IT in development of express method for consumer goods quality control

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Abstract. Implementation of IT significantly increases opportunities of the leading operators on the commodity market in the sphere of efficient quality and safety monitoring throughout the food products life cycle. Development of the compact analytical equipment for control of physical and chemical parameters regulated by the applicable technical standards at production, storage and marketing of food products is the important task having social implication. Represented in the article as an IT application solution is the express method for determination of casein concentration in dairy products packed with the help of the units using nuclear magnetic resonance (NMR) effect. With the aid of this express method the adulterated dairy products (milk, condensed milk, curd, etc.) can be revealed which are produced on the basis of dry skimmed milk containing a dry milk serum by substitution of the milk protein — casein. According to the preliminary assessment the minimum concentration of casein reported by such method is approx. 0.5%. The method is based on investigation of the hydration process of casein micelles participating in formation of structural-mechanical properties of protein coagula created at fermented milk products generation.

1. Introduction

Food products take a leading position in the sector of everyday products. As such, their quality and safety monitoring becomes increasingly important trend in the consumer goods segment. Non-conformance of food products to requirements of the regulatory documents has a serious negative impact on reputation of not only manufacturers, but also the leading operators of retail network. Consumers are at liberty to have complete confidence in that food products they everyday consume are not adulterated and correspond to quality and safety parameters declared on the packing [1].

One of the topical issues of food industry in the frames of the innovative transformation of economy on the basis of its digitization is development of the compact analytical equipment for economical control of the rated physical-chemical parameters at production, storage and output quality control of the products. At the present time a new type of cost-effective desktop instruments came into being the operating principle of which is based on the use of nuclear magnetic resonance (NMR) effects. The main advantage of NMR-instruments is absence of invasive and destructive methods of the diagnosis performed [2–6]. The known use of NMR in the food industry is ISO standard on...
determination of solid fat concentration in dairy products [7–9]. Besides, the following methods are known: NMR-spectral method on determination of acetic acid concentration as an indicator of vine degradation in closed containers [10]; NMR-analyzer manufactured by Intermagnetics company for quality control of dairy products [3]; application of ‘NMR-mouse’ instrument with a one-sided magnet and a sensor for determination of solid fat concentration in fishery products and food emulsions [11, 12], and dissolved oxygen in hyper-aerated mineral water [13]. Relatively not long ago the results have been received on that the speed of spin-spin relaxation $1/T_2$ of water protons in the model mixtures containing micellar casein, serum protein and lactose is directly proportional to casein concentration [14]. Represented in this article are the results of investigation of products with different fat status which have shown that the speed of relaxation $1/T_2$ of water protons is proportional to crude protein concentration.

2. Targets and methods of research

Samples taken for research have a concentration of fat from 0 to 6%, that of casein — from 0 to 3%. Composition of samples under research is given in table 1.

Table 1. Parameters of thermal conditioning and organoleptic characteristics of samples under research.

| Name of objects | Product composition being compared, % | Relaxation time $T_2$, ms | Characteristics of packing |
|-----------------|--------------------------------------|---------------------------|---------------------------|
| Ultra-pasteurized drinking milk (1 l) | proteins: 2.8, fats: 6, carbohydrates: 4.7 | 100 (two components found) | OP<sup>a</sup> (packing contains aluminium foil) |
| | proteins: 2.8, fats: 1.5, carbohydrates: 4.7 | 155 + 40 | OP (packing contains aluminium foil) |
| Ultra-pasteurized drinking milk (0.5 l) | proteins: 2.8, fats: 3.2, carbohydrates: 4.7 | 155 + 40 | OP (packing contains aluminium foil) |
| Pasteurized drinking milk ‘Snezhok’ (1 l) | proteins: 2.8, fats: 2.5, carbohydrates: 4.7 | 222 + 37 | CP<sup>b</sup> (polyethylene) |
| Pasteurized drinking milk ‘LATEO’ (1 l) | proteins: 2.8, fats: 0.5, carbohydrates: 4.7 | 226 + 37 | CP (plastic bottle) |
| Pasteurized serum ‘Laktis’ (1 l) | crude protein: 2.8 + 0.2 (a), casein: 3, fats: 2.5, carbohydrates: 4.7 | 229 + 37 | Titratable acidity 20 °T. pH = 6.51. CP (plastic bottle) |
| | crude protein: 0.61 + 0.02 (b), casein: 0, fats: 0.05, carbohydrates: 4.6, lactose: 3.6, 1.0 (c) | 1559 + 126 | CP (polyethylene) |

<sup>a</sup> Opened package.  
<sup>b</sup> Closed package.
The experiments have been carried out at a temperature of objects being studied and ambient air of 20 °C. Time of spin-spin relaxation $T_2$ of water protons in milk was measured with the aid of clinical NMR-tomograph Vectra manufactured by General Electric Medical Systems (USA). The tomograph field density is 0.5 T (NMR frequency at hydrogen atomic nucleus is 21.6 MHz). In addition to getting tomograms the tomograph also is used to measure the time of spin-spin relaxation $T_2$ with the help of Carr, Purcell, Meiboom and Gill pulse sequence (PS) (fast SE sequence). This PS was used for approximate measurement of time $T_2$ of protons in milk and milk serum. The measured values $T_2$ are satisfactory compared with the known literature data since the single-exponential relaxation curve is observed in milk and serum [15, 16]. Considered as a source of errors may be restriction to maximum pause $TR = 6000$ ms, since the time $T_1$ in milk is more than the time $T_2$ of protons. $T_1$ of protons is from 1 to 2 s [4]. In particular, when measuring $T_2$ of protons with the help of the same PS in 3% solution of native phosphorus caseinate the pause was 10 s [14]. There is a possibility in the used tomograph to approximate by different functions of experimental points obtained in fast SE PS for the random region of interest (ROI) which allows determining the relaxation time $T_2$ in the process of experiment. It is advisable to select the attenuating single exponent without the constant voltage component in the receiver as the approximating function. Protein concentration was determined with the help of formol titration method (a) and Kjeldahl method (b). Lactose concentration is determined by iodometric method (c). In the rest cases milk composition corresponds to that stated on the manufacturer's packing.

Table 1 contains the forecast values of two relaxation times on the assumption of the biexpotential curve.

In almost in all experiments the spin-spin relaxation time $T_2$ of water protons was measured in milk in the closed packing. Packs containing aluminium foil were an exception, table 1. The electromagnetic radiation at a frequency of 21.6 MHz does not penetrate inside this packing due to small thickness of skin-layer in aluminium and NMR signal from milk in such packing is absent. As an exception, these milk samples were placed in glass non-magnetic container in order to obtain NMR-tomograms.

Measurements of time $T_2$ were repeated thrice for each sample; root-mean-square deviations are given in table 1.

3.2. Discussion of obtained results
The investigations performed have shown that the time $T_2$ of water protons in milk with 0–3.2% fat concentration does not depend on fat concentration within the measurement error. These results are similar to the work [4], where the same consistency for two-dimensional distribution functions D–$T_2$, $T_1$–$T_2$ was noted but for wider interval of fat content change. The availability of biexpotential
dependence for the relaxation curve in individual samples of milk with 6% fat content was also noted in experiments, table 1. On the other hand, the measured values $T_2$ of water protons in milk of other samples were the same, table 1.

Comparing the literature data obtained under similar conditions (NMR frequency, temperature, pH of samples) inference should be drawn that the values $T_2$ of milk and serum insignificantly depend on the mass fraction of dry substances in semi-skimmed milk, slight changes in temperature and pH. Slightly overestimated values $T_2$ obtained in the experiment can be explained by the error in experimental data approximation. The obtained values $T_2$ of milk and serum protons are in satisfactory fit with the literature data, which can serve as confirmation that correct method is selected for measurement of times $T_2$ of protons on NMR tomograph. It is seen from tables 1 and 2 that relaxation time $T_2$ in milk ‘LATEO’ with a concentration of fat 2.5 % and casein 3% coincides with a value $T_2$ obtained in 3% solution of native phosphorous caseinate. The findings can be given on that the relaxation speed $1/T_2$ of water protons in milk is approximately proportional to casein concentration.

$\textbf{Table 2.}$ Relaxation time $T_2$ of water protons in adulterated milk ‘LATEO’ with 2.5% fat content

| Casein content, % | Relaxation time $T_2$, ms |
|------------------|--------------------------|
| 3.00             | 220                      |
| 1.50             | 290                      |
| 0.75             | 410                      |

Confidence estimation of the obtained results has been carried out by comparing the graph in figure 1 with a similar dependence [14] obtained for model mixtures containing phosphorus caseinate, serum protein and lactose.

![Figure 1](attachment:image.png)

$\textbf{Figure 1.}$ Dependence of relaxation speed $1/T_2$ of water protons in milk on casein concentration in serum.

The slope ratio of relaxation speed $1/T_2$ linear dependence on casein concentration obtained in the present investigation and in the earlier mentioned one [14]. Results are given in table 3.
Table 3. Comparison of dependence linear regression parameters on figure 1 with the work data [14].

| Regression equations | Reduced slope ratio<sup>a</sup> | Correlation factor | Titratable acidity, pH |
|----------------------|----------------------------------|--------------------|------------------------|
| Investigations performed | 123 + 25                          | 0.958              | 6.51                   |
| Acc. to A. Le Dean [14] | 152.2 + 1.1                       | 0.999              | 6.60                   |

<sup>a</sup>values in the second column were multiplied by the corresponding factor in order to obtain the slope ratio in the same coordinates as in the work by A. Le Dean et al. [14].

4. Conclusions

The performed investigations can be taken as a basis for a new express-method with the use of nuclear magnetic resonance effects in order to reveal adulteration of the packed dairy and fermented milk products manufactured with application of dry milk serum substituting the protein — casein. The preliminary assessment of the minimum concentration of casein reported by such method is less than 0.5%.

The theoretical basis of this method is measurement of spin-spin relaxation speed 1/T<sub>2</sub> of water protons. It is known that this value is proportional to a number of hydrogen atoms connected with casein micelles and influences chemical exchange and hydration. The new method can be used for investigation of hydration processes of casein micelles exerting a great influence over protein micelle stability in milk. Consequently, changes take place in the structural-mechanical properties of protein coagula created at making fermented milk products and in the consistency of, for example, ready-to-use cheese, which is one of the main indications of its quality.

Implementation of informational technologies can lead to serious changes in the food products monitoring. Among these are: special-purpose analytical programs, Internet of things and other technological solutions for control over logistics operations on the basis of artificial intelligence; new types of marketing developments and documentation management, as well as for provision of products safety and quality management. Digitization of consumer goods monitoring will find wide application in the future to reveal virtually any violations and non-conformances of products to the applicable regulations.

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