairy fats with various types of vegetable fats. For consommer it is important the possibility to determine what kind of milk used in food.

This topic has particular importance and for products intended for children, which requires strict control on raw milk.

Materials and methods

Was conducted the monitoring of drinking milk quality, selected from homesteads pasteurized to +63°C for 30 minutes and from the markets, manufactured in some industrial enterprises from Romania, Russian Federation, Ukraine and Belarus. In order to respect the confidentiality of information, may bring some harm producers/ importers, milk samples are coded without their names.

Laboratory investigations were carried out on the basis of new physical and chemical indicators, which are: fat content, lactic dry skim residue, density, protein content, lactose content, freezing temperature, conductivity, pH and titratable acidity according to [5]. The lactic fat extracted in the milk samples was determined fatty acid composition by gas-liquid chromatography method, and the use of the preparation procedure of the methyl esters of fatty acids using sodium methylate [6-9].

Determination of fatty acids in milk samples was investigated on „Chrom-5" chromatograph performed with a flame ionization detector. As the column filler was used Cromaton N-AW-DMCS (0.16 to 0.20) $x10^{-6}$m filing phase Reoplex-400 at 15%.

Chromatography conditions:

- temperature in thermostat of chromatographic column 150 ^{0}C;
- temperature of evaporator 200 ^{0}C;
- temperature of detector 210 ^{0}C;
- Consumption of lead gas (helium) 30 cm^3/min;
- Consumption of air 350 cm^3/min;
- consumption of hydrogenium 30 cm^3/min;
- speed mouvement of tape recording device 19 cm/hour.

The quantitative composition of the fatty acids was determined by norming peaks method, and the content of each fatty acid was calculated from the chromatogram, was expressed as a percentage with reference to the sum of the triglycerides acids extracted from the milk fat.

Results and discussions

After monitoring has been established, that typically Moldovan enterprises on sale pasteurized milk reconstituted from powder milk, packed in polyethilene packets and bottles of polymer material with storage period of 3 to 4 days. The importers on sale UHT milk packed in laminate cardboard with storage period from 48 days to 12 months. (Table 1).

Table 1. Milk samples selected from the markets

№	Country	Fat content, %	Packing	Storage period	Method of heat treatment
1.	**Moldova**	1,5; 2,5; 3,5	polyethylene packets plastic bottles	72 hours 96 hours	pasteurized
2.	**Moldova**	1,5; 2,5; 3,5 3,6-6,0	polyethylene packets plastic bottles	72 hours 96 hours	pasteurized
3.	**Moldova**	1,5; 3,2	polyethylene packets	72 hours	pasteurized
4.	**Moldova**	2,5	polyethylene packets	72 hours	pasteurized
5.	**Moldova**	2,5	polyethylene packets	168 hours	pasteurized

№	Country	Fat content, %	Packing	Storage period	Method of heat treatment
6.	**Moldova**	1,5; 3,5	polyethylene packets	72 hours	pasteurized
7.	**Russia**	0,5; 1,8; 3,5	cardboard box (tetra pack - 1litru)	6 months	ultrapasteurized
8.	**Ukraine**	0,5; 1,5; 2,6; 3,2	cardboard box (tetra pack - 1litru)	6 months 4 months	ultrapasteurized
9.	**Romania**	1,5; 3,5	cardboard box (tetra fino - 1litru)	6 months	ultrapasteurized
10.	**Ukraine**	1,5; 2,5 3,2; 6,0	cardboard box (tetra pack - 1litru)	12 months	ultrapasteurized
11.	**Belarus**	1,5; 3,1; 6,0	cardboard box (tetra pack - 1litru)	6 months	ultrapasteurized

According preventive results have selected four trademarks of production for carrying out laboratory investigations. As the fifth sample of the study served fresh cow's milk from farms (table 2).

The evaluation of physico-chemical parameters was performed according to the standards for the product, on the methods of testing, as well as data obtained from the device „Milcosan". Of milk samples studied, fully meets the requirements of SM 104 only cow's milk selected from farms. Higher deviations of fat content and titratable acidity were found in sample Nr.1. Based on the deviations from the established norms in the technical documentation it can be seen that the product is non-compliant if the information is not included on the product label.

Table 2. Physic-chemical indices of milk samples

Physic-chemical indices	**established norm in ND**	**Milk sample**				
		№1 2,5%	**№7 1,8%**	**№10 3,1%**	**№2 6,0%**	**milk selected from farms**
Fats, %	0,05-9,0	2,6	1,8	3,1	3,6	3,3
Dry lactic skimmed residue,%	>8,2	8,2	8,3	7,9	8,0	8,6
Density, gr./cm^3	1,027	1,027	1,029	1,027	1,027	1,030
Proteins, %	min. 28	3,1	3,0	3,0	3,0	3,2
Freezing temperature, ^{0}C	55,0	53,8	55,1	52,1	53,1	55,9
Lactose, %	min. 4,5	4,5	4,7	4,4	4,4	4,7
Conductibility, ohm/cm^3	4,5	4,5	4,2	4,4	4,1	4,7
pH	-	7,2	7,2	7,3	6,9	6,88
Titratable acidity, ^{0}T.	16-20	15	16	16,5	15,5	16,5

The following studies have been directed to the study of the structure of fat milk using gas-liquid chromatography. At the moment, are identified 45 lactic fat fatty acids, which vary by molecular weight isomerism spatial level of unsaturated hydrocarbon chain and the location of double bonds. Milk fat for authentication is enough to control

the ratio 5-10 fatty acids in samples tested to basic methodology [8]. As the reference sample was used natural fresh milk, pasteurized for 30 minutes at a temperature of + 63°C. The investigation results are presented in Table 3.

Table 3. Fat acids composition in lactic fat, extracted from milk samples

Samples (milk fat)	**The mass fraction of individ. fatty acids (% of triglycerides amount)**						
Norm according to GOST R 52253-2004	**Lauric**	**Miristic**	**Palmitic**	**Stearic**	**Oleic**	**Linolic**	**Linolenic**
	2,0-4,0	8,0-13,0	22,0-33,0	9,0-13,0	22,0-32,0	3,0-5,5	to 1,5
Natural pasteurized milk	2,30	12,86	31,63	12,65	28,90	2,15	traces
	2,22	12,55	31,83	12,22	28,57	1,95	traces
Sample nr.2	3,06	9,75	32,37	13,12	24,69	2,76	<0,2
	2,94	9,30	32,85	12,65	23,72	2,55	<0,2
Sample nr.2"a"	2,90	9,64	32,15	10,12	25,24	2,45	<0,2
	2,89	9,83	32,44	9,91	24,86	2,68	<0,2
Sample nr.8	2,87	9,95	33,23	13,50	27,70	2,43	<0,2
	2,90	10,20	32,94	13,10	28,20	2,55	<0,2
Sample nr.7	3,63	11,94	33,42	9,80	28,43	2,77	<0,2
	3,40	11,74	32,95	10,43	28,39	2,80	<0,2
Sample nr.1	2,21	9,72	33,44	14,27	26,71	2,31	0,34
	2,00	9,85	33,89	13,24	27,63	2,80	0,38
Sample nr.1„a"	1,28	4,09	36,40	6,28	36,55	6,46	0,45
	1,34	5,00	36,80	6,44	36,85	6,74	0,48

Mass fraction of lauric acid, myristic, palmitic, stearic, oleic fat milk is in the range of variation established for these components. Linoleic acid content is usually below the limit set for this component, but its amount is lower by 0.2%, or as "traces". The exception make sample 1 and 1"a", which fatty acids composition do not fall within established normative documents. The results of investigations on the composition of the fatty acids, the samples 2, 2"a", 7 and 8 are indices regulated in the standard. In the same place, the samples 6 and 7 have essential deviations of fatty acid content -palmitic, stearic, oleic and linoleic, which confirm the total or partial replacement of milk fat with vegetable fat.

Such replacement of milk fat with vegetable fats not only change the calorific value of dairy product but may decrease the price put you ahead of other producing companies. Such type of competition cannot be considered fair because it violated index "price-quality" and cause confusion. Milk product in question shall be offered to the consumer at a lower price and with the account information on the packaging about a correction of product chemical composition, such as consumer able to decide, what purpose this product can be used - in culinary as milk drinking or component to feed children etc.

Studies show that on the Moldovan market in same time with products complying normative documents it is placed drinking milk that may be considered non-compliant or clearly falsified. If information about the chemical content is not indicated

on the product label, that non-compliance is attributed to the category of falsifying content (replacing milk fat with the vegetal origin, the addition of excess water, etc.) and informational.

Conclusions

1. It was made the quality monitoring of drinking milk produced in Moldova and from the import.
2. It was found a wide range of milk quality indicators selected from markets.
3. It is established the possible ways to fake milk, which is dilution with water and partial replacement of milk fat with different vegetables fats.

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