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Uniform Field Resonators for EPR Spectroscopy: A Review

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Abstract

Cavity resonators are often used for electron paramagnetic resonance (EPR). Rectangular TE₁₀₂ and cylindrical TE₀₁₁ are common modes at X-band even though the field varies cosinusoidally along the Z-axis. The authors found a way to create a uniform field (UF) in these modes. A length of waveguide at cut-off was introduced for the sample region, and tailored end sections were developed that supported the microwave resonant mode. This work is reviewed here. The radio frequency (RF) magnetic field in loop-gap resonators (LGR) at X-band is uniform along the Z-axis of the sample, which is a benefit of LGR technology. The LGR is a preferred structure for EPR of small samples. At Q- and W-bands, the LGR often exhibits nonuniformity along the Z-axis. Methods to trim out this nonuniformity, which are closely related to the methods used for UF cavity resonators, are reviewed. In addition, two transmission lines that are new to EPR, dielectric tube waveguide and circular ridge waveguide, were recently used in UF cavity designs that are reviewed. A further benefit of UF resonators is that cuvettes for aqueous samples can be optimum in cross section along the full sample axis, which improves quantification in EPR spectroscopy of biological samples.

Keywords

Uniform field; EPR; Loop-gap resonator; Ridge waveguide; Dielectric tube resonator; Q-band; W-band

Introduction

When observing the electron paramagnetic resonance (EPR) signal from a microwave cavity, such as a cylindrical TE₀₁₁ or rectangular TE₁₀₂ cavity, the microwave magnetic field (H_1) varies as a cosine in intensity along the axis of the sample (Z-axis¹). Many EPR samples are

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¹In this work, we define the static magnetic field (H_0) to be along the X-axis and, therefore, the RF magnetic fields along Y- and Z-axes give rise to EPR transitions.

in capillaries that extend through the cavity, which results in variation of the microwave radio frequency (RF) magnetic field along the axis of the sample.

In ordinary continuous wave (CW) EPR at nonsaturating incident microwave powers, the spectral response varies in absolute intensity but not in relative intensity across the spectrum. Therefore, the only consequence of microwave field variation along the sample is loss of signal intensity. The spectral shape is unaffected.

If the relative response of the sample at a particular spectral point is not linearly proportional to H_1 , this is evidence that CW saturation effects are occurring. The relative response of the sample across the spectrum in this case depends on the variation of H_1 along the sample. Most pulse EPR experiments, as well as CW saturation-type experiments, belong to this category. In this review article, we summarize microwave cavity design approaches that have been made to achieve sample-axis uniformity of the component of H_1 that is orthogonal to H_0 in commonly used microwave cavities.

A solution to the problem of cosinusoidal variation of field intensity along a sample tube is proposed in a series of publications (1–4). Figure 1, derived from these papers, illustrates three methods of generating matching end sections that can be used with cylindrical TE_{011} electromagnetic field distributions at the operating frequency of the central waveguide, which is designed to be at the cut-off condition. The cut-off condition of a waveguide is defined as the lowest frequency of propagation and is only a function of the waveguide cross section, not the length. In microwave engineering and communications, it is commonly known that a waveguide is operable only above the cut-off frequency. As the operating frequency approaches the cut-off frequency, the wavelength inside the waveguide approaches infinity and the phase velocity approaches zero, impeding wave propagation. When the operating frequency is below the cut-off frequency, the propagating wave becomes evanescent at a rate proportional to the operating frequency. When the operating frequency is strictly at the cut-off frequency, the wavelength is infinite. At the cut-off condition, it is instructive to compare the magnetic field in the waveguide to the magnetic field in an infinitely long solenoid. A difficulty becomes apparent because Maxwell's equations dictate that the divergence of the magnetic field must be zero. Therefore, for cavity designs, end sections, illustrated in Fig. 1, are devised that are above the cut-off condition and the resonance frequency is tuned (by adjusting the end sections) to the cut-off frequency. This whole structure (cut-off region, end section, and sample) resonates at a single frequency that is determined by the geometry and properly matches the boundary conditions, satisfying Maxwell's equations. Since the central section remains at cut-off, change of length does not alter the microwave resonant frequency, and the variation of H_1 along the axis where the sample lies is minimal. In the middle, it is slightly dishd if the resonant frequency is just below cut-off and slightly domed if it is just above. The first section of this review discusses these pioneering papers.

Recent progress in uniform field (UF) technology for EPR spectroscopy has been in several directions. The first of these is development of methods for improved uniformity of loop-gap resonators (LGRs), particularly at Q- and W-bands (5,6). The LGR exhibits good uniformity along the Z-axis in the range of 1 to 10 GHz, but cosine-like variations appear at higher

frequencies. It is noted that an infinitely long metallic tube with a central loop-gap structure is a type of transmission line having a waveguide length that is greater than a free space wavelength. Methods developed to achieve uniformity in cavity resonators have been extended to LGRs. Other advances that are reviewed here include (a) structures based on circular waveguide that contains dielectric tubes (7), and (b) extension of UF technology to ridge circular waveguide or perhaps other re-entrant metallic geometries (8).

A classification system of sample type was introduced by Hyde to aid in the selection of resonators (9). It is based on three sample categories: dielectric loss, noting that an aqueous sample is particularly challenging; amount of available sample; and whether or not an experiment requiring high microwave power such as CW saturation or pulse EPR is contemplated (9). “Yes” or “no” answers to these three categories lead to eight sample types, which can be an aid in selection of an optimum resonator in the experimental design. Primarily, UF technology is concerned with line samples oriented along the Z-axis. Aqueous samples in capillaries have been considered in much of the UF literature.

The article concludes with a discussion of the impact of UF technology on experimental design for EPR spectroscopy. Although extension of UF technology was a motivation for the paper on dielectric tube resonators (DTRs) (7) as well as the paper on circular ridge re-entrant metallic geometries (8), both can be viewed as enabling extensions of cavity technology to lower microwave frequencies. And at X-band, both designs lead to miniaturization for enhanced sensitivity with samples of limited volume. Hyde *et al.* and Sidabras *et al.* provide new insight into resonator design for EPR beyond the stated goal of achieving UF over the sample (7,8).

The efficiency parameter Λ , introduced by Hyde and Froncisz (10), is useful in evaluating the uniformity of the magnetic field along the sample axis. It is defined as

$$\Lambda = H_1/P_0^{1/2}$$

where P_0 is the microwave power incident on a matched resonator, and H_1 is the value of the RF magnetic field at a point inside the resonator.

Consider an EPR sample speck that exhibits microwave power saturation. Further imagine that a series of experiments is carried out where the position of the sample is varied along the sample axis. The incident microwave power is readjusted in each experiment to bring the sample to the same level of saturation (say a power level that results in half of the signal intensity that would be expected in the absence of power saturation, which is the so-called half power level, $P_{1/2}$). Then, the signal at each point will be proportional to the product ΛV , where V is the sample volume. In this manner, the variation of Λ along the sample can be experimentally determined, and a number that is proportional to the average value, Λ_{ave} , can be calculated. A measure of the uniformity of the field along the sample axis expressed as a percentage is given by the equation

$$\Delta\Lambda = [(\int |\Lambda_{\text{ave}} - \Lambda| dV) / \Lambda_{\text{ave}} V] \times 100\%.$$

Experimental measurements of the uniformity of the efficiency parameter are difficult or impossible in the case of a complex cell geometry filled with aqueous sample. Commercially available finite-element software can be used to calculate the magnetic field, which in turn allows calculation of Λ and its variation along the sample axis. This calculation can be carried out in sample geometries that include, for example, the complex valued dielectric constant of an aqueous sample as well as the dielectric constant of the wall of the sample tube. In these cases, the calculation of Λ can influence the choice between alternative sample-cell geometries.

Uniform Field Cavity Resonators

A UF cavity consists of three sections: a center section and two end sections. See Fig. 1, which is based on the cylindrical TE_{011} cavity. The three structures in this figure are each the subject of a paper (1–3), and these three papers are the foundation of UF EPR cavity design. The papers also consider UF modes based on the rectangular TE_{102} mode. The center sections, which contain the sample, are identical in Fig. 1. They are designed using the equation for the resonant frequency of the cylindrical TE_{011} mode by assuming that the cavity length has been set to infinity, which implies that the guide wavelength is infinite. A value for the radius of the center section is then known. The length of the center section can be any value, as determined by the particular experiment of interest.

Three types of end sections were analyzed. In each type, it can be imagined that if the two end sections were joined, a resonant cavity, called a matching pseudocavity, would be formed that was $\frac{1}{2}$ wavelength long. For Fig. 1c, the matching pseudocavity would be completely filled with dielectric and would have the same diameter as the center section. For Fig. 1a, there is a challenge, since the end section diameter is greater than the central section, and a septum joins the end sections to the center section. The septum is indicated in Fig. 1a by horizontal lines $\lambda/4$ from the ends of the structure. The matching pseudocavity must include the septum, and lines of RF magnetic flux must flow around it. Nevertheless, it resonates at the same frequency as the other matching pseudocavities, Refs. (1–3), and the fields closely resemble the cylindrical TE_{011} mode.

The matching pseudocavity formed from Fig. 1b has the same diameter as the center section. It contains two re-entrant nine-element rings. Each ring consists of nine metal sectors cut from a closed circular loop with dielectric material separating adjacent sectors. It is a ring of capacitors that are electrically in series because of the metal sectors. Again, the fields of the matching pseudocavity closely resemble the cylindrical TE_{011} mode and could be characterized as a two-loop-nine-gap LGR.

In general, it can be said that the purpose of the end sections is to provide a return path for the lines of magnetic flux that flow over the sample and back along the cylindrical walls. They provide a proper impedance match to the open ends of the central section of the resonator, which require an effective “open” circuit. The cut-off frequency of the matching

pseudocavity will always be lower than the central section in order to allow propagation at the central cut-off frequency.

The end sections are compared in the third foundation paper (3). The transition regions between end and central sections in particular are analyzed. The dielectric end section of Fig. 1c is ideal in the transition region facing the central section, since the RF fields ($H_{\perp}$, $E_{\parallel}$) are required to be continuous across the interface between the end and central sections in this geometry. However, the region changes less abruptly along the Z-axis when a hole is made in the dielectric for a sample or a Dewar insert. Another problem is that the Q-value is somewhat lower because placement of the dielectric against metallic walls increases RF currents in the metal that are induced by the adjacent intense RF magnetic field.

The geometry of Fig. 1a has been most widely used because it is so convenient. It would appear to be the only practical way to design a dielectric tube UF resonator, as discussed later in this paper. It is remarkable that the uniformity of the RF magnetic field in the central section can be fully maintained even by end sections with large, abrupt cross-sectional discontinuities. The central section acts as a spatial filter supporting only the fundamental UF mode. The transition region is analogous to the localized fields near discontinuities in waveguides. In Fig. 1a, the transition region is somewhat long, which affects the uniformity of the magnetic field along the entire sample. Although in the preceding portions of this section we limited the discussion of UF cavities to the cylindrical TE_{01U} mode, Refs. (1–4) also consider UF versions of the familiar rectangular TE_{102} mode. The first practical uniform field cavity in this mode was developed at W-band (5) and is pictured in Fig. 2. It is based on the “septum” design of Fig. 1a. It was designed to accommodate so-called “flat cells,” and to allow sample irradiation of the plane of the sample with light from a small laser through a slotted array. A dual iris was developed, which is described in the paper. It is apparent that the RF field is uniform both along the Z-axis, and also along the axis corresponding to the “0” index. See Fig. 2c. A shield structure is shown in Fig. 2b that prevents contributions to the signal from sample material in the end regions. The shield thickness of 0.1 mm is accounted for in the simulation of the end section and is designed to be of practical dimensions with minimal perturbation.

The geometry of Fig. 1b has not been explored as much because of difficulties in construction. However, with the advancement of lithography techniques, this geometry may prove useful in reducing the end section length, thus reducing the need for a sample shield.

Study of the papers under review in this section will reveal a number of ways in which further progress can be made in development of UF technology for EPR. Some of these are listed below.

- The sample and sample tube can alter the UF condition by changing the cut-off condition. This perturbation is discussed by Mett *et al.* (1). UF resonators can be optimized for particular samples and sample tubes.
- UF resonators can be designed for use with Dewar inserts, as shown in Ref. (11), resulting in temperature-controlled UF EPR spectroscopy.

- Cutting of slots in the walls of the cylindrical TE₀₁₁ cavity to allow penetration of 100 kHz magnetic field modulation is a common practice. Application of UF technology to the rectangular TE₁₀₂ class of resonators is expected to enable extension of the slot cutting approach to this familiar EPR cavity.
- Cutting of slots for improved light irradiation can be facilitated, as described in (5).
- UF resonators can be optimized for specific types of aqueous sample cuvettes including flat cells and the various geometries discussed by Sidabras *et al.* (12) and Hyde and Mett (13), thereby increasing the concentration sensitivity.
- Shielding of sample tubes (Fig. 2) can probably be developed with the various cuvettes of the previous bullet. It already has been established for the flat-cell sample geometry of (5).
- The concentration sensitivity can be further increased if relatively large amounts of sample are available by optimization of the combination of specific cuvettes and the overall length of the UF sample region, which is limited only by the available microwave power to compensate for the reduction of resonator efficiency.
- An increase of concentration sensitivity using UF technology may be particularly useful at high frequencies—Q- and W-bands for example—because the sample volume is very small nevertheless.
- The UF technology can be extended to the spherical mode, which results in hemispherical end sections and an increase in Q-value.
- The diameter-to-length (D/L) ratio of the UF sample region is a free parameter, allowing improved performance not only for central regions as long as one or two free space wavelengths, but also with somewhat short central regions that are tailored in length to specific samples.

Uniform Field Loop-Gap Resonators

The LGR was originally developed for use in the microwave frequency range of 0.5 to 8 GHz, where cavity resonators are too large to be practical (10). It was soon extended to X-band for EPR studies of spin-labeled proteins. Initially, there were two motivating aspects for the extension to X-band: relative to a cavity, the amount of required protein was less, and, in addition, the Λ -value was higher. These benefits allowed experiments to be performed at higher values of H_1 at the sample for the available microwave power. Specifically, measurement of the accessibility of the spin-labeled site to dissolved molecular oxygen by CW saturation became feasible. Studies of this type over a range of spin-labeled sites, which is called “spin scanning,” yielded useful information about molecular structure. The small sample size enabled more samples to be prepared without requiring excessive amounts of protein.

An additional benefit of X-band LGRs was soon recognized: the uniform microwave field along the sample access yielded improved data for all EPR experiments at high microwave

fields, including pulse EPR. At X-band and lower, the uniformity of the RF microwave magnetic field over the sample was found to be very good, as expected, because the lumped-circuit model for the structure worked well. However, it was natural to extend LGR technology to higher microwave frequencies. Development of LGR technology at Q- and W-bands took place that was driven by the very high Λ -values as well as broadband performance because of the low Q-values. At Q- and W-bands, dimensions of the LGRs can be of the order of magnitude of the wavelength, 1 cm to 3 mm, and standing waves can lead to nonuniformity of H_1 along the sample tube. Formation of cosinusoidal variation of the intensity of the RF field along the sample axis is due to the LGR electric and magnetic fields becoming more distributed in the geometry. This problem is considered in this section.

Figures 3a and 3a' show preferred LGR cross sections for X-band and lower frequencies, 3b and 3b' for Q-band, and 3c and 3c' for W-band. Here, Figs. 3a,b,c have rather small sample loops, resulting in high values of the resonator efficiency parameter Λ , while corresponding Figs. 3a',b',c' have larger sample loops, allowing increased sample volume. The figure illustrates one aspect of the tradeoff that is possible between sample volume and Λ -value. The other aspect is the length of the sample loop, which affects both volume and Λ -value.

The RF electric field vectors in the structures of Fig. 3 lie in planes that are perpendicular to the sample axis. Thus, the microwave modes in an LGR can be classified as "transverse electric" (TE) with a propagation direction that is parallel to the axis of the sample loop and perpendicular to the planar cross sections illustrated in the figure. This review article concerns uniformity of the RF magnetic field H_1 along the sample axis. It is based on two published papers, one at Q-band and one at W-band (5,6).

The three-loop-two-gap LGR was first described by Wood, Froncisz, and Hyde for use in the 2 to 4 GHz range (14). The LGR was extended to Q-band by Froncisz, Oles, and Hyde using a two-loop-one-gap design (15). A three-loop-two-gap resonator was used by Hyde *et al.* (16) at Q-band as part of their multifrequency study of spin label T_1 values. Mett *et al.*, following a suggestion by Froncisz, developed an analytical model at Q-band for the LGR (6). Further insight was that an LGR can be modeled as ridge waveguide. It followed logically that the three methods that were first developed to produce a UF in rectangular or cylindrical waveguide-based cavities at X-band (1–3) could be extended to Q-band. These authors carried out the LGR analysis using the ridge waveguide analogy and validated it using finite-element calculations. They considered a resonator with the configuration of Fig. 3b. (See the figure caption.)

Conclusions of their work can be summarized as follows: (a) The sample can be more than one wavelength long with near-perfect uniformity along the sample tube, see Fig. 4. Not only is the quality of the data improved, but also the concentration sensitivity can be increased. (b) A limitation arises if the length is sufficient to allow higher-order modes. (c) Residual RF fields at the ends of the resonator become negligible over a distance along the sample tube that is of the order of the inner diameter of the LGR. Figure 4 is extensively discussed in Ref. (6).

Point (c) is under continuing development. It is possible to introduce a metallic shield to eliminate the RF magnetic field “seen” by the sample as it passes through the end regions where the LGR is “trimmed,” as illustrated in Fig. 4. In this case, the RF field becomes negligible in a distance along the sample tube that corresponds to the inner diameter of the shield, which approximately equals the outer diameter of the sample tube, rather than the inner diameter of the LGR.

Sidabras *et al.* extended the LGR technology to W-band, 94 GHz, and compared the results with a cylindrical TE₀₁₁ cavity tuned to the same frequency (17). The LGR configuration resembled Fig. 3c'. They found that the sensitivities were similar, but the bandwidth of the LGR was much higher. The high bandwidth enabled the frequency sweep studies of Hyde *et al.* (18) and led to a full paper on broadband W-band (19).

Sidabras *et al.* developed a UF W-band LGR in 2017 (5). It has six outer loops, which enabled the sample diameter to be increased relative to the previous design. It is an interesting observation that LGR technology can allow the sample loop not only to be extremely small, but also can permit somewhat larger aqueous sample tubes than normally are used with cavity resonators. Increase of diameter facilitated the introduction of the gas exchange method for sample degassing. Mainali *et al.*, working under the direction of W. K. Subczynski, applied this LGR to saturation recovery studies of samples prepared from the eye lenses of a single human donor (20). This is felt to be a particularly significant application of UF technology. Use of UF methods contributes to the development of quantitative saturation recovery EPR, since all portions of the sample respond to the saturating pulse and the observing field in the same way.

Uniform Field Dielectric Tube Resonators

The DTR was introduced by Hyde and Mett in 2017 (7). Their work was motivated by the early patent by Rempel *et al.*, which discloses the use of a quartz Dewar inserted into an X-band cavity for temperature control (11). It was immediately discovered that insertion of the Dewar at room temperature resulted in shift of the resonant frequency to a lower frequency accompanied by increase in EPR signal intensity of a standard sample by about a factor of two. Mett and Hyde investigated this effect using computer modeling of various tubes inserted into cylindrical TE₀₁₁ cavities of various sizes such that the resonant frequency remained always constant at 9.5 GHz (X-band). They systematically varied the diameter of the dielectric tube and the value of the dielectric constant while maintaining a hole in the center for a sample tube. The D/L ratio of all resonators was set to one. The dielectric tubes abutted the ends of the cavity with no provision for actual sample tube insertion. Tube dimensions were as small as a conventional sample tube and could be sufficiently large to fill the resonator. Dielectric constants introduced to the model were 4 (quartz), 10 (sapphire), and 100 (rutile, TiO₂).

For each dielectric, two densely populated colorized contour plots were produced. See Fig. 5. To use these plots, the wall thickness and average radius of the dielectric tube are found on the X- and Y-axes. The first contour plot provides the diameter of the DTR, and the second contour plot provides the Λ -value. Calculations were based on the analytical

formulation and confirmed at selected points by finite-element calculations, which also yielded three-dimensional plots of the RF electric and magnetic field vectors or magnitudes.

Q-values were also calculated and found to be somewhat lower than pure-mode dielectric resonators because of RF currents in the cavity walls. The DTR resonator is not the same structure as a dielectric resonator: it can be viewed as an intermediate or hybrid structure that lies between the pure-mode dielectric resonator and the free-space metallic resonator. The waveguide can be characterized as a partially filled waveguide and, therefore, the cut-off frequency is reduced according to the percentage filled, placement, and dielectric constant.

For rutile, the resonator sample volume at X-band was 1000-fold smaller than the corresponding free space structure. Dimensions were in fact similar to those of a free space cylindrical resonator at W-band. It was apparent that the inner diameter for the sample tube could be manipulated to optimize performance for a selected sample volume. A conclusion is that the rutile DTR would allow multifrequency studies, say W- and X-bands, on a sample with very limited volume. For some samples, particularly spin-labeled proteins, the free-space cylindrical TE_{011} cavity is somewhat large at X-band.

The DTRs can be sufficiently small that they can be inserted into a Dewar, which can be expected to yield increased temperature stability. There is a two-fold benefit: reduced problems from the temperature dependence of the dielectric, and more precise control of the temperature of the sample.

Finite-element calculations were required to develop a UF DTR. The methods follow the published papers on free-space UF design. The dielectric tube has constant cross-sectional dimensions, end-to-end. The diameter of the cylindrical metallic cavity walls is smaller in the central UF region and larger in the end sections to achieve uniformity. The length of the central section is arbitrary up to a wavelength or two. See Fig. 6. A tentative conclusion of the paper is that a sapphire DTR might be a useful general-purpose EPR cavity.

The work described here is an example of design by computers rather than the trial-and-error of most previous resonator design publications. The design approach allows optimization of multiple interacting design parameters. The next steps involve the development of microwave power coupling structures, sample tube openings and supports, and field modulation slots. An effort was made in Ref. (7) to cite every paper on dielectric resonators. This was done in part as a convenience to the reader, and in part to define the difference between the dielectric resonator and the DTR. The presence of the surrounding metallic wall of the DTR is expected to be central to the development of practical configurations.

Uniform Field Q-Band EPR Cavity Using Ridge Circular Waveguide

This section is based on improving the quality of pulse EPR at Q-band relative to a standard TE_{011} cavity of about 1 cm length, and reviews the work of Sidabras, Reijerse, and Lubitz (8). The standard sample tube used in the laboratory of the authors is a quartz capillary 2.8 mm outer dimension, 1.8 mm inner dimension. The sample volume it follows is typically 25 μ L. Frozen aqueous samples are envisaged. Presumably, the sample can be classified as having negligible dielectric loss and being readily saturable. The design goal was to achieve

a uniform Λ -value over the entire region of interest that was the same as could be achieved at the center of the standard cavity. This would result in improved quality of the data, and in addition would yield increase of sensitivity.

For any waveguide, propagation can be described by a series of modes, beginning with the lowest frequency, or fundamental mode. For the microwave frequency of interest, there will always exist a fundamental resonant cavity if the waveguide is terminated at the ends and the length is one half of a guide length. This paper is based on quadruple-ridge circular waveguide. C-C Chen is credited in the literature for the earliest report of circular waveguide with internal ridges (21). The paper under review here may be the first report of a resonant cavity based on ridge circular waveguide.

A. J. Sangster and J. Grant published a study of modes in ridge circular waveguide (22). Figure 7, reproduced from their paper, illustrates dual-ridge geometry (upper semicircle when mirrored in the horizontal diameter), quad-ridge geometry (lower left quadrant when mirrored in the horizontal and vertical diameters), and octo-ridge geometry (lower right quadrant suitably mirrored). Each ridge has two free parameters, labeled “w” and “h” in Fig. 7, resulting in a parameter space of some complexity.

Figure 8 illustrates the quad-ridge cross section used by Sidabras *et al.* (8). The text refers to the ridges as “fins.” They rounded off the ends of the ridges, selected a reasonable value for the “w” parameter, and varied the “h” parameter for best performance. The length of the ridges was 10 mm, and the end sections were filled with polystyrene (Rexolite) to satisfy the condition for uniformity following the techniques previously published (1–3). Figure 9 superimposes simulated profiles of the RF magnetic field along the axis of the UF and standard cavities normalized to the same peak intensity. The benefit of the UF cavity is apparent.

One consequence of using ridge waveguide in the cut-off section is the opportunity to use a combination of matching methods in the pseudocavity end sections. In the work of Sidabras *et al.* (8), a matching pseudocavity that combines Fig. 1a and Fig. 1c was used. Since the ridges lower the cut-off frequency of the waveguide, the overall diameter must be decreased to maintain the frequency. By removing the ridges in the end section but keeping the overall diameter constant, the cut-off frequency of the matching pseudocavity is decreased. Inserting dielectric material in this region further reduces the cut-off frequency. The height is adjusted to match the UF condition. This combination significantly reduces the needed length of the end sections. The advantage of this technique is illustrated by the simulations shown in Fig. 9, where the overall length of the resonator is reduced by approximately 4 mm compared with a UF resonator designed by using the matching pseudocavity of Fig. 1a. This diminishes the need for a sample shield compared with other UF cavities.

A notable feature of the paper by Sidabras *et al.* is the use of the EPR nutation technique to demonstrate improvement in pulse data by employing UF technology (8). It is well known that for a point sample in a microwave cavity, the nutation length diminishes at an exponential rate related to T_2 . As the sample fills the cavity, it is affected by nonuniformities of the microwave magnetic field and destructive interference reduces the nutation length. By

comparing the nutation lengths, a quantitative evaluation of the resonators can be performed. Experimental sensitivity profiles were also measured using the technique of “perturbing metal spheres” (23) and found to be in good agreement with simulations. The peak Λ -value in the UF cavity was only about 40% of that in the standard cavity. However, the UF cavity was prototyped in brass; significant improvement can be expected from the use of silver.

It is apparent that there is a certain similarity of the UF quad-ridge circular waveguide structure used by Sidabras *et al.* at Q-band (8) and the LGRs used by Sidabras *et al.* at W-band (5). Since it was established that LGRs can be modeled as ridge waveguides, the re-entrant TE_{01U} geometry explores the gap between LGRs and microwave cavities. The Q-band UF cavity design would appear to be suitable for larger samples than the LGR designs, although there may be overlap where either approach could be used for a particular sample size. Additionally, the ridged geometry provides a reduction of electric field in the sample, similar to LGR geometries, by better defining electric potentials between the ridges, Fig. 8c. This has an effect on the interaction of the sample dielectric and the cut-off frequency of the ridged UF resonator. Simulations show a 40% reduction of cut-off frequency shift compared with a UF resonator designed by the method of Fig. 1a.

Finally, Y. Rong considered generalized rectangular and circular ridge waveguide (24). Although most of his attention was paid to rectangular guide, analysis was carried out on one circular structure of low symmetry. He called it the “Double Antipodal Ridge Circular Waveguide.” Rong’s point of view is quite different from that of the EPR spectroscopist, but it is appropriate to realize, as he did, that the range of possible waveguide cross sections is without limit. Finite-element software allows this design parameter space to be probed.

Concluding Remarks

Variation of the RF magnetic field over the sample should be avoided for quantitative EPR, experiments carried out under saturating powers, passage experiments, and pulse experiments. Additionally, as arbitrary waveform generators become more commonplace in the EPR setup, the interaction of the microwave magnetic field, which can vary along the sample axis, with the EPR sample becomes increasingly important. The use of UF resonators as described in this article is a general approach to satisfy these requirements. A simpler approach is to use short samples that lie near the center of the resonator, but this has a disadvantage of reducing EPR sensitivity, and sample placement becomes tedious.

Development of a capability for resonator design and construction has become a realistic alternative because of the commercial availability of finite-element computer programs. For example, in Ref. (7), the finite-element simulations were done using ANSYS High-Frequency Structure Simulator (HFSS) (Canonsburg, PA) version 17.1 running on a Dell Precision Tower 7910 with 24 Intel Xeon dual-core processors with hyper-threading and 512 GB of RAM. Upgrades are frequent. In addition, ultraprecision electric discharge machining, which is available in many urban centers and major research institutions, is commonly used for construction. AutoDesk Inventor (or similar 3D CAD software) provides a useful interface between computer-simulated geometries and production. High-end manufacturers accept 3D geometry files (*e.g.*, STL, STP, IGES) and directly program the

geometries into CNC (computer numerical control) machinery. Commercially available custom PTFE (polytetrafluoroethylene) extrusions and tubing in many sizes provide convenient sample tubes. Reference (12) provides access to the work of the authors in their development of this capability.

We have used high purity silver, and have refined the use of slots to allow penetration of magnetic field modulation. The Λ -value is so high in many resonators that incident power is no longer a source of noise. In addition, use of low-noise amplifiers greatly reduces receiver noise. The fundamental rationale for use of 100 kHz field modulation was re-examined in a recent study at W-band (19). Use of lower field modulation frequencies will not lead to a decrease in the signal-to-noise ratio in many experiments, which alleviates one of the main difficulties in construction of self-designed resonators.

Mention has been made of two potential problems when using UF resonators. The first of these is that the dielectric properties of the sample as well as sample-tube affect the microwave cut-off frequency and should be included in the design. The second is that if the sample is exposed to microwave fields in the end sections, the benefits of the UF technology are reduced. The UF ridge cavity addressed both of these issues. Figure 4 illustrates the use of a metallic shield around the sample tube in the end sections, which effectively solves the second problem.

The general point is made that every microwave transmission line can be the basis for development of a UF cavity. The choice that is made depends on the sample and the experiment. Rectangular, circular, ridge rectangular, and circular ridge waveguides have been considered here. The addition of a dielectric material of any shape and placement extending along the inner space of any of these four metallic waveguides leads to another transmission line. One might collectively label these as dielectric tube waveguides. A centered tube in a circular waveguide is the basis of the DTR.

Waveguides and cavities are known as distributed circuits. They explicitly involve electromagnetic fields and are analyzed by Maxwell's equations. Dimensions are typically about the same as a wavelength, which leads to a practical value of about 1 GHz as the lowest frequency that can be labeled "microwave." At sufficiently low frequency, the engineering vocabulary changes to "resistors, capacitors, and inductors," which are known as lumped circuit components.

The LGR was originally conceived as a lumped circuit structure that could be used at microwave frequencies because it was so small. The lumped circuit vocabulary works well at 10 GHz and lower frequencies. At higher frequencies, 140 GHz being the highest thus far, the LGR is a hybrid structure where the lumped circuit vocabulary is useful in considering the cross section, and distributed circuit concepts become useful in discussing the dimension along the sample tube. One might say that the LGR at high frequencies is based on an "incipient" transmission line. The RF field along the sample begins to exhibit sinusoidal properties due to mismatched impedances at the ends. The homogeneity can be made uniform using methods that are similar to those developed for microwave cavities.

The authors and their colleagues have published a number of papers on use of aqueous sample cuvettes, Refs. (12,25,26). Three principles of design were recognized: first, constraining the sample to a region of zero RF electric field; second, constraining the sample to regions that are perpendicular to the RF electric field, which results in a discontinuity of the electric field vector; and, third, use of bundles of capillaries where the fields in each capillary can be characterized as arising from two lines of polarization charges. True optimization of cuvettes based on these three principles would lead to different dimensions along the sample in the case of a cosinusoidal variation of electric field, but this is impractical. Use of these structures in UF resonators leads to cuvettes that are uniform and optimum along the sample axis (13). One must recognize that use of aqueous sample cuvettes may affect the cut-off condition in UF resonator design. However, since the effect of the aqueous sample dielectric properties on the resonant frequency is minimal when using these cuvettes, this possible complication may not be significant.

Since the introduction of UF cavities, several practical designs have been implemented and used as general-purpose resonators. Current developments of UF resonators show the diversity of resonant geometries useful for EPR spectroscopy. The usefulness of these geometries will only increase as more complicated pulse sequences and non-linear EPR experiments are envisioned.

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Figure 1.

Methods for creating UFs in cavities. Region of interest at cut-off is matched to end-section (a) oversized with connecting septum, (b) re-entrant ring with capacitive posts (black circles), (c) dielectric section of length $\lambda/4$. Magnetic field vectors are illustrated with dotted lines (Figure derived from (5)). Reprinted from Journal of Magnetic Resonance, 282, JW Sidabras, T Sarna, RR Mett, JS Hyde, Uniform Field Loop-Gap Resonator and Rectangular TEU02 for Aqueous Sample EPR at 94GHz, 129-135, Copyright 2017, with permission from Elsevier.)

Figure 2.

(a) Half-structure drawing illustrating the W-band rectangular TE_{U02} geometry with oversized end-sections, sample access port, light access, and sample end-section shield, (b) magnetic field magnitude profile showing the 6 mm region-of-interest, and (c) magnetic field magnitude profile with dual iris (thickness 0.1 mm) and sample placement (dashed). Dotted line represents the cavity wall illustrating the light access slots beyond cut-off. Red is large magnetic field and dark blue zero magnetic field

Figure 3.

LGR cross sections. Shaded areas are sample loops. **a,a'** are one-loop-one-gap; **b,b'** are three-loop-two-gap; **c,c'** are five-loop-four-gap. **a,b,c** have small sample loops and large return flux loops. **a',b',c'** have inner and outer loop sizes reversed

Figure 4.

Cross-sectional profiles of axial RF magnetic field energy H_z^2 in a plane bisecting the three-loop-two-gap resonator through the gaps obtained for the $n = 0$ mode by computer simulation. Red to blue indicates a maximum to zero intensity. (a) 1 mm long LGR. (b) 10 mm long LGR, untrimmed for RF magnetic field uniformity. (c) 10 mm long LGR, trimmed for RF magnetic field uniformity using metal strips bridging the gaps (Figure obtained from (6). Reprinted by permission from Springer Customer Service Centre GmbH: Springer Nature, Applied Magnetic Resonance, Uniform radio frequency fields in loop-gap resonators for EPR spectroscopy, RR Mett, JW Sidabras, JS Hyde, 2007.)

Figure 5. Contour plots of the cavity radius (**a**) and lambda value (**b**) for sapphire as functions of the average tube radius and thickness at 9.5 GHz (Figure obtained from (7). Reprinted by permission from Springer Customer Service Centre GmbH: Springer Nature, Applied Magnetic Resonance, EPR Uniform Field Signal Enhancement by Dielectric Tubes in Cavities, JS Hyde, RR Mett, 2017.)

Figure 6.

Cross-sectional views of the magnitude of (a) electric field and (b) magnetic field inside a metallic cavity designed with two end sections that support an axially uniform RF field in the central section. The polycrystalline dielectric tube extends uniformly along the axial extent of the structure (Figure obtained from (7). Reprinted by permission from Springer Customer Service Centre GmbH: Springer Nature, Applied Magnetic Resonance, EPR Uniform Field Signal Enhancement by Dielectric Tubes in Cavities, JS Hyde, RR Mett, 2017.)

Figure 7. Visualization of a dual-, quad-, and octo-ridge waveguide. The design parameters R , w , h are defined (Figure obtained from (22), reproduced courtesy of The Electromagnetics Academy.)

Figure 8.

(a) Cross-sectional view of the circular ridge waveguide. (b) Side view of the reentrant cavity showing region-of-interest. (c,d) Ansys HFSS simulations corresponding to a and b (Figure obtained from (8). Quantitative data on Fig. 8d are given in Table 1 (8). Reprinted by permission from Springer Customer Service Centre GmbH: Springer Nature, Applied Magnetic Resonance, Uniform Field Re-entrant Cylindrical TE_{01U} Cavity for Pulse Electron Paramagnetic Resonance Spectroscopy at Q-band, JW Sidabras, EJ Reijerse, W Lubitz, 2017.)

Figure 9.

Ansyz HFSS simulation showing the normalized H_1 field of the cylindrical re-entrant TE_{01U} (short dashed line) compared with the cylindrical TE_{011} cavity (long dashed line). The vertical dotted lines mark the region-of-interest. The solid line was calculated using the method of Fig. 1a for the matching pseudocavity