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(71) Applicant: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; Twelfth Floor, 1111 Franklin Street, Oakland, California 94607-5200 (US).

(72) Inventors: **HAN, Song-I**; 1251 North Ontare Road, Santa Barbara, California 93105 (US). **SIAW, Ting Ann**; Apt. B, 4410 Hollister Avenue, Santa Barbara, California 93110 (US). **ZENS, Albert**; 12327 Maravilla Drive, Salinas, California 93908 (US).

(74) Agent: **COLLINS, Michael**; Billion & Armitage, Suite 425, 7401 Metro Blvd, Minneapolis, Minnesota 55439 (US).

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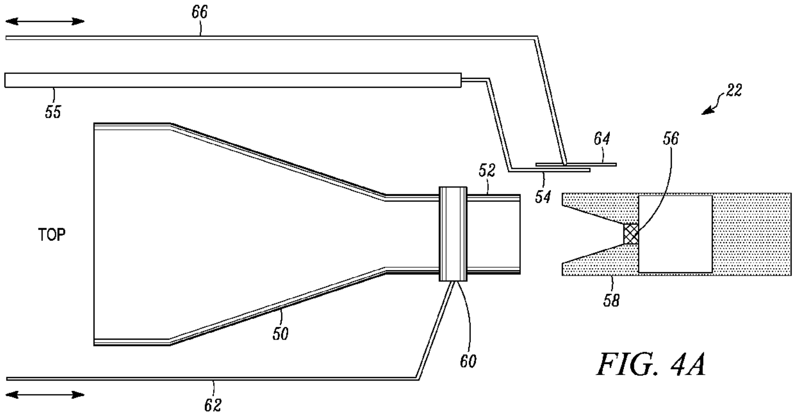

FIG. 4A

(57) Abstract: A nuclear magnetic resonance (NMR) probe utilized within a magnetic field and in conjunction with a dynamic nuclear polarization (DNP) instrument includes a coupling loop, a radio-frequency coil, a cylindrical waveguide extension, and a sliding capacitor ring. The RF coil includes a central bore for receiving a sample to be analyzed, wherein the RF coil is inductively coupled to the coupling loop. The cylindrical waveguide extension is configured to overlap, at least in part, with the RF coil to deliver microwave energy to the sample contained within the bore of the RF coil. The sliding capacitor ring is located at an outer circumference of the cylindrical waveguide extension that is actuated via a tuning rod to modify the location of the sliding capacitor ring relative to the RF coil to modify the resonance frequency of the RF coil.

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APPARATUS AND METHOD FOR NUCLEAR MAGNETIC RESONANCE UTILIZING DYNAMIC NUCLEAR POLARIZATION

TECHNICAL FIELD

[0001] The present disclosure is related generally to nuclear magnetic resonance (NMR) spectroscopy/imaging at high magnetic field, and in particular to apparatus that utilize dynamic nuclear polarization (DNP) to enhance NMR sensitivity.

BACKGROUND

[0002] The present invention is related to nuclear magnetic resonance (NMR) spectroscopy/imaging systems. A typical NMR system applies a constant and static magnetic field, B_0, generated by a superconducting magnet to the sample being studied. The applied B_0 magnetic field polarizes (i.e., aligns) the magnetic nuclear spins of the sample being measured. Application of an electromagnetic pulse (e.g., radio-frequency pulse) B_1 transverse to the B_0 field at a resonant Larmor frequency of the nuclear spins will cause a perturbation of the aligned nuclear spins. This perturbation on the aligned nuclear spins and the coherent and incoherent recovery of these nuclear spins to equilibrium is detected by an NMR probe, providing information on the structure/chemical composition/materials property of the sample. The signal detected by this probe is referred to as an NMR signal, the strength, width, frequencies and dispersion of which depends on a number of factors, including the chemical and physical properties of the material being studied.

[0003] In recent years, dynamic nuclear polarization (DNP) principles have been applied to increase the strength of the monitored NMR signal. DNP is a method by which electron spin polarization, typically of a stable free radical, is transferred to the nuclear spins of the sample such that the NMR signal is enhanced. This transfer of electron spin polarization requires irradiation of the sample with transverse B_1 magnetic fields in approximately the microwave frequency range; wherein this frequency is resonant within the range of or close to the Larmor frequency of the electron spins of interest at a given applied B_0 magnetic field strength. Upon application of microwave irradiation in the manner just described, polarization transfer from the electron spins to nuclear spins within the sample occurs spontaneously in response to the magnetic interaction and coupling between the electron spins, between the electron spins and the surrounding nuclear spins, as well as between the nuclear spins.

[0004] However, one of the drawbacks of utilizing DNP is the cost and technological challenges associated with the microwave source and other components required to operate effectively for the purpose of achieving the desired DNP efficiency. In addition, the expertise required to operate these apparatus is very high, especially if different sample types, geometries and temperatures ranging from liquid helium temperatures to above room temperatures are to be accommodated with ease, which in the current state of technology requires different NMR probes to be built and installed within the system depending on the nuclei to be studied, sample types and sample temperatures. Each time a different NMR probe is installed, expertise in re-aligning components responsible for efficient microwave irradiation from the source to the sample, such as mirrors and waveguides are required. It would therefore be desirable to provide an NMR-DNP apparatus that is cost efficient, optimally tailored to the sample and experiment of interest, while easily operable.

SUMMARY OF THE INVENTION

[0005] According to an embodiment of the present invention, a nuclear magnetic resonance (NMR) probe is described for use in conjunction with a dynamic nuclear polarization (DNP) instrument. The NMR probe includes a coupling loop, a radio-frequency coil, a waveguide extension, and a sliding capacitor ring. The NMR probe is operational at a wide range of temperatures spanning liquid helium temperatures to above room temperature. The NMR probe module is the non-stationary and removable part of the NMR probe, and includes the RF coil that encompasses within its central bore or nearby the sample to be analyzed and the sliding capacitor ring, wherein the RF coil is inductively coupled to the coupling loop. The cylindrical waveguide extension is configured to overlap, at least in part, with the RF coil to deliver B_1 fields in the microwave frequency range to the sample contained within the bore of or close to the RF coil. The sliding capacitor ring is located at an outer circumference of the cylindrical waveguide extension that is actuated via a tuning rod to modify the location of the sliding capacitor ring relative to the RF coil to modify the resonance frequency of the RF coil.

[0006] Another aspect of the present invention includes a dynamic nuclear polarization (DNP) apparatus that includes a quasi-optical (QO) microwave transmission device coupled to a solid-state microwave source. In addition, a superconducting magnet having a centrally located bore generates a magnetic field, and a microwave waveguide located within the bore of the superconducting magnet is coupled to QO microwave transmission device to receive microwave energy. A nuclear magnetic resonance (NMR) probe includes a stationary coupling loop and a NMR probe module removably coupled to the microwave waveguide. The NMR probe module includes a RF coil inductively coupled to the stationary coupling loop for communicating NMR signals to and from the NMR probe module.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 is a schematic diagram of a magnetic resonance setup that includes a nuclear magnetic resonance (NMR) probe compatible with dynamic nuclear polarization (DNP) according to an embodiment of the present invention.

[0008] Figure 2 is a schematic diagram illustrating placement of a waveguide and NMR probe within a cryostat that will be placed within the bore of a superconducting magnet, as illustrated in Figure 1 and according to an embodiment of the present invention.

[0009] Figure 3 is a schematic that illustrates the NMR probe, which includes a NMR probe module and a coupling loop according to an embodiment of the present invention.

[0010] Figure 4a is an exploded schematic view illustrating the placement of a number of components included as part of the removable NMR probe module and the coupling loop according to an embodiment of the present invention.

[0011] Figure 4b is a schematic view illustrating the location of a waveguide extension into position, adjacent to a modified A-G coil according to an embodiment of the present invention.

[0012] Figures 5a-5g are schematic diagrams illustrating the assembly of a modified A-G coil according to an embodiment of the present invention.

[0013] Figures 6a and 6b are schematics illustrating various types of RF coils, such as a surface coil, a coil tuned to multiple frequencies at once (not shown) or more than one coil placed within or near each other as part of one probe module (not shown), that may be utilized as part of or as an alternative to a modified A-G coil.

[0014] Figures 7a-7c are schematic views illustrating a sample holder according to various embodiments of the present invention.

[0015] Figure 8 is a schematic view illustrating a mechanism utilized to measure the microwave beam power or performance at or near the sample using a pyroelectric detector, as a built-in part of the NMR probe according to an embodiment of the present invention.

DETAILED DESCRIPTION

[0016] The present invention is directed to a nuclear magnetic resonance (NMR) apparatus that utilize dynamic nuclear polarization (DNP). In particular, the NMR apparatus includes an NMR probe comprised of several parts inductively coupled to allow an NMR probe module that includes the RF coil component of the NMR probe and auxiliary components to be modified and/or replaced without having to disconnect or otherwise disturb other components of the NMR probe apparatus. In addition, the NMR probe module is configured to mate with a waveguide extension component that connects to the complete waveguide to deliver a microwave beam efficiently from the microwave source to the sample.

[0017] Figure 1 is a schematic diagram of the NMR apparatus 10 according to an embodiment of the present invention that includes microwave source 12, quasi-optical transmission apparatus 14, cryostat 18, superconducting magnet 20, and NMR probe 22, In general, NMR probe 22 is a mechanical structure that removably fits within cyrostat 18 and is connected to an NMR spectrometer (not shown) via cables. As described in more detail below, NMR probe 22 is comprised of a number of components, some of which are visible in Figure 1 – such as waveguide 16, waveguide taper 50, waveguide extension 52, and removable probe module 23 - and some of which are not – including a coupling loop (shown in Figure 3). In addition, as described in more detail below, a number of components of NMR probe 22 are removable. The removable components are referred to generally as comprising NMR probe module 23, and include an RF coil (shown in more detail in Figure 3), a guard ring (shown in more detail in Figures 5d-5f, and optionally waveguide extension 52.

[0018] In general, the present invention provides enhanced spectroscopy/imaging of a sample placed within NMR probe 22. As discussed above, the principle of nuclear magnetic resonance polarizes (i.e., aligns) the magnetic nuclear spins of the sample being analyzed via application of a constant and static magnetic field, B_0, generated by superconducting magnet 20. The alignment of the nuclear spins are perturbed via application of a time-dependent electro-magnetic (e.g., radio frequency (RF) pulse) field, B_1, that is perpendicular to the B_0 field and is generated by NMR probe 22, wherein the frequency of the RF pulse is dependent on the B_0 magnetic field and the type of nuclei and sample being observed or studied. That is, an RF pulse provided at the correct frequency will result in resonant absorption by the nuclei, wherein this magnetic resonant interaction is then detected by NMR probe 22. NMR is utilized in a variety of applications ranging from spectroscopy of materials, pharmaceutical compounds to drug molecules to medical and clinical imaging (MRI).

[0019] The sensitivity of NMR apparatus 10 is improved via utilization of dynamic nuclear polarization (DNP), which is a method by which electron spin polarization is transferred to the nuclear spins of the sample such that the NMR signal is enhanced. As discussed above, electron spin polarization transfer requires irradiation of the sample with a transverse magnetic field in approximately the microwave frequency range (referred to herein as a "microwave beam signal"); wherein the frequency is resonant with the electron spins of interest at a given magnetic field strength. In response, the polarization occurs spontaneously due to the magnetic interaction and coupling between the electron spins and the surrounding nuclear spins.

[0020] In the embodiment shown in Figure 1, microwave source 12 generates the desired microwave beam signal, which is transmitted via the QO transmission apparatus 14 to the sample contained within the NMR probe 22. For example, in the embodiment shown in Figure 1, microwave source 12 is a solid-state device that emits radiation in the frequency range of 193-201 GHz as compatible with the electron paramagnetic resonance (EPR) frequency at a magnetic field B_0 of 7 Tesla, although it should be understood that other radiation frequency ranges may be utilized, especially if magnetic fields B_0 is greater than or less than 7 Tesla. In one embodiment, microwave source 12 utilizes a ~12 GHz synthesizer containing a yttrium indium garnet (YIG) crystal oscillator, whose frequency is multiplied 16 times to generate the 193-201 GHz frequency range, as well as its microwave power amplified to yield >50 mWatt of power. In other embodiments, other types of microwave sources may be utilized, but a solid-state microwave source provides the benefit of lower cost and versatility in its utility over other types of microwave sources, such as gyrotons or vacuum devices.

[0021] The microwave output generated by microwave source 12 is modified via the plurality of components included as part of quasi-optical transmission apparatus 14. Modification of the microwave output may include modification to create a pulsed output, a continuous wave output, a frequency modulated output, and further allows modification of frequency tuning, power adjustment and irradiation in CW and pulsed modes, as well as microwave pulse shaping. In the embodiment shown in Figure 1, quasi-optical components include optical horn 21, elliptical mirrors 24a-24c, planar mirrors 26a-26c, 45° wire-grid polarizer 28, Faraday rotors 30a-30b, absorber 32, horizontal wire grid polarizer 34, fixed roof mirror 36, adjustable roof mirror 38, and elliptical mirror 40 for directing the microwave beam downward and into waveguide 16, as discussed in more detail below. In general, quasi-optical components are designed to refocus the beam as it diverges from microwave source 12, and ultimately focus the beam into waveguide 16, while minimizing power loss. Furthermore, in the embodiment shown in Figure 1, the quasi-optical apparatus or QO bridge 14 is mounted on an aluminum breadboard, wherein various QO components are mounted onto the aluminum breadboard. As shown in Figure 1, QO bridge 14 is supported above superconducting magnet 20. Although not shown in Figure 1, QO bridge 14 would be supported by a support structure that consists of aluminum extrusions, tracks and mechanical actuators that allow the horizontal position, vertical position, and angle of QO bridge 14 to be adjusted relative to waveguide 16 to provide precise alignment between the output of QO bridge 14 and waveguide 16. Proper alignment between the output of QO bridge 14 and waveguide 16 minimizes the loss of microwave power during transmission of the microwave signal. Although a specific configuration of quasi-optical components are illustrated in Figure 1, in other embodiments various other quasi-optical components may be utilized to deliver the desired microwave beam to waveguide 16. In the embodiment shown in Figure 1, waveguide 16 is a cylindrical metallic tube that is corrugated internally in order to transport the microwave beam provided by QO bridge 14 to the sample being studied. Here, alignment between QO bridge 14 and waveguide 16 is crucial to maximize the microwave energy delivered to the sample. Therefore, once aligned properly it is beneficial to retain the relative locations of the QO bridge 14, waveguide 16 and superconducting magnet 20. A benefit of the present invention is the ability to remove and modify NMR probe module 23, either together with waveguide extension 52 or separate from waveguide extension 52, without requiring the removal of all components associated with NMR probe 22 – such as waveguide 16.

[0022] NMR probe module 23 is discussed in more detail below. In general, NMR probe module 23 includes a RF coil or multiple RF coils placed at the center of the magnetic field B_0 created by superconducting magnet 20. The sample being studied is placed at a location near the termination of the waveguide responsible for transmitting microwave signals to the sample to provide the desired dynamic nuclear polarization effect. To begin analysis of the sample being studied, cryostat 18 is operated to control the temperature of the sample as desired – typically cooled anywhere between below room temperature down to liquid helium temperatures (e.g. 4 Kelvin). Microwave signals generated by microwave source 12 and communicated via QO bridge 14 and waveguide 16 are communicated to the sample, within the magnetic field B_0 generated by superconducting magnet 20. NMR signals are then analyzed by an NMR spectrometer to detect characteristics of the sample being studied. As discussed above, the NMR signal analysis relies on the physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation provided by NMR probe 22 at a specific resonance frequency, which is a function of magnetic field B_0, the nuclei manipulated and the sample studied. The re-emitted electromagnetic radiation allows the observation of specific quantum mechanical magnetic properties of the atomic nucleus, which in turn offers insight into the chemical, dynamic, physical and materials property of the sample of interest.

[0023] In addition, as discussed in more detail below, elements used to tune NMR probe 22 are inductively and/or capacitively coupled to NMR probe module 23, allowing NMR probe module 23 to be removed from NMR probe 22 and replaced by another such structure having a different resonance frequency or geometry for analysis of different types of nuclei and/or samples, without requiring disconnection of the tuning elements and removal of all aspects of the NMR probe 22. In addition, the embodiment shown in Figure 1 illustrates tuning rod 48 connected to tuning elements (not shown) associated with NMR probe 23. Tuning rod 48 allows one or more tuning elements inductively and/or capacitively coupled to the coil structure or coil structures of NMR probe module 23 to be modified, while NMR probe module 23 is configured to be externally tunable, when inductively coupled to the rest of the NMR probe 22, as described in more detail below.

[0024] Figure 2 is a schematic diagram illustrating attachment of NMR probe module 23 to waveguide 16 and placement of NMR probe 22 – including NMR probe module 23 and waveguide 16 - within cryostat 18. In the embodiment shown in Figure 2, cryostat 18 utilizes liquid helium to control/cool the sample being analyzed, wherein liquid helium is flowed through input port 44 and out via output port 46. This cryostat can also be used with liquid nitrogen as the coolant. In addition, the embodiment shown in Figure 2 utilizes clamp 47 to secure NMR probe 22 within cryostat 18.

[0025] In addition, the embodiment shown in Figure 2 illustrates the inclusion of waveguide taper 50 extending from a distal portion of waveguide 16, and waveguide extension 52 placed at a distal end of waveguide taper 50. During operation, waveguide taper 50 (as part of waveguide 16), waveguide extension 52, and NMR probe module 23 are connected. In the embodiment shown in Figure 2, waveguide taper 50 is a short, metallic taper segment of waveguide 16 that reduces the diameter of the microwave beam to a size that is optimal for irradiating a sample of interest that may have lateral dimensions on the order of millimeters. In addition, the embodiment shown in Figure 2 illustrates attachment of waveguide extension 52 to the end of waveguide 16. Waveguide extension 52 is a short piece of straight cylindrical waveguide which may also be metallic or made of a different material with a metallic coating on the inside. Waveguide extension 52 is configured to terminate very close to the sample being studied. In this way, the free space that must be traversed by the microwave signal is minimized, thereby reducing loss associated with the microwave signal while at the same time preventing any loss in performance of the radio frequency power associated with NMR probe 22. In addition, as discussed in more detail below, the location and positioning of waveguide extension 52 relative to the RF probe (not shown) and sample (not shown) is important to the ultimate results obtained, as performance can be altered if the gap and/or angle between the end of the waveguide extension and RF probe is modified. In the embodiment shown in Figure 2, the position of waveguide 52 relative to NMR probe module 23 is fixed.

[0026] Figure 3 is a schematic that illustrates NMR probe module 23 and the coupling loop 54, both of which are part of the NMR probe 22, in additional detail according to an embodiment of the present invention. In the embodiment shown in Figure 3, NMR probe 22 includes waveguide taper 50 that is a part of waveguide 16 (only taper is shown), waveguide extension 52, coupling loop 54, chip capacitor 56, modified A-G coil 58, sliding capacitor ring 60, first tuning rod 62, foil plate 64, second tuning rod 66, sample holder 68, and silver mirror 70. NMR probe module 23 – which includes components removable from the rest of NMR probe 22 - includes chip capacitor 56, RF coil 58 (e.g., modified A-G coil, surface coil, etc.), sample holder 68 and silver mirror 70. NMR probe module 23 may also include waveguide extension 52 formed as an integral aspect of NMR probe module 23, or may be separate from one another. The structure of RF coil 58 may be tuned to more than one NMR frequency at once and/or may include multiple RF coils at once, whose geometry can be an A-G coil, but may also be of a different coil architecture, as long as RF coil(s) 58 can be inductively coupled to coupling loop(s) 54 of NMR probe 22 and whose geometry it concurrently optimized for NMR, DNP and EPR experiments. As discussed above with respect to Figure 2, waveguide taper 50 has a tapered geometry (i.e., decreasing diameter) that acts to focus or reduce the diameter of the microwave beam to a size that is optimal for irradiating a sample of interest. Waveguide extension 52 is mechanically coupled to and aligned with waveguide taper 50, and acts to deliver the microwave beam to the sample being studied.

[0027] As shown in Figure 3, NMR probe 22 includes coupling loop 54 and RF coil 58 (e.g., modified A-G coil), which are inductively coupled with one another to communicate NMR signals. In the embodiment shown in Figure 3, coupling loop 54 comprises a loop of wire connected/soldered to a cable that is in turn connected to a spectrometer. The function of coupling loop 54 is to communicate NMR pulses and receive NMR signals from RF coil 58. If there is more than one RF coil, there may be more than one coupling loop as part of NMR probe 22. As discussed in more detail below, RF coil 58 is comprised of etched copper foil and includes one or more chip capacitors 56 and sliding capacitor ring 60. Sliding capacitor ring 60 is coupled to tuning rod 62, which is actuated to change the position of capacitor ring 60 relative to RF coil 58. In this way, RF coil 58 is tuned to a desired resonant frequency. In particular, RF coil 58 receives RF pulses from coupling loop 54 and transmits the RF pulses to the sample being studied, located within sample holder 68. In addition, RF coil 58 receives NMR signals from the sample and communicates this information to coupling loop 54. Matching of resonant frequencies between coupling loop 54 and RF coil 58 is accomplished via selective actuation of foil plate 64 by second tuning rod 66. As illustrated in the embodiment shown in Figure 3, there is no physical contact between RF coil 58 and coupling loop 54. Rather, RF coil 58 and coupling loop 54 are inductively coupled. A benefit of utilizing second tuning rod 66 and foil plate 64 is it allows matching of resonant frequencies without having to move/adjust coupling loop 54, which is connected to the spectrometer (not shown) via coaxial cable (55).

[0028] The exact frequency at which RF coil 58 resonates is tuned/controlled, among others, by actuating tuning rod 62, thereby moving sliding capacitor ring 60 up and down relative to RF coil 58. Although not visible in the embodiment shown in Figure 3, sliding capacitor ring 60 is not in physical contact with RF coil 58, but rather is separated from RF coil 58 by a dielectric material (e.g., quartz, sapphire or other dielectric materials). Tuning rod 62 may be controlled/actuated at a location external to superconducting magnet 20, thereby allowing tuning and matching of the resonant frequency of NMR probe 22 after the NMR probe is installed within the superconducting magnet 20, while the sample is cooled within cryostat 18 and during experimental runs. In addition, because RF coil 58 is inductively coupled to coupling loop 54, NMR probe module 23 – which is the removable portion that does not include coupling loop 54 - can be detached from waveguide 16 without the need to unsolder or physically disconnect any elements such as coupling loop 54.

[0029] The embodiment shown in Figure 3 also illustrates the location of sample holder 66 within RF coil 58. Sample holder 68 is positioned at the distal end of waveguide extension 52, such that the focused microwave beam is provided to sample holder 68. In the embodiment shown in Figure 3, sample holder 68 includes silver mirror 70 that acts to reflect microwaves passing through the sample back to the sample, at least once more. One embodiment that may be utilized in conjunction with the apparatus shown in Figure 3 is the utilization of stable, radical-based samples that are designed to mimic reactants or ligands in chemical or biochemical or adsorption or separation reactions and processes for DNP-enhanced NMR characterization of samples for the purpose of selectively characterizing surface sites, local sample volumes or locations targeted by these tailored, spin-labeled, reactant mimics.

[0030] The NMR apparatus described with respect to Figure 3 provides several advantages. For example, magnetic/inductive coupling between RF coil 58 and coupling loop 54 allows RF coil 58 to be removed and replaced with another RF coil or a different RF coil setup. In this way, an RF coil having a first set of characteristics (e.g., resonance frequency) can be quickly replaced with a different RF coil having a second or different set of characteristics such as different resonance frequency or different geometry for various types of samples. In addition, this design allows for external tuning and matching of the respective components via tuning rods 62 and 66, with components capable of operation at low temperatures (e.g. liquid helium temperatures). For example, variable capacitors are typically used in tuning applications, but the O-rings utilized in typically variable capacitors are apt to freeze-up at low temperatures, thereby disabling the tuning mechanism. While a modified A-G coil architecture is described with respect to Figure 3, other RF coil architecture can be developed, as long as the RF coil (or RF coils) inductively couples to the coupling loop (or coupling loops). Finally, as described in more detail with respect to Figures 4a and 4b, waveguide extension 52 minimizes microwave losses between the source and the sample by coupling and/or overlapping with RF coil 58 or another suitable RF coil, and is a built-in part of NMR probe module 23.

[0031] In one embodiment, the following steps/procedures may be utilized to operate the apparatus described with respect to Figure 3. First, the type of microwave beam desired for a given experiment is selected and quasi-optical components to be utilized are selected for transmission through and within the QO bridge 14 (shown in Figure 1). Next, a pyroelectric detector (utilized to measure amplitude or power of a microwave beam, shown in Figure 8) is attached and built-into the NMR probe 22, so that adjustments can be made in the alignment between QO bridge 14 and waveguide 16 to maximize the microwave power delivered by waveguide 16 to the sample being studied, while the NMR probe is installed within the superconducting magnet 22 and during experimental runs. The pyroelectric device may be attached at the end of waveguide taper 50, at the end of waveguide extension 52, to the side of waveguide extension 52 as part of the NMR probe 22 or at the sample holder location itself. Having located the maximum pyroelectric value, the pyroelectric detector may remain a permanent part of the NMR probe setup. If the pyroelectric detector is installed such that part of the transmitted microwaves is measured by diverting a sizable (e.g. 10-20%) part of the transmitted microwaves to the detector, an externally actuatable mechanism needs to be built in to ensure full transmission of micrwaves to the samples when needed versus partial divertion to the pyroelectric detector. If the pyroelectric detector is installed such that it reads a very small portion (e.g. <5%) or reflected/scattered portion of the transmitted microwaves, the divertion of microwaves do not need to be externally actuatable. The sample is prepared with a solution of water/glycerol/nitroxide, which is added to sample holder 68 along with the sample being studied. Next, sample holder 68 and RF coil 58 as part of NMR probe module 23 are connected to NMR probe 22, whereby waveguide extension 52 and waveguide taper 54 are aligned and connected, and then the NMR probe 22 loaded into cryostat 18. Liquid helium (or liquid nitrogen) is flowed through cyrostat 18 to cool the sample, and NMR probe 22 is tuned while installed in cryostat 18 using tuning rods 62, 66 to the desired RF frequency or frequencies. NMR signals are acquired from the sample via the RF coil setup. In one embodiment, a saturation recovery sequence with a solid echo read-out pulse is utilized. To obtain a DNP signal, the microwave source is maintained in a continuous wave mode and the DNP-enhanced NMR signal is compared to the NMR signal with microwaves Off to determine the signal enhancement value. In addition to signal enhancement value, we also obtain DNP frequency sweep profiles (e.g., signal enhancement vs. microwave irradiation frequency) and DNP power curves (signal enhancement vs. microwave irradiation power) measurements, as well as nuclear spin-lattice relaxation time and DNP buildup time, T_{1n} and T_{DNP}, respectively.

[0032] Figure 4a is an exploded view illustrating the placement of a number of components making up NMR probe 22 according to an embodiment of the present invention. Visible in the embodiment shown in Figure 4a is waveguide taper 50, waveguide extension 52, coupling loop 54, coaxial cable 55, chip capacitor 56, RF coil 58, sliding capacitor ring 60, first tuning rod 62, foil plate 64, and second tuning rod 66. In particular, Figure 4a illustrates the ability to remove RF coil 58, as part of NMR probe module 23, without requiring removal or disconnection of wires soldered or otherwise connected to the spectrometer via coaxial cable. While the removable NMR probe module 23 is envisioned to often include waveguide extension 52 as part of its design, a design in which the removable NMR probe module 23 does not include waveguide extension 52 can be chosen, depending on experimental and mechanical requirements.

[0033] Figure 4b illustrates location of waveguide extension 52 into position adjacent to RF coil 58. The view illustrated in Figure 4b is rotated 90° from that shown in Figure 4b, as evidence by the "window" defined within RF coil 58 no longer being visible. The embodiment shown in Figure 4b illustrates how waveguide extension 52 is designed to couple with RF coil 58. In particular, the embodiment shown in Figure 4b illustrates how waveguide extension 52 overlaps RF coil 58, with the result being that the microwave beam communicated via waveguide 16 (shown in Figures 1 and 2) are delivered directly to the sample being studied. As discussed above, this minimizes the loss of microwave power provided between the microwave source and the sample. In addition, because components utilized to provide tuning and matching between coupling loop 54 and RF coil 58 remain in place (e.g., foil plate 64 and sliding capacitor ring 60), tuning and matching characteristics remain in place while allowing RF coil 58 to be removed. For example, the resonant frequency of NMR probe 22 may be modified by replacing RF coil 58 with a different RF-type coil designed for a different resonant frequency – while waveguide taper 50, foil plate 64, coupling loop 54, and sliding cap-band tune mechanism 60 remain in place. The waveguide extension 52 may or may not remain in place, at the distal end of waveguide 16. Similarly, RF coils capable of single, dual, or triple resonance capabilities may be easily interchanged without requiring removal of the entire NMR probe – and as a result without requiring calibration of the entire system after changing to a different RF coil. A benefit of this design is that a majority of the components remain in place, and therefore are not subject to the wear and tear associated with most NMR probes in which the entire structure is removed in order to modify/tune the probe. Although operation of the embodiment described with respect to Figures 3-4b have been provided with respect to NMR and DNP experiments, the described apparatus may also be utilized for electron paramagnetic resonance (EPR) spectroscopy and measurements.

[0034] Figures 5a-5g are schematic diagrams illustrating assembly of RF coil 58 (in this example, a modified A-G coil) according to an embodiment of the present invention. Figure 5a is a flattened view of modified A-G coil 58. Figure 5b is a perspective view of modified A-G coil 58. Figures 5c-5g are side views that illustrate assembly of modified A-G coil 58 with guard rings 70.

[0035] The embodiment shown in Figure 5a is a flattened view that illustrates construction of modified A-G coil 58. In particular, modified A-G coil 58 is comprised of first and second modified H-shaped conductive (e.g., copper) foils 72a, 72b separated by capacitors 56a, 56b on a "left" side of modified A-G coil 58.

[0036] Figure 5b is a perspective view that illustrates modified A-G coil 58 in a non-flattened (i.e., normal) configuration. As shown, modified A-G coil 58 has a central opening that allows modified A-G coil 58 to slip over guard rings, shown in Figures 5c-5g.

[0037] In the embodiments shown in Figures 5c-5e, modified A-G coil 58 coil is shown to further include guard ring 70, which was hidden from view in the embodiments shown in Figures 4a-4b. In the embodiment shown in Figure 5c, the arrow indicates that modified A-G coil 58 is placed over guard ring 70 during assembly. In the embodiment shown in Figure 5c, guard ring 70 includes a continuously conductive (e.g., ring-like) shield that act to protect the sample being analyzed from high electric field regions. When assembled as shown in Figure 5d, guard ring 70 is hidden from view within the right-hand side of modified A-G coil 58.

[0038] In the embodiment shown in Figure 5e, the arrow indicates placement of A-G coil 58 over waveguide extension 52. Figure 5f illustrates the final assembly of A-G coil 58, including placement of A-G coil 58 over guard ring 70 (as described with respect to Figures 5c-5d) and placement of A-G coil 58 over waveguide extension 52. A benefit of the embodiment shown in Figures 5e and 5f is that the portion of waveguide extension 52 that extends into modified A-G coil 58 acts as a guard ring, providing protection to the sample being analyzed from high electric field regions. A benefit of locating waveguide extension 52 within a portion of modified A-G coil 58 include provision of the microwave beam communicated via waveguide extension 52 directly to the sample being analyzed, thereby decreasing loss of microwave power. In addition, waveguide extension 52 obviates the need for a separate guard ring.

[0039] Figure 5g illustrates modified A-G coil 58 in the assembled state, but rotated 90° from that shown in Figure 5f. The slots extending from capacitors 56 to the left-side of modified A-G coil 58 are illustrated on the top and bottom of this side view.

[0040] Figures 6a and 6b illustrate various types of RF coils that may be utilized as an alternative to modified A-G coil 58. In both embodiments, the point illustrated is that the RF coils may be removed without having to change the tuning mechanism of the NMR probe with each different type of coil. For example, Figure 6a illustrates surface coil 80 installed over ring guard 70 and waveguide extension 52. Likewise, Figure 6b illustrates multiple turn coil 82 installed over ring guard 70 and waveguide extension (not visible in this view). A benefit of the present invention is that different types of RF coils may be removed from the test apparatus and replaced with different types of RF coils with a different resonance frequency or different geometry for analyzing different types of nuclei and sample types without requiring hard-wire disconnects/reconnects.

[0041] Figures 7a-7c illustrate sample holder 68 according to various embodiments of the present invention. Figure 7a is a perspective or angled view of sample holder 68; Figure 7b is a cross-sectional view of sample holder 68; and Figure 7c is a cross-sectional view of sample holder 68 installed in conjunction with waveguide extension 52.

[0042] In the embodiment shown in Figures 7a and 7b, sample holder 68 includes bottom portion 86 and top portion 88. The interior portion of bottom portion 86 (shown in yellow) is a thin-walled metal sleeve coating/plating that acts to reflect/contain microwave signals provided by waveguide 16 (i.e., minimizes losses associated with the microwave beam), while at the same time the thin-walled metal sleeve is "invisible" to RF signals transmitted to and from the sample by NMR probe 58. In this way, the thin-walled metal sleeve coating/plating of sample holder 68 acts to contain microwave fields while allowing RF signals to pass through as desired. The coating and the geometry of this metal sleeve is designed to maximize the microwave B_1 field strength transmitted to the sample. One benefit of this design is it prevents background noise associated with the microwave signal from being communicated external of the sample holder to NMR probe 22.

[0043] The embodiment shown in Figure 7c illustrates mechanical attachment of sample holder 68 directly to waveguide extension 52. A benefit of this arrangement, in addition to securely holding sample holder in place, is the ability to provide the microwave beam transmitted via waveguide 16 directly to the sample being analyzed. In this way, losses associated with microwave transmission are minimized.

[0044] Figure 8 is a schematic view that illustrates the addition of mechanism 90 to the NMR apparatus to allow waveguide 16 to provide microwave beams to either pyroelectric detector 92 (i.e., a device for measuring the magnitude of microwave energy) or NMR probe 22. In the embodiment shown in Figure 8, mechanism 90 is a rotatable waveguide capable of re-directing the microwave beam provided by waveguide 16 to either pyroelectric detector 92 or to NMR coil 22. In another embodiment, mechanism 90 may utilizer a splitter that diverts a small fraction of the microwave beam to pyroelectric detector 92 for analysis.

[0045] A benefit of this arrangement is that both pyroelectric detector 92 and NMR probe 22 may be installed and locked into place. Mechanism 90 is adjusted to direct the microwave beam provided by waveguide 16 to pyroelectric detector 92, which is utilized to measure the amplitude of the microwave beam and adjust components accordingly to maximize the power delivered by the microwave beam. Having calibrated delivery of the microwave beam, mechanism 90 is adjusted to deliver the microwave beam to NMR probe 22, allowing analysis to commence on the sample being studied.

[0046] While the invention has been described with reference to an exemplary embodiment(s), it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment(s) disclosed, but that the invention will include all embodiments falling within the scope of the appended claims.

Claims:

1. A nuclear magnetic resonance (NMR) probe utilized in conjunction with a dynamic nuclear polarization (DNP) instrument with the NMR probe comprising:
   a waveguide connected to receive a microwave beam;
   a waveguide extension coupled to the waveguide to direct the microwave beam received by the waveguide to a sample being analyzed;
   a sliding capacitor ring located at an outer circumference of the waveguide extension, wherein the sliding capacitor ring is actuated via a tuning rod to modify the location of the sliding capacitor ring;
   a coupling loop; and
   a NMR probe module removably coupled to the waveguide extension, wherein the NMR probe module comprises a radio-frequency (RF) coil inductively coupled to the coupling loop and tuned via selective actuation of the sliding capacitor ring.

2. The NMR probe of claim 1, wherein the RF coil is a modified A-G coil, a surface coil, another RF coil type or multiple RF coils that can be inductively coupled to the coupling loop.

3. The NMR probe of claim 2, wherein the modified A-G coil includes a guard ring.

4. The NMR probe of claim 3, wherein the guard ring includes a cylindrical guard portion that when received within the RF coil is located within a portion of the RF coil distal to the waveguide extension.

5. The NMR probe of claim 4, wherein the portion of the waveguide extension received within the RF coil acts as a ring guard for the portion of RF coil located proximate to the waveguide extension.

6. The NMR probe of claim 2, wherein the sample is encased within a thin metallic foil that is transparent to radio frequency for NMR detection, but is not transparent to the microwave frequency as employed for DNP experiments.

7. The NMR probe of claim 1, wherein the sliding capacitor ring is separated from the RF coil by a dielectric material.

8. The NMR probe of claim 1, further including:
a second tuning rod; and
a foil plate coupled to the second tuning rod and located adjacent to the coupling loop, wherein resonant frequency between the coupling loop and the RF coil is matched via selective actuation of the second tuning rod.

9. A dynamic nuclear polarization (DNP) apparatus comprising:
a solid-state microwave source;
a quasi-optical (QO) microwave transmission device coupled to the solid-state microwave source;
a superconducting magnet having a centrally located bore, wherein the superconducting magnet generates a magnetic field;
a microwave waveguide located within the bore of the superconducting magnet and coupled to the quasi-optical microwave transmission device; and
a nuclear magnetic resonance (NMR) probe that includes a stationary coupling loop and a NMR probe module removably coupled to the microwave waveguide, wherein the NMR probe module includes a RF coil inductively coupled to the stationary coupling loop for communicating NMR signals to and from the NMR probe module.

10. The DNP apparatus of claim 9, wherein the NMR probe includes a waveguide extension coupled to the microwave waveguide and to the NMR probe module for

communicating the microwave beam provided by the microwave waveguide to a sample located within the NMR probe.

11. The DNP apparatus of claim 10, wherein the waveguide extension overlaps with the RF coil of the NMR probe module.

12. The DNP apparatus of claim 10, wherein the NMR probe further includes a sliding capacitor ring located at an outer circumference of the waveguide extension that is actuated via a tuning rod to modify the location of the sliding capacitor ring.

13. The DNP apparatus of claim 10, wherein the waveguide extension is comprised of a material selected based on the sample being investigated.

14. The DNP apparatus of claim 10, wherein the waveguide extension has a geometry selected based on the sample being investigated.

15. The DNP apparatus of claim 10, wherein the NMR probe further includes a pyroelectric detector to measure relative microwave power near the sample being analyzed.

16. The DNP apparatus of claim 9, with which DNP signal enhancement is recorded as a function of microwave power to yield an experimental dataset termed the DNP power curve, whose shape is exploited as a diagnosis tool to optimize sample conditions for DNP and EPR experiments.

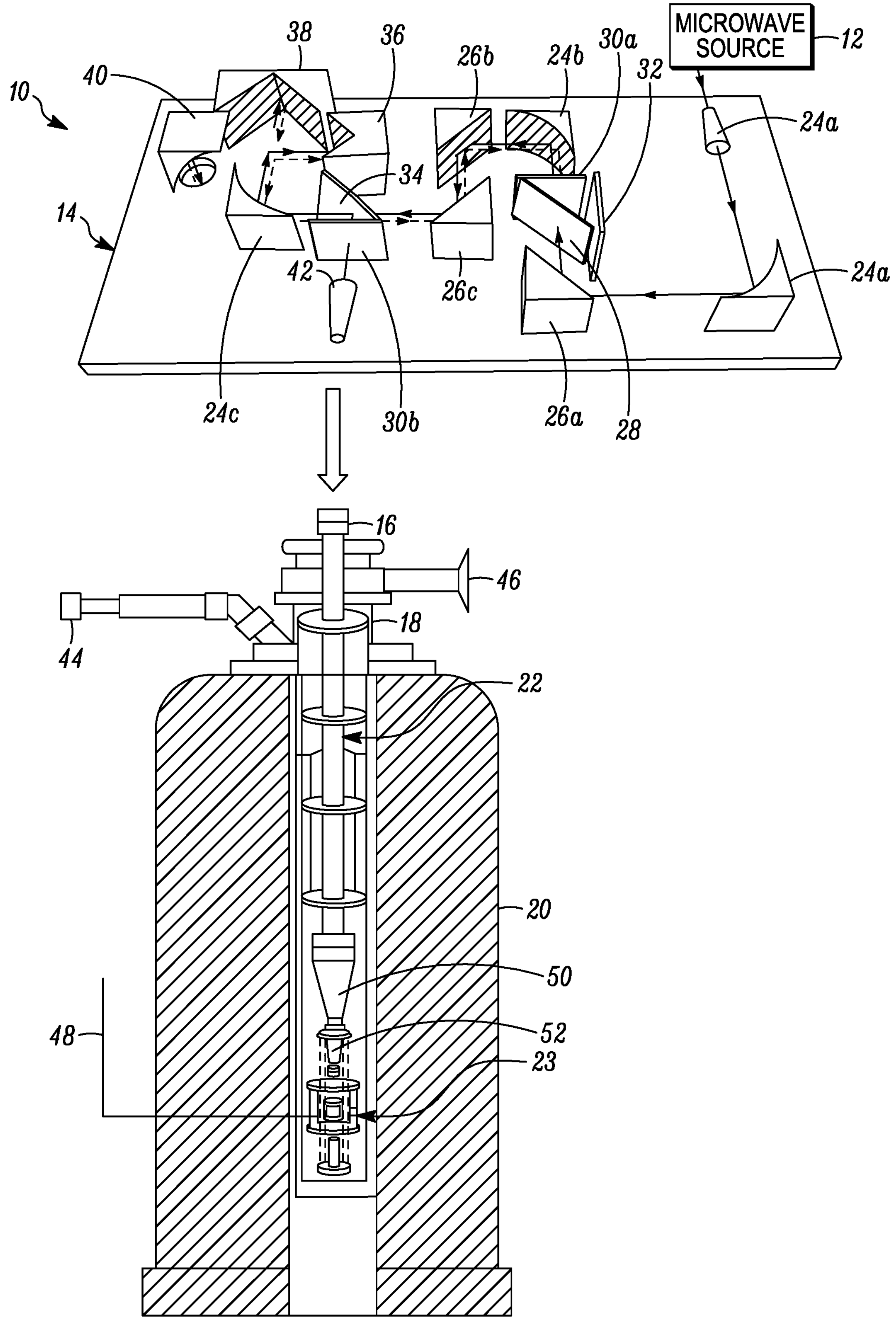
17. The DNP apparatus of claim 9, further including:
a second tuning rod; and
a foil plate coupled to the second tuning rod and located adjacent to the stationary coupling loop, wherein resonant frequency between the stationary

coupling loop and the RF coil is matched via selective actuation of the second tuning rod.

18. The DNP apparatus of claim 9, wherein the RF coil is a modified A-G coil, a surface coil, another RF coil type or multiple RF coils that can be inductively coupled to the stationary coupling loop.

19. The DNP apparatus of claim 18, wherein the modified A-G coil includes a guard ring.

20. The DNP apparatus of claim 19, further including a waveguide extension coupled to the microwave waveguide to direct the microwave beam received by the microwave waveguide to a sample being analyzed, wherein the guard ring includes a cylindrical guard portion that when received within the RF coil is located within a portion of the RF coil distal to a waveguide extension.


MICROWAVE SOURCE
12
10
14
40
38
36
34
26b
24b
30a
32
24a
24a
42
26c
24c
30b
26a
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52
23

FIG. 1

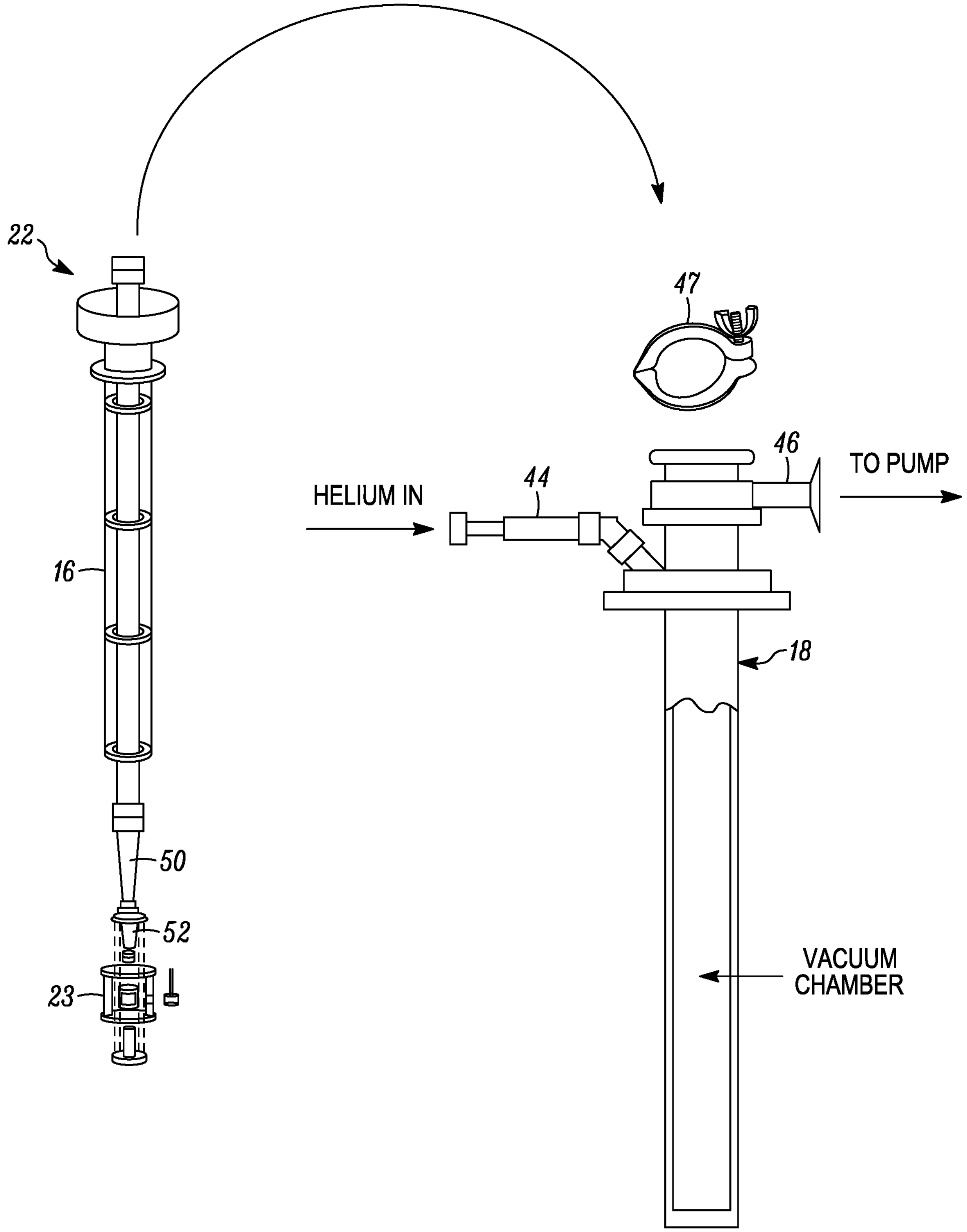

FIG. 2

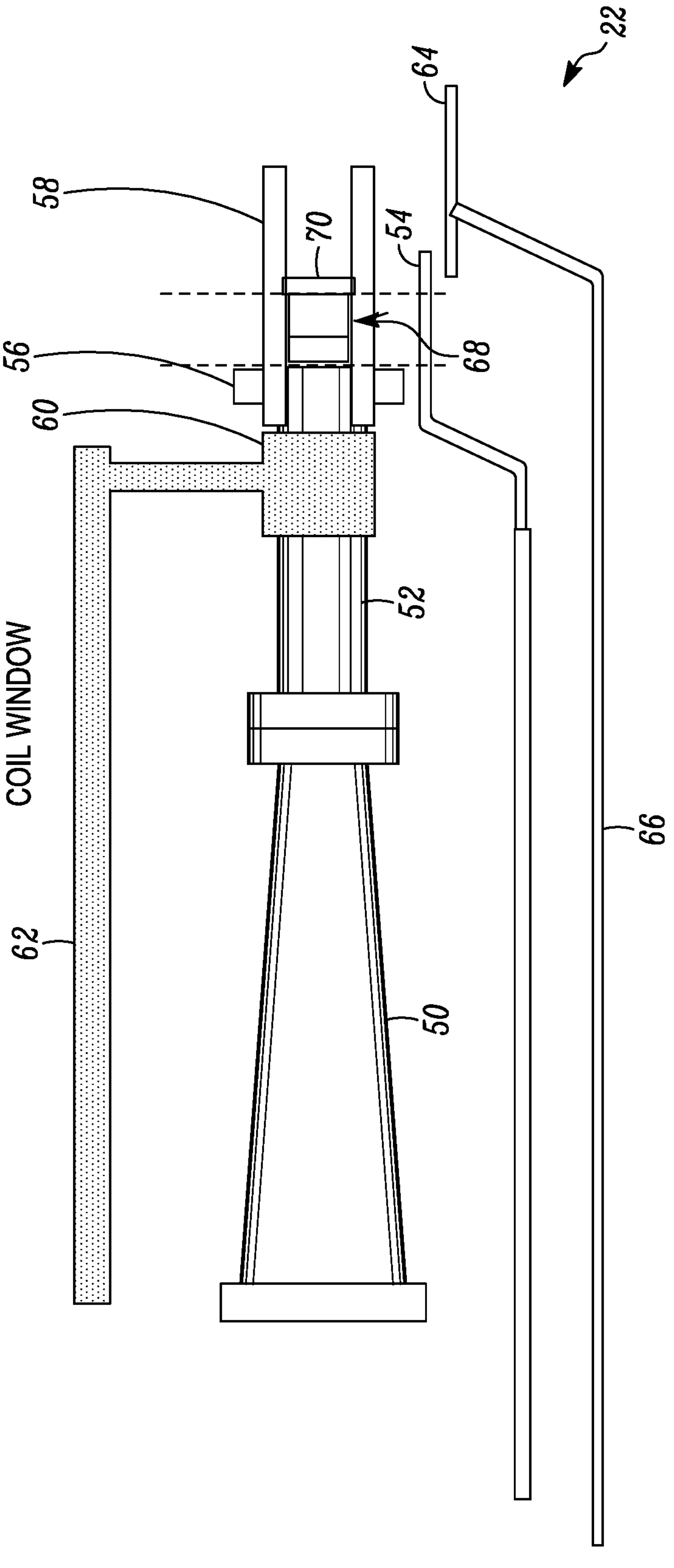

FIG. 3

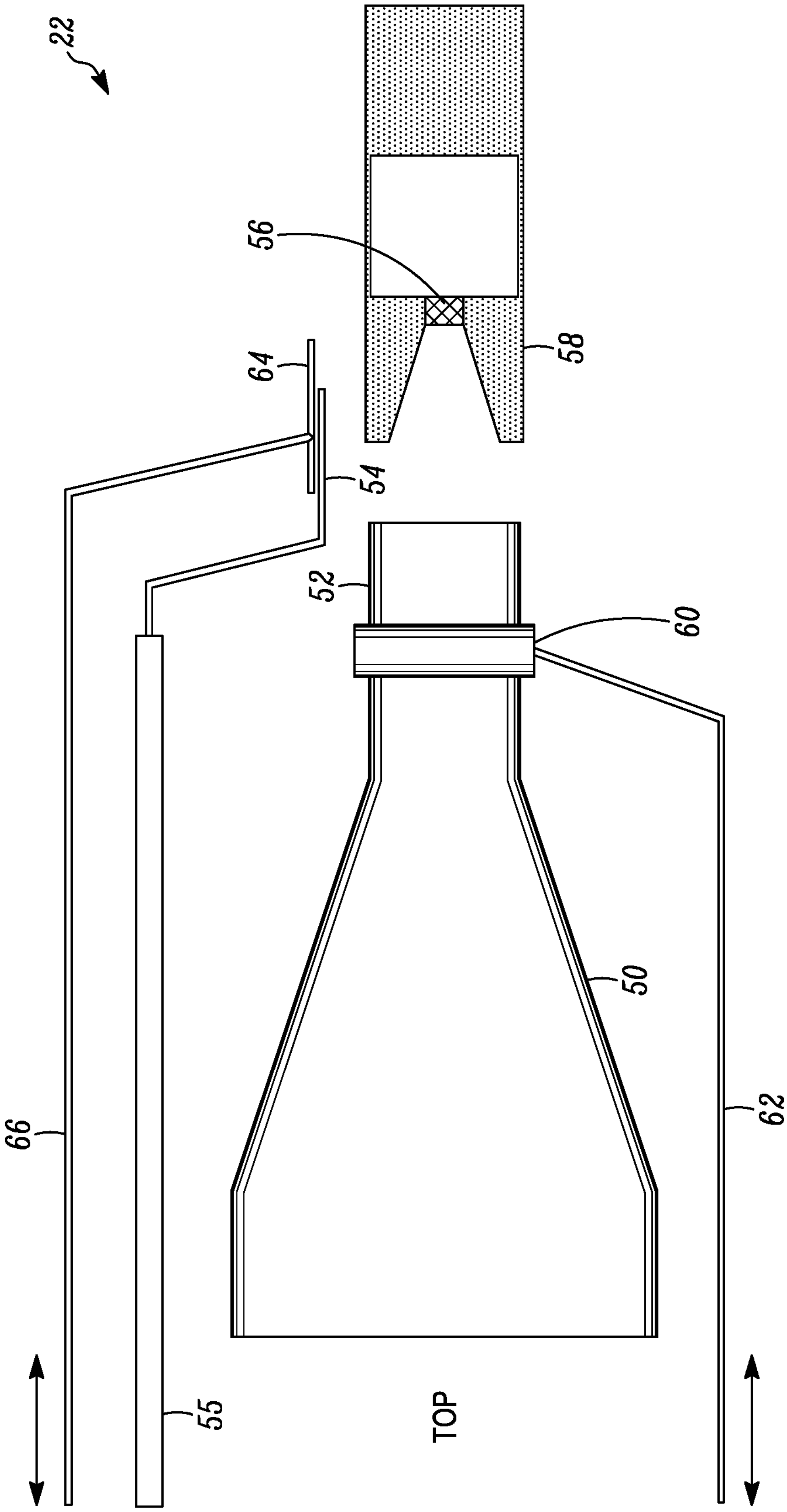

FIG. 4A

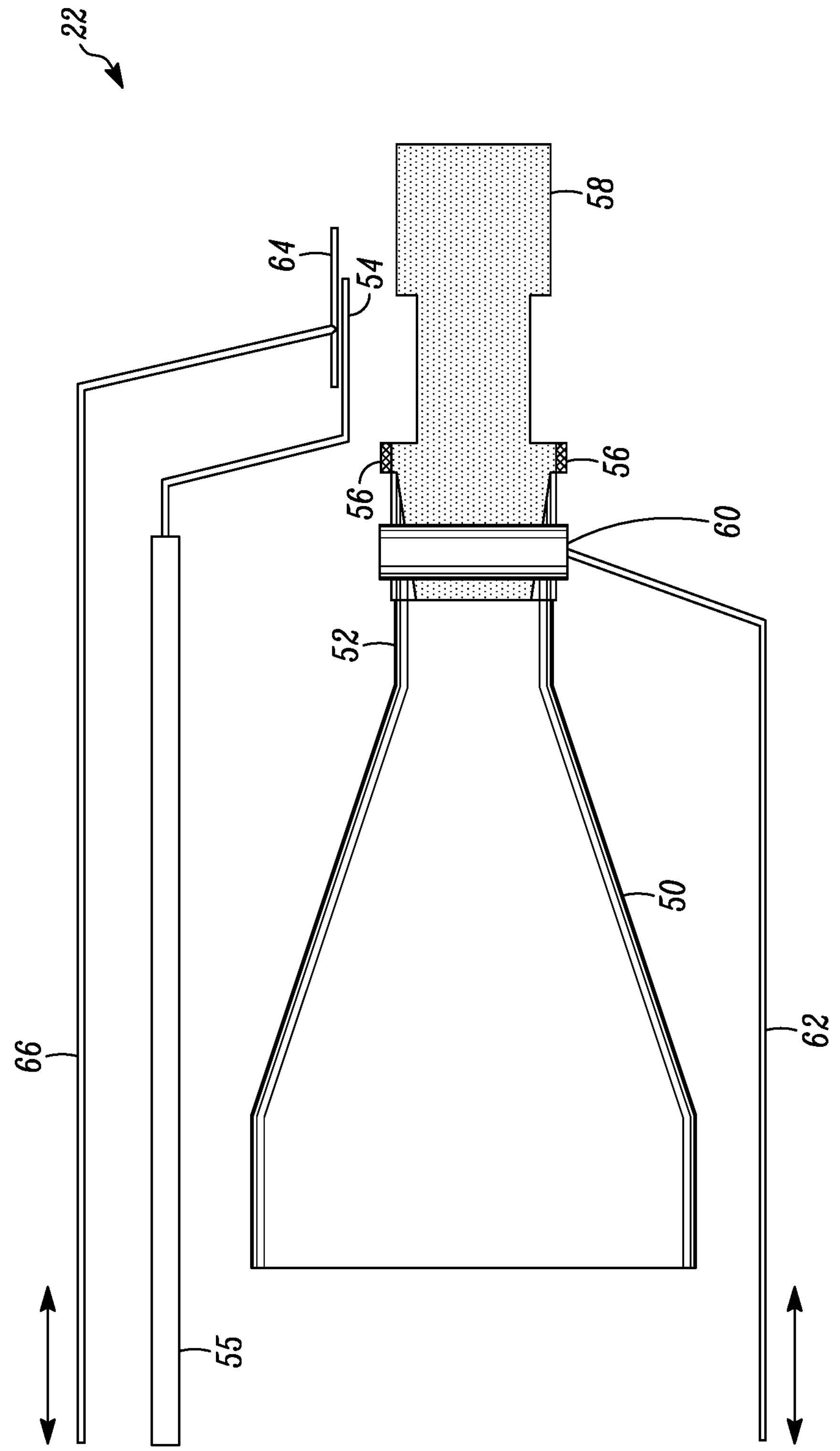

FIG. 4B

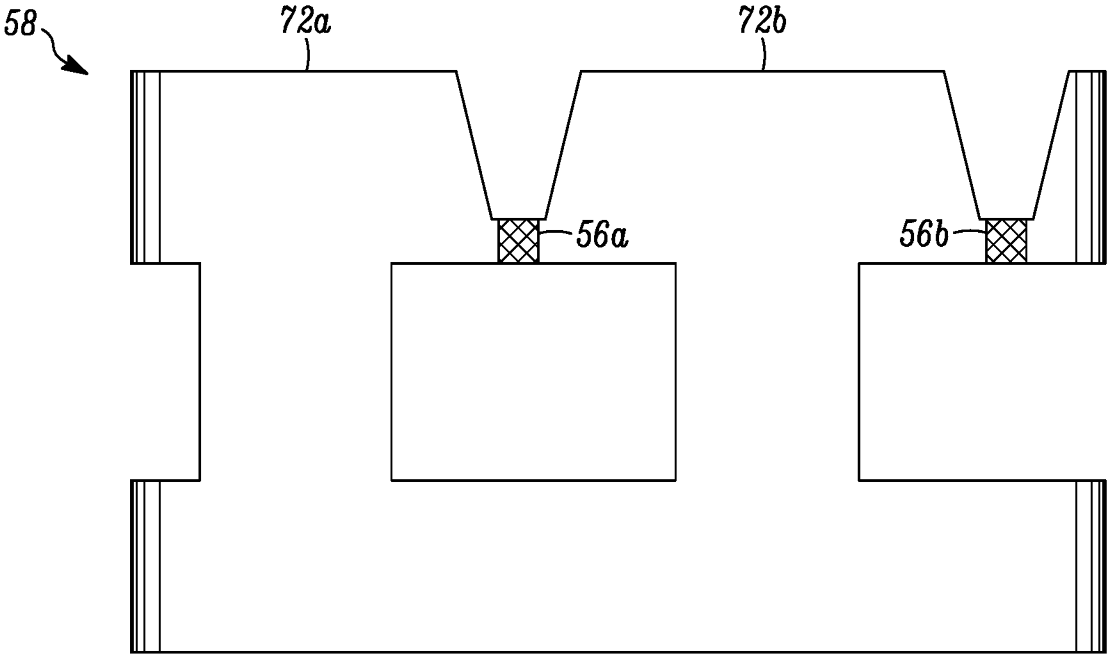

FIG. 5A

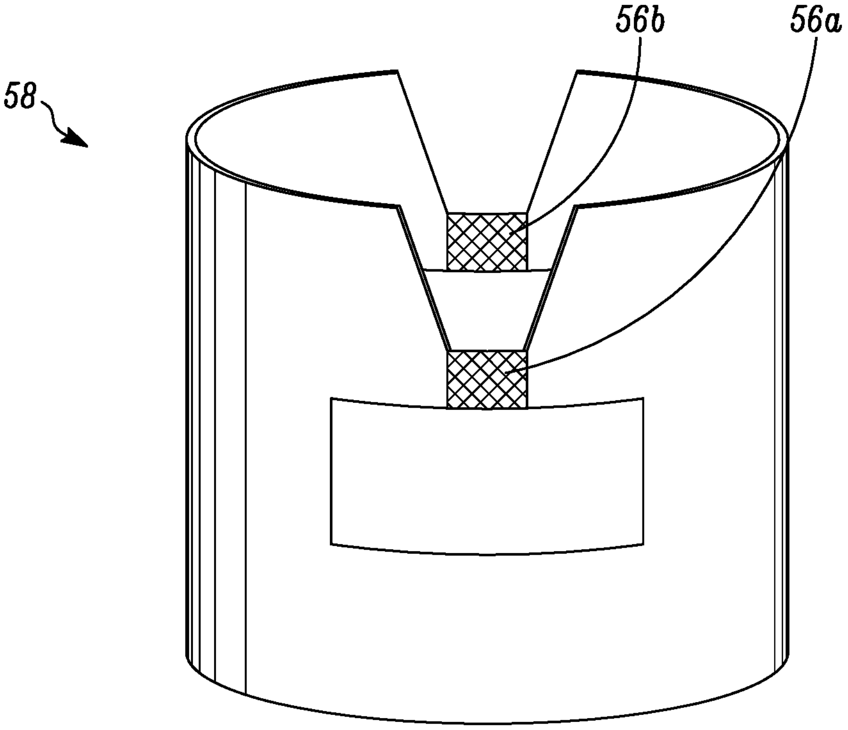

FIG. 5B

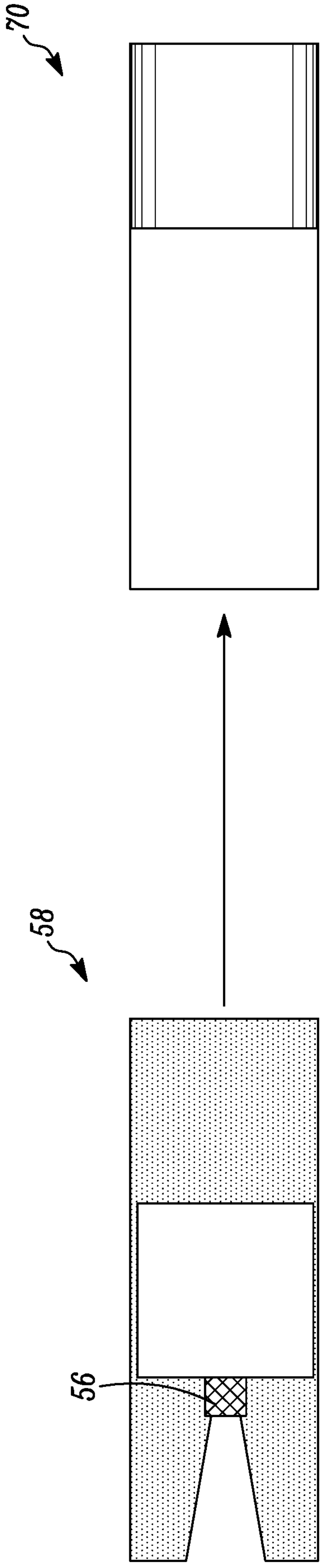

FIG. 5C

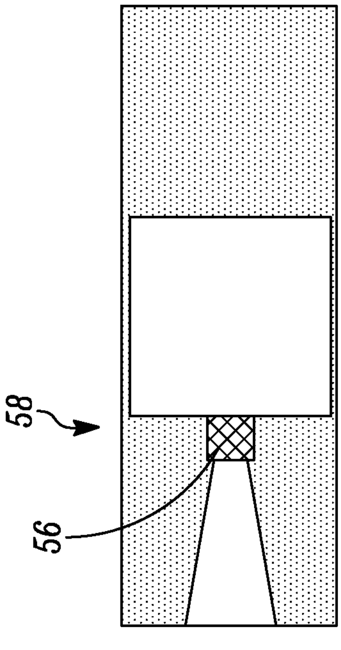

FIG. 5D

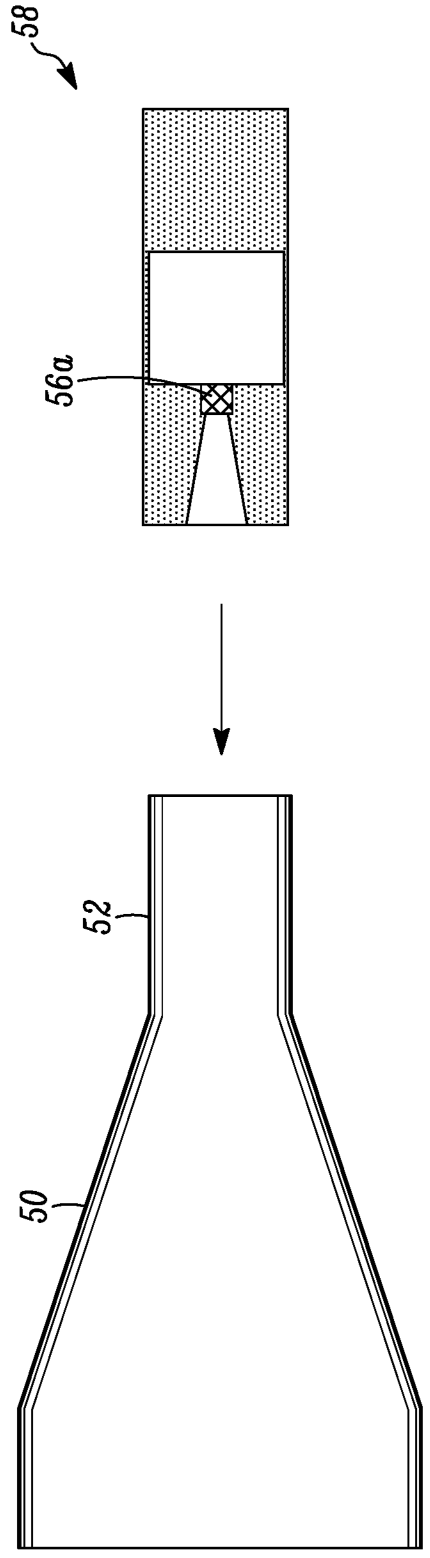

FIG. 5E

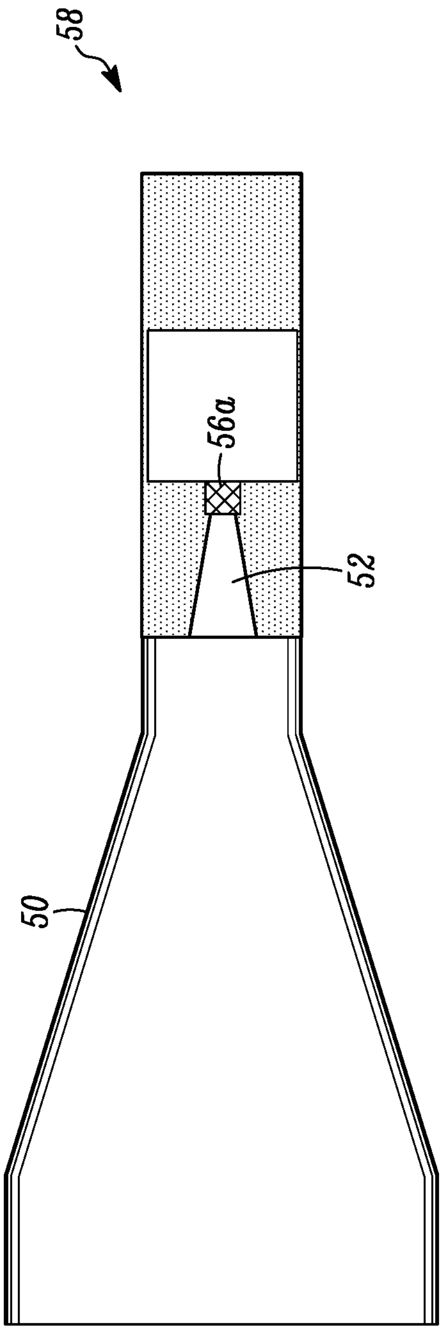

FIG. 5F

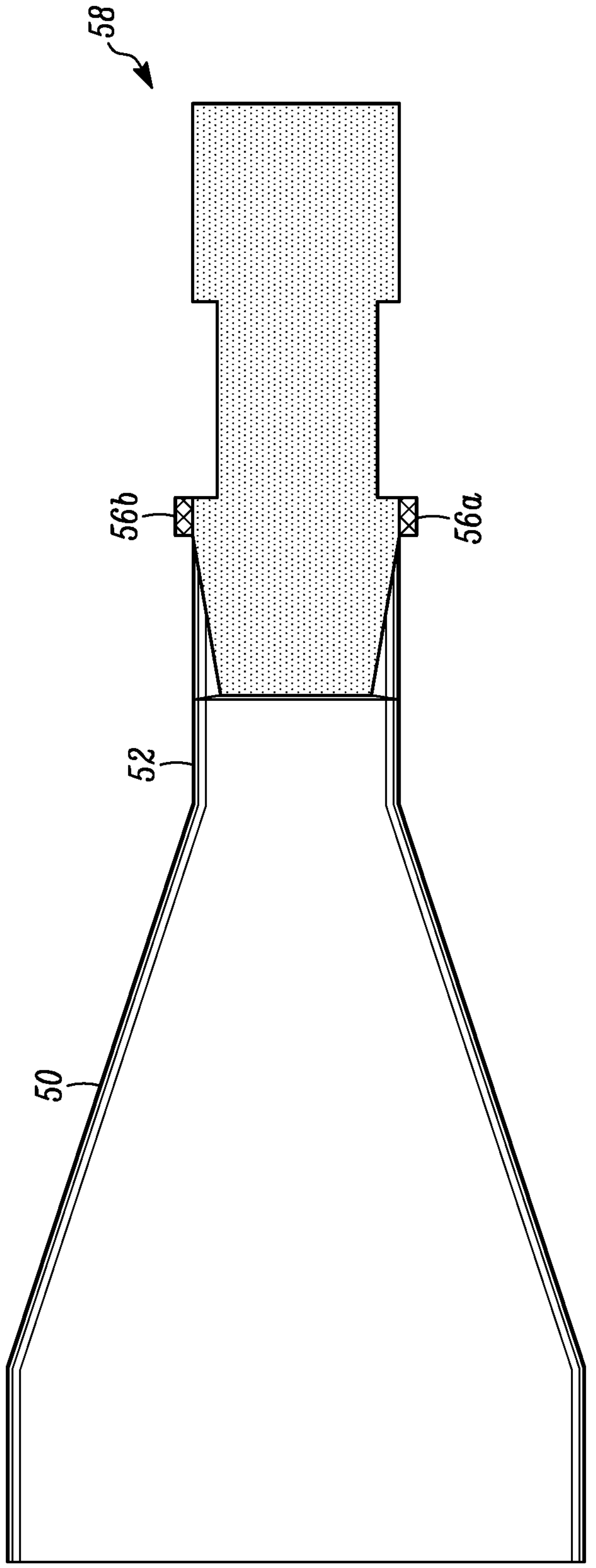

FIG. 5G

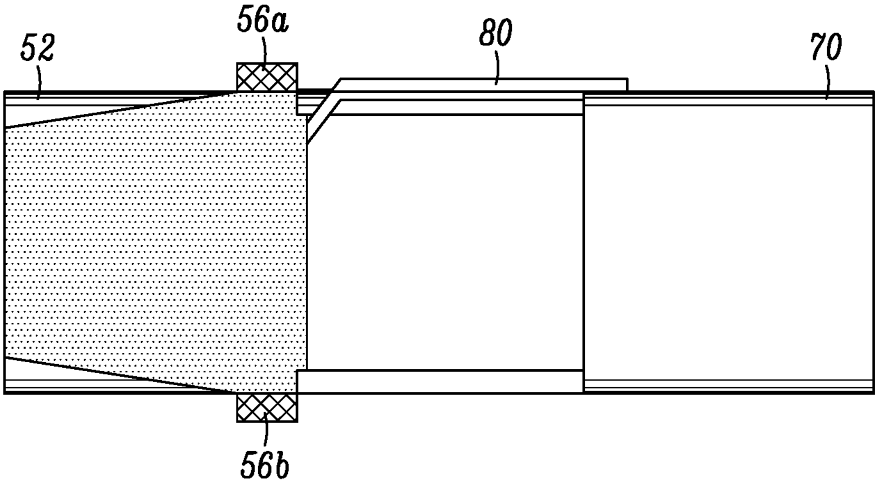

FIG. 6A

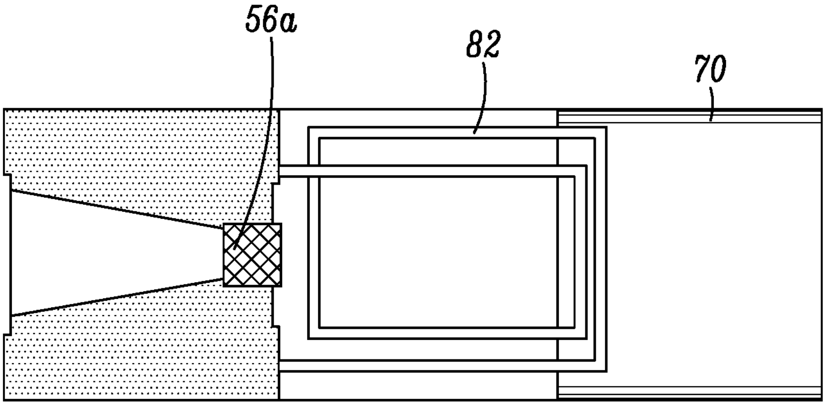

FIG. 6B

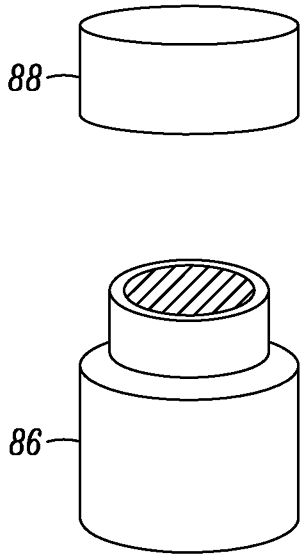

FIG. 7A

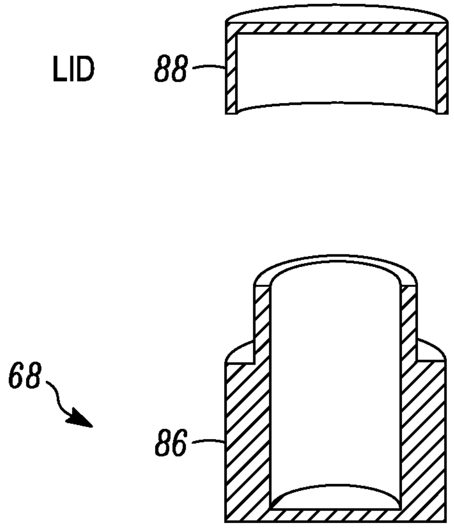

FIG. 7B

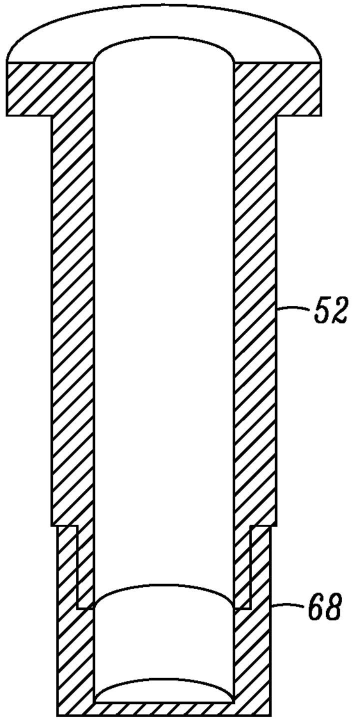

FIG. 7C

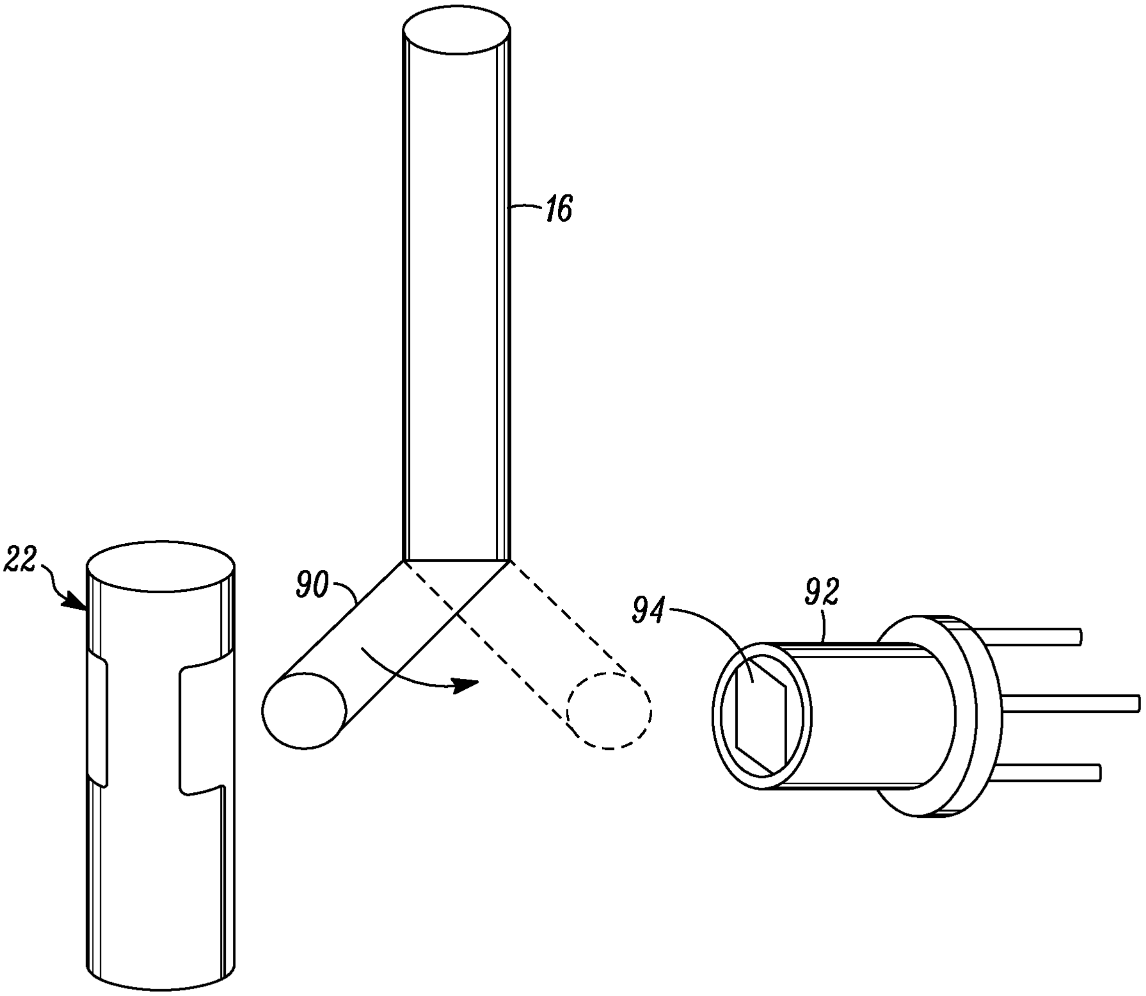

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/031272

A. CLASSIFICATION OF SUBJECT MATTER

G01R 33/341(2006.01)i, G01R 33/345(2006.01)i, G01R 33/36(2006.01)i, G01R 33/46(2006.01)i, G01R 33/48(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01R 33/341; G01V 3/00; G01R 33/20; G01R 33/345; G01R 33/28; G01R 33/30; G01R 33/36; G01R 33/46; G01R 33/48

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: NMR(Nuclear Magnetic Resonance), DNP(Dynamic Nuclear Polarization), microwave, capacitor, ring, modify

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008-0290869 A1 (HUTTON et al.) 27 November 2008 See paragraphs [1],[52],[59],[67] and figures 1,5.	1-20
A	US 2006-0192559 A1 (ARDENKJAER-LARSEN et al.) 31 August 2006 See paragraphs [17]-[18],[47],[52] and figure 1.	1-20
A	US 2004-0222796 A1 (MUNSON et al.) 11 November 2004 See paragraphs [30],[45] and figures 1-3.	1-20
A	US 2014-0117988 A1 (ANNINO et al.) 01 May 2014 See figures 1A-1D.	1-20
A	WO 2015-018640 A1 (BRUKER BIOSPIN GMBH) 12 February 2015 See figures 1-3.	1-20

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 16 August 2016 (16.08.2016)	Date of mailing of the international search report **16 August 2016 (16.08.2016)**
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer KIM, Yeon Kyung Telephone No. +82-42-481-3325

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Information on patent family members

International application No.
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