AUTOMATED NMR-RELAXOMETRY FOR CONTROL OF PRODUCTION AND QUALITY

Bekmurza Aitchanov[1], Anatoli Voronin[2], Janusz Partyka[3], Aitkul Aldibekova[4]

[1]Kazakh National Technical University after K. I. Satpaev, [2]Almaty Technological University, [3]Lublin University of Technology Department of Devices and High Voltages Technologies, [4] Kazakh National Technical University after K. I. Satpaev Instytut of information and telecommunication technologies

Abstract. In this work we show the possibility of using of nuclear magnetic resonance at low magnetic fields for the purpose of establishing a system of automated process of control and quality of dairy products.

Keywords: nuclear magnetic resonance (NMR), relaxometry, chemical shift, automated control system

AUTOMATYCZNY RELAKSOMETR NMR DO KONTROLI PRODUKCJI I JAKOŚCI

Streszczenie. W pracy przedstawiono możliwość użycia jądrowego rezonansu magnetycznego dla słabych pól magnetycznych do stworzenia zautomatyzowanego systemu kontroli procesu i jakości produktów mlecznych.

Słowa kluczowe: jądrowy rezonans magnetyczny, relaksometr, przesunięcie chemiczne, zautomatyzowany system kontroli

Introduction

There are various methods to control the quality of products based on the use of various physical and chemical effects. This paper describes the possibility of using NMR spectroscopy for the purposes of automated quality control of milk using a magnetic field. By studying the NMR spectra of isotopes that are part of the milk, you can unambiguously identify the product, in other words to determine its authenticity.

1. Method and equipment of NMR spectroscopy

The use of NMR spectroscopy is well known for controlling the manufacturing process [1].

Under the influence of an external magnetic field, atomic nuclei can receive and emit radio waves. Their frequency v_0 is proportional to the strength B_0 of the magnetic field:

$$\omega = 2\pi v_0 = \gamma B_0 \qquad (1)$$

here, the coefficient of proportionality is the gyromagnetic ratio γ. It is a constant value for a particular nuclear isotope.

The content of certain isotopes in the nature and the corresponding frequencies of the radiation are given below:

Table 1. Properties of several atomic nuclei

Nuclear isotopes	Content in the nature	v_0 at $B_0 = 1$ T
^{1}H	99,98%	42,57 MHz
^{13}C	1,108%	10,71 MHz
^{14}N	99,63%	3,08 MHz
^{19}F	100,0%	40,05 MHz
^{129}Xe	26,44%	11,78 MHz

Nuclear magnetic resonance (NMR) is a peculiar form of telecommunications in the magnetic field, because the NMR frequency determined by the value of the magnetic field at the point where the core is. Atomic nuclei are surrounded by electrons and in the compounds, which are formed by different atoms
i.e. molecules, electrons can be shared, forming a chemical bond. The orbits of binder electrons are characteristic of the chemical structure of molecules. As is well known electrons carry an electrical charge, movement of which is induces a magnetic

field. The internal magnetic field induced by electrons that are moving in an external magnetic field B_0, is usually proportional to this field and shields the nucleus from it.

The induced magnetic field causes a shift of the resonant frequency:

$$\omega_L = 2\pi v_L = \gamma(1-\sigma)B_0 \qquad (2)$$

where σ is a constant of magnetic shielding for a given chemical group.

Value of $\delta = (v_L - v_{ref})/v_{ref}$ is the chemical shift of this group. It does not depend on the strength of the magnetic field B_0. Chemical shifts can be calculated from the chemical shift increment tables, as well as on the basis of the laws of quantum mechanics. Value of v_{ref} is a reference frequency, for example, the resonant frequency of tetramethylsilane (TMS) for ^{1}H and ^{13}C. In liquids the resonance signal typically has a width of 0,1 Hz.

The distribution of the resonance frequencies defines the NMR spectrum, which displays the structure of the molecule. On the Figure 1 NMR spectrum is shown ^{13}C in polyethylene. Identification of NMR spectrum of molecules in solutions is a standard method of analysis for the further chemical synthesis and accordingly the quality of a particular type of the manufactured products.

In recent years the NMR is widely used for control and management of various technological processes, for example, in the manufacture of medical preparations in the pharmaceutical manufacturing [9], for monitoring the quality of agricultural products [2, 3, 5, 6].

It is known that applicable in spectrometers permanent magnets depends on the temperature. Nevertheless, such spectrometers which measure the echo or signal induced in the coil after the initiation of the pulse − is a free induction decay (FID) in weakly inhomogeneous fields are widely used for characterizing a variety of types of products, for example, foods, cosmetics, polymers. FID frequency analysis in using Fourier transformation gives you the opportunity of obtaining NMR spectrum with linewidth

$$\Delta\Omega = 1/(\pi T_2) \qquad (3)$$

where T_2 is the transverse relaxation time, which is determined by local magnetic fields dependent or independent of the time. With the proper conduct of the experiment the accuracy of such measurements is 0,1%.
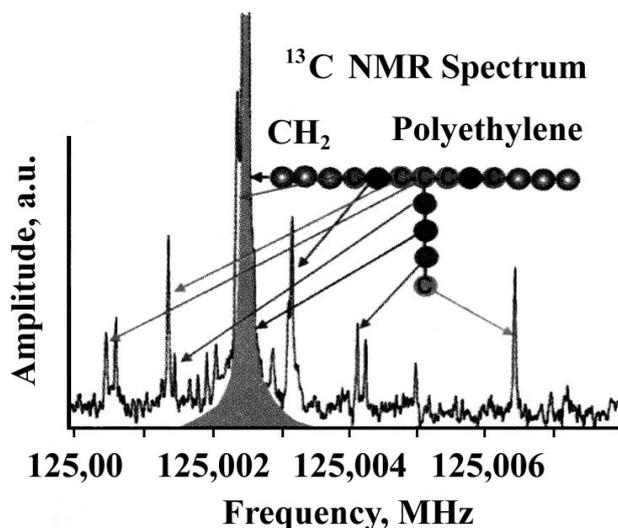
Fig. 1. Chemical structure

NMR with a weak field can be reproduced with the help of a small and low-cost equipment, value of which can be obtained in the range from 0,5 to 1 T by using electromagnets. NMR with a weak field in the homogenous fields can be used to control the manufacturing process, for example, petroleum refining or other types of products, for example the quality of milk. For optimizing the product stream after the spectrometric analysis the return signal is generated from the parameter ^{1}H of NMR spectrum.

2. Description of the automated system for determining the quality of milk

This paper considers the automatic control system (ACS) of the milk quality when it is processing by the magnetic field. In recent years, paid much attention to the processing by physical fields of liquids [7, 8, 10].

We have attempted to use the magnetic field for milk processing with a view to its better storage. For controlling parameters of quality of milk have developed an automated control system (ACS), which is regulated by the seven parameters (fat mass fraction, the mass fraction of milk solids non-fat (MSNF), the density, the mass fraction of added water, the temperature, the mass fraction of protein, the acidity). Moreover for controlling the magnetic field with a high accuracy NMR signal of hydrogen applied ^{1}H and of carbon ^{13}C, which by the chemical shift indicate the presence of microbial flora in the milk.

A block diagram of the device shown at the Figure 2. Milk from the reservoir via delivery pipe (1) supplied to the sliding shutter (2), which regulates the velocity of the fluid. Next, the milk supplied to a system for electromagnetic treatment of milk (3), consisting of several pairs of quadrupole lenses (EM-1, EM-2 etc.), which have a special configuration of the magnetic tips. Value of the magnetic field strength is measured with a high accuracy up to 10^{-5} by an NMR sensor (4), which is in the area of fields of the quadrupole lenses.

The parameters of milk (as input (7), and output (8)) are controlled by sensor devices, installed in the analyzers «Laktan-4», «AKM-98 Farmer». They allow to register up to 6 parameters of milk quality.
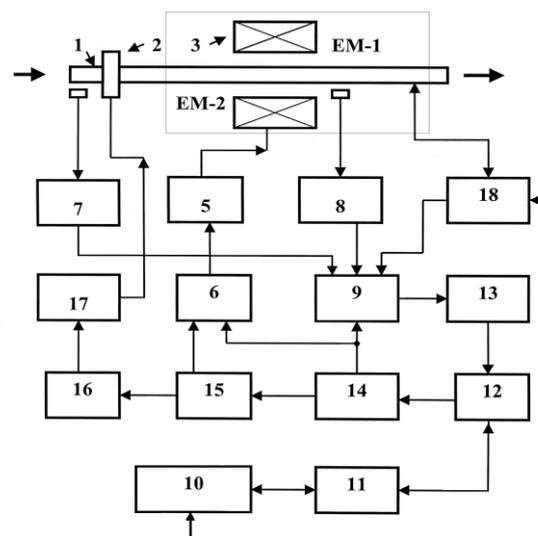

Fig. 2. The block diagram of the ACS: 1 – delivery pipe; 2 – sliding shutter; 3 – device for electromagnetic treatment of milk; 4 – NMR sensor; 5 – power amplifier; 6 – digital-to-analog converter (DAC); 7 – input sensors of properties of milk; 8 – output sensors of properties of milk; 9 – controlling signal switch; 10 – personal computer; 11 – LPT-port; 12 – interface; 13 – registrar of receiver; 14 – registrar of control; 15 – data recorder; 16 – switch of the stepper motor; 17 – stepper motor; 18 – NMR spectrometer

Input and output data from the sensors are supplied to the controlling signals switch (9) through the appropriate interface and LPT-port (11) to the personal computer (10). In the personal computer, there is a required software, designed to control the strength of the magnetic field of quadrupole lenses. The magnetic field is generated by electromagnets, supplied and controlled by a DC voltage source (5), control signals from the PC via the digital-to-analog converter (DAC) (6).

The second branch of the adjustment of the fluid velocity is given through the registrar switch management of the stepper motor with the corresponding electronic equipment, given at the Figure 1. Milk flow rate through the delivery pipe can be adjusted in the range from 0 to 6 m/s. with accuracy of 0,15%.

In the present paper uses the method of analysis of the asymptotic stability developed and [1] designed to obtain frequency stability conditions of subsystems of direct digital control of regime parameters of considered technological processes.

3. Identified results

We have experimentally determined, magnetic treatment of milk for field strengths up to 0,5 T reduces the deposition of salts and the formation of milk stone up to 3 times, which contributes to lower heat and power costs, prime cost of dairy products, their quality improvement. Magnetized milk has a higher viscosity (up to 16-18%), critical shear stress of milk coagulum (up to 23-28%), electrical conductivity (up to 14-16%), the surface tension of the milk is reduced up to 11-15%.

An important indicator for establishing the expiration date is the acidity.

Titratable acidity is a key indicator of freshness of milk and dairy products. It reflects the concentration of milk components having acidic character. It is known that the active acidity is one of the indicators of quality, it is determined by the concentration of hydrogen ions. On the pH value depends the colloidal state of the milk proteins, growth of beneficial and harmful microflora, thermostability of milk and activity of the enzymes.
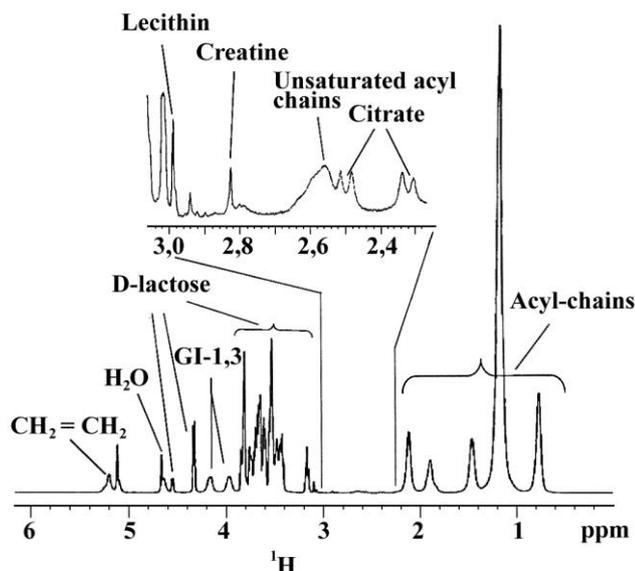
Fig. 3. ^1H NMR spectrum of milk

Thus, a constant magnetic field is a biologically active factor of the external environment that may affect to the liquid systems and bacteria.

Great interest attaches the NMR technique of determining the chemical shift of the hydrogen, carbon, phosphorus, which characterize the nuclear-physical parameters of milk.

As an example, Figure 3 shows a portion of the NMR spectrum signal of milk for hydrogen-1 isotope.

4. Conclusions

This paper shows the feasibility of establishing a system of automated quality control of liquid milk using NMR, having a high accuracy of determination of manufactured products.

References

[1] Ajtchanov B. H.: Chastotnye kriterii stohasticheskoj ustojchivosti odnogo klassa sistem s zapazdyvaniem, Vestnik Vostochno-Kazahstanskogo gosudarstvennogo tehnicheskogo universiteta im. D. Serikbaeva. 21 (2003), nr 3, pp. 83-86.

[2] Andreotti G., Trivellone E., Lamanna R., Luccia A. D., Motta A.: Milk identification of different species: 13C-NMR spectroscopy of triacylglycerols from cows and buffaloes' milks. Dairy Sci. 83 (2000), pp. 2432-2437.

[3] Belloque J., Carrascosa A. V., Fandino R. L.: Changes in phosphoglyceride composition during storage of ultrahightemperature milk, as assessed by 31P-nuclear magnetic resonance. Possible involvement of thermoresistant microbial enzymes. Food Prot, 64 (2001), pp. 850-855.

[4] Bljumih B.: Osnovy NMR. Moskva, Tehnosfera, 2007.

[5] Fangyu Hu, Kazuo Furihata, Mie Ito-Ishida, Shuichi Kaminogawa, Masaru Tanokura.: Nondestructive Observation jf Bovine Milk by NMR Spectroscopy: Analysis of Existing States of Compounds and Detection of New Compounds, Agric. - Food Chem. (2004), nr 52(16), pp. 4969-4974.

[6] Kaminogawa S., Sagano C., Horono A., Eds.: The Science of MilksNew Function of Milk. National Plant Dairy Industry of Agricultural Cooperative Association. Tokyo, Japan, 2000.

[7] Kunizhev S. M., Shuvaev V. A:, Novye tehnologii v proizvodstve molochnyh produktov. Moskva, DeLi Print, 2004.

[8] Poljanskaja I. S.: Magnitnaja obrabotka biologicheskih sistem: teoreticheskoe obosnovanie, Tezis- doklad. nauchno-prakticheskoj konferencii v ramkah III Molochnogo Foruma, Vologda-Molochnoe: IC VGMHA, 2009.

[9] Rutger F., Jurgen F..: Automatisiertes NMR-Screening in der Medikamententwicklung. BIOspektrum: (2010), nr 5, pp. 687-688.

[10] Starikova A.F., Poljanskaja I.S., Noskova V.I., Neronova E.Ju.: Proizvodstvo funkcional'nogo tvoroga s primeneniem jelektromagnitnoj obrabotki moloka. Molochnohozjajstvennyj vestnik, (2011), nr 3, pp. 36-41.

Prof. Bekmurza Aitchanov Husainovich
e-mail: berait@rambler.ru

Professor, Academician of the International Academy of Information and Academician of the Kazakhstan National Academy of Natural Sciences. He published more than 205 research papers. He teaches the following disciplines: «Information technologies», «Theory of the information», «Designing of information systems». His experience of scientific and pedagogical activity is 37 years.

Prof. Anatoli Voronin Mikhailovich
e-mail: voronin.ski@rambler.ru

Professor, expert in nuclear physics and accelerators, Full Member of the International Engineering Academy (instrument engineering), Academician of the National Engineering Academy of the Republic of Kazakhstan (accelerators of charged particles). At present he works as a professor of the chair of physics at the Almaty Technological University. Fields of interest: nuclear physics; high-frequency systems of charged-particle accelerators; radioecology; information and communication technologies; electronic pedagogy in high-education institutions.

Prof. Janusz Partyka
e-mail: j.partyka@pollub.pl

A graduate of the Leningrad Electrical Engineering Institute, Department of Electrophysics. His first (Ph.D. level) doctoral degree in physics was obtained in 1990 at the Maria-Curie Sklodowska University in Lublin, and his higher doctoral degree (doctor habilitatus) – in 2005, at the Belarusian State University in Minsk, Department of Physics. Presently he is employed at the Lublin University of Technology, Department of Electrical Engineering and Information Science as a university professor. He is the author or co-author of over 150 scientific publications and has been a supervisor of several dozen of graduate theses. He has chaired scientific committees of a number of cyclical symposia concerning problems of the electrical engineering domain. The subject scope of his lectures includes: material engineering, physical fundamentals of electronics, electrical engineering and architecture of computer systems. His research interests focus on electronic materials and technologies.

M.Sc. Aitkul Aldibekova
e-mail: aitkul_86 @mail.ru

A Ph.D. student of Satpayev Kazakh National Technical University in "Automation and Control." A co-author of eight publications.