Detection of Selected Chemical Substances by Means of Nuclear Quadrupole Resonance

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Abstract— Nuclear Quadrupole Resonance (NQR) is an advanced diagnostic method for the spectroscopy of solid state substances. NQR exploits the presence of the electrical quadrupole moment of the atomic nuclei of certain isotopes. A broad set of substances, both inorganic and organic, have their quadrupole resonance in the range of ones to tens of MHz. An important fact is that recognizable quadrupole resonance can be detected in the case of substances present in explosives, drugs, and medicaments. The utilization of NQR constitutes a promising perspective for non-contact, non-destructive diagnostics in chemical research, material science, and security applications. A compact experimental NQR spectrometer has been built at the DTEEE, Brno University of Technology. The spectrometer enables us to experimentally verify the impact of various functional blocks on the detection abilities. Selected chemical substances containing chlorine and nitrogen isotopes were analyzed with the spectrometer.

1. INTRODUCTION

The principles of NQR spectroscopy can be found in reference [1]. Although this technique seems to be very promising for the detection of explosives [2], it is presently too slow and not very suitable for field applications [3]. The detection of explosive materials via NQR is now used as a confirmatory method in airport scanners. This type of detection is mostly based on the presence of nitrogen isotope ^{14}N. In addition to this, NQR spectroscopy can also be used to detect a variety of other chemicals, such as those based on chlorine, bromine, or lithium. In this way, it is then possible to identify drugs, which often contain some of the detectable isotopes.

The experimental NQR spectrometer in our laboratory is designed to measure within the frequency range of up to 100 MHz. Its design, which is based on paper [4], utilizes a SpinCore radioprocessor and is equipped with a 250 W rf power amplifier. A photograph of the experimental NQR setup is shown in Figure 1.

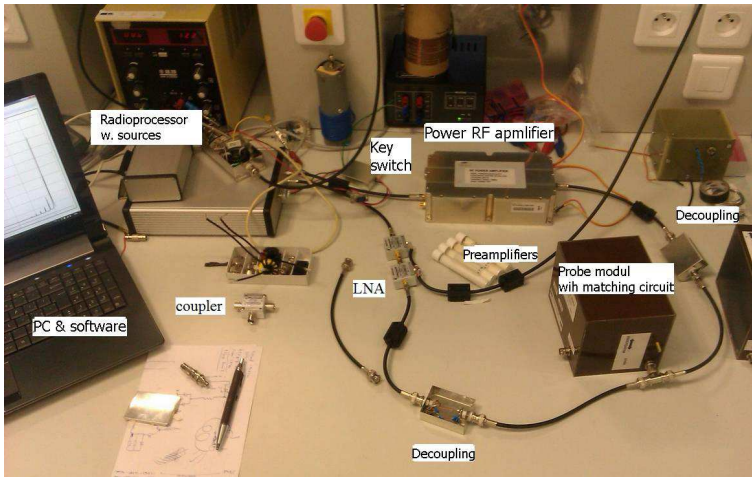

Figure 1: The NQR setup during the experiment.

We examined the possibility of detecting some of the compounds and explosive mixtures introduced in Table 1, and we also verified the minimum detectable amounts. These obviously depend on the specific design of the spectrometer, in particular on the volume of the measuring coil and the associated power of the rf amplifier. Other aspects significant in determining the minimum amounts include the sensitivity and low SNR of the amplifiers and acquisition circuitry.

Table 1: Resonant frequencies of some substances.

Substance	Resonant frequency
$KClO_3$	28.09 MHz
$NaClO_3$	29.93 MHz
$NaNO_2$	3.6 and 4.64 MHz
RDX	3.41 and 5.192 MHz
HMX	5 and 3.5 MHz
PETN	1 MHz

2. EXPERIMENT

A key part of the spectrometer is the rf preamplifier. We tested an AU-1647 low-noise amplifier by Miteq and a cascade of two MiniCircuits ZFL-1000LN amplifiers. The best obtained SNR value was 27 dB for the pair of ZFL-1000LN and 38 dB for the AU-1647; furthermore, the cascade comprising an AU-1647 + 2 × ZFL-1000LN was examined, with the resulting SNR of 22 dB. It is therefore evident that the increasing number of amplifiers also causes the SNR to decrease.

As an example, we will now describe the results obtained from the measurements of two substances: potassium chlorate ($KClO_3$) and sodium nitrite ($NaNO_2$). The acquired FID signals are presented in the graphs in Figures 2 and 3; here, the values on the y-axis are in units of output from the A/D converter, and the x-axis shows time in seconds. The blue and red curves represent the components I and Q of the quadrature detection. The applied parameters of the NQR experiment are given in the description of the image.

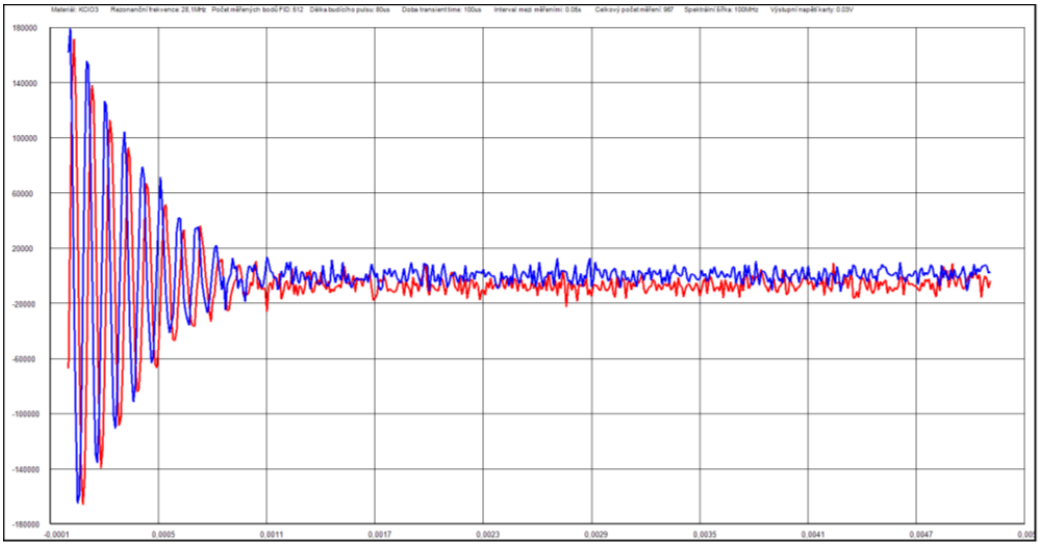

Figure 2: The FID of the $KClO_3$ sample at the frequency of 28.1 MHz (number of measured points: 512; excitation pulse length: 80 µs; dead time: 100 µs; interval between the measurements 50 ms; spectral width: 100 kHz; output voltage level: 30 mV). The response time is about 1 ms.

After the time accumulation, the signal was transformed into the frequency domain; the received spectrum can be seen in Figures 4 and 5. The x-axis is in kHz, while the y-axis is in relative units of the A/D converter. The spectrum shown here was computed from the signal accumulated from 1000 implementations.

As the resonant frequency of the LC probe slightly shifted after the insertion of the sample, it is appropriate to tune the resonant circuit only in the presence of the sample. During the measurement, the spectral response often exhibited narrowband artifacts; these unwanted components can be caused by phenomena such as nonlinearities in the circuit or interferences from nearby appliances. We also verified the impact of slight changes (within the scale of kHz) in the excitation signal frequency on the spectrum. Artifacts unrelated to the measured sample remained at the same position in the spectrum, while the response of the sample was shifted to the other frequency.

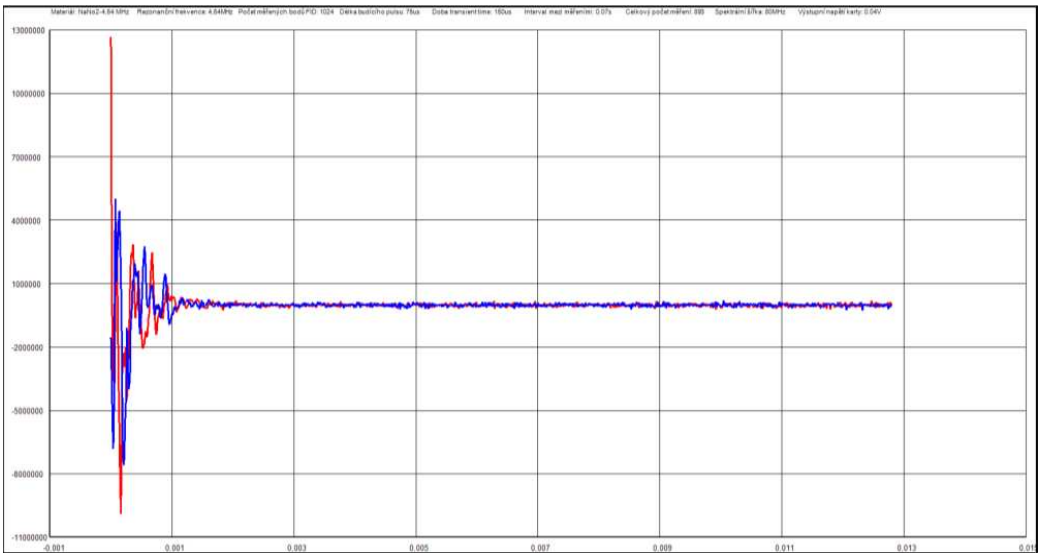

Figure 3: The FID of the $NaNO_2$ sample at the frequency of 4.64 MHz (number of measured points: 1024; excitation pulse length: 75 µs; dead time: 150 µs; interval between the measurements: 70 ms; spectral width: 80 kHz; output voltage level: 40 mV). The response time is about 1 ms.

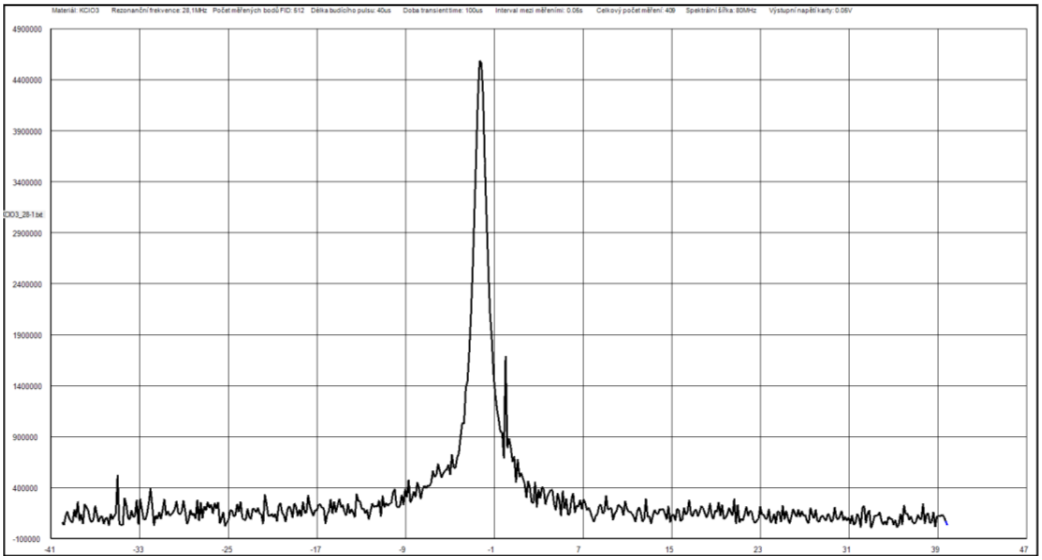

Figure 4: The spectral response of the $KClO_3$ sample at the excitation frequency of 28.1 MHz.

This approach can be used to identify and eliminate artifacts in the measured spectrum.

The spectral response depends on the excitation parameters, especially on the duration of the excitation pulse: for the strongest spectral response, it is necessary to find its optimal value. When measuring potassium chlorate, the intensity of the main spectral lines increased with the excitation pulse lengthening up to 80 microseconds and remained strong up to 200 microseconds. Further excitation pulse lengthening has an opposite effect, and thus the signal fades. Equally important to proper detection is the excitation level: at an excessively high level, the sample is overexcited, and weak or even no NQR response is obtained. A prerequisite for the FID acquisition is the correctly set dead time, which must be optimally selected to recover the preamplifier transients after the excitation pulse; simultaneously, the time must not be too long to preclude FID decay.

The averaging methods require us to measure n implementations of the signal. To ensure high sensibility, this value should be large enough to facilitate the visibility of even small signals; conversely, a too large n causes measurement time extension and amplifies the artifacts as well as the correlated noise, which leads to a relative decrease in the signal intensity (despite the fact that its absolute value increases). The usual number of implementations was therefore around 1000.

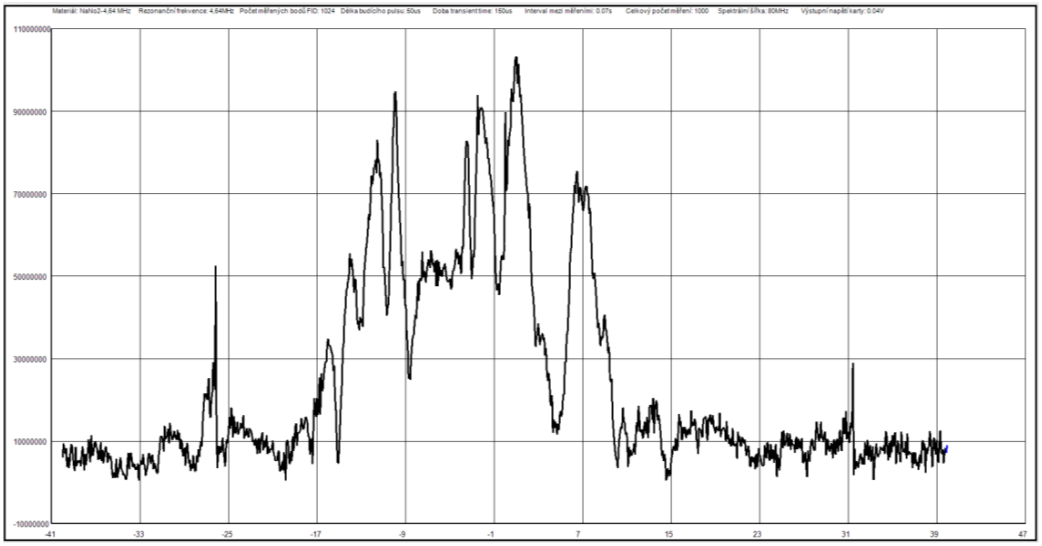

Figure 5: The spectral response of the $NaNO_2$ sample at the excitation frequency of 4.64 MHz.

In accordance with the theoretical knowledge, we observed the influence of the ambient temperature and atmospheric pressure on the experiment. In some cases, we failed to find the NQR response when the laboratory was too warm or when the atmospheric pressure dropped before a storm.

3. DETECTABLE AMOUNT OF SAMPLES

The basic parameters for the NQR signal strength are the probe coil volume and duty cycle, i.e., the ratio of the volume of the measured substance to the working volume of the coil. A major problem lies in the electromagnetic field distribution in such a coil; thus, the signal depends on the location of the sample in the coil. In this paper, we present the results obtained from several measurements with varying amounts of potassium chlorate ($KClO_3$) excited at the frequency of 28.09 MHz. The experimental arrangement of the test is shown in Figure 6. In a coil having the volume of about 30 cm^3 and with a 17 cm^3 test tube, the minimal detectable amount of $KClO_3$ was approximately 7 g. For substances with a weaker NQR signal, the measurement in the given configuration does not make sense. It turned out that any prior mechanical movement affecting the powder sample exerted strong influence on the NQR signal; it is therefore suitable to let each sample recrystallize for several hours before measurement.

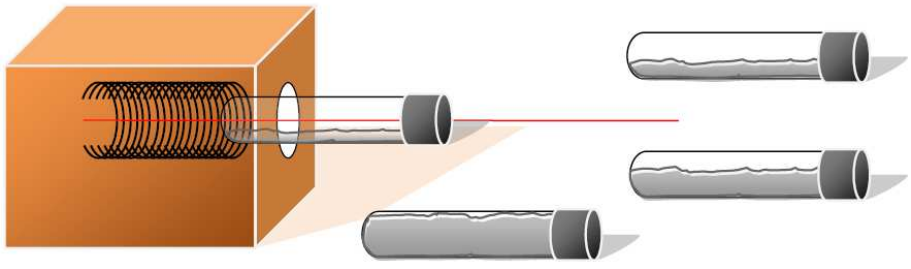

Figure 6: The experiment with the minimum detectable amount of $KClO_3$. The red abscissa indicates the center of the coil with the maximum electromagnetic field; the tube filled with over a half of the volume thus exhibits a substantially higher signal value.

ACKNOWLEDGMENT

The presented activities were supported by the project No. FEKT-S-14-2545/2014, Brno University of Technology internal science fund. Further, the research utilized financial assistance from the project No. CZ.1.07.2.3.00.20.0175 within the Education for Competitiveness Operative Programme.

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