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Magnetic resonance imaging method of rapid remote control of casein concentration in milk products in unopened packages

Summary

The following article is devoted to the issue of a new nuclear magnetic resonance (NMR) method of rapid remote determination of casein concentration in dairy products in sealed packages. This method can have two directions of possible practical applications. With this remote rapid method the casein content adulteration in foods in sealed packages can be detected. For example, milk, condensed milk, cottage cheese produced on the basis of the adulterated skimmed milk containing whey. According to preliminary estimates, the minimum concentration of casein recorded with this method is less than 0.5%. The method is based on measuring the water protons spin-spin relaxation time T_2^{-1}, which is proportional to the number of hydrogen atoms bound to casein micelles due to chemical exchange and hydration. Therefore, the method may be used for research purposes of casein micelles hydration processes that influence vastly the stability of the micelles in the milk protein, the structure and mechanical properties of protein coagulum formed in the production of sour milk products, the consistency of the finished cheese. Therefore, this method that uses NMR imaging could be used for remote research of the spatial distribution of hydration parameters (hydration properties, the mobility of water in the hydration shells, etc.) in the foods that are produced and kept in sealed containers, and storage control quality.

Key words: *Nuclear magnetic resonance (NMR), casein concentration, water proton spin-spin relaxation time (T_2^{-1})*

Metoda obrazowania rezonansem magnetycznym w szybkiej zdalnej kontroli koncentracji kazeiny w szczelnie zapakowanych produktach mlecznych

Streszczenie

W niniejszym artykule omówiono zagadnienie wykorzystania nowej metody magnetycznego rezonansu jądrowego (NMR) w celu szybkiego określenia koncentracji kazeiny w szczelnie zapakowanych produktach mlecznych. Metodę tę w praktyce można wykorzystać na dwa sposoby. W celu szybkiego i zdalnego wykrycia zafałszowania zawartości kazeiny w szczelnie zapakowanej żywności. Przykładowo w mleku, mleku zagęszczonym, twarogu produkowanym na bazie zafałszowanego, odtłuszczonego mleka zawierającego serwatkę. Według wstępnych szacunków minimalne stężenie kazeiny wykryte za pomocą tej metody wynosi mniej niż 0,5%. Metoda oparta jest na pomiarze czasu relaksacji wodnych protonów spin-spin T_2^{-1}, proporcjonalnego do ilości atomów wodoru związanych w micelach kazeiny, wynikającej z wymiany chemicznej i uwodnienia. Z tego względu metodę można wykorzystać w badaniach procesu uwodnienia kazeiny, który wpływa znacząco na stabilność miceli w białku mleka, strukturę i mechaniczne właściwości skrzepu białkowego wytworzonego podczas produkcji kwaśnych produktów mlecznych, konsystencję wytworzonego sera. W związku z tym, że w metodzie korzysta się z obrazowania NMR, może ją zastosować do zdalnego badania rozkładu przestrzennego parametrów uwodnienia w żywności produkowanej i przechowywanej w szczelnych opakowaniach oraz do kontroli jakości przechowywania m.in. właściwości uwodnienia, mobilność wody w uwodnionej warstwie, itp.

Słowa kluczowe: *magnetyczny rezonans jądrowy (NMR), koncentracja kazeiny, czas relaksacji protonów wody spin-spin (T_2^{-1})*

Introduction

Development of analytical equipment for the economical rapid control of the required maintenance of physical and chemical parameters during the foods production and storage and its quality control are the urgent problems in food industry. The advantage of the NMR-phenomenon based devices is non-invasive and non-destructive diagnostics. Nowadays, new types of energy-efficient desktop NMR devices, such as NMR-mouse, are being introduced. They have a much wider range of possibilities: one-way magnet sensor remote measurements, 1H NMR spectroscopy with a resolution of more than 0.20 ppm in volume of 0.4 cm^3, the liquid velocity distribution measurements, translational self-diffusion coefficients measurements, NMR relaxation time distribution measurements, two-dimensional spectra of the various NMR parameters measurements (Blümich 2005; Hurlimann et al. 2006; Perlo et al. 2007).

One of the well-known NMR applications in the food industry is the ISO standard method for determining the concentration of the solid fat in dairy products (Wahlgren and Drakenberg 1995). Wider application of the NMR-based techniques is limited by relatively small number of joint researches conducted by NMR specialists, engineers and scientists at the food industry aiming at development of the analytical methods, required by particular enterprise.

There is a small number of remote NMR-methods developed for the foods analysis in sealed packages in the food industry: NMR spectroscopic method for determining the acetic acid content as an indicator of wine spoilage in a sealed bottle (Weekley et al. 2002); NMR-analyzer from "Intermagnetics" company for dairy products quality control (Blümich 2005); the application of unilateral NMR-mouse with sensor for determining the concentration of solid fat in the fish, food emulsions (Pedersen et al. 2003; Veliyulin et al. 2005) and dissolved oxygen in the hyper carbonated mineral water (Stork et al. 2006).

Recently the following results were obtained: in model mixtures that contain micellar casein, whey protein and lactose the spin-spin relaxation T^{-2} of water protons is directly proportional to the concentration of casein (Le Dean et al. 2004). Research of different fat content in dairy products sold in retail stores has shown that the relaxation rate T^{-2} of water protons is proportional to the concentration of total protein and does not dependent on the concentration of fat (Hurlimann et al. 2006). According to the data published, the dependence of T^{-2} of water protons on the concentration of casein in milk of different manufacturers sold in retail stores with a different fat concentration in sealed package has not been researched yet (Mariette 2008). Currently there are no studies of the NMR imaging of dairy products using this method (Mariette 2008).

This article presents the results of NMR tomography of the spin-spin relaxation time T_2 of water protons in the milk sold in retail stores with casein concentration of 0 – 3%, fat - of 0.5 – 6%. The milk is produced by various manufacturers of the Leningrad region. In many experiments the T_2 relaxation time of water protons was measured in the diary products in sealed package. According to the research results the NMR method for remote rapid determination of casein concentration in milk in sealed package is suggested and options for its practical application are presented.

Materials and methods

The research objects are represented with milk samples and whey, bought in various retail shops of Saint-Petersburg. The samples have fat concentration in a range of 0 – 6%, casein concentration in a range of 0 – 3% and were produced by different manufacturers of Leningrad Region, Russia. The list of the milk samples and producers is shown in Table 1. The water proton spin-spin relaxation time (T_2) in milk depends a lot on pH and temperature. Titratable acidity in the measured milk samples was not more than 20°T, that corresponds approximately to pH = 6.51. The experiments were conducted under the temperature of 20°C.

NMR-imaging unit. The water proton spin-spin relaxation time T_2 in milk was measured with the medical NMR-imaging unit Vectra of General Electrics Medical Systems (the USA). The magnetic field is 0.5 tesla (NMR frequency on nucleus of hydrogen atom – 21.6 MHz).

Pulse sequence. In addition to obtaining tomograms, this NMR-imaging unit gives possibility to measure the spin-spin relaxation time T_2 using the pulse sequence Carr – Purcell – Meiboom – Gill (fastSE sequence). This pulse sequence has been used to measure the approximate time T_2 of protons in milk and whey. The maximum number of echo signals equals 16, which stipulates the existing measurement error of T_2 time. Nevertheless the measured value T_2 corresponds satisfactory with the results shown in literature data obtained under similar conditions (see Table 2). This is particularly due to the fact that single-exponential relaxation curve is observed in milk and whey (Roef 1989; Mariete 2008). Note that the measurement errors of T_2 in this paper may also be caused by the absence of the 90- and 180-degree pulses settings before the measurement. Also errors may be caused by the limitation of the maximum pause TR = 6000 msec. It is known that in milk the T_1 time is bigger than T_2 of protons. T_1 of protons value is in the range of 1 – 2 sec (Hurlimann et al. 2006). In particular, when measuring T_2 of protons with the same pulse sequence in the 3% solution of native phosphocaseinate the pause was 10 sec. (Le Dean et al. 2004).

The parameters of the pulse sequence fast SE, used to measure T_2: TR = 6000 msec (maximum value in the NMR-imaging unit); TE is from 50 to 300 msec (selected values are not multiple of pause TR and cover the time interval from 0 to 3 T_2); number of accumulations NEX = 1; size of image matrix 160 x 160; FOV = 25 cm; cut thickness - 5 mm; the distance between cuts 2 mm; number of cuts –2÷6.

Note that the choice of the TE parameter can influence the measured value of T_2 of water protons in milk using the pulse sequence Carr – Purcell – Meiboom – Gill due to proton exchange (Mariete 2008). However, according to the paper (Gottwald et al. 2005) at NMR frequency less than 20 MHz this dependence can be neglected.

Approximation of relaxation data. In Vectra NMR-imaging unit it is possible to approximate the various functions of the experimental points, obtained in pulse sequence fastSE for any selected area (ROI) (Fig. 2). This allows determining the relaxation T_2 time right with the NMR-imaging unit. At this stage damped single exponential without the voltage constant component at the receiver was chosen as the approximating function. Consideration of constant voltage component in the approximating function is important in the presence of a noisy signal. Calculations show that at T_2 < 300 msec for our experimental conditions (number of points and value of the constant component), approximation of the experimental points of a single exponential gives values of T_2 overestimated for approximately 15%. In the following experiments, this error will be corrected. Note that for the values of T_2 > 500 error due to not taking into account the constant component in the calculation of T_2 is less than 5%.

Also note that experimental data obtained with Vectra NMR-imaging unit were also approximated in Mathcad and Origin software programs. Both programs with single exponential data approximation give approximately same relaxation time T_2, which is shorter than the relaxation time T_2 defined on Vectra NMR-imaging unit for about 10% in the range of 190 ÷ 500 msec for T_2 relaxation time. The source of this discrepancy is not clear.

Let us point out the contribution of other milk components to the measured T_2 relaxation of protons. Note that the T_2 proton relaxation curve reflects not only the water protons relaxation but also all other compounds: solid and liquid fat, protein and lactose. Observation of these components depends on their concentration and time of experimental points sampling. If the time interval of points sampling is small, about 20 msec, in the

time range from 0 to 1 msec the relaxation curves of solid fat and protein protons contribute to the relaxation curve of water proton. Furthermore, the relaxation time T_2 of liquid fat protons is comparable with the time T_2 of water protons. This fact complicates the interpretation of relaxation data with increasing concentrations of fat, e.g. in cream 18 and 36% fat. Sampling interval in our experiment is very large, fat concentration is relatively small, so we assume that we observe only the water protons signal. However, when measuring milk "Klever", 6% fat, the obtained relaxation curve was not monoexponential. Table 1 shows the estimated values of two relaxation times assuming biexponential relaxation. This fact requires further study.

The package influence. Almost in all NMR experiments the measurement of spin-spin relaxation time T_2 of water protons was conducted in milk in sealed package. Packages, containing aluminum foil, were the exceptions (Table 1). Electromagnetic radiation at frequency of 21.6 MHz cannot penetrate this package, due to the small thickness of the skin-layer in aluminum. Therefore, the NMR signal from the milk is absent in such package. These milk samples were placed in a glass jar in order to get the NMR-images.

For each sample, the time T_2 measurements were repeated three times, and the standard deviations are shown in Table 1. Photo of milk samples, whey and beer in sealed package before the NMR-imaging is shown on Figure 1.

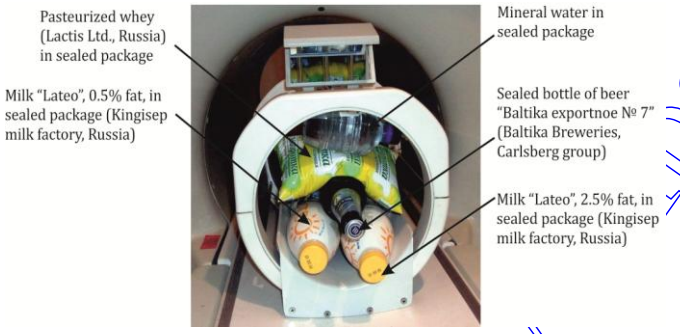

Fig. 1. MR-imaging unit is ready for remote measurements of NMR-relaxation time of water protons in foods in sealed packages ("Lateo" milk 0.5% and 2.5% fat, "Baltika exportnoe №7 beer, pasteurized whey are placed into the transceiver RF coil)

Rys. 1. Stanowisko do obrazowania jądrowym rezonansem magnetycznym, przygotowane do zdalnego pomiaru czasu relaksacji protonów wody w szczelnie zamkniętej żywności (mleko "Lateo" 0,5% i 2,5%, piwo "Baltica exportnoe №7 " i pasteryzowaną serwatkę umieszczono w cewce transceiver RF)

Theory

T_2 relaxation time of water protons in the milk is significantly smaller than the relaxation time of pure water protons. Recently using model mixtures, containing casein, whey protein and lactose it was shown that a small value of T_2 of water protons in milk is due to the exchange between protons of free water and slow-moving protons that are constrained by the casein micelles (Le Dean et al. 2004). The small value of water protons T_2 is due to the fact that the slow-moving protons have very short relaxation time T_{2s}. On condition of fast protons exchange between the two states it is not their relaxation times that takes place, but reciprocal – the relaxation rates (with coefficients reflecting the relative concentration of protons in each state). As the relaxation rate of pure water is T^{-20} due to its small value (about 0.3 sec^{-1}) it could be neglected, the experimentally observed relaxation rate T^{-2} of water protons in milk is determined by the concentration of slow-moving protons and their time T_{2s}.

According to the numerous studies the following model of the spin-spin relaxation of water protons in milk is the convention. T_2 relaxation time of protons (the nucleus of hydrogen atom) of water is determined by the exchange (by circulation) of protons between two states (two phases of NMR), where protons have different NMR parameters: concentration (P_0 and P_s), the spin-spin relaxation times (T_{20} and T_{2s}) and NMR frequencies (ω_0 and ω_s). The first state (P_0, T_{20} and ω_0) is protons of pure water. The second state (P_s, T_{2s} and ω_s) is protons with significantly lower mobility than in pure water. This proton exchange corresponds with the condition of rapid exchange. This means that the proton exchange rate (transition) τ^{-1} between these states is that large in comparison with the observed relaxation rate T^{-2} and the difference of the NMR-frequencies $\omega_0 - \omega_s$, which protons have in two states, that we can assume that we see one relaxation time T_2, averaged for a system of two states. In the NMR experiment in this case the spin-spin relaxation time curve is measured, which is presented by an exponential function of a form:

$$S(t) = Se^{-\frac{t}{T_2}} = Se^{-t\left(\frac{P_0}{T_{20}}+\frac{P_s}{T_{2s}}\right)}, \quad \frac{1}{T_2} = \left(\frac{P_0}{T_{2f}}+\frac{P_s}{T_{2s}}\right), \quad P_0 + P_s = 1, \tag{1}$$

where:

T_2 – the measured in NMR-experiment spin-spin relaxation time of water protons in milk;
T_{20} – spin-spin relaxation time of protons in pure water (beyond the hydration shell of casein micelles);
T_{2s} – spin-spin relaxation time of slow-moving protons (see further);
S – constant, proportional to the proton amount in the sample.

By experimental data function approximation (1), in this paper the spin-spin relaxation times T_2 of water protons in milk of different fat content and casein concentration were calculated. Since we know the proton relaxation time in pure water T_{20}, as well as the proton concentration in the bulk free water P_0, then, according to (1), the relaxation rate T_2^{-1} of water protons in milk depends on two parameters: the relative proportion of slow-moving protons P_s and their relaxation time T_{2s}. Nowadays there is no single meaning what protons are slow-moving and, therefore, it brings ambiguity in the definition of P_s and T_2. Generally two possibilities are suggested:

1. Slow-moving protons are protons of a number of casein molecules chemical groups, in particular in -OH, -NH, -NH2, COOH groups (chemical exchange model).
2. Slow-moving protons belong to the bound water molecules in the hydration shells of casein micelles (model of bound water).

Both models approximate the experiment data (Gottwald et al 2005). We present a formula reflecting the dependence

of the relaxation rate of water protons T_2^{-1} on the casein concentration. This formula is valid for both models (Le Dean et al. 2004).

$$\frac{1}{T_2} = \frac{1}{T_{20}} + nC_p\left(\frac{1}{T_{2s}} - \frac{1}{T_{20}}\right), \quad (2)$$

where:

C_p – mass concentration of casein;

n – mass fraction of slow-moving protons per weight unit of casein.

According to the first model, n is the fraction of casein protons that exchange with protons of free water. According to the second model, n is the degree of hydration of the casein molecules.

Formula (2) is confirmed experimentally in model mixtures, containing native phosphocaseinate, whey protein and lactose (Le Dean et al. 2004). However, according to the authors, there are no published studies in which this formula was tested in the finished milk sold in retail stores with different fat concentrations and of different manufacturers.

The results of the experiment

General patterns

In this paper it was shown that remote rapid measurement of T_2 relaxation time of the proton using the proposed NMR tomography (or other remote NMR-method, such as NMR-mouse) can be performed for a wide range of dairy products in sealed packages or containers. The key restriction to the NMR-method is the metal parts in the package. For example, products in aluminum foil packages cannot be studied in sealed containers (see paragraph "Materials and Methods"). All measured values of T_2 of water protons in milk are shown in Table 1.

Table 1. Measured water proton relaxation times T_2 in dairy products in sealed and opened package

Tabela 1. Pomiar czasu relaksacji protonów wody w produktach mlecznych szczelnie zamkniętych oraz produktach otwartych

Name of product	Content (%)	Relaxation time T_2 (msec)	Conditions for NMR measurement
UHT milk "Klever" (Saint-Peteresburg milk factory "Piskarevskii" Ltd.) (1.0 l)	protein: 2.8 fat: 6 carbohydrate: 4.7	100 1454 (2 components detected)	OP (package contains aluminum foil)
	protein: 2.8 fat: 1.5 carbohydrate: 4.7	155 ± 40	OP (package contains aluminum foil)
UHT milk «Tyoma» ("Milk factory Petmol" subsidiary, JSC "Unimilk") (0.5 l)	protein: 2.8 fat: 3.2 carbohydrate: 4.7	155 ± 40	OP (package contains aluminum foil)
"Snezhok" ("Laktis" Ltd., Veliky Novgorod) (1.0 l)	protein: fat: 2.5 carbohydrate:	222 ± 37	SP (polyethylene)
Pasteurized milk "LATEO" (JSC "Kingisep milk factory") (1.0 l)	protein: 2.8 fat: 0.5 carbohydrate: 4.7	226 ± 37	SP (plastic bottle)
	crude protein: 2.8 ± 0.2[a] casein: 3 fat: 2.5 carbohydrate: 4.7	229 ± 37	Titratable acidity 20°T; pH=6,51; SP (plastic bottle)
Pasteurized whey ("Laktis" LTD, Veliky Novgorod) (1.0 l)	crude protein: 0.61 ± 0.02[b] casein: 0 fat: 0.05 carbohydrate: 4.6 lactose:3.6 ± 1.0[c]	1559 ± 126	SP (polyethylene)

Where:

a – Protein concentration was determined using Formoltitration

b – Protein concentration was determined using Kjeldahl method

c – The concentration of the lactose was determined using iodometric method

In the rest cases the milk content corresponded with the information given by the producer.

SP – sealed package

OP – opened package (for measurements the object was placed into a nonmagnetic container (for packages with aluminum foil)

Figures 2÷4 show the examples of measuring T_2 of protons in milk «LATEO» with fat concentration of 0.5% and 2.5% and casein concentration of 3%, and also whey with the casein concentration of 0%. The increase of T_2 time of protons in whey, containing only whey proteins with concentration of 0.6% conforms with the hypothesis of the concentration of casein predominant influence on the relaxation of water protons. This correlation is studied in section below.

Studies have shown that the time T_2 of water protons in milk with fat concentration of 0 – 3.2% does not depend on the concentration of fat in the range of measurement error. These results are similar to the results in paper (Hurlimann et al. 2006), which points out the same correlation for the two-dimensional distribution functions $D - T_2$, $T_1 - T_2$ but in broader range of fat concentration, including cream (more than 36% of fat) and condensed milk. In our experiments the presence of double-exponential dependence of the relaxation curve for milk "Klever", 6% of fat (see Table 1) was revealed. These results require further study.

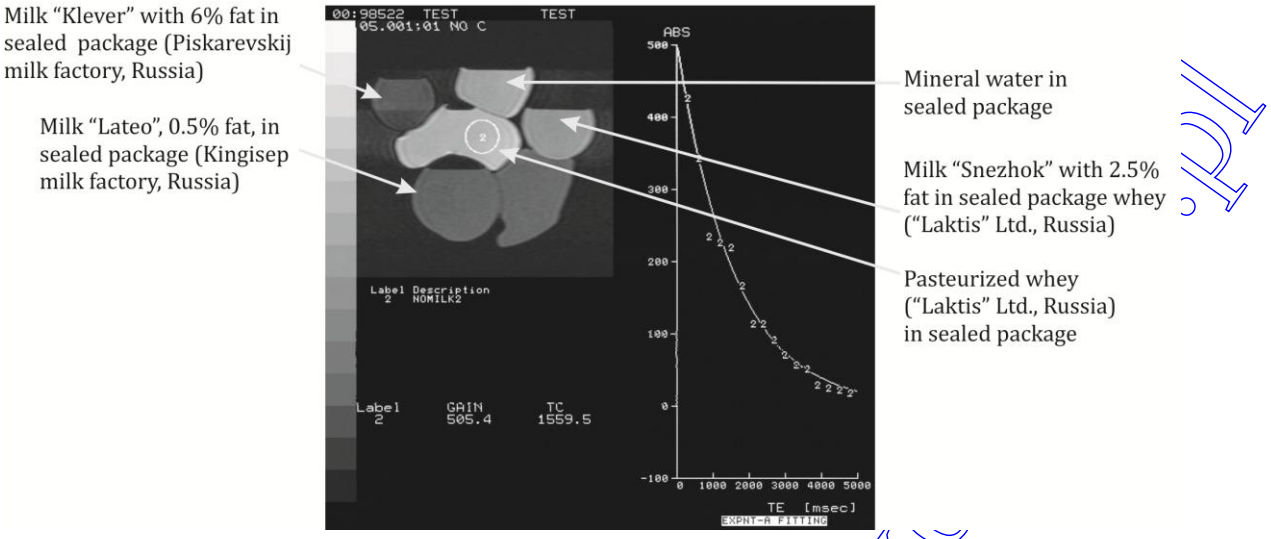

Fig. 2. Determination of the T_2 of the water protons in whey in sealed package. Casein concentration in whey equals zero

Rys. 2. Wyznaczanie protonów wody T_2 w serwatce w szczelnym opakowaniu. Stężenie kazeiny w serwatce jest równe zeru

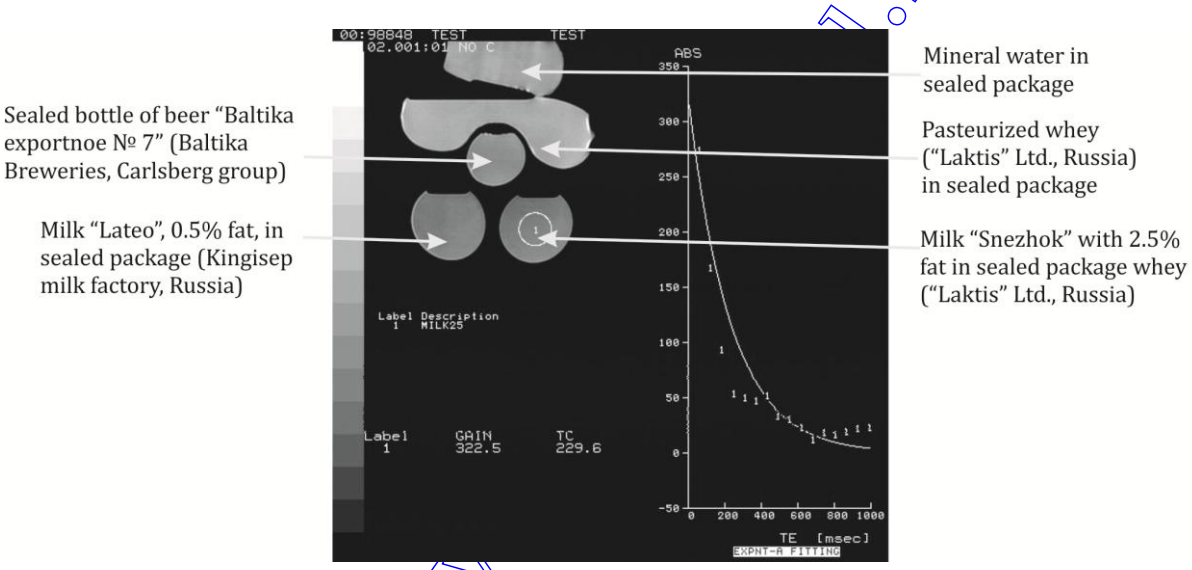

Fig. 3. Determination of T_2 protons of water in milk "LATEO" with 2,5% of fat and casein concentration of 3% in sealed package

Rys. 3. Wyznaczenie protonów wody T_2 w mleku "LATEO" o 2,5% zawartości tłuszczu i 3% stężeniu kazeiny w szczelnie zamkniętym opakowaniu

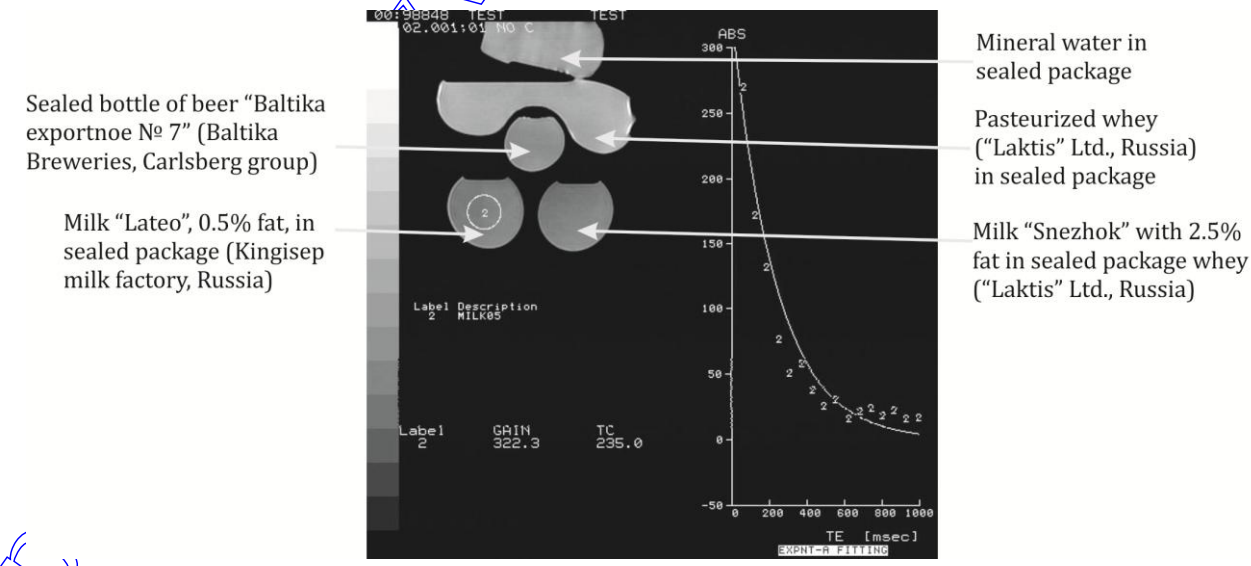

Fig. 4. Determination of T_2 protons of water in milk "LATEO" with 0.5% of fat in sealed package

Rys. 4. Wyznaczenie protonów wody T_2 w mleku "LATEO" o 0,5% zawartości tłuszczu w szczelnie zamkniętym opakowaniu

Comparison with literature data

Table 2 is to compare the values of the relaxation time T_2 of protons of milk and whey (the values were taken from literature data), obtained under similar conditions (NMR frequency, temperature, pH). The following conclusion can be drawn: the values of milk and whey T_2 depend slightly on geographical location of the manufacturer, fraction of total mass of solids in the skimmed milk, small changes in temperature and pH. Slightly overestimated values of T_2, obtained during this study, may be due to an error of approximation of the experimental data, see paragraph "Materials and Methods". It can be concluded that the obtained values of T_2 of milk and whey protons are in satisfactory correspondence with literature data, what proves the correctness of the measuring methodology of the T_2 proton with NMR-tomograph .

Table 2. Comparison of measured values of T_2 of water and whey protons with literature data

Tabela 2. Porównanie zmierzonych wartości T_2 protonów wody i serwatki z danymi literaturowymi

Source	Sample content	Relaxation time T_2 of water protons (msec)	NMR frequency on nucleus of a hydrogen atom (MHz)	Temperature (°C)	pH
This paper	Lateo 0,5 % fat. (CB: 8.2%)	226 ± 37	21.6	20	6.5
	Pasteurized whey "Laktis" Ltd. (CB: 5.26%)	1559 ± 126	21.6	20	-
Roef 1989 (the Netherlands)	Skimmed milk, of powder (CB:12%)	165 ± 15	20	20	6.35–6.6
	Skim milk ultrafiltrate (see above) molecular weight cutoff membrane - 10 pKa	1450 ± 70	20	20	4.5–6.6
Hurliman 2006 (the USA)	Skimmed milk and whole milk of supermarket	200 ± 30	5	20	-
Mariette 1993 (France)	Skimmed milk, of powder (CB: 9%)	200 ± 2	10	40	6.6
	Milk whey (obtained by adding rennin to skimmed milk, see above)	1800 ± 20	10	40	-
Mariette 2004 (France)	Aqueous solution, containing 3% native phosphocaseinate, 0.03% whey protein, 4.9% lactose	164.2 ±0.5	20	40	6.4
	3% native phosphocaseinate solution	162.8-203.5[a]	20	40	6.2

a – minimum and maximum values are shown

Remote casein mass fraction determination in finished milk in sealed containers

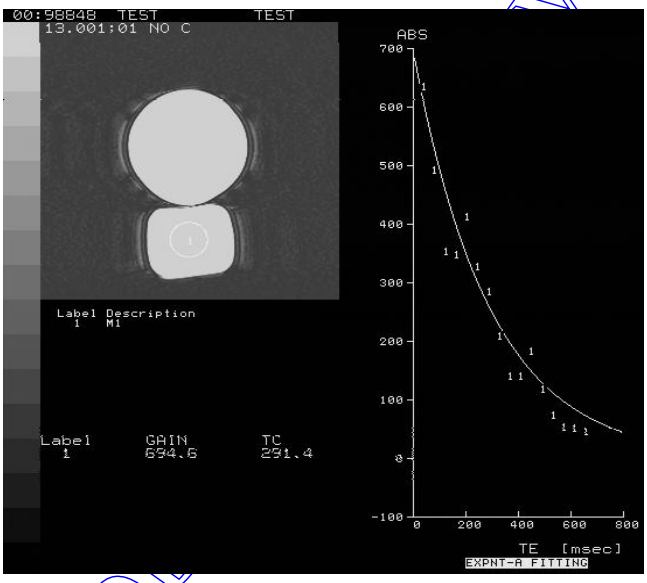

Fig. 5. Determination of T_2 of water protons in milk with casein concentration 1.5% (after two fold dilution of milk «LATEO» 2.5% of fat)

Rys. 5. Wyznaczenie protonów wody T_2 w mleku o 1,5% stężeniu kazeiny (po dwukrotnym rozcieńczeniu mleka «LATEO» 2,5% tłuszczu)

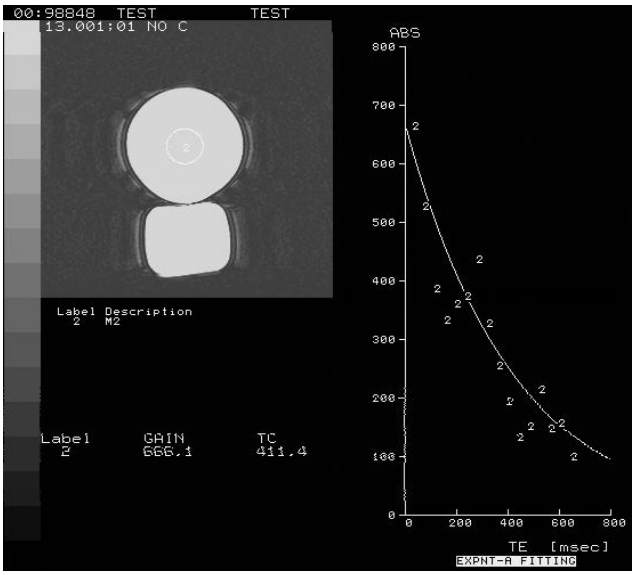

Fig. 6. Determination of T_2 of water protons in milk with casein concentration of 0.75% (after four fold dilution of milk «LATEO», 2.5% fat)

Rys. 6. Wyznaczenie protonów wody T_2 w mleku o 0,75% stężeniu kazeiny (po czterokrotnym rozcieńczeniu mleka «LATEO» 2,5% tłuszczu)

As it was noted in the introduction and theoretical paragraphs, it has been shown that the relaxation rate T_2^{-1} of water protons to a first approximation is proportional to the casein concentration and does not depend on the concentration of whey proteins and lactose in model mixtures that contain native phosphocaseinate. However, according to the authors, these experiments have not been carried out with the finished milk sold in retail stores, with different fat concentration and of different manufacturers.

In this paper, such measurements were carried out using the method of dilution. Casein concentrations in whey and milk «LATEO», 2.5% of fat, were measured. The values were 0 and 3% respectively. Then we chose the filtered tap (filtered with household filter) in order to dilute. This water had the T_2 relaxation time equal to T_2 of the whey. We diluted 2 and 4 times the original milk «LATEO», 2.5% of fat. Four measured values of the relaxation rate T_2^{-1} of protons were plotted as a function of the casein concentration; see Table 3 and Figures 5–7. Experimental points are described by a linear function, i.e. relaxation rate T_2^{-1} of protons is a linear function of the concentration of casein.

Table 3. Relaxation time T_2 of water protons in milk «LATEO», 2.5% of fat

Tabela 3. Czas relaksacji protonów wody T_2 w mleku «LATEO» 2,5%

Casein concentration (%)	Relaxation time T_2 (msec)
3	220
1.5	290
0.75	410

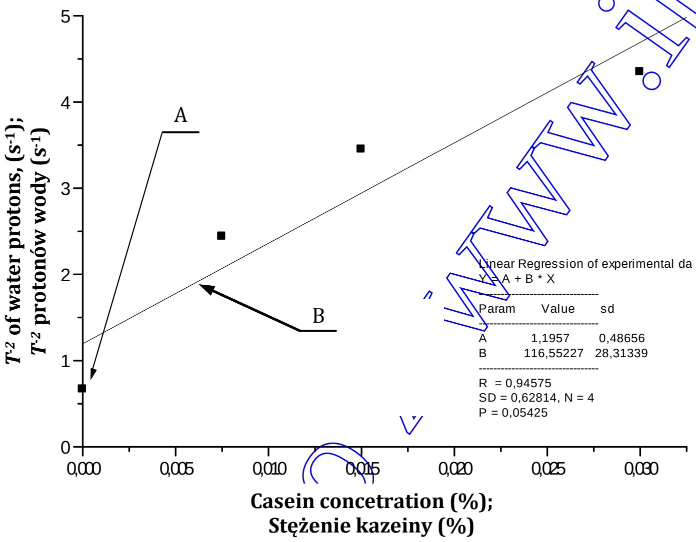

Fig. 7. Relaxation rate T^{-2} of water protons in milk and whey as a function of casein concentration

Rys. 7. Rys. 7. Szybkość relaksacji T^{-2} protonów wody w mleku i serwatce, jako funkcja stężenia kazeiny

Then we compared the graph in Figure 7 with the similar dependence (Le Dean et al. 2004) obtained for model mixtures containing phosphocaseinate, whey protein and lactose. In Tables 1 and 2 it is shown that the relaxation time T_2 in milk «LATEO», 2,5% of fat and 3% of casein, coincides with the value of T_2 obtained in 3% native phosphocaseinate solution. After that we compared the slope of the linear function of the relaxation rate T_2^{-1} of the casein concentration, obtained in our research, and in the previously mentioned study (Le Dean et al., 2004). The results are shown in Table 4. We can conclude that the relaxation rate T_2^{-1} of water protons in the finished milk sold in the store is approximately proportional to the casein concentration.

Table 4. Comparison of the linear regression on Figure 7 with the data (Le Dean et al. 2004)

Tabela 4. Porównanie regresji liniowej z Rysunku 7 z danymi literaturowymi

Reference	Slope	Correlation coefficient	pH
This work	116 ± 28	0.96	6.51
Le Dean et al., 2004	152.2 ± 1.1	0.999	6.6

Conclusions

The article deals with the NMR-method of rapid remote measurement of casein concentration in dairy products in sealed packages. This method may have two possible ways of practical implication.

1. Using this rapid remote method the adulteration of casein concentration in dairy products, particularly in sealed packages can be detected. For example, milk, condensed milk, cottage cheese produced with the use of adulterated skim milk powder containing whey powder. According to the preliminary estimation the minimum casein concentration recorded with the method proposed is less than 0.5%.

2. The method is based on measuring the water protons spin-spin relaxation time T_2^{-1}, which is proportional to the number of hydrogen atoms bound to casein micelles due to chemical exchange and hydration. Therefore, the method may be used for research purposes of casein micelles hydration processes that influence vastly the stability of the micelles in the milk protein, the structure and mechanical properties of protein coagulum formed in the production of sour milk products, the consistency of the finished cheese. Therefore, this method that uses NMR imaging could be used for remote research of the spatial distribution of hydration parameters (hydration properties, the mobility of water in the hydration shells, etc.) in the foods that are produced and kept in sealed containers, and storage control quality.

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