United States Patent [19]

Hyde

[11] **3,714,550**

[45] **Jan. 30, 1973**

[54] **MICROWAVE SPECTROMETER APPARATUS**

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

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[21] Appl. No.: **85,851**

[52] **U.S. Cl.** ....**324/.5 R**
[51] **Int. Cl.** **G01n 27/78**
[58] **Field of Search** ...324/.5 A, 58 C, 58.5 C, .5 AC, 324/.5 AH

[56] **References Cited**

UNITED STATES PATENTS

3,350,633 10/1967 Hyde..324/.5

FOREIGN PATENTS OR APPLICATIONS

1,103,622 2/1968 Great Britain.......................324/.5 A
960,927 6/1964 Great Britain.......................324/.5 A

OTHER PUBLICATIONS

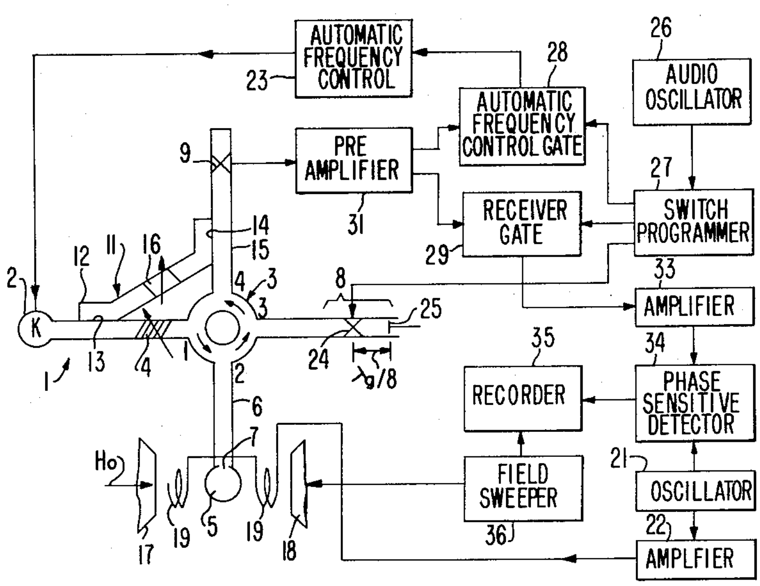
H. C. Pradduade, 100KHz Homodyne, 35 GHz Reflection Cavity Spectrometer with Phase–Lock of the Reference Signal and Low Frequency Field Modulation, Rev. of Sci. Instr., 38(3), March, 1967, pp. 339–347.

Primary Examiner—Michael J. Lynch
Attorney—Vincent W. Cleary and Stanley Z. Cole

[57] **ABSTRACT**

A microwave spectrometer is disclosed which employs a microwave reflection cavity bridge. The bridge includes a 4 port circulator having a source of microwave power applied to its first port, a matched sample cavity resonator coupled to the second port, a phase modulator coupled to the third port for phase modulating the microwave reflected cavity signal, and a microwave detector coupled to the fourth port. A reference channel interconnects the microwave source and the microwave detector for providing a reference phase. The phase of the reflected cavity signal is modulated by 90° and/or 180° and the detected output is synchronously detected against the phase modulation to obtain improved spectrometer response.

19 Claims, 19 Drawing Figures



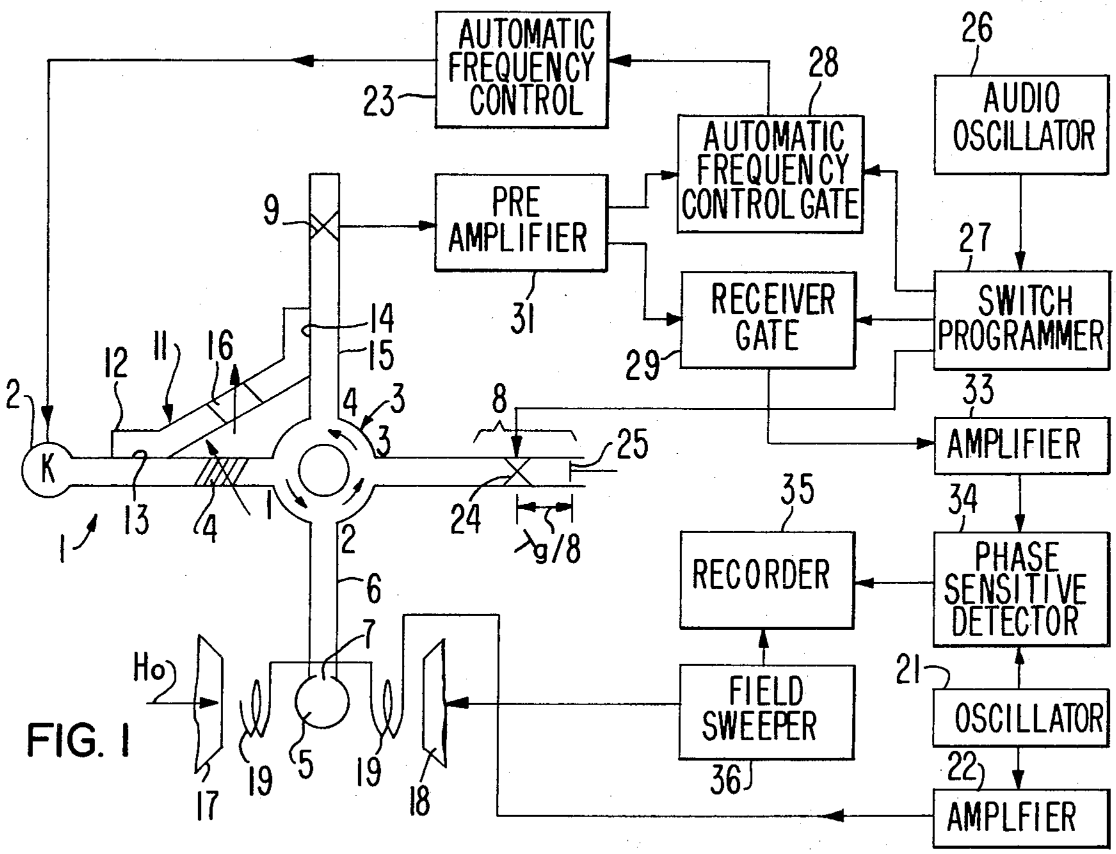


FIG. 1

FIG. 2A

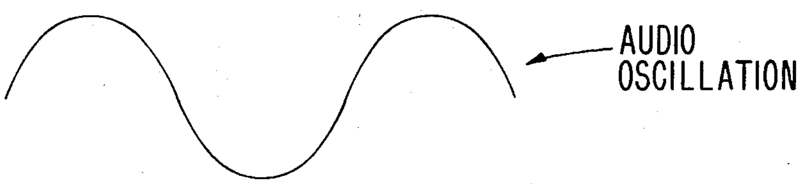


FIG. 2B

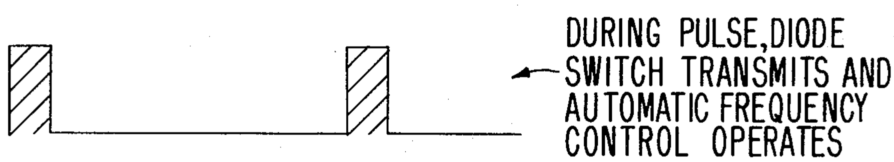
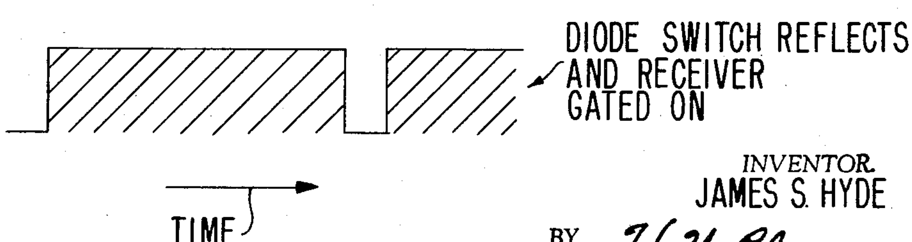


FIG. 2C



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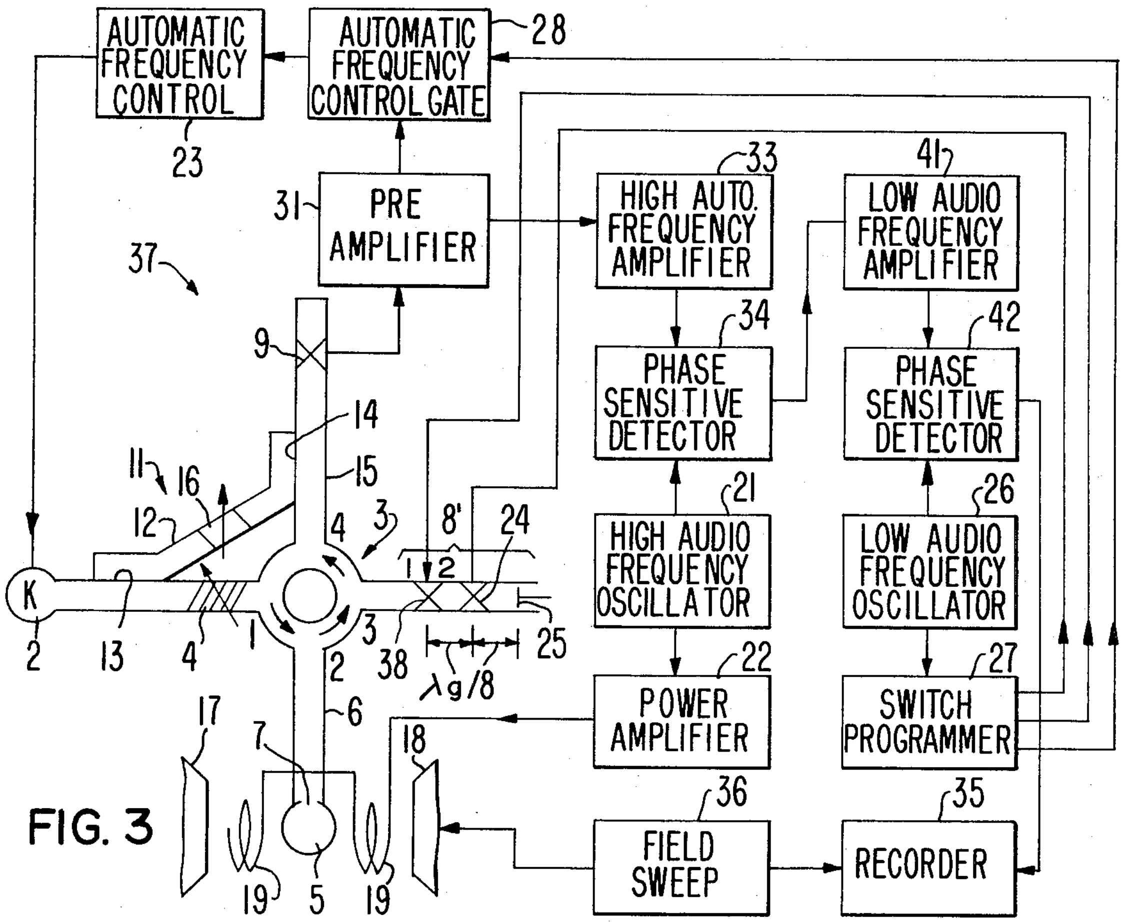

FIG. 3

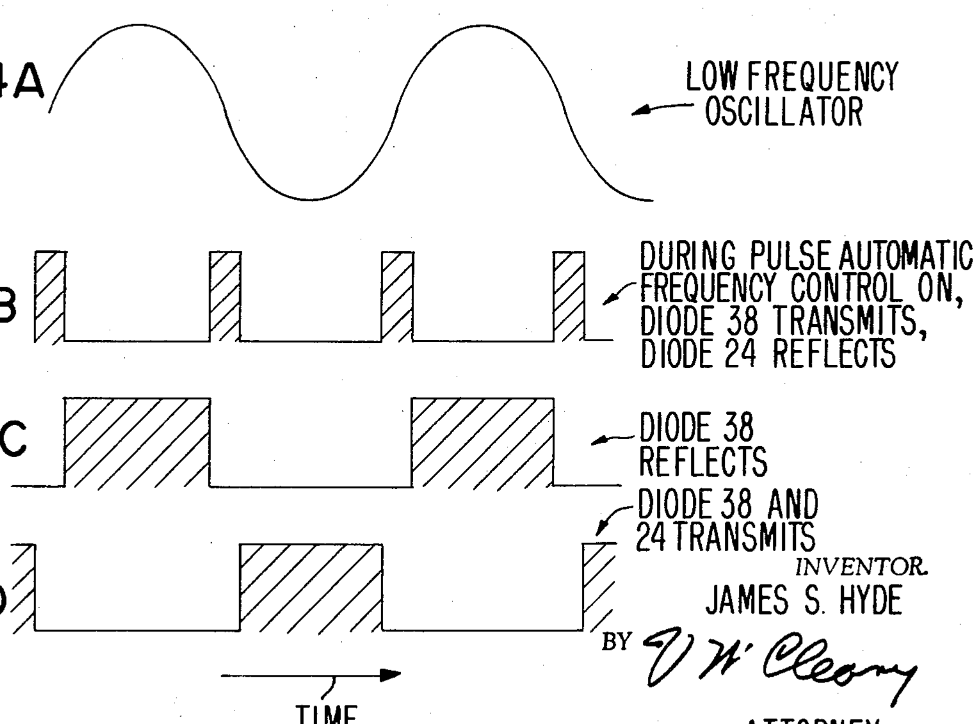

FIG. 4A

FIG. 4B

FIG. 4C

FIG. 4D

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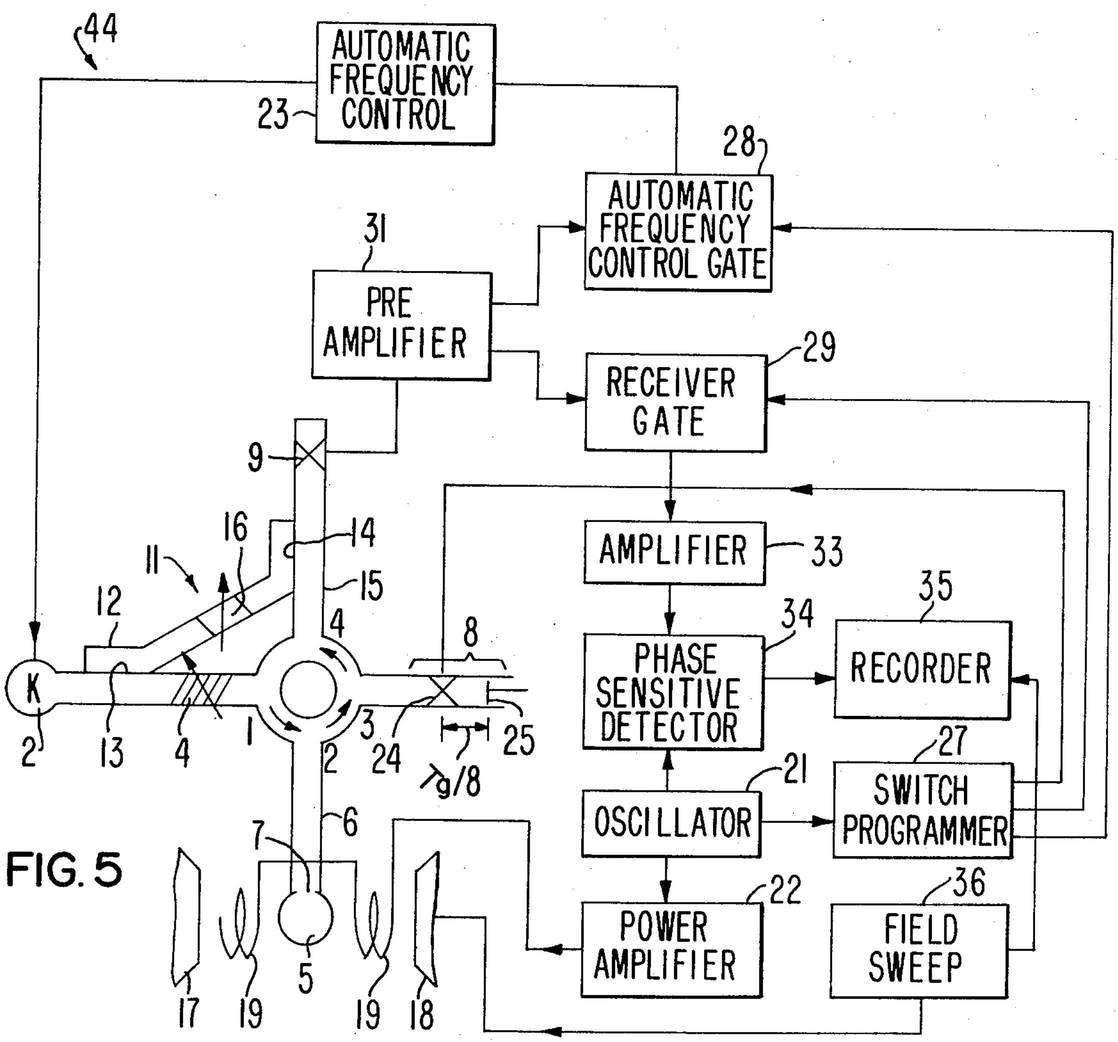

FIG. 5

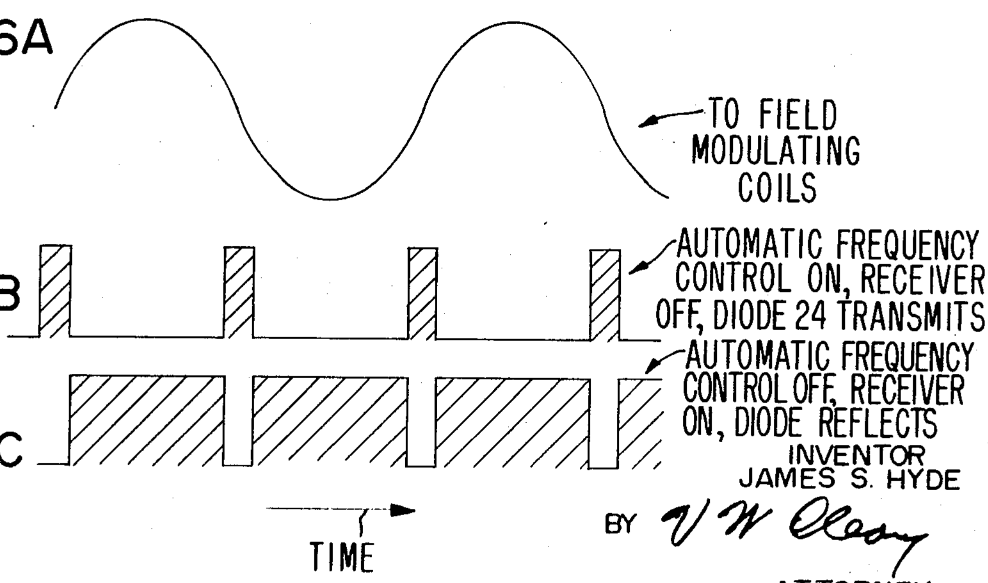

FIG. 6A

FIG. 6B

FIG. 6C

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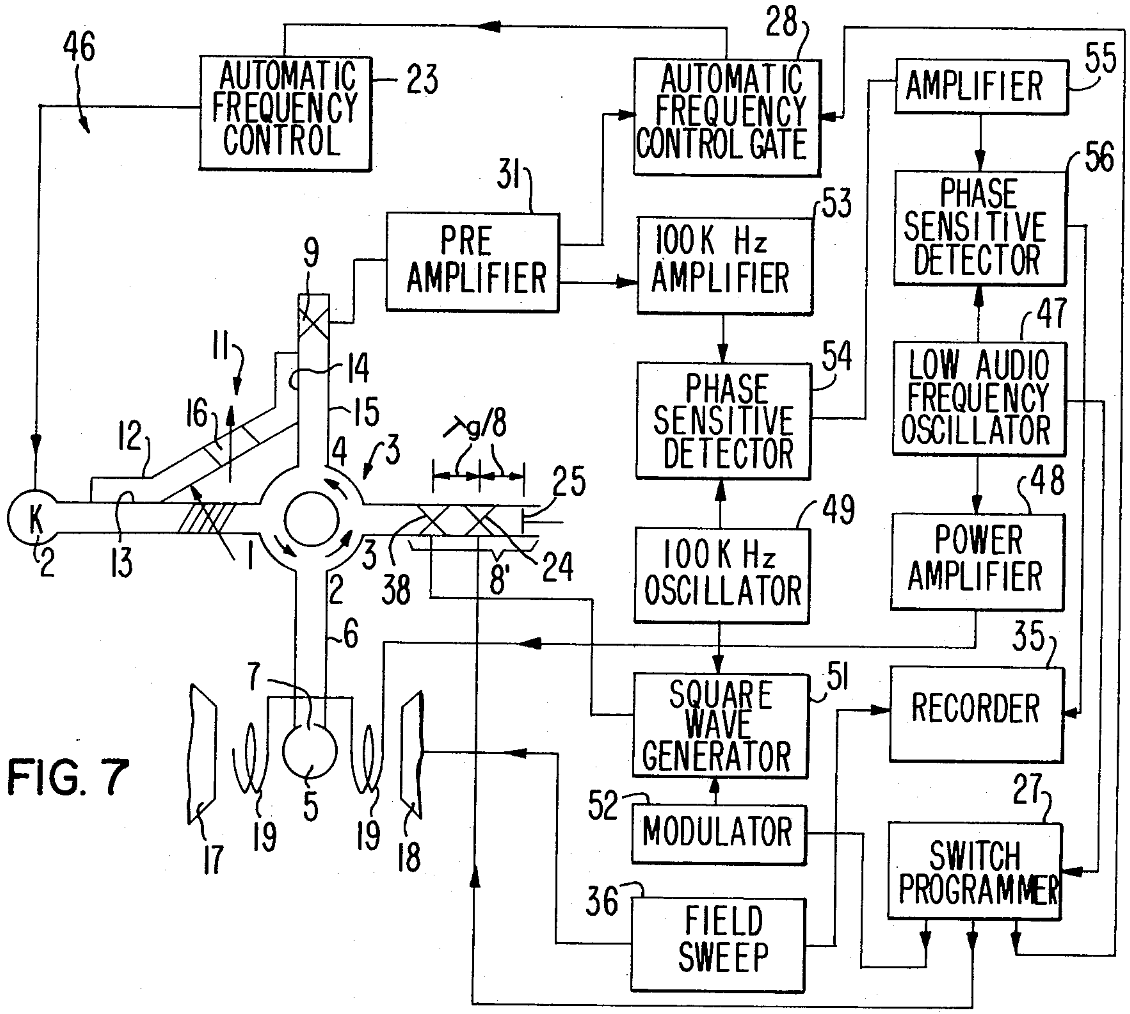

FIG. 7

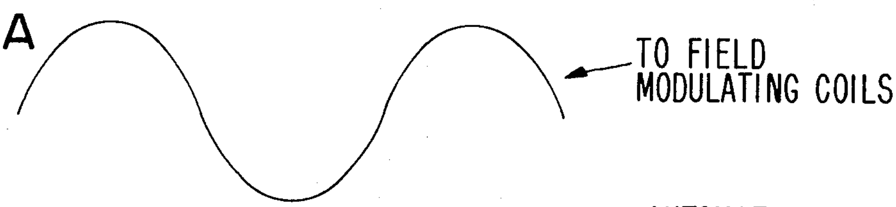

FIG. 8A

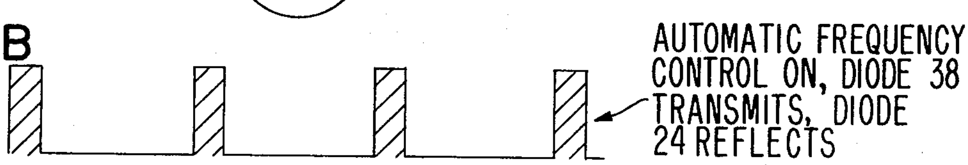

FIG. 8B

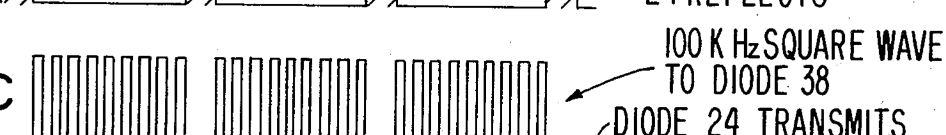

FIG. 8C

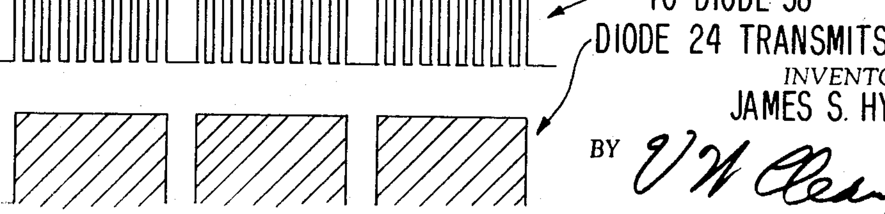

FIG. 8D

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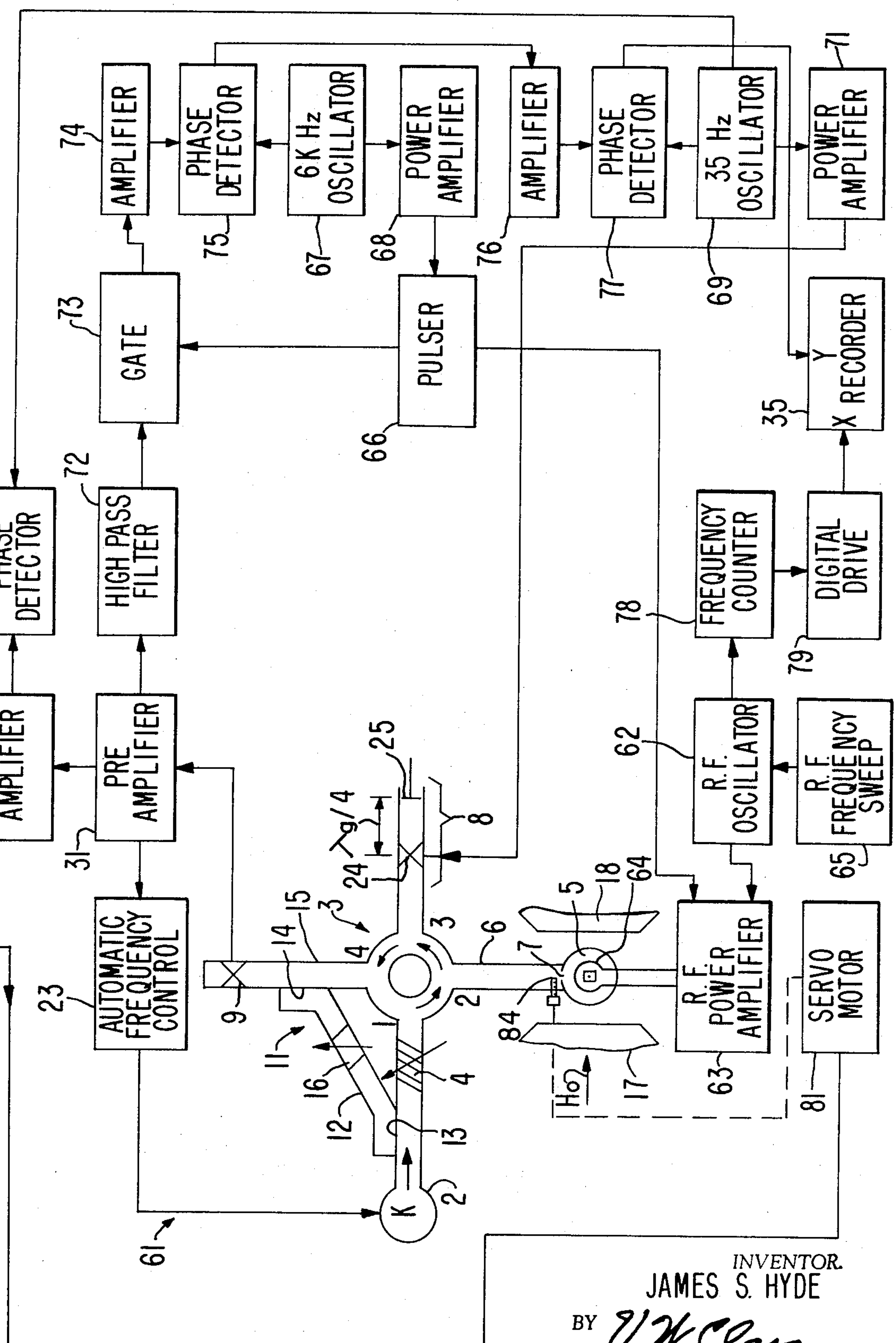

FIG. 9

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MICROWAVE SPECTROMETER APPARATUS

DESCRIPTION OF THE PRIOR ART

Heretofore, microwave reflection spin resonance spectrometers have included a microwave bridge having a microwave circulator for applying microwave energy to an electron spin sample in a matched reflection cavity. In addition, a reference channel has been provided for applying a sample of the microwave source signal to the detector for supplying a reference phase. In one prior art spectrometer, a relatively complex arrangement of microwave was provided which included a pair of microwave detectors, one detector observing the in-phase reflected microwave cavity signals and the other detector observing the 90° out-of-phase or dispersive reflected cavity signals. Such a spectrometer is disclosed and claimed in U.S. Pat. No. 3,350,633, issued Oct. 31, 1967, and assigned to the same assignee as the present invention. While such an arrangement provided a means for separately observing absorption and dispersion mode electron spin resonance the microwave bridge is relatively complex and a simplified arrangement of microwave plumbing is desired.

In another prior art electron spin resonance spectrometer, the microwave plumbing was similar to that previously described above with regard to U.S. Pat. No. 3,350,633 with the exception that phase modulation was obtained in the reference channel. In addition, the reflected microwave cavity signal was modulated by a ferrite modulator at a relatively high modulation frequency, as of 100 kHz. The first phase modulation of the reference signal was employed for obtaining a proper phase reference for observing pure absorption or pure dispersion resonance signals. The 100 kHz modulation of the reflected cavity signal served to reduce the noise factor of the microwave detector. The magnetic field modulation component, at a relatively low frequency, was phase sensitive detected and separated from the 100 kHz signal after detection and amplification of the 100 kHz signal. Such a spectrometer is disclosed in an article appearing in the Review of Scientific Instruments, Volume 38, No. 3, pages 339 – 347 of March, 1967. While such microwave resonance spectrometer has the advantage of reducing the detector noise, it would be desirable to obtain the same result with a much less complicated arrangement of microwave plumbing.

SUMMARY OF THE PRESENT INVENTION

The principal object of the present invention is the provision of an improved microwave spectrometer apparatus.

One feature of the present invention is the provision, in a microwave spectrometer apparatus, of a microwave circulator having first, second, third and fourth ports with a microwave source connected to the circulator via the first port, a reflection cavity containing the sample under analysis coupled to the second port for reflecting a cavity signal to the circulator, a variable phase shifter coupled to the third port, and a microwave detector coupled to the fourth port. A reference channel is provided interconnecting the source of microwave energy and the detector for supplying a reference phase to the detector. The phase shifter is modulated for modulating the phase of the cavity signal reflected to the detector whereby the phase of the reflected cavity signal is variable between **90°** and **180°** by means of a relatively simple arrangement of microwave plumbing.

Another feature of the present invention is the same as the preceding feature wherein the phase shifter coupled to the third port consists of an electrical discharge device spaced from a wave reflective discontinuity and wherein the phase of the reflected cavity signal is switched between 90° and 180° by pulse modulating the conductivity of the electrical discharge device causing the wave energy to be alternately reflected from the electrical discharge device and from the wave reflective discontinuity.

Another feature of the present invention is the same as any one or more of the preceding features including the provision of synchronously switching the reflected phase modulated cavity signal at a frequency related to the phase modulation frequency for separating signals of one phase from signals of another phase.

Another feature of the present invention is the same as any one or more of the preceding features including the provision of means for producing a polarizing magnetic field in the cavity and of means for modulating the polarizing magnetic field at a modulation frequency and wherein the phase modulation is synchronized with the field modulation.

Another feature of the present invention is the provision of a second variable phase shifting means coupled to the third port of the circulator for modulating the reflected cavity signal with a second phase modulation frequency.

Another feature of the present invention is the same as any one or more of the preceding features including means for variably controlling the coupling of the wave energy between the circulator and the cavity resonator and phase detecting the modulation reflected cavity signal to derive a control output, and feeding the control output to the cavity coupling control for causing the coupling control means to automatically match the impedance of the cavity to the impedance of the circulator.

In another feature, during each cycle of a reference oscillator, the cavity signal is phase modulated by 180° with a duty cycle less than 50 percent and the detected absorption mode signal output is fed to an AFC circuit in synchronism with the phase modulation for an AFC duty cycle substantially less than 50 percent, and for substantially more than 50 percent of each cycle the cavity signal is phase modulated by 90° and the dispersion mode signal is fed to the receiver circuits and to a recorder.

Other features and advantages of the present invention will become apparent upon a perusal of the following specification taken in connection with the accompanying drawings, wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a circuit diagram, partly in block diagram form, of a microwave spectrometer incorporating features of the present invention,

FIGS. **2A** – **2C** are a composite waveform plot depicting the waveforms for certain of the signals of the circuit of FIG. **1**,

FIG. 3 is a schematic block diagram of a microwave spectrometer incorporating alternative features of the present invention,

FIGS. 4A – 4D are a waveform diagram depicting the waveforms for various signals of the circuit of FIG. 3,

FIG. 5 is a schematic block diagram of a microwave spectrometer incorporating alternative features of the present invention,

FIGS. 6A – 6C are a composite waveform plot depicting waveforms in the circuit of FIG. 5,

FIG. 7 is a schematic block diagram of a microwave spectrometer incorporating alternative features of the present invention,

FIGS. 8A – 8D are a composite waveform plot depicting waveforms for certain of the signals in the circuit of FIG. 8, and

FIG. 9 is a circuit diagram, partly in block diagram form, depicting a microwave spectrometer incorporating alternative features of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIGS. 1 and 2, there is shown an electron spin resonance microwave spectrometer 1 incorporating features of the present invention. The spectrometer 1 includes a source of microwave energy 2, such as a reflex klystron oscillator, coupled to one port of a microwave circulator 3 via the intermediary of a variable attenuator 4 for controlling the power level of the microwave energy applied to the circulator 3. The circulator 3 should have relatively high isolation between ports. For example, the eight isolations over 8.5 to 9.6 GHz in dB are: 2–1 (>56), 3–2 (>20), 4–3 (>55), 1–4 (>20), 2–4 (>30), 4–2 (>28), 3–1 (>28), 1–3 (>28).

A sample cavity resonator 5 for containing a sample of matter to be investigated, such as an electron spin resonance sample, is coupled to the second port of the circulator 3 via the intermediary of a length of waveguide 6 and a coupling iris 7. The iris 7 is adjusted to obtain a perfect impedance match between cavity 5 and circulator 3 at the resonance frequency of the cavity 5 which is the frequency of the microwave energy supplied to the cavity 5. A variable phase shifter 8 is coupled to the third port of the circulator 3 for varying the phase of the microwave cavity signal reflected from the cavity 5 back to the circulator 3 and thence into the phase shifter 8. The phase shifter operates to variably control the phase of the microwave cavity signal as reflected back to the circulator 3 from whence it is fed to a microwave detector 9 coupled to the fourth port of the circulator 3. Energy flow being in the direction of the arrows as shown in the circulator 3.

A reference channel 11 interconnects the microwave source 2 and the detector 9, and comprises a short section of waveguide 12 provided with directional couplers 13 and 14 at its respective ends which connect to the source 2 and detector arm 15 of the circulator 3, respectively. A variable phase shifter 16 is provided in the reference channel for controlling the phase of the reference signal fed from the microwave source to the detector 9.

The cavity 5 is shown immersed in a polarizing magnetic field H_0 produced between the pole pieces 17 and 18 of a powerful electromagnet, not shown. The cavity 5 is oriented such that the microwave magnetic field is essentially perpendicular to the polarizing magnetic field H_0. A pair of field modulation coils 19 are shown disposed to modulate the polarizing magnetic field H_0 at a suitable modulation frequency derived from a field modulation oscillator 21. A typical field modulation frequency is on the order of 10 to 100 kHz. The output of the field modulation oscillator 21 is amplified by power amplifier 22, the output of which drives the field modulation coils 19.

An automatic frequency control channel 23 is provided for tuning the frequency of the microwave source 2 to the resonant frequency of the microwave cavity 5. The automatic frequency control circuit 23 includes a frequency modulator for frequency modulating the microwave source 2 at a convenient modulation frequency, as of 5 kHz.

The variable phase shifter 8 consists of a diode switch 24, such as a PIN diode, disposed an odd integral number of ⅛ wavelengths from a wave reflective wall 25 taken along the path of the microwave cavity signal. The switch 24 and wall 25 are adjusted such that when the switch 24 is in the transmission state to allow the microwave signal to pass to the wall and to be reflected from the wall 25, the reflected microwave cavity signal will be in-phase with the phase reference signal at the microwave diode 9. However, when the diode switch 24 is wave reflective, the reflected microwave cavity signal will be reflected from the diode 24 and not from the wall 25 such that the microwave cavity signal will be 90° out of phase with the reference microwave signal at the microwave diode 9.

A reference audio oscillator 26 of a frequency, as of 35 Hz, supplies an input to a switch programmer 27. This programmer 27 has one output which operates the phase shifter 8 by rendering the switch 24 transmissive or reflective and which has other outputs driving an automatic frequency control gate 28 and a receiver gate 29, respectively. The gates 28 and 29 are connected to receive the output of a pre-amplifier 31 which amplifies the output of the microwave detector 9. Thus, the phase shifter 8 is modulated by the output of the switch programmer 27 with a modulation frequency synchronized by the output of the audio oscillator.

In addition, the phase shifter 8 is operated with a duty cycle as shown by waveforms (b) and (c) of FIG. 2 in relation to the output of the audio oscillator 26, such that the microwave detector 9 "sees" an in-phase microwave cavity signal during such time as the microwave switch 24 is transmissive and sees a 90° phase shifted out-of-phase microwave cavity signal when the microwave switch 24 is reflective i.e., the diode is rendered conductive for reflecting wave energy from the diode switch 24. The in-phase microwave cavity signal is employed for automatic frequency control and the duty cycle for the switch 24 is preferably selected such that during a preponderance of the time, as of 90 percent, the dispersion mode of 90° out-of-phase microwave cavity signal is gated through the receiver gate to a receiver amplifier 33 whereas during a relatively short period of time, such as 1/10 of the time, the absorption mode or in-phase microwave cavity signal is gated through the preamplifier and automatic frequency control gate 28 to the automatic frequency control circuit 23.

The automatic control channel **23** includes a phase sensitive detector, not shown, which phase sensitive detects the AFC modulation component in the detected cavity signal against the modulation signal employed for frequency modulating the microwave source **2** to derive an error signal for controlling the center frequency of the microwave source **2** to the frequency of the cavity **5**. The AFC circuit **23** generates a frequency correction signal and includes a memory circuit which stores and applies the corrected frequency setting of the microwave source **2** during the interval between successive absorption mode pulses gated to the AFC circuit **23**.

The 90° out-of-phase reflected microwave cavity signal (dispersive cavity signal) is gated by the receiver gate **29** to the input of an amplifier **33** wherein the field modulation produced component in the detected microwave cavity signal is amplified and thence fed to one input of a phase sensitive detector **34** for phase sensitive detection against the field modulation frequency, derived from the output of oscillator **21**, to obtain a dispersive mode electron spin resonance signal. The resonance signal is fed to a recorder **35** for recording as a function of time or as a function of magnetic field sweep derived from a field sweeper **36** which serves to sweep the intensity of the polarizing magnetic field H_0 across the spectrum of the sample under analysis. Thus, the output of the recorder **35** is a dispersive mode spectrum of the sample under analysis.

The spectrometer of FIG. **1**, as contrasted with the prior art, exemplified by U.S. Pat. No. 3,350,633,and considerably less expensive to make.

Referring now to FIGS. **3** and **4**, there is shown an alternative microwave spectrometer **37** incorporating features of the present invention. Spectrometer **37** is substantially the same as that of FIGS. **1** and **2** with the exception that the variable phase shifter **8'**, which is connected to the third port of the circulator **3**, includes a second diode switch **38** which is spaced an odd number of quarter wavelengths from the wave reflective wall **25**. The reference phase shifter **16**, in the reference channel **11**, is adjusted such that the reflected microwave cavity signal is in-phase with the reference signal at the detector **9** when diode switch **38** is transmitting and diode switch **24** is reflective to reflect wave energy from the diode **24** to the circulator **3**. In addition, the switching programmer **27**, is synchronized by the output of the low audio frequency oscillator **26**, as shown by waveform (a) of FIG. **4**, to cause the in-phase reflected cavity signal to be reflected from diode **24** twice per cycle of the frequency of the low frequency oscillator signal by causing diode **38** to be transmissive and rendering diode switch **24** reflective. Switching programmer **27** is also synchronized by the output of oscillator **26** to reflect the 90° out-of-phase dispersive mode cavity signal from the first diode **38** once per cycle of the low frequency oscillator signal, as shown by waveform (c), by causing diode **38** to be reflective during the cross hatched portion of waveform (c). In addition, during the other intervals, as indicated by waveform (d), both diodes **38** and **24** are rendered transmissive, by biasing the diodes off, to reflect a dispersive mode signal from end wall **25** to the detector **9**.

Spectrometer **37** operates substantially in the manner as previously described with regard to the spectrometer of FIG. **1**. More particularly, the high frequency field modulation signal is amplified by high frequency amplifier **33** and phase detected in phase detector **34** against a sample of the high frequency field modulation signal derived from high frequency oscillator **21** to derive a dispersive mode output signal having superimposed thereon a low frequency component and the frequency of the low frequency audio oscillator **26**, as of 35 Hz. This low frequency signal is amplified in a low audio frequency amplifier **41** and phase detected in phase detector **42** against a sample of the low audio frequency oscillator signal derived from oscillator **26** to obtain a dispersive mode resonance signal which is recorded in recorder **35** as a function of the field sweep signal derived from field sweep generator **36**. The provision of the second phase sensitive detector **42** serves to exclude any possible absorption signals (present when the AFC is on) in the output of the phase sensitive detector **42** due to the fact that the AFC repetition frequency is twice the frequency of the low frequency oscillator. The advantage of the spectrometer **37** is that the separate receiver gate has been eliminated and that the AFC rep rate has been increased for a given low frequency reference oscillator.

Referring now to FIGS. **5** and **6**, there is shown an electron spin resonance spectrometer **44** incorporating alternative features of the present invention. Spectrometer **44** is essentially identical to that of FIG. **1** with the exception that the audio oscillator **26**, of FIG. **1**, has been replaced by the field modulation oscillator **21**. The switching programmer **27** is synchronized with the field modulation waveform (a) of FIG. **6**, as shown by waveform (b) of FIG. **6**, to sample the in-phase reflected cavity signal at twice the frequency of the field modulation signal by synchronizing the operation of AFC gate **28** with switching of the diode switch **24**. The spectrometer is initially set up for the in-phase mode with diode switch **24** transmissive, such that the microwave reflected cavity is reflected from end wall **25**. Thus, by switching diode switch **24** to a wave reflective state, wave energy is reflected therefrom to observe the dispersive mode of the cavity signal.

The field modulation component present in the dispersive mode cavity signal is fed via the receiver gate **29** to the amplifier **33** and thence to one input of a sensitive detector **34** for detection against a sample of the field modulation signal derived from field modulation oscillator **21** to produce the electron spin resonance dispersive mode signal which is recorded as a function of the field sweep derived from field sweep generator **36**. The receiver gate **29** can be omitted, if desired, since the phase sensitive detector **34** will discriminate against the absorption signal since it is at the second harmonic of the field modulation signal.

Referring now to FIG. **7** and **8**, there is shown an alternative electron spin resonance spectrometer **46** incorporating features of the present invention. More specifically, the spectrometer **46** employs a relatively low frequency field modulation within the cavity **5** which is superimposed upon a relatively high frequency phase modulation of the microwave cavity signal fed to the microwave detector **9** to avoid the noise produced by the microwave detector **9** at low frequencies. This principle is disclosed in a prior art publication, namely, the aforecited Review of Scientific Instruments Article.

The variable phase shifter **8'** is arranged relative to the phase of the reference channel **11** such that, when diode switch **24** is reflecting wave energy and diode switch **38** is transmissive, the detector **9** detects the in-phase microwave cavity signal.

A low audio frequency oscillator **47**, as of 35 Hz, provides an output signal which is fed to a power amplifier **48** and thence to the field modulation coils **19** for modulating the polarizing magnetic field H_o at the low audio frequency oscillator frequency. The field modulation signal is also fed to the switch programmer **27** for synchronizing the diode switches **38** and **24** such that diode **38** transmits and diode **24** reflects at twice the field modulation frequency as indicated by the waveforms (a) and (b) of FIG. **8**. The switching programmer **27** also switches the automatic frequency control gate in synchronism with waveform (b) for automatic frequency control.

A relative high frequency oscillator **49**, as of 100 kHz, provides an output to a square wave generator **51** for generating a square wave at the frequency of the high frequency oscillator **49**. The output of the square wave generator **51** is fed to diode switch **38** such that diode switch **38** is rendered alternately wave reflective and transmissive at the frequency of the high frequency oscillator **49** to produce a 100 kHz phase modulation of the reflected microwave cavity signal. When the cavity signal is reflected from diode **38** the cavity will be 90° out-of-phase with the reference signal such that the dispersive mode of the cavity signal is seen at the output of the microwave detector **9**. The switching programmer **27** modulates the square wave generator **51** at twice the frequency of the field modulation signal such that the diode **38** is rendered transmissive in accordance with the AFC waveform as indicated by waveform (b) and (c) of FIG. **8**. Diode switch **24** is rendered transmissive in accordance with waveform (d) of FIG. **8** such that the high frequency phase modulation is 180° phase modulation.

The output of the pre-amplifier **31** is fed to a 100 kHz amplifier **53**, and thence to one input of a phase sensitive detector **54** for phase detection against a reference derived from the high frequency oscillator **49** to obtain a dispersive mode output signal, the output signal is fed to amplifier **55** and thence to one input of a second phase sensitive detector **56** for phase detection against the field modulation signal derived from low frequency oscillator **47**. The output of the phase sensitive detector **56** constitutes a dispersive mode electron spin resonance signal which is fed to the recorder **35** for recording as a function of the field sweep signal derived from field sweep generator **36**.

The advantage of the spectrometer of FIG. **7** is that high frequency field modulation cavity losses are avoided and yet the high frequency modulation produced by oscillator **49** serves to overcome the inherent low frequency detector noise to obtain improved signal to noise ratio. As in the previous embodiments, the output of the pre-amplifier **31** need not be gated to the resonance receiver **53**, as the second phase sensitive detector **56** will discriminate against absorptive signals at twice the frequency of the field modulation frequency.

Referring now to FIG. **9**, there is shown an electron-nuclear double resonance spectrometer generally of the type disclosed and claimed in U.S. Pat. No. 3,358,222 issued December 12, 1967 and assigned to the same assignee as the present invention. Briefly, in such a spectrometer, a nuclear resonance spectrum is obtained by observing the effect on the electron spin resonance due to exciting resonance of the nuclei which are coupled to the electrons. The spectrometer is similar to that previously described with regard to FIG. **1**, with the exception that the phase shifter **8** is arranged such that the microwave diode switch **24** is spaced a quarter wavelength from the reflective wall **25** such that the phase of the microwave cavity signal reflected to the crystal detector **9** is varied by 180° depending upon whether the cavity signal is reflected from the microwave switch **24** or from the reflective wall **25**. An RF oscillator **62** applies RF energy to a power amplifier **63**, and thence to an RF coil **64** integral of the cavity **5** for applying a radio frequency magnetic field to the sample at right angle to the polarizing magnetic field H_o to excite nuclear resonance of the sample. The RF frequency of the oscillator **63** is swept through the nuclear resonance spectrum by means of an RF frequency sweep generator **65**. The RF energy applied to the sample is pulse modulated at a relatively high frequency, as of 6 kHz by means of a pulser **66** which is driven from a 6 kHz oscillator **67** via the intermediary of a power amplifier **68**.

Phase shifter **8** and phase shifter **16** are adjusted such that the reference microwave signal is in-phase or 180° out-of-phase with the microwave signal reflected from the cavity to the diode **9** via the phase shifter **8**. The phase of the microwave cavity signal is modulated at a relatively low phase modulation frequency, as of 35 Hz, derived from a 35 Hz oscillator **69** having its output amplified by power amplifier **71**, the output of which is fed to the diode switch **24**. The cavity signal is amplified in pre-amplifier **31** and one output is fed to the input of the automatic frequency control circuit **23** for controlling the frequency of the microwave source **2**, as previously described. Another output of the pre-amplifier **31** is fed via a high pass filter **72** which is tuned to pass the 6 kHz modulation in the microwave cavity signal. The output of the high pass filter **72** is gated via gate **73**, at the 6 Khz frequency derived from the 6 kHz oscillator **67** to obtain an absorption mode resonance output which is fed to a second low frequency amplifier **76**. The output of amplifier **76** is fed to a phase detector **77** for phase detection against a sample of the low frequency phase modulation signal derived from oscillator **69** to obtain an output resonance signal which is fed to the Y axis of the recorder **35** for recording as a function of the swept frequency of the RF oscillator **62**. The sweep signal is derived by a frequency counter **78** which counts the RF oscillator frequency and obtains an output fed to digital drive **79** for driving the X axis of the recorder **35**.

The impedance match between the circulator **3** and the cavity **5** is automatically maintained by amplifying with the amplifier **82** the signal at the 35 Hz appearing on the output of preamplifier **31**, phase detecting in phase detector **83** and feeding the output to a servo motor **81** for controlling the adjustment of a screw **84** which projects into the iris **7** between the circulator **3** and the cavity **5** for automatically adjusting the coupling between the cavity and the circulator **3** to maintain a perfect impedance match therebetween.

The automatic frequency control 23 will properly lock for either phase of the reflected cavity signal if the power incident on the cavity 5 is greater than 4 times the power in the reference channel 11. At lower incident powers, the AFC must be gated for one of the phases. As an alternative, the reference phase of the AFC phase sensitive detector, not shown, may be switched by 180° at the phase modulation frequency, i.e., 35 Hz.

Since many changes could be made in the above construction and any apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a microwave spectrometer apparatus, circulator means having first, second, third and fourth ports, microwave energy source means coupled to said first port of said circulator for supplying microwave energy to said circulator means, cavity resonator means for containing a sample to be investigated and coupled to said second port of said circulator for applying microwave energy to the sample and for reflecting a cavity microwave signal to said circulator, variable phase shifter means having a first and second state coupled to said third port of said circulator for receiving the cavity microwave signal and reflecting such signal with a first and second phase relative to a reference phase derived from said energy source, microwave detector means having an output signal, said detector being coupled to said fourth port of said circulator means for receiving the microwave cavity signal with a phase relation which is a function of the phase shift produced by said phase shifter means, means independent of said circulator for coupling said microwave energy source to said microwave detector means for applying microwave energy from said source to said detector means to provide said reference phase for said detector, and means for causing said microwave detector signal output to selectively change from a pure absorption mode signal to a pure dispersion mode signal, said means comprising means to cyclically switch said variable phase shifter between said first and second state.

2. The apparatus of claim 1 including an audio oscillator wherein said means to switch said variable phase shifter is responsive to said audio oscillator for controlling the sequence of switching between said first and second state.

3. The apparatus of claim 2, including means for coupling said detector output signal to an AFC circuit for tuning the frequency of said microwave energy source when said signal represents an absorption mode signal and for coupling said detector output signal to a receiver when said signal represents a dispersion mode signal, said means for coupling being responsive to said audio oscillator.

4. The apparatus of claim 3, including, means for producing a polarizing magnetic field in said cavity resonator, means for modulating the polarizing magnetic field in the cavity at a high field-modulation frequency, said high modulation frequency being provided said receiver to enable synchronous detection of said dispersion signal.

5. Apparatus of claim 3 wherein said variable phase shifter comprises a first and second spaced apart electrical discharge means spaced from a reflective wall structure, and wherein said means to switch said variable phase shifter is responsive to a first and second related pulse sequence connected respectively to said first and second electrical discharge means.

6. Apparatus of claim 2 wherein said means to switch said variable phase shifter comprises means for switching between said first and second state at least twice during each cycle of said audio oscillator.

7. Apparatus of claim 5, including field modulation windings coupled to said audio oscillator wherein said first related pulse sequence is a low multiple of the frequency of the audio oscillator driving the field modulation windings and said second related pulse sequence is a high frequency pulse train which occurs between pulses of said first related pulse sequence.

8. The apparatus of claim 3 including, means for modulating the frequency of the microwave energy supplied to said circulator means and thence to said cavity resonator from said microwave energy source means to produce modulation of the microwave cavity signal reflected to said detector means at a second modulation frequency which is a function of the frequency of the frequency modulation, means for detecting the second modulation component in the microwave cavity signal during said period that said detector signal represents the absorption mode signal, means responsive to the detected second modulation component for determining and storing a frequency correction signal, and means for tuning the frequency of said microwave energy source to the resonant frequency of said microwave cavity means responsive to said stored correction signal.

9. The apparatus of claim 3 wherein said means for coupling includes a gate responsive to said audio oscillator for gating the cavity output signal of said detector means such that the cavity signal components of one phase are gated to one receiver and components of a second phase are gated to a second receiver.

10. The apparatus of claim 5 wherein said first and second electrical discharge means are spaced from said wave reflective wall along the path of the microwave cavity signal by an odd number of ¼ and ⅛ wavelengths, respectively, for modulating the phase of the microwave cavity signal at the first and second phase modulation frequencies by 180° and 90°, respectively.

11. The apparatus of claim 1 including, means for variably controlling the coupling of wave energy between said circulator means and said cavity resonator means, means for modulating the phase shift produced by said phase shifter means at a modulation frequency to produce a modulation signal component in the detected cavity signal at a frequency which is a function of the phase modulation frequency, means for phase detecting the modulation signal to derive a control output, means for feeding the control output to said cavity coupling control means for causing said control means to automatically impedance match said cavity to said circulator means.

12. The apparatus of claim 1 including automatic frequency control means for tuning the frequency of said microwave energy source to the resonant frequen-

cy of said microwave cavity means, and means for synchronizing operation of said automatic frequency control means to the absorption mode portions of said microwave detector output.

13. In a microwave spectrometer apparatus, circulator means having first, second, third and fourth ports, microwave energy source means coupled to said first port of said circulator for supplying microwave energy to said circulator means, cavity resonator means for containing a sample to be investigated and coupled to said second port of said circulator for applying microwave energy to the sample and for reflecting a cavity microwave signal to said circulator, variable phase shifter means coupled to said third port of said circulator for receiving the cavity microwave signal and reflecting such signal with a certain phase relation to said circulator means, microwave detector means coupled to said fourth port of said circulator means for receiving the microwave cavity signal with a phase relation which is a function of the phase shift produced by said phase shifter means, and means independent of said circulator for coupling said microwave energy source to said microwave detector means for applying microwave energy from said source to said detector means to provide a reference phase for said detector, wherein said phase shifting means comprises a wave reflective wall structure and an electrical discharge means responsive to the modulation signal and spaced from said reflective wall structure, said electrical discharge means serving to reflect the microwave cavity signal back to said circulator means when said electrical discharge means is rendered wave reflective in response to the modulation signal, and said wall serving to reflect the microwave cavity signal when said electrical discharge means is rendered wave transmissive.

14. The apparatus of claim **13** wherein said electrical discharge means includes a diode.

15. The apparatus of claim **13** wherein the spacing from said electrical discharge means to said wave reflective wall structure is an odd integral number of one eighth wavelengths at the resonant frequency of said cavity resonator, whereby a 90° phase modulation of the microwave cavity signal is obtained at the phase modulation frequency.

16. In a microwave spectrometer apparatus, circulator means having first, second, and third ports, microwave energy source means coupled to said first port of said circulator for supplying microwave energy to said circulator means, cavity resonator means for containing a sample to be investigated and coupled to said second port of said circulator for applying microwave energy to the sample and for reflecting a cavity microwave signal to said circulator, microwave detector means, variable phase shifter means coupled to said third port of said circulator for receiving the cavity microwave signal and transmitting said signal with a certain phase relation to said microwave detector means, means independent of said circulator for coupling said microwave energy source to said microwave detector means for applying microwave energy from said source to said detector means to provide a reference phase for said detector, automatic frequency control means for tuning the frequency of said microwave energy source to the resonant frequency of said microwave cavity means, means for cyclically modulating the phase of said variable phase shifter, and means for synchronizing operation of said automatic frequency control means with the phase modulation cycle, said means for synchronizing including means for rendering said automatic frequency control means responsive only during certain portions of the cycle of said modulation of said variable phase shift.

17. The apparatus of claim **16** wherein said means for synchronizing said automatic frequency control means with the phase modulation cycle includes a gate for gating the detected cavity signal of one phase to said automatic frequency control means, and means for applying a cyclical gating signal to said gate in synchronism with the phase modulation cycle of the cavity signal.

18. The apparatus of claim **16** including, means for producing a polarizing magnetic field in said cavity resonator, means for modulating the polarizing magnetic field in the cavity at a field modulation frequency responsive to an oscillator, and wherein said phase modulation frequency is also responsive to said oscillator such that the phase modulation of the cavity signal is synchronized with the field modulation frequency.

19. The apparatus of claim **16** including means for applying radio frequency energy to the sample in said cavity resonator at a nuclear resonance frequency of nuclei of the sample, and means for sweeping the frequency of the radio frequency energy.

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