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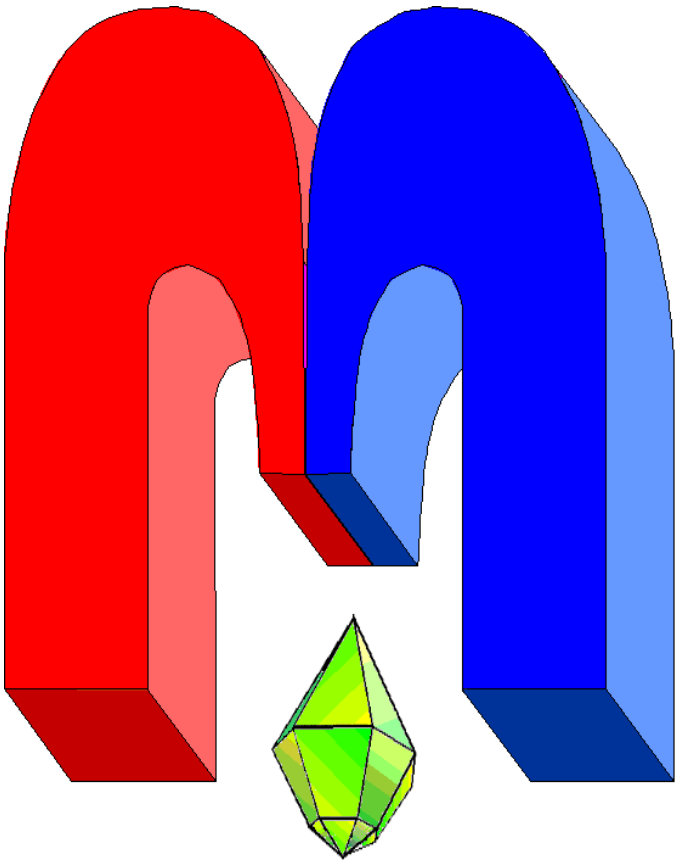

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

The home-built pulse NMR spectrometer with CPMG sequence for ^{3}He research at low temperatures†

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The home-built pulse NMR spectrometer for ^{3}He investigations is described in this article. It operates in the 1.5–4.2 K temperature range, 0–850 mT magnetic field range, and 3–150 MHz frequency range with a dead time as short as 8 μs at 8 MHz that makes possible multinuclear NMR measurements. The spectrometer includes: saturation-recovery and inversion-recovery pulse sequences for spin-lattice relaxation time measurements by FID and Hahn echo amplitude measuring, CPMG pulse sequence for spin-spin relaxation time measurements, pulse gradient coils for diffusion measurements and a possibility to modify surface of porous samples by preadsorption of certain amount of nitrogen. The block diagrams of the spectrometer, the transmit-receive path and the amplifier are also presented.

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Keywords: pulsed NMR, CPMG, diffusion, ^{3}He, low temperatures.

1. Introduction

The pulsed nuclear magnetic resonance (NMR) technique allows to measure nuclei magnetization spin-lattice and spin-spin relaxation times T_1 and T_2 respectively. These parameters are often used for the characterization of porous media. The ^{3}He is a helium isotope ($I = 1/2$) suitable for NMR porous media characterization due to the large magnetic moment, the absence of a nuclear quadrupole moment, sufficiently long intrinsic T_1 relaxation times and because of small sizes of molecules (0.32 Å) [1–6].

It is also known that confined geometry (pore sizes <10 nm) influences on nuclear magnetization relaxation process and makes it different compared to bulk relaxation [7]. The pore sizes of nanoporous media may be varied by preadsorption of certain amount of inactive or noble gas on its surface. The spectrometer gas system includes possibility to add nitrogen gas to the porous sample. That amount of nitrogen represents a different numbers of solid monolayers on the sample surface at 1.5-4.2 K temperature range [8]. This allows us to study confined geometry more correctly.

Nowadays it is possible to average NMR signal to increase signal-to-noise ratio by using analog-to-digital converter (ADC) and digital accumulation, but that requires a high sampling rate. The spectrometer described here contains radiofrequency pulse generator with the possibility of changing the pulse frequency, amplitude and phase, and ADC oscilloscope with 500 MS/s (2 ns for point) maximal sampling rate. The spectrometer software is programming by LabVIEW code which makes it flexible to any additional improvements like new pulse sequences, different data processing for different goals, and etc. All spectrometer units are matched to 50 Ω.

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2. The spectrometer block-diagram

2.1. The transmit-receive path

A schematic diagram of the transmit-receive path is shown on Fig. 1a. The outputs of the generator and the inputs of the oscilloscope are displayed on the front panel. An image of the front panel with signed pins is shown in Fig. 1b.

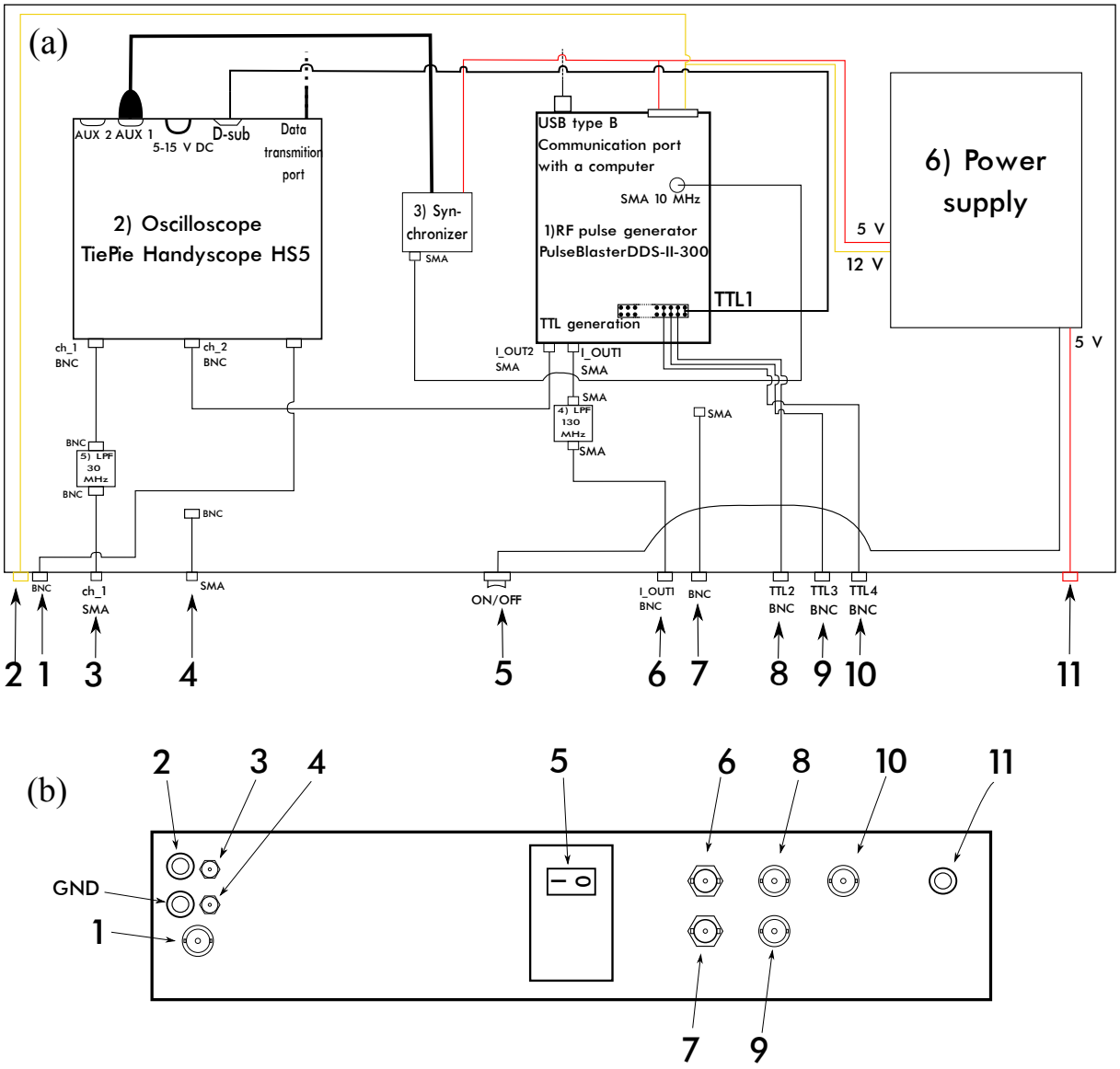

Figure 1. (a) Block diagram of the transmit-receive path. (b) An image of the front panel of the transmit-receive path. The numbers indicate the following parts:
1 – The generator output built into the TiePie Handyscope HS5 oscilloscope (BNC);
2 – The 12 V power output from the power supply;
3 – The input of the first channel of the oscilloscope (ch1) (SMA);
4 – The input, which can be connected to the second channel of the oscilloscope;
5 – The toggle switch power supply;
6 – The first output of the generator (BNC);
7 – The output that can be connected to the second channel of the generator;
8-10 – The TTL outputs from PulseBlasterDDS DDS II 300;
11 – The 5 V power output from power supply.

The transmit-receive path includes:

1) "PulseBlasterDDS DDS-II-300" radio frequency (RF) pulse generator with 2 RF and 4 digital channels (TTL). The generator is designed to send RF pulses with adjustable phase and amplitude at a frequency of 5 kHz to 150 MHz.
2) The TiePie Handyscope HS5-540 XM oscilloscope that contains 2 input channels with sensitivity from 200 mV to 80 V and 500 MS/s maximum sampling rate. The first channel takes signals up to 250 MHz, the second one operates up to 100 MHz. This oscilloscope includes its own RF generator with one output channel with maximum signal amplitude of 12 V and a frequency in the range from 1 μHz to 40 MHz.
3) The generator and oscilloscope synchronization unit.
4) The 130 MHz low-pass filter (LPF) at the generator output.
5) The 30 MHz low pass filter at the input of the oscilloscope.
6) The power supply.

The first generator output (6) is used to transmit (via a pulsed amplifier) a RF pulse of desired frequency, phase and amplitude to the circuit with the sample. The first input of the oscilloscope (3) receives a sample response NMR signal that passes through the "MITEQ AM 1581" preamplifier. The second output of the generator provides a reference signal to the second input of the oscilloscope. The TTL1 channel delivers a sync pulse to the oscilloscope. The TTL2 channel is used to instantly turn on the amplifier. The TTL3 channel is used for switching on and off of gradient coils creating a gradient field for diffusion measurements.

2.2. The pulsed amplifier

For NMR measurements a high power of radio-frequency pulses is required. Therefore after the pulse generator generates pulses they are amplified by a pulsed amplifier, which is turned on only for the duration of the radio frequency pulse. Block diagram of the amplifier is shown on Fig. 2.

The amplifier includes three voltage transformers, three protection stages (current protection, power control and approval control), a high-pass filter, two amplifiers stages (10 and 600 W) and a FOD8342 opto-isolator. The Opto-isolator is used for drive the pulse mode of the amplifier. 50 V output is used to supply the power amplifier stage of the pulsed amplifier, 15 V output is used to supply the preamplifier stage of the pulsed amplifier and 12 V output is used for transistor biasing. Block diagrams of the amplifier stages with blanking part are shown on Figs. 3 and 4.

The preamplifier stage amplify a RF pulse before sending it to the input of the power amplifier stage. The TTL pulse from the pulse generator activates the FOD8342 opto-isolator (250 ns input signal rise and fall times) which opens up 12 V BIAS voltage on transistors of the power amplifier stage. 12 V BIAS goes through voltage divider and RC circuit that reactively matches with the transistors. Reactive matching provides biasing without significant time delays ($<$15 μs).

2.3. The gas handling system, glass cryostat, magnet and gradient coils

For low temperature ^{3}He NMR experiments electromagnet with magnetic field up to 850 mT, glass cryostats and ^{3}He/^{4}He/N_2 gas handling system are used. The magnetic field value is set by the power supply current. The NMR experimental cell with the sample is located in a bath of liquid helium. Due to the pumping of helium vapors, it is possible to make experiments in temperature range of 1.5-4.2 K. Block diagram of this part is shown on Fig. 5.

The experimental cell is connected to the vacuum tight gas handling system. It allows to inject ^{3}He into a porous sample for NMR experiments, cover the sample surface with various amount of solid nitrogen layers at low temperatures [8], add ^{4}He to eliminate the ^{3}He adsorption layer during the experiment. Before NMR experiment the sample is flushed by ^{4}He several times at 95°C temperature with subsequent pumping out. The NMR coil and the sample is placed in the bath of liquid helium. The capacitive part of the tank circuit is located at room temperature in order to be able to change the NMR frequency. If it is necessary to study small NMR signals, it is possible to use a cold circuit at a certain frequency [9]. The NMR signal from the sample passes to the oscilloscope trough the "MITEQ AM 1581" preamplifier with the dead time ca. of 3 μs. Following calibrated resistors are used for temperature measurements: Pt-1000 Ω for 4.2-300 K temperature range and 62 Ω Allen-Bradley for 1.5-4.2 K temperature range. Magnetic field is driven by "BK precision XLN8018" power supply with the 18.5 A maximum current value and varies in range from 0 up to 850 mT. Besides, the pair of gradient coils produces a constant 90% homogeneity gradient of magnetic field G_x, G_y and G_z up to 3.3 mT/cm. The magnetic field gradient provides possibility of diffusion measurements [10].

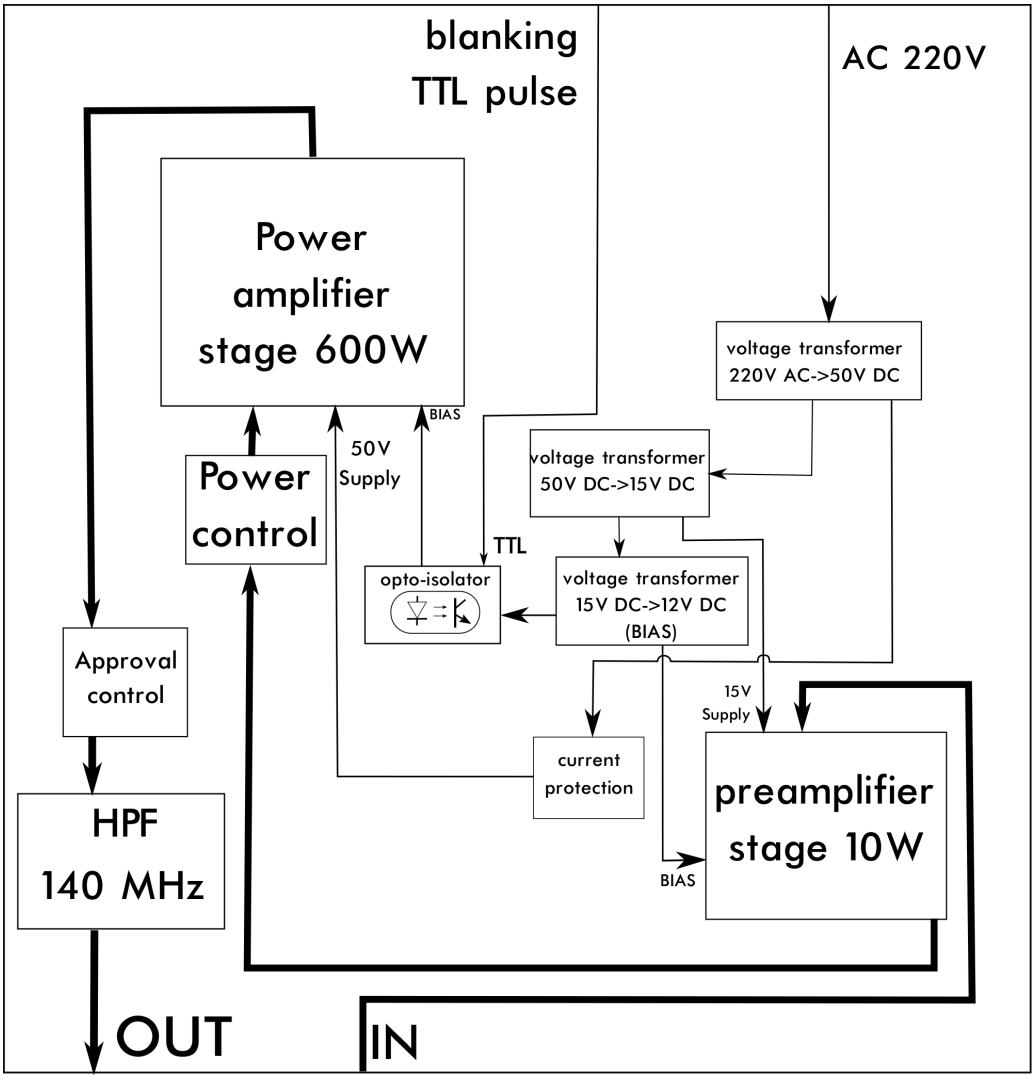

Figure 2. Block-diagram of pulsed amplifier used in the spectrometer.

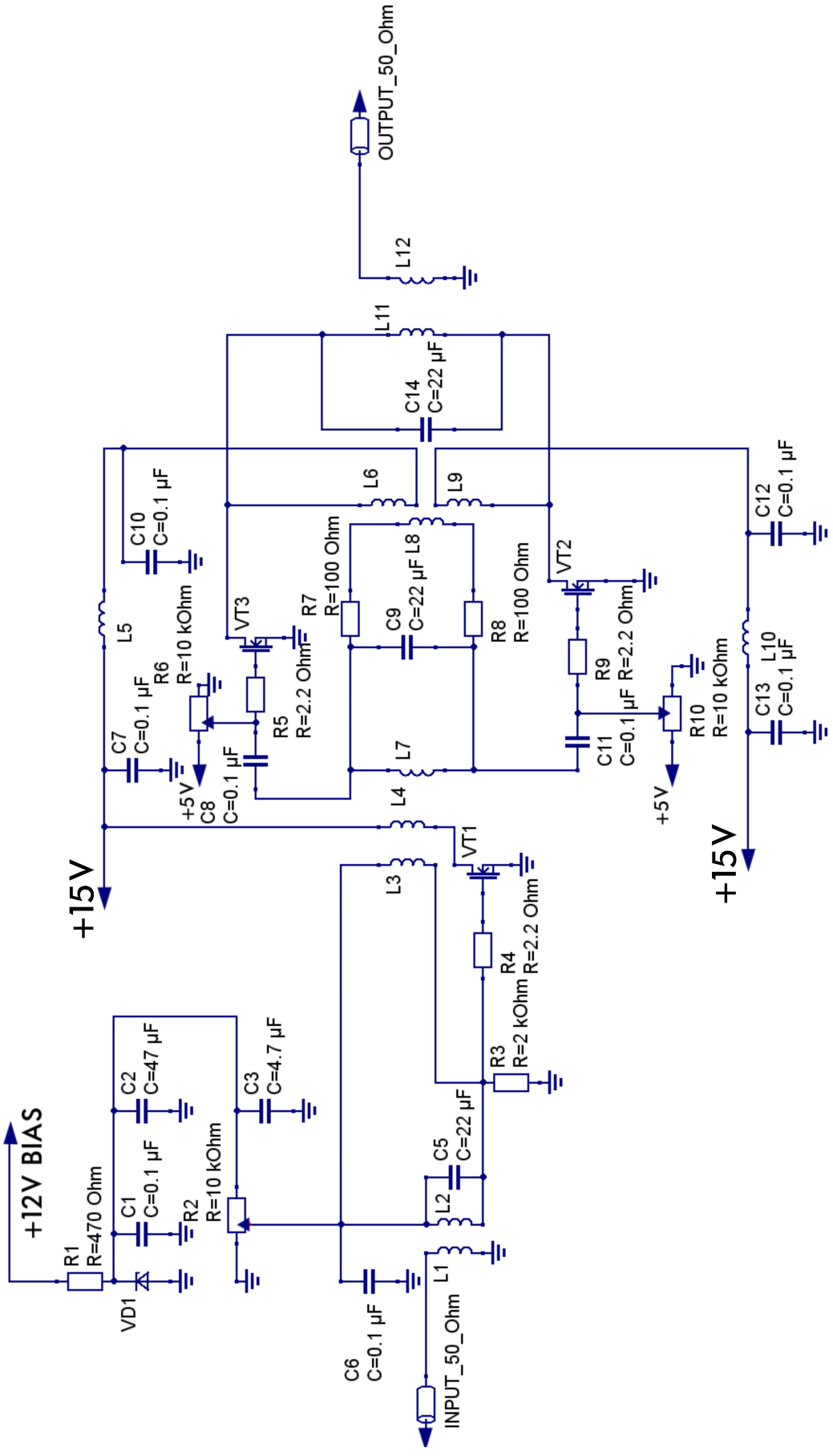

Figure 3. Block diagram of the 10 W preamplifier stage.

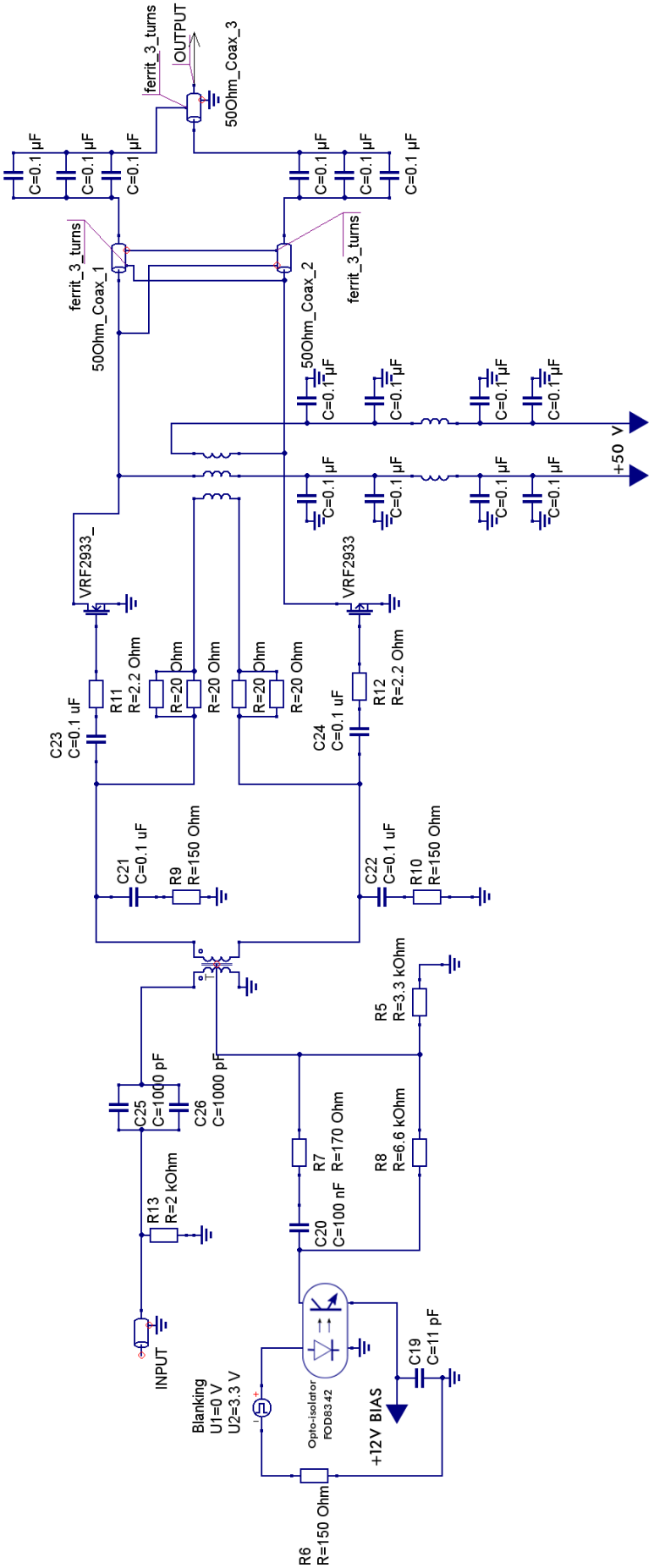

Figure 4. Block diagram of the 600 W RF pulse power amplifier stage with blanking control.

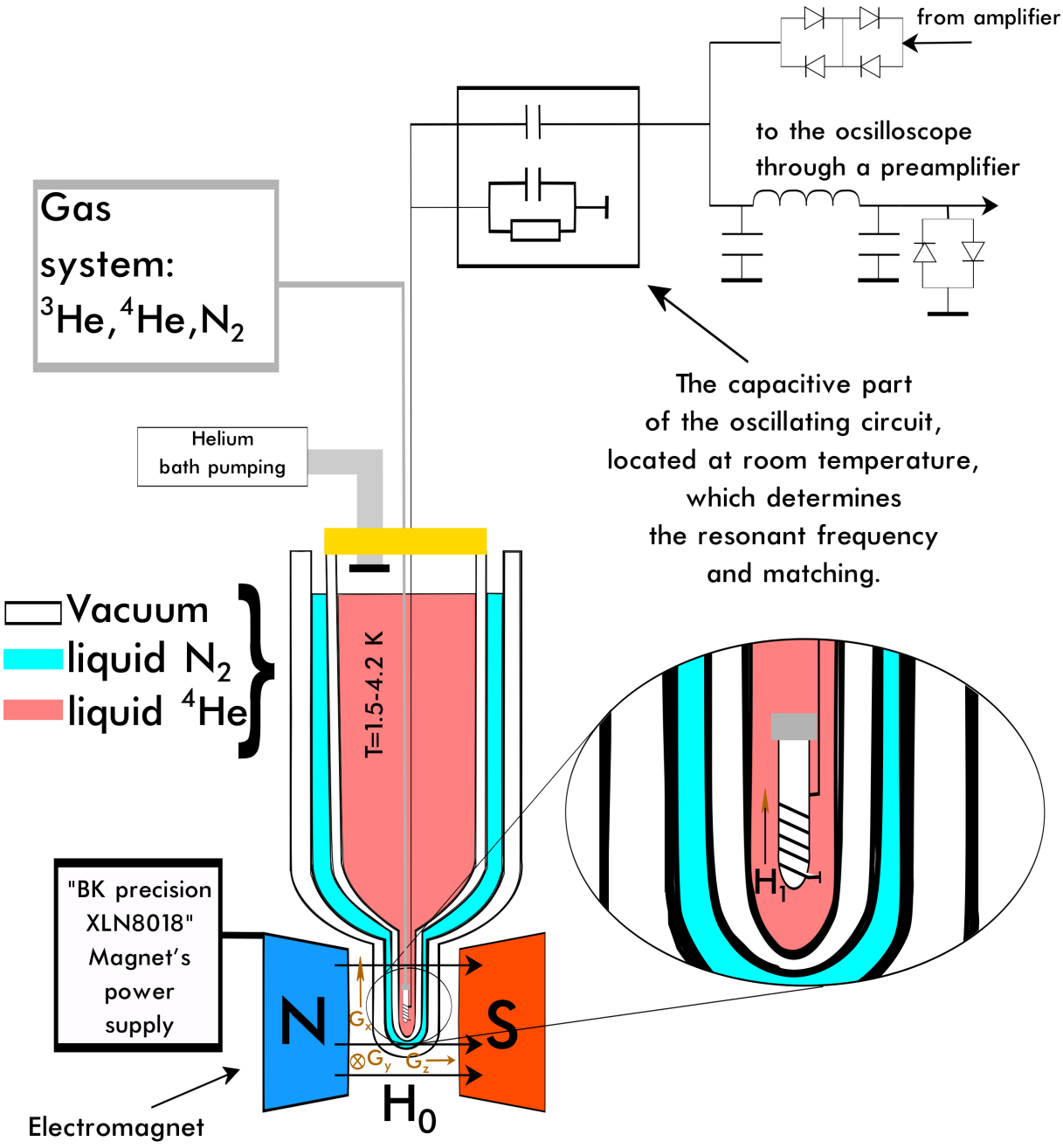

Figure 5. Block-scheme of glass cryostat, magnet and gas system.

3. The spectrometer software and pulse sequences

The spectrometer software is implemented by LabVIEW programming code. The front panel of LabVIEW program includes three tabs for five types of NMR measurements (FID, Hahn Echo, T_1, T_2 Hahn echo, T_2 Carr-Purcell-Meiboom-Gill (CPMG)) and the digital low pass filter. There is an opportunity to vary sampling frequency. Screenshot of the written NMR software is shown on Fig. 6. The program performs a digital signal averaging and quadrature detection. More details about quadrature detection are described in the article that describes previous version of the spectrometer [9]. The NMR signal from sample (FID, Hahn echo) is shown at the left window, while signal amplitude value versus time (longitudinal magnetization recovery,

transverse magnetization decay) is deposited on the right window. The CPMG signal (one scan) from adsorbed ^{3}He above nitrogen monolayer in contact with TiO_2 nanopowder at 1.5 K and 18.9 MHz is given as an example (Fig. 7).

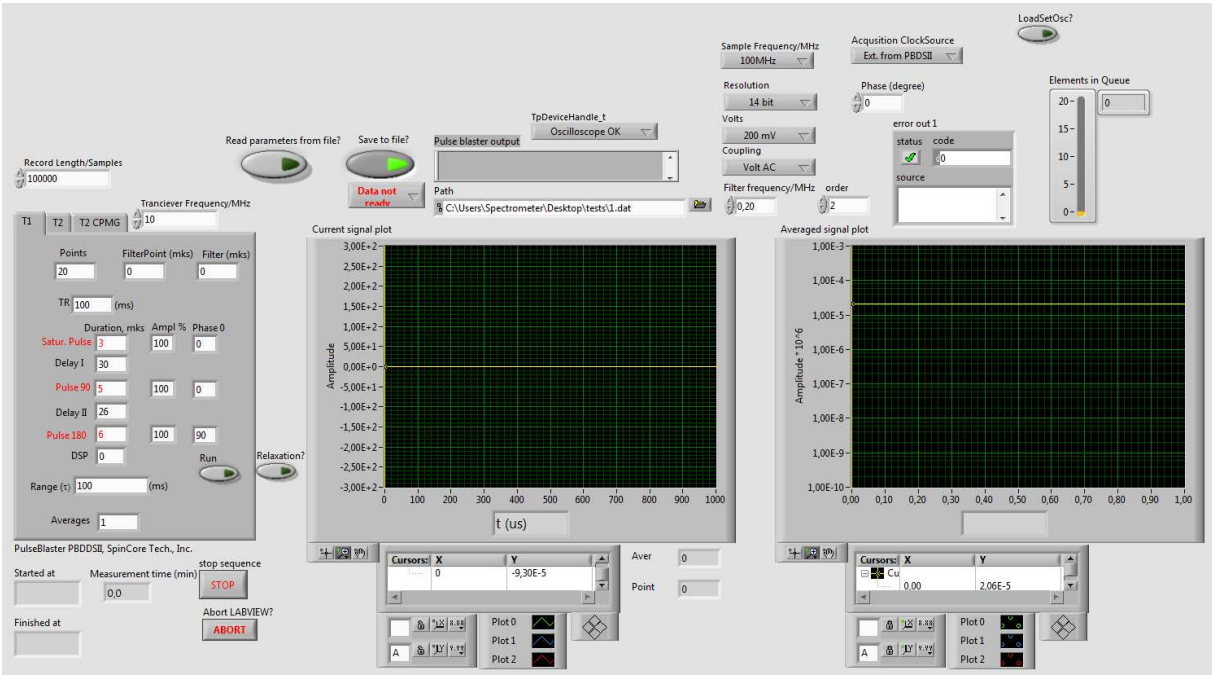

Figure 6. Screenshot of the written NMR software.

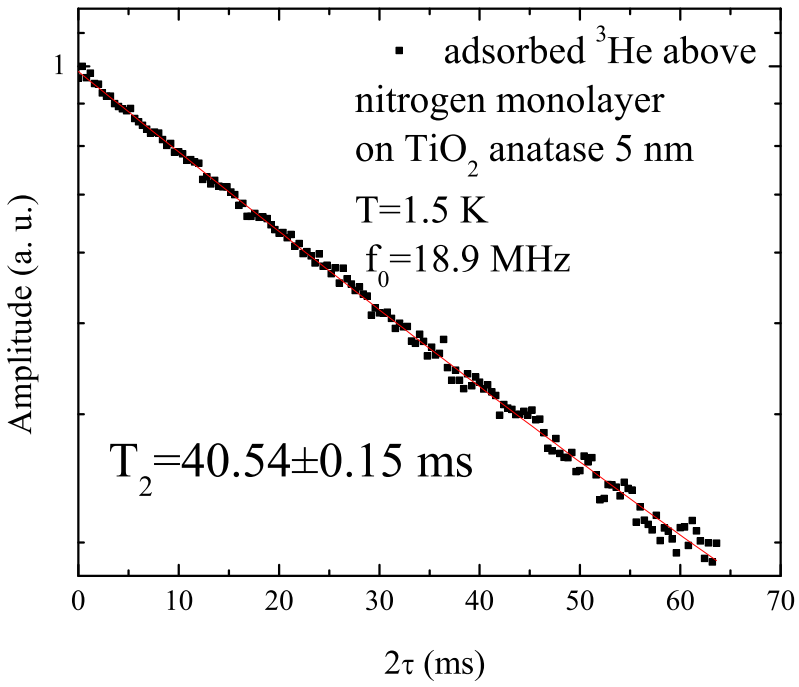

Figure 7. The example of the transverse magnetization decay of ^{3}He nuclei received by CPMG sequence application to adsorbed ^{3}He above nitrogen monolayer in contact with TiO_2 nanopowder at 1.5 K and 18.9 MHz.

4. Conclusion

The main features of the pulse NMR spectrometer described here are:

- The high sampling frequency (500MS/s) ADC and RF pulse generator with variable frequency, amplitude and phase of pulses are used.
- The digital quadrature detection allows to avoid synchronization problems.
- The possibility of adding nitrogen and helium-4 into the experimental cell allows to expand the range of possible experiments with confined geometry in nanoporous samples.
- The availability of gradient coils allows diffusion measurements.
- The analog and digital filtration and opportunity of averaging gives better signal to noise ratio.

Acknowledgments

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