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A New Probe Head Design for the Weak Field Double Resonance Spectrometer

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Abstract

In order to observe low field σ EPR spectra of free radicals a new probe head was designed to work at 1.53 mT. As a double resonance spectrometer, at 1.53 mT the probe head includes both NMR and EPR rf coils. To induce the σ transitions EPR rf coil must produce an rf field parallel to the main static field. Various coil designs were examined for this aim and the best results was obtained with a solenoid NMR coil and saddle shaped single turn EPR coil design combination.

1. Introduction

In magnetic resonance, if the irradiation field is applied perpendicular to the main magnetic field, π transitions and if it is applied parallel to the main field, σ transitions are observed. As the angle between the irradiation field and main field has a value between 0° and 90° both type of transitions are observed simultaneously [1,2,3]. Recent EPR imaging studies on biological samples revealed the fact that low radiation fields should be used to avoid the heating of samples. Afterwards, low field DNP studies became important again because of DNP imaging applications [4,5]. In this respect an experimental study of σ transitions was performed at 6.8 mT [6]. Although theoretical calculations related to σ transitions at about 1.5 mT field region were present in the literature [7,8], there were no experimental observations in this field. In our previous studies, with the probe head used in the double resonance spectrometer [9] only π transitions could be observed. In this first probe head both NMR and ESR coils were solenoids. Since the fields produced by these coils were perpendicular to main static field, the only possible transitions were π type (Figure 1). New designed probe head made the observation of σ, π and both σ and π transitions possible.

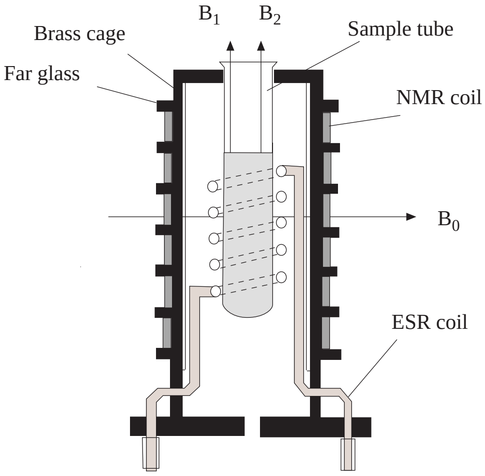


Figure 1. Cross-sectional view of the previously designed probe head

2. Theory

The most important parameters in the design of a magnetic resonance coil are signal to noise ratio ε/N, the coil resistance, quality factor and homogeneity of the magnetic field. The NMR coil is used both as an emitter and a receiver. The rf irradiation that induces transitions between nuclear energy levels is applied by means of this coil, and it also detects the magnetization within the sample. The effective value of signal to noise ratio is

$$\left(\frac{\varepsilon}{N}\right) \propto \frac{CV_s B_2}{\sqrt{R_C T_C}}. \tag{1}$$

Here, T_C is the coil temperature, R_C is the resistance of the coil, C is the number of resonant spins per unit volume and B_2 is the strength of the inducing NMR magnetic field [10,11,12]. CV_S is the number of spins at resonance within the total volume. Therefore signal to noise ratio can be increased by decreasing the temperature of the coil T_c and increasing the ratio of $V_S B_2/\sqrt{R_C}$. However, B_2 rf field is not completely independent of the resistance of the coil and an optimum value should be found. Sample volume related to the filling factor η, which determines the fraction of the coil volume occupied by the sample. For this reason an increase in η provides an increase in the signal to noise ratio. If the temperature of the coil is kept constant along the experiment, signal to noise ratio depends upon $V_S B_2/\sqrt{R_C}$ and η. The values of these quantities should be made as high as possible.

At frequencies greater than 5 MHz, current flows in a cylindrical shell through the coil's windings. For this reason the AC resistance of the conductor may be much greater than DC resistance of the conductor [13]. Then the resistance of the coil can be rewritten to include this effect.

$$R_C = \rho \frac{l}{2\pi r\delta}, \tag{2}$$

Here, ρ is the resistivity of the material from which coil is made, l is the length of the wire, r is the radius of the wire and δ is the skin depth. Skin depth is given by

$$\delta = \sqrt{\frac{\rho}{\pi\nu\mu}}. \tag{3}$$

Here, ν is the frequency, μ is magnetic permeability. For copper skin depth is $66.2/\sqrt{\nu}$ mm. Other contributions to the resistance of the coil arise from the "proximity effect" and "sample losses". Proximity effect comes into existence when the coil has more than one turn. In this case, the magnetic field created by a current passing through of one part of the conductor effects the current in the other parts of the conductor by self induction. This causes an increase in the resistance of the coil by a factor between 3 and 6. Then the resistance of the coil takes the form:

$$R'_C = \xi R_C. \tag{4}$$

The sample itself might also create an increase in the resistance of the coil as a result of dielectric and inductive losses and resultantly cause a decrease in the ε/N ratio [14].

The quality factor of a coil is given as

$$Q = \frac{\omega L}{R_C}, \tag{5}$$

where ω is the angular frequency and L is the inductance of the coil. Quality factor is a measure of the transformation of rf power into electromagnetic energy and therefore its value should be kept as high as possible. Except that the amplitude of the rf voltage produced at the ends of resonance circuit during resonance depends on the quality factor, Q [15]. However Q is not a completely reliable parameter in the performance of a coil [16]. In the rf region Q depends on the frequency roughly by $\nu^{1/2}$. In application, as the frequency of irradiation increased, the number of turns should be decreased.

The homogeneity of the produced rf fields in a coil is another factor that plays important role in the resonance signal shape obtained.

In the design of a coil having good ε/N ratio all the above discussed parameters should be taken into consideration. However optimum performance can only be reached with experimental tests.

3. Experimental

Experiments were performed first with NMR coils. Afterwards, in order to design the new probe head of the double resonance spectrometer, both NMR and EPR coils were used in combination in the measurements.

NMR Coils NMR coil is used both to produce the magnetic field B_2 at 65 kHz resonance frequency and also to receive the resonance signal. Therefore good signal to noise ratio is necessary in the coil design. Two coil geometries were examined. One of them was a circular solenoid and the other was a square turn coil. In order to test optimum coil parameters five separate coils were wound and numbered from 1 to 5. Four of the coils were selonoids; coil number 4 was square. Their dimensions and measured parameters are listed in Table 1. Measurements were performed with a 22kHz-70MHz Q-meter HP 4242A and a 5Hz-13MHz LF impedance analyzer HP 4192A. NMR coil works at 65 kHz, and for this frequency the skin depth was calculated from Eq. 3 to be 0.26 mm. Since the radii of wires used in these coils were changed over the range of 0.15 mm-0.23 mm, $\delta > r$ and the skin effect can be neglected. On the other hand, the number of turns were high and the turns were close to each other, therefore proximity effect exist. This results in an additional increase in the coil resistance. The coil resistances were calculated using the measured Q values and Eq. 5 and ξ factors were obtained from the ratio of resistance of the coil R_C to the measured DC resistance of the coil by an ohmmeter. To determine ε/N ratios experimentally, a 4-hydroxy-TEMPO(TANOL)/water 1mM sample (11 cm^3 in volume) was prepared under vacuum and measurements were performed at the spectrometer by the successive replacement of the NMR coils to be tested.

Table 1. Measured parameters and experimental ε/N ratios of NMR coils. 2a is average coil diameter in cm, 2g is coil height in cm, N is number of turns, ψ is diameter of conductor in mm

	coil # 1	coil # 2	coil # 3	coil # 4	coil # 5
Dimensions of coil	2a = 3.1 2g = 5.0 $N = 157 \times 6 = 942$ $\psi = 0.45$	2a = 3.1 2g = 5.0 $N = 157 \times 6 = 1002$ $\psi = 0.30$	2a = 3.8 2g = 4.3 $N = 120 \times 6 = 720$ $\psi = 0.35$	2a = 3.8 2g = 4.5 $N = 600$ $\psi = 0.30$	2a = 3.8 2g = 4.3 $N = 120 \times 6 = 720$ $\psi = 0.30$
Q	24.0	60.0	67.5	55.7	83.4
L(mH)	11.0	12.0	12.3	11.8	12.0
$R_{DC}(\Omega)$	10.6	22.6	16.7	20.0	21.3
$R_C(\Omega)$	187.2	81.7	74.4	86.5	58.8
ξ	17.7	3.6	4.5	4.0	2.8
η	0.30	0.29	0.23	0.17	0.23
ε/N	0.50	1.25	0.80	0.70	0.95

EPR Coils In a double resonance spectrometer, EPR coil is used to pump the transitions between the electronic energy levels. This results in an increase in the NMR signal detected by NMR coil [17]. The important points be attentive to in the design of an EPR coil are the homogeneity and strength of the B_1 field. Greater the B_1/R_C ratio, the stronger the field obtained. To produce a field parallel to main field three coil geometries were examined. These were a saddle shaped coil, rectangular coil and Helmholtz coil. The homogeneity conditions of the coils were obtained from the literature [11,18,19,20,21]. The frequency range covered by EPR coil is 5-120 MHz. From Eq.3 for 60 MHz, as an average value, skin depth is approximately 8μm. Since the wire diameter used 3 mm, $\delta \ll r$ and skin depth should be taken into account in the resistance of the coil. All the coils were single turn coils and there was no additional resistance sourced from proximity. Therefore their resistances were calculated from Eq.2. To perform B_1/R_C ratio of the EPR coils experimentally a small coil was wound and inserted into the center of the EPR coils while the EPR coils were driven at a frequency of 42 MHz. This is a practical way of measuring the B_1/R_C ratio. The results are listed in Table 2.

Table 2. Measured parameters and experimental values of EPR coil. N is number of turns, ϕ is diameter of conductor in mm and α is the coil angle. (See Fig. 2 for coil dimensions)

	Saddle shaped coil	Rectangular coil	Helmholtz coil
Dimensions	2g = 4.2 2a = 3.0 N = 1 $\phi = 3$ $\alpha = 120°$	2d = 3.0 2g = 4.4 2a = 2.7 N = 1 ϕ	2g = 8.5 2a = 3.0 N = 1 $\phi = 3$
Inductance L (μH)	0.760	0.750	2.000
$R_C(\Omega)$	0.614	0.635	1.130
Induced voltage (V)	2.8	1.0	0.1

Double Resonance Probe Head Using the above mentioned coil types three different probe heads were designed (Fig. 2).

a) NMR: coil # 2, EPR: Helmholtz,
b) NMR: coil # 5, EPR: saddle shaped,
c) NMR: coil # 4, EPR: rectangular.

For probe head (a) NMR coil was inserted into the EPR coil, but the order was reversed for the other two heads. The best designed head should give a high signal to noise ratio, highest observed enhancement $(P_Z \pm P_0)/P_Z$ [17] and its B_1 field must be homogeneous. The test performed with probe head (a) indicated that the EPR field produced was insufficient and did not reach the sample as a result of screening effect by the NMR coil. Therefore this coil was eliminated and measurements were completed with the use of the other two coils. When EPR coils were inserted into NMR coils, the Q values of NMR coils decreased by an average of 33% from their original values. Experiments were performed at 82 MHz, keeping the ratio $V/\nu = 1$ (Volt/MHz). The sample used was an aqueous solution of 4-hydroxy-Tempo at 1mM concentration. 82 MHz is the resonance frequency of the sample for a π transition. Both for $B_0//B_1$ (σ condition) and $B_0 \parallel B_1$ (π condition) P_0, P_Z and enhancement factors were obtained. Here P_0 is the signal intensity without EPR irradiation and P_Z is the signal intensity in the presence of EPR irradiation. If we consider one of the resonance transitions, e.g. a π transition, then in theory for $B_0 \perp B_1$ the intensity should be high and for $B_0//B_1$ it should be zero. However, experimental results indicated the presence of the contribution of the other type in each spectrum. This is in fact a measure of the inhomogeneity of the field and the enhancement ratio

$$\frac{G(P)_\sigma}{G(P)_\pi} = \frac{\left(\frac{P_Z - P_0}{P_0}\right)_\sigma}{\left(\frac{P_Z - P_0}{P_0}\right)_\pi} \tag{6}$$

gives the inhomogeneity percentage. Smaller this ratio the more one directional and homogeneous a field is observed. The results are given in Table 3.

Table 3. Enhancement factors and field inhomogenities for the probe heads designed to perform a double resonance experiment. A is NMR: coil #5 and EPR: saddle shaped coil, B is NMR: coil #4 and EPR: rectangular coil. (ν = 82 MHz)

	$B_0 \parallel B_1$			$B_0 \perp B_1$			
	P_0	P_z	$G(P)_\sigma$	P_0	P_Z	$G(P)_\pi$	$G(P)_\sigma/G(P)_\pi$ (%)
A	0.95	0.65	0.32	0.95	4.60	5.84	6
B	0.85	0.58	0.32	0.87	1.66	2.91	11

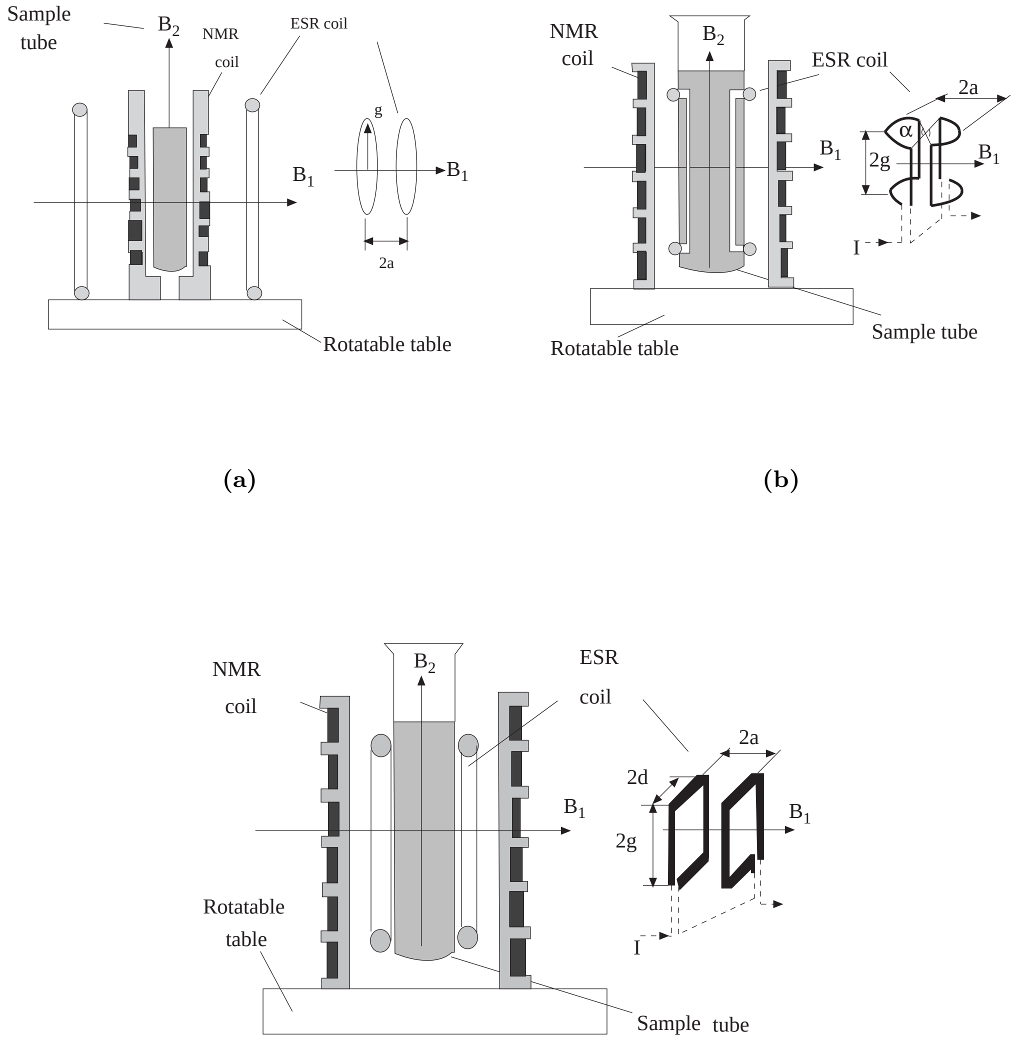
4. Results and Discussion

A consideration of Table 1 and Fig. 3 indicates the consistency of the experimental and calculated signal to noise ratios for each coil. In order to calculate signal to noise ratios from $V_S B_2/\sqrt{R_C}$, at first for each coil geometry, the magnetic field was calculated [21]. The best result was obtained for coil #2. A comparison of the results obtained for quality factors and filling factors of the coils revealed the fact that although these parameters give complementary information, they alone were not sufficient in the determination of ε/N ratio. From Table 1 the proximity factor of coil #1 is higher than expected. The reason for this was the thick wire used. As a result the turns were not ordered sufficiently and the quality factor of the coil decreased.

From an inspection of Table 2 and Fig. 4 the harmony between measured and calculated values could be seen. The best result belongs to the saddle shaped coil.

The above discussion was made for NMR and EPR coils separately. However, since a double resonance instrament requires the combination of these coils, the best result might be different from the separate tests. This was the case in this study. NMR coil #2 was used together with the Helmholtz type EPR coil and the screening effect arose. This was overcomed by inserting the EPR coil into the NMR coil, therefore, instead of coil #2, coil #5 was used. This coil shows the second best signal to noise ratio and used together with the saddle shaped coil which was the best among EPR coils. A comparison with the previous probe head revealed the fact that the enhancement factors obtained with the new probe head were lower. The reason was the saddle shaped coil used for EPR. In other words this was the cost paid for the change of the direction of the EPR field.

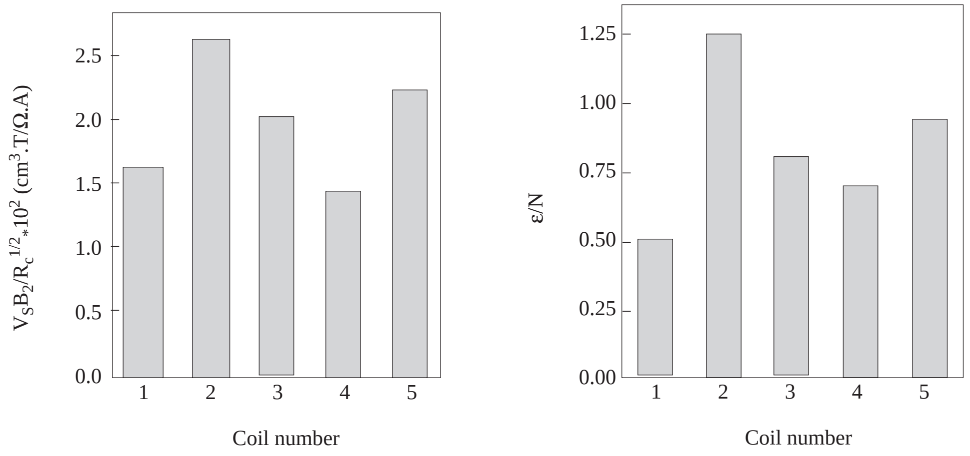
In conclusion, for the first time in the 1.53 mT field region, a probe head has been created which made possible the observation of the transitions parallel to the main static field. The probe head still might be improved by replacing the wires with thin metal stripes and may be by decreasing the length of coil and connection wires. Our studies in this direction are continuing.



(a) **(b)**

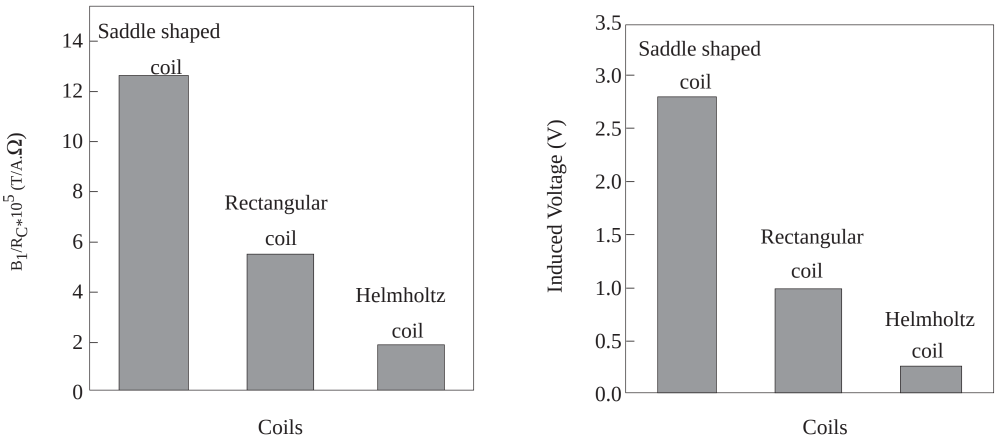
(c)

Figure 2. The cross-sectional views of the double resonance probe heads. Static field B_0 is in the horizontal plane. a) NMR: circular solenoid, EPR: Helmholtz, b) NMR: circular solenoid, EPR: saddle shaped, c) NMR: square turn coil, EPR: rectangular coil



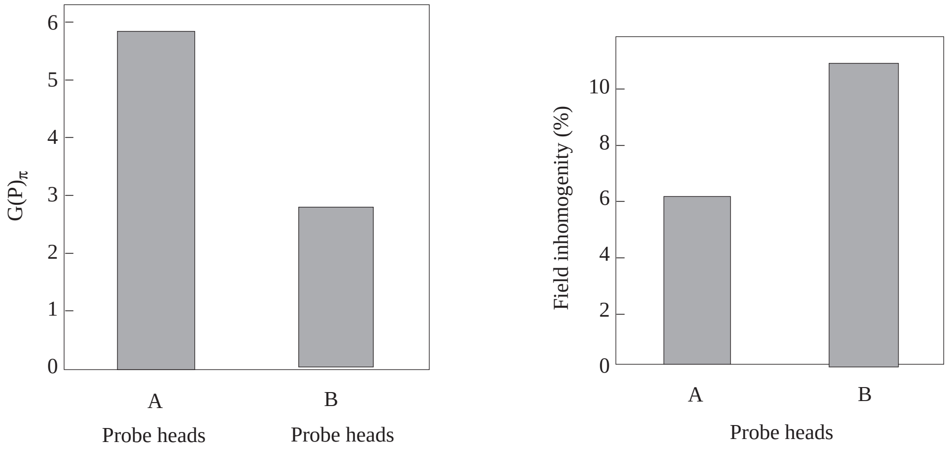
(a) **(b)**

Figure 3. The comparison of a) theoretical $V_S B_2/R_C^{1/2}$ and b) measured ε/N values for designed NMR coils



(a) **(b)**

Figure 4. The comparison of a) theoretical B_1/R_C and b) measured induced voltage values of designed EPR coils



(a) **(b)**

Figure 5. The measured values of a) enhancement factors and b) field inhomogeneity percentage of the two new designed probe heads. (Probe head A: solenoid NMR and saddle shaped EPR. Probe head B: square turn coil NMR and rectangular EPR)

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