SURFACE DIELECTRIC RESONATORS FOR X-BAND EPR SPECTROSCOPY

Sergey V. Petryakov¹, Wilson Schreiber^{1,*}, Maciej M. Kmiec¹, Benjamin B. Williams^{1,2} and Harold M. Swartz^{1,2}

¹Department of Radiology, EPR Center for the Study of Viable Systems, Geisel School of Medicine at Dartmouth, Hanover, NH, USA

²Division of Radiation Oncology, Department of Medicine, Dartmouth-Hitchcock Medical Center, Lebanon, NH, USA

*Corresponding author: wilson.schreiber@dartmouth.edu

A new resonator for X-band electron paramagnetic resonance (EPR) spectroscopy, which utilizes the unique resonance properties of dielectric substrates, has been developed using a single crystal of titanium dioxide. As a result of the dielectric properties of the crystal(s) chosen, this novel resonator provides the ability to make *in vivo* EPR spectroscopy surface measurements in the presence of lossy tissues at X-band frequencies (up to 10 GHz). A double-loop coupling device is used to transmit and receive microwave power to/from the resonator. This coupler has been developed and optimized for coupling to the resonator in the presence of lossy tissues to further enable *in vivo* measurements, such as *in vivo* EPR spectroscopy of human fingernails or teeth to measure the dose of ionizing radiation that a given individual has been exposed to. An advantage of this resonator for surface measurements is that the magnetic fields generated by the resonator are inherently shallow, which is desirable for *in vivo* nail dosimetry.

INTRODUCTION

Electron paramagnetic resonance (EPR) at X-band (9–10 GHz) delivers high sensitivity in non-lossy samples by using volume resonators. These resonators are conventionally used in a wide variety of EPR applications where a small sample can be placed in a glass capillary and inserted into the resonator. *In vivo* EPR nail and tooth dosimetry require development of surface resonators in order to make a measurement on living (or extracted) tissues where the sample cannot otherwise be placed in the small volume (relative to the tissue being measured) of a volume resonator. In order for the use of surface resonators to be feasible at X-band, the resonator must be designed with a high filling factor in order to maximize the detected signal amplitude. This is particularly important when measuring samples where lossy materials (i.e. tissues that contain water) that do not contribute to EPR signal amplitudes are present in/around the measurement site. Optimization of the filling factor should be prioritized over optimization of the quality-factor (Q), as the overall Q for the measurement will be dominated by the lowest Q of the entire measurement setup (i.e. the Q of the resonator and the losses attributed by the tissues). A high filling factor can be achieved with this resonator, as the depth of the microwave field generated by the dielectric resonator is localized near the sensing surface of the resonator and does not penetrate deep into the measurement site (i.e. nail bed of the finger or pulp of the tooth). The use of materials with higher dielectric constants than that of the tissue to be measured are advantageous

for surface resonators as they localize the transverse microwave B_1 field in the target tissue and constrain the extent of the microwave E field. Dielectric resonators also have the advantage of having only one resonance mode, which is dictated by its physical geometry. This eliminates undesirable resonance modes that are of similar frequency, which can cause unwanted measurement and/or tuning artifacts, and ultimately do not contribute to measuring an EPR signal. This allows the microwave energy that is coupled into the resonator to stimulate the desired resonance which will stimulate spins within a measurement sample.

DESIGN OF THE RESONATOR

To be useful for study of signals close to the surface of a sample, the resonator design goals include localization of the microwave B_1 such that there will be a high filling factor for spins within the target geometry, high Q to enhance signal amplitude, and minimal E field (and hence microwave loss) in the region of lossy samples such as aqueous tissues. A simplified and isolated cylindrical dielectric substrate geometry was first calculated⁽¹⁾ to determine an approximate diameter of the resonator to have a fundamental mode between 9 and 10 GHz, given a titanium dioxide (TiO_2) dielectric substrate with a Miller index of 001 (dielectric constant 120–180). The selection of TiO_2 was based on previous developments of EPR resonators at this frequency⁽²⁾. The length of the cylindrical substrate was restricted to what could be readily purchased from a crystal

supplier (1.0 mm from MTI Corp. of Richmond, CA). This resulted in a diameter of ~ 5 mm diameter with a resonance frequency of ~ 9.2 GHz.

In previous resonator designs, we have observed unwanted noise in our EPR spectra which can potentially confound our measurement results (i.e. signal amplitude). Common noise sources include mechanical vibrations, continuous or spurious electromagnetic interference, instrumental instability and sample motion. The effects of these noise sources can be minimized through optimized instrumental design and experimental procedures. We have observed a separate type of noise seemingly not due to any of the aforementioned sources that has been observed independent of the spectrometer used, and therefore intrinsic to the resonator itself. This noise has the unique characteristic that it is observed as an unexpected and highly variable spectral feature present in all of the collected EPR scans, as if it were a baseline or background signal. As observed for true EPR signals, the amplitude of this noise is coherent with the magnetic field sweep and does not decrease with simple averaging of repeated scans. The shape and location of this noise is seemingly only changed as a result of physical perturbation to position of the resonator relative to the main magnetic field and not as a result of a physical change to the position of the measurement sample relative to the main magnetic field or the resonator. We have observed that this noise can be reduced by either replacing the resonator on the sample or rotating the magnetic field relative to the resonator and sample and then averaging EPR spectra collected under these varied conditions. We have observed that in controlled perturbation methods (such as magnet rotation or computer controlled placement of the resonator) that we are able to reproduce this noise for a given position of the resonator, albeit when the resonator is placed very precisely (sub-millimeter/degree precision). As resonator positioning is not precisely reproducible under *in vivo* measurement conditions, the noise is also not reproducible and it is not possible to simply subtract the noise in post-processing of the data. We have also observed that careful selection of resonator materials and thorough resonator cleaning practices can reduce the likelihood of this type of noise. For the sake of clarity throughout this manuscript, this type of unwanted noise is referred to as ‘baseline distortion’.

In order to avoid baseline distortions in EPR spectra collected with dielectric resonators, we observed that it was desirable to have a hole in the center of the dielectric resonator, which will shift the frequency slightly.

A 3D model of the resonator was constructed within a finite element analysis and computer aided design (CAD) software packages (Ansoft High Frequency Structure Simulator (HFSS), and Solidworks

respectively) in order to visualize the magnetic and electric fields in the desired/various physical configuration(s) (see Figure 1).

The cross section of the resonator (Figure 1) shows that a magnetic field is generated inside the hole, within the dielectric, and extends beyond its top and bottom surfaces. The magnetic field that extends beyond the surface of the resonator will have the largest contribution in stimulating the spins during a surface measurement. If the dielectric constant is too large, the electric and magnetic field will not extend beyond the surface of the dielectric. If the dielectric is too small, the fields will propagate further than necessary. The ideal balance is to have a dielectric constant that is similar, but slightly higher, than the material to be measured. This will ensure that an optimal value of energy is deposited into the measurement site. In order to further ensure that there are no unwanted spectral features and minimal baseline distortion, the dielectric substrate is cleaned in hydrochloric acid. Hydrochloric acid is used based on successful reduction of baseline distortion observed in empirical testing of cleaning solvents and acids within our lab in attempts to ameliorate baseline distortion in various types of resonators. Unlike other resonators that have been constructed from silver or copper, and that possibly incorporate some plastic (Rexolite, Teflon, etc.), a crystal dielectric substrate can withstand extensive cleaning in high concentrations of hydrochloric acid to further ensure that a majority of the unwanted contamination is eliminated from the resonator.

Figure 1. (a) CAD design of resonator in the machined holder. (b) HFSS visualization showing the magnetic field protruding from the top/bottom sensing surfaces of the dielectric resonator; (c) the HFSS model showing the visually transparent metallic shield; and (d) HFSS visualization of the electric field in the dielectric resonator. For sub-figures (b) and (d): Higher field values approach white, and lower values approach black.

DESIGN OF THE COUPLER

In order to effectively transmit microwave power to/from the dielectric resonator, a coupler designed specifically for dielectric resonators is needed. An inductively-based coupling system is typically employed for this type of resonator. The resulting equivalent circuit diagram of the intended prototype of the surface dielectric resonator is shown in Figure 2.

Any partial reflection from the coupling loop reduces power that is delivered to the resonator, and ultimately the sample being measured. An ideal load on the coupling loop (the resonator on the sample) is one whose inductance equals 50 ohms at resonance frequency. Any reflections that are not caused by the spin system (i.e. from partial reflections from a nonideal load) ultimately reduce the absolute sensitivity of the EPR spectrometer, and therefore an emphasis on designing a resonator with minimal reflections is highly advantageous in detecting weak EPR signals. The two segments of the coupling loop have load-dependent impedance: when there is a large load (i.e. one with very lossy sample), the coupling loop impedance is reduced by the total losses of the measurement setup, and at low load (i.e. minimal losses in the sample) the coupling loop impedance increases. Minimal reflection occurs when the impedance of the coupling loop is twice the impedance of the driving microwave source, and the transmission lines leading to the coupling loop are equal to twice that of the feeding transmission line. Therefore, since a 50 ohm transmission line is conventionally used in microwave bridges, the 50 ohm transmission line that leads to the coupling loop must then feed a 100 ohm transmission line leading to a 100 ohm coupling loop. This can be comprised of a two-loop segment, and two symmetrical transmission lines connected symmetrically to the grounded housing,

Figure 2. Simplified, equivalent circuit diagram of the variable magnetic coupling mechanism of the surface resonator. This mechanism utilizes two balanced loops to transfer energy (M) from the 50-ohm transmission line into the resonator through varying the distance of the coupling loops to the resonator for a wide range of resonator loads or impedances. The dielectric resonator is shown as an ideal LC-resonator. The enclosure of the resonator is shown as a rectangular box around the coupler and resonator, with an 8 mm diameter sensing aperture.

which can be seen in Figure 3. As a result of matching these impedances, a balun is not required.

The optimal length of the coaxial transmission line from the internal wall of the enclosure to the coupling loop is a length equal to an odd-integer value of the quarter wavelength of the resonators frequency. We will use 21 wavelengths due to physical restrictions and machining limitations. This reduces unwanted partial reflections at the connector. There is a limit to the diameter of the coupling loops, because the length of the circumference of the loop should be small compared with the one-quarter wavelength in the wire loop^(3, 4). The diameter of the coupling loop should also be as large as possible to ensure that a maximal amount of energy is delivered to the dielectric resonator. The coupling loop (4.4 mm diameter) is connected to the end of the 50-ohm coaxial transmission line using two symmetrical 100-ohm quarter wavelength lines. As a result of doubling the characteristic impedance of the transmission line that is delivering power to the coupling loop, there are minimal unwanted reflections back from the coupling loop, thus a maximal amount of energy is transmitted to the coupling loop, and therefore the dielectric resonator.

Given that the coupling loop could be in close enough proximity to the resonator that the magnetic fields generated by the resonator could stimulate spins in the coupling loop itself, and that the modulation field generated by the modulation coils of the magnet will likely penetrate through the aperture and resonator assembly, the coupling loop must also

Figure 3. A two-segment coupling loop designed for high coupling capability to a dielectric resonator measuring lossy samples. The parallel gaps between the wire is then filled with an appropriate capacitor (typically copper clad Teflon) to create the desired impedance (100 ohms).

Figure 4. The resonator assembly is comprised of the following components: 1, 50-ohm Coaxial cable (rigid); 2, SMA connector; 3, Brass threaded rod; 4, Aluminum body of the resonator; 5, Clamp cap; 6, Clamp ring; 7, Rexolite spacer; 8, Inner dielectric plate holder; 9, Outer dielectric plate holder; 10, Coupling adjustment knob; 11, Spring; 12, Teflon washer; 13, Dielectric substrate; 14, Coupling loop.

Figure 5. S11 measurement performed on an Agilent E5071C calibrated network analyzer showing a single resonance mode with reasonable Q (~ 580 unloaded) of the dielectric surface resonator within the desired 9–10 GHz frequency range.

be free of possible contamination. A contaminated loop could cause unwanted baseline distortions or spectral features. Therefore, the coupling loop and transmission lines are also cleaned with hydrochloric acid.

RESULTS

After the aforementioned considerations, the resulting construction of the resonator assembly can be seen in Figure 4. The resulting resonant response (Figure 5) shows that this design provides a single resonance frequency rather than multiple resonance frequencies. This efficiency of the resonator, quantified by a conductive perturbing sphere⁽⁵⁾ provides an

Figure 6. Measured sensitivity of the resonator performed using the perturbing metallic sphere method described in Reference (5), and measuring the effect of the frequency shift on the resonance mode.

indication of the filling factor of the resonator as a function of distance from the center surface of the dielectric resonator, which is shown in Figure 6.

EPR data was then collected using a standard Bruker EMX X-Band spectrometer. Custom modulation coils were constructed, installed and calibrated using evacuated LiPc for this resonator. For each of the samples mentioned below, the following instrumental parameters were used:

RF Power: ~ 1.5 mW
 Time Constant: 10.24 ms
 Modulation Freq. 100 kHz
 Modulation Amp. ~ 3 Gauss
 Scan Time: 10.5 seconds
 Number of Scans: Varies

A two micro-molar concentration TEMPO solution in ~200 ml was created and placed within the center of the hole of the dielectric resonator. This resonator and sample assembly was then placed into the Bruker EMX spectrometer to collect EPR data. The resulting EPR spectra, shown in Figure 7, indicate that the resonator can indeed collect a small concentration (i.e. low number of spins) in a lossy medium (water).

Two extracted, irradiated human incisors were also measured to demonstrate that surface measurements of teeth can also be made with this resonator. The resulting EPR spectra (shown in Figure 8) provide indication that the radiation induced signal can easily be detected, in 2 Gy teeth, and possibly lower doses, given the SNR of the spectra (~7).

In previous *in vivo* nail studies Kapton25 and Kapton35 tape were used as an surrogate standard for simulating the radiation induced signal that are present in human finger nails that have been

subjected to ionizing radiation⁽⁶⁾. A sample of Kapton35 (equivalent to ~30 Gy) was placed on the sensing aperture of the surface dielectric resonator and EPR data were collected (Figure 9). The resulting SNR of ~10 for the surrogate radiation induced signal provides an indication that this resonator could be considered for future works and investigations into *in vivo* nail dosimetry.

CONSIDERATION OF OTHER DIELECTRIC SUBSTRATES/CRYSTALS

Other laboratories have previously reported developments on dielectric resonators^(2, 7-10), which used TiO₂, potassium tantalate (KTaO₃) and other crystals as their dielectric substrate. Isotropic ceramic resonators have also been developed⁽⁷⁾.

Two kinds of single-crystalline dielectrics, KTaO₃ and TiO₂, were tested at our facility. Single crystals are likely to be very pure and free of contamination, and therefore free of unwanted baseline distortion or spectral features that would otherwise confound our EPR amplitude measurements. However, we have found that the TiO₂ crystals may have an EPR signal that interferes with our EPR signals of interest (radiation induced signals) that we have found strongly depends on the crystal orientation relative to the orientation of the static magnetic field, and can be reduced virtually completely via precise positioning of the dielectric in the resonator housing.

We have observed that KTaO₃, unlike TiO₂, does not have dielectric anisotropy, does not have a strong background signal, and can be used in any orientation with respect to the constant magnetic field. KTaO₃ has a very high dielectric constant (~300), which determines the maximum aperture of the cavity surface. We constructed an aperture with a sensing diameter of 2.7 mm with a 1 mm hole. The thickness of the crystal was 0.5 mm. The concentration of the magnetic energy in this crystal was so great that we were only able to measure a signal when the microwave power was reduced to at least

Figure 7. Approximately 200 ml of two micro-molar solution of TEMPO in a polyethylene test tube, resulting in a SNR of ~7, provides an indication of the sensitivity of this resonator. Spectral fit is overlaid on the EPR data. Twenty-five scans were collected.

Figure 8. A 2 Gy and a 60 Gy (added dose) extracted human upper incisor tooth (whole) held in a rubber mold pressed against the aperture of the dielectric resonator. Fifty scans were collected on each tooth.

Figure 9. A 10 mm $\times$ 10 mm sample of Kapton35 tape overlaid on the aperture of the resonator. Fifty scans were collected.

–30 dB from the Bruker EMX Bridge; otherwise we observed saturation of the EPR signal. We also found strong temperature instability of the resonator, which is further amplified by the application of microwave power over the course of a given measurement, and is likely to be a problem for *in vivo* measurements.

TiO₂ has strong dielectric anisotropy. The anisotropy of the dielectric constant makes the orientation of the TiO₂ plate is critical in the manufacturing of surface dielectric resonator. In the final version of the resonator, the crystal was oriented in a plane perpendicular to the permanent magnet field to eliminate the background signal completely.

CONCLUSION

A surface resonator based on a single crystal of TiO₂ crystal with 8 mm sensing aperture was designed, constructed and tested. A two-element inductive coupling loop was designed to provide a wide range of adjustment for a variety of loads/impedances. The resonator can work with very lossy samples, such as measuring TEMPO in a relatively large volume of water, which indicates that this resonator could be applicable detecting weak signals for *in vivo*

measurements, such as what is required for *in vivo* EPR nail dosimetry.

Surface dielectric resonators appear to be promising in the development of EPR dosimeters for *in vivo* nail dosimetry and other biological applications of EPR measurements as a result of their unique high-Q resonance mode, a single resonance response, high filling factor, high sensitivity and ease of cleaning of unwanted contaminants from the dielectric substrate with previously identified cleaning procedures.

REFERENCES

1. Kaifez, T. D. and Guillon, P. *Dielectric Resonators* (Atlanta, GA: Nobel) (1998).
2. Blank, A., Stavitski, E., Levanon, H. and Gubaydullin, F. *Transparent miniature dielectric resonator for electron paramagnetic resonance experiments*. *Rev. Sci. Instrum.* **74**(5), 2853 (2003).
3. Schelkunoff, S. A. and Friis, H. *Antennas Theory and Practice* (New York: John Wiley and Sons, Inc.) (1952).
4. Petryakov, S., Samouilov, A., Kesselring, E., Wasowicz, T., Caia, G. L. and Zweier, J. L. *Single loop - multi gap resonator for whole body EPR imaging of mice at 1.2 Ghz*. *J. Magn. Reson.* **188**(1), 68–73 (2007).
5. Poole, C. P. *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*. 1st Ed. (New York: Wiley) (1983).
6. Grinberg, O., Sidabras, J. W., Tipikin, D., Krymov, V., Mariani, M., Feldman, M., Kmiec, M., Petryakov, S., Brugger, S., Carr, B., Schreiber, W., Swarts, S. G. and Swartz, H. M. *Dielectric-backed aperture resonators for x-band in vivo EPR nail dosimetry*. *Radiat. Prot. Dosim.* [this issue].
7. Dykstra, R. W. and Markham, G. D. *A dielectric sample resonator design for enhanced sensitivity of EPR spectroscopy*. *J. Magn. Reson.* **69**(2), 350–355 (1969).
8. Sienkiewicz, A., da Costa Ferreira, A. M., Danner, B. and Scholes, C. P. *Dielectric resonator stopped-flow electron paramagnetic resonance*. *J. Magn. Reson.* **136**(2), 137–142 (1999).
9. Mett, R. R., Sidabras, J. W., Golovina, I. S. and Hyde, J. S. *Dielectric microwave resonators in TE₀₁₁ cavities for electron paramagnetic resonance spectroscopy*. *Rev. Sci. Instrum.* **79**(9), (2008).
10. Webb, A. *Cavity- and waveguide-resonators in electron paramagnetic resonance, nuclear magnetic resonance, and magnetic resonance imaging*. *Prog. Nucl. Magn. Reson. Spectrosc.* **83**, 1–20 (2014).