**United States Patent** [19]

**Hyde**

[11] **3,757,204**

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[54] **CAVITY RESONATOR STRUCTURE FOR AN EPR SPECTROMETER EMPLOYING DIELECTRIC MATERIAL FOR IMPROVING RF ELECTRIC AND MAGNETIC FIELD UNIFORMITY ALONG THE SAMPLE**

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[73] Assignee: **Varian Associates**, Palo Alto, Calif.

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[21] Appl. No.: **229,788**

[52] **U.S. Cl.** .................................. **324/0.5 R**, 333/83

[51] **Int. Cl.** .............................................. **G01n 27/78**

[58] **Field of Search** ................... 324/0.5 R, 0.5 AH, 324/0.5 AC, 58.5 C, 58 C; 333/24.1, 24 G, 83

[56] **References Cited**

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*Primary Examiner*—Michael J. Lynch

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[57] **ABSTRACT**

In an electron paramagnetic resonance cavity resonator having a line sample therein, a dielectric material positioned near the sample and along at least a portion of its length, and extending into the RF electric field region near the sample, changes the gradient of the electric field intensity and, as a result, the RF magnetic field intensity along the line sample so as to make both the RF electric and magnetic field intensities more uniform along the sample length. The dielectric material may take the form of a shaped sleeve surrounding the sample, or two shorter sleeves extending over the sample from either end and spaced apart at the center region, or parallel plates on either side of the sample,

**12 Claims, 7 Drawing Figures**

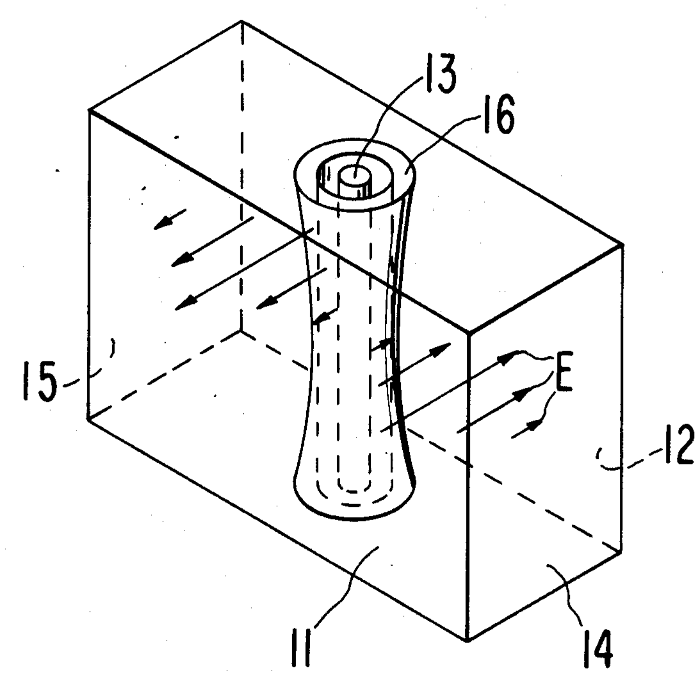


FIG.1

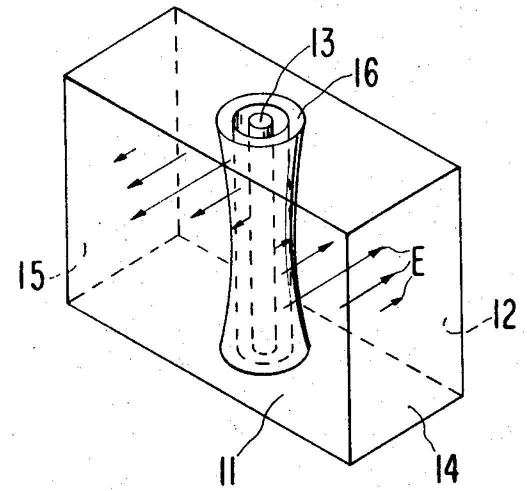



FIG.2

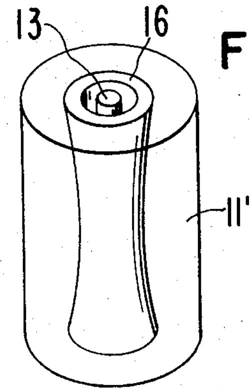



FIG.6

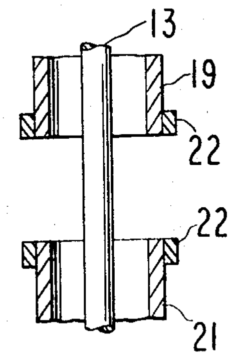



FIG.4

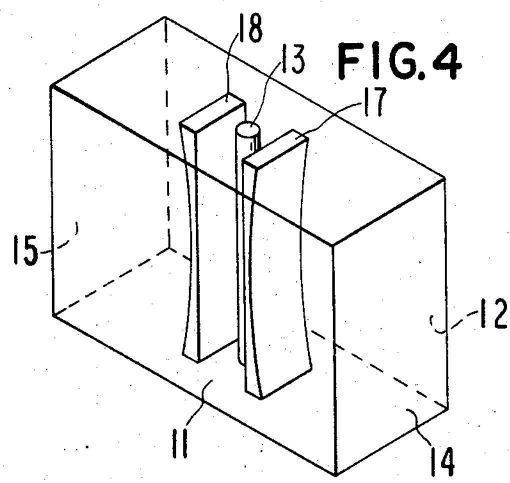



FIG.5

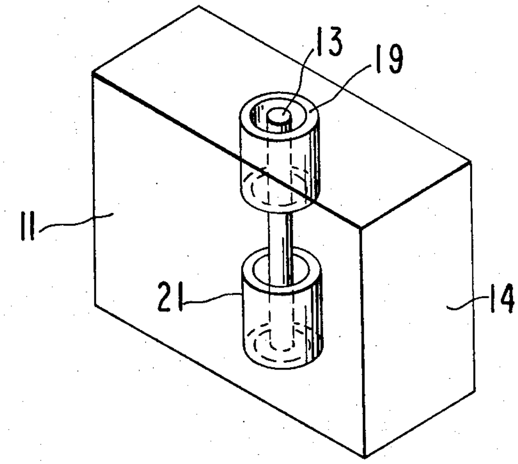



FIG.7

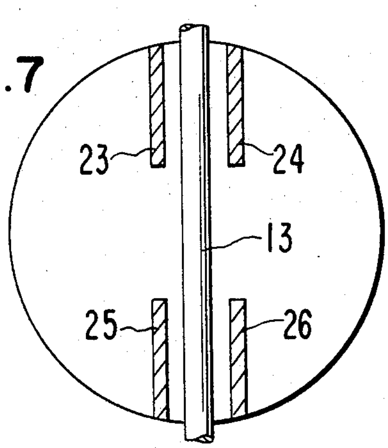
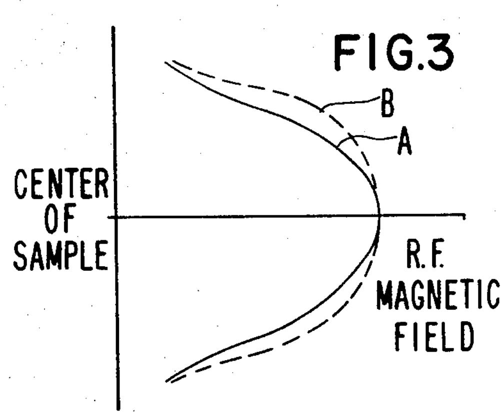



FIG.3



# CAVITY RESONATOR STRUCTURE FOR AN EPR SPECTROMETER EMPLOYING DIELECTRIC MATERIAL FOR IMPROVING RF ELECTRIC AND MAGNETIC FIELD UNIFORMITY ALONG THE SAMPLE

## BACKGROUND OF THE INVENTION

The two most widely used cavity resonators in electron paramagnetic resonance spectrometers are the rectangular $TE_{102}$ mode and the cylindrical $TE_{011}$ mode cavities, while the cylindrical $TM_{110}$ mode cavity is used to a much lesser extent. These cavity resonators form one arm of a microwave bridge and are positioned in the magnetic field gap of the polarizing magnet with the elongated sample cell extending down into the cavity along a line vertically through the center of the cavity and parallel to the magnet pole faces. Typical forms of such cavity resonators are shown in U.S. Pat. No. 3,122,703 issued on Feb. 25, 1964 to R.C. Rempel et al entitled "Gyromagnetic Resonance Method and Apparatus" and U.S. Pat. No. 3,197,692 issued June 27, 1965 to J.S. Hyde entitled "Gyromagnetic Resonance Spectroscopy".

The radio frequency power delivered to the cavity resonator at the electron resonance frequency, for example 9.5 GHz, produces the driving RF magnetic field along the sample length, this RF magnetic field intensity varying as sin $(X\pi/L)$, where $L$ is the length of the cavity along the sample and $x$ is the position of a point along the sample length measured from the bottom of the cavity, for the rectangular $TE_{102}$ mode cavity and the cylindrical $TE_{011}$ mode; a somewhat similar function exists for the RF magnetic field intensity in a cylindrical $TM_{110}$ mode cavity. The RF magnetic field intensity is therefore stronger at the central region of the sample length than at the two regions on either end of the central region. As the RF power incident on the cavity increases, that part of the sample at the central region ($x = L/2$) experiences microwave power saturation first, and, if the power continues to increase, the parts of the sample removed from the central region saturate.

Several problems arise because the RF magnetic and electric field intensities are not constant along the line sample extending through the cavity. Measurement of relaxation parameters, for example the spin lattice relaxation time (often called $T_1$) and the spin-spin relaxation time (often called $T_2$), is performed by varying the power incident on the cavity, and, if there is a spatial variation of the RF magentic field intensity along the sample, this presents a difficult problem in making accurate measurements. Also, dielectric heating of the sample may occur, and the change in temperature of the sample may change the resonance characteristics of the sample. Diffusion tends to minimize thermal gradients, but significant temperature variation may still occur along the length of the sample if the RF electric field intensity varies along this length, which makes it difficult to study the resonance characteristics with precision. Additionally, in a specific situation involving nitroxide radical spin labels in water, when the sample is inserted into the cavity the temperature dependence of the dielectric constant of the water causes an undesirable variation in time of the balance of the microwave bridge because of sample heating. The sample is, in addition, relatively easy to saturate with the RF magnetic field. In order to obtain the largest magnetic resonance signal from the sample and at the same time minimize the variation in bridge balance after the sample is inserted into the microwave cavity, it is desirable to have both RF electric and RF magnetic field intensities more nearly constant along the sample length.

## BRIEF SUMMARY OF THE PRESENT INVENTION

In the EPR cavity resonator of the present invention, a dielectric material is positioned in the RF electric field near the sample so as to change the RF electric and magnetic field intensities and to make them more uniform along the sample length, so as to minimize spatial variation of the RF magnetic field intensity along the sample length, minimize thermal gradients along the sample, and/or minimize bridge inbalance while optimizing the magnetic resonance signal output.

In one embodiment, the dielectric material is in the form of a cylinder surrounding the sample and extending into the electric field region in the cavity, the wall of the cylinder being concave with its thinnest portion in the central region of the sample. In a variation of this embodiment, the cylinder is replaced with a pair of dielectric plates, one on each side of the sample, the plates being concave.

In another embodiment, the dielectric is in the form of two hollow cylindrical members extending over the sample regions on either side of the central region, with the central region clear of the dielectric. In a variation of this embodiment, each separate cylinder is replaced by a pair of plates positioned on opposite sides of the sample and in planes normal to the broad sides of the cavity resonator.

## DESCRIPTION OF THE DRAWINGS

FIGS. **1** and **2** are perspective diagramatic views of a rectangular $TE_{102}$ mode EPR cavity resonator and a cylindrical $TE_{011}$ mode EPR cavity resonator, respectively, incorporating one embodiment of the present invention.

FIG. **3** is a plot of RF magnetic field obtained with and without the use of the present invention, illustrating the increase in uniformity of the RF magnetic field along the sample with the present invention.

FIG. **4** is a diagramatic view of another rectangular cavity resonator incorporating another embodiment of the present invention.

FIGS. **5** and **6** illustrate still another embodiment of the present invention.

FIG. **7** is another structural form of the invention as utilized in a cylindrical $TM_{110}$ mode cavity resonator.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. **1**, there is shown a typical form of rectangular $TE_{102}$ mode cavity resonator which is placed in the gap of a strong magnet in an EPR spectrometer such that the two broad sidewalls **11** and **12** are parallel to the magnetic pole faces and normal to the direction of the magnetic field lines in the gap. Means are provided (not shown) for supplying RF power to the cavity resonator at the magnetic resonance frequency of the electrons in the sample held in the cylindrical sample cell **13** extending vertically in the center of the resonator.

The electric field lines E in the cavity resonator extend normal to the two sidewalls **11** and **12** in a sinusoidal function with zero electric field strength at the center of the cavity where the sample is positioned, and maximum electric fields, in opposite and alternating directions, midway between the sample 13 and the two end walls 14 and 15. The RF magnetic field lines extend in an alternating manner parallel to the elongated sample, with the maximum field strength in the center of the cavity at the sample position.

The RF magnetic field intensity along the sample varies approximately as sin ($x\pi/L$ ), where L is the length of the cavity along the sample, as illustrated by the solid line curve A in FIG. 3. The ordinate in FIG. 3 represents distance from the center of the sample to either end of the sample, and the abscissa represents RF field intensity in arbitrary units. It can be seen that the RF field intensity is maximum at the center region of the sample and decreases in the regions along the sample on either side of the center region.

As the RF power applied to the cavity resonator is increased, the sample in the center region experiences microwave power saturation first, followed by saturation at the upper and lower regions as the power continues to increase. Undesirable heating of the sample results from sample dielectric loss, and is concentrated in the center region. It is therefore desirable to make the RF magnetic field intensity more uniform along the central region so that saturation can occur over an increased sample length at the same power incident on the cavity, and it is desirable to reduce the spatial variation of the RF electric field intensity along the sample length so that the sample temperature will be more uniform.

It is known from earlier experiments, discussed for example in the Varian Associates Technical Information Bulletin, Fall, 1965, pages 13 and 14, that the RF magnetic field intensity at a sample position can be increased by placing a sleeve of dielectric material, such as quartz, about the sample. However, a simple increase or decrease of RF magnetic field in the present instance will not solve the problem caused by the RF magnetic field concentration at the cavity sample center; what is desired is control over the RF field distribution in the cavity to obtain more RF magnetic field intensity uniformity over greater sample length.

In the embodiment of the present invention shown in FIG. 1, a sleeve 16 of dielectric material, such as quartz, having a concave outer surface is placed over the sample, the walls of the sleeve extending into the region of the electric field lines E on either side of the sample. This dielectric material in the electric field changes the gradients of the electric field intensity which in turn give rise to changes in the intensity of the RF magnetic field. The thinner walled section of the dielectric material at the center region of the sample causes very little change in the RF magnetic field intensity at that region whereas the thicker walled section of the sleeve in the regions on either side of the center sample region result in an increase in the intensity of the RF magnetic field in these regions, in comparison to the uncompensated resonator. As a consequence of the increase in the intensity of the RF magnetic field on either side of the central region, the RF magnetic field intensity becomes more uniform over the sample. This result is illustrated by the dotted line B in FIG. 3.

Spatial variation of the RF magnetic field intensity with changing incident power is reduced. More uniform sample temperature along the length of the sample exists due to the more uniform RF electric field intensities along the sample. Saturation of the sample will also occur more uniformly along the length of the sample. As a result of the more uniform RF electric and magnetic field intensities along the sample length, more sensitivity is obtained in experiments where the sample is near saturation and more faithful representation of the line shape in the region near saturation is obtained, more uniform sample temperature occurs, and more reliable measurements of saturation characteristics of lines results.

A similar form of dielectric sleeve for controlling the relative intensity and orientation of the RF electromagnetic field vectors along the sample length in a cylindrical $TE_{011}$ mode EPR cavity resonator 11 is illustrated in FIG. 2.

Referring to FIG. 4, the dielectric cylinder of FIG. 1 is replaced with a structure approximating the cylinder and comprising a pair of dielectric plates 17, 18 extending on either side of the sample and in the electric field. The outer surfaces of the two plates are concave so that the material is thinner at its center region than at the areas on either side of the center. This results in a more uniform RF magnetic field as represented by curve B in FIG. 3.

In another embodiment of the invention, as shown in FIG. 5, two cylindrical sleeve section 19 and 21 with uniform wall thickness may be employed to make the RF magnetic field intensity more uniform along the sample. The sleeves extend over the sample from either end thereof, leaving the central region free from dielectric material. Further control over the field uniformity may be accomplished by increasing the thickness of the sleeve wall slightly at the inner ends of the sleeves, as by annular dielectric ring portions 22 affixed thereto as shown in FIG. 6.

Referring now to FIG. 7, there is shown a diagrammatic view of a cylindrical $TM_{110}$ mode cavity resonator with still another embodiment of the invention utilized therein. A typical form of such resonator for X-band has about a 1.5 inch diameter and is 0.17 inch wide. Two pairs of plates 23, 24 and 25, 26 of dielectric material extend from the wall of the resonator along either side of the elongated sample 13 located in the center of the cavity. The plates extend about one-third of the way into the cavity from each side, leaving the middle third of the length along the sample free of dielectric. With a sample cell diameter of about 0.16 inch, good results were obtained with quartz plates about 0.04 inch thick and spaced about 0.20 inch from the axis through the sample.

Although the sizes and shapes of the dielectric material can be selected to accomplish the desired results, it has been found that if the dielectric extends too far into the RF electric field, there is a tendency for the change in the RF magnetic field intensity to be reversed in direction.

In the various embodiments, the dielectric material may be quartz, which has a low loss and a high dielectric constant or it may be of other suitable material such as polyethylene, teflon or corundum.

What is claimed is:

1. Apparatus for use in testing samples in an electron paramagnetic resonsance spectrometer system comprising

a cavity resonator having an aperture therethrough to receive an elongated sample cell and to apply a radio frequency magnetic field to said sample cell along a substantial portion of its length to produce electron paramagnetic resonance therein, and

a dielectric material positioned in the electric field near said sample cell aperture for controlling the relative intensity of the radio frequency magnetic field applied to a cell along the sample cell length wherein a greater thickness of dielectric material is present at regions of the sample cell length on opposite sides of the central region of the cell length than at the central region.

**2.** Apparatus as claimed in claim **1** wherein said cavity resonator operates in the rectangular $TE_{102}$ mode.

**3.** Apparatus as claimed in claim **1** wherein said cavity resonator operates in the cylindrical $TE_{011}$ mode.

**4.** Apparatus as claimed in claim **1** wherein said cavity resonator operates in the cylindrical $TM_{110}$ mode.

**5.** Apparatus as claimed in claim **1** wherein said dielectric material has a concave shape with the thin section near the central region.

**6.** Apparatus as claimed in claim **5** wherein said dielectric material is a hollow cylindrical member surrounding the elongated sample cell and with a concave outer surface.

**7.** Apparatus as claimed in claim **1** wherein said dielectric material comprises at least two sections extending near the two end regions of the sample cell removed from the central region.

**8.** Apparatus as claimed in claim **7** wherein each of said sections comprises a hollow cylinder surrounding the sample cell.

**9.** Apparatus as claimed in claim **1** wherein said dielectric material at each side region comprises a pair of plates extending parallel to the sample cell and being positioned on opposite sides of the cell.



**10.** Apparatus as claimed in claim **9** wherein the inner ends of the plates near the central region of the sample cell are thicker than the remaining portion of the plates extending away from the central region.

**11.** A cavity resonator for an EPR spectrometer including, means for sustaining electric and magnetic field intensity waves in said resonator, said resonator including an aperture defining an axis therethrough for receiving an elongated sample cell, said magnetic field intensity being non-uniform along said sample cell axis, the improvement comprising:

means for converting said non-uniform magnetic field intensity along said sample cell axis into a more nearly uniform magnetic field intensity along the said sample cell axis, said means comprising a dielectric material being interposed between said sample cell and at least a pair of cavity walls, said dielectric material includes a surface wherein the cross section of the surface through said axis includes elongated elements parallel to said axis.

**12.** A cavity resonator of claim **11** wherein said means comprising a dielectric material is configured with respect to the cavity so as to have less effect upon the cavity magnetic field at the region of maximum magnetic field than in the zones removed from the region of maximum magnetic field, said dielectric material being thinner at said region of maximum magnetic field.

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