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Abstract. The article substantiates the need to use express control to check the quality of various products in the form of a liquid, gel or bulk materials. A technique for express control of quality of various products based on the phenomenon of nuclear magnetic resonance is proposed. This technique makes it possible to obtain information on the results of research in digital form and automatically place it on the Internet. Within the framework of the 'Internet of things' concept, leave online for users of this medium their opinion on the quality of goods. The results of experimental studies of liquid media are presented.

1. Introduction

Currently, there is a constant increase in prices for many groups of goods associated with higher taxes, crisis phenomena in various industries and businesses (for example, in the fuel and energy sector, construction, etc.) [1]. In this regard, many manufacturers are trying to reduce the cost of production of goods in order to maintain their affordable prices [2]. This often leads to a deterioration in product quality and production safety. In some cases, automatic product quality control is disabled on production lines [3].

In various sectors of the economy, various ways of hiding the low quality of goods offered to the consumer are used [4]. For example, in the food industry, numerous additives are used to preserve the appearance and taste of the products. Numerous checks of purchased products show the excess of their permissible concentrations. The consumption of such products adversely affects people's health [5].

In some cases, undeclared components (for example, palm oil) are added to products to reduce production costs. These components are cheaper than raw materials and are relatively safe for health. The quality of this food product, and especially its energy value for a person, decreases.

In a number of countries, the problem of the quality of motor fuels and oils, technical lubricants and other necessary hydrocarbon media for mobile mechanisms is quite acute. Manufacturers often make mixtures of these media, which are adjusted to a given state with various additives and chemical processes. For example, a mixture of two gasoline or motor oils. A dye is added to the oil to create the desired color. The substances created in this way, when used, cannot provide the necessary parameters for the operation of mechanisms in comparison with quality products. This creates big problems for consumers [6].

In some cases, it is possible to determine the low quality of food or perfumery products in an organoleptic way (for example, to feel some discomfort). However, in most cases, it is quite difficult to return low-quality products to the seller in this situation. In other situations, problems from the consumption or use of low-quality products appear later [7].

Therefore, if doubts arise in the quality of products, it is advisable to check them at the place of purchase, especially in the case of large purchases on the spot. This applies primarily to hydrocarbon media, soft drinks (e.g. mineral water), etc. [8].

Chemical analysis of samples of this product at the place of its purchase (outside the laboratory) is a complex and time-consuming task [9]. In most cases, each liquid medium requires its own reagents [10]. Therefore, there is a need for a reliable, affordable, easy-to-use mobile measuring device that allows you to quickly conduct studies of liquids and media in the express mode on the spot (for example, at the time of their purchase, etc.) [11].

It should be noted that in the current situation, customer feedback on product quality is an important factor in its sales [12]. There are many sites that collect user feedback and product reviews based not only on subjective experience, but also on objective measurements. Unfortunately, even this approach has disadvantages. Firstly, the same products can be produced at different plants, on which its quality may depend. In this case, a detailed review of the product will show its quality only for a particular plant. Secondly, it often happens that on such sites information about the low quality of the product is placed after a long period of time, when many have already purchased this product. This is due to the fact that people want to check it in the laboratory, so as not to provide false information. The solution to these problems may be to use the 'Internet of things' approach for measuring and processing data. If a relatively large number of users will have a portable device that allows you to measure the parameters of purchased products in express mode, share it with other users and compare with their results, consumers will be able to quickly assess the quality of goods, as well as undeclared changes in its quality over time.

However, in order for such a device to be included in the mass segment, it must be universal, accurate (error not higher than 1.5%), compact and at the same time have an affordable price [13]. To do this, it is necessary to solve another problem related to the search for a device that meets the above criteria and is able to carry out measurements in the express mode (to carry out express control) [14]. At present, a large number of devices using various physical phenomena have been developed for express control of liquid media [15]. For example, express analyzer 'IT-1' for determination of the water percentage in engine or transformer oil and diesel fuel, the portable photometer pHotoFlex (for determination of the water condition and pH), the visible light portable spectrophotometer DR 190 manufactured by HACH-LANGE for the liquid media condition control with the turbidity not more than 10 FNU, etc. But all of them are designed to solve a narrow range of problems and do not have extensive functionality to determine the state of a large number of liquid media [16].

In addition, in recent years, increased demands have been placed on express control methods, one of which has become paramount in most cases. The conducted study of the environment should not change its chemical composition and physical structure [17]. This is necessary to obtain confirmation of the identified deviations in this sample of the medium in the stationary laboratory [18].

One device that meets the above requirements can be developed by us compact nuclear magnetic spectrometer. The only condition for its use is the presence of a sufficient number of nuclei with a large magnetic moment in the liquid under study [19]. Almost all liquid media contain hydrogen

nuclei (protons) [20], which are most sensitive to the method of nuclear magnetic resonance and one of the largest magnetic moments, compared with other nuclei contained in various substances [21].

2. Compact nuclear magnetic spectrometer and control method

The main parameters of any condensed (liquid or solid) medium, by which it is possible to instantly determine the change in its state (temperature increase, appearance of impurities, etc.), are the times of longitudinal T_1 and transverse T_2 relaxation [22]. By measuring the values of T_1 and T_2 at the sampling site and comparing them with the baseline (corresponding to the standard state of the medium under study), you can instantly determine its state [23]. This is enough to refuse to purchase this product.

We have developed a new method that allows in some cases (for example, for gasoline and motor oils) to determine the composition of the mixture by the measured relaxation times T_1 and T_2 and the form of the recorded nuclear magnetic resonance (NMR) signal. This significantly expanded the functionality of the compact NMR spectrometer developed by us. Its scheme is presented in figure 1.
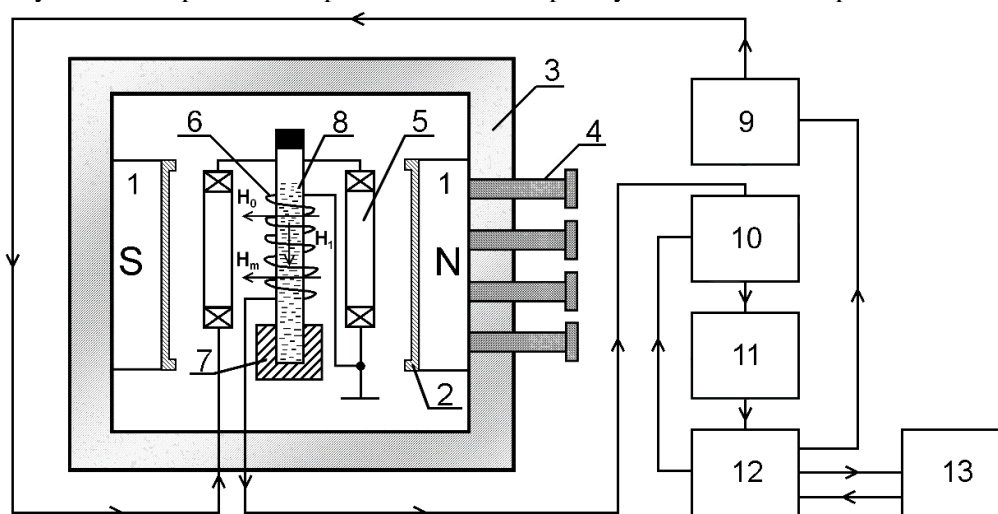
Figure 1. Structural scheme of compact NMR spectrometer: 1 — permanent magnet; 2 — inserts; 3 — neutral for the placement and alignment of the magnets; 4 — adjusting screws; 5 — modulation coil; 6 — NMR signal registration coil; 7 — locking device for the container with the researched medium; 8 — container with the researched medium; 9 — RF generator; 10 — registration scheme; 11 — analog-to-digital converter; 12 — processing and control unit; 13 — electronic device (e.g. laptop, tablet, smartphone).

The principle of operation, the method of recording the NMR signal, as well as the description of the main components of the device is presented in [24]. We developed a specialized measuring probe using a sample of the medium under study with a volume of less than 0.5 ml (figure 2) for faster monitoring of the media state in the field (outside the laboratories).

Figure 2. Measuring probe and container for the studied medium.

It consists of a registration coil 6, modulation coil 7 and a device for placing a container (cuvette) 4 (figures 1 and 2). The inner diameter of the container is 3.2 mm and the outer diameter is 4.8 mm. For example, in high-resolution NMR spectrometers (e.g. BRUKER) the cuvette diameters are 3.0 and 4.6 mm respectively.

In addition, we have developed a new processing and control scheme 12 based on the STM32 microcontroller (ARM Cortex M3 — STM32F100RBT6B) for the operational information processing, as well as for the automation of the measurement process (automatic adjustment of the registration device parameters to ensure the minimum measurement error). Additionally, the NMR signal accumulation scheme was implemented on the basis of STM32 microcontroller. The use of the accumulation scheme makes it possible to measure T_1 and T_2 in media containing few protons. Another new element in the small NMR spectrometer scheme is a 16-bit analog-to-digital Converter (ADC) 11. The use of this device allows you to continue to work only with digital signals, which meets the requirements of the digital economy [25].

From the outputs of the microcontroller digital NMR signal and measured values T_1 and T_2 come to the input of the electronic device 13, e.g. tablet. Then, depending on the type of environment you are exploring, you can perform various actions on your tablet. The main action is the comparison of the measured values T_1 and T_2 with the standard ones. These results determine the state of the environment (its quality) [26]. Further, through the mobile application, the result can be posted on the Internet within a few seconds (within the concept of 'Internet of things'). From this moment on, operational information about this product becomes available to other users.

Additional tasks may include the method we have developed for determining the concentration of mixtures of gasoline, kerosene and gasoline, motor oils, etc. [27], as well as the launch of the spectrum registration program. The latter takes quite a long process and thus should be used only in case of serious need [28].

3. The results of experimental studies of hydrocarbon media and their discussion
To demonstrate the feasibility of the proposed concept of determining product quality with the posting of results on the Internet, we selected hydrocarbons as test media. In many countries of the world, there are low-quality motor oils, as well as cases of mixing two gasolines for various reasons.

Figure 3 shows, as an example, NMR signals from synthetic motor oil ZIC XQ 5W-40 at a temperature T = 291.6 K
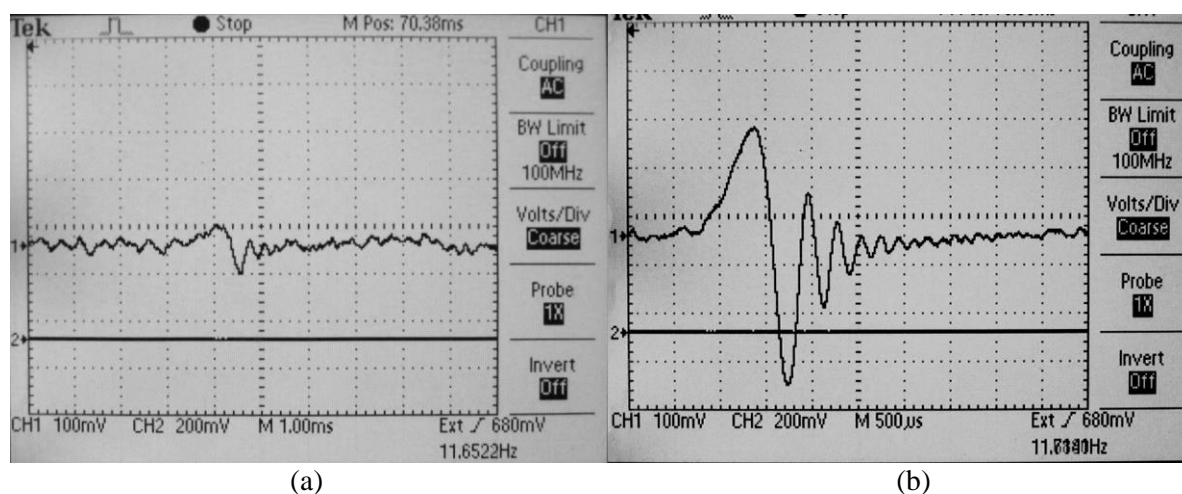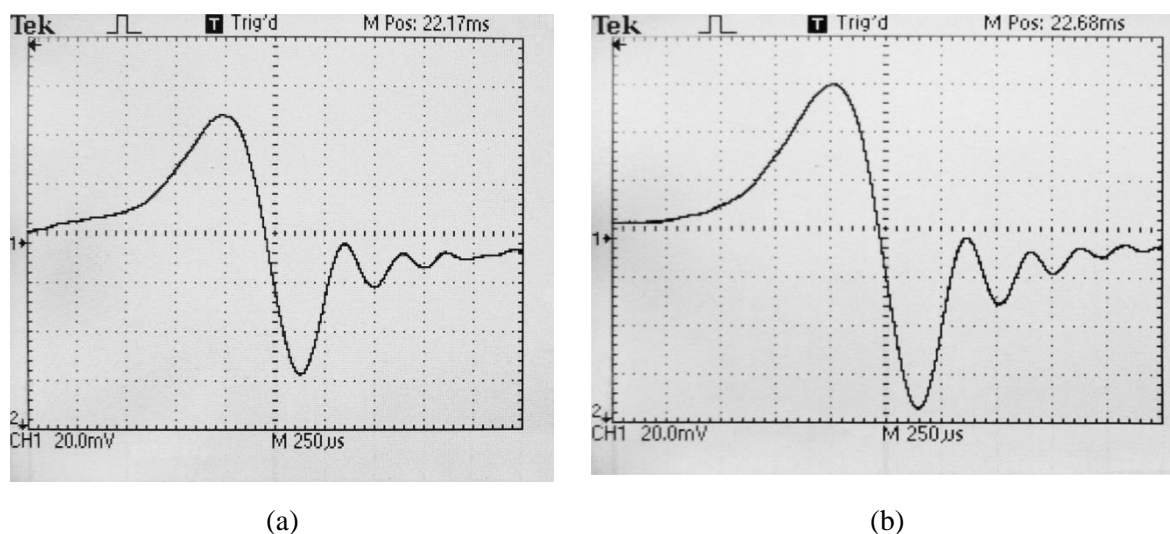
Figure 3. Registered NMR signal from the engine oil: (a) — without accumulation;
(b) — after accumulation.

The analysis of presented in the figure 3 NMR signals shows that we have to use accumulation schemes, because without them it is impossible to be sure that the S/N ratio will be greater than 3.0 which is necessary for the measurement with an accuracy higher than 1.5%.

It should also be noted that the use of a probe developed by us allows NMR signal registration from the investigated medium volume V_R less than 0.3 ml. This is important because for precision measurement we have to know sample temperature. If the studied medium contains in a small volume, after 10–15 s its temperature becomes equal to air temperature, which we can measure using standard instruments with high precision. Use of small container with volume V_R is one of the advantages of the compact NMR spectrometer in comparison with other devices.

The measured values of relaxation times $T_1 = 1.021 \pm 0.005$ s and $T_2 = 720.36 \pm 3.59$ µs coincided with the standard error. This shows that this engine oil is of good quality. In addition, a sample of this oil at the same temperature was studied on a stationary NMR relaxometer Minispec mq 20 (firm BRUKER). The following results were obtained on this device: $T_1 = 1.0207 \pm 0.0021$ s, $T_2 = 718.94 \pm 1.44$ µs. Comparison of the results of two measurements of T_1 and T_2 values confirms the reliability of the data obtained using the method developed by us and the conclusions made about the quality of engine oil.

Figure 4 shows as an example the registered NMR signals from AI-95 gasoline and its mixture with AI-92 gasoline in a ratio of 75% to 25%.

(a)   (b)

Figure 4. Registered NMR signal from (a) — gasoline AI-95, (b) — gasoline mixture AI-95 and AI-92 in the proportion of 75% to 25%.

According to the form of the recorded NMR signal, it can be visually determined that there are impurities in the AI-95 gasoline. This is confirmed by the measured values of relaxation times T_1 and T_2. For the studied substances they differ by more than 20%. For example, for pure AI-95 relaxation time $T_2 = 1.227 \pm 0.012$ ms, while the relaxation time of the mixture $T_2 = 0.872 \pm 0.008$ ms.

In the case of reducing the concentration of gasoline AI-92 in the mixture, the difference in the recorded signals in appearance becomes insignificant. In this case, the presence of impurities can be determined only by the measured values T_1 and T_2 (or using more complex methods, such as spectrum registration).

Experiments have shown that the developed device allows you to set changes in the relaxation times T_1 and T_2 caused by a slight addition of impurities, for example, when mixing 1000 ml of main gasoline and 10 ml of impurity gasoline. However, this ratio may vary for other substances.

4. Conclusions
The results show the high efficiency of the proposed method of express control of consumer goods compatible with the concept of the 'Internet of things'. Information about low-quality goods quickly becomes available to many Internet users and helps prevent various unpleasant situations. For example, with refueling a car on the highway. The same applies to the purchase of food products not in stationary large stores, etc.

The device developed by us can be connected to a regular smartphone (if the necessary software is available) as the data we use are digitized. This allows you to quickly mark on online maps outlets in which you think they sell low-quality products. People who are on the track in cars almost always listen to the news and exchange information in real time. As soon as the demand for goods falls at such outlets, the quality of the offered products will improve. This is one of the actual examples showing how, using fast and reliable express control together with the Internet services, it is possible to improve the quality of the goods offered to us.

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