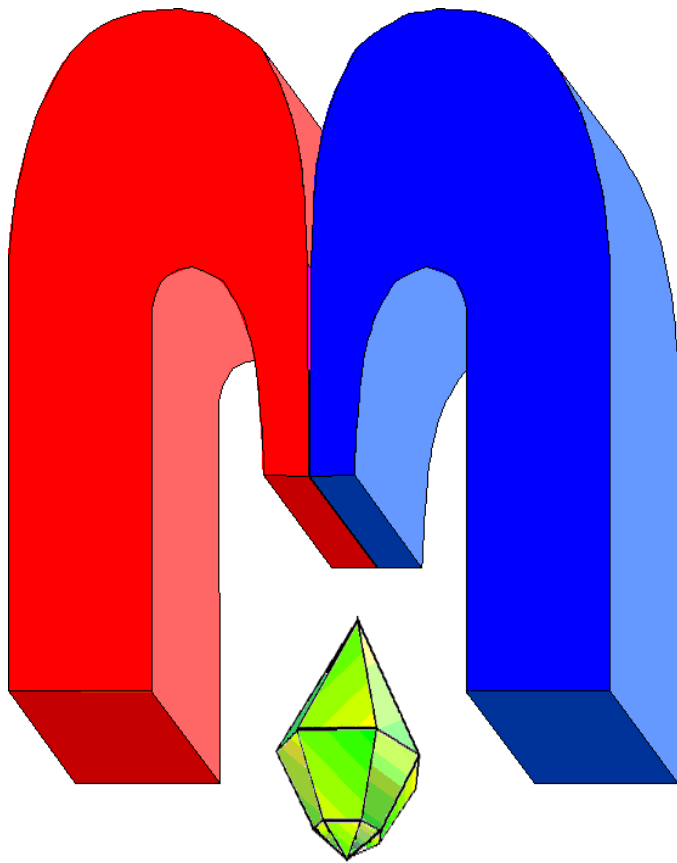


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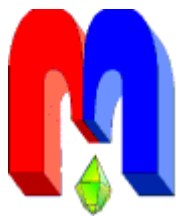
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Pulsed NMR spectrometer with dynamic nuclear polarization for weak magnetic fields

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Pulsed nuclear magnetic resonance (NMR) spectrometer operating in weak magnetic field (~ 100 Oe) with the dynamic nuclear polarization (DNP) is described. The spectrometer is designed to study the Overhauser DNP effect in natural hydrocarbons for potential using DNP techniques to enhance the ^1H NMR signal in crude oil and petroleum products. The unit was tested on a sample of the ethylene glycol chromium complex at room temperature. A DNP enhancement of $\varepsilon = -50$ for ^1H NMR signal from solvent protons by pumping $^{52}\text{Cr}^{5+}$ electronic transitions with the optimized pumping parameters was achieved.

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Keywords: magnetic resonance, Overhauser effect, dynamic polarization of nuclei, NMR, DNP.

1. Introduction

Investigation of the reservoir characteristics such as porosity, permeability, fluid saturation, type of saturating fluid, etc. is an important task for the oil industry. One of the most effective, non-destructive and express method for measuring these characteristics is nuclear magnetic resonance (NMR) [1, 2]. However, despite the rapid development, an important problem in the field of NMR logging still remains the low sensitivity of the method at near room temperatures (RT). This is primarily due to the low nuclei magnetization (thermal polarization) at RT in weak magnetic fields (~ 100 Oe) used by the borehole logging devices. In addition, the fluid saturation of reservoir usually does not exceed a ten percent which means a low filling factor of the receiving antenna. It leads to the weak signal-to-noise ratio or increases the acquisition time, which is very crucial for logging application.

One of the ways to increase the NMR signal is to enhance the nuclei magnetization by the methods of dynamic nuclear polarization (DNP) based on the effect of transfer the polarization from electronic spins S (paramagnetic centers) to a system of nuclear spins I (see for example [3–5]). In liquids the Overhauser mechanism (ODNP) makes the largest contribution to the polarization transfer [6]. The ODNP enhancement can be factorized as:

$$\varepsilon = \frac{P_z - P_0}{P_0} = \zeta f s \frac{\gamma_S}{\gamma_I}, \quad (1)$$

where P_0 is equilibrium polarization of I spins, P_z is enhanced polarization of I spins, ζ is coupling factor, f is leakage factor, s is saturation factor for electronic spin S , γ_S and γ_I are gyromagnetic ratios of the electron and nuclear spin systems, respectively [7]. Such a transfer requires the presence of paramagnetic centers in the system under study, as well as the presence of a magnetic coupling between such centers and the nuclei subsystem. In the mid-1950s the paramagnetism of hydrocarbon containing systems mainly due to the presence of stable carbonaceous free radicals was discovered [8, 9]. Already in 1958 a fifteen-fold amplification of the ^1H NMR signal of an oil sample due to DNP in the magnetic field of 15 Oe was demonstrated [10].

However, in later reports on this topic not native hydrocarbons, but oil asphaltene / asphalt solutions, as containing the highest amount of free radicals, were investigated by ODNP [11–13] in the magnetic fields of 14-74 Oe. Probably it is connected with the great diversity of the qualitative and quantitative composition of oils meaning that only in some of them the magnetic coupling between paramagnetic centers and protons, as well as their mutual mobility, are sufficient to observe a perceptible ODNP effect.

The goal of this work was to create a pulsed NMR spectrometer with DNP for magnetic field of 100 Oe to study the ODNP effect in natural hydrocarbons and to increase the NMR signal of hydrocarbons for NMR logging applications.

2. Apparatus

The block diagram of the designed setup is shown in Fig.1. The setup includes an NMR subsystem and a system of pulsed saturation of the electron paramagnetic resonance (EPR) line of paramagnetic centers. An NMR logging device magnetic system (MS) was used to generate the external magnetic field H_0 . The MS consists of two cylindrical permanent SmCo magnets 120 mm in diameter and 500 mm in height, directed by the analogous poles to each other. The distance between the poles of the magnets was 500 mm. This configuration creates an axially symmetric relatively uniform magnetic field of 99.4 Oe directed along the radial axis (see Fig. 1) at 180 mm distance from the center (O) of the magnetic system. Magnetic field gradients at this area was estimated as $\frac{\partial H_0}{\partial x} \approx \frac{\partial H_0}{\partial z} \approx 2$ Oe/cm. The ^1H NMR frequency in this field is 423 kHz.

The NMR subsystem consists of an NMR sensor, a receiver amplifier RA, a power amplifier PA, a pulse sequence programmer PP, and an RTO1012 oscilloscope. The NMR sensor radiofrequency (RF) circuit is built according to the Fig.2. The circuit was developed to match to the preamplifier constructed earlier in our group, which has an input impedance of $50\ \Omega$ and a low noise factor $K \sim 1$ dB. The sensor consists of a transceiver parallel oscillating circuit L_0C_0 , matched to $50\ \Omega$ by C_1 , a quarter-wave line equivalent circuit $C_2-L_1-C_3$, and a cross-

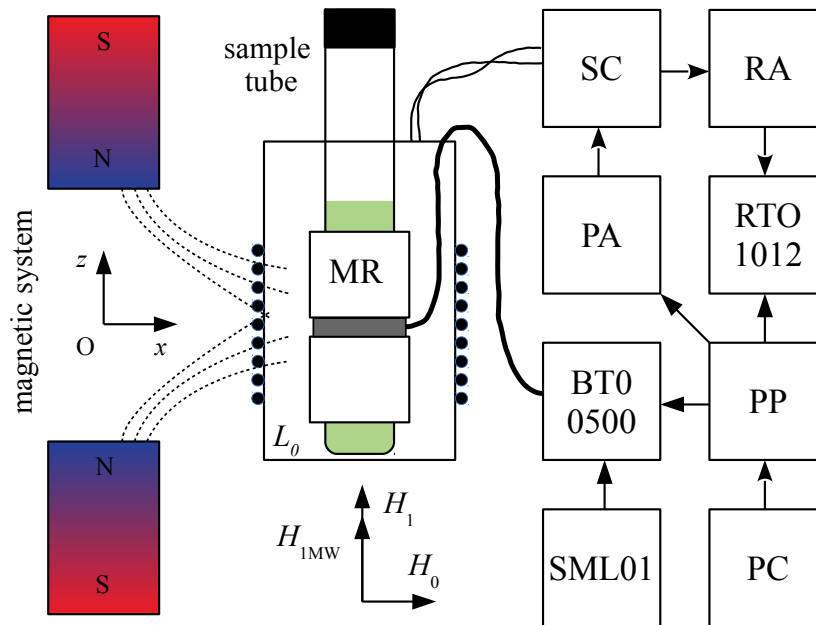


Figure 1. Scheme of the designed setup: resonator MR, sensor circuit SC, receiver amplifier RA, RF pulse power amplifier PA, pulse sequence programmer PP, personal computer PC. More details are given in the text.

diode switches VD_1 - VD_2 , VD_3 - VD_4 . The antenna L_0 is a solenoid 20 mm in diameter and 80 mm in height, made of copper wire 0.35 mm in diameter. The inductance of the antenna is $L_0 = 126 \mu\text{H}$, the quality factor $Q = 45$. By choosing the capacitance C_0 , the NMR sensor is tuned to the resonance frequency. By choosing the capacitance C_1 the output impedance of the sensor is matched to 50Ω . The quarter-wave line circuit is tuned by trimming the inductance L_1 .

The electrical circuit of the receiver amplifier RA is shown in the Fig. 3. The RA is a selective amplifier, it has 50Ω input and output impedance, 67 dB total gain, 20 kHz bandwidth (-3 dB) and 60 dB dynamic range. The RMS noise voltage at the output of the RA with the input loaded by 50Ω is $60 \mu\text{V}$. The RA consists of a two-stage preamplifier assembled on MRF571 transistors according to a common emitter circuit, and a two-stage end amplifier assembled on

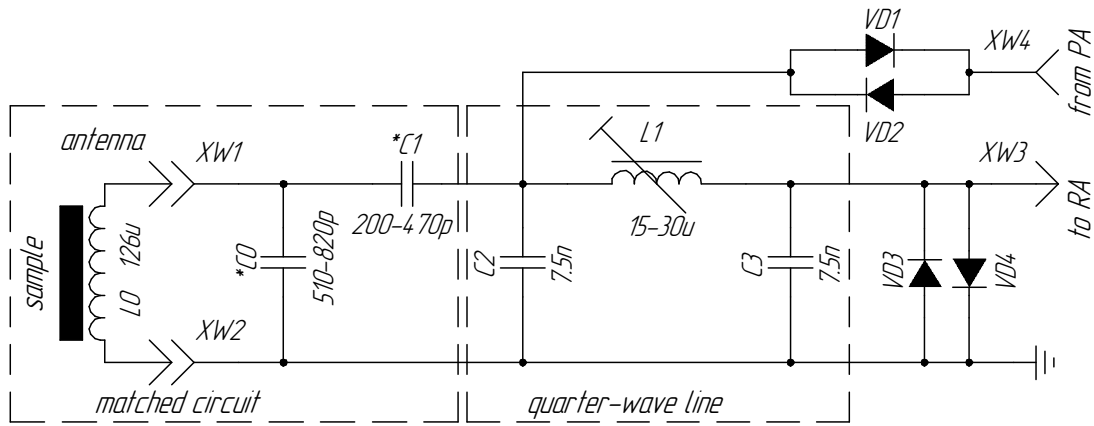


Figure 2. The electrical circuit of the NMR sensor.

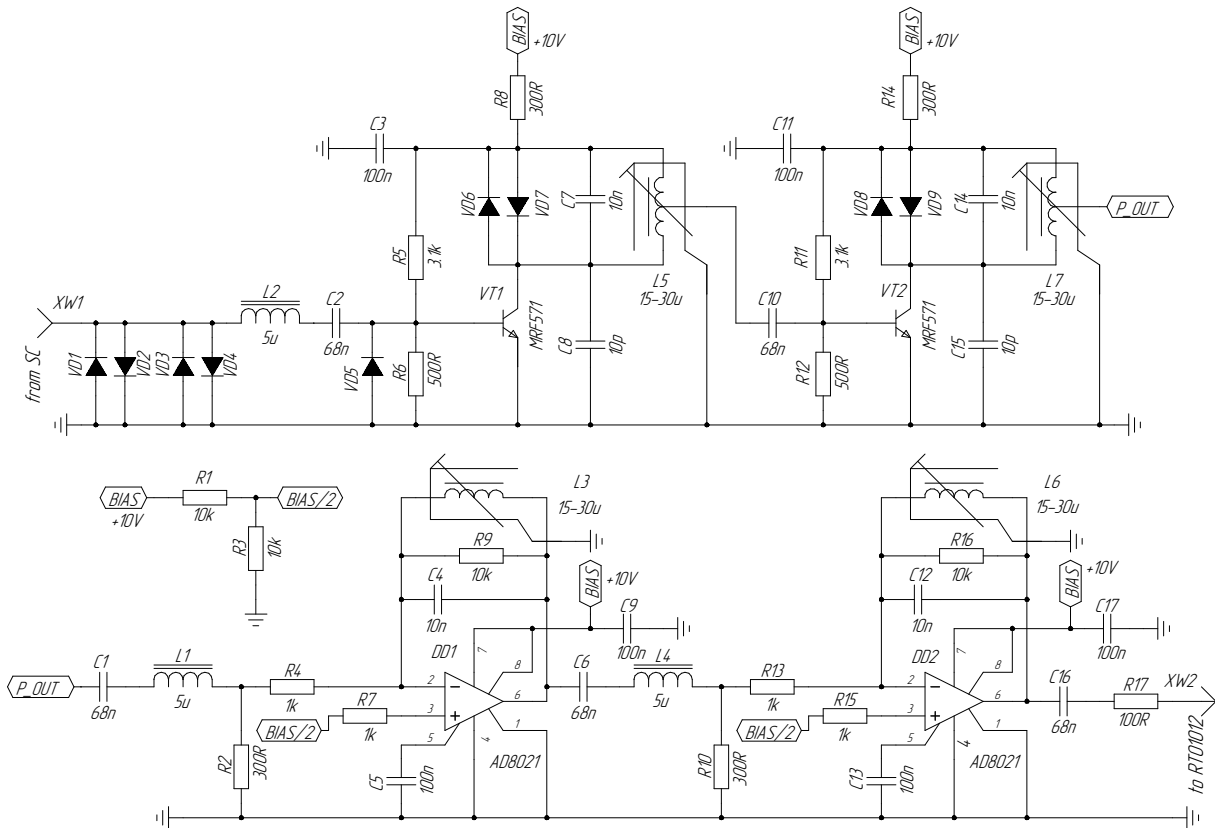


Figure 3. The electrical circuit of the receiver amplifier RA.

AD8021 ICs according to an inverting amplifier circuit. Selectivity is provided by a distributed filter consisting of LC circuits in each amplifying stage.

The electrical circuit of the power amplifier PA is shown at Fig. 4. The output stage of the amplifier was built on IRFPS3810 MOSFETs using a push-pull scheme. IR2113 IC is applied to drive IRFPS3810. The power supply voltage of the amplifier is up to 35 V. In the output stage 3:1 transformer T_1 made on the ferrite ring M1500HM 35 x 20 x 10 is applied. The output impedance of the PA is 50 Ω , the maximum pulse power is 100 W at nominal load.

The NMR signal was detected by spin echo spectrum using an RTO1012 oscilloscope with an integrated Fourier transform function. The control and synchronization of all devices was carried out by the pulse sequence programmer PP, designed on the SPARTAN6 FPGA IC. The programmer generates radio-frequency $\pi/2$ - and π -pulses, a trigger pulse for RTO1012 oscilloscope, and a gating pulse for EPR line saturation. The programmer is controlled from a conventional computer via the TCP/IP interface and homemade software.

The electronic transition saturation system consists of an R&S SML01 generator used as a reference high frequency generator, a TOMCO BT00500 power amplifier and a MR resonator. The H_{1MW} pulse is formed by applying a logic level pulse from PP to the gating input of the TOMCO BT00500 amplifier. The MR resonator (Fig. 5) was calculated and assembled according to the detailed description given by Diodato [14]. The MR is a double loop-gap resonator with

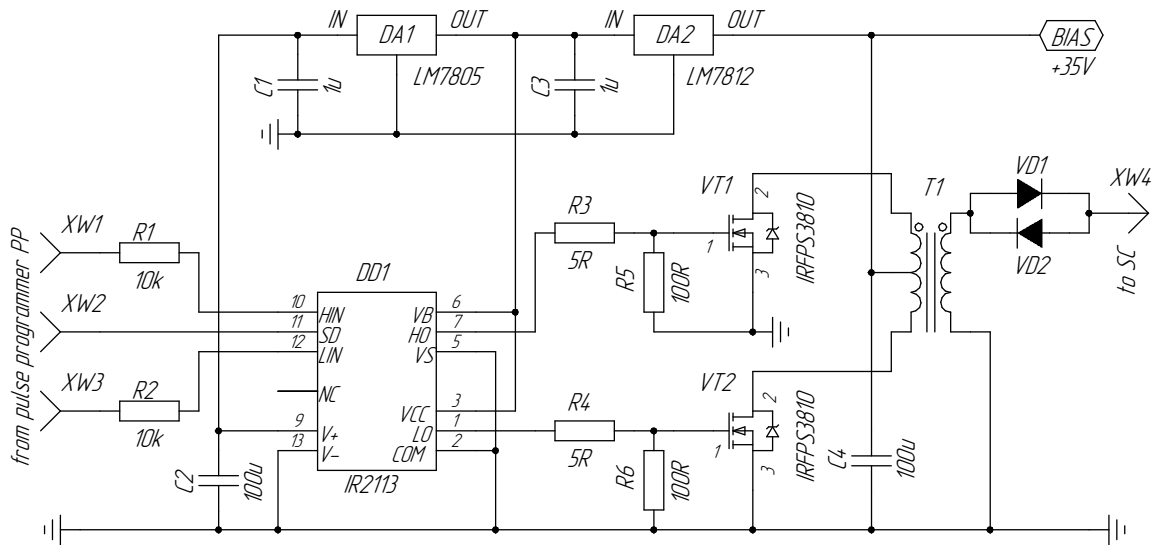


Figure 4. The electrical circuit of the power amplifier PA.

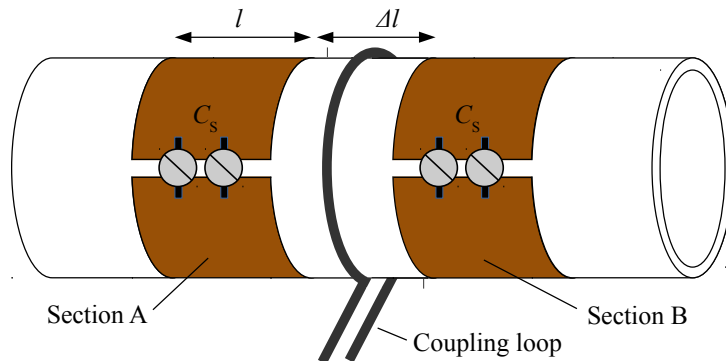


Figure 5. The scheme of the resonator MR by Diodato [14].

10 mm internal diameter and 40 mm section height. The resonator was tuned by trimming the capacitance C_S . The output impedance of the resonator was matched to 50Ω by a broadband coupling loop. Precise matching could be easily achieved by varying the distance Δl from both sections to the coupling loop (Δl was varied between 5-10 mm). The quality factor of the resonator is 557 at 280 MHz. The alternating magnetic field H_{1MW} is directed along the Oz axis and equals 2.1 Oe at $P_{MW} = 16$ W supplied to the resonator. According to Poindexter [10] that is sufficient to observe a significant DNP effect on oil protons.

3. Results

The designed setup was tested on an ethylene glycol Cr^{5+} complex sample. The parameters of this paramagnetic center in organic solvents are rather well studied [7, 15] with the estimated $\varepsilon = -50$ and the corresponding coupling factor $\zeta = 0.077$. Concentration of the prepared ethylene glycol Cr^{5+} complex was 0.01 mol/L, the volume was 8 mL. EPR spectrum of the sample is due to the presence of chromium ^{52}Cr isotope ($I = 0$), giving a narrow (4 Oe) intense EPR line with a g -factor equal to 1.981. Odd ^{53}Cr isotope ($I = 3/2$) with natural content of 9.5%, gives 4 lines of low intensity in EPR spectrum caused by the hyperfine interaction [16]. Intensive $^{52}\text{Cr}^{5+}$ line was saturated to provide DNP, in the field of 99.4 Oe this line has Larmor frequency $f_{MW} = 275.39$ MHz.

The tests were performed using the pulse sequence “ $T_{MW} - \pi/2_{NMR} - \tau - \pi_{NMR}$ ”. It is started with the pulse H_{1MW} with duration T_{MW} and power P_{MW} for EPR line saturation and then followed by NMR detection sequence. The duration of $\pi/2$ - and π -pulses were 10 and 20 μs , respectively, the time $\tau = 600 \mu\text{s}$

The results for the ethylene glycol Cr^{5+} complex are presented in the Fig. 6. Figure 6 shows the absolute values of the experimentally measured ODNP enhancements ε as functions of P_{MW} and T_{MW} . Changes in the NMR signal begin to appear already at $T_{MW} = 10$ ms and $P_{MW} = 0.1$ W. With an increase of P_{MW} , the NMR signal first decreases to zero, then changes its sign and further grows as described in literature for the predominant dipole electron-nuclear coupling [3]. The maximum enhancement $\varepsilon = -50$ was achieved that agrees well with Fedotov [15]. For $T_{MW} > 150$ ms and $P_{MW} > 2$ W, the ODNP enhancement is found to be

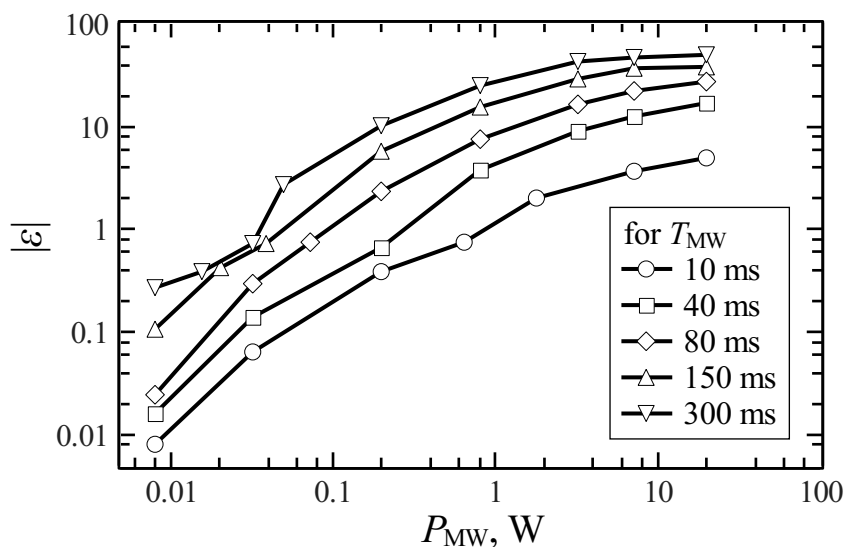


Figure 6. ^1H ODNP enhancement for the ethylene glycol Cr^{5+} complex as a function of the EPR pumping P_{MW} power and duration of the EPR line saturation pulse.

independent of the applied power. It can be assumed, that in this case the EPR line is completely saturated, and therefore the saturation factor $s \approx 1$. The leakage factor was estimated as $f = 0.7$ by the measurements of nuclear spin-lattice relaxation time T_1^{IS} of ethylene glycol Cr^{5+} complex protons and nuclear spin-lattice relaxation time T_1^I of pure ethylene glycol protons ($f = 1 - T_1^{IS}/T_1^I$ [7]). Using these parameters, we have estimated the coupling factor from Eq. 1 as $\zeta = 0.11$, which also agrees well with Fedotov [15].

4. Summary

NMR / DNP spectrometer has been designed and produced for studying DNP on samples up to 10 mm in diameter with the continuous and pulsed saturation of electronic transitions with a maximum value of the alternating magnetic field of about 2 Oe in a permanent magnetic field of about 100 Oe. Test experiments were performed to measure the effect of ODNP on protons of the ethylene glycol chromium complex. The designed setup can be exploited for DNP investigation of native hydrocarbons, their components and solutions as well as for the estimation of optimal parameters necessary for the effective NMR enhancement in NMR logging applications.

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