

NMR Express-analyser for quality monitoring of motor fuel

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Abstract. A method for the rapid analysis of motor fuel quality was developed by artificial increase of the octane number through dissolving ferrocene in a low-octane gasoline ($C_{10}H_{10}Fe$). Measurements of the spin-lattice relaxation time of nuclear magnetic resonance is used for determination of ferrocene presence in standardized and real fuel from gas stations. The results of measurements of the relaxation characteristics among certain grades of motor fuel with dissolving ferrocene therein are presented.

1. Introduction

Problem of motor fuel quality at gas stations becomes very important since the presence of heavy metal salts and iron in gasoline leads to failure of the expensive machinery and environmental deterioration. Standard laboratory techniques, which are used in oil refining, usually give results not earlier than 2 to 3 hours. In this paper it is proposed to conduct a rapid analysis of the fuel quality in 3 to 4 minutes with an instrument, based on the measurement of the spin-lattice relaxation time of protons (T_1) of nuclear magnetic resonance (NMR), which has high precision and reproducibility of the obtained data and small measurement duration.

It is known that by mixing two substances with different viscosity or between molecules which have a chemical interaction, the spin-lattice relaxation time T_1 decreases versus time T_1 in the pure liquid. Note that this time also depends on other factors, such as type of nucleus, the magnetic field strength, mobility of spins (microviscosity), and temperature. Furthermore, due to the presence of the magnetic moments of atoms and molecules, real substances have paramagnetic properties. A particularly strong influence on the time T_1 have paramagnetic ions that may be contained in materials, through which the octane number of gasoline can be increased. As it is known, a magnetic moment of a paramagnetic ion is of the order of the Bohr magneton, and almost 10^3 times greater than nuclear magnetic moment. Paramagnetic ions (Mn^{2+} , Cu^{2+} , Fe^{2+} , Gd^{3+}) contain unpaired electrons whose reorientation creates a very strong fluctuating magnetic field that leads to a substantial decrease of the relaxation time. In this case, even a small concentration of paramagnetic ions in solutions containing such ions has a significant impact on the value of the spin-lattice relaxation time T_1 NMR. For example, the content of 0.01 mol of iron salt in a solution reduces the magnitude of T_1 compared with deoxygenated water from 3.6 to 0.01 s [2]. Thus, the effect of the paramagnetic ions in a liquid sample may significantly reduce the spin-lattice relaxation time.

In practice, ferrocene ($C_{10}H_{10}Fe$) is commonly used to increase the octane number of fuel by dissolving it into the fuel with a lower octane number. Ferrocene is the cheapest and most effective means for the octane number magnification. In order to increase the octane number by 4 to 5 units, it is enough to add 1 t of gasoline to 170 g of ferrocene.

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In this paper, studies on influence of the dissolved ferrocene concentration in pure gasoline Ai-92 and Ai-95 on the spin-lattice relaxation time were carried out with the help of NMR relaxometer [3, 4], which was described in [2]. Ferrocene was used for studies in which the content of free iron was about 0.03%, and the contents of other substances insoluble in gasoline did not exceed 0.5%.

2. Experimental procedure

In this paper measurement of the spin-lattice relaxation time T_1 is performed by magnetic resonance absorption at the double modulation of the magnetic field by sawtooth pulses of low frequencies and sinusoidal vibrations of sound frequencies. The use of dual modulation can significantly increase the signal to noise ratio and thereby reduce error in determining the time T_1 .

Signal amplitudes arising from the implementation of the nuclear resonance condition are measured in the device. This condition is described by equation of Larmor:

$$f = \gamma \cdot H_0, \quad (1)$$

where f – frequency of the HF generator, γ – gyromagnetic ratio (for a proton γ is equal to 42.58 MHz/T), H_0 – the constant magnetic field strength, in this case amounted to 0.37 T.

Information about the spin-lattice relaxation time T_1 is retrieved from the formula:

$$T_1 = \tau \left(-\ln \left(1 - \frac{A(\tau)}{A_1} \right) \right)^{-1} \quad (2)$$

where A_1 – amplitude of the first signal (saturation), which is always greater than the second signal and remains the same during the measurement, $A(\tau)$ – amplitude of the second signal, τ – time between a pair of signals (see figure 1).

The range of values of the first signal determines the measurement error T_1 . In contrast to the signal processing method described in [3, 4], in this research the period between a pair of absorption pulses was set from 0.9 to 1.0 s.

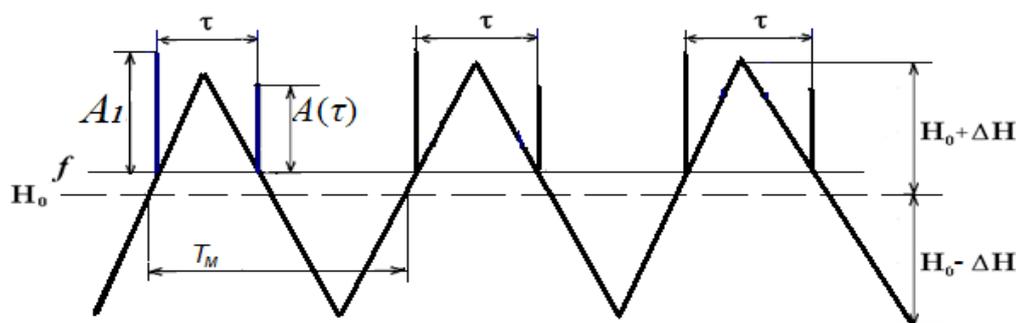


Figure 1. Form of absorption signals at a fixed frequency of HF generator. At this frequency, period between absorption signals was set at about 1.0 s. T_M is a period of triangular modulation.

One of the conditions for optimum operation of the device is that triangular modulation period should be from 3 to 5 times larger than the spin-lattice relaxation time T_1 , i.e. $T_M = (3-5) T_1$. Inside the couple of absorption signals, the time delay must be less or comparable to T_1 . Then all the information about changing of the second signal amplitude goes to a computer where a specially designed program starts processing of this data array. The relaxation time is determined by a number of a predetermined amount of measurements (up to 30), averaged and displayed at the measurement results panel (see figure 2).

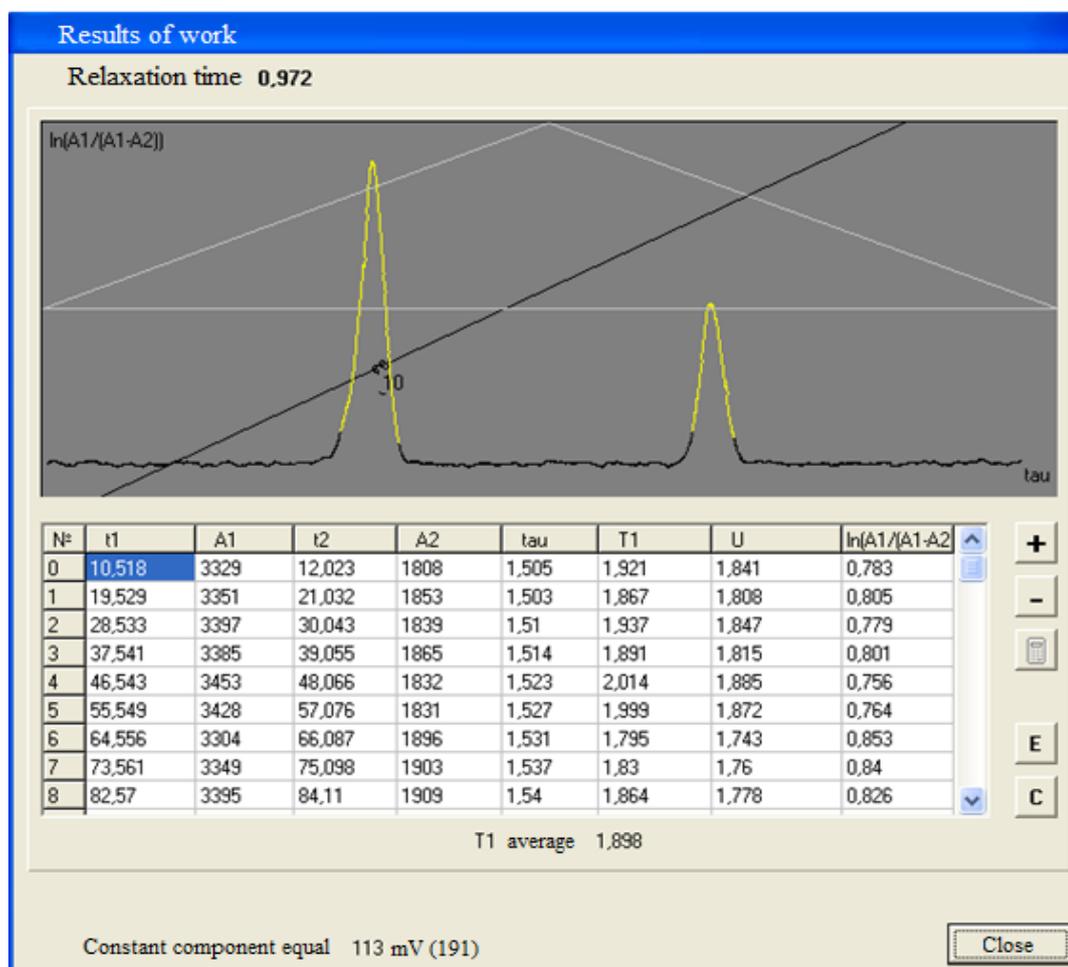


Figure 2. The measurement results panel.

In the case of such device realization in the automotive industry and energy sector, it is supposed to adhere to the following algorithm of device operation. Amplitude data and information about the spin-lattice relaxation time (T_1) of fuels, which correspond to their standardized quality at a suitable temperature, are programmatically entered in a computer.

The device automatically measures the specified parameters of the real fuel, compares them with the ideal fuel parameters, which are set in the program, and if they do not match the standard, a warning signal is triggered. Differences of the characteristics of the fuel from the standard can be fixed with an accuracy of $\pm 5\%$. Device control and signal processing is performed using the built-in processor, excluding the manual adjustments.

3. Measurement results

To check the correct operation of relaxometer, test measurements of time T_1 of distilled water were conducted. This time period was equal to 2.42 s. The actions have been taken to exclude the fuel evaporation during conduction of the measurement. About 3.0 ml of the fuel was required for this analysis. The measurements were performed three times by 30 points for each fuel grade, and then the average T_1 was calculated. Table 1 shows the measurement data regarding time T_1 at the temperature of 21°C for various grades of fuel produced at different gas stations in Moscow and Moscow area.

Table 1. The spin-lattice relaxation time dependence on fuel type

| Fuel type | T_1 , s |
|--------------------------------|-----------|
| Diesel fuel | 0.78±0.05 |
| KO brand Kerosene | 0.93±0.05 |
| Kerosene “Ekspohimtreyd” | 1.15±0.05 |
| Gasoline “The galosh” | 2.45±0.05 |
| Gasoline Ai-95 (2015 year) | 3.16±0.07 |
| Gasoline Ai-95 (ten years old) | 2.54±0.07 |
| Gasoline Ai-92 (2015 year) | 3.62±0.07 |
| Gasoline Ai-92 (ten years old) | 2.40±0.05 |

As it can be seen from the table, the relaxation time decreases significantly with the increase of fuel storage period. Presumably, it can be associated with the fact that during long storage period various photochemical processes can occur, and also evaporation of the fuel’s light fraction leads to the increase of viscosity which consequently decreases the relaxation time.

To measure the influence of ferrocene concentration on the spin-lattice relaxation time T_1 , the appropriate amount of ferrocene was dissolved in 20 g of gasoline Ai-92.

Figure 3 shows a graph of time T_1 dependence on the concentration of ferrocene in gasoline Ai-92 and Ai-95.

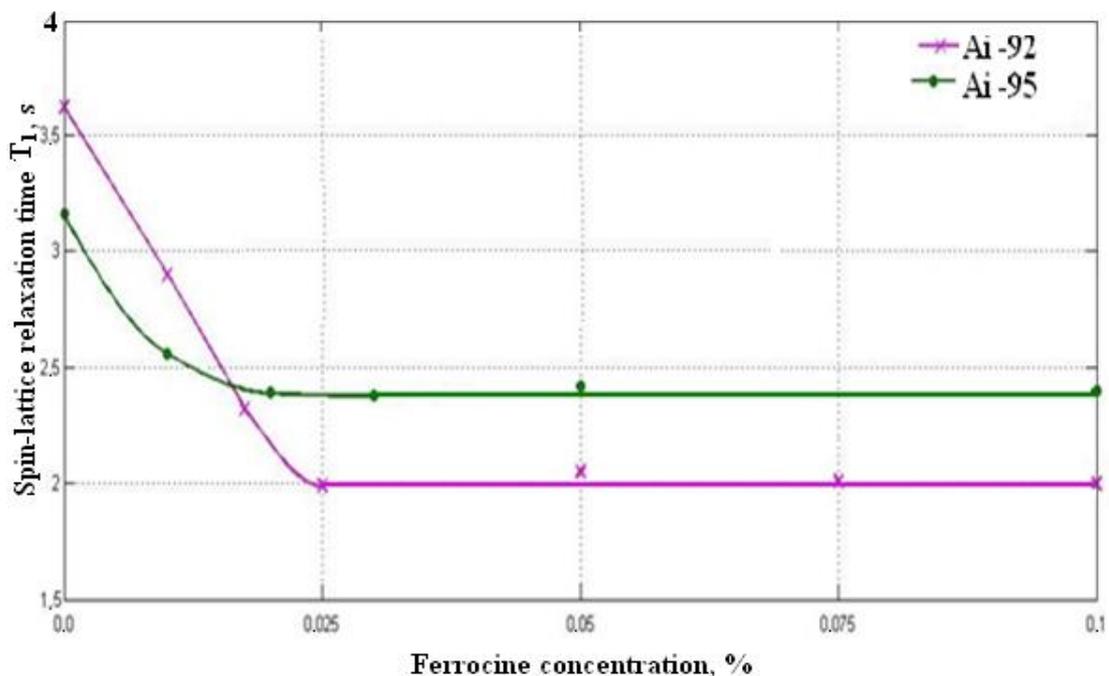


Figure 3. Spin-lattice relaxation time T_1 dependence on the concentration of ferrocene dissolved in gasoline Ai-92 and Ai-95.

Comparing the data for gasoline Ai-92 and Ai-95, it can be concluded that in measured gasoline Ai-95, ferrocene probably was already present.

As it can be seen from the graph, at ferrocene concentration of 0.025% and higher, the relaxation time T_1 within the margin of error ceases to depend on the amount of ferrocene, i.e. there is a saturation effect. Obtained error is mainly associated with the inaccuracy of components' weighing. Nature of the saturation effect is unknown yet and requires further research. Presumably, in this case the presence of free atoms of iron in ferrocene matters, which in its turn can prevent heat exchange between nuclear moments and the lattice.

Thus, the time difference of the spin-lattice relaxation time between pure Ai-92 gasoline and gasoline dissolved therein with ferrocene concentration even less than 170 grams per ton of gasoline is 1.5 s. This fact allows to implement a reliable detection of this substance presence in gasoline.

Acknowledgments

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