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NMR Spectroscopy in the Earth's Magnetic Field

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Abstract

Today, magnetic imaging systems used are quite expensive and are generally used for medical purposes. Apart from this purpose, there are many scientific fields of study whose internal structure is desired to be displayed. Especially in science, different from the techniques used to understand the internal structure of matter, magnetic imaging techniques are also needed. Therefore, the interest in more useful and smaller magnetic imaging systems is increasing. For this purpose, studies on magnetic particle imaging and magnetic resonance imaging techniques have gained momentum. The magnetic resonance imaging technique, which is one of the magnetic imaging systems based on the NMR phenomenon, has passed through numerous stages and has become smaller and more useful. This study examines the basic components of the NMR images made in the earth's magnetic field for different liquids, the T_1 and T_2 proton relaxation parameters, and the technique of the obtained two-dimensional images with the EFNMR system.

1. Introduction

There are various imaging techniques in the field of biomedical and medical physics. Among the imaging techniques, magnetic resonance imaging (MRI) is an effective, powerful, and reliable method. Medical physicists are finding better opportunities by working towards the design of this imaging technique every day [1,2]. MRI is widely used to visualize the structures and functions of living systems and protozoa. However, MRI is an imaging technique that is also used in medical radiology and has no harmful effects. It is best today, especially for anatomical images of organ tissues [3,4]. Nuclear magnetic resonance (NMR) spectroscopy is a complementary method in determining the structure and behavior of solid-state materials [5-7]. This technique is often used in many fields of materials research, as it can provide comprehensive information at the atomic scale [8,9].

The magnetic resonance imaging technique is based on the resonance phenomenon, which is the nuclear magnetic resonance phenomenon, which is realized by stimulating the protons in a uniform magnetic field with a radio frequency field of appropriate frequency. In order to obtain an image of the molecular structure and dynamics that are desired to be visualized, a magnetic field environment as homogeneous as possible is required. Thanks to the perfection of the magnetic medium, the signal intensities obtained are large and this affects the quality of the images. The source of the signals is due to the spin property inherent in NMR-sensitive nuclei. Atoms with an odd number of protons or neutrons such as hydrogen (^{1}H), oxygen (^{17}O), fluorine (^{19}F), sodium (^{23}Na), phosphorus (^{31}P), and potassium (^{39}K) have a spin property and these atoms are used as signal sources in MRI [10]

In magnetic resonance imaging, hydrogen, also known as the proton, which has a spin feature is used. Especially in organic chemistry, NMR signals of protons give essential information about the internal structure of compounds. Chemical shift, spin-spin interactions, diffusion coefficients, and spin relaxation times are the most important NMR parameters used to determine the characteristic structure of liquids. The NMR signal intensity also presents information about the proton density of the sample. The spin relaxation times of the nuclei and the intensity of the signals they generate form the

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basis of NMR imaging. These images obtained depending on the parameter they are used, are T_1, T_2, and proton density (PD) images, respectively [11]. How NMR signals are formed has been reported in detail in the literature [12,13].

The spins of the protons that make up water in tissues have a magnetic moment because they are also charged particles. These magnetic moments, which are one of the basic components of magnetic resonance imaging systems and under the influence of the external magnetic field, are aligned in the same direction with the field and have an average magnetic moment. It is the average magnetic momentum of this spin ensemble that will give the MR signal. This mean is called the magnetization of the spin ensemble. It is not the hydrogen nuclei themselves that align with the outer field, but the individual magnetic moments of the hydrogen nuclei. Since it represents only two possible energy states of the proton, spins can only align in one of two directions, parallel to the field or in the opposite direction. The hydrogen nucleus itself does not change direction, it just rotates on its axis. The NMR signal is the sum of the individual spins. If it is found from which parts of the tissue these NMR signals come, we obtain a magnetic resonance image of the tissue. Field gradients are used to accomplish this. Field gradients, which are part of the magnetic imaging system, determine the spatial position of the tissue. If the direction of the external magnetic field is accepted as the z-axis, a linearly increasing magnetic field change along the z-axis and gradient $G_z = dB_z/dz$ is applied to measure the NMR signals of the image on this axis. The spectrum obtained with the magnetic field gradient applied along one of the axes and along the axis of the NMR measurement should accurately reflect the geometry of the sample.

$$\omega(z) = \gamma(B_0 + zG_z) \qquad (1)$$

Here, ω is the frequency of the radio signal applied perpendicular to the external magnetic field and γ is the gyromagnetic ratio constant of the spin system. This constant also determines the resonance frequency of the spin system. These NMR signals, which are formed in the time dimension, are subjected to two consecutive Fourier transform. The first transform provides a transformation to the position space corresponding to the time signals, the data in this position space called k-space is subjected to a Fourier transform again to display the internal structure of the tissue or the examined sample. NMR signals are pure data [14,15]. The known original magnetic resonance image is created by twice Fourier transform of pure NMR signals.

This study is about the use of spectroscopy, relaxivity, and magnetic resonance imaging method, whose theory is too broad to fit in this article, in the laboratory environment. In recent years there has been an increasing interest in nuclear magnetic resonance spectroscopy (EFNMR) in the Earth's magnetic field [9, 16, 17]. The purposes of this paper are to measure the parameters T_1 and T_2 relaxation times for ^{1}H nuclei in different chemical environments; to study two-dimensional (2D) imaging in the earth’s magnetic field; and to demonstrate the benefit of the EFNMR method to characterize relaxation parameters consisting of five different chemical solvents in the earth’s magnetic field (the typical earth magnetic field in Bursa, Turkey, is 0.047 mT) at room temperature. The described EFNMR system does not have a permanent magnetic field generator. It uses the very smooth but very weak (about 0.047 mT) magnetic field of the Earth. Such a method is very advantageous due to the minimum cost of purchase, installation, and maintenance.

2. Material and Method

In this study, T_1 and T_2 relaxation times of five different chemical compounds, namely Bromobenzene, Chlorobenzene, Iodobenzene, Ethanol, and distilled water, were measured using Terranova-MRI imaging device produced by Magritek company in New Zealand. In addition, two-dimensional images of the ethanol from the top (transverse), front (sagittal), and side (coronal) were recorded.

2.1. Polarization Coil

This system consists of three base units with a nested three-component probe, an ultra-low frequency spectrometer, and a computer-operated Prospa software package. Figure 1 shows the internal structure of this coil set [18].

2.2. B_1 Transmit/Receive Coil

This most inwardly positioned coil generates radio frequency, first stimulating the spin system in the sample and then detecting the NMR signals coming from the spin ensemble. This coil is connected to a series of capacitors. By changing the capacitance values, the B_1 coil is adjusted to the Larmor frequency of the spin ensemble. The value of the Larmor resonance frequency varies according to the value of the local magnetic field. This frequency, which is usually in the range of 1-3 kHz, should be found experimentally.

2.3. B_1 Gradient Coil

It is necessary to deregulate the Earth's magnetic field in a very controlled manner to encode spatial information into the NMR signal so that the magnitude of the field changes in the direction of the desired spatial coding. This is succeeded using a three-axis gradient coil set.

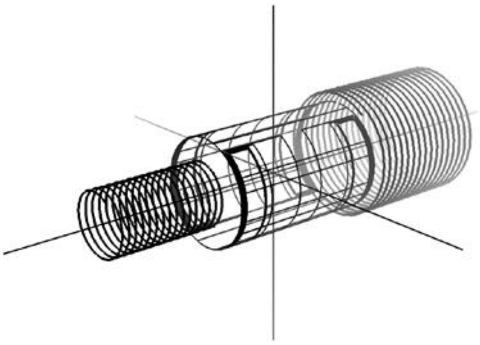

Figure 1. A schematic of the three-coil probe

2.4. Ultra-Low Frequency Spectrometer

In a sense, the Terranova-MRI device is the essence of EFNMR spectroscopy. It is controlled by a digital signal processor (Digital Signal Processing) driven by a personal computer running its software, Prospa. In a typical earth field NMR (EFNMR) experiment, Prospa sends a precompiled DSP pulse packet and all necessary parameters to the DSP unit via the computer's USB port. It then starts running this program. This program controls the entire NMR experiment by sending pulses to the B_P, gradient and B_1 coils and then receiving the NMR data at appropriate time intervals. After this data is collected, it is displayed, all necessary analyzes are made, and then the experiment is terminated or, if desired, the experiment is repeated by sending new parameters to the DSP.

2.5. Ethanol Tube

To obtain two-dimensional images of ethanol in the EFNMR experiment, the nested tube system shown in Figure 2 was made. The inner tube is filled with ethanol and placed in a large tube filled with distilled water. These two tube systems, insulated from each other, represent two separate tissue samples.

2.6. Determination of the Relaxation Parameters

The first of the NMR parameters expected to be measured in an NMR spectrometer is the measurement of the relaxation times. All chemicals used are technical and at least 99% pure. In the measurement of T_1 relaxation times, also known as spin-lattice or longitudinal relaxation time, the time intervals between the applied B_p polarization pulse and 90^o pulses are changed and measured by repeating the desired number of steps (measurements) one after the other. The obtained T_1 relaxation time graphs are presented in Figure 3 and the numerical data are summarized in Table 1.

In the measurement of T_2 relaxation times, also known as spin-spin or transverse relaxation times, T_2* values are measured in conjunction with T_1 spin-lattice relaxation. T_2* is shorter than T_2 because of the unevenness of the field. For this reason, spin-echo pulse sequences are used.

Figure 2. Nested tube system used for imaging

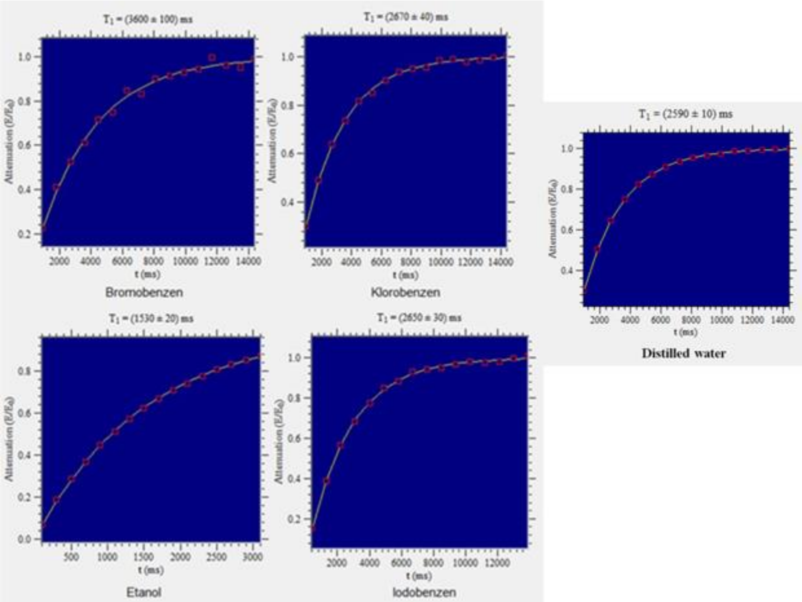

Figure 3. The obtained T_1 relaxation times

The application of a spin-echo pulse array refocuses the phase dissolution of the spin ensemble caused by the non-uniform field, allowing accurate measurement of T_2. Disruption of phase harmony between spins is known as phase dissolution. The EFNMR system uses shimming coils, to minimize the effect of this phase dissolution. For samples with weak signal strength, the system must first be calibrated for the homogeneity of the field.

T_2 relaxation time graphs obtained using spin-echo pulse sequences are presented in Figure 4 and numerical data are summarized in Table 1.

3. Results and Discussion

When the T_1 relaxation times in Table 1 are examined, it is seen that the relaxation times of the benzene group are close to each other. The T_1-weighted image obtained using an ethanol tube in distilled water is given in Figure 5. T_1-weighted images will be clear as there is a difference between the relaxation times of distilled water and ethanol. When Figure 5 is examined, it is seen that the images of distilled water and ethanol are clearly separated. The presence of the tube is noticeable in the top and side views. In both of these images, it is seen that the redness does not continue between the two bright red spots. The reason is that there is an air gap there. In the front (sagittal) view, the presence of ethanol is clearly visible.

In the table, it is noticed that the T_1 and T_2 relaxation values of the benzene group are actually close to each other. This is due to the closeness of T_1 and T_2 relaxation times in liquids. However, it seems that distilled water does not comply with this rule.

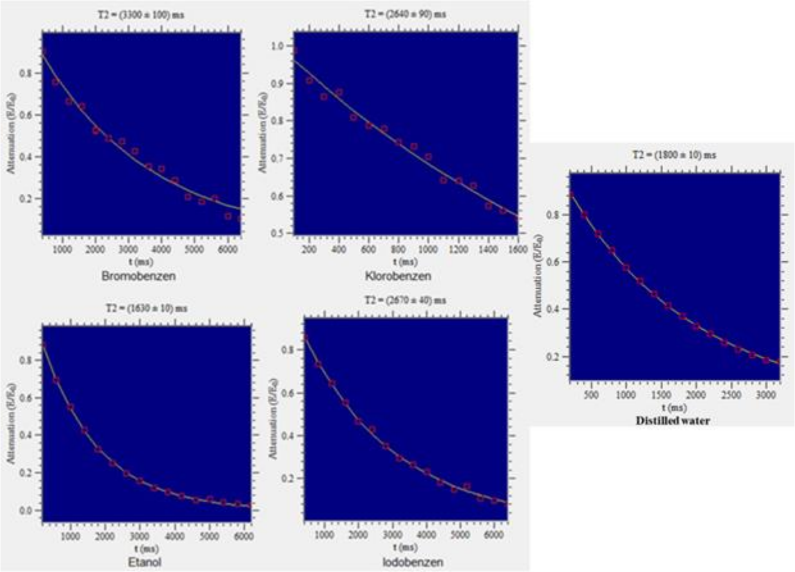

Figure 4. The obtained T_2 relaxation times

Table 1. T_1 and T_2 relaxation times of the compounds used

Solvent	T_1 (ms)	T_2 (ms)
Bromobenzene	3600 ± 100	3300 ± 60
Chlorobenzene	2670 ± 40	2450 ± 50
Iodobenzene	2650 ± 30	2670 ± 40
Ethanol	1530 ± 20	1630 ± 10
Distilled Water	2590 ± 10	1800 ± 10

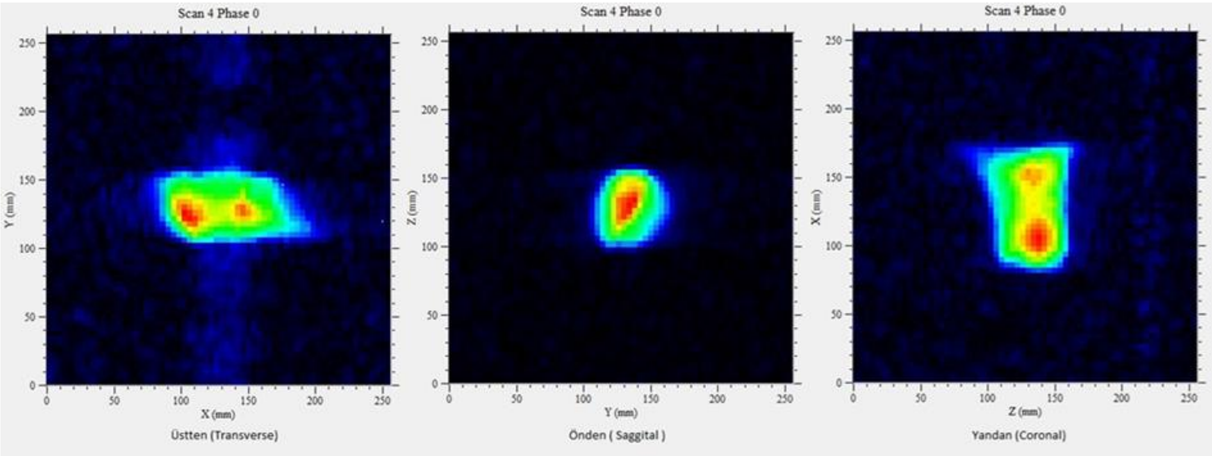

Figure 5. The T_1-weighted image of ethanol obtained using an ethanol tube in distilled water.

In addition, the homogeneity of the magnetic field of the EFNMR system must be calibrated before the T_1 or T_2 weighted images of this group are taken. In addition, the homogeneity of the magnetic field of the EFNMR system must be calibrated before the T_1 or T_2 weighted images of the studied solvents are obtained. For this, the NMR signal of pure water can be used. The free induction decay (FID) and NMR signal of pure water obtained in its calibrated form are shown in Figure 6. In Figure 6, it can be seen that the magnetic field is perfect in a wide band gap.

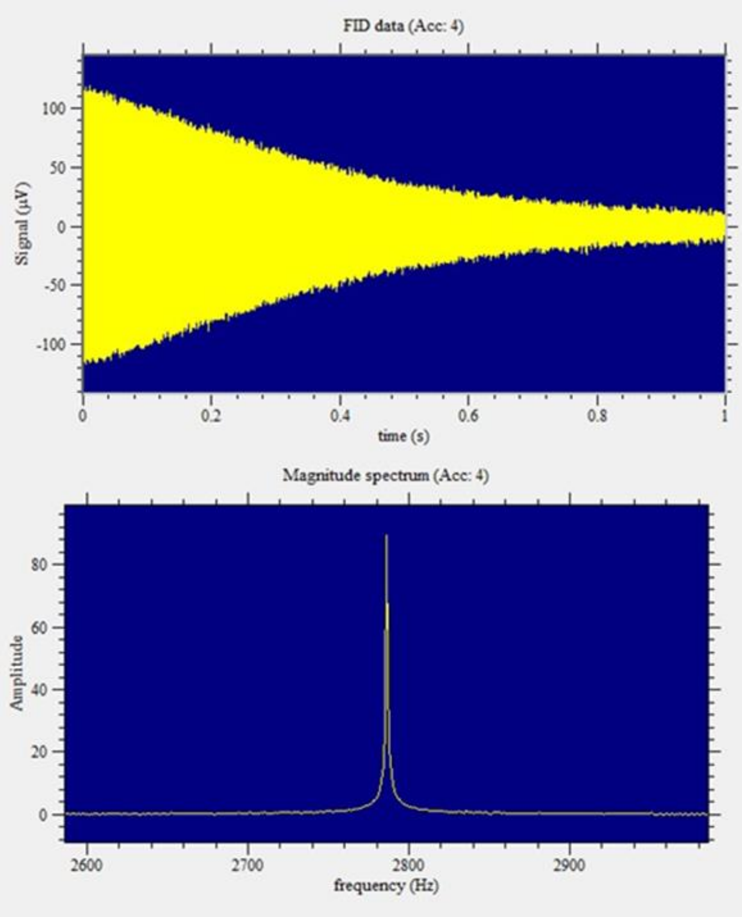

Figure 6. FID and NMR signal of pure water

4. Conclusion and Suggestions

Newly developed mobile NMR devices using weak magnetic fields, namely EFNMR desktop magnetic resonance imaging systems, have now turned into a functional examination method in the laboratory environment due to their small size, low weight, and mobility.

T_1 and T_2 relaxation times of five different solvents and two-dimensional ethanol-water image studies were performed in the world's magnetic field, which is a less costly option. Using NMR with a small and affordable permanent magnet, it was investigated whether it was possible to distinguish between different liquids. It was demonstrated that basic FID envelopes may be utilized in the laboratory to study the relaxation of hydrogen-atom-containing materials using EFNMR. NMR measurements at a high magnetic field can be replaced by magnetic field measurements of the earth, which is a less costly option and has a lower magnetic field.

Using T_1 and T_2 parameters or including information about signal strength can help improve identification accuracy. Thus, additional information can be provided on samples and structures of new solvents in the future. From the measurements of the T_1 and T_2 parameters and 2D image studies, it was finally concluded that the EFNMR method is useful for characterizing relaxation parameters in various solvents in Earth’s magnetic field. Experimental applications of the technique demonstrated that EFNMR data with spatial resolution output may be obtained in a matter of minutes. The use of a low magnetic field (the earth’s magnetic field is roughly 0.0047 mT) contributes to this field since there is little work in this field.

This paper is the study of NMR studies, which were previously done in a high magnetic field, in a very low magnetic field. With researchers working with EFNMR, these devices can be programmed at peak performance and used to understand the spin behavior of liquids.

Contributions of the authors

All authors contributed equally to the study.

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The authors declare that this study complies with Research and Publication Ethics

References

[1] C. Kurz, G. Buizza, G. Landry, F. Kamp, M. Rabe, C. Paganelli, G. Baroni, M. Reiner, P. Keall, C.A.T. Berg, and M. Riboldi, “Medical physics challenges in clinical MR guided radiotherapy,” *Radiat. Oncol.*, vol. 15, no. 93, pp. 93-109, 2020, doi: 10.1186/s13014-020-01524-4.

[2] D. Qiu, Y. Cheng, and X. Wang, “Gradual back-projection residual attention network for magnetic resonance image super-resolution,” *Comput. Methods Programs Biomed.*, vol. 208, pp. 106252, Sept. 2021, doi: 10.1016/j.cmpb.2021.106252.

[3] H. L. Ring, Z. Gao, A. Sharma, A., Z. H. Han, C. Lee, K. G. M. Brockbank, E. D. Greene, K. L. Helke, Z. Chen, and L. H. Campbell, “Imaging the distribution ofiron oxide nanoparticles inhypothermic perfused tissues,” *Magn. Reson. Med.*, vol. 83, no. 5, pp. 1750-1759, Dec. 2020, doi: 10.1002/mrm.28123.

[4] T. Abe, R. S. Thiebaud, and J. P. Loenneke, “The mysterious values of adipose tissue density and fat content in infants: MRI-measured body composition studies,” *Pediatric Res.*, vol. 90, no. 5, pp. 963-965, Jan. 2021, doi: 10.1038/s41390-021-01376-y.

[5] A. Abraham, E. Salager, D. Krishnan, and Y.C. Su, “Advances of solid-state NMR spectroscopy in material sciences,” *Magn. Reson. Chem.*, vol. 58, no. 11, pp. 987, Oct. 2020, doi: 10.1002/mrc.5086.

[6] P. Chien, K. J. Griffith, H. Liu, Z. Gan, and Y. Hu, “Recent Advances in Solid-State Nuclear Magnetic Resonance Techniques for Materials Research,” *Annu. Rev. Mater. Res.*, vol. 50, no. 1, pp. 493-520, May. 2020, doi: 10.1146/annurev-matsci-091019-011049.

[7] S. Bjorgvinsdottir, and L. Emsley, “Bulk hyperpolarization of inorganic materials,” *Chimia*, vol. 75, no. 4, pp. 333-337, Feb. 2021, doi: 10.2533/chimia.2021.333.

[8] G. Foran, N. Verdier, D. Lepage, C. Malveau, N. Dupre, and M. Dolle, “Use of solid-state NMR spectroscopy for the characterization of molecular structure and dynamics in solid polymer and hybrid electrolytes,” *Polymers*, vol. 13, no. 8, pp. 1207-1241, Apr. 2021, doi: 10.3390/polym13081207.

[9] H. Ovalıoğlu, “Application of nuclear magnetic resonance/magnetic resonance imaging techniques to estimate proton relaxation parameters at earth field,” *Emerg. Mater. Res.*, vol. 11, no. 3, pp. 303–312, Sept. 2020, doi: 10.1680/jemmr.21.00180.

[10] Z. Yüksel, “Manyetik Rezonans Görüntüleme, Fizik Temelleri ve Sistem Bileşenleri,” *BSJ Eng. Sci.*, vol. 2, no. 2, pp. 57-65, Apr. 2019.

[11] W. Catherine, C. K. Roth, and J. Talbot, *MRI in Practice, 4*th ed. USA, Wiley-Blackwell Publishing Ltd., 2011, pp: 21-58.

[12] M. Balcı, *Basic 1H- and I3C-NMR Spectroscopy*. Ankara-Turkey, Elsevier, 2005. pp. 9-23.

[13] G. Harald, *NMR Spectroscopy* , Weinheim-Germany, Wiley-VCH Verlag GmbH&Co, 2013, pp: 13-27.

[14] M. S. Hansen, and P. Kellman, P., “Image reconstruction: An overview for clinicians,” *Magn. Reson. Imaging,* vol. 41, no. 3, pp. 573-585, Jun. 2015, doi: 10.1002/jmri.24687.

[15] G. A. Wright, “Signal acquisition and processing for magnetic resonance imaging,” in *Proc. ICIP-94, IEEE Comput. Soc. Press 1st Int. Conf. on Image Proc.*, Aug. 2002, pp. 523–527, doi: 10.1109/ICIP.1994.413751.

[16] E. Balci, B. Rameev, H. Acar, G.V. Mozzhukhin, B. Aktas, B. Colak, P.A. Kupriyanov, A.V. Levlev, Y.S. Chernyshev, and V.L. Chizhik, “Development of Earth's Field Nuclear Magnetic Resonance (EFNMR) technique for applications in security scanning devices,” *Appl. Magn. Reson.*, vol. 47, no. 1, pp. 87-99, Oct. 2015, doi: 10.1007/s00723-015-0730-z.

[17] M. Trybus, “Measurements of Longitudinal and Transverse Relaxation Times of Selected Liquids Using the EFNMR Scanner,” *Przeglad Elektrotechniczny,* vol. 963, pp. 115-118, Oct. 2020, doi: 10.15199/48.2020.10.21.

[18] M. E. Halse, “Multi-acquisition and multi-dimensional earth’s field nuclear magnetic resonance spectroscopy,” Ph.D. dissertation, Dept. Phys., Victoria Univ. of Wellington, Wellington, New Zealand, 2009.