

Preprint

An electronically tuned wideband probehead for NQR spectroscopy in the VHF range

Hermann Scharfetter

Institute of Medical Engineering, Graz University of Technology, Stremayrgasse 16, 8010
Graz

Published article: Hermann Scharfetter, *An electronically tuned wideband probehead for NQR spectroscopy in the VHF range*, Journal of Magnetic Resonance, Volume 271, October 2016, Pages 90-98, ISSN 10907807, <http://dx.doi.org/10.1016/j.jmr.2016.08.008>.

Abstract

Nuclear quadrupole resonance spectroscopy is an analytical method which allows to characterize materials which contain quadrupolar nuclei, i. e. nuclei with $\text{spin} \geq 1$. The measurement technology is similar to that of NMR except that no static magnetic field is necessary. In contrast to NMR, however, it is frequently necessary to scan spectra with a very large bandwidth with a span of several tens of % of the central frequency so as to localize unknown peaks. Standard NMR probeheads which are typically constructed as resonators must be tuned and matched to comparatively narrow bands and must thus be re-tuned and re-matched very frequently when scanning over a whole NQR spectrum. At low frequencies up to few MHz dedicated circuits without the need for tuning and matching have been developed, but many quadrupole nuclei have transitions in the VHF range between several tens of MHz up to several hundreds of MHz. Currently available commercial NQR probeheads employ stepper motors for setting mechanically tuneable capacitors in standard NMR resonators. These yield high quality factors (Q) and thus high SNR but are relatively large and clumsy and do not allow for fast frequency sweeps. This article presents a new concept for a NQR probehead which combines a previously published no-tune no-match wideband concept for the transmit (TX) pulse with an electronically tuneable receive (RX) part employing varactor diodes. The prototype coil provides a TX frequency range of 57 MHz with a center frequency of 97.5 MHz with a return loss of ≤ -15 dB. During RX the resonator is tuned and matched automatically to the right frequency via control voltages which are read out from a previously generated lookup table, thus providing high SNR. The control voltages which bias the varactors settle very fast and allow for hopping to the next frequency point in the spectrum within less than 100 μs . Experiments with a test sample of ZnBr_2 proved the feasibility of the method.

Keywords: nuclear quadrupole resonance, wideband probehead, resonator, varactor diodes, tuning and matching

Highlights

- A new concept for fast tuneable wideband coils for NMR and NQR spectroscopy is presented
- combining a wideband TX and a resonant RX coil allows varactors to be used for tuning/matching
- fast scanning of wideband NQR spectra with a bandwidth of $\geq 50\%$ of the center frequency
- electronic tuning/matching by varactors does not require any mechanical parts

Introduction

Nuclear quadrupole resonance (NQR) spectroscopy (NQRS) is an analytical method which relies on the interaction of the electric quadrupole moment of nuclei with spin ≥ 1 with the electric field gradient (EFG) at the nuclear site [1]. The interaction leads to a characteristic energy level structure, analogous to the Zeeman splitting in NMR which is due to the interaction between the nuclear magnetic moment and a magnetic field. As the EFG strongly depends on the electronic environment of the quadrupole nucleus, the characteristic transition frequencies are very sensitive to changes of e.g. the chemical bonding structure and of the crystallographic configuration in crystals.

The transitions can be observed with the same techniques as in NMR, but, unlike NMR spectroscopy NQRS does not require a static magnetic field. So-called zero-field NQRS has the advantage that e.g. in powders the peaks are not broadened like in NMR. Moreover, due to the lack of the static magnet, the instrumentation is simpler and less expensive, even allowing for miniaturization. Recently a low-frequency NQRS system with a weight of no more than 3kg was reported for the characterization of compounds which contain ^{14}N [2]. The applications of NQRS range from solid state physics for the investigation of chemical bonds and crystal structures [3][4] over the real-time detection of specific toxic species (e.g. arsenic) in minerals [5], the detection of explosives [6] and drugs [7] to the characterization of pharmaceutical products [8]. The author of this article applies NQRS in the context of a research project (see acknowledgement) on new contrast mechanisms for magnetic resonance imaging (MRI) which rely on the interaction of quadrupolar nuclei with water protons. The respective measurements have to be carried out at frequencies in the VHF range.

In principle NQRS can be carried out with standard NMR methods. However, while NMR usually operates with comparatively small bandwidths, NQRS frequently requires the scanning of very wide frequency bands, sometimes over many tens of MHz. Thus the typical resonators in NMR probeheads are not automatically well-suited for NQRS because of their small bandwidth, even if they are built for two or more discrete resonance frequencies (multinuclear spectroscopy) [9]. Many published, so-called 'wideband' concepts refer to coils for solid state NMR adopted for NQRS, whereby many authors use the term 'wideband' already for bandwidths of no more than several 100 kHz. Bandwidths between 250 kHz und

2 MHz are sometimes called 'ultra-wideline' [10]. They are usually employed in the context of special approaches like the double-frequency sweep method [11] or related concepts e.g. in [12] [13] as well as for the so-called WURST-QCPMG sequence [10][14]. Large bandwidths are always achieved at the cost of the quality-factor (Q) and consequently also at the cost of the SNR, which is proportional to the square root of Q. [15]. Q-factors as low as 17 have been reported [14].

In this article 'wideband' shall refer to bandwidths of many tens of per cent of the central frequency, i. e. usually several tens of MHz. In order to scan over such wide NQRS bands classically a frequency hopping method is being used, which means a series of subsequent scans of neighboring frequency bands with several 100 kHz of width. When changing the band, the resonator must be re-tuned and re-matched to the new center frequency. Wideband probeheads used so far (some are available commercially) typically consist of NMR resonators which are automatically tuned and matched for each frequency point of the spectrum to be acquired. Though this approach provides the highest possible SNR it has one drawback: Automatic tuning and matching a transmit coil at power levels of 100W and more requires mechanically tuneable high-voltage capacitors controlled by stepper motors ([5],[16]). This makes the probeheads large and clumsy and prevents fast re-tuning and re-matching, whereby fast means in the range of 1ms or less. Spectrometers using motor-controlled probeheads thus typically do not scan one spectrum after another before averaging but instead perform the averaging for a single frequency point before hopping to the next frequency. The wideband spectrum is not available before concatenating all individual scans, i. e. before the end of the complete data acquisition. As the latency time between neighboring frequency points is determined by the mechanical re-tune/re-match process it can become the dominant factor for the overall acquisition time, especially in the case of only few averages.

If the re-tune/re-match process of a resonating probehead could be achieved by electronic components such as varactor diodes, the abovementioned shortcomings could be overcome easily. Whole spectra could then be obtained by mimicking the operation of a spectrum analyzer, i. e. by acquiring individual complete wideband spectra with single, fast frequency sweeps. Such a concept allows for the immediate visualization of the full wideband spectrum and the early recognition of spectral features while the averaging of whole spectra goes on continuously. There is no need for waiting until the end of the whole scanning process which may take considerable time. The latency time of a varactor-controlled circuit depends only on the ringdown-time of the RF filters of the biasing network. This time typically can be made as small as several tens of μs in the VHF range.

In this article we present a hybrid approach which allows for the use of varactors by splitting up the probehead into a no-tune/no-match wideband TX part and a resonant RX part which, in the absence of the high power RF pulse, can be tuned and matched electronically.

Methods

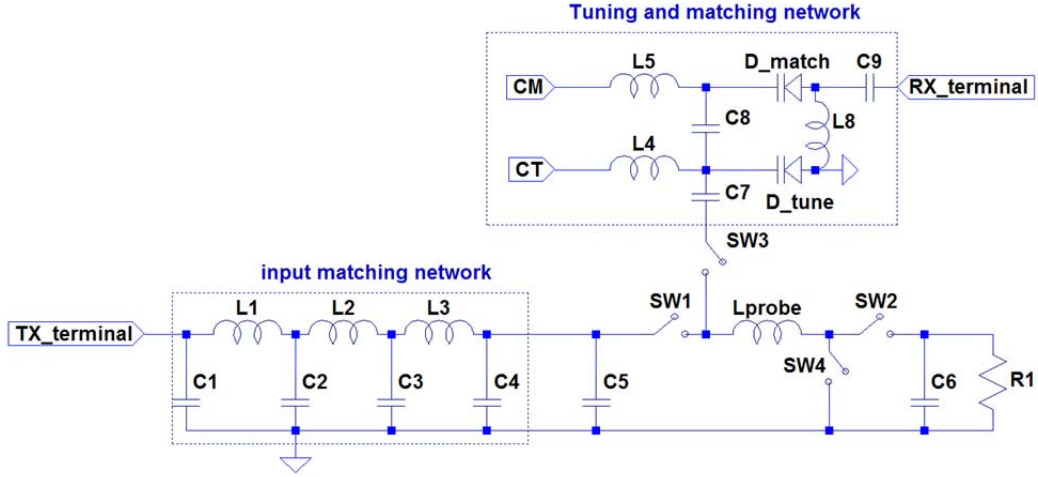
In a previous publication [17] we presented a no-tune no-match ultra-wideband coil which is based on the approximation of an exponential transmission line by lumped elements consisting of 5 L-C-lowpass sections. While providing a very large useful bandwidth (about 50% of the center frequency) this coil yields a very low Q-factor of around 2. Thus the coil is very beneficial during TX but lacks SNR during RX and is therefore only useful for large samples with low molecular weights which provide strong and narrow peaks. In the proposed new implementation the wideband concept of [17] is being used only during TX and switched to resonator mode during RX so as to achieve high Q ('Q-switching'). As no high power is applied during RX, varactor diodes can be employed for automatic tuning and matching in synchrony with the frequency sweep of the spectrometer.

The basic schematic of the hybrid coil is shown in fig. 1A. During TX (fig. 1B) the RF switches SW1 and SW2 are closed and the input matching network together with the final pi-section $L_{probe}/C5/C6$ constitutes a lumped exponential transmission line (LETL) with 4 sections (1 less than in [1]). The LETL transforms the termination resistance $R1$ (in our case 5Ω) to the 50Ω input impedance over a large bandwidth, thus providing optimal transfer of power from the port 'TX_terminal' to the terminator and, at the same time, maximum current in the probe coil L_{probe} . During TX the probe coil is isolated from the sensitive tuning/matching circuitry by the open switches SW3 and SW4. During RX (fig. 1C) L_{probe} is isolated from the power path by opening SW1 and SW2 and connected to the tuning/matching section by closing SW3 and SW4. Then the NMR signal is received in resonator mode and passed to the 50Ω port 'RX_terminal'. Tuning and matching is achieved with the varactors D_{tune} and D_{match} which are controlled via the reverse bias voltages provided at the ports CT and CM. In an actual implementation SW2 may be omitted because, during RX, the termination is short circuited by SW4 anyway.

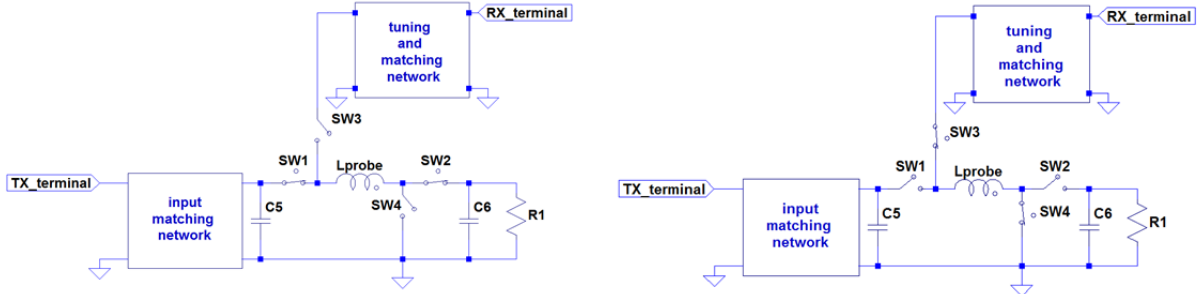
In practice the switches can be realized by RF relays or by PIN diodes. Relays have low losses and may thus be preferred, but their switching speed is limited and frequent switching shortens their lifetime. PIN diodes provide fast switching without mechanical degradation but have higher losses due to their relatively high on-resistance (typically 0.5Ω under normal biasing conditions). According to the general definition of the Q-factor we have

$$Q = \frac{2\pi f L_{probe}}{r} \quad (1)$$

whereby f is the operating frequency and R the total series resistance of the coil, including the switches.



A



B

C

Fig. 1. A: Schematic of a possible circuit for wideband TX and tuned/matched RX. B: simplified schematic showing the state during TX. The tuning/matching network is decoupled from the probe coil L_{probe} by switches SW3 and SW4. C: simplified schematic showing the state during RX. L_{probe} is decoupled from the transmit path by opening SW1 and SW2. Simultaneously the received signal is passed to the tuning/matching network via the closed switches SW3 and SW4.

The basic design rules for the LETL network [18] require the inductance of the probe to obey the condition

$$L_{probe} = \frac{Z_{0,final}}{2\pi f_c} \quad (2)$$

where $Z_{0,final}$ is the characteristic impedance of the final pi-section $L_{probe}/C_5/C_6$ and f_c is the central frequency of the operating band. There is a recursive law for calculating $Z_{0,final}$ which relates $Z_{0,final}$ with R_1 in a non-linear manner. However, with a number of pi-sections ≥ 4 and R_1 values between 10Ω and 200Ω we obtain approximately

$$Z_{0,final} \approx R_1 \rightarrow L_{probe} \approx \frac{R_1}{2\pi f_c} \quad (3)$$

Substituting (3) into (1) we thus obtain

$$Q \approx \frac{f}{f_c} \frac{R_1}{r} \quad (4)$$

It is thus possible to achieve higher Q when changing the transform ratio between the terminator R_1 and the 50Ω output impedance of the power amplifier (PA) while preserving full wideband operation. In principle the same coil can be applied for TX and RX, but then the Q at RX is determined by the TX termination. Higher Q-factors are possible when increasing R_1 , but there are practical limits which arise from (1) parasitic capacitances, especially at high frequencies, and (2) insulation problems because of high voltages which are built up across the probe coil and the termination resistance during RX. In turn it may also be desirable to choose R_1 lower than 50Ω in order to have lower voltages across L_{probe} and the PIN diodes SW3 and SW4 during TX at high RF powers. In this case, unfortunately, the Q can become considerably low.

This shortcoming can be circumvented. As eq. (4) only limits the Q of the TX coil, the use of a separate RX coil with high inductance allows for higher Q which then is only limited by the resistances of the coil and of the switches SW3/SW4. This concept is illustrated schematically in fig. 2, where a low inductance, low-Q TX coil (blue) is coupled with a high-inductance, high-Q RX coil (red).

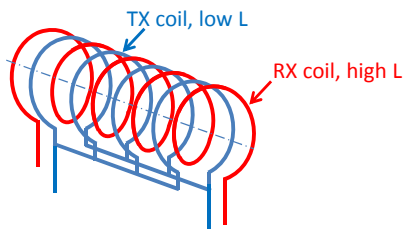


Fig. 2: Schematic of the double coil consisting of two interleaved coils. The TX coil (blue) consists of several parallel loops, thus providing very low inductance L . The RX coil is a spiral with several windings so as to yield high inductance. The magnetic field of both coils is concentrated in approximately the same volume which, at the same time, acts as the sample volume.

Both coils must be approximately equally sensitive to the sample volume which requires a tight magnetic coupling. Our prototype according to fig. 2 employs a TX coil with an inductance of 12 nH in order to re-use the same TX network as in [17]. The RX coil has an inductance of 180nH. SW4 was omitted and hence the series resistance of the secondary was reduced by $0.5\ \Omega$. Assuming a typical coil resistance of about $0.3 - 0.4\ \Omega$ the overall Q-factor can theoretically be made as high as 125 @100MHz with an expected improvement of the SNR by more than 7 compared to the coil in [17]. The resulting generic circuitry of the complete system is shown in fig. 3.

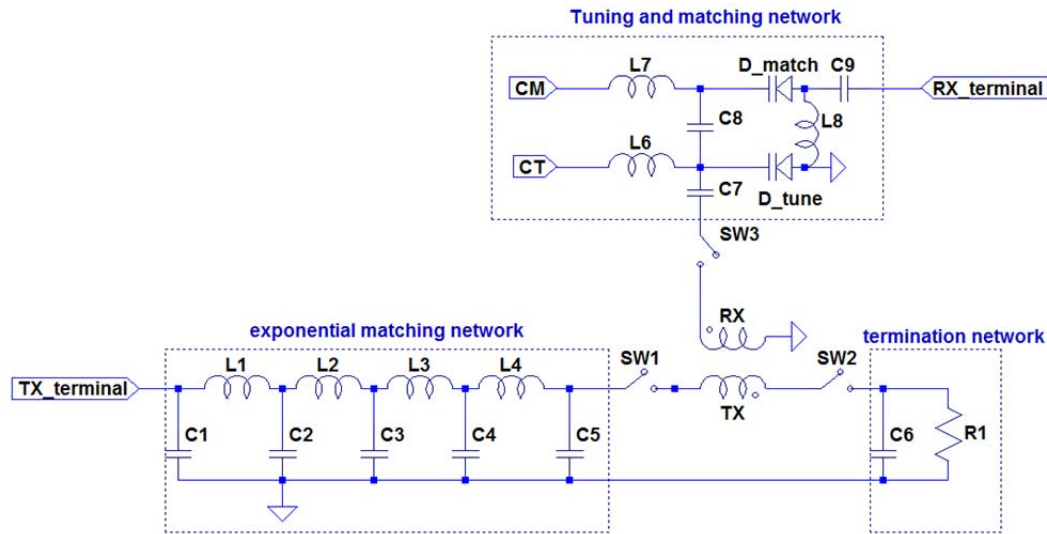


Fig. 3: Generic transformer-coupled probehead.

As the two coils constitute a tightly coupled transformer any load connected to the primary side (here the TX coil) is transformed to the secondary (here the RX coil) and vice versa. A proper functioning of the input matching network during TX requires the secondary to remain unloaded because otherwise the TX coil does not present the appropriate electrical parameters. Thus the tuning and matching network must be disconnected via SW3. During RX the primary load which is constituted by C5, C6, the input matching network and the termination resistance must be disconnected via SW1 and SW2. In principle SW2 can be omitted but in our implementation it was retained in order to keep parasitic capacitances acting on the RX coil as low as possible.

During TX the sensitive varactor diodes must be protected from high RF voltages which appear across the RX coil. In principle the open SW3 should provide this protection. However, the PIN diodes used by us have a parallel capacitance of 0.7 pF which provide a certain shunting path at high frequencies and thus at 100 MHz a complete isolation cannot be guaranteed. Therefore we added a limiter diode antiparallel to a Schottky diode for shunting residual RF currents to ground.

The detailed final implementation is illustrated in fig. 4 and 5. Fig. 4 shows the transmit path. SW1 and SW 2 are realized by two PIN diodes (MA4P7104F-1072T, MACOM) the biasing network of which consists of the L-R-series combinations L9/R2 and L10/R3 whereby the 39Ω resistors limit the bias current to a typical value of approximately 100 mA per PIN diode when applying +5V at the control port LV. The ground return of the biasing current is provided by L11. During RX the diodes are reverse biased with -5V so as to completely unload the TX coil. C10 and C11 serve for DC decoupling. The termination resistance was 5Ω according to [17]. Fig. 4 also contains transmission lines T1 and T2. These represent the connections of the central pi-section LTX/C5/C6 to the input matching network and to the terminator, respectively. T2 is necessary for establishing a certain distance between the

probe coil and the terminator in order to prevent heating of the sample due to RF power dissipation in R1. Moreover T1 and T2 render possible that the sample coil protrudes from the rest of the electronics by a certain distance which is useful if the probe should e.g. be placed inside of a cooling chamber or a magnet. The characteristic impedance Z_0 of T1 must match R1, thus two commercially available semi-rigid coaxial cables with $Z_0=10\Omega$ were paralleled. According to [18] the Z_0 of T2 must be the geometric mean of the characteristic impedances of the two connected pi-sections, i. e. section LTX/C5/C6 and the last one of the input matching network. In our case this is a value of approximately 12Ω which was approximated by two paralleled coaxial cables with $Z_0 = 25\Omega$, each.

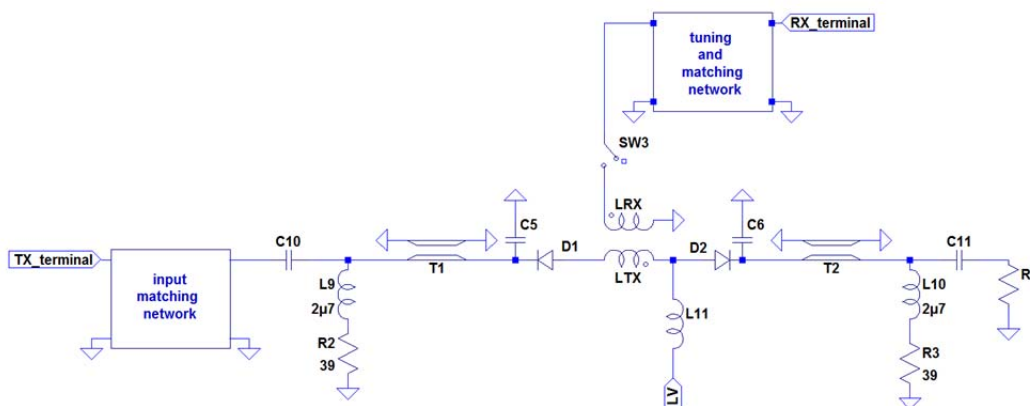


Fig. 4: Detailed implementation of the TX path.

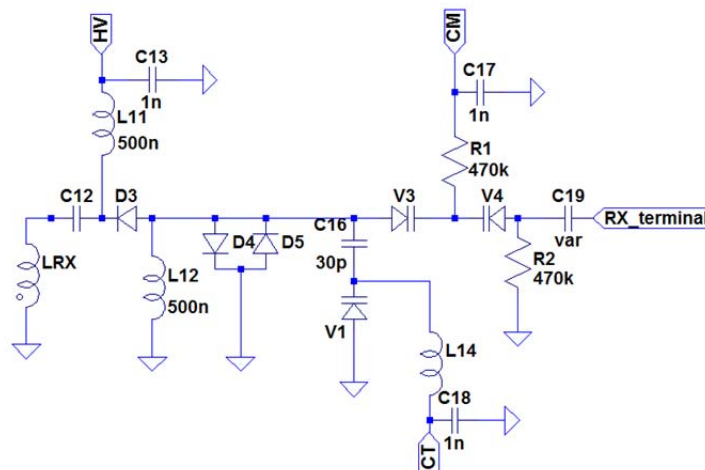


Fig. 5: Detailed implementation of the RX path.

Fig. 5 shows the receiving part in detail. PIN diode D3 acts as switch SW3 and is reverse biased during TX with 250V via the biasing network L12/C13/L13 from port HV. D4 is a limiter

diode (UM9989, Microsemi) which together with the Shottky diode D5 (BAV99W, NXP) shorts residual RF currents which leak through the parasitic capacitance of D3 once the respective voltage drop exceeds the diode's threshold voltage. During RX +5V are applied both at ports HV and LV so that D3 gets forward biased. In this state the probe coil LRX forms a resonant circuit together with the series of C16 and the varactor V1. The tuning voltage CT is provided via the biasing network L14/C18 while the matching varactors V2 and V3 are being controlled from port CM via the simpler resistor network R2 and R3. The resistances must be high (here 470 k Ω each) in order not to load the RF signal and compromise the Q-factor. Such large resistors cannot be used in the tuning circuit because they form R-L-C-circuits together with the capacitance of V1, C16 and L13, which render the time constant for settling of the bias voltage too long for fast operation. In contrast the matching circuitry contains only very small capacitances (usually < 10pF) of the varactors and thus the settling times are sufficiently small (on the order of several μ s). As tuning varactor the SMV1249 (Skyworks solutions) was used because it provides a high tuning range within a reverse voltage range of only 4 V. For the matching varactors two BBY57 (Infineon) was applied. All biasing coils (L9-13) were wound as air coils from enamelled copper wire (diameter 0.5mm) so as to provide high Q-factors because otherwise the overall Q of the resonator would be compromised.

The sample coil was built for the frequency range centered about 97.5 MHz. In order to obtain an optimal S_{11} frequency response the inductance of the TX coil must be considerably small (no more than 9.4 nH) for the chosen termination resistance. The envisaged application of the coil, however, requires the following constraints: diameter = 10 mm, length = 12 mm, maximally homogeneous magnetic flux density distribution inside the coil volume and operation up to 125 MHz. In [17] similar conditions were achieved with a single turn of copper stripe which, however, would cause considerable eddy current losses and thus Q-reduction in the RX coil. This was prevented by mounting four single circular turns in parallel as shown in fig. 2. They were made of enamelled copper wire (diameter 0.6mm) on a thin cylindrical plastic former (diameter 10.5 mm).

The new coil was first simulated with COMSOL Multiphysics (Comsol Multiphysics, Germany) and the distance between the individual windings was optimized for best field homogeneity. Due to the volume constraints the inductance was somewhat higher than the optimal value, i. e. approx. 12 nH. The RX coil consists of a solenoid with 4 windings which is interleaved with the TX coil and possesses an overall inductance of approximately 180 nH.

Spectrometer

The performance of the new coil was tested against that of a TX/RX wideband coil of the same type as published in [17], however with a slightly different sample volume of approximately 1 ml. The volume of the new coil was roughly 1.14ml, hence the sample volumes of the two coils were comparable.

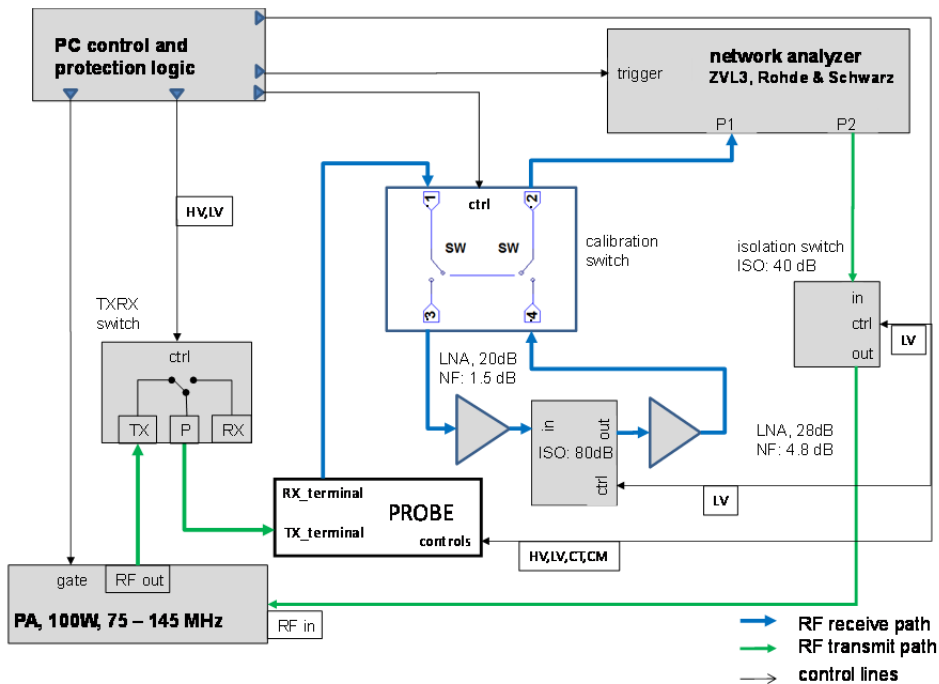


Fig. 6: Block schematic of the spectrometer. The grey shaded parts are the same as in [17] while the white blocks represent the new probe and a calibration switch for auto-tuning and matching.

The spectrometer described in [17] was extended according to fig. 6. Most parts remained the same (grey shaded blocks). The only changes were the new coil and the calibration switch (white blocks). The software was extended by an automated tuning and matching function. The control voltages CT and CM are interpolated from a lookup table which contains the optimal control voltages for the varactors as functions of the frequency. The lookup table is generated automatically before spectroscopy by switching the calibration switch to the position shown in fig. 6 so that the RX terminal of the probe is connected directly to port 1 of the network analyzer (NWA). Then, the tuning control voltage is swept through typically 50 equidistant values and at each value the matching voltage is again swept through 50 values, thus giving a total of 2500 S_{11} spectra. For each voltage pair the frequency with the minimum S_{11} value is recorded together with the respective control voltage pair CM and CT and stored in a lookup table after sorting along the frequency column. During NQR spectroscopy the calibration switch is set so that the RX terminal is connected to the preamplifier and the amplifier output is connected to port 1 of the NWA (normal operation as in [17]). The control voltages at ports CT and CM are then interpolated from the lookup table at each NWA frequency and provided as analog output voltages of free DAC-channels of the I/O interface (USB6351, National Instruments).

Experimental procedures

Coil characterization

The matching of the TX coil was measured by scanning the S_{11} parameter between 40 and 140 MHz with the same NWA which was used in the spectrometer. As the useful TX bandwidth we defined the frequency range within which the return loss remained below -15dB. This is less rigorous than the -20dB limit used in [17], but the suboptimal inductance value of the TX coil forced us to relax the specification somewhat. However, as modern RF PAs usually accept return losses of more than -10dB, this bandwidth definition for TX was still considered as appropriate. Tuning and matching of the RX circuit was tested within the spectrometer as described in the previous section. As useful RX bandwidth we defined the frequency range within which S_{11} could be kept below -20dB.

Spectroscopy and SNR measurements

As test substance we applied the same as in [17], i. e. $ZnBr_2$. For a fair comparison the same powder volume (1.2 cm^3) was used in both coils. The $ZnBr_2$ powder (anhydrous form, 99.9% pure, Sigma Aldrich, USA) was filled as densely as possible into a 3ml plastic syringe which fitted snugly into the small probe coil. The powder was gently pressed so as to yield a density of 2492 kg/m^3 . As the density of pure $ZnBr_2$ is 4200 kg/m^3 , the filling factor was thus 0.59.

The tip of the syringe was immediately sealed hermetically with a 2-component glue (UHU Schnellfest, UHU GmbH & Co. KG, Germany) in order to prevent hydration of the highly hygroscopic powder. The syringe with the powder was placed inside of the probe coil and a spin echo sequence ($T_R = 5\text{ms}$, $T_p = 60\mu\text{s}$, $T_E = 250\mu\text{s}$) was started. After a run-in period of 10 minutes for thermal equilibration of the sample the spectra were acquired with 100 averages for the new coil and 1000 averages for the coil from [17]. The NWA was set to a centre frequency of 97 MHz and a span of 5MHz, the number of points per spectrum was 400, the IF bandwidth was set to 20kHz. As the TX coils of the two probeheads had a very similar shape they differed only very little in the magnetic flux density and hence the pulse length T_p for the $\pi/2$ pulse could be made the same, thus allowing for the same pulse protocol.

The spectra obtained with the two coils were compared by means of the achieved SNRs, calculated as the ratio between the peak amplitude and the RMS value of the noise in the baseline interval.

Results

Coil characterization

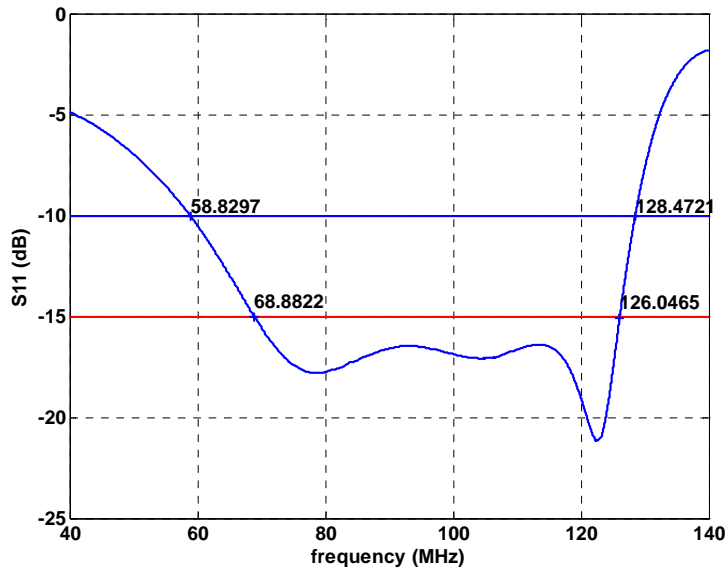


Fig. 7: S_{11} of the new coil. The -15dB bandwidth lies between 69 and 126 MHz, i. e. 57MHz in total.

Fig. 7 shows the matching of the TX network during the closing phase of D1 and D2. As can be seen the -15 dB bandwidth is 57 MHz with a center frequency of 97.5 MHz. When accepting -10dB return loss, a value which is usually tolerated by modern RF power amplifiers, the bandwidth can even be extended to about 69 MHz. The useful RX bandwidth was found to lie between 60 and 130 MHz, thus overlapping nicely with that of the TX coil. In general the matching provided by the automatic RX coil characterization procedure always yields a return loss of better than -30dB.

Spectroscopy

Fig. 8 shows the NQR spectrum of the ^{79}Br isotope of ZnBr_2 measured with the new coil after $N=100$ averages. The three peaks of the characteristic triplet are considerably broadened probably due to a large number of crystal defects in the crystallites of the powder. The SNR was 135 while the noise voltage was close to that of a 50Ω resistance, as expected in the case of good matching. In comparison the SNR of the standard wideband coil was 41.4 after $N=1000$ averages. Thus, assuming an increase of the SNR with \sqrt{N} the new coil provides a 10.3 fold improvement of SNR and thus a shortening of the measurement time by a factor of 106.

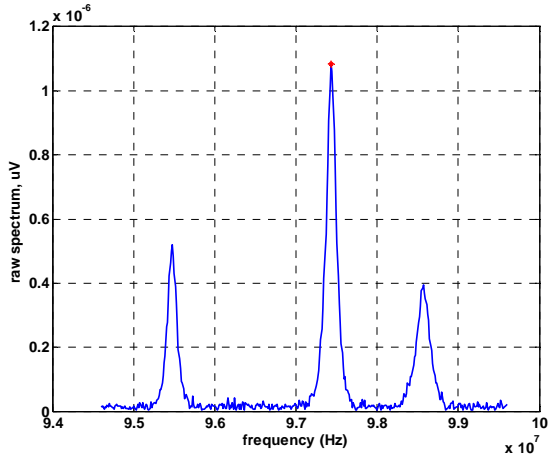


Fig. 8a: NQR spectrum of the ^{79}Br isotope of ZnBr_2 measured with the new coil. Results are given in absolute induced voltages. SNR=135, **N = 100**.

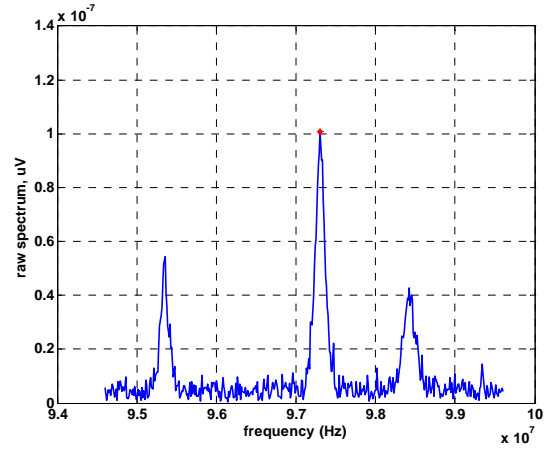


Fig. 8b: NQR spectrum of the ^{79}Br isotope of ZnBr_2 measured with the coil published in [17]. Results are given in absolute induced voltages. SNR=41.4, **N = 1000**.

Discussion

We have demonstrated the feasibility of a hybrid NQR probehead which combines a non-resonating wideband TX path with a resonating RX path which is electronically tuned and matched while scanning spectra over a range of several tens of MHz. In contrast to standard probeheads tuning and matching is achieved with simple and cheap varactor diodes rather than with mechanically driven high power capacitors. The settling time of the control voltages is with $\leq 100 \mu\text{s}$ considerably less than usual repetition times and thus fast scanning over a complete wideband spectrum is possible. The RX coil can be tuned and matched over a range of approximately 70 MHz with a centre frequency of 97.5MHz. The useful -15dB TX bandwidth is 57 MHz, but when allowing for up to -10dB return loss the range can be extended to the full RX bandwidth. The SNR of the coil was assessed by scanning a 6 MHz wide part of a ZnBr_2 spectrum with a custom-built spectrometer. After 100 averages the SNR was 136 while the noise voltage was close to that of a 50Ω resistance, as expected.

Using an NWA as spectrometer enables the immediate visualization of the full wideband spectrum and the early recognition of spectral features while the averaging process goes on continuously. There is no need for waiting until the end of the whole experiment, which is desirable for quick raw scanning when searching for unknown peaks. Thus a single sweep spectrum of the ZnBr_2 spectrum could be achieved within 2s.

In contrast typical frequency-hopping approaches with motor-controlled NMR probeheads acquire one narrowband spectrum after another, going through all averages before stepping to the next center frequency. Consequently the complete wideband spectrum is not available before the end of the complete data acquisition and concatenation of the

individual narrowband spectra, which may be cumbersome when scanning over a wide frequency range.

The downside of our implementation is that the Q-factor at RX is typically lower than that of mechanically tuned and matched solenoid coils because of the on-resistance of the PIN diodes. Our results correspond to a Q-factor at RX of 72, which is below the theoretically expected one. Limiting factors are the Q-factors of the varactor diodes, the on-resistance of the PIN diodes as well as losses in the biasing inductors which, from the RF viewpoint, lie in parallel to the resonator. There is certainly room for improvement e. g. by paralleling PIN diodes so as to reduce the total loss resistance of the resonator. Also increasing the inductance of the RX coil could still increase the quality, but this measure is limited by the target frequency range and the parasitic capacitances in the RX path.

Another limiting factor caused by the PIN diodes is the high voltage required to reverse bias D_3 in fig. 5. As a rule of thumb the RF can be safely blocked if the reverse bias voltage is at least the peak RF voltage $V_{p,RF}$ and the reverse breakdown voltage of the PIN diode is $2 V_{p,RF}$ [19]. Depending on the width of the i-region, the RF pulse duty cycle and the applied frequency blocking can still be achieved with reverse bias less than $V_{p,RF}$, but this depends on the chosen type of PIN diode. A pulse with a power of 100 W produces a voltage drop of approximately 44V along LTX, which is uptransformed to 176V at the four windings of the RX coil. Thus a safe reverse bias is approximately 200 V and the required reverse breakdown voltage V_{br} 400V. The used PIN diodes (MA4P7104F-1072T, MACOM) fulfill this specification. For higher powers PIN diodes with higher reverse breakdown voltages are required.

Alternatively one could apply RF relays for SW3/4 which would, most probably, enhance the Q-factor significantly. However, the settling time could then not be brought below several ms which is only admissible for correspondingly long repetition times. Moreover typically such relays are specified for several millions of switching cycles only. Assuming 10^7 allowable cycles would thus a replacement after 100 spectra with 1000 points and 100 averages, respectively, which means an impractically short lifetime.

Our concept was implemented successfully also for other bands with central frequencies from 30 MHz up to 100 MHz, thus covering a total spectral range from 20 MHz up to 130 MHz. Lower frequencies are accessible relatively easily from the technical point of view, but then the sensitivity of the method decreases because of the strong frequency dependence of the NQR signals. At very low frequencies (up to several MHz) there is no need for a resonator, even during RX. In [20],[21] a non-resonating circuit was published which exhibits excellent SNR. Instead of a tank circuit a simple solenoid RX/TX coil is coupled to a FET amplifier via a transformer. Due to voltage transformation and the very high input impedances of FETs this solution provides an extremely low noise figure. Unfortunately the approach is restricted to fairly low frequencies and can hardly be realized in the VHF range

due to the gate-capacitances of the FETs which lower the input capacitance to unacceptably low values and which forms parasitic resonators together with the RX coil.

The upper frequency limit of our concept is determined by the inductances of the TX coil and the termination resistance according to eq (2). Assuming that we want to preserve the sample volume of 1 ml, the coil inductance cannot be made smaller than somewhat more than 10 nH. In our prototype we had 12 nH with one effective winding. When terminating with an R_1 of 50Ω this yields, according to eq (2), a central frequency of 663 MHz. Thus it should be possible to build wideband coils up to the UHF range.

Acknowledgements

This project has received funding from the European Union's *Horizon 2020 research and innovation programme* under grant agreement No 665172

References

- [1] Das T P and Hahn E L 1958 *Solid State Physics: Supplement 1: Nuclear Quadrupole Resonance Spectroscopy* (Academic Press Inc)
- [2] Beguš S, Jazbinšek V, Pirnat J and Trontelj Z 2014 A miniaturized NQR spectrometer for a multi-channel NQR-based detection device *J. Magn. Reson.* **247** 22–30
- [3] Freude D and Haase J 1993 Quadrupole Effects in Solid-State Nuclear Magnetic Resonance *Special Applications NMR Basic Principles and Progress* ed P D H Pfeifer and D P Barker (Springer Berlin Heidelberg) pp 1–90
- [4] Freude D 2006 Quadrupolar Nuclei in Solid-State Nuclear Magnetic Resonance *Encyclopedia of Analytical Chemistry* (John Wiley & Sons, Ltd)
- [5] Lehmann-Horn J A, Miljak D G, O'Dell L A, Yong R and Bastow T J 2014 Rapid detection of arsenic minerals using portable broadband NQR *Geophys. Res. Lett.* **41**2014GL061386
- [6] Blinc R, Apih T and Seliger J 2004 Nuclear quadrupole double resonance techniques for the detection of explosives and drugs *Appl. Magn. Reson.* **25** 523–34
- [7] Garroway A, Buess M L, Miller J B, Suits B H, Hibbs A, Barrall G, Matthews R and Burnett L J 2001 Remote sensing by nuclear quadrupole resonance *IEEE Trans. Geosci. Remote Sens.* **39** 1108–18
- [8] Kyriakidou G, Jakobsson A, Althoefer K and Barras J 2015 Batch-Specific Discrimination Using Nuclear Quadrupole Resonance Spectroscopy *Anal. Chem.* **87** 3806–11

- [9] Mispelter J, Lupu M and Briguet A 2006 *NMR Probeheads for Biophysical and Biomedical Experiments: Theoretical Principles & Practical Guidelines* (Imperial College Press)
- [10] O'Dell L A and Schurko R W 2008 QCPMG using adiabatic pulses for faster acquisition of ultra-wideline NMR spectra *Chem. Phys. Lett.* **464** 97–102
- [11] Kentgens A P M 1991 Quantitative excitation of half-integer quadrupolar nuclei by a frequency-stepped adiabatic half-passage *J. Magn. Reson.* **95** 619–25
- [12] Haase J and Conradi M S 1993 Sensitivity enhancement for NMR of the central transition of quadrupolar nuclei *Chem. Phys. Lett.* **209** 287–91
- [13] Veenendal E van, Meier B H and Kentgens A P M 1998 Frequency stepped adiabatic passage excitation of half-integer quadrupolar spin systems *Mol. Phys.* **93** 195–213
- [14] Gregorovič A and Apih T 2013 WURST-QCPMG sequence and ‘spin-lock’ in (^{14}N) nuclear quadrupole resonance. *J. Magn. Reson.* **233C** 96–102
- [15] Rossini A J, Hamaed H and Schurko R W 2010 The application of frequency swept pulses for the acquisition of nuclear quadrupole resonance spectra *J. Magn. Reson.* **206** 32–40
- [16] Kubàsek R and Alkhaddour M 2012 Building NMR/NQR Spectrometer *Progress In Electromagnetics Research Symposium Proceedings Progress In Electromagnetics Research Symposium* pp 163–6
- [17] Scharfetter H, Petrovic A, Eggenhofer H and Stollberger R 2014 A no-tune no-match wideband probe for nuclear quadrupole resonance spectroscopy in the VHF range *Meas. Sci. Technol.* **25** 125501
- [18] Gonzalez-Posadas V, Martin-Pascual C, Jiménez-Martín J L and Segovia-Vargas D 2008 Lumped-Element Balun for UHF UWB Printed Balanced Antennas *IEEE Trans. Antennas Propag.* **56** 2102–7
- [19] Caverly R H and Hiller G 1990 Establishing the minimum reverse bias for a p-i-n diode in a high-power switch *IEEE Trans. Microw. Theory Tech.* **38** 1938–43
- [20] Mandal S, Utsuzawa S, Cory D G, Hürlimann M, Poitzsch M and Song Y-Q 2014 An ultra-broadband low-frequency magnetic resonance system *J. Magn. Reson.* **242** 113–25
- [21] Mandal S and Song Y-Q 2014 Two-dimensional NQR using ultra-broadband electronics *J. Magn. Reson.* **240** 16–23