UNCLASSIFIED

AD NUMBER

AD021087

CLASSIFICATION CHANGES

TO: **unclassified**

FROM: **confidential**

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAY 1953. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203.

AUTHORITY

ONR ltr, 29 Sep 1959; ONR ltr, 13 Sep 1977

THIS PAGE IS UNCLASSIFIED

CONFIDENTIAL
SECURITY INFORMATION

VARIAN ENGINEERING
REPORT NO. 129-4

COPY NO. 38
JUNE 1953

FINAL REPORT
MEASURING LOW MAGNETIC FIELDS

Prepared for

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
Contract NOnr - 791(00)

By

VARIAN ASSOCIATES
611 Hansen Way
Palo Alto, California

NOTICE:
This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18 U.S.C., Sections 793, 794, 795. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

This document has been reviewed in accordance with OPNAVINST 5510.17, paragraph 5. The security classification assigned hereto is correct.

Date: 12/4/53 Gould Hunter
By direction of
Chief of Naval Research (Code 427)

CONFIDENTIAL
SECURITY INFORMATION

VARIAN ENGINEERING
REPORT NO. 129-4

COPY NO. 38
MAY 1953

FINAL REPORT
MEASURING LOW MAGNETIC FIELDS

Prepared for

OFFICE OF NAVAL RESEARCH
Contract NOnr-791(00)

Prepared by:

Arnold Bloom
Edwin Jaynes
L. Malling

Approved by:

W Myrl Stearns
W. Myrl Stearns
Vice-Pres. and Gen. Manager

Robert L Jepsen
Robert L. Jepsen
Director of Research

John W Clark
John W. Clark
Contract Administrator

ABSTRACT

A theoretical investigation was undertaken to investigate the measurement of small changes in the earth's magnetic field by means of paramagnetic resonance methods.

A study was made of the effects of line shape, sensitivity of apparatus, geometry, and the chemical and physical properties of free radical and metal-in-ammonia samples. Single and cross-coil systems were considered as well as their associated electronic circuits.

It is felt that an air-borne detector can be designed capable of detecting magnetic field changes of the order of one millionth gauss and insensitive to changes in orientation with respect to the field, provided certain conditions can be met.

TABLE OF CONTENTS

Page No.

PART I - THEORY

PART II - APPARATUS

APPENDIX A

APPENDIX B

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (CONT.)

LIST OF ILLUSTRATIONS (CONT.)

LIST OF TABLES

PART I - THEORY

1. Introduction

The purpose of this report is to discuss the possibilities of using paramagnetic resonance as a means for measuring very small changes in the earth's magnetic field. The report is divided into two parts. Part I deals with the theoretical aspects of paramagnetic resonance and the theoretical consideration upon which a device using paramagnetic resonance for measuring the earth's field has to be built. Part II discusses the possible mechanism for achieving this result and discusses in detail circuit diagrams and other electronic considerations.

Before discussing paramagnetic resonance in detail, it is necessary to consider what requirements must be imposed on the apparatus which we intend to design for measuring small changes in the earth's magnetic field. The apparatus must be designed to be flown in an airplane or towed in a bird and to detect, in flight, changes of the order of at least 0.1 gamma (Γ) and possibly as small as 0.01 gamma. (One gamma = 10^{-5} gauss.) These measurements must be carried out over a frequency range of from approximately 0.01 to 1 cps. In other words, we are not concerned at the moment with the absolute value of the earth's field (about 1/2 gauss) but only with changes in a value of the field of the order of 1 cps or less. It is desirable that the apparatus be rugged, easy to install and maintain, and require a minimum of attention in flight. It is also expected that personnel should not have to be very highly trained in order to perform routine maintenance operations and checks on the apparatus. The measurements made by this apparatus should be completely insensitive to the motion of the airplane and should be capable of being operated off the airplane power mains with a minimum need of additional regulation. The sensing element should be small.

We should now consider what paramagnetic resonance is and why it has been considered in the design of an air-borne magnetometer. Paramagnetic resonance is a form of spectroscopy in which transitions are induced between Zeeman levels corresponding to the two possible spin states of a free electron. To observe the resonance, a steady magnetic field is needed, in this case the earth's field, which defines the z-direction along which the electron spins are aligned either parallel or anti-parallel. A r-f magnetic field perpendicular to the d-c field will then induce transitions between the spin states if the angular frequency ω of the r-f field is close to the resonance frequency of the electrons; i.e., we require that $\hbar\omega$ equals the energy difference between the Zeeman levels. In common with many Zeeman effects, the energy difference for this one is proportional to the applied magnetic field so that we have the following relation:

$$\omega_0 = \gamma H_0 \qquad (1\text{-}1)$$

$\omega_0/2\pi$ is the so called resonance frequency, H_0 is the steady magnetic field, and γ is a constant determined by the ratio of the magnetic moment of the electron to its spin. In round numbers, $\gamma = 2\pi \times 2.8$ mc per gauss.* Thus,

---

* Throughout this report γ is the absolute value of the true gyromagnetic ratio of the electron.

since the earth's magnetic field is of the order of 1/2 gauss, the resonance frequencies which we expect are within what we may call the broadcast range. The transitions induced by the r-f field are magnetic dipole transitions along the z-axis which result in resonance radiation which is radiated throughout the xy-plane. Thus there have arisen two methods of detecting paramagnetic resonance. (These methods were originally developed to observe nuclear magnetic resonance at much higher field strengths; however, this same physical principle applies, and the same type of apparatus may be used for both cases, except for the strength of H_o.)

One method of detecting paramagnetic resonance was developed by Purcell and his collaborators(1) and detects the resonance radiation in the x-direction, that is to say, in the same direction as the applied r-f field. Since the resonance radiation subtracts from the applied r-f field, the net effect upon the coils producing the field is that of an absorption of energy by the sample. Thus, one uses a single coil to produce the r-f magnetic field and observes the resonance as a loss of energy inside the sample. This method will be referred to hereafter as the single-coil system. The other method, developed by Bloch and his collaborators,(2) detects the resonance radiation at right angles to the applied r-f field. In this method the resonance is observed as an induced voltage in the coils at right angles to the r-f field. These coils, when properly adjusted, do not couple with the applied field unless there is paramagnetic resonance present to produce the resonance radiation. This method will be referred to hereafter as the cross-coil method. Both methods have theoretically the same ultimate sensitivity for detecting small changes in the earth's magnetic field. However, this point will be discussed in more detail in Part II of this paper.

The phenomenon of paramagnetic resonance can be explained in terms of a very simple analogy in classical mechanics. The electron, possessing a spin and a magnetic moment, may be considered to be a magnetic gyroscope whose poles are in the direction of the axis of spin. This spinning magnet will, after a certain length of time determined by frictional forces, find itself aligned with the magnetic field. If one now applies a magnetic field impulse at right angles to the earth's field so as to knock the gyroscope out of alignment with the earth's field, a torque is imposed upon the gyroscope which causes it to precess at a frequency known as the Larmor frequency. These Larmor precessions about the z-axis will damp out in time unless the impulses are applied once each Larmor cycle, i.e., each time the gyroscope comes around to the point where the field can impart the maximum torque. Thus, a resonance is set up which occurs at the Larmor frequency given by ω_o. According to Bloch, the motion of a spinning magnet of magnetic moment M may be described as follows. The motion of the spinning magnet, due to the torque imposed upon it by a magnetic field, is given by

$$\frac{d\vec{M}}{dt} = -\gamma \vec{M} \times \vec{H} \tag{1-2}$$

where γ is the same quantity as given in formula (1-1). The effect of frictional forces, which are actually caused by collisions between the electrons, is described by Bloch(3) by the traditional frictional damping term

$$\frac{d\vec{M}}{dt} = \frac{\vec{M}_o - \vec{M}}{\tau} \tag{1-3}$$

where M_0 is the equilibrium magnetic moment distribution and τ is a quantity called the relaxation time. Bloch further assumed that these two formulas could be combined to give the equation of motion of a substance in paramagnetic resonance. This combined formula is given in Section 2.

Returning to spectroscopic terms, the quantity $1/\tau$, having units of frequency, may be defined to be proportional to the line width of this spectroscopic line. In units of magnetic field, we define the quantity $\lambda = 1/(\gamma\tau)$ as the line width in terms of changes of magnetic field. This quantity will be of fundamental importance in our discussion. The line width λ for substances showing paramagnetic resonance varies widely, depending on the substance, from values of a fraction of a gauss to values of several hundred gauss or more.

One of the reasons paramagnetic resonance has appeared to be important as a possible method of measuring the earth's field is the fact that it is possible to eliminate the need for any biasing field in connection with the measurement. All other sensitive methods of measuring changes in field require the use of some bias field to set the apparatus to a standard field, which is the field that is actually measured. As is shown in Section 4, the use of even a very small bias field imposes severe requirements on the stabilization of the apparatus because the probe must then point exactly in the direction of the earth's field. In the case of paramagnetic resonance, however, it appears that biasing fields can be done away with because the biasing, so to speak, is done by adjusting the resonance frequency. Thus, the possibility develops that a magnetometer could be designed which does not need to be oriented with respect to the earth's field. The extent to which this is true will be discussed in Section 4.

2. Line Shape

The behavior of any apparatus utilizing paramagnetic resonance will depend upon the shape and intensity of the resonance line as a function of both frequency and magnetic field. The principal features of the line shape may be deduced from the classical assumptions of Bloch(3), which hold rigorously if the line shape is Lorentzian(4). According to these assumptions, the paramagnetic substance may be considered to be made up of a classical system of gyroscope magnets of gyromagnetic ratio γ which precess at a Larmor frequency $\omega_o = \gamma H_o$. In the absence of any r-f field, the gyroscope magnets are to assume equilibrium positions such that the net moment, M_o, is given by Curie's Law,

$$M_o = \chi_o H_o = \left(\frac{I + 1}{3I}\right) \frac{N_o \mu^2}{kT} H_o \qquad (2\text{-}1)$$

Here, I is the spin of the electron in units of $\hbar$, N_o is the number of free electrons per unit volume, μ is the magnetic moment of the electron, and kT is the thermal energy.

If M is the macroscopic moment of a sample, the equations of motion are

$$\frac{d\vec{M}}{dt} + \frac{\vec{M} - X_o\vec{H}}{\tau} + \gamma \vec{M} \times \vec{H} = 0 \qquad (2\text{-}2)$$

which are Bloch's equations(3) modified to include the case, $H_1 \simeq H_o$. H_1 is one half the magnitude of the r-f field. We will assume only one isotropic relaxation time for this particular case and define $\gamma \lambda = 1/\tau$.

We are concerned with the steady state solution for which

$$H_x = 2H_1 \cos \omega t$$
$$H_y = 0 \qquad (2\text{-}3)$$
$$H_z = H_o = \frac{\omega_o}{\gamma}$$

and for which M_z = constant. This last condition implies a weak r-f field, i.e.,

$$H_1 < \lambda \qquad (2\text{-}4)$$

In quantum-mechanical terms, equation (2-2) is the macroscopic equation of motion for a system of magnetic moments obeying Curie's Law, for which the lifetime in a given Zeeman level is determined by the time between collisions. A collision may be roughly defined to be a process which destroys the coherence of the electron wave function and returns the electron to the equilibrium distribution. The theory of the collision-broadened line shape for the particular case of absorption as observed in a single-coil system is also developed quantum-mechanically in reference$^{(5)}$.

For our purposes we need the general steady state solution of equation (2-2) with the conditions of equation (2-3). If we define

$$F = M_x + iM_y \qquad (2\text{-}5)$$

then the solution is

$$F = \frac{2\chi_o H_1 (\gamma\lambda - i\omega_o)\left[(\gamma\lambda - i\omega_o)\cos \omega t + \omega \sin \omega t\right]}{(\gamma\lambda - i\omega_o)^2 + \omega^2} \qquad (2\text{-}6)$$

The real part of F gives us the solution seen by a single-coil system, while the imaginary part gives us the solution observed by a cross-coil system. Furthermore, in the single-coil system the absorption mode is given by the sine terms and the dispersion mode by the cosine terms, but in the case of the cross-coil system the reverse is true, the absorption mode being given by cosine terms and the dispersion by sine terms. The reason for this reversal is simply the fact that it takes a quarter of a cycle for the precessing moments to move from a position where they will be observed in the single-coil system to one where they will be observed in a cross-coil system. The voltage that is induced in a coil surrounding a sample will be given by time derivatives of F, i.e. by $\frac{dM_x}{dt}$, $\frac{dM_y}{dt}$. The magnetic moment, M, can be broken up into a dispersion component, u, and an absorption component, v.

The voltage developed across the receiver coil in the different cases is then proportional to the following formulas. By "proportional" we mean that we have omitted geometrical factors given in formula (3-1):

Single-coil absorption:

$$\frac{dv_x}{dt} = \gamma \chi_0 H_1 \omega^2 \lambda \left[\frac{1}{\gamma^2\lambda^2 + (\omega_0 - \omega)^2} + \frac{1}{\gamma^2\lambda^2 + (\omega_0 + \omega)^2} \right] \cos\omega t \quad (2\text{-}7)$$

Single-coil dispersion:

$$\frac{du_x}{dt} = -\gamma \chi_0 H_1 \omega \lambda \left[\frac{(\gamma^2\lambda^2 + \omega_0^2)^2 + (\gamma^2\lambda^2 - \omega_0^2)\omega^2}{\gamma^2\lambda^2 + \omega_0^2 + \omega^2} \right] \times$$

$$\left[\frac{1}{\gamma^2\lambda^2 + (\omega_0 - \omega)^2} + \frac{1}{\gamma^2\lambda^2 + (\omega_0 + \omega)^2} \right] \sin\omega t \quad (2\text{-}8)$$

Cross-coil absorption:

$$\frac{dv_Y}{dt} = \gamma \chi_0 H_1 \omega^2 \lambda \left[\frac{1}{\gamma^2\lambda^2 + (\omega_0 - \omega)^2} - \frac{1}{\gamma^2\lambda^2 + (\omega_0 + \omega)^2} \right] \sin\omega t \quad (2\text{-}9)$$

Cross-coil dispersion:

$$\frac{du_Y}{dt} = \frac{\chi_0 H_1 \omega}{2} (\gamma^2\lambda^2 + \omega_0^2 - \omega^2) \times \left[\frac{1}{\gamma^2\lambda^2 + (\omega_0 - \omega)^2} - \frac{1}{\gamma^2\lambda^2 + (\omega_0 + \omega)^2} \right] \cos\omega t \quad (2\text{-}10)$$

In the event that $\omega_0 >> \gamma\lambda$, the single and cross-coil formulas become identical in the vicinity of resonance and become the familiar Lorentzian absorption and dispersion curves:

Absorption:

$$\omega v = \gamma \chi_0 H_1 \omega^2 \lambda \left[\frac{1}{\gamma^2\lambda^2 + (\omega_0 - \omega)^2} \right] \quad (2\text{-}11)$$

Dispersion:

$$\omega u = \chi_0 H_1 \omega \left[\frac{\gamma^2\lambda^2 + \omega_0(\omega_0 - \omega)}{\gamma^2\lambda^2 + (\omega_0 - \omega)^2} \right] \quad (2\text{-}12)$$

Our study, however, has included paramagnetic substances in which the reverse is true, i.e., ω_0 is of the same order of magnitude as $\gamma\lambda$. The resulting asymmetry of the curves about resonance will have considerable effect on the sensitivity of an apparatus using these curves for its operating characteristics. For examples of typical line shapes see Figures (2-1) to (2-6).

The actual line shapes observed in given materials often differ from the ideal Lorentzian shape given in formulas (2-7) through (2-12) owing to interactions between electrons which have no classical analogue(6). A small change in the shape of the curves does not affect the results presented in this report, and in general we shall find it convenient to consider as our operating curves formulas (2-11) or (2-12) or curves derived from them. These formulas give the basic considerations on which our discussion must depend.

Of more interest to us, however, is the possibility that the position of the resonance may change as a function of instrumental parameters. Thus, we may want to know whether there will be apparent changes in the resonance positions, and therefore spurious changes in the earth's field, due to factors that may ultimately be traced to variations of power supply voltage, for example, or other factors which change the conditions under which the instrument operates. Such factors which may change both the shape of the resonance curve and the position of resonance are the following:

a. Electrical conductivity in the sample. This causes some mixing of the absorption and dispersion modes and thereby changes the shape of the signal which is observed in either case. This effect is discussed in reference(7). This mixing may cause a shift in the apparent resonance which is constant and, therefore, does not interest us unless the conductivity changes during operation. It is probable that the conductivity of metal-ammonia solutions changes slightly as a function of temperature; however, over the permissable operating range of temperatures the change is probably not sufficient to cause us any concern.

b. Line broadening by strong r-f fields. The effect of a strong r-f field is to reduce the height of the resonance maximum and thereby give the effect of a broadened curve. The theory of this effect for single-coil systems is discussed in reference(8). See also references (1) and (3). The criterion that a r-f field be strong enough to produce line broadening is that

$$H_1 > \lambda \tag{2-13}$$

If the resonance line is narrow, then the principal effect of line broadening is to reduce the sensitivity. However, if the line is broad so that formulas (2-7) thru (2-10) hold in weak fields, then a line broadening also shifts the position of maximum absorption or zero dispersion.

c. The Bloch-Siegert effect(9). It has been shown that a resonance curve of the form given by formula (2-11) or (2-12) may have its resonance shifted by a factor proportional to $\frac{H_1^2}{16\ H_o^2}$ if the r-f field is sufficiently strong so that line broadening is also present. This effect however will be negligible for the ranges of H_1 and H_o for which we are interested. A similar effect is observed if the r-f field is not perpendicular to H_o and if formula (2-13) applies. (See Appendix.) These effects would be of importance if it were necessary to operate the apparatus under conditions such that H_1 were comparable to H_o, for in that case the position of the resonance might be sensitive to power supply variations or other factors which might change the value of H_1 slightly. It turns out, fortunately, that optimum operation is obtained under conditions in which the r-f field is weak, (i.e. formula (2-4) applies). Under these conditions variations in the value of H_1 may cause changes in sensitivity but not in the position of resonance. The manner in which the effects of changes in sensitivity are minimized is discussed in Section 4 of this paper.

d. Effects of changes of direction of the earth's field relative to the probe. These effects are discussed in some detail separately in Section 4.

In general, we expect an instrument which is designed to employ paramagnetic resonance to give an indication which is a function of the magnetic field, and which will be related in some way to one of the resonance curves given by formulas (2-7) thru (2-12). The particular indication that it gives we shall call the operating curve or operating characteristic. It will become apparent in subsequent discussion that the best type of operating characteristic is one which is approximately linear in a region in which the output signal changes sign. An example of such a characteristic is that of formula (2-12), illustrated in Figure (2-6), in which the desired property is observed in the region around resonance. The sensitivity of the apparatus is then proportional to the slope of this operating characteristic in the region of interest. In this particular case the slope is given by

$$\frac{d\,(\omega u)}{d\,\omega_0} \simeq \chi_0 H_1 \frac{\omega^2}{\gamma^2 \lambda^2} \qquad (2\text{-}14)$$

in which we neglect a very small effect due to the fact that the characteristic does not go through zero exactly at resonance. Formula (2-14) will be fundamental in our calculations of the sensitivity of the apparatus.

Another desirable operating curve is obtained by employing the absorption curve (2-11) with a magnetic sweep modulation, which is a sinusoidal sweep of the form

$$H_s \cos \omega_m t \tag{2-15}$$

and then, looking only at the component of the output which is at the modulation frequency, $\omega_m/2\pi$. It can be seen from Figure (2-7) that the output or operating characteristic obtained in this way is, for small values of H_s, approximately proportional to the derivative of the absorption curve, and the resulting curve has approximately the same shape as the dispersion curve (2-12) although it is not identical to it. The characteristic obtained for an arbitrary amount of sweep modulation can be obtained in the following manner. Let us define the quantities $\frac{\omega_0 - \omega}{\gamma \lambda} = a$, and $\frac{H_s}{\lambda} = b$. Then the instantaneous signal produced by the sample is given by

$$\omega v(t) = \frac{\chi_0 H_1 \omega^2}{\gamma \lambda} \left[\frac{1}{1 + (a + b \cos \omega_m t)^2} \right] \tag{2-16}$$

If we expand (2-16) in a Fourier series we find that the component at the modulating frequency $\omega_m/2\pi$ is given by

$$J = \frac{\chi_0 H_1 \omega^2}{\pi \gamma \lambda} \int_{-\pi}^{+\pi} \frac{\cos \omega_m t}{1 + (a + b \cos \omega_m t)^2} \, d(\omega_m t) \tag{2-17}$$

which is equal to

$$J = - \frac{2\chi_o H_1 \omega^2}{b \gamma \lambda} \left[\frac{a - i}{\sqrt{(1 + ai)^2 + b^2}} + \frac{a + i}{\sqrt{(1 - ai)^2 + b^2}} \right] \qquad (2\text{-}18)$$

where the complex square roots are to be taken with real parts positive. An example of such a curve is shown in Figure (2-8). The slope of this characteristic where it crosses the axis is given by

$$\left.\frac{dJ}{da}\right|_{a = o} = - \frac{2\,b}{(1 + b)^{3/2}} \qquad (2\text{-}19)$$

Formula (2-19), plotted in Figure (2-9), has a broad maximum at the value $b = 0.707$. Thus, the optimum response is obtained when the peak value of the modulation is 0.707 times the line width. This particular value of b was used to plot Figure (2-8). The slope of this curve at resonance is 0.77 times the slope of the corresponding dispersion curve for the same sample.

The use of a sweep modulation introduces another parameter upon which sensitivity and position of the resonance may depend. The resonance position may vary slightly if the sweep modulation field is not parallel to the field to be measured. This effect is discussed in detail in Section 4. Concerning variations due to changes in the magnitude of H_s, due for example to power supply variations, we observe from Figure (2-9) that the broad maximum insures that the sensitivity does not vary much with small changes in H_s. A change in H_s will produce no change in the apparent value of the earth's field if the original absorption characteristic is symmetrical around resonance.

However, if the absorption characteristic is asymmetrical as, for example, those shown in Figures (2-1) and (2-2), then obviously the zero indication may be a very sensitive function of the magnitude of the sweep field and would imply that H_s would have to be highly regulated. This is an argument in favor of using narrow linewidths, such as those obtained from metal-ammonia solutions, which give characteristic curves described most nearly in terms of formulas (2-11) and (2-12).

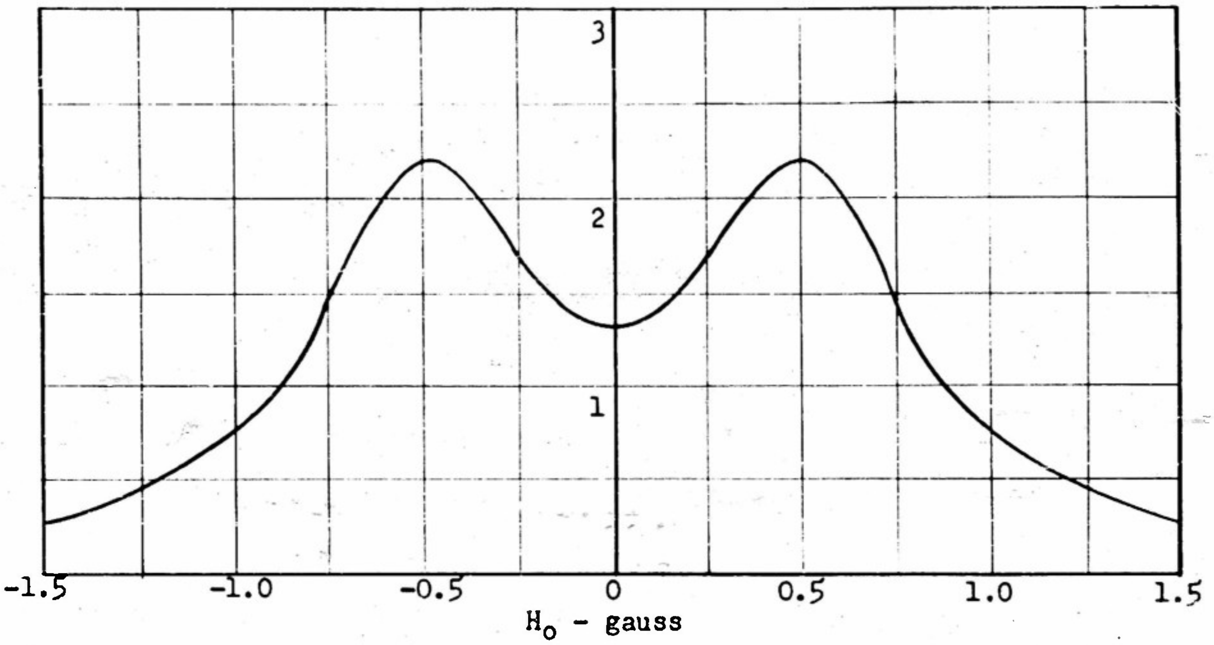


FIGURE 2-1

RESONANCE CURVE FOR SINGLE-COIL ABSORPTION

λ = 0.35 gauss, ω = 1.4 mc,

ordinates in arbitrary units

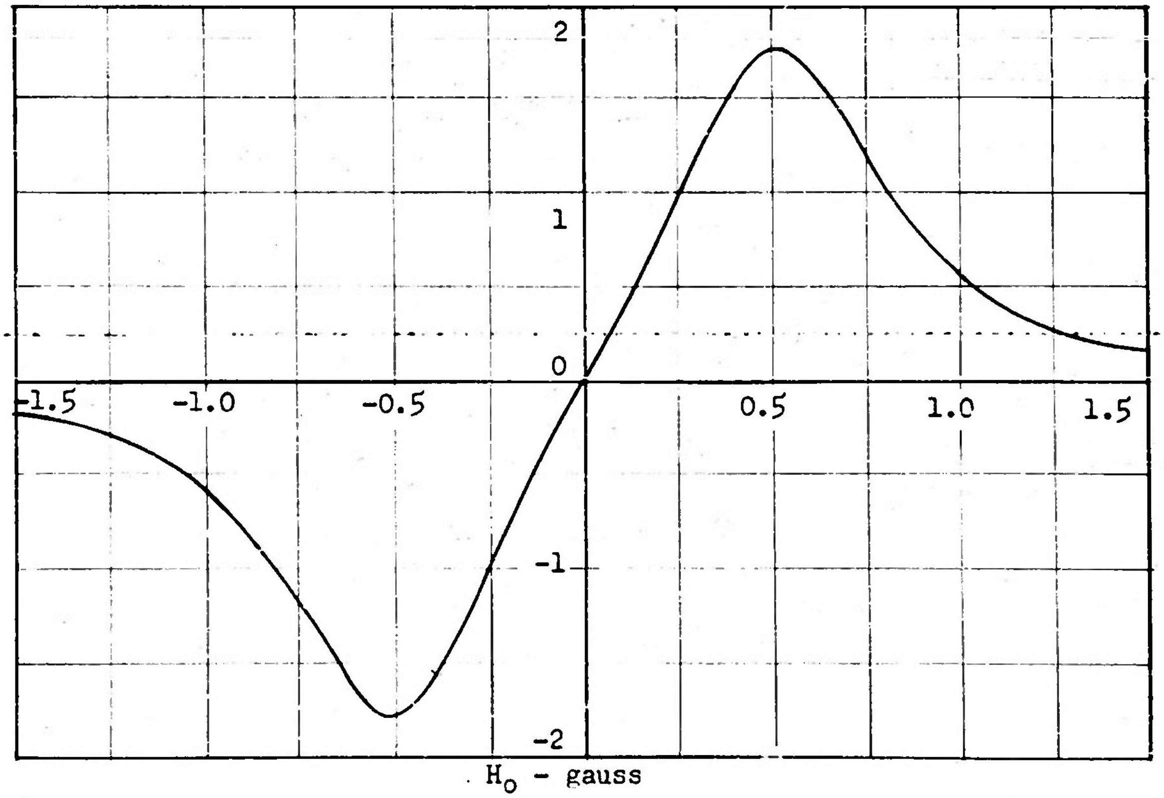


FIGURE 2-2

RESONANCE CURVE FOR CROSS-COIL ABSORPTION

λ = 0.35 gauss, ω = 1.4 mc,

ordinates [illegible] units

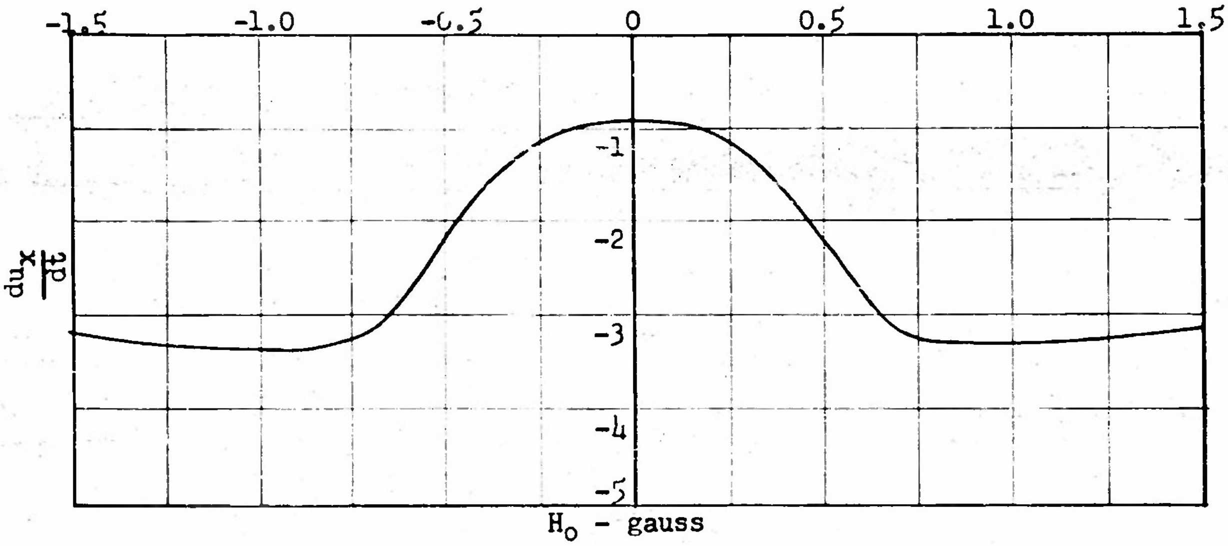


FIGURE 2-3

RESONANCE CURVE FOR SINGLE-COIL DISPERSION

λ = 0.35 gauss, ω = 1.4 mc,

ordinates in arbitrary units

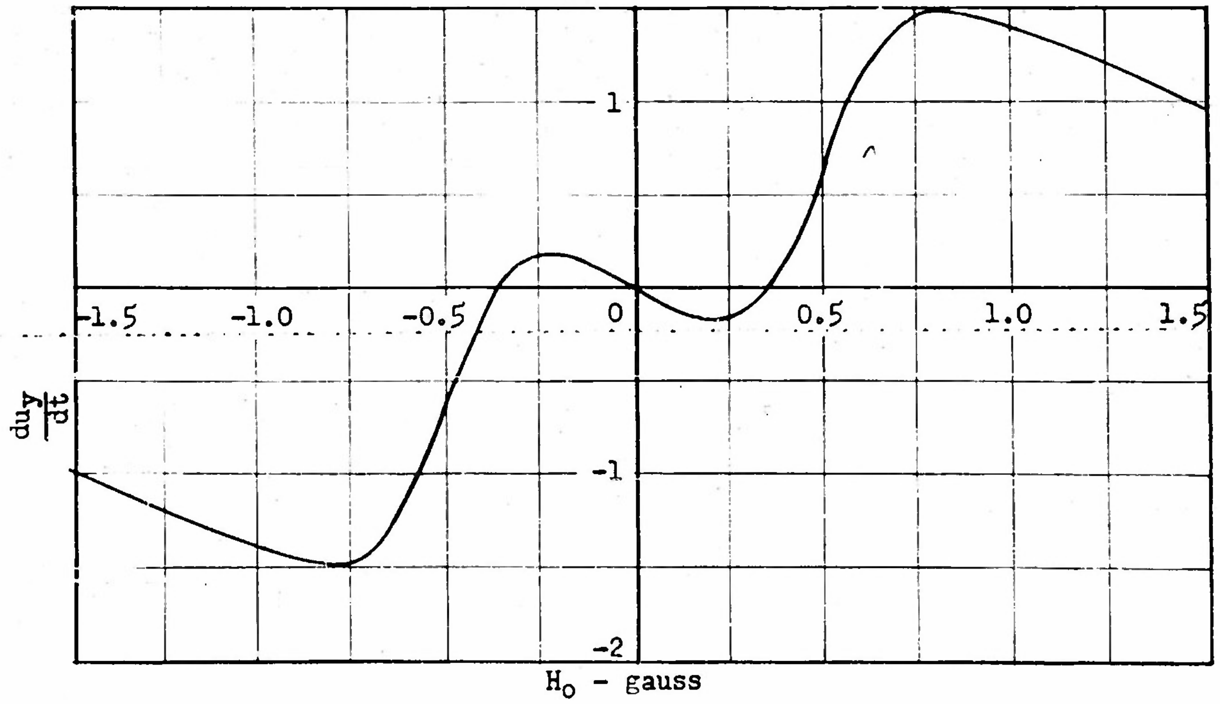


FIGURE 2-4

RESONANCE CURVE FOR CROSS-COIL DISPERSION

λ = 0.35 gauss, ω = 1.4 mc,

ordinates in arbitrary units

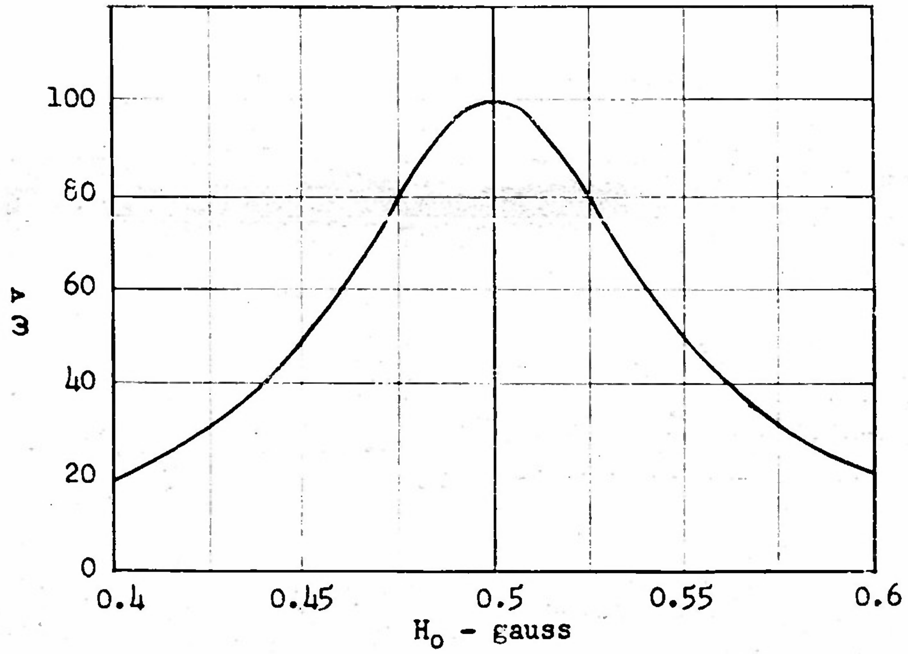


FIGURE 2-5

ABSORPTION RESONANCE CURVE

$\lambda = 0.05$ gauss, $\omega = 1.4$ mc,

ordinates in % maximum height of absorption

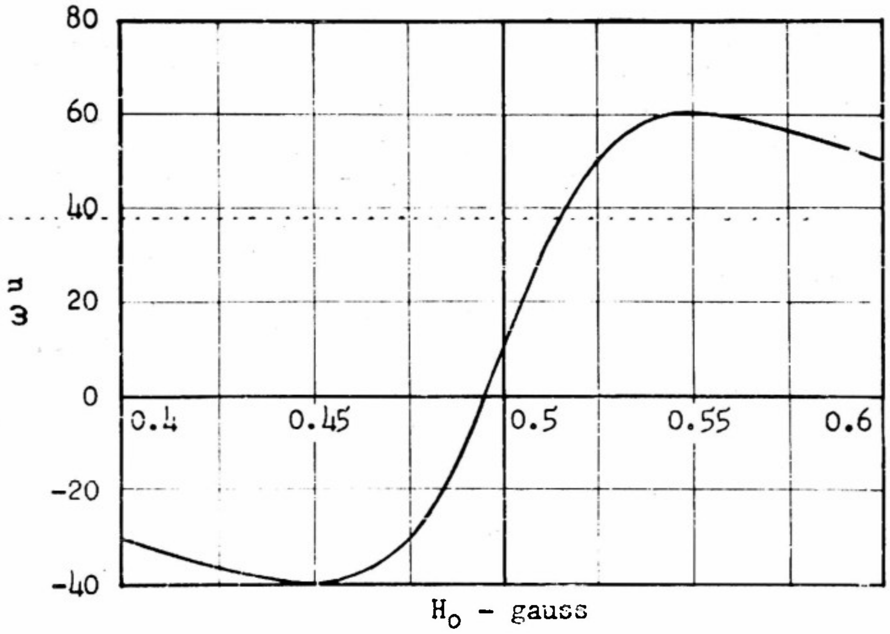


FIGURE 2-6

DISPERSION RESONANCE CURVE

$\lambda = 0.05$ gauss, $\omega = 1.4$ mc,

ordinates in % maximum height of absorption

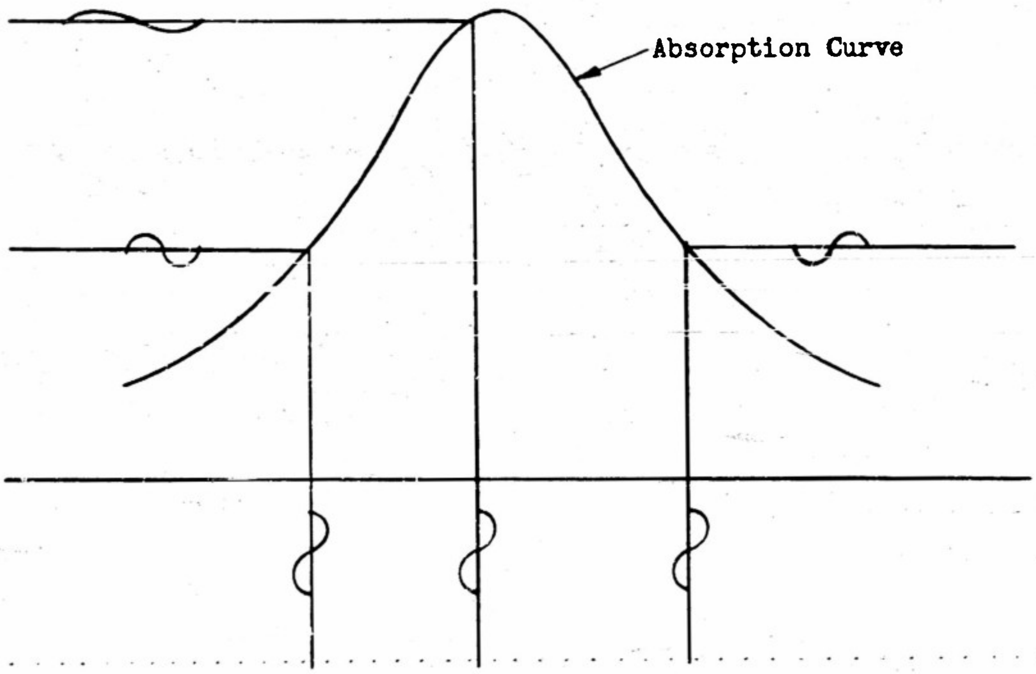


FIGURE 2-7

ILLUSTRATION OF HOW AN OPERATING CHARACTERISTIC IS OBTAINED FROM SWEEP MODULATION OF THE ABSORPTION CURVE

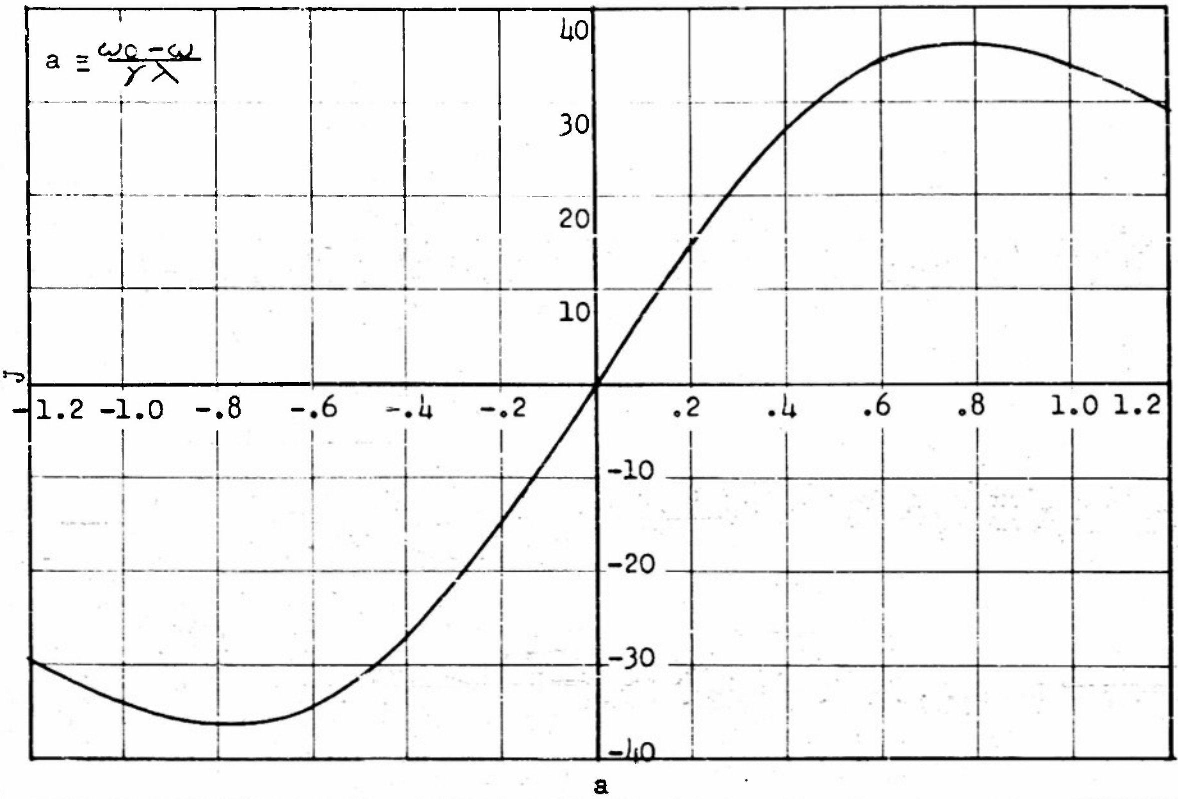


FIGURE 2-8

DERIVED CURVE FROM SWEEP MODULATED ABSORPTION CURVE

Ordinates in % maximum height of absorption.

This is the sweep-modulated characteristic.

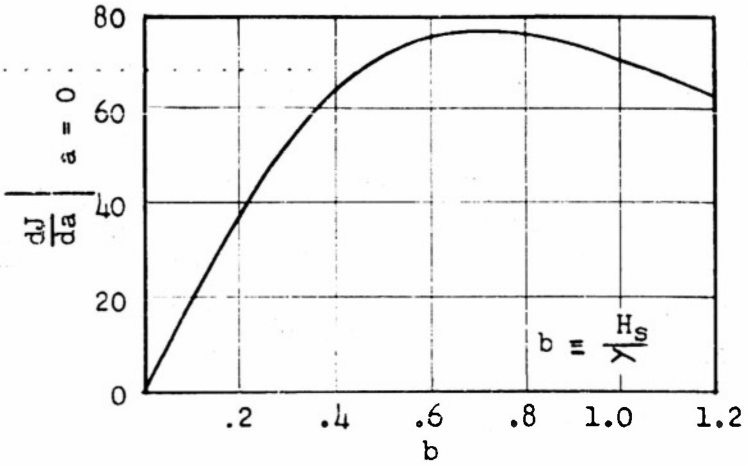


FIGURE 2-9

MAXIMUM SLOPE OF SWEEP-MODULATED CHARACTERISTIC AS A FUNCTION OF SWEEP AMPLITUDE

Ordinates in % maximum slope of dispersion curve.

3. Theoretical Sensitivity of the Apparatus

The smallest change in the earth's magnetic field which can be detected by an apparatus using paramagnetic resonance is governed only by the ratio of the signal amplitude to the noise level of the apparatus. (All noise figures given in this paper are in terms of voltage signal-to-noise ratio). Since the total magnetic moment producing a signal is proportional to the number of electrons and therefore to the volume of the sample, there is theoretically no limit to the sensitivity that may be achieved thru paramagnetic resonance if the sample volume can be made large enough. Actually a limitation exists when a point is reached at which the sample must be too large to be used in a practical apparatus, either because it is too large to be fitted into the desired space, or because it becomes prohibitively difficult to make the sample in large quantities.

If a spherical sample of volume Ω is used, then the voltage induced across the receiving coil has been shown(10) to be equal to

$$V_s = \frac{4\pi}{\sqrt{2}} \frac{NQ\Omega}{\sqrt{h^2 + d^2}} \left\{ M\omega \right\} \times 10^{-8} \qquad (3\text{-}1)$$

where N is the number of turns in the coil, Q is the Q of the entire tuned circuit of which the receiver coil is part, h and d are the height and diameter of the coil respectively, and the quantity in brackets refers to whichever of formulas (2-7) to (2-12) is applicable in this particular instance. Formula (3-1) has been derived on the assumption that the radio-frequency field H_1 is constant across the sample as is generally the case in cross-coil systems.

In a single-coil system a small correction must be applied to formula (3-1) to take account of the fact that H_1 may not be uniform across the sample.

In the types of apparatus to be described in Section 2 of this paper we need to know, not the total EMF developed across the receiver coil, but only the change in EMF due to a small change in magnetic field. Thus, in formula (3-1) we wish to replace the quantity $\left\{ M\omega \right\}$ by $\frac{d}{dH} \left\{ M\omega \right\}$, which equals $\gamma \frac{d}{d\omega_o} \left\{ M\omega \right\}$. If we use as the operating characteristic the dispersion curve given by formula (2-12), then it can be easily verified that the change in EMF for a change in the field of 1 gamma is given by

$$\frac{\Delta \left\{ M\omega \right\}}{\Delta H} = \frac{\chi_o H_1 \omega_o^2}{\gamma \lambda^2} \times 10^{-5} \qquad (3-2)$$

If the modulated absorption curve shown in Figure 2-9 is used as the operating curve, then the change in EMF will be 0.77 x formula (3-2), and the slope of other operating curves will always be some constant factor times formula (3-2). Inserting (3-2) into (3-1) we find that the voltage change for a field change of 1 gamma is given by

$$V_s = \frac{4\pi}{\sqrt{2}} \frac{NQ\Omega}{\sqrt{h^2 + d^2}} \frac{\chi_o H_1 \omega_o^2}{\gamma \lambda^2} \Delta H \times 10^{-13} \qquad (3-3)$$

where ΔH is expressed in gammas.

The noise level of the apparatus is ultimately limited by the Johnson noise in the tuned receiver circuit. The rms noise voltage is given by the familiar formula (3-4)

$$V_n = \sqrt{4R\,kT\,(\Delta\nu)} \qquad (3\text{-}4)$$

Thus the signal-to-noise ratio for a small change in magnetic field is given by

$$\frac{V_s}{V_n} = \pi\sqrt{2}\left(\frac{NQ}{\sqrt{h^2 + d^2}}\right)\frac{\chi_0 H_1 \omega_0^2 \times 10^{-13}\ \Omega(\Delta H)}{\gamma \lambda^2 \sqrt{R\,kT\,(\Delta\nu)}} \qquad (3\text{-}5)$$

where R is the equivalent noise resistance across the grid of the input tube of the receiver, and $\Delta\nu$ is the bandwidth in cycles per second at the output of the entire system.

Formula (3-5) provides us with the basic criteria necessary for determining the optimum signal-to-noise ratio and the size of sample which is required. The factor in parentheses is a function only of the geometry of the coil and of its tuned circuit. The quantity λ is the linewidth; thus it is evident that, other things being equal, the substance having a narrow linewidth is by far preferable to one having a wider linewidth. The dependence of the signal on the resonance frequency ω_0 is already evident in formulas (2-7) thru (2-12), as is the dependence on the susceptibility. The dependence on the r-f field H_1 must be understood to apply only when condition (2-4) applies, i.e. $H_1 < \lambda$, and would have to be seriously modified for a strong r-f field. The linear dependence on the volume assumes that the quantity in brackets in equation (3-5) is a constant for all volumes. This is not necessarily true, as it is desirable to fit the coil closely around the sample. However, experience has shown that over a very wide range the Q of the tuned circuit will be determined by factors other than the Q of the receiver coil alone; thus, since it and the other factors in the bracket are constant, one may take a linear dependence on Ω as a good approximation.

We are now in a position to perform a sample calculation to find the minimum volume of sample necessary when we use a good paramagnetic substance. Let us consider, as sample material, a solution of 0.1 molar Na in ammonia, for which the constants χ_o and λ can be obtained from Table 5-2. We take H_1 = 10 milligauss which is equivalent to a r-f field $2H_1$ of 14 milligauss rms; for ω_o we take 2π times 1 mc, corresponding to the lowest earth's magnetic field one may desire to measure. Experience has shown that for $N/\sqrt{h^2 + d^2}$ we may take approximately 15, and for Q approximately 75. The bandwidth $\Delta\nu$ is expected to be 1 cps, and the equivalent shunt resistence R for a typical low noise input circuit is about 25,000 ohms. Inserting all these numbers into formula (3-5) we find that

$$\frac{V_s}{V_n} \simeq 0.1\,\Omega\,(\Delta H) \tag{3-6}$$

Thus, if we expect to distinguish between changes of 0.1 gamma, we need a sample volume Ω of 100 cc. This number will be used in future calculations.

Further discussions on the sensitivity, based on formula (3-5), will be carried out in Section 4 and Part II of this paper.

4. Geometrical Factors

It is important that we explore fully the effect of changes in direction of the d-c field on paramagnetic resonance. In the previous discussions we have always assumed that the earth's field defined a direction, which we call the z-direction, and the r-f field was perpendicular to it, in what we will define as the x-direction. One would then look for signals due to varying magnetic moments appearing in either the x- or y-direction. Laboratory experiments on paramagnetic resonance are usually performed with the aid of a modulating or sweep field which is also in the z-direction, and in addition, in the laboratory there may also be steady biasing fields in this direction. We must now consider what effects there are on the resonance characteristics and on the sensitivity if out of all these fields only the direction of the earth's field is changed. We will consider in order changes in direction relative to (1) a biasing field, (2) a magnetic sweep modulating field, and (3) the r-f field.

a. Biasing field.

The total magnetic field seen by the instrument must be the vector sum of the earth's field and the biasing field (Figure 4-1). If θ is the angle of tilt between the two fields, then the absolute value of the observed field is

$$H = \sqrt{H_e^2 + H_b^2 + 2H_e H_b \cos \theta} \qquad (4-1)$$

where H_e is the earth's field and H_b is the biasing field. If the bias field H_b is very much less than the earth's field, H_e, and if the tilt angle θ is small, equation (4-1) becomes approximately

$$H = H_e + H_b - H_b \frac{\theta^2}{2} \tag{4-2}$$

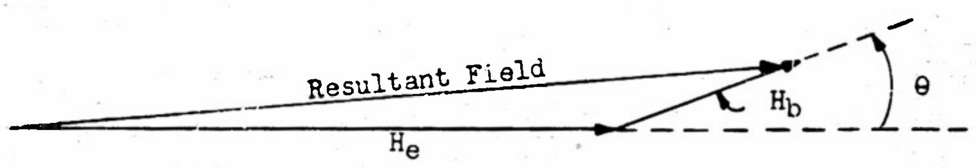


FIGURE 4-1

VECTOR DIAGRAM OF EARTH'S FIELD AND BIAS FIELD

Thus, there is a change in the absolute value of H directly proportional to H_b and to θ^2. For example, if we wish our apparatus to tolerate a 5 degree tilt with a variation in H of less than 0.1 gamma, we can allow a biasing field no larger than 20 gammas, (Figure 4-2). Thus, for our apparatus to be even moderately independent of direction we should exclude the idea of a steady biasing field.

b. Sweep field.

We assume in this case that the apparatus detects resonance by sweeping through it with a sinusoidally varying magnetic field, $H_s \cos \omega_m t$. We wish to know both the apparent change in the earth's field and the apparent change in the amplitude of the sweep field as a function of the angle of tilt, θ. Let H_s be the peak value of the sweep field. Then as a function of time

$$H = \sqrt{H_e^2 + H_s^2 \cos^2 \omega_m t + 2H_e H_s \cos \omega_m t \cos \theta} \tag{4-3}$$

If $H_s \ll H_e$ we can expand equation (4-3) as a Fourier series in ω_m and as a power series in the small quantity (H_s/H_e). The result is

$$H = H_e \left(1 + \frac{H_s^2}{4 H_e^2} \sin^2 \theta + \frac{H_s}{H_e} \cos \theta \cos \omega_m t + \ldots.\right) \tag{4-4}$$

where the missing additional terms are either of higher than second order in the small quantity (H_s/H_e), or are harmonics of the sweep frequency. We assume that the detection system will discard these harmonics. Thus, we see that the modulation amplitude is a second-order function of the tilt angle θ, and changes in the apparent value of the earth's field are of second order in both the modulation amplitude and the angle of tilt (Figure 4-3). For example, if H_s is 1000 gammas, a good sweep field for metal-ammonia solutions, then a tilt of 5 degrees produces an apparent shift in the earth's field of less than 0.1 gamma (Figure 4-4). Thus, it appears practical to consider a paramagnetic resonance apparatus using a magnetic field sweep of the order of 1000 gammas (10 milligauss). Devices using organic free radicals, however, would require a sweep of at least 10,000 gammas, which would produce an apparent shift in the earth's field of 6 gammas for a 5 degree tilt. This is one of many reasons for preferring metal-ammonia solutions over organic free radicals.

c. Radio-frequency changes in sensitivity.

The effect of a tilt of the earth's field relative to the r-f part of the probe is partly to change the sensitivity. (Changes in line shape and resonance position will be considered later.) We find, however, that the effect of tilt is different for single-coil and cross-coil systems. Let θ be the angle of tilt between the earth's field and z-direction of the probe. Then for a single-coil system and for tilts in the xz-plane we can see that the effectiveness of the r-f is reduced by a factor cos θ, while the effectiveness of the coil for receiving emitted radiation is also reduced by the factor cos θ; therefore, the sensitivity goes as $\cos^2 \theta$, if the tilt is in the xz-plane, and the coil axis is in the x-direction (Figure 4-5).

However, it can be seen from the cylindrical symmetry of a single-coil system that a tilt in the yz-plane will have no effect on sensitivity since the z-axis may be defined anywhere in this plane. Thus, there is a preferred direction for motion in a single-coil system, which may be an advantage in certain applications. For arbitrary deviations, however, the change in sensitivity is a function not only of θ but also of the longitudinal angle ϕ (Figure 4-6).

For a cross-coil system the following considerations apply:

Let the transmitter coil axis lie in the x-direction and the receiver coil in the y-direction. If we perform the tilt so it is in the xz-plane (Figure 4-7), then the r-f is effectively reduced by the factor cos θ, whereas the effectiveness of the receiving coil is unchanged. Conversely, if the tilt is in the yz-plane (Figure 4-8), the effectiveness of the r-f is unchanged, but the effectiveness of the receiving coil is changed by the factor cos θ. Actually, it can be shown that the sensitivity is always reduced by the factor cos θ, irrespective of the angle ϕ. Thus, unlike single-coil systems, cross-coil systems have no preferred directions of tilt, for sensitivity changes; and the change of sensitivity in a cross-coil system, for small θ, is approximately half the maximum change to be expected in a single-coil system.

We may also remark, for the sake of completeness, that rotations about the direction of the earth's field have no effect on sensitivity.

The importance of changes in sensitivity can be evaluated by the following considerations: The airplane or towed bird on which the apparatus is mounted will pitch and yaw in times which give frequency components in the same frequency range in which the desired signals are to be picked up. Now, although small changes in sensitivity over long periods of time are not important, rapid changes in sensitivity might, under certain conditions, produce effects which look like the signals which one desires to detect. This is illustrated in Figure 4-9. Here an instrument, using curve 1 as an operating characteristic, is set so as to operate at Point A. A change in field produces a change in signal level by moving the operating point to B. However, the same signal change can be produced by a decrease in sensitivity, making curve 2 the operating characteristic, so that the instrument operates at Point C. Obviously, we must be able to keep such effects below the noise level of the instrument. One way to do this is to operate the instrument as a null detector, at Point 0 on the characteristic. This can be done, for example, by operating the instrument in the dispersion mode, (Figure 2-6) without sweep or with square-wave sweep so the signal at resonance is zero, or by operating the instrument with sweep in the absorption mode and looking at the output at the sweep frequency (Figure 2-9). Now, changes in sensitivity will not give changes in the zero indication of the instrument; however, changes in the magnetic field will give deviations from null which can then be detected and interpreted. In actual operation it may not be possible, for electronic reasons, to track the resonance frequency continuously with the earth's field so as to operate at the null point at all times. A similar problem existing in other types of magnetometers is solved by step-wise changes in the bias field and may be solved in our case by step-wise changes in radio frequency. In our case it is important to know how far off resonance one can operate before changes in sensitivity due to motions of the airplane will be large enough to appear as signals. If we consider the signal to be a linear function of the field in the neighborhood of resonance, then a 5 degree tilt will produce a change of sensitivity of the order of 1 per cent in the single-coil system and somewhat less in the cross-coil system. We see that if we are within 10 gammas of the resonance field, the effects of motion will still be less than 0.1 gamma; thus, we have a freedom of approximately 20 gammas within which we can work at the same operating frequency (Figure 4-10). This assumes no changes in sensitivity from any other source. If we are using a sweep field, there is a small additional change due to the last term included in equation (4-4).

Since the sensitivity of a single-coil system varies as $\cos^2 \theta$, it is possible to design a system, based on single-coil principles, which is completely insensitive to tilt. Let α be the angle between the earth's field and the axis of the coil (thus $\cos^2 \theta = \sin^2 \alpha$). Suppose now the single coil is replaced by three mutually perpendicular coils, each with its own sample, connected in series but otherwise decoupled from each other. The signal will then be the sum of the signals in each coil. Let α_1, α_2, α_3 be the respective angles between the earth's field and the axis of the coils. Then the signal is proportional to

$$\sin^2 \alpha_1 + \sin^2 \alpha_2 + \sin^2 \alpha_3$$

$$= (1 - \cos^2 \alpha_1) + (1 - \cos^2 \alpha_2) + (1 - \cos^2 \alpha_3) = 2$$

since the sums of the squares of the direction cosines is equal to one. Thus, irrespective of the direction of the earth's field, the signal will always be equal to the maximum signal that can be produced by two of the three samples. Electrical problems and line-shape considerations are the same as in any other single-coil system; this should be kept in mind in Part II of this paper. Note that each coil must have its own sample; if several coils are wound about one sample their fields merely add vectorially.

d. Radio-frequency directional effects in the single-coil system.

If $\omega_0\tau >> 1$ (natural line width small compared to earth's field), then making certain approximations, valid in the neighborhood of resonance, the absorption component of susceptibility for a single-coil system, given by equation (A-29) Appendix A, reduces to:

$$\chi = \chi_0 \left\{ \frac{\sin^2\theta}{\omega\tau} + \frac{1}{2}\,\frac{\omega_0\tau\cos^2\theta}{1+(\omega_0-\omega)^2\tau^2} \right\} \qquad (4\text{-}5)$$

where χ_0 is the static susceptibility, and $(90^\circ - \theta)$ is the angle between the earth's field and the coil axis. This represents a normal resonance curve of amplitude $\frac{1}{2}\chi_0\omega_0\tau \cos^2\theta$, with a superimposed term that shifts the apparent resonant frequency to a lower value ω'. The fractional change is found by differentiating to be

$$\frac{\omega_0 - \omega'}{\omega_0} = \frac{\tan^2\theta}{\omega_0^4\tau^4} = \left(\frac{\lambda}{H_0}\right)^4 \tan^2\theta \qquad (4\text{-}6)$$

where $\lambda + 1/(\gamma\tau)$ is the natural line-width, expressed in gauss. In the case of a sodium-ammonia solution, $\lambda \sim 0.02$ gauss; and we have

$$\left(\frac{\lambda}{H_0}\right)^4 \simeq \left(\frac{.02}{.5}\right)^4 = 2.5 \times 10^{-6}$$

so that a directional error of 45 degrees leads to an error of apparent field of only 1.25×10^{-6} gauss, or 1/8 gamma. If angles are held to ± 10 degrees, the error is reduced to 0.004 gamma.

It should be noted that these favorable numbers depend entirely on the fact that the natural line width is so narrow. Since in a single-coil system the directional error varies as the fourth power of the natural line width, use of any organic free radical compound thus far discovered would lead to such a bad directional effect that it, rather than sweep field considerations, would limit the angular tolerances.

In the tilt-independent system having three mutually perpendicular coils, the small directional effects mentioned here have a negligible effect because they affect only the coil or coils whose contribution to the total signal is small.

e. Radio-frequency directional effects in the cross-coil system.

In the analysis of Appendix A, the x-axis is chosen in the direction of the field of the transmitter coil, $H_t = 2H_1 \cos \omega t$, while the z-axis is located by the condition that the earth's field lies in the xz-plane. Then the field H_r due to unit current flow in the receiver coil, being perpendicular to H_t, must lie in the yz-plane. Let the angle between H_r and the y-axis be ψ (Figure 4-11). Then the orientation of the cross-coil system is specified by the two angles θ, ψ, which are ideally both zero.

The voltage induced in the receiver coil depends only on the component

$$P_r = P_y \cos \psi + P_z \sin \psi$$

of polarization along H_r. This is, from equation (A-27), Appendix A:

$$P_r = - \frac{\omega \chi_0 H_1 \cos\theta}{2} \left\{ \frac{2 i \sin\theta \sin\psi}{\frac{1}{\tau} + i\omega} + \frac{\cos\psi - i \sin\theta \sin\psi}{\frac{1}{\tau} + i(\omega + \omega_0)} - \frac{\cos\psi + i \sin\theta \sin\psi}{\frac{1}{\tau} + i(\omega - \omega_0)} \right\} \qquad (4\text{-}7)$$

The last term in the brackets is the dominant resonance term, while the first two terms represent rather complicated corrections. From equation (4-7) we could give a discussion of all details of the directional effects on the u- and v-modes, but for the present the only important thing about the correction terms is that once again their magnitudes are small compared to the dominant resonance term.

The serious effect lies in the factor

$$\cos\psi + i \sin\theta \sin\psi \qquad (4\text{-}8)$$

which occurs in the resonance term. According to this, the phase of the induced signal is shifted relative to the driving field by an angle ξ determined by

$$\tan\xi = \sin\theta \tan\psi \,. \qquad (4\text{-}9)$$

Using any particular phase reference, this causes the observed signal to be a linear combination of u- and v-modes, the combination varying with θ and ψ. This is in a sense a quadratic effect, since if <u>either</u> $\theta = 0$ or $\psi = 0$, it is absent. It can cause the apparent magnetic field to shift by an uncomfortably large fraction of a natural line width, if indication is based on phase information. Thus, if $\theta = \psi = 10$ degrees, the phase shift is

$$\delta = 1.8 \text{ degrees}$$

Since variation of $(\omega - \omega_0)\tau$ from -1 to +1 changes the phase by 90 degrees, the apparent magnetic field is shifted by a fractional amount

$$\frac{1.8}{90} = .02$$

of the natural line width. In the case of a metal-ammonia sample this amounts to 40 gammas.

Thus we observe that in all cross-coil systems there is a directional effect, purely geometric in origin, that shifts the resonance position by such a large fraction of a line width as to make a simple cross-coil system completely impractical unless a paramagnetic substance is found with a line width of 5 gammas or less. An oversimplified explanation of this effect is that the projections of the coils on the plane of the precessing electron moments are not necessarily 90 degrees apart, and thus the apparent "angle between coils" is a function of the tilt. This same oversimplified argument also suggests a way out of the difficulty, which is to have two cross-coil systems with the coils displaced 90 degrees from each other (i.e., system 1 has transmitter and receiver coils along the x- and y-axes, and system 2 along the y- and (-x)-axes respectively), and connect the two receiver coils in series. Since the sum of the "angle between coils" in the two systems must be 180 degrees, one expects the directional effect to be equal and opposite in the two receiver coils. A more detailed argument shows that the cancellation is not complete, but that at small angles of tilt (10 degrees, for example) it may be sufficient to allow the use of a metal-ammonia sample in such a system.

f. Differential and bias systems.

Under the terms of NOnr Contract 791(00), we have also been requested to investigate the possibility of using biasing fields in order to raise the resonance frequency to the microwave region. In this case the biasing field would be very much larger than the earth's field. However, the same considerations apply as were discussed previously, in that a very high degree of mechanical stabilization would be required. In addition, if such a system were used, the biasing field would have to be regulated to a very high degree of accuracy inasmuch as variations would have to be kept below the level of the smallest variation in the earth's field which one expects to detect. It therefore does not seem practical to consider the use of very large biasing fields in order to raise the frequency into the microwave region for one sample alone. However, there is also the possibility of employing a differential system consisting of two paramagnetic resonance apparatus located at some distance from each other. In this case, one would devise the electronics to detect not the resonant frequency, but the difference in resonance frequencies or fields between the two samples. In order to do this, one should employ the same r-f oscillator to drive both systems, the same current should be passed through both biasing coils, and the apparatus must be devised so that the z-axes of both systems are kept rigidly parallel. If this can be done, then it is apparent that the apparatus will be relatively insensitive to changes in bias field or in direction relative to a uniform field. However, since the field gradient is a tensor quantity, the apparatus will still be sensitive to changes in direction if the field is even slightly nonuniform and will, therefore, require some mechanical stabilization.

The absolute sensitivity, in order to make such an apparatus useful as a differential instrument, must be several orders of magnitude greater than the present apparatus. The instrument should, in fact, be able to detect changes of the order of 10^{-3} gamma or less. This would not be difficult at microwave frequencies, since the sensitivity of the apparatus for any given sample size increases approximately as the square of the frequency. Therefore, theoretically the samples could be approximately the same size as those suggested for the low field apparatus. Problems may arise, however, in fitting a large sample into the waveguide system in such a way that the dispersion does not detune the system.

A differential system (gradiometer) can be expected to have several advantages over a magnitude-of-field system. First of all, requirements on mechanical stabilization are of a very low order because the changes in gradient due to the presence of a "nearby object" are at least of the same order of magnitude as the existing gradient of the earth's field. Insofar as the gradient is concerned, one does not have to look for small differences in a large quantity, and the small differences that occur due to directional effects are of little importance. Secondly, the natural noise level due to small changes in the earth's field would be very low because most such noises tend to cancel out in the two areas of the gradiometer. Most of the magnetic noise in such a system will probably be produced by the waves in the sea and by eddy currents in the airplane. In general, the sensitivity of the instrument to the presence of a magnetic dipole will be a function of the "nearness" of the dipole to the instrument; thus the waves and the submarine, several hundred yards away, should produce much more signal than the earth, whose center is 4000 miles away.

It is obvious from the above remarks that the design of a gradiometer requires a different approach than the design of a simple field-reading instrument. For this reason we will not discuss gradiometers in the rest of this report, as we feel that the design of such an instrument should be the subject of a separate study.

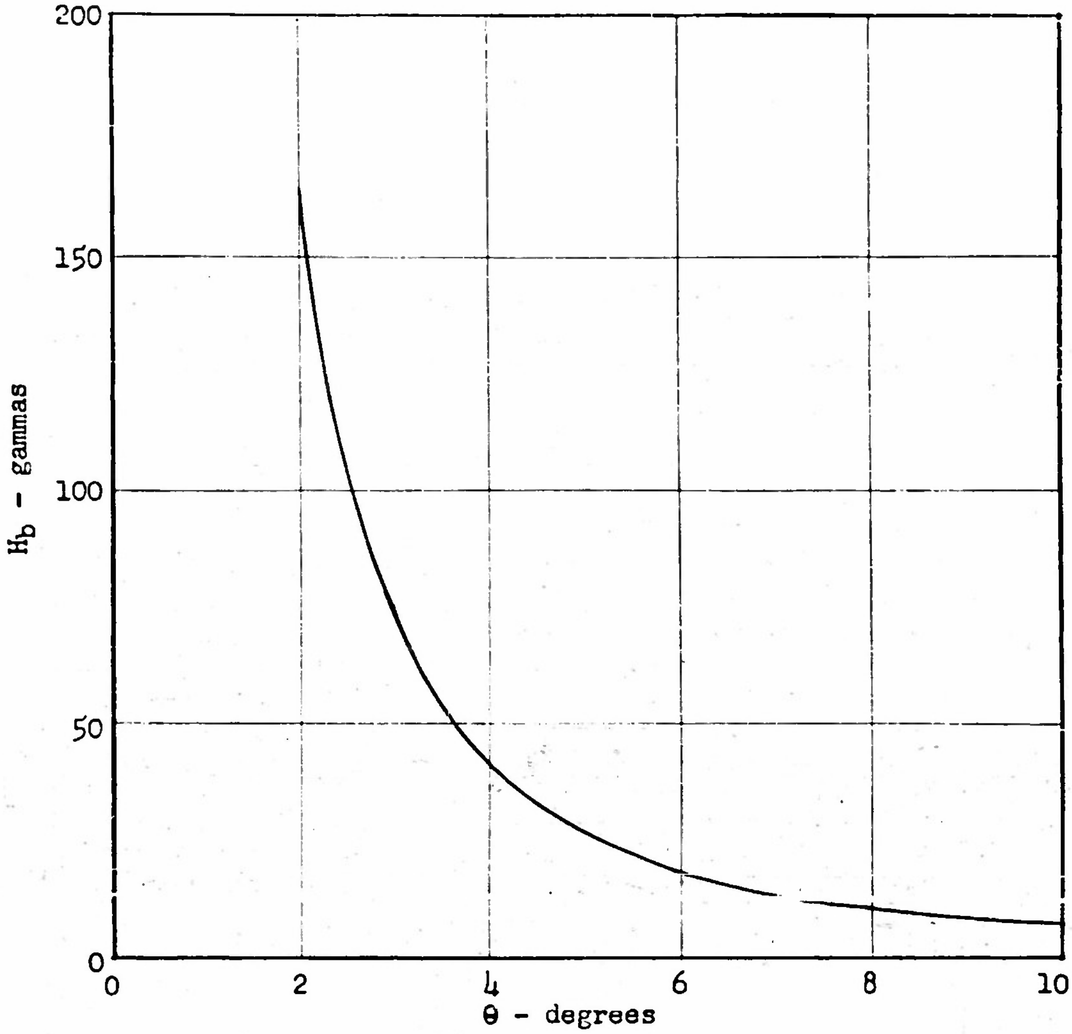


FIGURE 4-2

MAXIMUM ALLOWABLE BIAS FIELD TO PRODUCE ERROR OF $\leq$ 0.1 GAMMA AT TILT ANGLE θ.

For error of $\leq$ 0.01 gamma divide ordinates by ten.

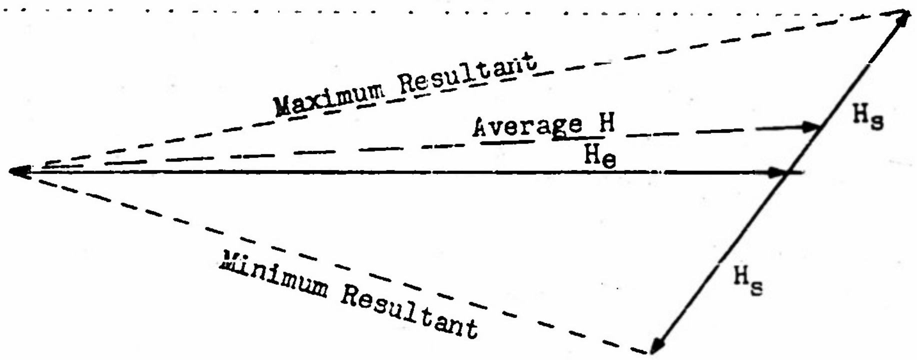


FIGURE 4-3

VECTOR DIAGRAM OF EARTH'S FIELD AND SWEEP FIELD

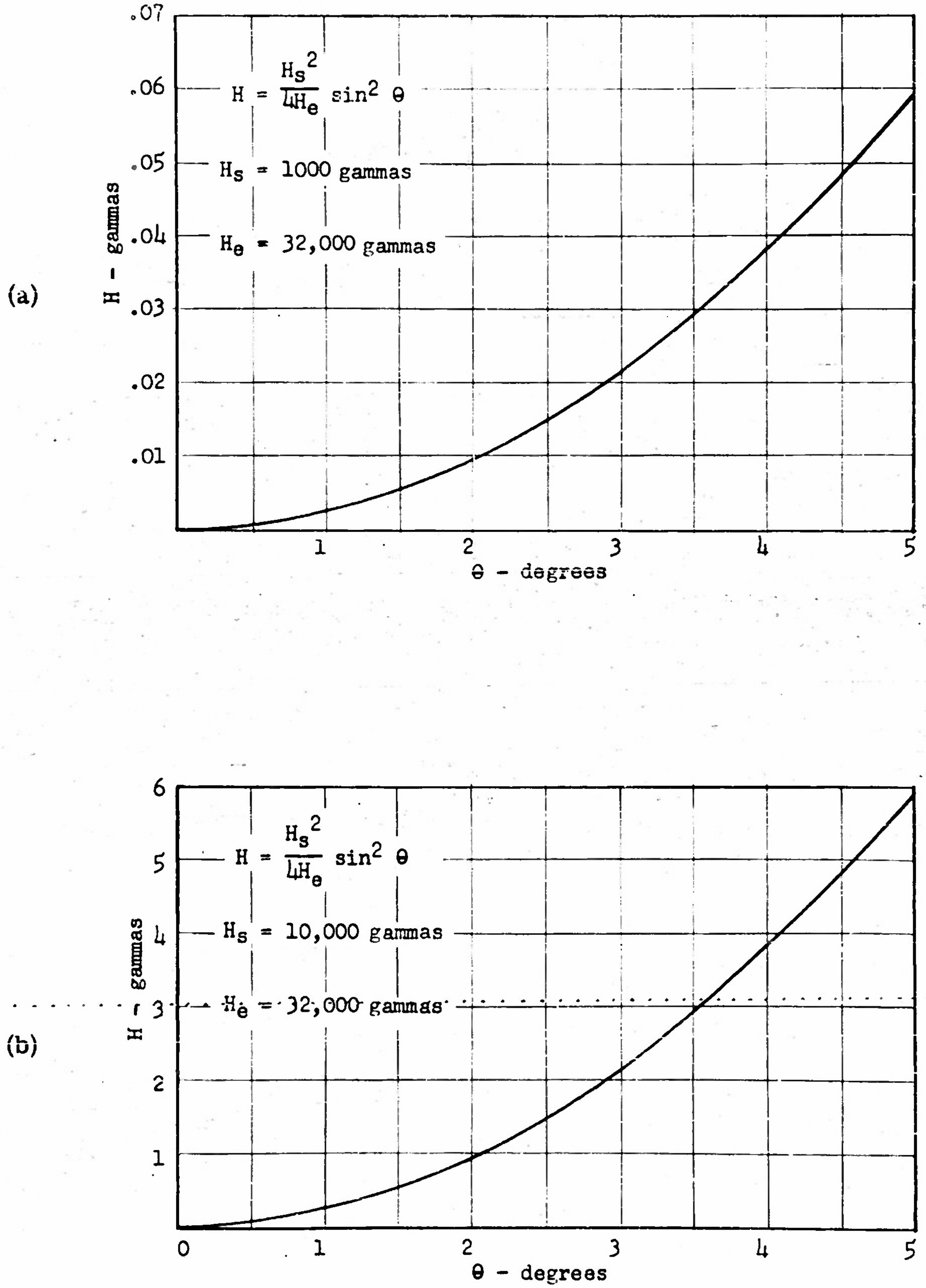


FIGURE 4-4 (a), (b)

ERROR IN EARTH'S FIELD INDICATION
AS A FUNCTION OF TILT ANGLE

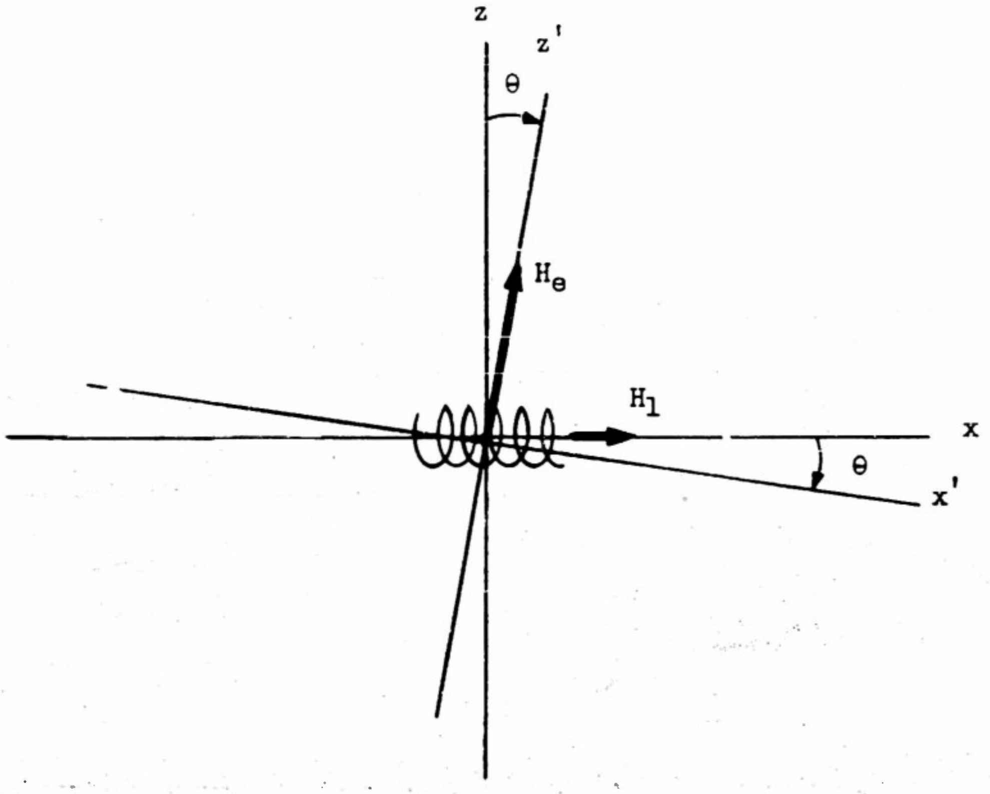


FIGURE 4-5
GEOMETRY OF SINGLE-COIL SYSTEM
WITH TILT IN XZ-PLANE

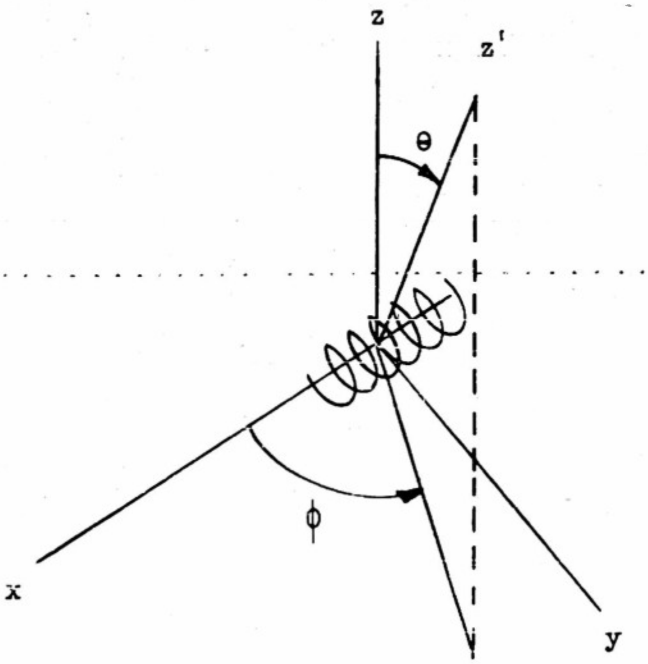


FIGURE 4-6

GEOMETRY OF SINGLE-COIL SYSTEM
WITH TILT IN YZ-PLANE

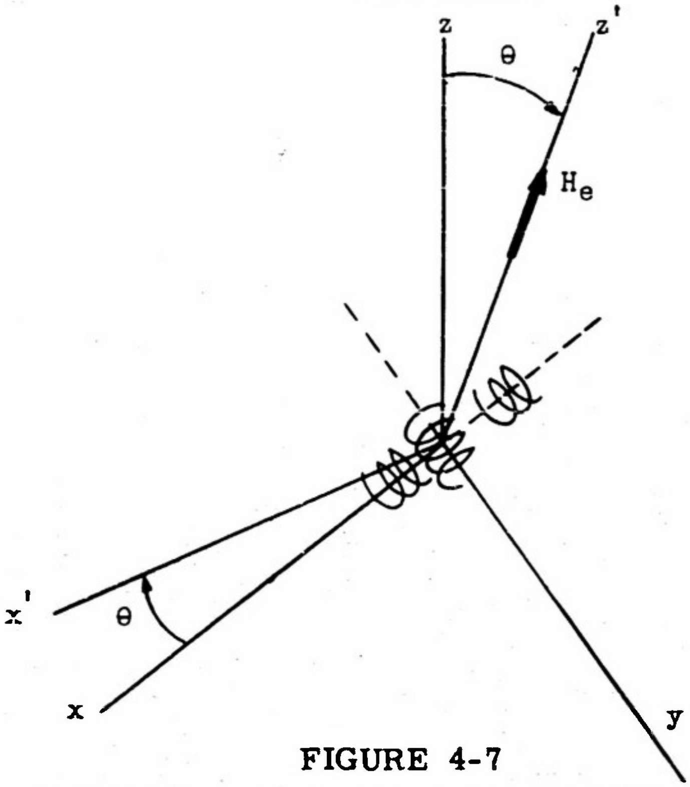


FIGURE 4-7
GEOMETRY OF CROSS-COIL SYSTEM WITH
TILT IN XZ-PLANE

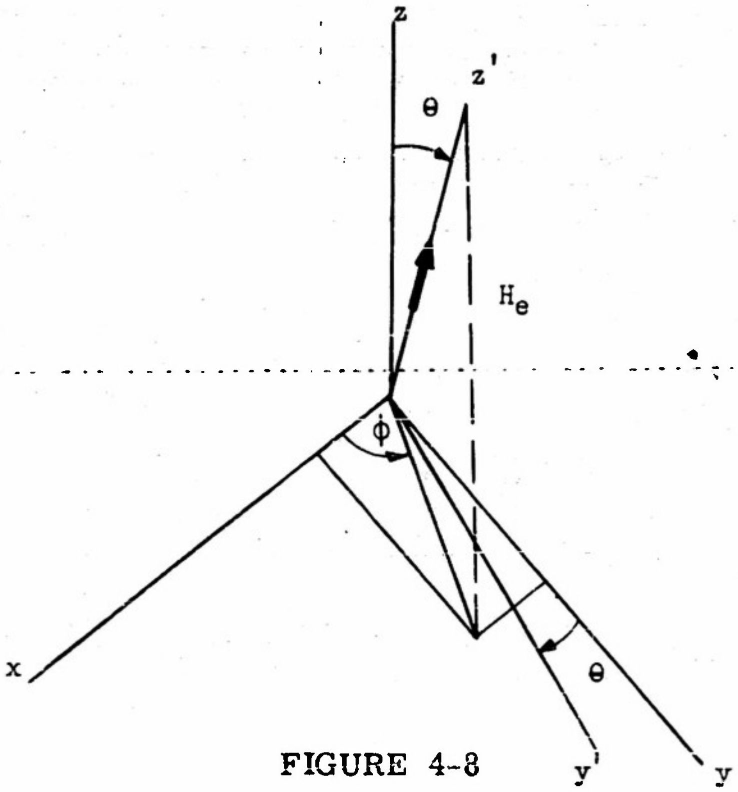


FIGURE 4-8
GEOMETRY OF CROSS-COIL SYSTEM WITH
TILT IN YZ-PLANE

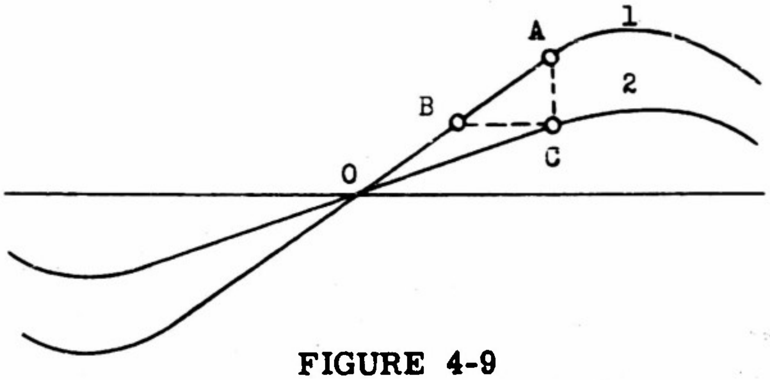
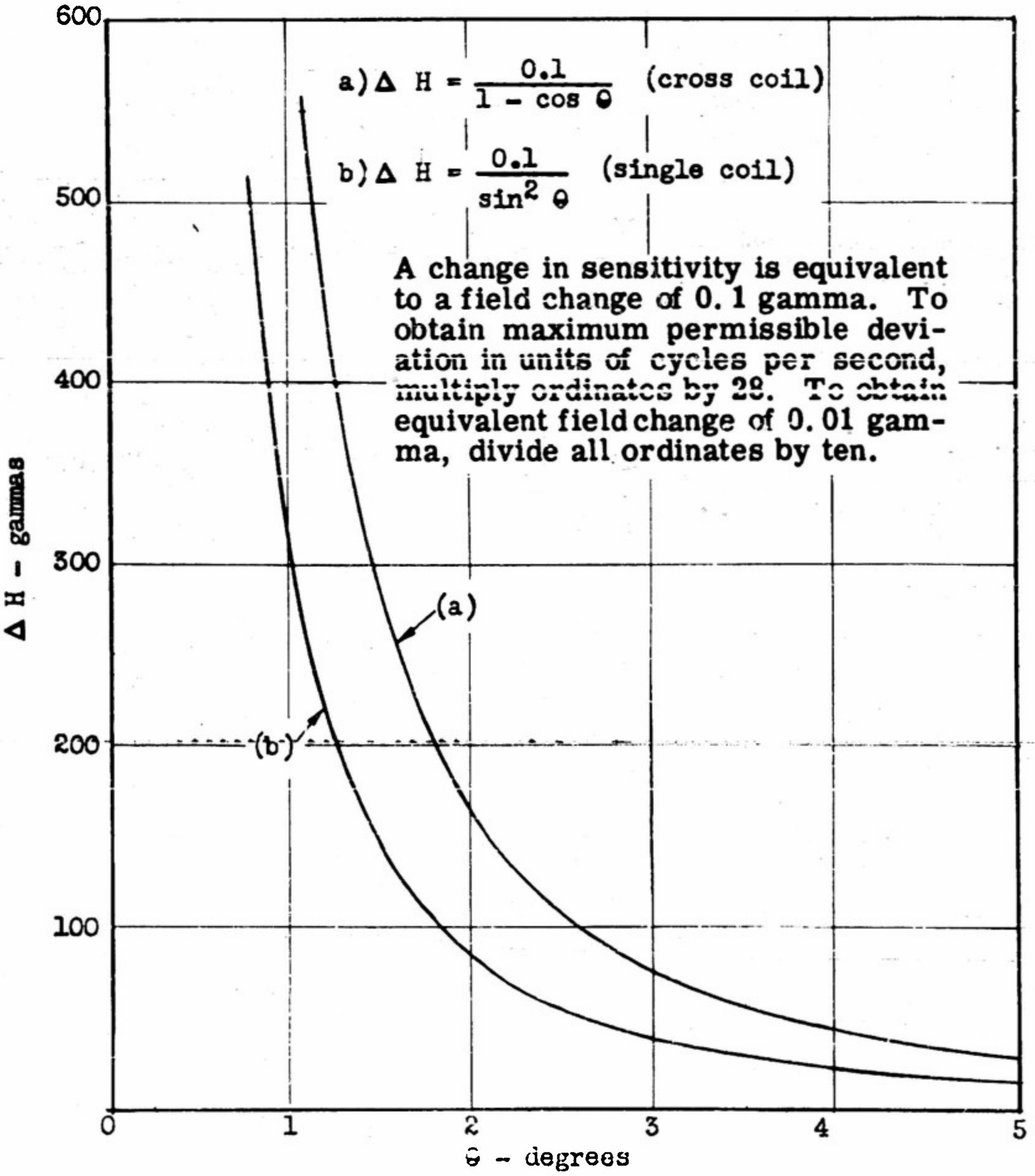


FIGURE 4-9

EFFECT OF CHANGES OF SENSITIVITY ON SIGNAL



a) $\Delta H = \dfrac{0.1}{1 - \cos\theta}$ (cross coil)

b) $\Delta H = \dfrac{0.1}{\sin^2\theta}$ (single coil)

A change in sensitivity is equivalent to a field change of 0.1 gamma. To obtain maximum permissible deviation in units of cycles per second, multiply ordinates by 28. To obtain equivalent field change of 0.01 gamma, divide all ordinates by ten.

FIGURE 4-10

MAXIMUM PERMISSIBLE DEVIATION FROM RESONANCE AS A FUNCTION OF TILT ANGLE

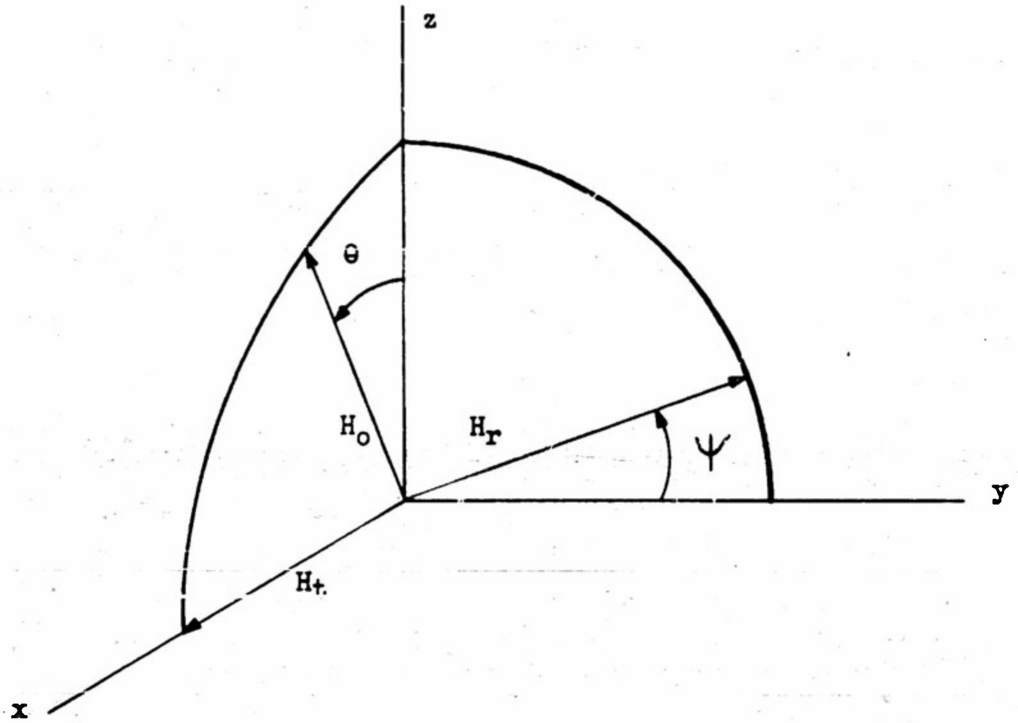


FIGURE 4-11

VECTOR DIAGRAM OF ORIENTATION
OF CROSS-COIL SYSTEM

5. Requirements of the Sample

The discussion of the previous sections has been based purely on the theory of magnetic resonance and would be applicable to any type of material which showed such resonance. We would now like to consider various materials available with a view of selecting one which best suits our purpose. To do this, let us first, on the basis of our previous discussion, list the requirements for what we might call an ideal sample material:

(1) There should be a large number of free electrons per unit volume, i.e., the absolute magnitude of the signal must be large. (2) From the discussion of Section 2, we see that a narrow line is preferable to a wide line, and in any case the line must be no wider than the field to be measured. A limitation on the narrowness of the line is imposed, however, by the available sweep frequency. We require that the line be considerably wider (expressed in frequency units) than the sweep frequency; otherwise the sweep, which is equivalent to a frequency modulation of the RF, will space the sidebands too far apart to reproduce the line shape faithfully. (3) The material to be used should be easily available in large quantities, easy to handle and to mold into the desired sample shape, and should last indefinitely. It should be insensitive to changes in temperature, pressure, or other external factors and should be isotropic. (4) The material should have a very low electrical conductivity in order to maintain a high Q in the receiving coil. (5) It should have a very low static susceptibility so that it does not appreciably perturb the earth's field in its immediate neighborhood.

Two types of material have been found which have lines narrow enough to deserve consideration. One group of these are certain organic free radicals, the other are the solutions of alkali metals in ammonia. The most satisfactory organic free radicals and their properties, relative to requirements (1) through (5) above, are shown in Table 5-1.* Of these materials Tris-p-nitrophenylmethyl, hereafter abbreviated as TPN, appears to be the most satisfactory from the point of view of requirements 3, 4, and 5, though it must be sealed in an inert atmosphere. In regard to its relative sensitivity, it is therefore necessary to calculate how much of the material would be needed in order to design an apparatus capable of detecting 0.1 gamma. This has been done, using the design constants given in the sample calculation of Section 3, and indicates that with this substance the desired sensitivity can be achieved with a sample volume of approximately 100 cc. Such a volume, corresponding to a spherical sample with a diameter of 2-1/2 inches, is certainly practical from the standpoint of size and does not require excessive amounts of material although it would require more TPN than is customarily produced in one batch at the present time. However, in this calculation we have assumed that we can use the optimum r-f field and the optimum sweep. Both of these are approximately 40,000 gammas peak-to-peak or, if the sweep is in terms of frequency modulation, approximately 1 mc. This much RF may be extremely

---

* The quantity λ in the tables and in subsequent discussion is defined to be the field difference between the maximum and half-voltage point on the absorption curve. Some investigators have reported their data in terms of field difference between points of inflection on the curve. In these latter cases we list λ = (field difference between points of inflection) x 0.866, a relation which is exactly true only in the case of a strictly Lorentzian curve.

difficult to produce under moderate power requirements and frequencies. Furthermore, if magnetic field sweep is used, the apparent value of the earth's field will be very sensitive to the amount of tilt, as has been shown in Section 2. Thus, with a sample of TPN we would either have to have much more stringent requirements on our electronics and on directional stability, or we would have to use much less RF and sweeps and correspondingly larger samples; however, it is probable that samples as large as a liter are impractical. It therefore does not appear that TPN or any of the other presently known free radicals are suitable substances.

Let us now consider the metal-ammonia solutions. The paramagnetic and electrical properties of metal-ammonia solutions for several concentrations are given in Table 5-2, and the principal physical properties of liquid ammonia are given in Table 5-3. Further information on these subjects may be obtained from the references given with the tables. The manufacture of metal-ammonia solutions requires commercial metallic sodium or potassium, compressed ammonia gas, and a high-vacuum system. The commercial ammonia is treated to remove moisture and oxygen, and both the metal and the ammonia are purified in the vacuum system just prior to being mixed in solution. There is no limit to the size of sample that can be made by this process. With regard to properties 1, 2, and 5 in the above list, the sample calculation in Section 3 gives a signal-to-noise ratio for small changes in field of about the same magnitude as for TPN. However, whereas in the case of TPN the optimum RF and sweep conditions are difficult to obtain, in the case of metal-ammonia solutions they correspond to about 3000 gammas peak-to-peak, conditions which are easy to obtain with conventional techniques. Furthermore, as shown in Section 2, the apparatus would be sufficiently free from tilt effects if a magnetic sweep modulation is used. Thus, following our previous calculations we may assume 100 cc to be a working number for the size of the sample required. We should also note that high Q coils of 2-1/2 inches diameter or larger can easily be designed for the 1 to 2 mc range. As regards properties (3) and (4) above, metal-ammonia solutions are not as satisfactory as organic free radicals. As is shown in Table 5-3, the sample must be operated at high pressures which become critical in tropical climates. Refrigeration or ice packing during operation may be possible but would constitute a nuisance factor. The fact that the sample is a liquid guarantees that it is isotropic and can be molded to the desired shape. However, the life of the sample is in general not indefinite. Impurities of alkali oxide in the solution may initiate the reaction, $2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$, which is self catalyzing so that in time the free ions in the solution must disappear completely. It has been found that by making samples sufficiently pure they may be kept with undiminished strength at room temperature for periods of at least several months, and possibly longer. However, the fact remains that for any given sample its life time is, within certain limits, unknown. Spoilage of a sample is indicated by loss of color and loss of signal. The self-catalyzed reaction does not occur so rapidly that one could not with certainty use a sample over a period of a day or so; however there is again considerable nuisance value due to the finite lifetime of samples. Thus, an apparatus using metal-ammonia solutions must be designed so that samples can be easily changed, and means must be available for testing samples to make sure that their strength is undiminished.

Information about the conductivity and skin depth of metal-ammonia solutions is given in Table 5-2. It is interesting to note that the line begins to broaden when the skin depth is just small enough to produce appreciable phase shifts in a 1 cc sample. Since practically all experiments on metal-ammonia solutions to date have been performed on samples about 1 cc in size, one can speculate as to whether higher concentrations would be useful if the sample could be split into sections .01 cc in volume or less. If a 100 cc sample could be split into a large number of such small units, then skin effect would be less of a problem, and it might be possible to use higher concentrations of samples with correspondingly greater sensitivities and without diminishing the Q of the receiver coils.

On the basis of the preceding arguments we have concluded that solutions of alkali metal in ammonia make satisfactory samples for an instrument using paramagnetic resonance and are definitely preferable to the presently known organic free radicals, even though the mechanical problems of handling metal-ammonia solutions are considerably more difficult. The problem of mass production and packaging of such samples is beyond the scope of the present study. However, we offer some suggestions which have come to mind as we have considered the chemical engineering aspects of the production of metal-ammonia solutions:

(1) Freedom from impurities of the ammonia is in the end governed by the cleanliness of the vacuum system in which it is liquefied. High

vacuum techniques now in use by industry are probably satisfactory for this purpose.

(2) In present methods of production the concentration of the samples cannot be determined without chemical analysis which destroys the sample. This is because it is difficult to determine by eye how much sodium has been introduced into the vacuum system. It has been suggested that an accurate method of introducing a known amount of sodium into the vacuum system would be to employ the method of electrolysis through heated glass. The sodium ions coming through the glass would be of unquestioned purity, and the amount could be determined with high accuracy.

(3) It has been suggested that some of the impurities which eventually destroy the sample come from the walls of the glass itself in the form of alkali oxide which is imperfectly fused into the glass. This source of contamination could be avoided by the use of glass internally coated with boron salts, as is done in the present manufacture of sodium vapor lamps.

(4) The present method of production requires that the capsule not be filled completely with liquid since the glass has to be sealed off by heat. This difficulty could be avoided by the use of a metal pinch-off seal, which would also eliminate a source of contamination which exists if alkali metal is present on the glass at the time it is heated.

(5) The requirement that a sample the size of 100 cc be split into a large number of small units suggests either (a) an emulsion or (b) a honeycomb structure inside the capsule. We do not know how much research

has been done, if any, on emulsions of liquid ammonia in other substances. With regard to honeycomb structure, it has been suggested that the new types of glass whose sensitivity to etching is determined by exposure to light could be useful here. Thus, the honeycombs could be produced out of laminations of thin sheets of this glass which have previously been etched out in the form of a large number of thin-walled holes. A sample packaged in this way would have the additional advantage that, should the solution in one cell of the honeycomb be destroyed, it would not destroy the rest of the sample and would effect the sensitivity of the sample by only a minute amount.

(6) Finally, paramagnetic resonance itself could be used to monitor the concentration of samples during manufacture and to assure a uniform product.

Nevertheless, the arguments presented in this section only emphasize the necessity for doing research in order to find paramagnetic substances with narrower lines and more tractable physical properties than metal-ammonia solutions.

TABLE 5-1

ORGANIC FREE RADICALS

Substance	Half-width at Half-maximum λ (*) (gauss)	References	Remarks (**)
diphenyl-picryl-hydrazyl	1.1	Holden, Kittel et al (11)	Stable in absence of moisture
tris-p-nitrophenylmethyl (TPN)	0.34	Hutchison (12) Pake & Weissman (13)	Stable in an inert gas
Substance believed to be tris-p-aminophenylaminium perchlorate	0.30	Hutchison (12) Torrey (12)	Stable in air. Only one specimen made

(*) See footnote on page 5-2.
(**) The static susceptibility of all these substances is about 3×10^{-6}.

TABLE 5-2

SOLUTIONS OF K OR Na in NH_3

Concentration (a) molar	Half-width λ at room temperature (a) (*) gauss	Static susceptibility (a)	Conductivity at NH_3 boiling pt. (b) ohm^{-1} cm^{-1}	Skin depth at 2 mc cm
0.4	0.070	10×10^{-8}	0.35	6
0.3	0.040	8×10^{-8}	0.25	7
0.2	0.030	6×10^{-8}	0.15	9
0.10	0.021	4×10^{-8}	0.06	14
0.09	0.021	4×10^{-8}	0.05	16
0.07	0.021	3×10^{-8}	0.03	20
0.05	0.021	3×10^{-8}	0.02	25
0.03	0.021	1.7×10^{-8}	0.01	35
0.01	0.021	0.6×10^{-8}	< 0.01	>35

(a) C. A. Hutchison, Jr., Reference (12)
(b) C. A. Kraus, Reference (14)
(*) See footnote on page 5-2. Experiments (Reference 12) have shown that the line shapes are Lorentzian, to a high degree of accuracy, over the region in which we are interested.

TABLE 5-3

AMMONIA (a)

Temperature degrees fahrenheit	Pressure lb/sq.in.	Specific Gravity liquid	gas
0	30.4	0.663	1.8×10^{-3}
10	38.5	0.656	2.2×10^{-3}
20	48.2	0.648	2.7×10^{-3}
30	59.8	0.640	3.3×10^{-3}
40	73.3	0.634	4.0×10^{-3}
50	89.2	0.625	4.9×10^{-3}
60	107.6	0.617	5.8×10^{-3}
70	128.8	0.610	6.9×10^{-3}
80	153.0	0.601	8.2×10^{-3}
90	180.6	0.592	9.6×10^{-3}
100	211.9	0.584	11.3×10^{-3}

(a) From Reference (15)

PART II - APPARATUS

6. Apparatus Using Two-Coil Systems.

In this section we shall discuss, first, general principles of two-coil systems and considerations regarding their use in an airplane for the specific purpose of a magnetometer. We shall then discuss possible operating characteristics that can be used and means for obtaining them.

a. General Considerations.

By "two-coil system" we mean either a cross-coil system or a system of the type used by Bloembergen, Purcell, and Pound,$^{(1)}$ in which the r-f voltage across a "single-coil" is compared with the voltage across another identical coil with no sample in it. The latter system is therefore a single-coil system insofar as line shape or directional effects are concerned; however, in common with the cross-coil system, it has separate receiver and transmitter circuits and the problem of correct balance in the probe. In these respects it differs from the single-coil circuits described in Section 7.

It has been shown in Section 4 that a simple cross-coil system of the type used in the laboratory cannot be used in our application because of serious directional effects. By "cross-coil system," therefore, we always imply the existence of two such simple systems, with receiver coils in series and coil geometries displaced 90 degrees with respect to each other, so that the directional effects are at least partly cancelled.

The basic elements in any cross-coil system are shown in Figure 6-1 and in reference (2). An oscillator of conventional broadcast frequencies design supplies r-f power to the two coils in the probe which lie in the x-direction. The receiver coil in the y-direction picks up the induced voltage from the precessing paramagnetic electrons, and this induced voltage is amplified by the receiver, also of conventional design, and rectified by the detector. In this apparatus the only critical part whose design and operation is not already thoroughly understood by radio personnel is the probe. The probe must be designed so that the total voltage induced across the receiver coil due to direct coupling from the transmitter coils, either electromagnetic or electrostatic, must be approximately 1/1000 the voltage across the transmitter coils or less. This coupling, to be referred to hereafter as "leakage," must remain constant throughout flight and preferably should be independent of operating frequencies. Although it may be possible to adjust the probe for zero coupling, it is usually desirable to have a certain amount of leakage in order to determine whether the absorption or the dispersion mode of the signal is to be detected. This is shown in Figure 6-2. Here it will be observed that a signal which has some arbitrary phase can be split into one or the other of its components if it is observed simultaneously with a leakage of the corresponding phase, which is considerably larger than the signal. The reason for this is that the component which is in phase with the leakage produces a first order change upon the absolute value of the vector (leakage + signal), whereas the other component, being at right angles to the leakage, produces only a second order effect and is therefore not observed. An additional reason for having leakage is that it enables the r-f amplifiers and the detector to operate in a linear region, which may not necessarily be the case if there were no leakage. This factor, together with the one concerning the determination of the phase of the signal, determines a lower limit on the amount of leakage which is desired. An upper limit is placed again by the requirement for linearity in the receiver and detector and also because of the fact that, since a certain amount of noise is present in the transmitter RF, it is desirable to minimize the amount of this noise which is carried on into the receiver circuit.

A detailed discussion of the mechanism which determines and controls leakage in cross-coil systems may be found in reference (16).

The other system, to be discussed together with the cross-coil system, we shall define as the twin-coil bridge.* A schematic of the probe circuit is shown in Figure 6-3. The bridge is balanced in the absence of a paramagnetic signal, and signal is indicated as a slight unbalance of the bridge. The balance can be made independent of frequency if the coils and their electrical and geometrical environments are identical. The "leakage" in this case is a residual unbalance of the bridge. Otherwise, all considerations just discussed relative to cross-coil systems hold here also.

. . . .

It has been shown in Section 4 of this report that it will be desirable to adjust the resonance frequency so that the instrument operates

---

* By "twin-coil" we wish to exclude bridged-tee or similar unsymmetrical bridges(17), which cannot be used here because the balance is extremely frequency-sensitive.

most of the time as a null indicator. Several possibilities exist in this connection. One of them is that the frequency adjustment be instantaneous and complete so that the output is always zero. In this case the recorder indication would be not the output voltage but rather the changes in frequency of the transmitter, governed by the feedback system which always sets the output to zero. We should note parenthetically that all of the operating characteristics which we are considering in this report have the form of an error signal so that they can be easily applied to an automatic frequency-control system. However, an instantaneous and complete frequency correction is rather difficult to obtain, particularly if it is necessary to have a mechanical unit, such as a servomotor, in the feedback system. It has another disadvantage is that steady changes of the earth's field during flight may eventually cause recorder indication to go off scale so that manual readjustment will be necessary. For these reasons we are proposing the following in all systems: The output of the detector, containing all frequencies up to 1 cps, would be shown on the indicator; however, the slow variations (1/10 cps and less) would constitute the error signal to be applied to the AFC. In this way the recorder would indicate zero on the average but would still be capable of indicating the desired signals with full sensitivity. Also, the problem of stability in the AFC feedback loop becomes considerably simplified.

The means by which the output signal is used to reset the transmitter frequency is a matter for considerable concern. One would first think of using a reactance tube circuit in the transmitter, in which one impresses the error signal on the grid of the reactance tube. Unfortunately it has been found that reactance tube circuits tend to be unstable. A better method, possibly, since the corrections are to be slow, is to employ a variable ganged condenser which is tuned by a servomotor. The driving mechanism in the variable condenser must be carefully designed so as not to introduce microphonic noises into the tuned circuits of the ganged condenser.

With regard to operation of the equipment in flight, neither the transmitter nor the receiver system should need any attention except possibly for gross changes in frequency. These could be done manually or automatically and can be done merely by the turning of a ganged tuning condenser. In the probe, however, the adjustments which determine the magnitude and phase of the leakage are so sensitive that they may shift slightly in flight owing to vibration. Small changes in the magnitude of the leakage are of no importance, and changes in phase of the leakage are equivalent to a small shift in the apparent resonance frequency; this again is of no importance if it occurs slowly enough. The probe, however, must be built so there is no "flutter" owing to the plane's vibration.

The amount of phase change due to vibration and temperature effects which can be tolerated can be estimated from the following simplified argument: A phase change of 90 degrees can be said to shift the "peak" of the resonance by λ. For $\lambda = 2100$ gammas and a deviation of the peak of 0.1 gamma the maximum permissible phase deviation is $(90 \text{ degrees}) \times \frac{0.1}{2100} \simeq 4 \times 10^{-3}$ degrees or about 15 seconds. This is the required short-time stability in the leakage. It would be less stringent for a narrower line width.

The maintenance of this equipment by the ground crew should be no problem for a crew that is already trained in the maintenance of conventional radio transmitters and receivers. Repairs on the probe should not be necessary except in cases of physical damage. In such cases, however, they require highly skilled personnel and probably should not be attempted in the field. The only critical adjustments which need to be made before flight are in the leakage, which should be adjusted, particularly when a new sample is placed in the probe. This adjustment is of the same order of complexity as the tuning up of the final stage of a transmitter and is one that should be easily learned by the average technician. When a new piece of equipment is being placed into service it may be necessary to first adjust the resonance frequency to correspond to the earth's field at that particular point. This adjustment can be made by rapidly changing the frequency until an indication in the output is observed, at which point the finer frequency adjustments are made so that the apparatus is at the proper operating point.

b. The Dispersion Component, No Sweep.

We will now consider three possible ways of using a two-coil probe to provide the desired output signal. The first of these employs the dispersion component without sweep as the operating characteristic (formula (2-12) and Figure 2-6). This is perhaps the simplest way of achieving a desirable operating characteristic and requires no sweep modulation of any kind. However we find that the simple diagram of Figure 6-1 is insufficient for our purpose because the output is not just the signal from the dispersion component alone, but is the signal plus the leakage which is in phase with the dispersion component. Thus, even though we operate at the position of zero dispersion component, i.e. at resonance, we are still getting a large output which may be a very sensitive function of the amplitude of the r-f field. Since we wish to avoid having the r-f amplitude highly regulated, a modified diagram must be used as shown in Figure 6-4. Here the signal from the detector, before going to the low frequency amplifier, is first mixed with a reference voltage consisting of rectified RF direct from the transmitter and of opposite sign to that of the signal. Thus the d-c component of the leakage is cancelled, and only the signal remains. The advantages of this type of system lie in the use of the dispersion mode with its high sensitivity and its simplicity due to the absence of any type of sweep modulation. There remain, however, the disadvantages of a d-c amplifier, with its drift and flicker noise, and the necessity for a very stable r-f amplifier. A modification of this type of system which is somewhat more practical is discussed in Section 9.

c. Magnetic Sweep Modulation.

The type of apparatus to be described here is most nearly like the type used in laboratory investigations and is probably the one about which most is known. It is also one of the types which we think is perhaps the most suitable for use in air-borne equipment.

A block diagram of this type of apparatus is shown in Figure 6-5. This system is operated in the absorption mode. A sweep oscillator supplies current at the sweep frequency to a third set of coils in the probe whose axis is in the direction of the earth's field. The induced voltage in the receiver coil consists of the absorption signal modulated at the sweep frequency plus the leakage; it is amplified in the receiver and rectified in the first detector. At this point it consists of a signal with components at the sweep frequency and at harmonics of the sweep frequency. The second detector is a so-called lock-in detector and is designed to reject all frequency components except those at the sweep frequency. The output of the lock-in detector is then placed on the recorder and on the AFC system.

This apparatus is only slightly more complex than the one shown in Figure 6-4. It has the advantage, however, that the operating characteristic is actually zero at resonance. Therefore, the apparatus is sensitive to changes in amplification only to the extent that it is sensitive to other changes of sensitivity, and these may be minimized by always operating near the resonance point. Since the signal which is actually observed is carried through the receiver and the first detector at the modulation frequency, it is sensitive only to flicker noise near the modulation frequency; and this is usually smaller than the low frequency flicker noise detected in the apparatus of Figures 6-4. The disadvantages are as follows: First of all, in a cross-coil system it is somewhat more difficult to adjust the probe for a pure absorption leakage than it is for a dispersion leakage. This difficulty can be minimized by good engineering. A second disadvantage is that the use of a magnetic sweep may cause slight changes in the apparent value of the earth's field in certain types of motion. This effect has been discussed in Section 4. Under certain conditions it may be a serious limitation on the operation of the equipment.

d. Frequency Modulation.

The scheme to be described here may not be practical with the presently known paramagnetic substances. However, should substances be discovered that have considerably narrower line widths than the metal-ammonia solutions, then this method would probably be more satisfactory than either of the previous two. For this reason we will go into it in some detail.

The method to be described here, shown in Figure 6-6, is similar to that of the preceding section, Figure 6-5, except that, instead of using a magnetic sweep modulation, a FM is used. In Figure 6-6 the transmitter frequency is simultaneously modulated by the sweep oscillator, producing FM at the sweep frequency, and by the slow automatic frequency control operated by a servomechanism which is identical to that in the other schemes. The only novel part of this system is the fast FM of the transmitter. For reasons that have been described previously, a reactance tube system is probably undesirable; instead, one might use rapidly rotating condensers (for example, Hammarlund high-speed type BFC) or possibly vibrating variable condensers. Assuming that the ideal FM can be achieved, this system has all the advantages of Figure 6-4 and in addition does not have any directional sensitivity due to the magnetic field sweep. The disadvantages, however, are as follows:

First of all, the FM in the transmitter is usually accompanied by a certain amount of amplitude modulation which must be eliminated by subsequent limiting. This introduces a certain amount of complexity in the transmitter which will depend on the amount of frequency modulation which is required, The second disadvantage is the fact that the probe and the receiving apparatus may have to be designed to accommodate a wider band of frequencies than is required with the other systems. This implies lower Q's in the tuned circuits and a correspondingly lower sensitivity than would be indicated by formula (3-1), or a setup in which the bandpass characteristics of the receiver are modulated simultaneously with the FM. The third disadvantage may be seen in formulas (2-7) through (2-12) and is the fact that all of these formulas have a factor ω^2 in addition to the resonance terms; thus, formulas (2-11), (2-12), and (2-18) no longer have the symmetry around resonance which they posses when magnetic sweep modulation is used.

The amount of FM which would be required to get useful sensitivity is as follows: for metal-ammonia solutions and 100 cc samples, a frequency shift must be approximately 20 per cent of the center frequencies. This amount of shift is much greater than is tolerated in any type of FM system now known in electronics. Although it may be possible to design such a FM system, the development involved may be so great as to make the system impractical compared to those involving magnetic sweep modulation. However, if paramagnetic substances can be found whose line widths are approximately 1/10 of those of metal-ammonia solutions, then obviously a system such as shown in Figure 6-5 may become quite practical.

FIGURE 6-1

BASIC DIAGRAM OF CROSS-COIL SYSTEM

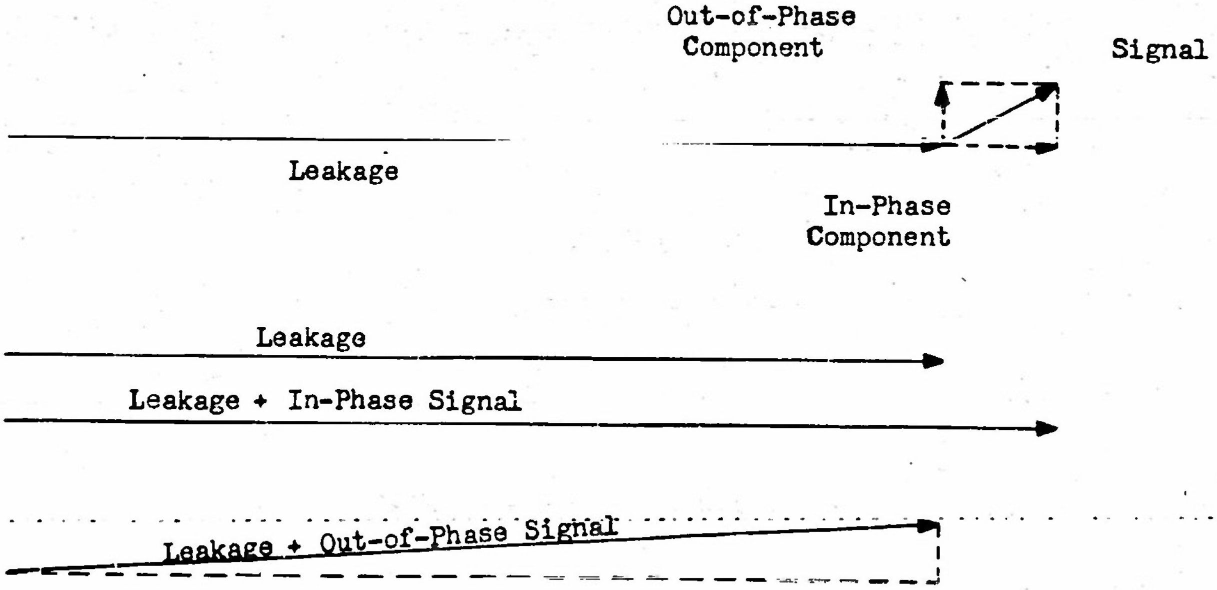


FIGURE 6-2

ILLUSTRATION OF HOW LEAKAGE
SELECTS PHASE OF SIGNAL

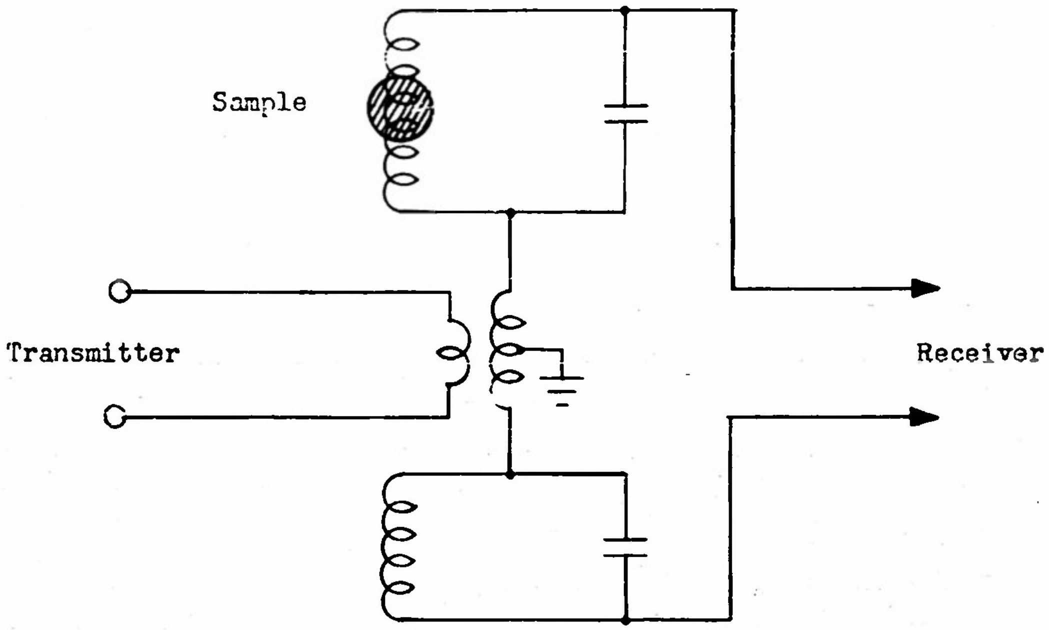


FIGURE 6-3

AN EXAMPLE OF A TWIN-COIL BRIDGE

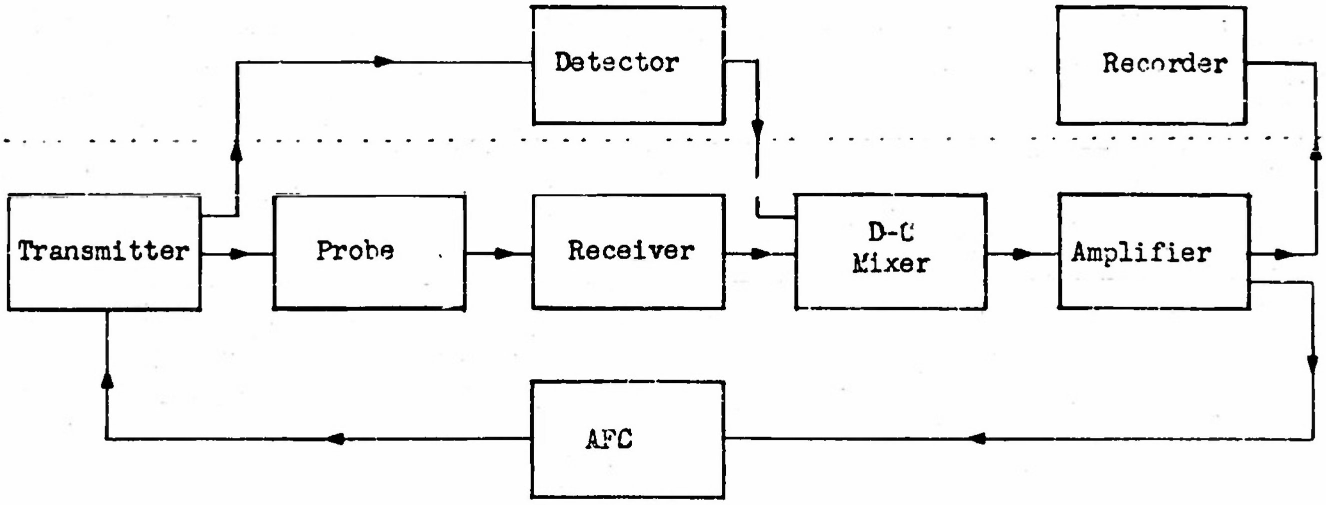


FIGURE 6-4

BLOCK DIAGRAM OF SYSTEM OPERATED
IN DISPERSION MODE, WITH NO SWEEP

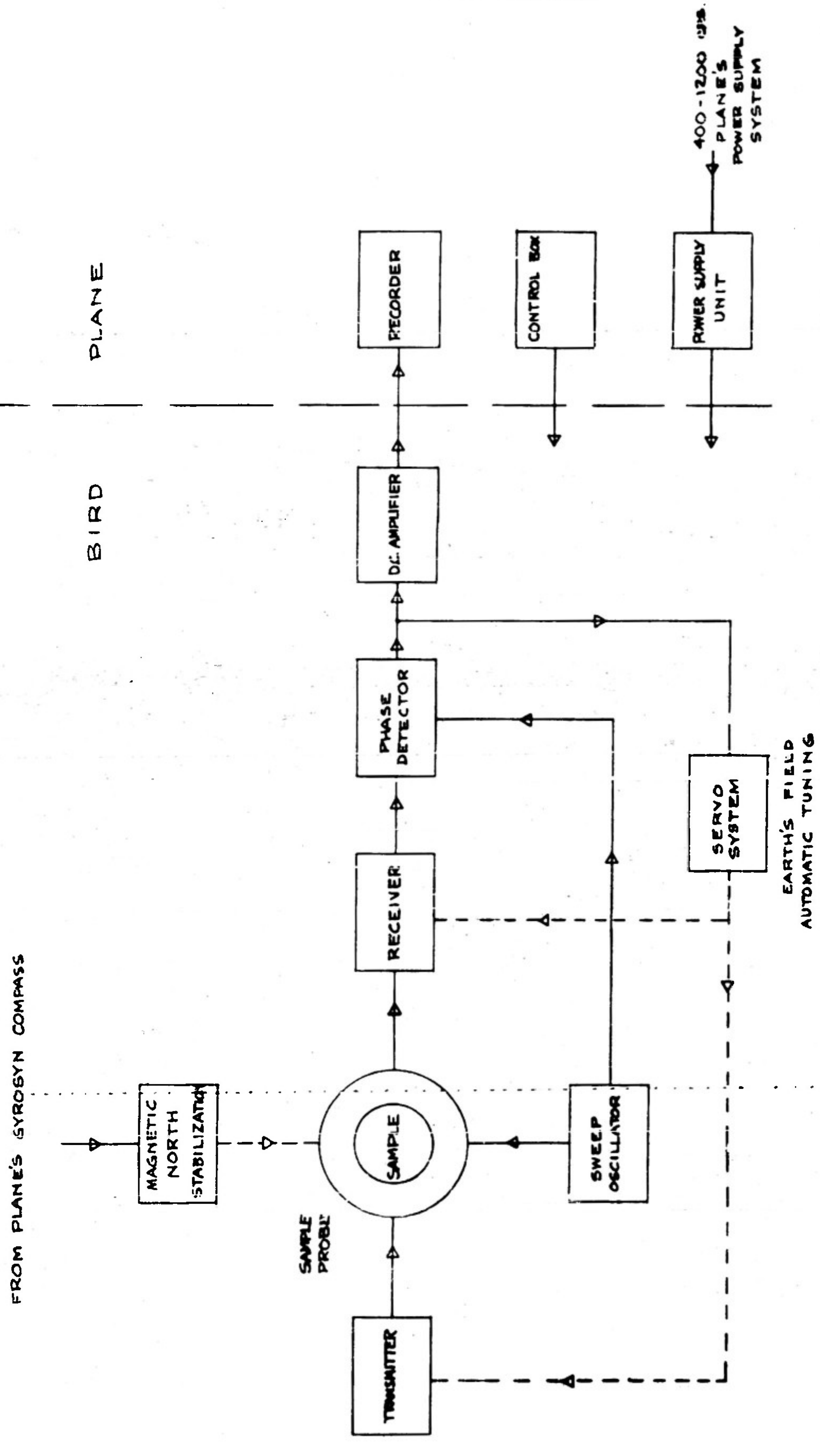


FIGURE NO. 6-5
SYSTEM NO. I, SIMPLIFIED

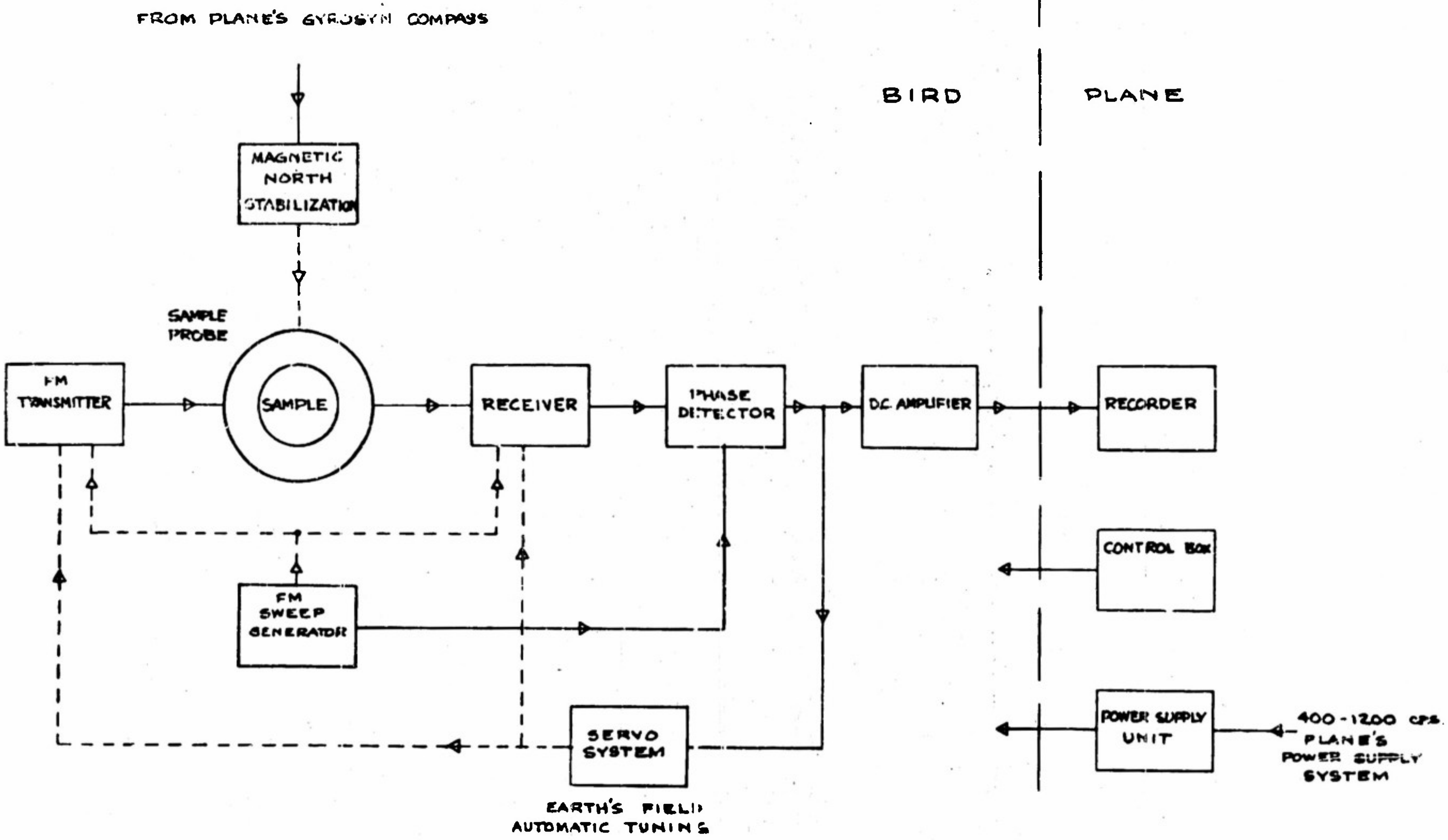


FIGURE NO. 6-6
SYSTEM NO. 3, SIMPLIFIED

7. Single-Coil Systems

In this section we shall discuss a type of single-coil system which enjoys wide popularity for laboratory work and which is usually known as the oscillating detector. See references (18) and (19).

In this type of circuit the single coil is the inductance of a negative-resistance oscillator circuit. The nature of this negative resistance oscillator is such that the vacuum tubes can feed only a limited amount of energy into the tuned circuit. At resonance, therefore, energy is being absorbed by the sample, and the amplitude of oscillation drops until the negative resistance characteristic changes are such that an equilibrium is re-established. Thus, the level of the oscillations can be amplified and detected to produce the signal. Strictly speaking the changes in amplitude in the single coil are produced only by the absorption mode of the resonance, since this has a resistive effect upon the coil. The effect of the dispersion mode is reactive and is to change the frequency of the oscillator, a change which can be shown to be proportional to the cube of the operating frequency. It turns out that, at frequencies of the order of 1 to 2 mc, this effect, at the very most, will be less than 1 cps and is therefore not of practical importance. Thus, this type of single-coil system can employ only the absorption mode.

Oscillating detector circuits have been produced in a variety of forms. They all have a distinguishing feature in their extreme simplicity. The entire apparatus which is equivalent to the transmitter, receiver, and first detector in a two-coil system is here represented only by a maximum of two or three tubes. There are no balancing problems in the probe, as only the absorption mode can be produced. In fact, the probe needs a minimum of attention in design and none during operation and maintenance. There are, however, serious difficulties in the operation of oscillating detectors which may make them impractical for use in an airborne magnetometer. These will be discussed later.

In a single-coil system of the oscillating detector type, two possible schemes are available for obtaining the desired operating characteristic. These are equivalent to c and d of the previous section. The system employing a magnetic field sweep is shown in Figure 7-1. Except for the replacement of the transmitter-receiver-detector by the oscillating detector, this instrument is identical with that of Figure 6-5. The same considerations regarding effects of amplifier noise, operational characteristics, and directional effects apply here as in Figure 6-5.

A circuit employing FM in an oscillating detector is also possible. The disadvantages discussed in the previous section hold here also, with one exception. In the circuit of Figure 6-5 it may be necessary to have low Q tuned circuits in order to get the necessary pass band for the RF. In the case of an oscillating detector, however, since there is only one tuned circuit in the entire system, it can be tuned to the instantaneous frequency of the oscillator. A circuit of this type, employing FM, has been constructed and used successfully in nuclear resonance work (19). However, the percentage of modulation in this case was very small. It is found that with larger amounts of modulation it is very difficult to get a FM without simultaneous AM, especially since the amplitude of the oscillation depends upon the shunt resistance of the tuned circuit, which is a function of frequency.

Another type of FM which appears to have some possible merit is one in which square wave FM is employed. This can be achieved, for example, by switching a capacity in and out of the tuned circuit. In this case the two frequencies of the square wave modulation should correspond to positions on equal and opposite sides of resonance. When the apparatus is at "resonance," the output should presumably be identical for both frequencies; but if the field changes, the output will be greater at one frequency than at the other, thus producing a detectible signal. Attempts were made experimentally to construct an apparatus of this sort, and they will be discussed in the following section.

In spite of the greater simplicity of oscillating detector systems relative to two-coil systems, the former have certain serious difficulties in operation which must be discussed in some detail. One of these is the fact that, since observation of the resonance depends on a particular type of tube characteristic, the circuit operation is very sensitively dependent on the condition of the oscillator tube. It is therefore extremely sensitive to vibration, which might shake the internal structure of the vacuum tube, and to aging effects. This factor in itself may make an oscillating detector impractical for use in an airplane unless special types of vacuum tubes are designed for it. An additional bad feature is the difficulty of making adjustments to get the optimum signal. Unlike a twin-coil system, where the only difficult adjustments are of a type that can easily be learned by average personnel, the adjustments in the oscillating detector system are sometimes not easily predictable even by experts and differ not only with each instrument but also with each vacuum tube. Thus, should one of these adjustments have to be changed in the middle of flight, it might mean that the apparatus would be out of operation for a period as long as 10 or 15 minutes, while the oscillator is being readjusted for optimum conditions. Needless to say, these adjustments are also very sensitive to bias voltages and other power supply conditions.

It is quite probable that these difficulties can be minimized by good engineering and, in fact, this has been done in some cases. (We should point out that the present cross-coil systems represent several years of engineering development and that the original cross-coil systems were far less satisfactory than they are now.) There is another type of disadvantage in the oscillating detector system, however, which is of a more subtle nature and which does not appear to be surmountable by any type of engineering design. This difficulty is the following:

The sensitivity of the detector to small changes in Q depends on the curvature of the tube characteristic, but the oscillation amplitude depends on the slope of the tube characteristic. Thus, it is possible for the oscillating detector to operate under conditions in which it appears to have normal oscillation amplitude and produces a normal noise level at the output, but is actually insensitive to the desired signal. This disadvantage is of considerable importance; for example, a gradual shift in the tube characteristic during flight may not be noticeable to the operator unless he inserts a test signal, and yet the apparatus might become so insensitive that the airplane could pass right over the target without noticing it. There is no comparable difficulty in the two-coil systems. In these systems loss of sensitivity may occur either because of a failure in the receiver circuit which would be immediately apparent to the operator by the complete absence of noise, or by failure in the transmitter circuit. The latter effect may be noticeable by a difference in noise level owing to the fact that the diode detector operates in a non-linear region of its characteristic; or, for a more satisfactory solution, it is a simple matter to place an output meter in the circuit to continually monitor the transmitter output.

The equivalent input noise level of an oscillating detector circuit is generally higher than that of a two-coil system. It is believed that with certain types of oscillating detector circuits one can get a noise level as low as that of a two-coil system in the limit of vanishingly small r-f fields. Vanishingly small RF, however, implies infinitely large samples. At the actual r-f level of about 1000 gammas which we propose to use, the best that can be expected of the existing oscillating detector circuits is 1/10 the sensitivity of the two-coil circuits.* This agrees with results we have obtained experimentally on oscillating detector systems. (See next section.) It is possible, of course, that systems with lower noise levels will be designed in the future.

---

* Private communications. A detailed discussion of the noise figures of oscillating detector circuits is given by G. D. Watkins, Ph.D. Thesis, Harvard University.

An additional difficulty of the oscillating detector circuit, discussed in Watkins' thesis but not found elsewhere in the literature, is the fact that the modulated signal is not in phase with the sweep which produces the modulation, and the phase difference is a function of the circuit adjustments. Thus, to the difficult adjustments of the tube operating conditions must be added an equally difficult adjustment of audio phase at the phase-sensitive detector, which may have to be corrected fairly often during flight.

On the basis of these arguments it appears that less engineering development would be required at the present time to produce a satisfactory two-coil system than would be required to produce a workable oscillating detector system. One must remember, however, that the condition for r-f phase stability in the two-coil system is extremely stringent, and that the r-f phase-stability problem does not exist in oscillating detector systems.

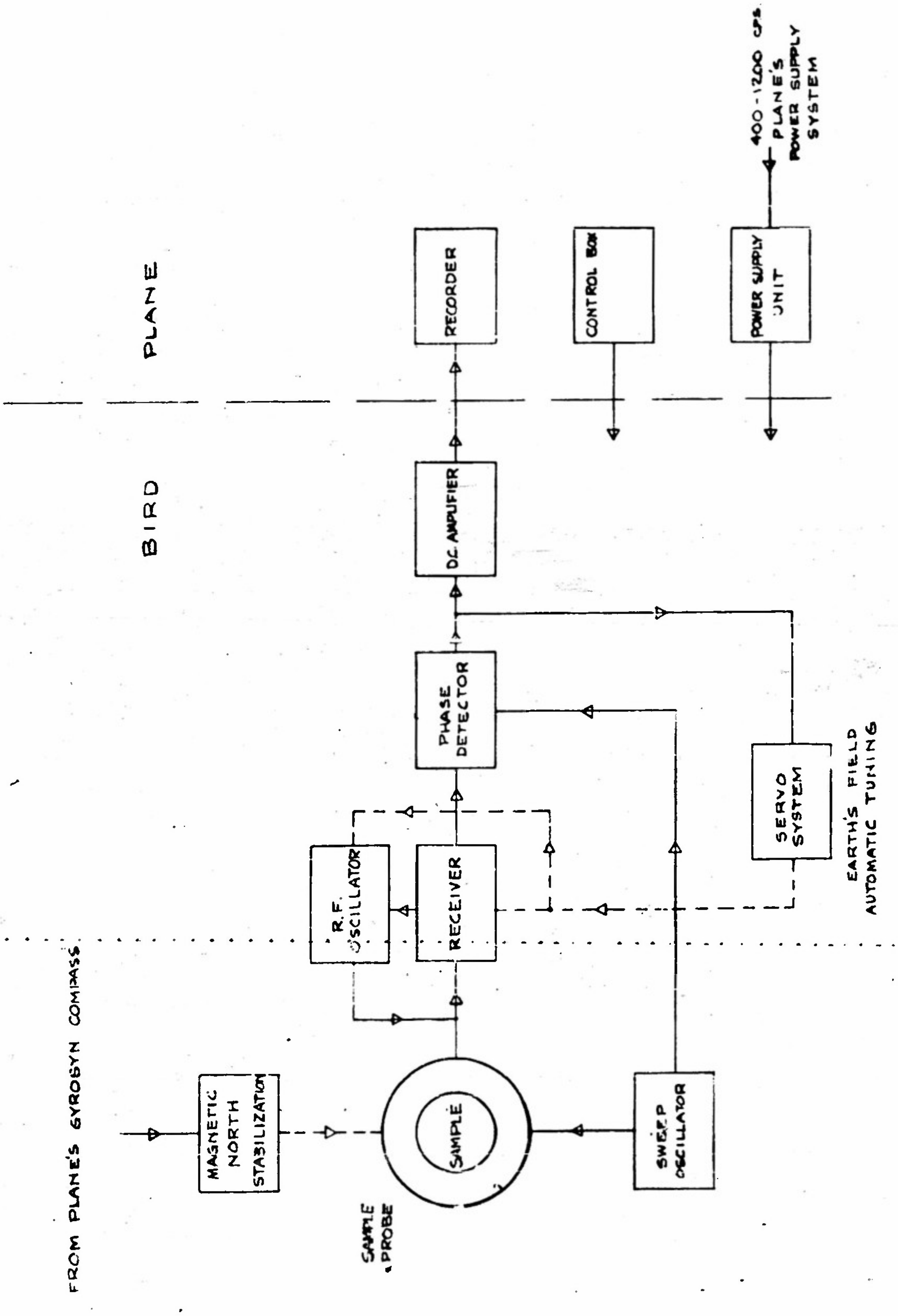


FIGURE NO. 7-1
SYSTEM NO. 4, SIMPLIFIED

8. Experimental Results

Most of the theoretical discussions of the past sections have been amply corroborated by experiments performed on nuclear and paramagnetic resonance. In this section we wish to discuss some experiments performed under this contract with the specific intent of obtaining information on how paramagnetic resonance apparatus would behave, relative to small changes in the value of a weak magnetic field.

To study two-coil systems, we carried out experiments on components of the Varian Associates Nuclear Resonance Radio-Frequency Spectrometer. This apparatus is basically a cross-coil system with magnetic sweep modulation of the form described in Figure 6-4. However, it does not have any AFC systems. The frequency range of the probe and the tuned circuits used in these experiments was from 2 to 4 mc, which is somewhat higher than the frequencies that would be used in the airborne equipment; however, one expects that the results at 2 mc can easily be extrapolated to the desired frequency range. The electrical constants of the apparatus, relative to signal-to-noise calculations, were approximately those used in the sample calculation of Section 3. The sample volume was of the order of 2 cc. The apparatus is designed to be relatively insensitive to vibrations of the type that are encountered in the laboratory.

The first experiments were performed with samples of the free radical diphenyl-picryl-hydrazyl. The apparatus, which is capable of a much wider range of r-f and sweep amplitude settings than would be needed in the airborne equipment, was first adjusted so as to give the pattern of Figure 2-2. The r-f field was then optimized (i.e., the signal adjusted to maximum) and the sweep then narrowed so that it was approximately equal to the observed width of the line. Tests on the sensitivity of the apparatus to small changes in field were made employing a current-carrying coil to produce a small perturbation of the d-c field. The apparatus was then allowed to run overnight, and a recording was taken on the recording meter. The sensitivity of the apparatus on the basis of the measurements made with the current-carrying coils was approximately 5 milligauss per large division (i.e., between heavy lines) on the chart. A section of the chart during a quiet part of the night is shown in Figure 8-1. It is believed that most of the short time noise variations shown in this chart are due to the random noise in the receiver circuit, while the long time variations are believed to be due to changes in leakage apparently caused by thermal variations in the probe geometry. (The cyclic variations correspond to operations of the building heating system.) The actual signal amplitude observed from the sample is quite large compared to the nuclear signals for which the apparatus is designed. Therefore, the range in which a compromise is made between correct balance conditions and linearity of the amplifiers is rather restricted. This accounts for the sensitivity of the apparatus to changes in leakage.

Further experiments of the same sort were carried out on samples of sodium dissolved in liquid ammonia, kindly supplied us by Prof. Clyde A. Hutchison, Jr., and Mr. R. C. Pastor of the Institute of Nuclear Studies, University of Chicago. The concentration of the sample is not exactly known, but the line width can be determined in the following manner. Figure 8-2 shows the absorption signal from this sample under conditions of a magnetic field sweep of approximately 2 gauss peak-to-peak. The distance between the two peaks of opposite sign must be equal to twice the value of the steady magnetic field at resonance. Since the operating frequency was 2.1 mc, the steady magnetic field must have been 0.75 gauss or 75,000 gammas. From visual inspection and assuming no line broadening due to electronic reasons, one would estimate λ at about 30 milligauss, corresponding to a sample whose concentration was 0.2 molar. The volume of this sample is approximately 2 cc. Measurements of the sensitivity of the apparatus with this sample by means of the current carrying coils proved unsatisfactory, possibly due to the fact that the field produced by these coils had an inhomogeneity greater than the line width of the line. Instead, a sensitivity measurement was made by varying the frequency and measuring the frequency difference necessary to produce a shift of one large division upon the recording chart. This measurement indicated a sensitivity of approximately 50 gammas per large division of the recording tape. The noise level shown in Figure 8-3, taken during a quiet part of the night, is approximately of the order of 20 gammas peak-to-peak. This number checks very well with the estimated noise level of the apparatus by calculations of the form described in Section 3 and gives one confidence that under good conditions an apparatus can be designed which will achieve performance consistent with that expected from theoretical considerations. It was found that, once the optimum operating conditions were known, it was possible to adjust the apparatus quickly to reproduce these conditions and that a balance adjustment of the form that would have to be performed when samples are changed could be reduced to a very simple process.

A difficulty which had been encountered in existing cross-coil systems was the sensitivity of the leakage, both in amplitude and in phase, to frequency changes. As had been mentioned before, the slow changes in leakage as a result of the slow changes in frequency are not of great importance in this problem. However, it had been observed on the existing laboratory equipment that there were often rapid changes in leakage corresponding to sudden movements of the tuning condenser, which appeared in the output as increased noise. Since our proposed two-coil systems are based on a variable oscillator in which the tuning condenser is often in motion, it was decided to incorporate a probe having a leakage that is essentially constant over a wide range of frequencies. Such a probe had previously been developed in connection with the Varian Associates Magnetic Field Meter, and this probe was adapted for this application. The geometry of the transmitter and receiver coils is adjustable from outside the probe, and it has been found possible to make the probe relatively frequency-insensitive over a 2-1 frequency range, which is ample for the present purposes. The adjustments are of a type that should be able to withstand severe vibration conditions and should be insensitive, or at least self-compensating, for variations in geometry due to thermal expansion. In a probe of this design one expects no spurious noises due to changes in either leakage or frequency.

A series of experiments was instituted to investigate the use of oscillating detector systems. One of the circuits investigated employed one oscillator tube having several control grids of the form described by Knoebel and Hahn (19) but with the 6AS6 oscillator tube replaced by type 6BN6, which is believed to have somewhat better characteristics for this particular purpose. An attempt was made to design a square wave f-m system with this circuit of the form described in the previous section. A moderate amount of success was achieved. Ordinarily the switching in of an additional condenser on the tuned circuit of the 6BN6 changes the amplitude of the oscillations as well as their frequency for reasons which are discussed in the previous section. However, it was found possible to compensate for this, at least partially, by simultaneously varying the bias on the first grid of the tube. Nevertheless, this bias adjustment appeared to be so full of complications and the overall sensitivity of the apparatus so low that further work on this circuit was abandoned. As would be expected, little difficulty was encountered in making the coil and sample holder of the oscillator; however, the oscillator tube characteristics were found to be extraordinarily sensitive to vibration. A further difficulty was encountered with the use of a 6BN6 tube because part of the grid structure, comprising in this case part of the tuned circuit, is unshielded. Therefore, the tube was also sensitive to motion of nearby objects. To eliminate these difficulties, it was necessary to mount the tube and its associated circuit components in a special shielded box designed to hold all components in a rigid position relative to one another. This box is shown in Figure 8-4.

Another type of oscillating detector circuit which was investigated was of the form described by Pound and Knight (18). This type of circuit has been used by a large number of investigators for laboratory experiments in nuclear and paramagnetic resonance and has been found by them to be quite satisfactory. In our experiments with this circuit, however, we were able to achieve a sensitivity only 1/10 of that available in the Varian Associates Nuclear Resonance Spectrometer, part of the difficulty apparently being vibration of the tube elements even though this part of the circuit was very carefully shock mounted. Whether or not this type of vibration sensitivity is inherent in the oscillating detector circuit or merely reflects our inexperience in the design of such circuits, we are not in a position to say at the present time. Other investigators have also found, however, that with an r-f field of the order of 1000 gammas a sensitivity about 1/10 that of a cross-coil system is about the best that can be expected of this type of circuit (see footnote, Section 7, page 7-5).

The directional effects common to all simple cross-coil probes, discussed at the end of Section 4, were not discovered by us until operations under this contract were almost completed. Previous to this time there appeared to be nothing to be gained by the use of a twin-coil bridge instead of the cross-coil system, and for this reason no experiments were performed on twin-coil bridges. However, since to the best of our knowledge the directional effects had not been observed in the laboratory previously, we performed an experiment to see if these effects actually exist. A sample of diphenyl-picryl-hydrazyl was used in a probe placed between Helmholtz coils, which provided a homogeneous field of several gauss. The magnetic field sweep was also placed on the Helmholtz coils. It was possible to twist the probe so that angles θ and ψ (Figure 4-11) of about 30 degrees could be obtained. Under these conditions one expects the phase shift to be such that a pure absorption mode is changed to approximately 90 per cent absorption and 10 per cent dispersion.

Figure 8-5 shows a plot of a 90 per cent absorption and 10 per cent dispersion together with a 100 per cent absorption Lorentzian curve. Figure 8-6 shows the experimental results. Both center curves are from a correctly aligned probe. The curves at the upper and lower left are the result of rotating about the receiver and transmitter axes respectively. As predicted by theory, there are changes in amplitude but not in shape of the curves. The curves in the upper and lower right are the result of twisting in different skew directions; in one case angle ξ (formula 4-9) is positive, in the other case it is negative. The distortions of these curves are in opposite directions, in agreement with theory, and they also agree with the amount of distortion predicted in Figure 8-5. We therefore believe that the directional effect in cross-coil systems actually exists.

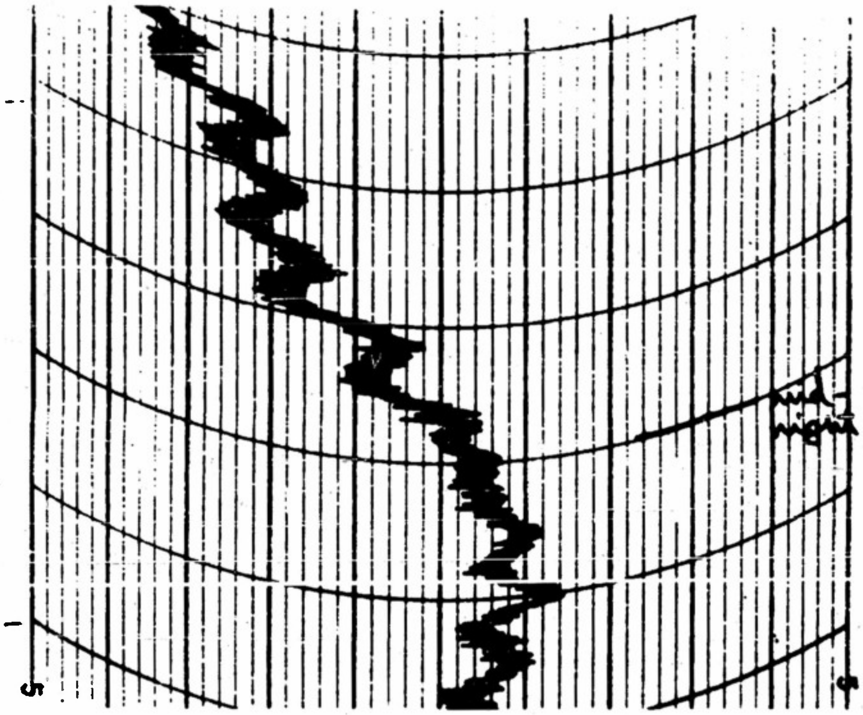


FIGURE 8-1

NOISE LEVEL AND LONG-TIME DRIFT EMPLOYING HYDRAZYL SAMPLE

Time scale: 1 division = 1 hour

Magnetic field scale: 1 division ≃ 500 gammas

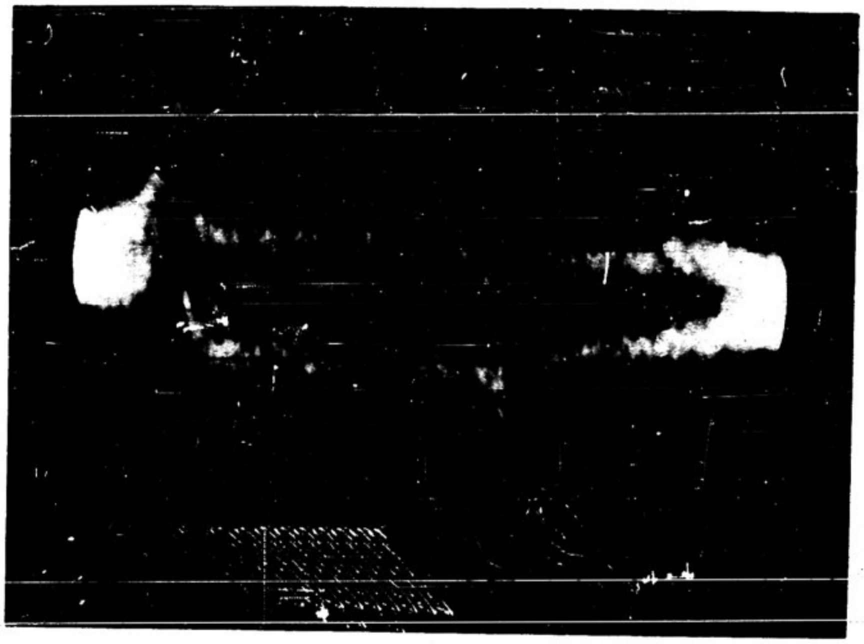


FIGURE 8-2

CROSS-COIL ABSORPTION SIGNAL FROM 0.2M Na IN LIQUID NH_3 AT 2.1 MC

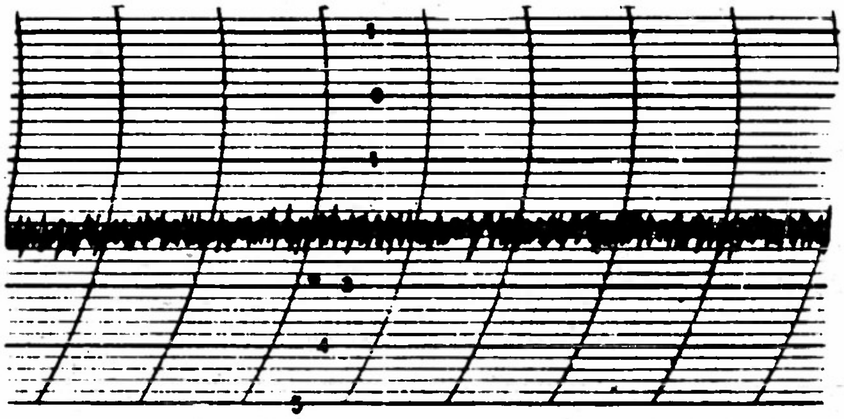


FIGURE 8-3

NOISE LEVEL EMPLOYING 2CC SAMPLE OF Na IN NH_3

Time scale: 1 division $\simeq$15 minutes

Magnetic field scale: 1 large division $\simeq$50 gammas

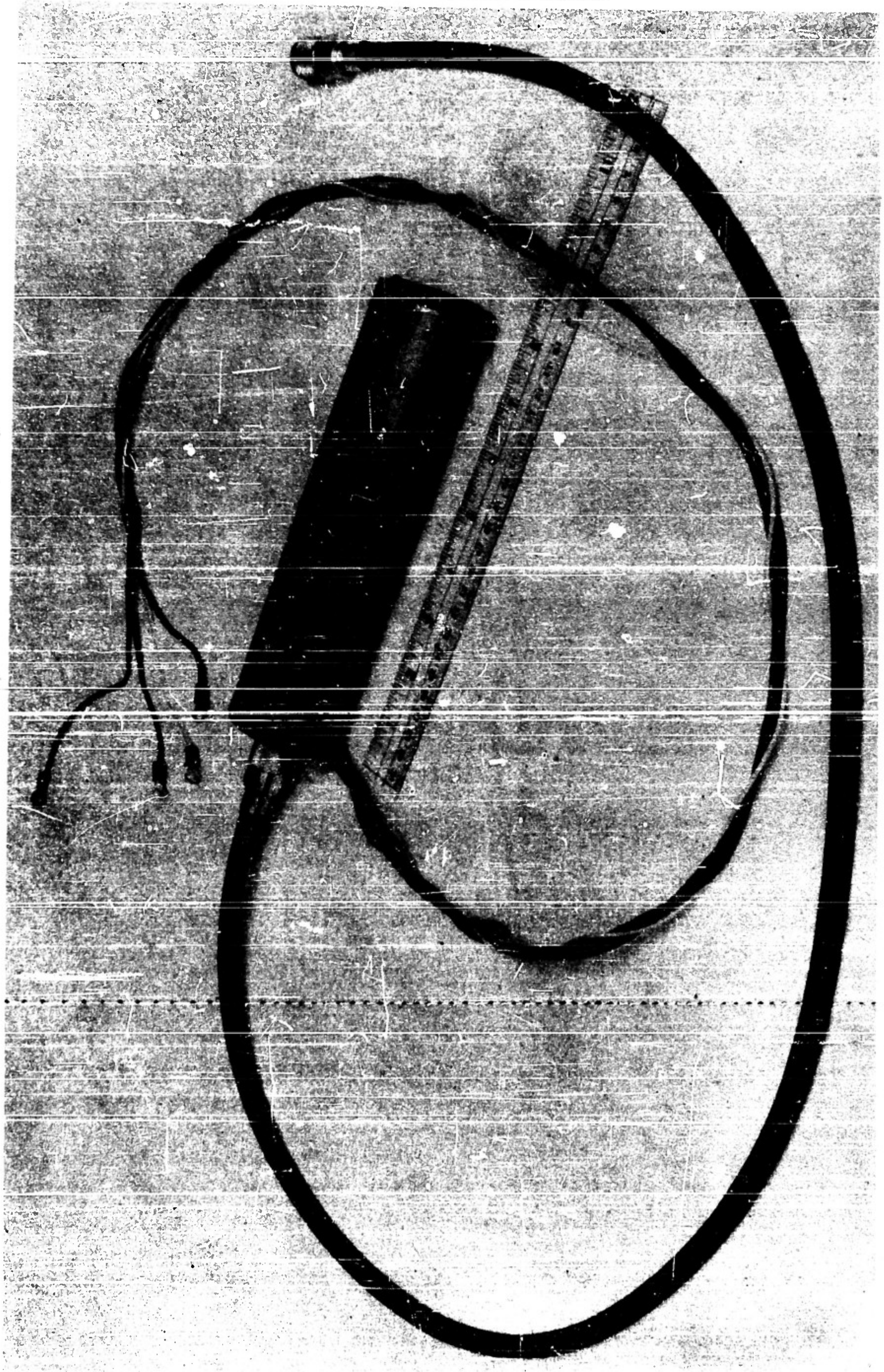


FIGURE 8-4A

SINGLE-TUBE OSCILLATING DETECTOR

The probe is connected to other end of coaxial cable.

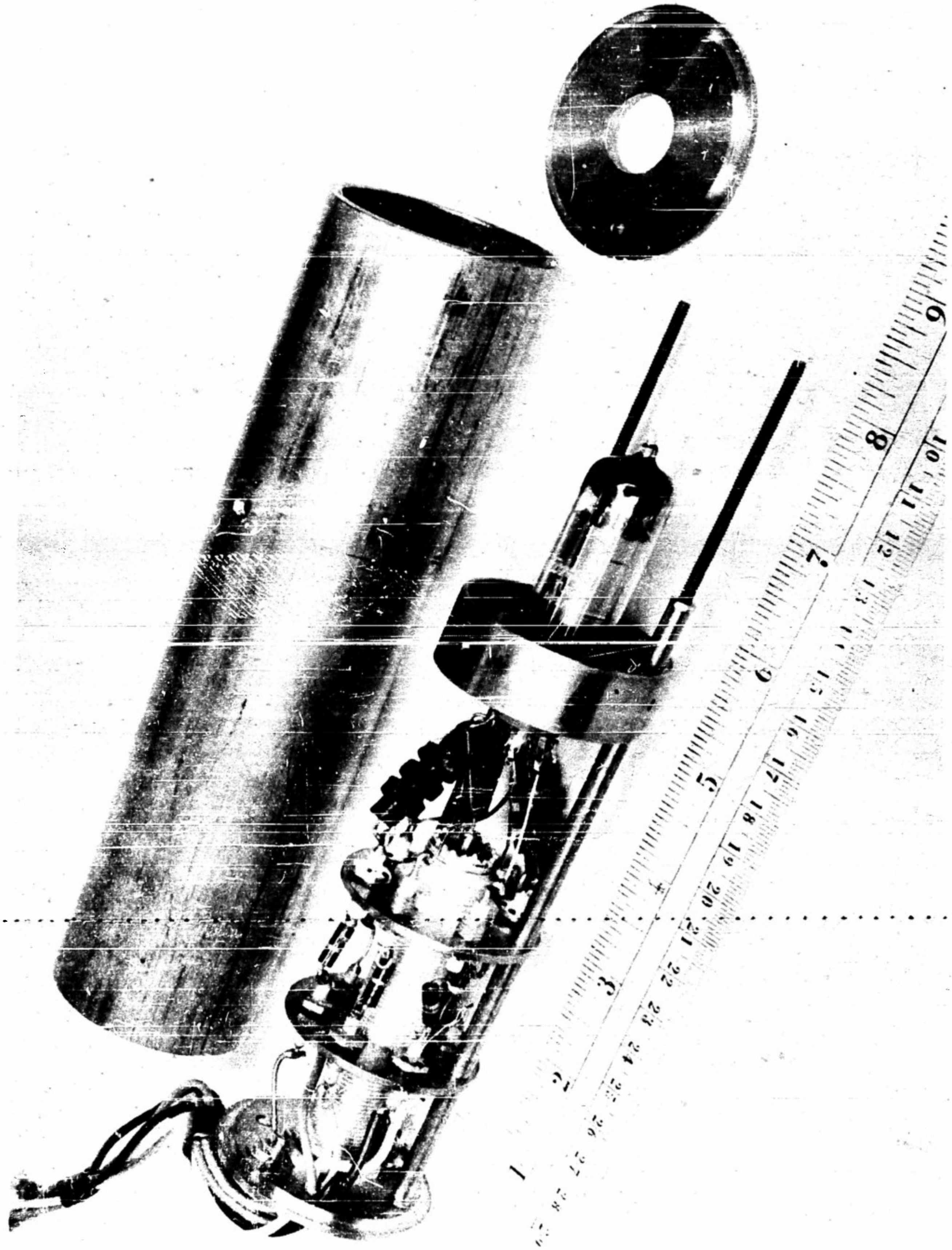


FIGURE 8-4B

DETAILED VIEW OF SINGLE-TUBE OSCILLATING DETECTOR

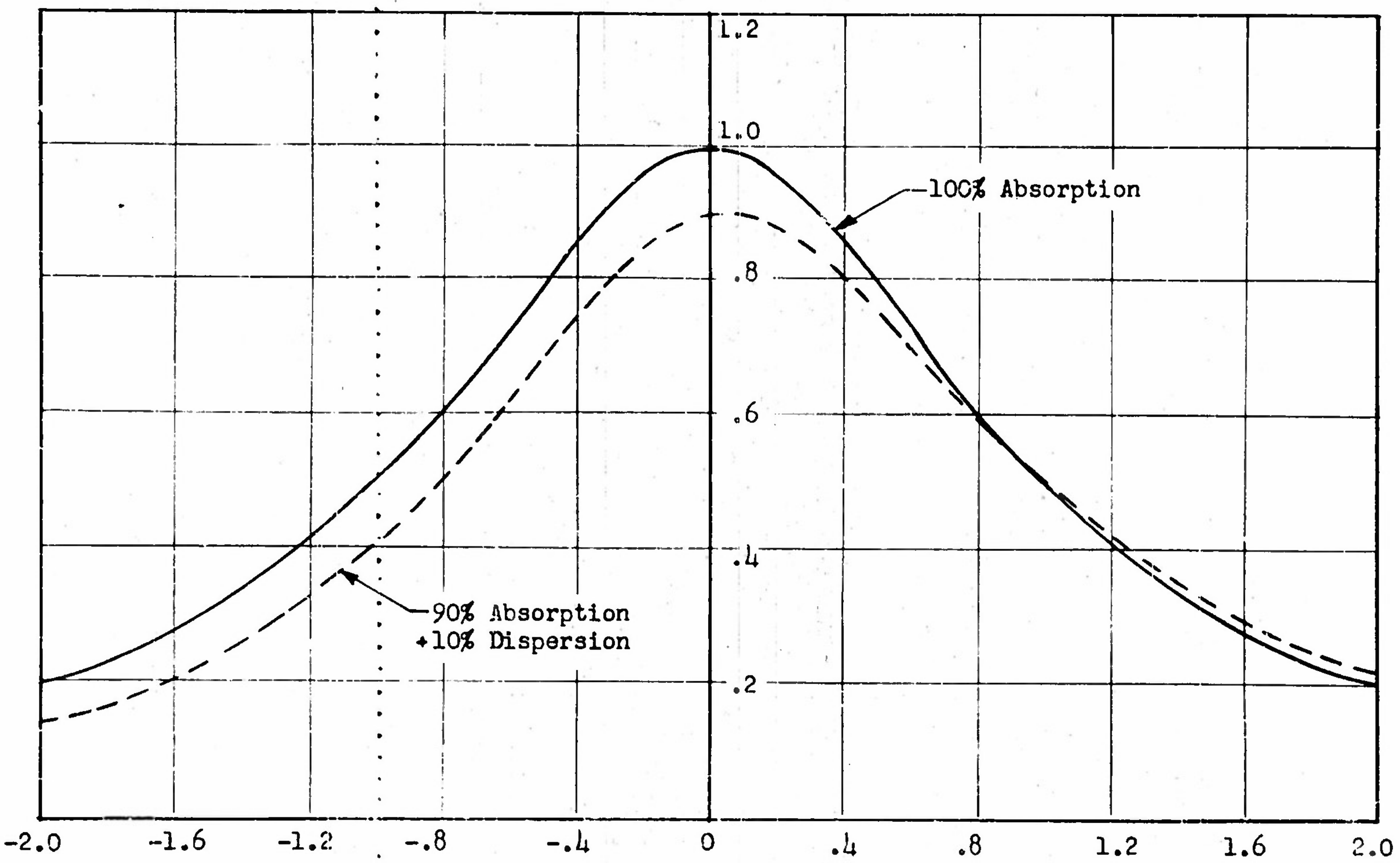


FIGURE 8-5

EFFECT OF MIXING A SMALL AMOUNT OF DISPERSION WITH THE ABSORPTION MODE

The units of both abscissas and ordinates are arbitrary.

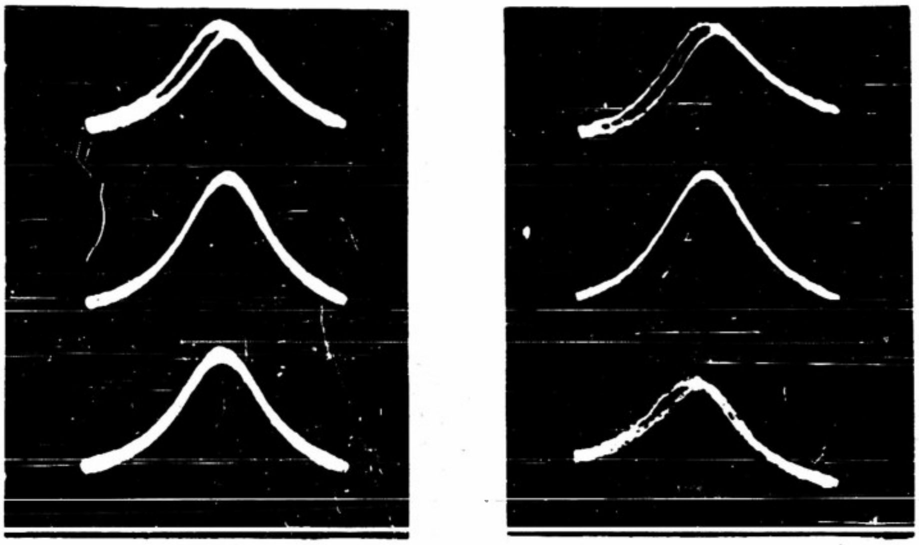


FIGURE 8-6

EXPERIMENTAL TRACES DEMONSTRATING DIRECTIONAL EFFECT OF CROSS-COIL PROBE

9. Proposals For Paramagnetic Resonance Magnetometers

In this section we propose a number of practical systems in which paramagnetic resonance is used in a magnetometer. In the drawings we show the main points of interest in the design of the systems. We have not worked out the minor engineering details; it is assumed that many of these can be worked out by conventional techniques. These systems are based on the block diagrams shown in Section 6. They are not the only systems that might successfully be used in a paramagnetic resonance magnetometer. However, they are systems that could be designed and built with a minimum amount of time spent in engineering development, since they are based on principles already well established in laboratory apparatus. The magnetometers shown here are designed to be towed in the bird. However, it is obvious that they could also be placed in the plane if desired.

Systems 1 thru 4 and the drawings 6-5, 6-6, 7-1, and 9-1 thru 9-9 refer to systems that use only one sample, or to the twin-cross-coil system employing two samples. The tilt-insensitive system employing three samples in mutually perpendicular coils will be referred to as "System 5" and is discussed separately at the end of this section.

. . . .

The principal design parameters around which the instruments must be designed are shown in Tables 9-1 and 9-2. Table 9-1 gives the parameters for systems in which the smallest observable variation is 0.1 gamma. Table 9-2 gives the corresponding numbers for a variation of 0.01 gamma. Following is an explanation of the columns in the tables.

Table 9-1

Design Parameters for ΔH = .1 Gamma

H_e = 0.32 gauss, λ = 0.021 gauss

1 Type of system	2 θ max. degrees	3 H_s peak gammas	4 $\Delta\nu$ max. kc	5 Ω cc	6 Sample diameter inches	7 Frequency stability ± cps
Dispersion mode						
Ideal*	20	--	--	100	2.3	45
System 2	20	--	--	140	2.6	45
System 5	--	--	--	70**	2.0	--
Absorption mode						
FM	20	--	20	180	2.8	45
Magnetic sweep	20	350	--	490	3.9	45
Magnetic sweep	10	700	--	170	2.7	180
Magnetic sweep	5	1400	--	130	2.5	1400

Table 9-2

Design Parameters for ΔH = .01 Gamma

H_e = 0.32 gauss, λ = 0.021 gauss

1 Type of system	2 θ max. degrees	3 H_s peak gammas	4 $\Delta\nu$ max. kc	5 Ω cc	6 Sample diameter inches	7 Frequency stability ± cps
Dispersion mode						
Ideal*	20	--	--	1000	4.9	4.5
System 2	20	--	--	1400	5.5	4.5
System 5	--	--	--	700**	4.4	--
Absorption mode						
FM	20	--	20	1800	6.0	4.5
Magnetic sweep	20	100	--	10,000	10.5	4.5
Magnetic sweep	10	200	--	5000	8.4	18
Magnetic sweep	5	400	--	1600	5.7	140

---

* Assuming a perfectly noiseless leakage reference

** Each of three samples

Column 1 - Type of System. This indicates which system is used, i.e., dispersion mode with no sweep, absorption mode with magnetic sweep, or absorption mode with FM.

Column 2 - This is the maximum angle of roll or pitch from the horizontal that the apparatus is designed to tolerate without producing spurious signals.

Column 3 - The peak value of the magnetic sweep field, in gammas. It is the smaller of either

a) $0.707\ \lambda$

or

b) the sweep field H_s which gives a barely noticeable shift in H (Formula 4-4) for a tilt of θ_{max} given in Column 2.

Column 4 - The maximum deviation from the carrier frequency, in the f-m system.

Column 5 - Volume of the metal-in-ammonia sample, in cubic centimeters. The calculation for the no-sweep cases was given in Section 3. (See also discussion on System 2.) For the other cases the relative increase in volume is computed from Figure 2-9, using either H_s from Column 3 or H_s equivalent = $2\pi \Delta\nu/\gamma$, using $\Delta\nu$ from Column 4. The "noise figure" of a good cross-coil system was included implicitly in the calculation of Section

3, in the equivalent input resistance R. For other types of circuits the noise figure may be somewhat higher, requiring a corresponding increase in volume.

Column 6 - Sample diameter, in inches, assuming a spherical sample.

Column 7 - Maximum frequency deviation from resonance which can be tolerated so that no spurious signals are produced by the tilt θ_{max} given in Column 2 (Figure 4-10). It is a measure of the accuracy to which the AFC system must be able to correct.

It will be observed that there are no safety factors in the calculations for these tables and that calculations for a maximum permissible perturbation are based on the assumption that other perturbations are absent. A safety factor exists, however, when the earth's field is larger than 32,000 gammas.

On the basis of the sample sizes shown in Table 9-2, we believe that it is not practical at the present time to design equipment for a sensitivity of a hundredth of a gamma, and as will be discussed in another report, we are not sure that there would be any advantage in designing equipment to such accuracy. For this reason the apparatus to be described is based on the design parameters of Table 9-1. The following points are of particular interest: The maximum tilt angle of 20 degrees in all systems has been selected on the basis of what is required to keep the recording needle on the tape. In other words, the maximum permissible deviation from resonance is about 15 times the smallest detectable variation in field, and this should be approximately the ratio of the maximum swing of the needle on the recording tape to the smallest observable motion. A latitude in tilt of 20 degrees also indicates that we do not have to be concerned with horizontal stabilization of the apparatus except possibly in extreme cases. For this reason, no such stabilization is indicated in the following drawings. The only type of stabilization required is orientation within 20 degrees in the direction of the earth's field. It is assumed that this can be accomplished by means of signals from the plane's gyrocompass.

When a magnetic field sweep is used, an additional restriction is placed on the magnitude of the sweep field because of the apparent variation in the magnitude of the field as a function of tilt, (formula 4-4). For this reason the table indicates the design parameters for maximum deviations of 20 degrees, 10 degrees, and 5 degrees, respectively; and note should be made especially of the variations in sample size and of necessary frequency stability. A relatively small sample is needed at 5 degrees, and correspondingly a small amount of frequency stability is needed. However, it is assumed that the vertical and horizontal stabilization under these conditions must be a good deal more stringent. The 10 degree maximum tilt represents a good compromise between conditions of small sample and minimum stabilization requirements.

Figures 6-5, 6-6, 7-1, and 9-1 thru 9-9 describe the proposed schemes in detail.

Figure 9-1 shows the probe for all two-coil schemes. The spherical sample at the center of the probe is closely surrounded by the transmitter and receiver, and these coils are rigidly potted in a spherical plastic globe. The sweep coils are mounted externally on the metallic shield surrounding the plastic globe. A bore through the plastic and a port in the shield make it possible to remove the sample. It has been found experimentally that the shield diameter must be about 3 times the diameter of the r-f coils in order that the leakage be accurately adjustable. This fact must be kept in mind in estimating maximum useful size of the sample.

The direction of the earth's field is to be approximately perpendicular to the plane of the sweep coils. The dip of the probe, corresponding to the dip of the earth's field, is adjusted by a thumbscrew worm adjustment on the horizontal probe pivot. This adjustment is made to correspond to the latitude in which operations are taking place, and one adjustment should be satisfactory for a radius of operations of several hundred miles or more. Electrical connection between the probe and the vertical pivot is made by means of short lengths of flexible cable.

The orientation of the probe is controlled to within the necessary accuracy (± 10 or ± 20 degrees) by a selsyn operated by signals from the airplane's gyrosyn compass. Since the probe may turn many times 360 degrees in the course of a flight, electrical connections through the vertical pivots must be of a movable type. For the transmitter and receiver connections, which are in high-Q circuits, coaxial joints, one in each pivot, are used. For the sweep coils a pair of slip rings is satisfactory. A snap-back arrangement, in place of movable contacts, is also possible.

The entire bird, and particularly the probe, must be carefully shielded; otherwise, the apparatus, properly tuned, makes an excellent receiver of broadcast stations.

System No. 1, absorption mode, two-coil bridge (or cross-coil) with magnetic field sweep, is substantially as shown in the simplified block diagram Figure 6-5. A more detailed diagram is shown in Figure 9-2. A sweep modulation of 5 kc is indicated. It is desirable to make the modulation frequency as high as possible, consistent with getting a large number of sidebands under the resonance curve so as to avoid flicker noise and power line interactions in the audio amplifiers. For $\lambda = 2100$ gammas there are, at 5 kc sweep, about 30 sidebands under the resonance curve, which should insure faithful reproduction of the signal. If a narrower line width is discovered, however, the sweep frequency should be correspondingly reduced.

Operation of the unit would be somewhat as follows. Some time before flight, and particularly if the sample is being changed, the unit is checked for correct leakage and r-f and sweep amplitude, as well as for correct operation of the electronics in general. These checks will require, in addition to the installed equipment, an oscilloscope and possibly an auxiliary sweep generator designed to produce large amounts of sweep. Just before flight the magnetic north stabilization is synchronized with the plane's compass. If the plane is being operated from a carrier, it is not possible to set the resonance frequency before flight because the residual field of the carrier may be vastly different from the earth's field. For this reason a unit called a "fast sweep, search and signal locking unit" has been incorporated into the AFC system. As the plane goes into flight this unit will make the AFC system rapidly scan back and forth over the entire frequency range until resonance is found. As the frequency approaches resonance, the output signal goes over a "hump" which is so large compared to the normal signals that it overloads the d-c amplifiers. This large signal, however, can be used to turn off the search unit, after which the normal error-correcting characteristic of the AFC pulls the frequency into resonance.

Operation of the unit in flight is completely automatic. For monitoring the operation, the operator needs only the recorder and a meter indicating the output of the amplitude detector. The latter is useful for indicating the condition of the r-f circuits and the leakage. No provision is indicated in the drawings for insertion of a test signal; however, this can easily be arranged by inserting a small d-c current on the sweep coils.

Figure 9-3 shows a system designed to use the dispersion mode, which is somewhat more elaborate than the simple scheme suggested in Figure 6-4. (Figure 9-4 is the simplified diagram.) The difficulty with putting Figure 6-4 into practice is that a d-c voltage must be subtracted from the output which is always exactly equal to the no-signal (i.e., leakage) output. In Figure 9-3 this is accomplished as follows: A square wave "sweep" modulation is applied to the sweep coils. For half a cycle no current flows through the sweep coil; the detector output is thus (signal + leakage). For the other half cycle a large bias current flows through the coils to bias the sample well off resonance; the detector then reads leakage only. The output of the detector is thus a square wave modulation of the dispersion mode. The additional electronics rectifies this modulation and provides information about its sign so that the proper sign of the error signal is maintained.

The theory of square wave modulation of a resonance is given in reference (20). It is necessary that the square wave frequency be less than half the line width (60 kc, in frequency units). The square wave biasing field can be made large enough so that the vector sum of it and the earth's field is essentially independent of the tilt angle; thus, no new directional effects are introduced. Since one effectively looks at the signal half the time and leakage all the time, the noise figure is increased by a factor of two over the ideal dispersion mode system, and the sample volume must be increased accordingly. This is shown in Tables 9-1 and 9-2.

Factors regarding maintenance, operation, search for resonance, etc. are the same in this and all other systems as in System 1, and will not be discussed further.

System 1a-2a, shown in Figure 9-5 and in simplified form in Figure 9-6, is to be considered alternatively to Systems 1 or 2 if it should be found in practice that the phase of leakage in the probe is not sufficiently stable under flight conditions. The phase reference, instead of being supplied by the leakage, is supplied by a phase-reference signal directly from the transmitter, which is mixed with the signal-plus-leakage in the r-f phase detector. The burden of stability is thus shifted to the r-f phase adjustment. The stability necessary for a metal-ammonia sample has been shown in Section 6 to be 15 seconds of arc for $\Delta H = 0.1$ gamma, and 1.5 seconds for $\Delta H = 0.01$ gamma. Variations in phase are not too important provided they occur more slowly than the time needed to make a measurement.

A system using FM of the absorption mode is shown in Figure 9-7 and in simplified form in Figure 6-6. The variable tuned circuits, varying at 400 cps, are independent of the AFC system and are tracked in both transmitter and receiver so as to allow higher Q circuits. This tracking implies considerable difficulty in initial alignment and field maintenance of the system. There are a larger number of moving parts and more ferrous material in the bird that is required in the other systems.

A probe for an oscillating detector circuit is shown in Figure 9-8. It differs from the probe shown in Figure 9-1 primarily in the design of the rotating coaxial joints. Since changes in Q of the single tuned circuit of this system are magnified many times, it is essential that the movable contacts be as noiseless as possible. It is suggested that the two joints - one at the horizontal and one at the vertical pivot (there is no flexible cable in this connection) - be patterned after the low-noise contacts used in variable microwave cavities. Actually the design of these joints is a major engineering problem in any event.

An oscillating detector circuit using magnetic field sweep is shown in Figure 9-9 and in simplified form in Figure 7-1. Except for the r-f circuits and probe it is identical to the other magnetic sweep system (Figure 9-2).

System 5 is the tilt-independent system employing three mutually perpendicular coils and three samples. The three coils are connected in series, with one tuning capacitor across them, and in all respects are equivalent to the single sample-containing coil of a conventional twin-coil bridge. Since the signal is for any direction equivalent to the signal produced by two of the three samples, it is necessary that each sample be at least half the size of the sample in a simple system with corresponding electronics, other factors being equal. This is indicated in Table 9-1 and 9-2, where the sample volumes are one half those of System 2. The geometrical efficiency of the three coils in series may not be as high as for a single coil with the same inductance; for this reason it may be necessary to increase the sample size from 70 cc, for example, to 100 cc.

In considering an electronic system for the tilt-insensitive setup, it is obvious that we do not want sweep modulation of the absorption mode, as it reintroduces directional effects. Frequency modulation also does not appear satisfactory because of the large number of tuning adjustments that are needed; so we are left with the equivalent of System 2, i.e., square wave modulation of the dispersion mode. The circuit of System 5 (Figures 9-10 and 9-11) is thus identical to that of System 2 except for the absence of the magnetic north stabilization.

The short-time frequency stability required for System 5 is determined not by directional effects but by amplifier stability and linearity of the operating curve. It is difficult to specify a number for this case, but probably a short-time stability of ± several kilocycles will be satisfactory.

The probe for System 5, not shown in the drawings, contains no moving parts, all coils being rigidly mounted with respect to the bird. It is not necessary that the coils be exactly perpendicular or that the coils or their samples be exactly identical; the directional sensitivity due to small variations in these factors would be negligible.

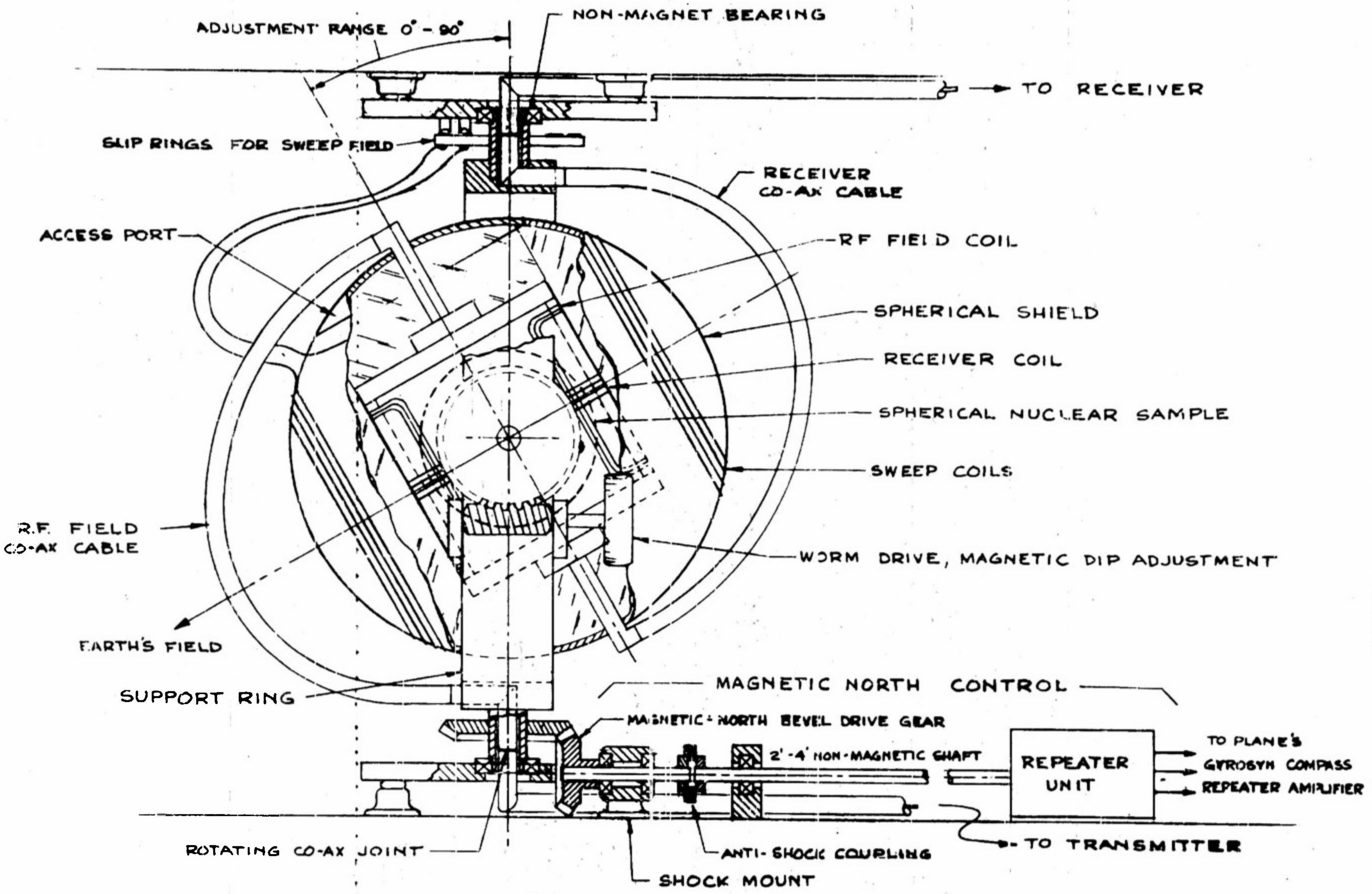


FIGURE NO. 9-1

CROSSED-COIL PROBE ASSEMBLY

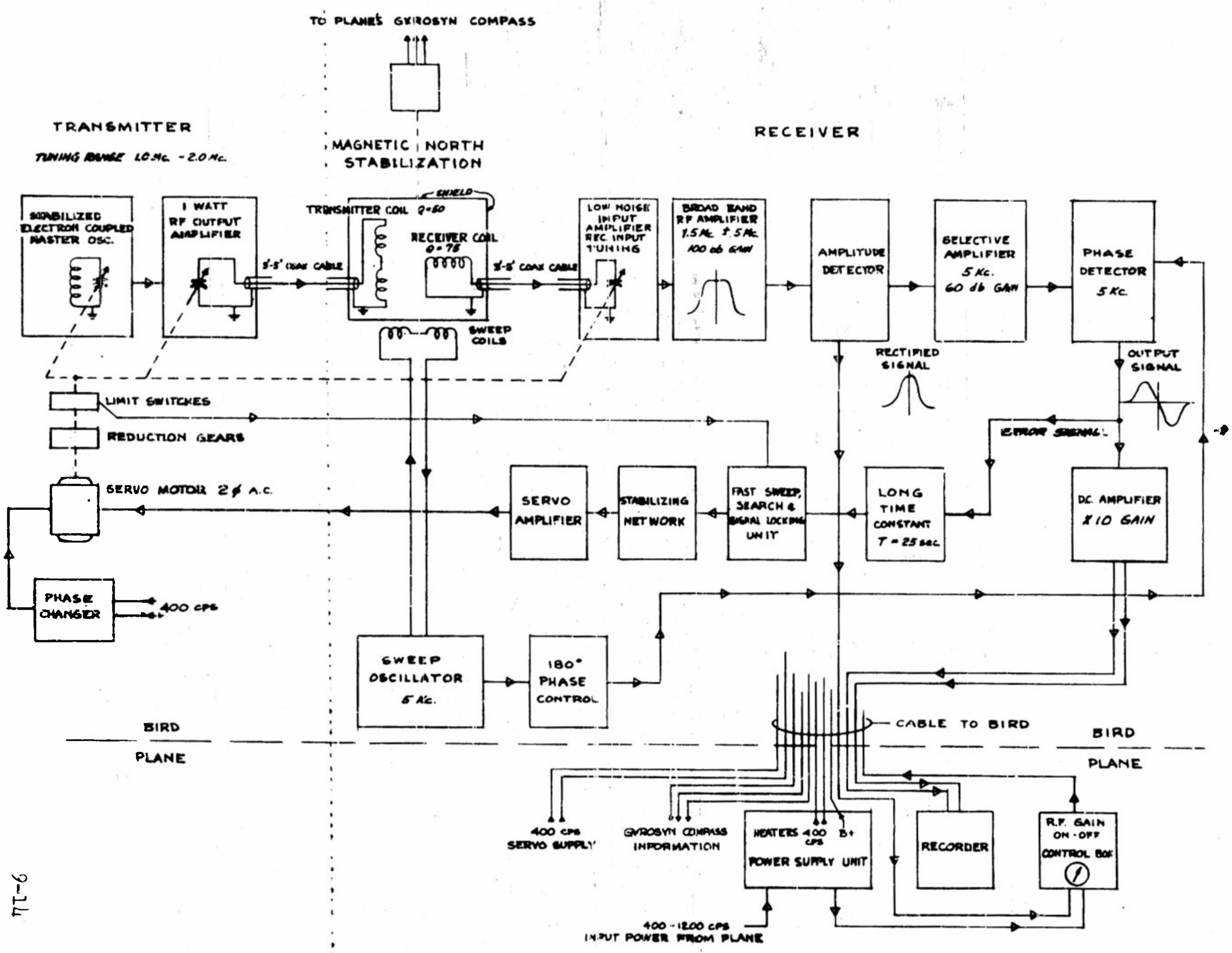


FIGURE NO. 9-2

SYSTEM NO. I

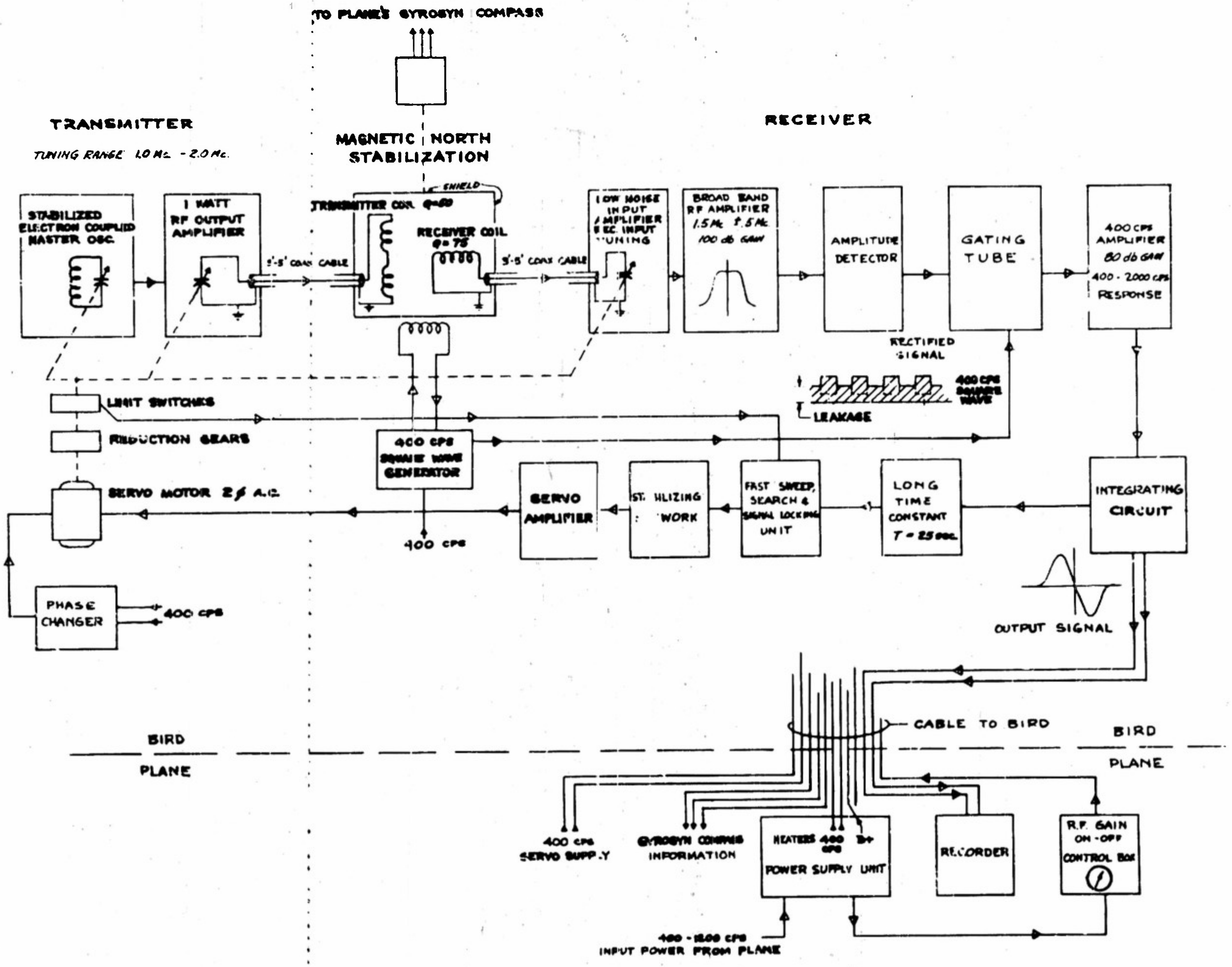


FIGURE NO. 9-3
SYSTEM NO. 2

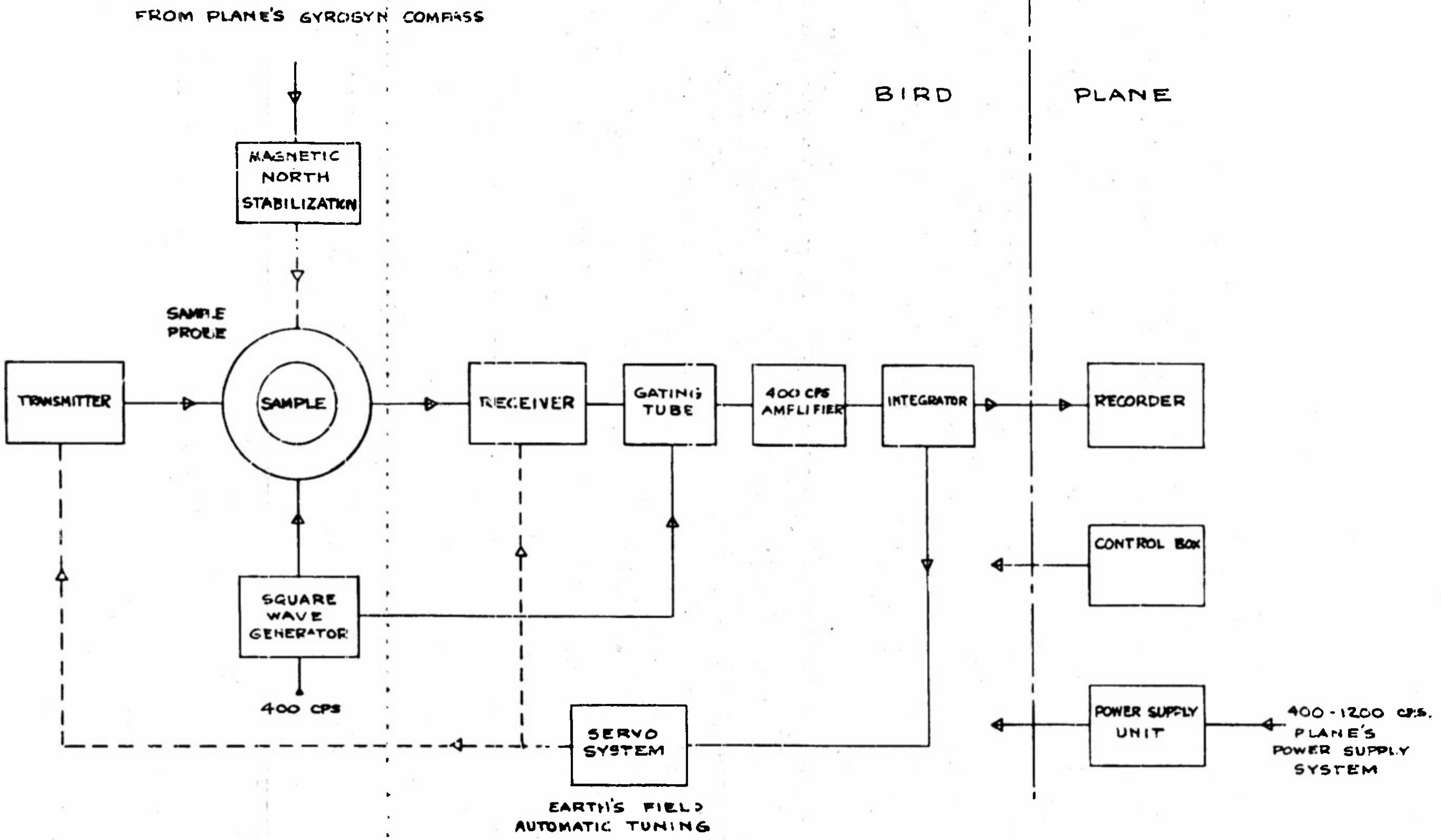


FIGURE NO. 9-4

SYSTEM NO. 2, SIMPLIFIED

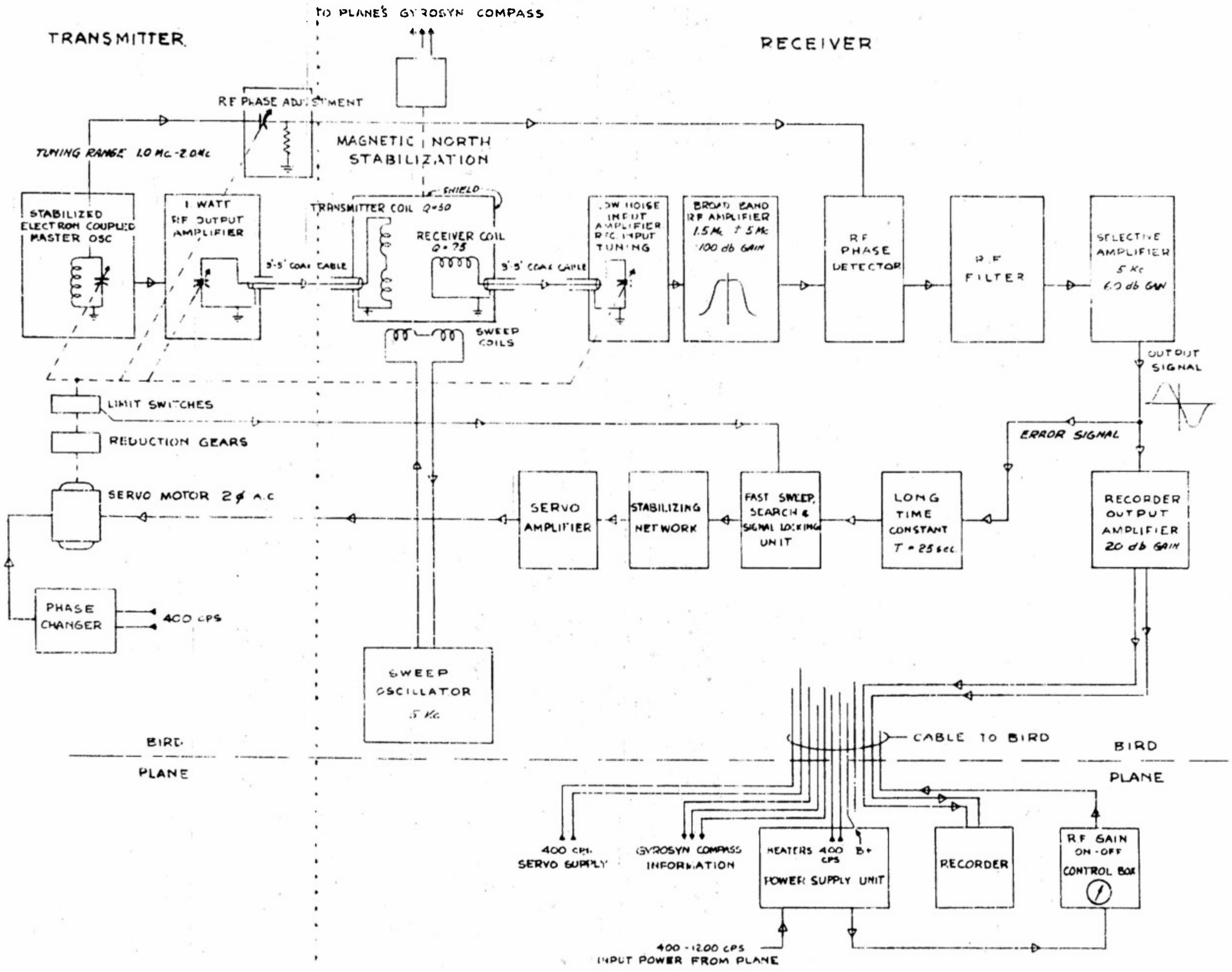


FIGURE NO. 9-5
SYSTEM Ia-2a

CONFIDENTIAL
SECURITY INFORMATION

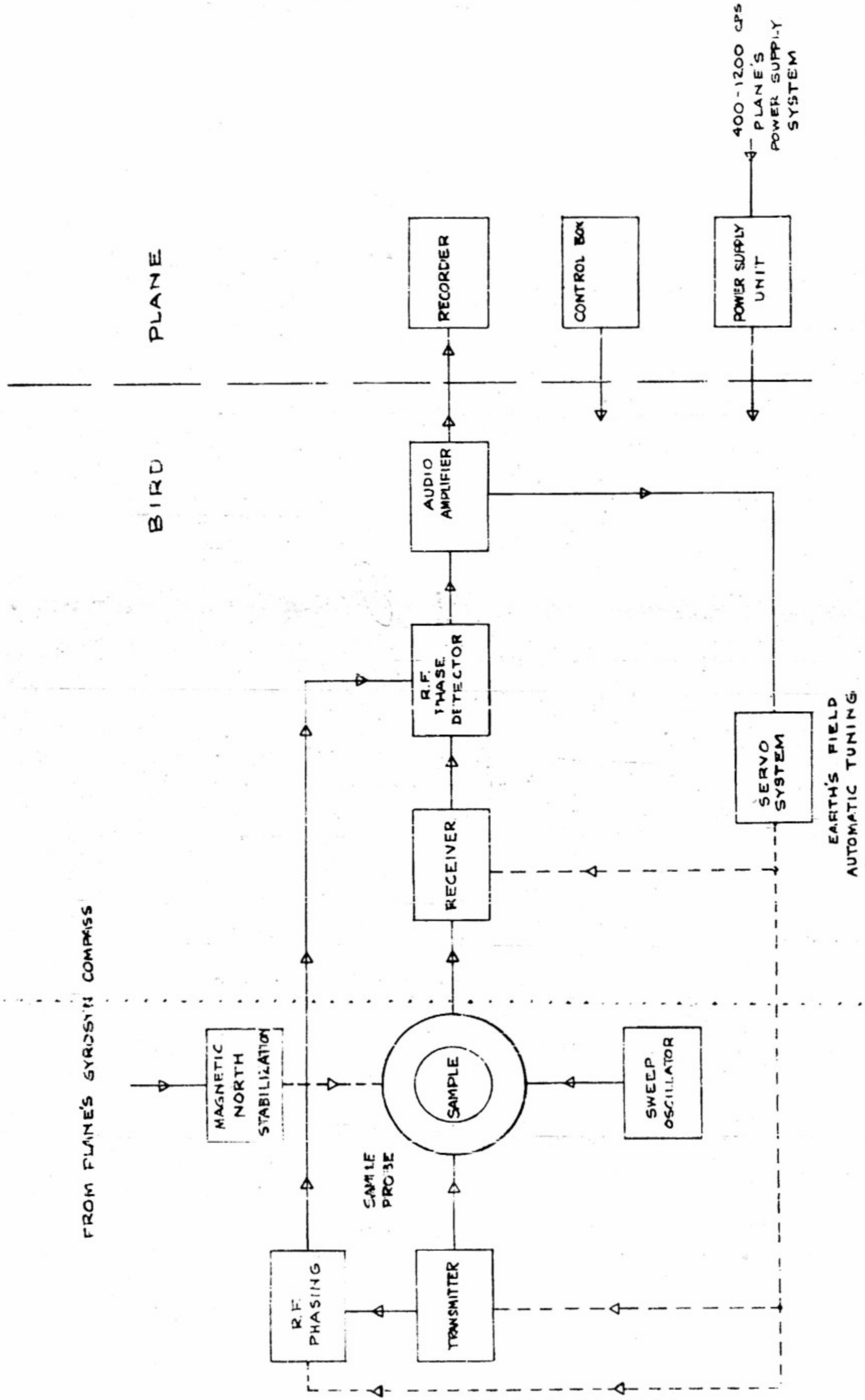


FIGURE NO. 9-6
SYSTEM NO. 1a-2a, SIMPLIFIED

CONFIDENTIAL
SECURITY INFORMATION

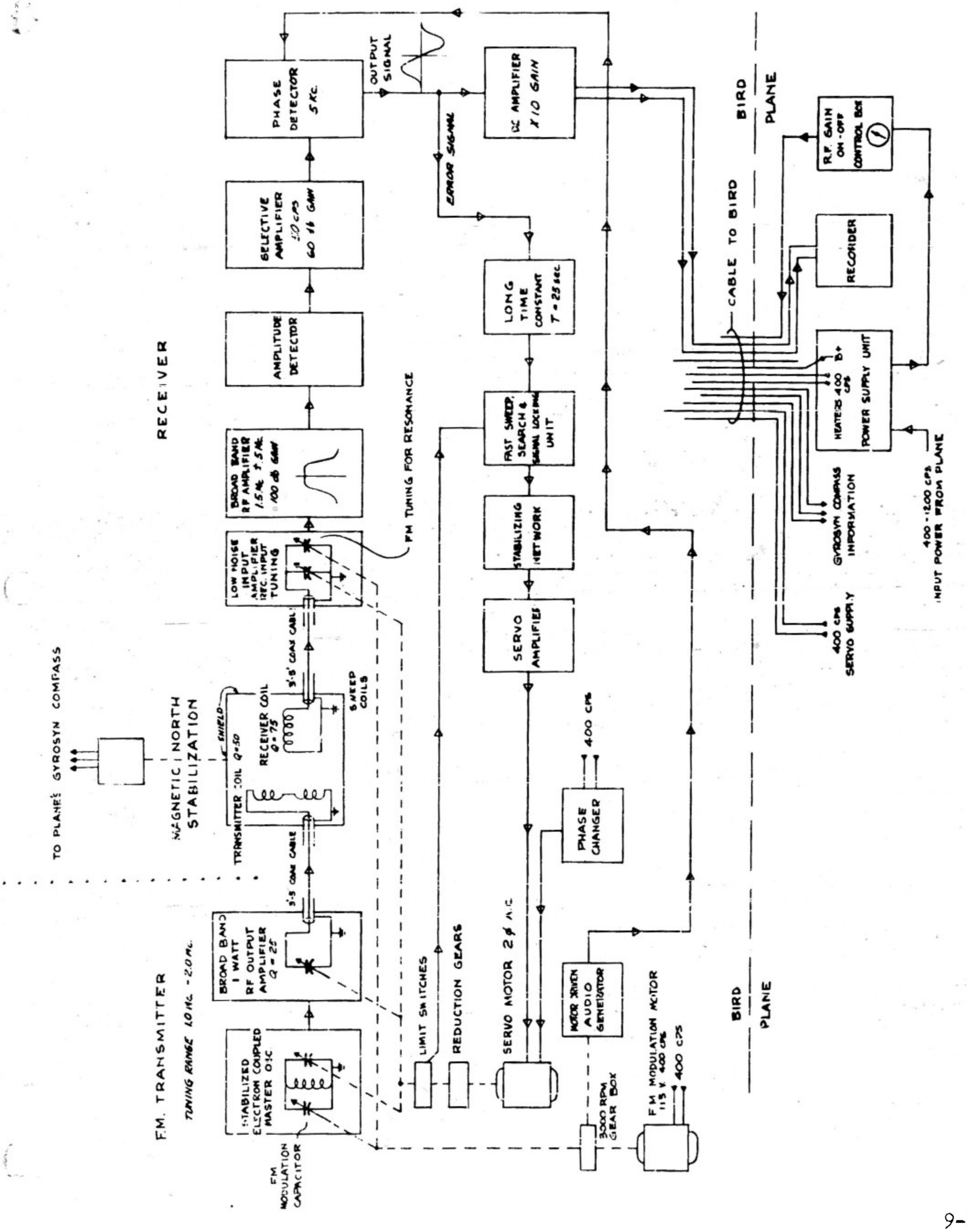
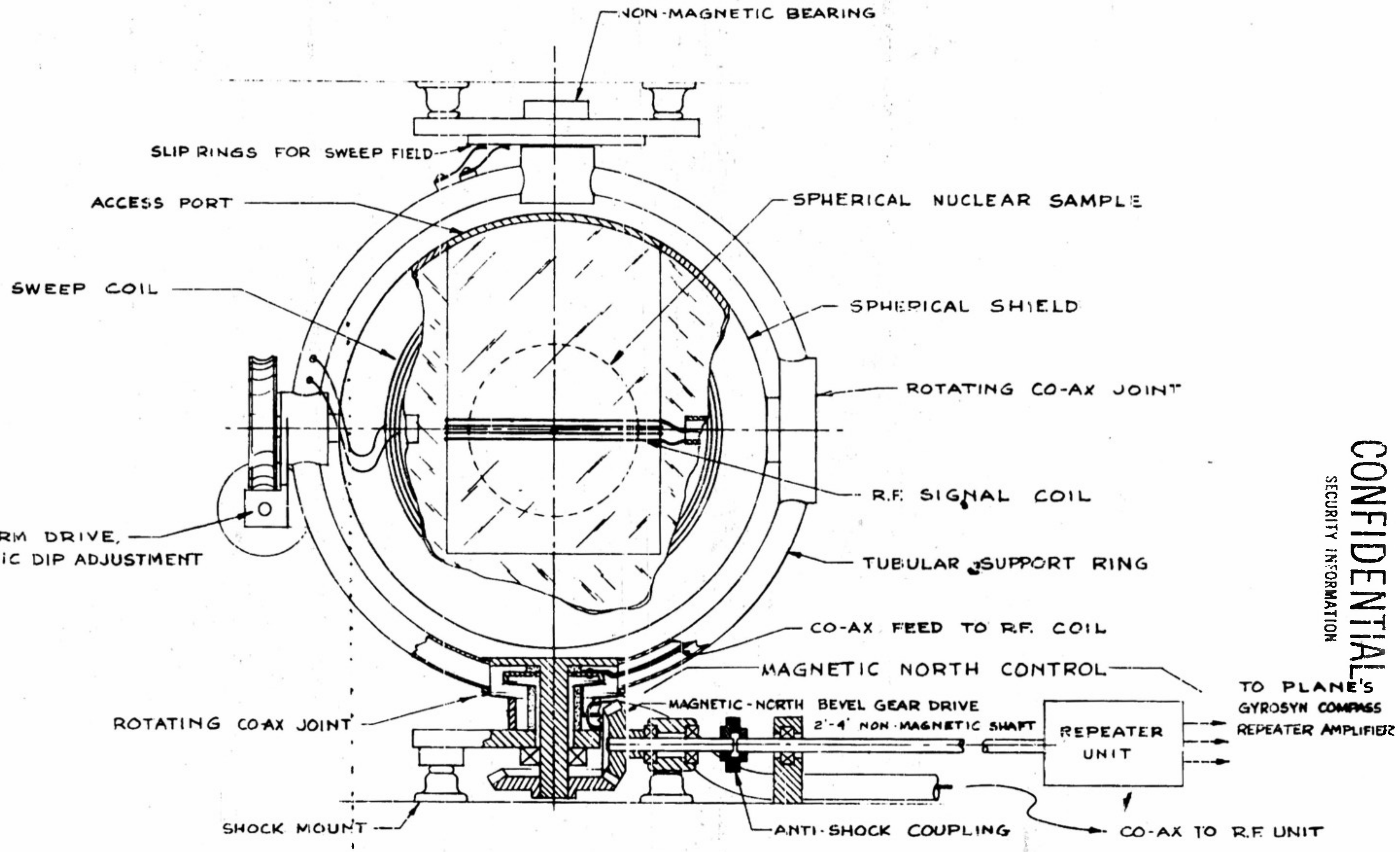


FIGURE NO. 9-7
SYSTEM NO. 3



NOTE:
EARTH'S FIELD NORMAL TO PAPER

FIGURE NO. 9-8

SINGLE-COIL PROBE ASSEMBLY

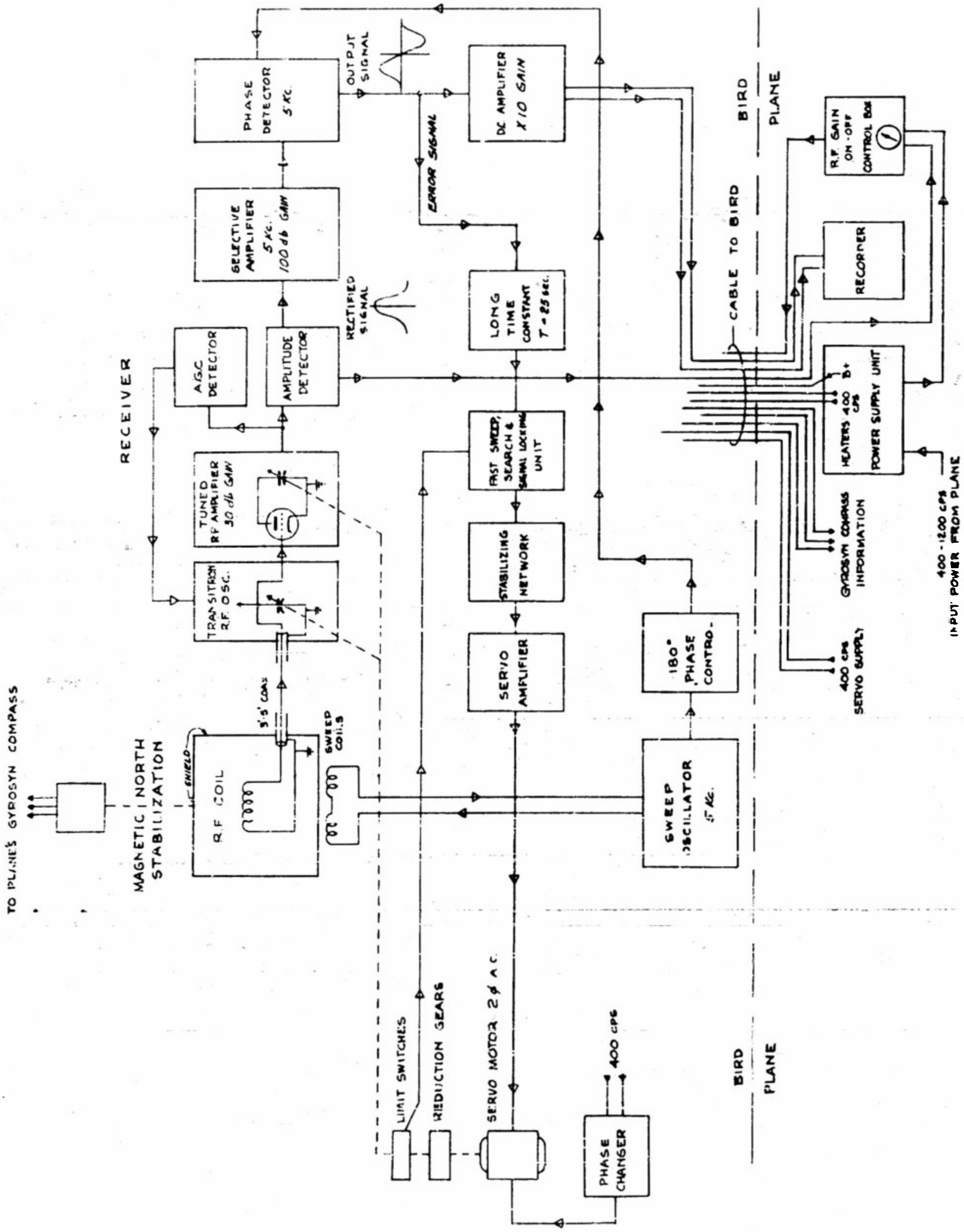


FIGURE NO. 9-9
SYSTEM NO. 4

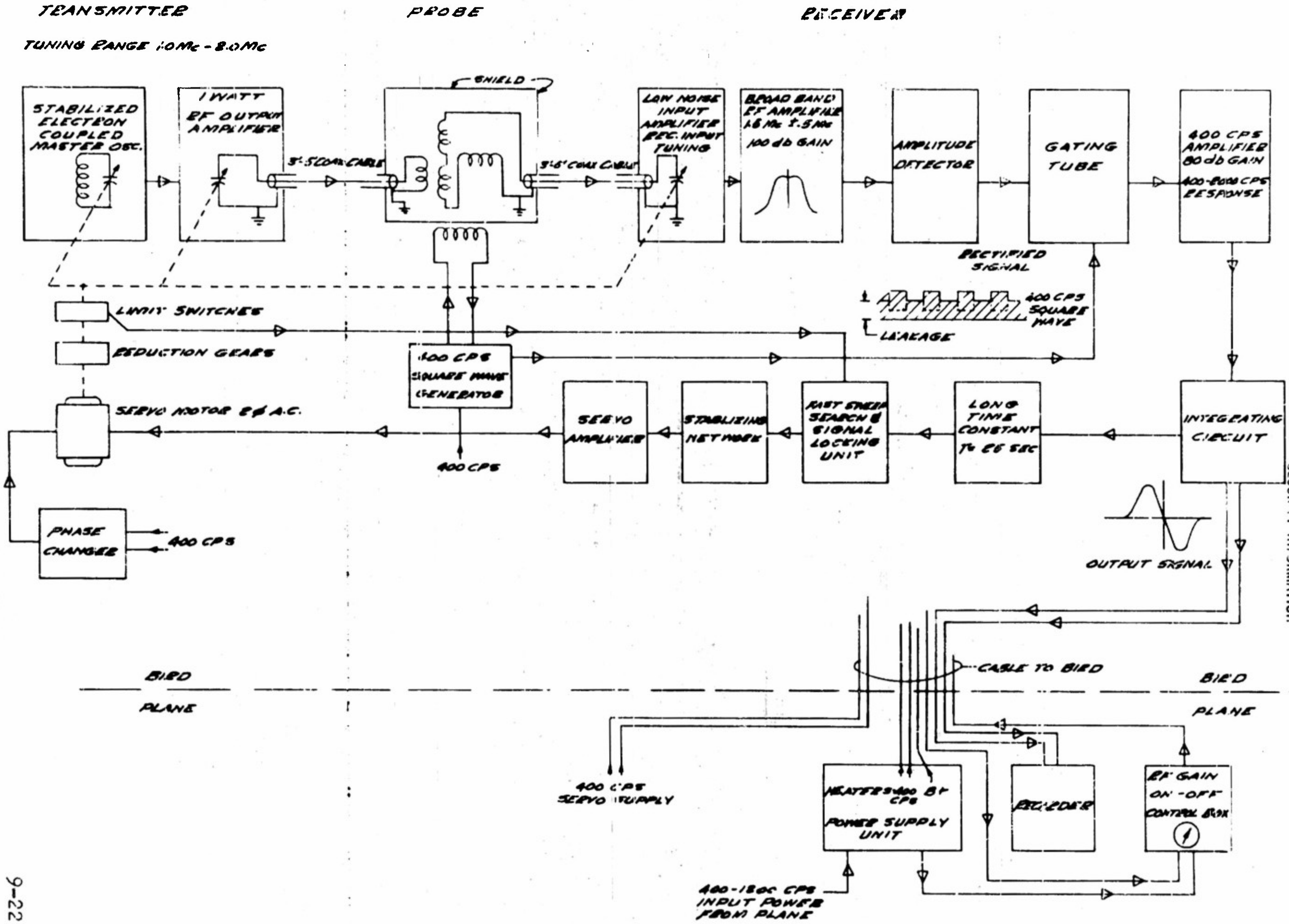


FIGURE NO. 9-10

SYSTEM NO. 5

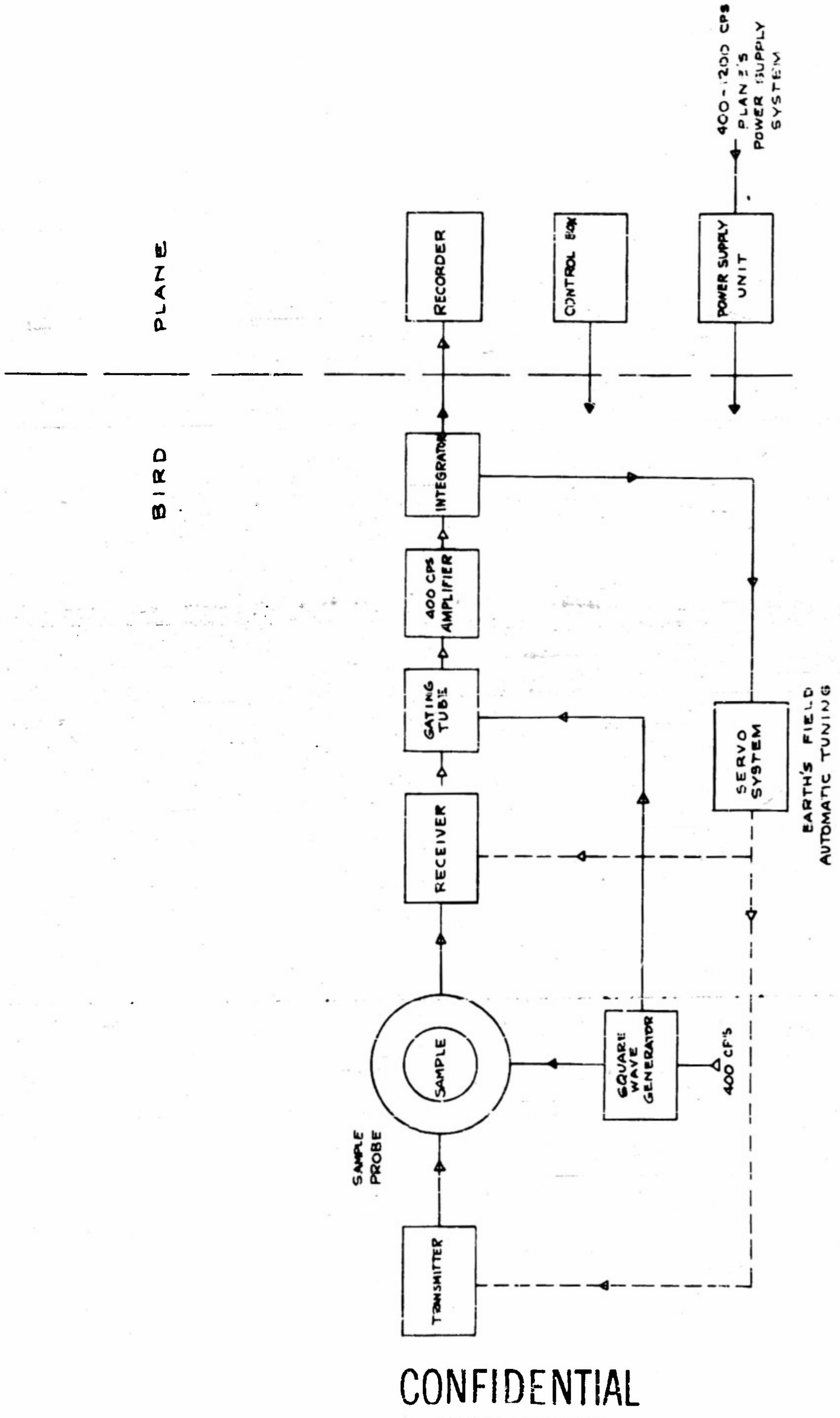


FIGURE NO. 9-11
SYSTEM NO. 5, SIMPLIFIED

10. Summary and Conclusions

A theoretical investigation has been made of the effects of line shape, sensitivity of apparatus, geometry, and the chemical and physical properties of the sample. Out of all these considerations we always come to the conclusion that it is desirable to use a paramagnetic substance in which the line width is narrow. Specifically the advantages of a narrow line width are as follows:

1. Symmetry of the line shape about resonance.

2. The strength of the RF required to produce the resonance is approximately equal to the line width expressed in units of magnetic field. Thus, narrow line widths imply less electronic equipment and less power for producing the r-f field.

3. Perturbations on the shape of the line due to geometric effects (i.e., motion of the probe relative to the earth's field) are generally proportional to the line width. Thus, narrower line widths imply smaller perturbations for a given effect.

4. If magnetic sweep modulation is used, a perturbation is produced which is proportional to the square of the sweep field amplitude. Since a sweep field amplitude must be of the same order of magnitude as the line width, a narrow line width again reduces the effect of this perturbation.

5. Other factors being equal, the sensitivity of an apparatus employing paramagnetic resonance is inversely proportional to the line

width. In general, smaller samples can be used with narrow line widths to achieve the same sensitivity.

The only possible disadvantage of a narrow line width is that it sets an upper limit to the modulation frequency of whatever type of modulation is used. These upper limits are very high even for the narrowest line widths known at the present time.

Among the various substances now known to have narrow line widths, the solutions of alkali metals in ammonia have the following advantages:

1. A line width, an order of magnitude narrower than that found in any other substance.

2. Being in liquid form, they are isotropic and can be molded to any shape.

3. They are relatively easy to manufacture.

The disadvantages are as follows:

1. They must be operated at high pressures.

2. They are perishable.

The first advantage outweighs all the disadvantages however.

A study has been made as to the relative merits of cross-coil and single-coil systems, particularly insofar as changes in direction introduce perturbations on the resonance signal. It has been found that the use of a simple cross-coil probe is impractical because of very serious directional effects. These effects may be minimized by the use of two cross-coil systems in series. In single-coil systems the directional effects are not serious and are primarily changes in sensitivity of the apparatus. The effect of changes in sensitivity can be minimized by designing the apparatus so that it always operates near a null region of the operating characteristic produced by the paramagnetic resonance. The use of such an operating characteristic has an additional advantage in that, used in this way, it provides an error signal which can be employed by the apparatus to correct for slow drifts in the earth's magnetic field or in the electronic constants of the apparatus.

A single-coil system employing one sample requires a moderate amount of stabilization in the earth's field so as to keep changes in sensitivity below a certain limit. The amount of stabilization required is only of the order of magnitude that can be provided by coupling with the airplane's magnetic compass. It is possible by employing three samples to devise an apparatus which is completely insensitive to the direction of the earth's field.

A study has been made of the various electronic systems which can be used with paramagnetic resonance. It is concluded that systems employing a separate transmitter and receiver circuit have the following advantages:

1. Ease and reliability of operation.
2. The circuits are all of conventional nature.

The chief disadvantage is a very stringent requirement on the stability of the phase reference signal.

Circuits of the oscillating detector type have the advantage of simplicity and of requiring no phase reference adjustment. They have the following disadvantages:

1. Relatively high noise levels.
2. Difficulty of adjustment for optimum operating conditions.
3. Unpredictability of this adjustment.
4. Dependence on operating characteristics of specific vacuum tubes.
5. Susceptibility to microphonics and vibration.

A comparison is made in Section 9 of several electronic systems in detail without recommendation at the present time as to which is likely to be superior to the others.

We conclude, therefore, that a magnetic air-borne detector employing paramagnetic resonance can be designed so as to detect changes in the earth's field of the order of 0.1 gamma and be insensitive to changes in orientation with respect to the direction of the field, provided the following conditions can be met:

1. If it is possible to manufacture samples, 100 cc or more in volume consisting of solutions of metal-in-ammonia, that have line widths of the order of 3000 gammas, have low electrical conductivity and long life, and are designed to withstand the internal pressure of the liquid ammonia.

2. If it is possible to either

a) design a two-coil probe such that the short-time phase stability of the leakage is 15 seconds of arc or less; or

b) design an oscillating detector circuit which is simple to adjust, is reliable in operation, whose sensitivity is not dependent on the characteristics of any individual vacuum tube, and which has a noise figure as low as that of a cross-coil system at the optimum r-f field level.

The problem of the design of such a system would be considerably simplified if a sample substance could be found with a line width as narrow or narrower than that of the metal-ammonia solutions and with considerably more suitable physical properties.

The design of an apparatus to detect changes of the order of 0.01 gamma or less does not appear practical at the present time, unless it can be considered practical to have several metal-ammonia samples each approximately a liter in volume. Such a system would be immediately practical, however, if a paramagnetic substance could be found with a line width approximately 1/10 that of the metal-ammonia solutions.

There appears to be no advantage in designing paramagnetic resonance systems biased so as to operate in the microwave region for field-magnitude systems. Differential systems (gradiometers) may be designed employing bias fields and microwave frequencies, but their design requires a different approach from the one used in this study.

APPENDIX A

Directional and Amplitude Effects

We wish to set up a general formalism that can be used for the discussion of effects arising from a finite r-f field strength and a variation in direction of the earth's field. The magnetization is assumed to follow the modified Bloch equation (2-2).

$$\dot{\vec{M}} + \frac{\vec{M} - \chi_0 \vec{H}}{\tau} = (\vec{M} \times \vec{H}) \quad . \qquad \text{(A-1)}$$

It will be convenient to talk not of M directly, but of its departure from the static value, given by the vector

$$\vec{P} \equiv \vec{M} - \chi_0 \vec{H} \qquad \text{(A-2)}$$

which satisfies the equation

$$\dot{\vec{P}} + \frac{\vec{P}}{\tau} = \gamma(\vec{P} \times \vec{H}) - \chi_0 \dot{\vec{H}} \quad . \qquad \text{(A-3)}$$

We investigate this for the case where there is a steady field H_0 in the direction of the unit vector $\vec{n}$, plus an alternating field in the x - direction, of magnitude $2H_1 \cos \omega t$. If we define

$$\omega_0 \equiv \gamma H_0 \quad , \qquad \omega_1 \equiv \gamma H_1 \qquad \text{(A-4)}$$

then the magnetic field is specified by

$$\gamma H_x = \omega_c n_x + 2\omega_1 \cos\omega t$$

$$\gamma H_y = \omega_o n_y \qquad (A-5)$$

$$\gamma H_2 = \omega_o n_z$$

and (3), written out in component form, is

$$\dot{P}_x + \frac{P_x}{\tau} = \omega_o(P_y n_z - P_z n_y) + 2\chi_o \omega H_1 \sin\omega t$$

$$\dot{P}_y + \frac{P_y}{\tau} = \omega_o(P_z n_x - P_x n_z) + 2\omega_1 P_z \cos\omega t \qquad (A-6)$$

$$\dot{P}_z + \frac{P_z}{\tau} = \omega_o(P_x n_y - P_y n_x) - 2\omega_1 P_y \cos\omega t$$

We are interested only in the steady-state solution, which will have the form

$$P_x = \sum_{n=-\infty}^{\infty} P_{nx}\, e^{in\omega t}$$

$$P_y = \sum_{n=-\infty}^{\infty} P_{ny}\, e^{in\omega t} \qquad (A-7)$$

$$P_z = \sum_{n=-\infty}^{\infty} P_{nz}\, e^{in\omega t}$$

Since each component of P is real, we have $P_{-ny} = P_{ny}^{*}$, etc. The equations of motion now become

$$\sum_n \left[\left(\frac{1}{\tau} + in\omega \right) P_{nx} + \omega_0 (n_y P_{nz} - n_z P_{ny}) \right] e^{in\omega t}$$

$$= i \chi_0 \omega H_1 (e^{-i\omega t} - e^{i\omega t}) \qquad \text{(A-8a)}$$

$$\sum_n \left[\left(\frac{1}{\tau} + in\omega \right) P_{ny} + \omega_0 (n_z P_{nx} - n_x P_{nz}) \right] e^{in\omega t}$$

$$= \omega_1 \sum_n P_{nz} \left[e^{i(n+1)\omega t} + e^{i(n-1)\omega t} \right] \qquad \text{(A-8b)}$$

$$\sum_n \left[\left(\frac{1}{\tau} + in\omega \right) P_{nz} + \omega_0 (n_x P_{ny} - n_y P_{nx}) \right] e^{in\omega t}$$

$$= -\omega_1 \sum_n P_{ny} \left[e^{i(n+1)\omega t} + e^{i(n-1)\omega t} \right] \qquad \text{(A-8c)}$$

Since these must be identities in t, we can equate terms of like frequencies, giving as the fundamental equations,

$$\left(\frac{1}{\tau} + in\omega \right) P_{nx} - \omega_0 n_z P_{ny} + \omega_0 n_y P_{nz} = i \chi_0 \omega H_1 (\delta_{n,-1} - \delta_{n,1})$$

$$\omega_0 n_z P_{nx} + \left(\frac{1}{\tau} + in\omega \right) P_{ny} - \omega_0 n_x P_{nz} = \omega_1 (P_{n-1,z} + P_{n+1,z}) \qquad \text{(A-9)}$$

$$-\omega_0 n_y P_{nx} + \omega_0 n_x P_{ny} + \left(\frac{1}{\tau} + in\omega \right) P_{nz} = -\omega_1 (P_{n-1,y} + P_{n+1,y})$$

or, in matrix form,

$$\begin{pmatrix} (\frac{1}{T} + in\omega) & -\omega_0 n_z & \omega_0 n_y \\ \omega_0 n_z & (\frac{1}{T} + in\omega) & -\omega_0 n_x \\ -\omega_0 n_y & \omega_0 n_x & (\frac{1}{T} + in\omega) \end{pmatrix} \begin{pmatrix} P_{nx} \\ P_{ny} \\ P_{nz} \end{pmatrix} = \omega_1 \begin{pmatrix} i\alpha\,\omega(\delta_{n,-1} - \delta_{n,1}) \\ P_{n-1,z} + P_{n+1,z} \\ -P_{n-1,y} - P_{n+1,y} \end{pmatrix} \qquad \text{(A-10)}$$

where

$$\alpha = \frac{\chi_0}{\gamma} \qquad \text{(A-11)}$$

The matrix

$$M_n = \begin{pmatrix} (\frac{1}{T} + in\omega) & -\omega_0 n_z & \omega_0 n_y \\ \omega_0 n_z & (\frac{1}{T} + in\omega) & -\omega_0 n_x \\ -\omega_0 n_y & \omega_0 n_x & (\frac{1}{T} + in\omega) \end{pmatrix} \qquad \text{(A-12)}$$

has the eigenvalues $(\frac{1}{T} + in\omega)$ and $(\frac{1}{T} + in\omega \pm i\omega_0)$, and is diagonalized by a transformation which consists of a rotation of coordinate axes bringing the new z-axis in the direction of $\vec{H}_0$, and using P_z and $(P_x \pm iP_y)$ as the variables in the new coordinate system.

We must now adopt a condensed notation in order to be able to survey the problem as a whole. If we define an additional vector P_n and a matrix N as

$$P_n \equiv \begin{pmatrix} P_{nx} \\ P_{ny} \\ P_{nz} \end{pmatrix}, \qquad N \equiv \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \tag{A-13}$$

then (10) can be written as

$$M_n P_n = \omega_1 N(P_{n+1} + P_{n-1}) + i\alpha\omega\omega_1 \begin{pmatrix} \delta_{n,-1} - \delta_{n,1} \\ 0 \\ 0 \end{pmatrix} \tag{A-10'}$$

which in turn can be written as a linear system in an infinite number of unknowns by introducing the super-matrices

$$M \equiv \begin{pmatrix} \ddots & & & & & & \\ & M_{-2} & & & & & \\ & & M_{-1} & & & & \\ & & & M_0 & & & \\ & & & & M_1 & & \\ & & & & & M_2 & \\ & & & & & & \ddots \end{pmatrix} \tag{A-14}$$

$$N \equiv \begin{pmatrix} \ddots & & & & & & \\ N & O & N & & & & \\ & N & O & N & & & \\ & & N & O & N & & \\ & & & N & O & N & \\ & & & & N & O & N \\ & & & & & & \ddots \end{pmatrix} \qquad \text{(A-15)}$$

and the super-vectors

$$P \equiv \begin{pmatrix} \vdots \\ P_{-2} \\ P_{-1} \\ P_o \\ P_1 \\ P_2 \\ \vdots \end{pmatrix} \qquad Q \equiv \begin{pmatrix} \vdots \\ O \\ O \\ +Q \\ O \\ -Q \\ O \\ O \\ \vdots \end{pmatrix}$$

where

$$Q \equiv \begin{pmatrix} i \propto \omega \\ 0 \\ 0 \end{pmatrix}$$

The entire system of equations now takes the form

$$\left(\mathbf{M} - \omega_1 \mathbf{N}\right) \mathbf{P} = \omega_1 \mathbf{Q} \qquad \text{(A-10'')}$$

and if we could diagonalize the matrix ($\mathbf{M} - \omega_1 \mathbf{N}$) we would have the exact solution. Actually, it is easy to diagonalize $\mathbf{M}$ along the lines mentioned for diagonalizing M_n. This doesn't help any as far as the exact solution is concerned because the transformation that diagonalizes $\mathbf{M}$ complicates $\mathbf{N}$ considerably. However, if we want approximate solutions for small ω_1 (weak r-f driving field), we can set up a perturbation problem in which diagonalization of $\mathbf{M}$ is useful.

Let us take ω_1 as the perturbation parameter, and find a solution in the form

$$\mathbf{P} = \mathbf{P}^{(0)} + \omega_1 \mathbf{P}^{(1)} + \omega_1^2 \mathbf{P}^{(2)} + \ldots \qquad \text{(A-17)}$$

Substituting into (10") we get the system of equations

$$\mathbf{MP}^{(0)} = 0$$

$$\mathbf{MP}^{(1)} - \mathbf{NP}^{(0)} = \mathbf{Q}$$

$$\mathbf{MP}^{(2)} - \mathbf{NP}^{(1)} = 0$$

$$\mathbf{MP}^{(3)} - \mathbf{NP}^{(2)} = 0$$

-------------, etc.,

or,

$$P^{(0)} = 0$$

$$P^{(1)} = M^{-1} Q$$

$$P^{(2)} = M^{-1} NP^{(1)} = M^{-1} NM^{-1} Q$$

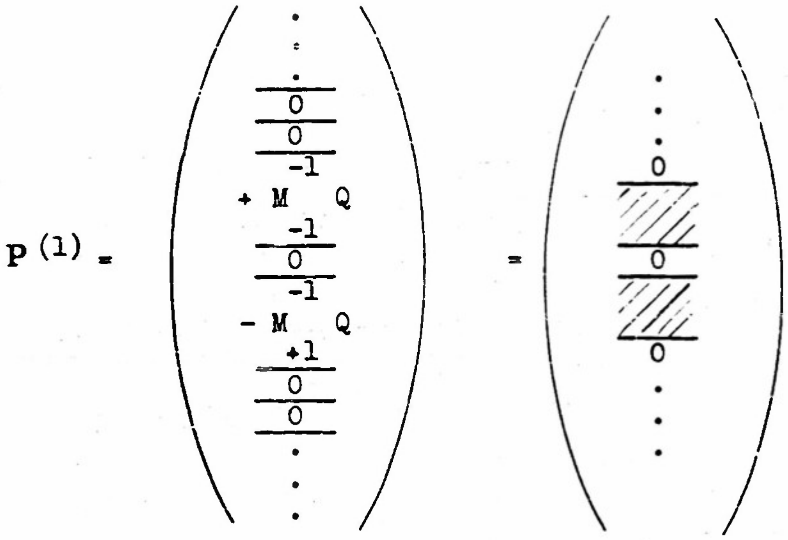
$$P^{(3)} = M^{-1} NM^{-1} NM^{-1} Q \qquad \text{(A-18)}$$

-----------, etc.

Note that, by definition, $\omega_1 P^{(1)}$ is that part of the polarization proportional to the first power of the amplitude of the r-f driving field, $\omega_1^2 P^{(2)}$ the part proportional to the 2nd power, etc. Now let us find which frequencies are contained in the terms of various orders. Since M^{-1} has the box structure

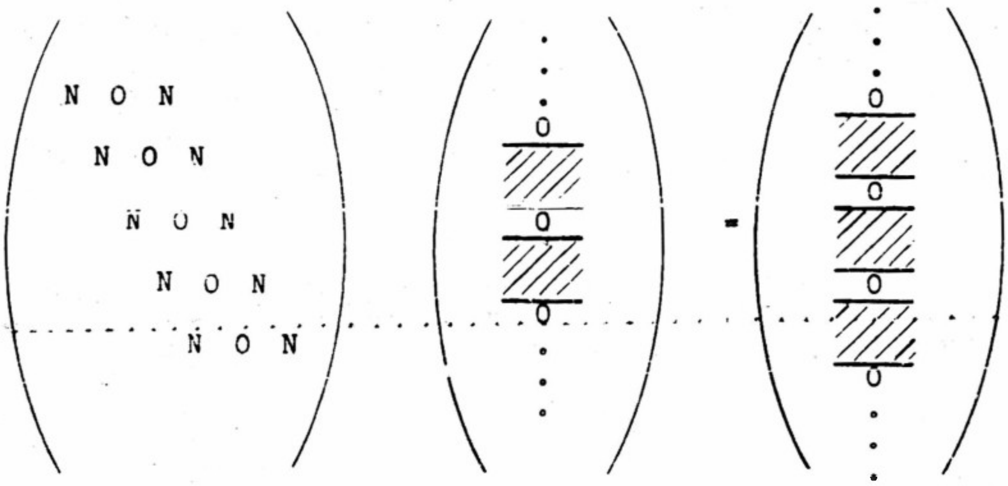
$$M^{-1} = \begin{pmatrix} M_{-2}^{-1} & & & & \\ & M_{-1}^{-1} & & & \\ & & M_0^{-1} & & \\ & & & M_1^{-1} & \\ & & & & M_2^{-1} \end{pmatrix} \qquad \text{(A-19)}$$

we see that



(A-20)

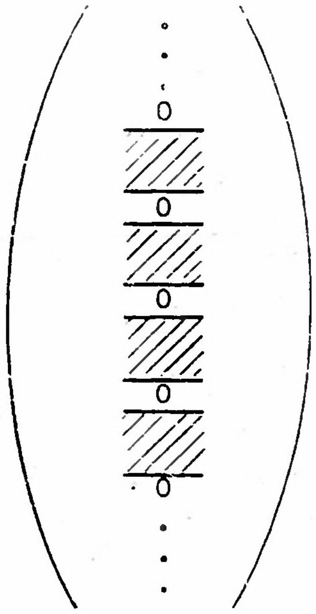
where the shading represents non-zero terms, and $P^{(1)}$ contains only terms of frequencies ± ω. $P^{(2)}$, however, will have the same box structure as $NP^{(1)}$, which is



(A-21)

and $P^{(2)}$ contains only "d-c" terms and second harmonic terms of frequency ± 2 ω. Similarly, $P^{(3)}$ has the same distribution of zeroes as $NP^{(2)}$, or

$P^{(3)} =$



(A-22)

which contains only terms of frequency $\pm \omega$ and $\pm 3\omega$. If our circuits are designed to detect only components of frequency $\pm \omega$, only $P^{(1)}$, $P^{(3)}$, $P^{(5)}$, ... will contribute to circuit operation; and if we consider terms through the second order approximation, $\omega_1 P^{(1)} + \omega_1^2 P^{(2)}$, to give a sufficiently accurate description of the system (which is undoubtedly the case if $2H_1 << H_0$), then we need calculate only $P^{(1)}$, and we are neglecting only terms proportional to third and higher harmonics of the driving frequency.

Directional Effects for Weak R-F Fields

The problem is reduced by the above considerations to the calculation of M^{-1}. We do this for the case that $n_y = 0$, i.e., the steady field H_0 lies in the xz-plane. Let the angle between H_0 and the z-axis be θ. Then $n_z = \cos \theta = C$, $n_x = \sin \theta = S$, and the unitary matrix

$$U = \begin{pmatrix} S & -\frac{1}{\sqrt{2}}C & -\frac{1}{\sqrt{2}}C \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ C & \frac{1}{\sqrt{2}}S & \frac{1}{\sqrt{2}}S \end{pmatrix} \qquad \text{(A-23)}$$

diagonalizes M_n: (A-24)

$$\Lambda_n = U^{-1} M_n U = \begin{pmatrix} (\frac{1}{T} + in\omega) & 0 & 0 \\ 0 & \left[\frac{1}{T} + i(n\omega + \omega_o)\right] & 0 \\ 0 & 0 & \left[\frac{1}{T} + i(n\omega - \omega_o)\right] \end{pmatrix}$$

Therefore,

$$M_n^{-1} = U \Lambda_n^{-1} U^{-1} \qquad \text{(A-25)}$$

and the desired part of the solution is

$$P_1^{(1)} = -U \Lambda_1^{-1} U^{-1} Q \qquad \text{(A-26)}$$

. . . .

The different steps of the calculation are as follows:

$$U^{-1}\,Q = \begin{pmatrix} S & 0 & C \\ -\frac{C}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & \frac{S}{\sqrt{2}} \\ -\frac{C}{\sqrt{2}} & \frac{i}{\sqrt{2}} & \frac{S}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} i\,\alpha\,\omega \\ 0 \\ 0 \end{pmatrix} = i\,\alpha\,\omega \begin{pmatrix} S \\ -\frac{C}{\sqrt{2}} \\ -\frac{C}{\sqrt{2}} \end{pmatrix}$$

$$\Lambda_1^{-1}\,U^{-1}\,Q = i\alpha\omega \begin{pmatrix} \dfrac{S}{\frac{1}{T} + i\omega} \\[2ex] \dfrac{-C}{\sqrt{2}\left[\frac{1}{T} + i(\omega + \omega_o)\right]} \\[2ex] \dfrac{-C}{\sqrt{2}\left[\frac{1}{T} + i(\omega - \omega_o)\right]} \end{pmatrix}$$

$$U\,\Lambda_1^{-1}\,U^{-1}\,Q = i\alpha\omega \begin{pmatrix} S & -\frac{C}{\sqrt{2}} & -\frac{C}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ C & \frac{S}{\sqrt{2}} & \frac{S}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \dfrac{S}{\frac{1}{T} + i\omega} \\[2ex] \dfrac{-C}{\sqrt{2}\left[\frac{1}{T} + i(\omega + \omega_o)\right]} \\[2ex] \dfrac{-C}{\sqrt{2}\left[\frac{1}{T} + i(\omega - \omega_o)\right]} \end{pmatrix}$$

$$= i\alpha\omega \begin{pmatrix} \dfrac{S^2}{\frac{1}{T} + i\omega} + \dfrac{C^2}{2}\left[\dfrac{1}{\frac{1}{T} + i(\omega + \omega_o)} + \dfrac{1}{\frac{1}{T} + i(\omega - \omega_o)}\right] \\ -\dfrac{iC}{2}\left[\dfrac{1}{\frac{1}{T} + i(\omega + \omega_o)} - \dfrac{1}{\frac{1}{T} + i(\omega - \omega_o)}\right] \\ \dfrac{CS}{\frac{1}{T} + i\omega} - \dfrac{CS}{2}\left[\dfrac{1}{\frac{1}{T} + i(\omega + \omega_o)} + \dfrac{1}{\frac{1}{T} + i(\omega - \omega_o)}\right] \end{pmatrix}$$

The first-order solution is therefore

$$P_{1x} = -i\omega\chi_o H_1 \left\{ \frac{\sin^2\theta}{\frac{1}{T} + i\omega} + \frac{\cos^2\theta}{2}\left[\frac{1}{\frac{1}{T} + i(\omega + \omega_o)} + \frac{1}{\frac{1}{T} + i(\omega - \omega_o)}\right] \right\} \qquad \text{(A-27a)}$$

$$P_{1y} = -\frac{\omega\chi_o H_1 \cos\theta}{2}\left[\frac{1}{\frac{1}{T} + i(\omega + \omega_o)} - \frac{1}{\frac{1}{T} + i(\omega - \omega_o)}\right] \qquad \text{(A-27b)}$$

$$P_{1z} = -\frac{i\omega\chi_o H_1 \sin\theta\cos\theta}{2}\left[\frac{2}{\frac{1}{T} + i\omega} - \frac{1}{\frac{1}{T} + i(\omega + \omega_o)} - \frac{1}{\frac{1}{T} + i(\omega - \omega_o)}\right] \qquad \text{(A-27c)}$$

from which directional effects in single-coil and cross-coil systems can be found. Equations (27a) and (27b) can be reduced to equation (2-6) for special case $\theta = 0$. In the case of a single-coil system, everything is determined by the effective susceptibility of the sample (remember that $M = P + \chi_0 H$):

$$\chi = \chi_0 \left\{ 1 - \frac{i\omega \sin^2\theta}{\frac{1}{T} + i\omega} - \frac{i\omega \cos^2\theta}{2} \left[\frac{1}{\frac{1}{T} + i(\omega + \omega_0)} + \frac{1}{\frac{1}{T} + i(\omega - \omega_0)} \right] \right\}$$

(A-28)

The power absorbed is proportional to the negative imaginary part of χ:

$$\text{Absorbed Power} \sim \chi_0 \left\{ \frac{\omega T}{1 + \omega^2 T^2} \sin^2\theta + \frac{\omega T \left[1 + (\omega_0^2 + \omega^2) T^2 \right]}{4\omega^2 T^2 + \left[1 + (\omega_0^2 - \omega^2) T^2 \right]^2} \cos^2\theta \right\}$$

(A-29)

APPENDIX B

GLOSSARY OF SYMBOLS

a	$(\omega_0 - \omega)/(\gamma\lambda)$
b	H_s/λ
d	Diameter of coil
h	Height of coil
h	Planck's constant
$\hbar$	Planck's constant divided by 2π
H_b	Biasing field
H_r	Receiver-coil field
H_t	Transmitter-coil field
H_o	Steady magnetic field
H_1	Half the magnitude of the r-f field
I	Spin of electron in units of $\hbar$
k	Boltzmann's constant
M	Macroscopic magnetic moment
N	Number of turns in the coil
N_o	Number per unit volume
Q	Q of coil or of tuned circuit
R	Resistance
T	Temperature
u	Dispersion component of magnetic field
v	Absorption component of magnetic field
V	Voltage

GLOSSARY OF SYMBOLS (CONT.)

V_s	Signal voltage
V_n	Noise voltage
α	Angle between earth's field and axis of coil
γ	Absolute value of gyromagnetic ratio; for electron, $\gamma = 2\pi \times 2.8$ mc/gauss
Γ	Unit of magnetic field strength; 1 gamma = 10^{-5} gauss
θ	Angle of tilt between earth's field and biasing field; $\cos^2\theta = \sin^2\alpha$
λ	Line width
μ	Magnetic moment of the electron
ν	Frequency
$\Delta\nu$	Bandwidth
ξ	Phase shift between induced signal and driving field; $\tan\xi = \sin\theta\tan\psi$
τ	Relaxation time
χ	Susceptibility
χ_o	Static susceptibility
ϕ	Longitudinal angle of tilt
ω	Angular frequency
ω_o	Resonance angular frequency (Larmor frequency); $\omega_o = \gamma H_o$
ω_1	Angular frequency corresponding to the r-f field; $\omega_1 = \gamma H_1$
ψ	Angle between H_r and y-axis where the y-axis is defined as being at right angles to H_o and H_t (See Figure 4-11)
Ω	Volume of sample

BIBLIOGRAPHY

1. Bloembergen, Purcell and Pound, Phys. Rev. 73, 679, (1948)

2. Bloch, Hansen and Packard, Phys. Rev. 70, 474, (1946)

3. F. Bloch, Phys. Rev. 70, 460, (1946)

4. R. K. Wangsness and F. Bloch, Phys. Rev. 89, 728 (1953)

5. J. H. Van Vleck and V. Weisskopf, Rev. Mod. Phys. 17, 227, (1945)

6. J. H. Van Vleck, Phys. Rev. 74, 1168, (1948)

   P. Anderson and P. Weiss, Rev. Mod. Phys. 25, 269, (1953)

7. N. Bloembergen, J. App. Phys. 23, 1383, (1952)

8. R. Karplus and J. Schwinger, Phys. Rev. 73, 1020, (1948)

9. F. Bloch and A. Siegert, Phys. Rev. 57, 522, (1940)

10. M. E. Packard, Thesis, Stanford University. See also references (2) and (3).

11. Holden, Kittel, Merritt and Yager, Phys. Rev. 77, 147 (1950)

12. C. A. Hutchison, Jr., and R. C. Pastor, Rev. Mod. Phys. 25, 285, (1953)

    C. A. Hutchison, Jr.; H. C. Torrey; and others:

    Report to the Paramagnetic Resonance Information Meeting (ONR), October 30, 1952, Washington University, St. Louis, Missouri (Mimeographed notes).

13. G. E. Pake, S. I. Weissman and others:

    Washington University, St. Louis, Missouri, "Paramagnetic Resonance of Free Radicals" (1st progress report under ONR Contract N6onr-20205 in the Departments of Physics and Chemistry).

14. C. A. Kraus, J. Am. Chem. Soc. 43, 755, (1921)

    (We are indebted to Dr. Hutchison for pointing out this reference.)

BIBLIOGRAPHY (CONT.)

15. Handbook of Chemistry and Physics, (29th ed. p. 1840)

16. H. E. Weaver, Jr., Phys. Rev. <u>89</u>, 923, (1953)

17. Waring, Spencer and Custer, Rev. Sci. Inst. <u>23</u>, 497, (1952)

18. R. V. Pound and W. D. Knight, Rev. Sci. Inst. <u>21</u>, 219, (1950)

19. H. W. Knoebel and E. L. Hahn, Rev. Sci. Inst. <u>22</u>, 904, (1951)

20. R. Karplus, Phys. Rev. <u>73</u>, 1027 (1948)