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AN INVESTIGATION OF
THE USE OF NUCLEAR MAGNETIC RESONANCE
TO DETERMINE MOISTURE CONTENT IN SOILS

A Thesis

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DEGREE OF MASTER OF SCIENCE
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This thesis of Nagalapur Sastry Haraprasad for the Master's degree,
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Moisture Content in Soils,"

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This Thesis Is Dedicated

TO MY MOTHER

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ABSTRACT

Nuclear Magnetic Resonance absorption appears as an interesting and useful technique for the study of nuclear secrets. The major objective of this study was to investigate the application of Nuclear Magnetic Resonance to determine the moisture content in soils. The Nuclear Magnetic Resonance apparatus built appeared to function normally but gave rise to inconsistent results. However, studies of soil moisture determination was continued in the Varian A-60 process analyzer of the physical science department. Fundamental defects in N.M.R. as a method are discussed.

CHAPTER I

HISTORICAL BACKGROUND

Historically, the first Nuclear Magnetic Resonance (hereafter abbreviated as N.M.R.) signals were observed during the late fall of 1945, in two independent physics laboratories located 3,000 miles apart on the American continent. Co-discoverers Edward M. Purcell at Harvard and Felix Bloch at Stanford announced almost simultaneously this interesting discovery in physics. They had found a way to "tune in" on the magnetic fields of spinning nuclei of atoms. The work was so important that in 1952 both Purcell and Bloch shared the Nobel Prize in Physics.

Some time ago Professor J. I. Hagen of the Electrical Engineering Department of the University of Idaho suggested to the writer that the phenomenon of N.M.R. should be explored as a means of measuring the moisture content of soils. The resonance could be tuned to the protons of the hydrogen nuclei of the sample and an external radio frequency field in such a manner that the number of hydrogen nuclei could be observed. A survey of the literature revealed that this could indeed be accomplished, and that the idea had been used to measure the moisture content of certain materials, such as dried potatoes, candies,¹ corn syrup, and various other dehydrated commodities.²

Of notable commercial interest is the Varian A-60 process analyzer which can be used to determine the moisture content of a

sample of almost anything to an accuracy of about 1 percent in a time of about 30 seconds. Equipment systems of a similar type are built by other companies, but the point to be noted here is that such systems are available at a minimum nominal cost of about \$17,000. The Varian A-60 uses an electro-magnet which weighs about 580 pounds with a magnetic field intensity of 14,092 gauss. The magnet has 10-inch diameter pole faces and a 3/8-inch air gap. This provides a sufficiently homogeneous field strength over a sample volume of 40 cc. such that broadline N.M.R. analyses can be made for that size volume.

A semi-technical article³ was noted, wherein very simple components were used to observe N.M.R. in water. It was felt that this approach could be examined as having potential for the soil moisture measurement. This apparatus in particular suggested the use of surplus magnetron magnets. If, indeed, this should prove to be workable for the purpose, it was seen that the apparatus could be small enough to be installed below ground, by utilizing weather-proof construction, etc. An alternate procedure might be almost as convenient for some applications wherein some samples of the soil might be handled with portable apparatus above ground.

It may be a point of interest to note here that all the work so far mentioned in the literature has been done with an actual N.M.R. analyzer (like the one maintained by the Chemistry Department at the University of Idaho). However, it was felt that a smaller, simpler system could be built using a magnetron magnet of perhaps 50 to 100 pounds weight that would analyze 5 cc. of material to an accuracy

of 2 to 3 percent. Such an instrument would be invaluable in the analysis of soil moisture where extreme accuracy is not nearly as important as reliability and repeatability of measurement. Such a system would have decided advantages over conventional electrical resistance methods of moisture analysis or the neutron scattering methods where a limited radiation hazard can be expected. The significant advantages of the N.M.R. approach are:

- (i) Speed—The time required for moisture determination ranges from 30 to 90 seconds. Furthermore, a projected modification of the analyzer to a "direct reading" system will substantially cut this time.
- (ii) Non-Destructive Technique—Samples may be retained for subsequent analysis.
- (iii) Minimum Sample Preparation—Almost all samples may be examined on an "as is" basis.
- (iv) Versatility—The method has been successfully applied to products routinely checked by vacuum-drying, azeotropic distillation, refractive index, and conductivity.
- (v) Flexibility—The method is completely independent of variables such as temperature, salinity, and the physical constants of the material being tested, except as noted later in this thesis.

In general N.M.R. has proven of great value in the study of atomic and nuclear structure. Today, chemists, geophysicists, electrical engineers, applied physicists, and biologists use N.M.R. in one or another of its forms.

CHAPTER II

INTRODUCTION AND THEORETICAL BACKGROUND

First of all, a review of the classical theory given in terms of the motion of a top and analogies to the proton situation in a steady magnetic field can be found and the nature of precession can be seen. In the more exact theory, resort must be made to quantum theory.

All matter is made up of atoms and molecules. The Rutherford's atomic model can be used which consists of a central positive nucleus surrounded by electrons in various orbits. The electron (charge) moves around the nucleus in a closed loop. Charge in motion constitutes a current. The conventional direction of the current is opposite to the direction in which the electron travels, as indicated in Figure 1. Thus, an electron in an orbit is analogous to a small current loop and as such experiences a torque in an external magnetic field. The torque tends to align the magnetic field produced by the orbiting electron with the external magnetic field. Since the magnetic field of the electron then adds to the external field, this simple picture would lead to the belief that the external magnetic field is always greater than it would be without the material present. This is true only in some cases, as a second motion of the electrons must be taken into account, i.e., electron spin.

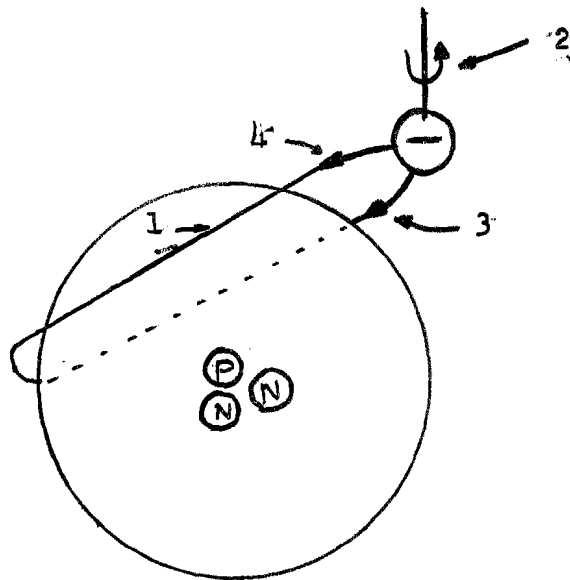


Figure 1.

Motion of the electron around the nucleus.

1. Orbital current loop.
2. Spin current loop.
3. Direction of current flow.
4. Direction of travel.

The physicists have shown that the electron spins about an axis passing through the electron itself as it orbits about the nucleus. This model is evidently patterned after the motion of a planet such as that of the earth moving about the sun. The spinning electron is

the equivalent to a second current loop, and the torque on this loop must also be considered in the presence of an external magnetic field. It turns out that these effects very nearly cancel each other in most atoms, as in the atoms of the constituents of wood, cotton, and milk of magnesia.

Magnetic Moment and Angular Momentum

If an electron is moving in a circular orbit, there exists a definite ratio between the magnetic moment and the angular momentum:

Let $\vec{\mu}$ represent the magnetic moment and \vec{J} represent the angular momentum of the electrons in orbit.

Then the magnitude of the angular momentum is

$$\vec{J} = mvr \quad (1)$$

and is directed perpendicular to the plane of the orbit,

where m = mass of the orbiting electron

v = velocity of the orbiting electron

r = the radius of the circular orbit.

The magnetic moment of the same orbit equals current times area :

$$\text{or } \vec{\mu} = \left(\frac{q}{t}\right) (\pi r^2) \quad (2)$$

$$\text{But } \frac{q}{t} = (q) (f) = (q) \left(\frac{v}{2\pi r}\right)$$

$$\therefore \vec{\mu} = \left(\frac{q}{t}\right) (\pi r^2) = (q) \left(\frac{v}{2\pi r}\right) (\pi r^2) = \frac{qvr}{2}$$

$$\text{But } \vec{J} = mvr \quad \text{----- from (1)}$$

$$\therefore \bar{\mu} = \left(\frac{q}{2}\right) \left(\frac{\bar{J}}{m}\right) = \left(\frac{q}{2m}\right) (\bar{J}) \text{ ----- (orbital motion)} \quad (3)$$

It is also directed perpendicular to the plane of the orbit. Both \bar{J} and $\bar{\mu}$ will be in the same direction, as shown in Figure 2.

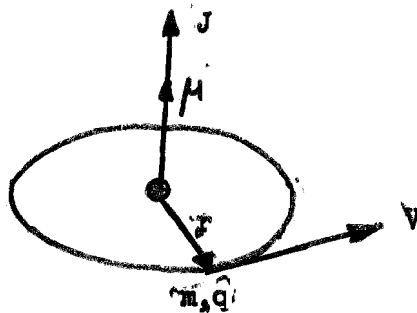


Figure 2.

For any circular orbit the magnetic moment

$\bar{\mu}$ is $\left(\frac{q}{2m}\right)$ times the angular momentum \bar{J} .

For an electron, the charge q is negative. Let it be $-q_e$.

$$\therefore \text{for an electron } \bar{\mu} = \left(\frac{-q_e}{2m}\right) \bar{J} \text{ ----- (electron orbital motion)} \quad (4)$$

This equation is true only for "orbital motion," but that is not the only magnetism that exists. The electron also has a spin (as noted earlier), and as a result of this spin, it has different values of \bar{J} and $\bar{\mu}$. It can be shown by quantum mechanics⁴ that for the "electron spin" the magnetic moment is twice that for orbital motion.

$$\text{i.e., } \bar{\mu} = (2) \left(\frac{-q_e}{2m}\right) (\bar{J}) = \frac{-q_e \bar{J}}{m} \text{ ----- (electron spin motion)} \quad (5)$$

In any atom there are, generally speaking, several electrons and many combinations of spin and orbital rotations which add vectorially to a total angular momentum and a total magnetic moment. But the ratio of the two, i.e., $\frac{\bar{\mu}}{\bar{J}}$, need not be either $(\frac{-q_e}{m})$ or $(\frac{-q_e}{2m})$, but somewhere in between, because there is a mixture of the contributions from the orbits and the spins.

Therefore, it is often written that $\bar{\mu} = g (\frac{-q_e}{2m}) \bar{J}$ where g is known as Lande's splitting factor. This factor is characteristic of the state of the atom. It would be 1 for pure orbital moment, or 2 for pure spin moment, or some other number between 1 and 2 for a complicated system like an atom. With the help of quantum mechanics,⁵ the value of the g -factor can be predicted for any particular atomic state. The above equation tells that the magnetic moment $\bar{\mu}$ is parallel to the angular momentum \bar{J} but can have any magnitude.

This can be extended to the nucleus also. In the nucleus there are protons and neutrons which may move around in some kind of orbit and at the same time, like an electron, have an intrinsic spin. Here again $\bar{\mu}$ is parallel to \bar{J} . Therefore, for the nucleus,

$$\bar{\mu} = g (\frac{+q_e}{2m_p}) \bar{J} \quad (6)$$

where m_p is the mass of the proton and now g is called the "nuclear g -factor," which is a number near 1, to be determined for each nucleus.

Another important difference for a nucleus is that the spin magnetic moment of the proton does not have a g -factor of 2, as the

electron does. For a proton, $g = 2$ (2.79) which has been obtained by the application of quantum mechanics.

The Precession of Atomic Magnets

One of the consequences of having the magnetic moment proportional to the angular momentum is that an atomic magnet placed in a magnetic field will precess. Suppose that the magnetic moment $\vec{\mu}$ is suspended freely in a uniform magnetic field \vec{H}_0 . It will feel a torque $\vec{\tau}$ equal to the cross product of $\vec{\mu}$ and \vec{H}_0 which tries to bring it in line with the field direction. But the atomic magnet is a gyroscope—it has the angular momentum \vec{J} . Therefore, the torque due to the magnetic field will not cause the magnet to line up. Instead, the magnet will precess. The angular momentum and with it the magnetic moment precesses about an axis parallel to the applied external magnetic field as shown in Figure 3. Now, consider Figure 4 which is a detailed reproduction of Figure 3. Suppose that in a small time, Δt , the angular momentum changes from \vec{J} to \vec{J}' , staying always at the same angle θ with respect to the direction of the magnetic field H_0 . Calling ω_p as the angular velocity of the precession, then, in the time Δt , the angle of precession is $\omega_p \Delta t$.

From the geometry of Figure 4, it is seen that the change of angular momentum in the time Δt is

$$\begin{aligned}\Delta \vec{J} &= (\vec{J} \sin \theta) (\Delta \theta) \\ &= (\vec{J} \sin \theta) (\omega_p \Delta t)\end{aligned}$$

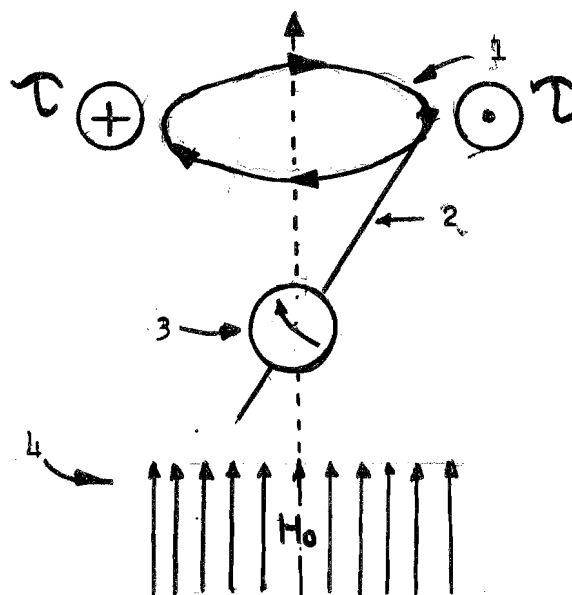


Figure 3.

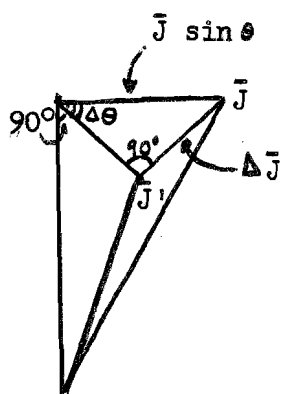
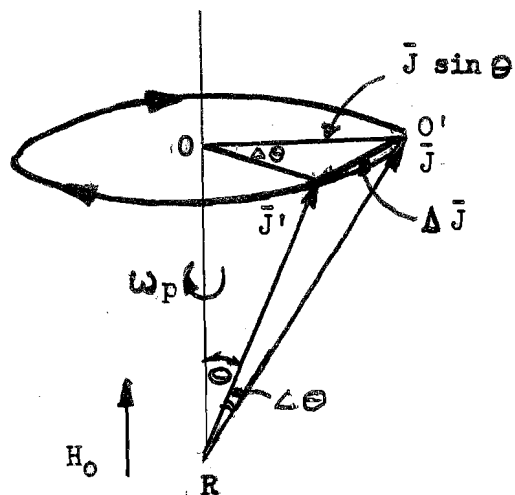
Motion of a nucleus in a magnetic field.

1. Precessional orbit.
2. Axis of rotation.
3. Spinning nucleus.
4. Direction of magnetic field H_0 .

$$\therefore \frac{\Delta \bar{J}}{\Delta t} = \bar{J} \sin \theta \omega_p \text{ ----- which must be equal to the torque } \bar{\tau}$$

$$\text{But torque } \bar{\tau} = \bar{\mu} \times \bar{H}_0 = \mu H_0 \sin \theta \bar{a}_n$$

Equating the magnitudes of the torques, $J \sin \theta \omega_p = \mu H_0 \sin \theta$ is obtained.



$$\sin \theta = \frac{OO'}{RO'} = \frac{OO'}{J}$$

$$\therefore J \sin \theta = OO'$$

$$OO' \Delta \theta = \Delta J$$

$$(J \sin \theta) (\Delta \theta) = \Delta J \quad (7)$$

$$\text{But } \Delta \theta = \omega_p \Delta t$$

$$\therefore (J \sin \theta) (\omega_p \Delta t) = \Delta J \quad (8)$$

Figure 4.

An object with angular momentum \vec{J} and a parallel magnetic moment $\vec{\mu}$ placed in a magnetic field \vec{H}_0 precesses with the angular velocity ω_p .

$$\therefore \text{the angular velocity of precession } \omega_p = \frac{\mu}{J} H_0 \quad (9)$$

$$\text{But from equation (6) } \mu = g \left(\frac{+q_e}{2m_p} \right) J.$$

$$\therefore \frac{\mu}{J} = \frac{gq_e}{2m_p} \quad (10)$$

Now, taking the magnitude of q_e and the mass of the proton, the proton resonance frequency is obtained. Substituting equation (10) in equation (9)

$$\begin{aligned} \omega_p &= \frac{\mu}{J} H_0 \\ &= \frac{gq_e H_0}{2m_p} \end{aligned} \quad (11)$$

Now, the proton precession frequency

$$P_{pf} = \frac{\omega_p}{2\pi} = \frac{gq_e H_0}{(2m_p)(2\pi)};$$

therefore, the precession frequency is proportional to the applied magnetic field, H_0 .

To show that the above equation is dimensionally the same:
in m.k.s. units,

$$\text{charge (coulombs)} = Q$$

$$\text{time (seconds)} = T$$

$$\text{magnetic flux density (Weber/meter}^2) = MT^{-1}Q^{-1}$$

$$\text{mass (kilograms)} = M$$

$$\text{So, left hand side, } P_{pf} = \frac{1}{\text{time}} = T^{-1}$$

$$\text{right hand side} = \frac{gq_e H_0}{2m_p 2\pi} = \frac{QMT^{-1}Q^{-1}}{M} = T^{-1}.$$

Since the left hand side and the right hand side both equal T^{-1} , the above equation is dimensionally the same.

Now, to find the proton precession frequency, the individual values are substituted:

the nuclear g-factor for the proton = $g = 2 \times 2.79$

the proton charge = $q_e = 1.6021 \times 10^{-19}$ coulombs

the magnetic flux density in Weber/meter² = H_0

the mass of the proton = $m_p = 1.67239 \times 10^{-27}$ kgs.

The proton precession frequency

$$= \frac{2 \times 2.79 \times 1.6021 \times 10^{-19} \text{ coulombs} \times H_0 \text{ (Weber/meter}^2\text{)}}{2 \times 1.67239 \times 10^{-27} \text{ kgs.} \times 2\pi}$$

$$= \frac{1.395 \times 1.6021 \times 10^8 \text{ coulombs} \times H_0 \text{ (Weber/meter}^2\text{)}}{1.67239 \times \pi \text{ kgs.}}$$

Converting Weber/meter² (which is in m.k.s. units) into gauss (which is in c.g.s. units), 1 Weber/meter² = 10^4 gauss.

$$\therefore P_{pf} = \left(\frac{1.395 \times 1.6021 \times 10^8 \text{ coulombs}}{1.67239 \times \pi \text{ kgs.}} \right) (H_0 \text{ Weber/meter}^2)$$

$$= (4.2408 \times 10^7 \frac{\text{coulombs}}{\text{kgs.}}) (H_0 \text{ Weber/meter}^2)$$

$$= (4.2408 \times 10^7 \frac{\text{cycles}}{10^4 \text{ gauss}}) (H_0 \text{ gauss})$$

$$= 4240.8 H_0 \frac{\text{cycles}}{\text{second}}$$

$$= 4240.8 H_0 \text{ Hertz.} \quad (12)$$

This means the proton will precess at a frequency of 4240.8 times the applied magnetic field (which is measured in gauss). Thus, by accurately measuring the value of H_0 , the proton precession frequency can be precisely determined.

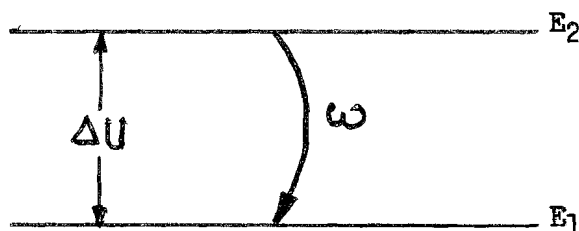
When the frequency of the rotating magnetic field (applied externally) and the proton precession frequency become equal, they are said to be in resonance. This phenomenon is known as "nuclear magnetic resonance."

Energy Absorption Process at Resonance

According to Plank's equation, when an atom has two levels, say E_1 and E_2 , which differ in energy by the amount ΔU , then it can make the transition from the upper level E_2 to the lower level E_1 by emitting a light quantum of frequency ω , which can be represented by the equation

$$\Delta U = h\omega \quad (13)$$

where h is known as Plank's Universal Radiation Constant.



This can be extended to the nucleus also. But, in the nucleus (if interest is only in the nucleus of ordinary hydrogen, namely the proton), the energy difference between the definite energy levels E_2 and E_1 is so small that the frequency does not correspond to light, but to radio frequencies. If there is an atom in a magnetic field, then transitions can be caused from one state to another by applying an additional electro-magnetic field of the proper frequency. In other words, if there is an atom in a strong magnetic field and if the atom is "excited" with a weak varying electromagnetic field, then there will be a certain probability of knocking it to another level, provided the frequency is near ω in the equation (13).

For an atom in a magnetic field, this frequency is just what was called earlier ω_p in equation (11). If the atom is excited with the wrong frequency, the chance of causing a transition is very small.

Thus, there exists a sharp resonance at ω_p in the probability of causing a transition. The energy absorption by lower levels of a proton takes place only in resonance, which can be detected.

It may be worthwhile to make an additional comment at this point. There is no apparent reason why there could not also be transition at the frequencies $2\omega_p$. But, with the oscillating magnetic field, the probability that a frequency $2\omega_p$ would cause a jump of two steps at once is zero. It is only at the frequency ω_p that transitions, either upward or downward, are likely to occur.⁶

The Use of N.M.R. to Determine Moisture Content in Soils

To begin with, the problem was attacked in the following manner:

Forgetting for awhile the soil portion of the test sample, it can be said that the remaining portion is mainly water. Water consists of hydrogen and oxygen atoms. Usually the isotopes present are the ordinary hydrogen atom, namely ${}^1_1\text{H}^1$, and the ordinary oxygen atom, ${}^{16}_8\text{O}$. Without much hesitation it can be said that the small concentrations of the other isotopes of hydrogen, ${}^2_1\text{H}$ and ${}^3_1\text{H}$, and oxygen, ${}^{17}_8\text{O}$ and ${}^{18}_8\text{O}$, are negligible.

In nuclear physics, the usual representation of any atom is ${}^A_Z\text{H}$ where Z stands for the Atomic Number and A stands for the Atomic Mass Number. It has been shown in the text by J. A. Pople⁷ that

- (i) If both the Atomic Number Z and the Atomic Mass Number A are odd, then the nuclear spin I is half integral, like 1/2, 3/2, 5/2... (${}^1_1\text{H}^1$ belongs to this case.
- (ii) If both the Atomic Number Z and the Atomic Mass Number A are even, then the nuclear spin I is zero. Nuclei with spin I = 0 have no nuclear magnetic spectra. (${}^{16}_8\text{O}$ belongs to this case. Hence no energy absorption by ${}^{16}_8\text{O}$ occurs.)

Hence whatever spectra obtained on the oscilloscope is only due to the energy absorption of the hydrogen nuclei (proton). The size (area) of the spectra depends on the number of protons present which in turn indicates the amount of moisture present. If the percentage of moisture is large, the number of hydrogen nuclei present is large, and hence the same spectrum appears with large area.

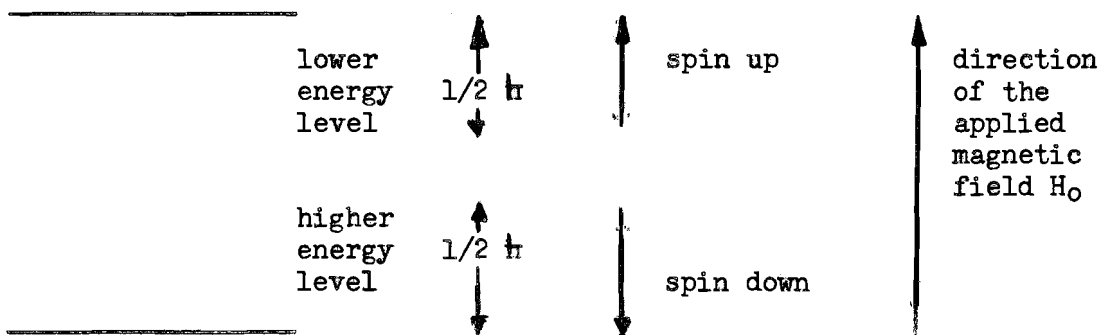
Proton Topology in the Resonance

It has been shown by quantum mechanics⁸ that, if I is the nuclear spin number (that is, the intrinsic angular momentum of the atomic nuclei), then, in the presence of a magnetic field, each energy level is split into $(2I + 1)$ equally spaced sub-levels.

For the hydrogen nuclei, i.e., the proton, the spin equals one-half.⁹ So the number of possible orientations

$$\begin{aligned}
 &= (2I + 1) \\
 &= [(2) (1/2) + 1] \\
 &= 2
 \end{aligned}$$

The protons will thus have two energy levels shown schematically in the sketch which follows. These are often referred to as "spin up" and "spin down." In each case, the projected magnitude of the spin momentum is $1/2 \left(\frac{h}{2\pi}\right)$, or $1/2 \hbar$ where \hbar is the Modified Plank's Constant.



The spin up position is considered to be a low energy or parallel orientation in which the atomic magnet is aligned with the field, and the spin down position corresponds to a high energy or anti-parallel

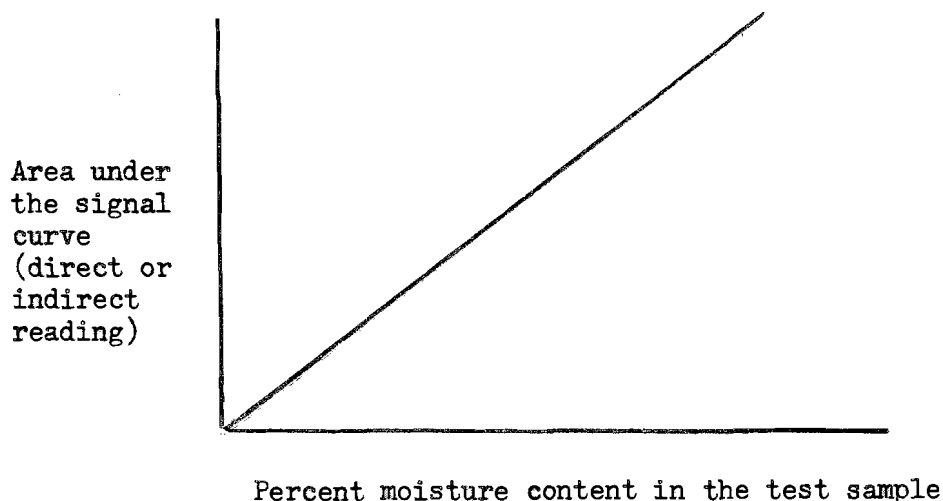
orientation in which it is aligned against the field. During the energy absorption the spin up position is re-oriented to the spin down position, this phenomenon being known as "Spin-Flip Transition."

As stated by Andrew,¹⁰ when the nuclear moments are in thermal equilibrium with the crystal lattice in which they are imbedded (which is the usual case), then the number of nuclei in the lower energy level should be somewhat greater than the number in the upper level.

Thus, the process that takes place in the resonance is the energy absorption by the lower state to become the higher state, this energy being given by the Radio Frequency Coil which surrounds the test sample. This Radio Frequency Coil also acts as a pickup element, sensing the signal induced which can be seen on the oscilloscope. The area under the signal curve, in turn, gives the amount of hydrogen present in the sample which, in turn, gives the amount of water present. Thus measuring the area under the signal curve directly or indirectly the moisture content is revealed. Finally, it is planned to draw a graph of the area under the signal curve on the ordinate and the percentage of moisture content in the test sample on the abscissa. It is hoped that a linear relationship will be obtained.

This statement is justified by the fact that the area under the signal curve depends on the number of hydrogen nuclei per unit volume of the sample. This, in turn, depends on the molar concentration of the hydrogen nuclei (the percent moisture content) in the unit volume of the sample. Developing this argument it can be stated that if the molar concentration of the hydrogen nuclei per unit volume is

less, the area under the signal curve is less and vice-versa. Hence a linear relationship as shown below can be expected.



Now, just by measuring the area of the signal curve, which can be done very easily, in a short time the percentage of moisture content in the test sample can be determined with the aid of the above graph.

Relaxation Processes

The relaxation processes have an extremely important effect on the spectra. Reference to this will be made again in Chapter IV, Section (C-1). A clear definition of relaxation processes has been given by Dyer.¹¹ The relaxation processes are various types of radiationless transitions by which a nucleus in an upper spin state returns to a lower spin state. Relaxation processes are of two kinds:

- (i) spin-lattice relaxation and
- (ii) spin-spin relaxation.

The term lattice refers to the framework of molecules containing the precessing nuclei. All of these molecules are undergoing

translational, rotational, and vibrational motions and have magnetic properties. Hence, a variety of small magnetic fields is present in the lattice. A particular small magnetic field, properly oriented in the lattice, can induce a transition in a particular precessing nuclear magnet from an upper state to a lower state. The energy from this transition is transferred to the components of the lattice as additional translational, rotational, and vibrational energy (spin-lattice relaxation, sometimes referred to as longitudinal relaxation). The total energy of the system remains unchanged. Thus, a nucleus is returned to a lower state from an upper state. This process maintains an excess of nuclei in a lower state, which is the condition necessary for the observation of the nuclear resonance phenomenon. The spin-lattice relaxation time is denoted by T_1 .

Spin-spin relaxation is effected by the mutual exchange of spins by two precessing nuclei in close proximity to one another. Associated with each precessing nucleus there is a magnetic vector component rotating in a plane perpendicular to the main field. If two nuclei are in close proximity, this small rotating magnetic field is exactly what is required to induce a transition in the neighboring nucleus. Although this mutual exchange of spins (spin-spin relaxation, sometimes called transverse relaxation) shortens the lifetime of an individual nucleus in the higher state, it does not contribute to the maintenance of the required excess of nuclei in a lower spin state. The spin-spin relaxation time is denoted by T_2 .

CHAPTER III

THE EXPERIMENTAL METHOD

In the first part, it was explained how the application of N.M.R. principles might be used to determine the moisture content in soils. In this section, the design and construction of the experimental apparatus will be considered. A variety of experimental problems were encountered. These will be explained in the proper places of the ensuing text.

First, the various parts of the N.M.R. spectrometer are described and the method of assembling the apparatus is given. The experimental procedure carried out to perform the test is then outlined.

Description of Various Parts of the N.M.R. Spectrometer

The apparatus consists mainly of five parts:

- (i) a magnet (either electro or permanent) capable of producing a very strong homogeneous field.
- (ii) a means of continuously varying the magnetic field over a svery small range—the magnetic field sweep.
- (iii) a radio frequency oscillator.
- (iv) a radio frequency receiver.
- (v) an oscilloscope.

CHAPTER IV

THE MAGNET

The magnet is a very important part of the N.M.R. spectrometer. Only in the presence of a magnetic field does the absorption of radio frequency radiation take place.

Both permanent and electromagnets have been employed to supply the magnetic field in N.M.R. spectroscopy. To obtain the hyperfine structure of the spectrum, the magnet should possess a field homogeneity of 1 part in 10^8 .¹² The homogeneous field is defined as the number of lines of magnetic force and the direction of the lines of magnetic force per unit area in the air gap should be of a constant value throughout the air gap.

A permanent magnet and an electromagnet were used. The permanent magnet consisted of two U-shaped magnetron magnets. The two magnets were connected in such a way that the field strength of each magnet was additive. That means the like poles of the two magnets were attached together as shown in Figure 5. By doing so, the field strength was increased from 900 gauss to 1,700 gauss.

Two circular pole faces made of steel were used. They were 4-inches in diameter and 1/4-inch thick, resulting in an air gap width of 3/4-inch. A small 1-inch cube of steel was welded to the center of the pole faces so that these pole faces could be held very neatly at the junctions of the two U-shaped magnets, S,S and N,N. To insure a uniform field, the faces of the circular pole pieces were made uniform and smooth. To get a good homogeneity, it was necessary

that great care be taken to remove the machining marks by using a very good polish. As mentioned by Bloom and Packard,¹³ the volume over which the field is homogeneous depends on the ratio of pole piece diameter to the air gap width. It has been stated by Robert G. Marcley¹⁴ that the ratio of the pole piece diameter to the air gap width should be at least 5. An electromagnet, while not so convenient for a laboratory setup, can be used if adequate care is taken to insure a stable field. This will require some method of automatic control and regulation of the magnetizing coil current. In the experimental setup the ratio of the pole piece diameter to the air gap width was 5.33.

As it was mentioned earlier, it is necessary to have a field homogeneity of at least 1 in 10^8 to get the required hyperfine structure of the spectra. With all the precautions taken to obtain a good homogeneous field, it was felt that the resolution obtained was about 1 in 10^3 . It has been pointed out by Robert G. Marcley¹⁵ that a field homogeneity of at least 1 in 10^3 is necessary or else the chances of getting the resonance is very remote.

Setup Procedure for Magnets

The two U-shaped magnets were connected as shown in Figure 5. The necessary mechanical jig and fixture arrangement was used to hold the two magnets (and hence the circular pole faces) in position. Extreme precaution was taken in setting up this arrangement since there will be an intense magnetic field present between the pole pieces. A non-magnetic material such as wood should be placed between the two pieces so that the fingers are not caught. If wood is used, precaution ought to be taken so that it may not spoil the shiny

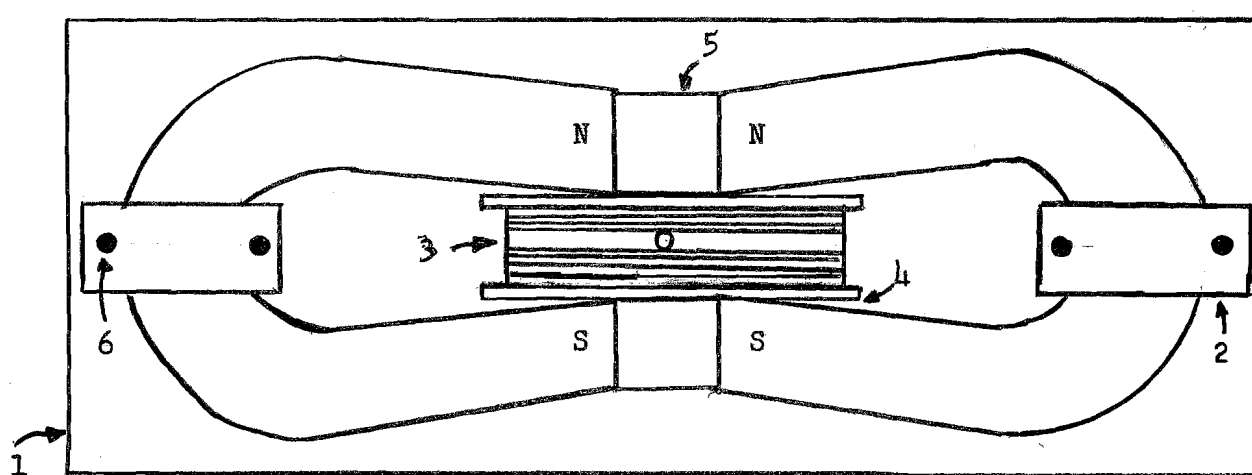


Figure 5.

Plan view for the arrangement of magnets.

1. A wooden plank of 16-inches x 5 1/2-inches x 1 1/2-inches.
2. A 3-inches x 1-inch x 1/4-inch steel strip with holes drilled at the ends for the insertion of bolts.
3. The air gap space between the pole faces for the test sample and the modulation coils.
4. 4-inches diameter circular pole face.
5. A 1-inch steel cube welded to the center of the pole faces.
6. 1/4-inch diameter steel bolt 3 1/2-inches in length.

surface of the pole pieces. Also, because of the danger of the magnetic field, wrist watches should be kept at a distance.

Measurement of the Magnetic Field

After the circular pole pieces were fixed to the magnet, the field strength was reduced considerably. It was reduced from 1,700 to 1,410 gauss. The field measured was exactly in the center of the pole faces. A micromanipulator was used to place the probe (and the gauss meter) exactly at the center of the pole pieces.

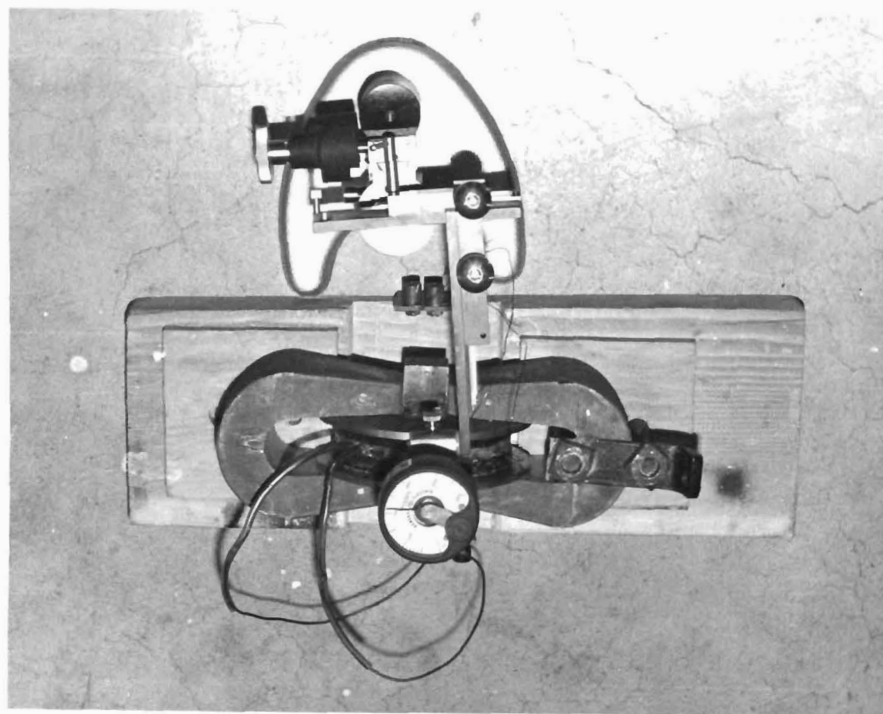


Figure 6.

Setup of the micromanipulator to measure the field strength.

The reading obtained with the gauss meter was 1,410 gauss. But the gauss meter, being uncalibrated, read 2,260 gauss on a standard magnet of 2,500 gauss. Hence a correction factor of $\left(\frac{2,500}{2,260}\right)$ was used. Thus, a better approach to the magnetic field at the center = $\left(1,410 \times \frac{2,500}{2,260}\right) = 1,560$ gauss.

The Electromagnet

The electromagnet used was the one built by the staff of the Electrical Engineering Department in the summer of 1966. Both the main and modulation coils are wound on the yoke. The magnet has approximately 700 turns of main winding and 100 turns of modulation winding. The wire used was 11 and 14 gauge copper wire respectively. It has a circular pole face of 1 3/4-inches diameter and 1 1/8 inches air gap width. There is a provision to adjust the air gap width. With this setup, the ratio of the pole piece diameter to the air gap width was 1.56.

The magnet had about 30 gauss of residual magnetism. This was because of the previous magnetization. This residual magnetism was completely demagnetized by sending a DC current in one particular direction in one period and in the next period in the reverse direction. This procedure was repeated, starting from 7 amperes down to 0 amperes, descending at an interval of .5 ampere each time. After repeating this procedure four times, the residual magnetism as checked by a gauss meter was very nearly zero.

Using a Hewlett Plackard "Harrison 6267A" instrument which gives a regulated supply of magnetizing coil current, the following

graph (Figure 6) of magnetizing coil current versus \bar{B} field in the air gap was drawn. The process of getting the graph of \bar{B} versus the current was repeated three times. Sometimes, it was observed that the reading of \bar{B} field obtained was slightly higher than the corresponding previous reading. This may have been due to the residual magnetism that was present because of previous excitation of the fields, or it may have been due to the instability of the gauss meter. An average was taken of the readings at each level of current (Table 1) and a final plot was made as shown in Figure 6.

Table 1.

Calibration of current versus magnetic field.

Ampere, I	Magnetic Field Strength, B			
	I	II	III	Average Gauss
0.0	75	75	65	72.00
.5	325	300	310	312.00
1.0	625	575	570	590.00
1.5	875	825	810	837.00
2.0	1,150	1,060	1,050	1,087.66
2.5	1,375	1,300	1,300	1,325.00
3.0	1,630	1,550	1,530	1,570.00
3.5	1,775	1,875	1,800	1,817.00
4.0	2,050	2,100	2,025	2,058.00
4.5	2,280	2,275	2,280	2,277.00

$\times 10^2$

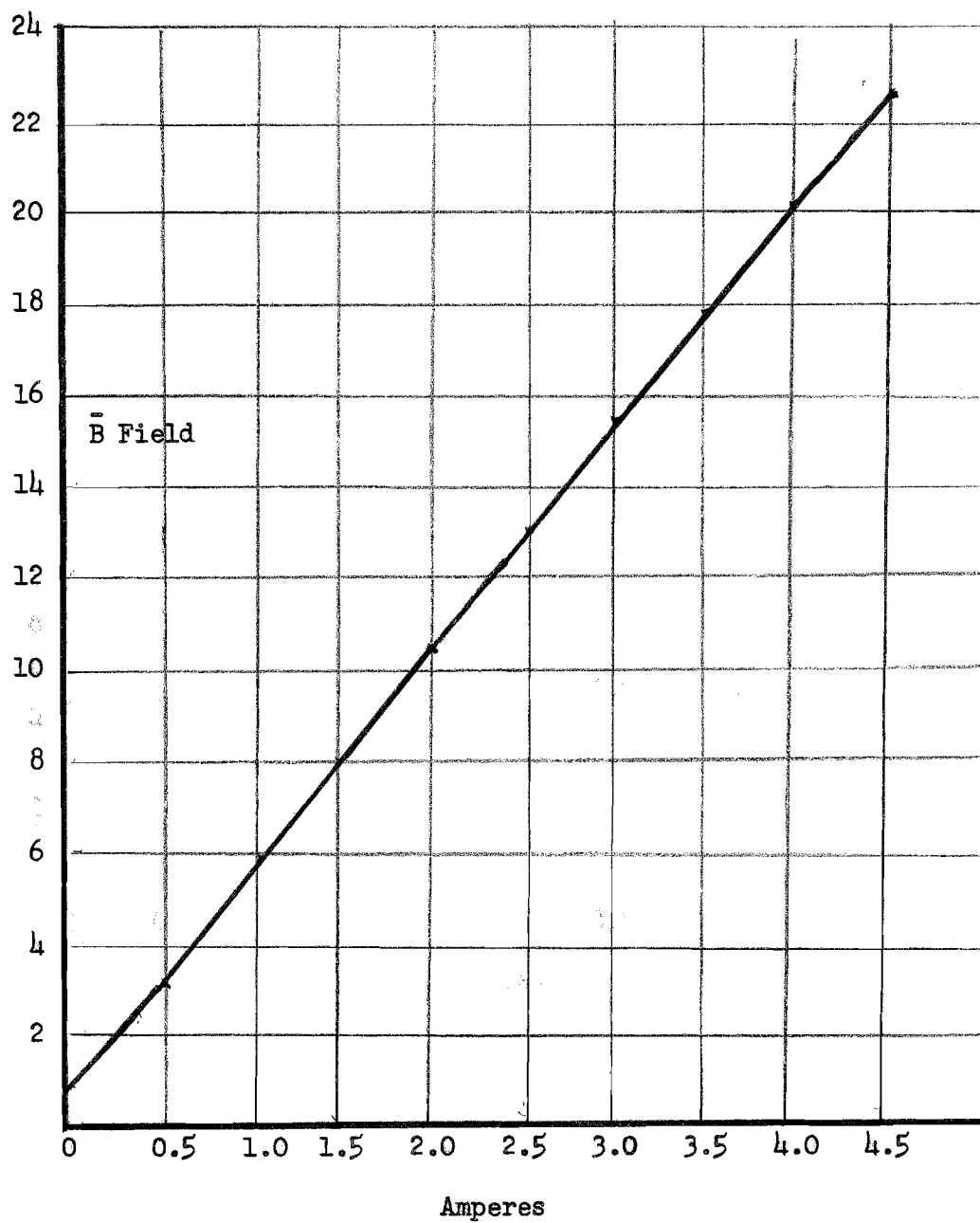


Figure 6.

Plot of magnetizing coil current versus magnetic field intensity in the air gap.

Effect of Stronger Magnetic Field

It is extremely desirable to have the strength of the magnetic field as high as is practically possible. The reasons for this are threefold:

- (i) The chemical shifts are proportional to the field strength. Hence, higher field strengths result in increased dispersion of the spectrum.
- (ii) As stated by Pople,¹⁶ for a given experimental arrangement at constant temperature and for $T_1 = T_2$ where T_1 is spin-lattice relaxation time and T_2 is spin-spin relaxation time, it is apparent that, at a given field, the signal strength (peak intensity) is proportional to

$$N_1 \left(\frac{I + 1}{I^2} \right) \mu^3 H_0^2 \quad (14)$$

where N_1 = number of nuclei (with spin 1/2)
per unit volume

I = the nuclear spin

μ = the magnetic moment

H_0 = the steady magnetic field.

Thus, the higher the strength of the magnetic field, the stronger the absorption signals.

- (iii) The strength of an absorption signal relative to the irreducible background of radio frequency noise varies with approximately one and one-half power of the field strength.¹⁷ Hence, when considering the above points, it is apparent that the higher field is always desirable.

CHAPTER V

MAGNETIC FIELD SWEEP

Earlier it was shown by equation (12) that the proton precession frequency was equal to the field strength (gauss) times 4,240.8. This means that resonance can be achieved through variation of the frequency of the rf field or by varying the magnitude of the static magnetic field, in order to satisfy the above condition. In this experiment, variation of the applied static field technique was employed.

The magnetic field sweeping coils may be constructed in two ways. The first method consists of winding a number of turns on the two pole pieces of the magnet. In the second method, an alternating current is fed into a pair of coils known as Helmholtz coils which flank the sample with their axes parallel to the direction of the static magnetic field of the magnet. The modulation coil (Helmholtz coil) is driven by a variable voltage transformer. The current in the modulation coil produces a small field. This field alternately reinforces and opposes that of the main magnet. Hence, this allows the effective value of the magnetic field H_0 to be varied over a small range without detriment to the homogeneity of the field.

Construction of the Helmholtz Coil

The Helmholtz coil was wound on a 3 7/8-inches diameter by 3/4-inch wide circular plexiglass material. The width of this tube is the same as the space between the circular pole pieces. A 5/16-inch

diameter hole was drilled in the center of the tube to admit the test tube in which the sample will be kept. Great care is required in drilling this hole. To begin with, a 1/32-inch hole was drilled by giving a feed of 1/64-inch each time. Then the diameter was increased at the rate of 1/32-inch until the diameter reached 5/16-inch. This job should be done with great patience or else the probability of breaking the tube is very high. To start with, the tube was wound with 20 turns of 23 gauge enameled wire on each side, wound in the same direction. Dupont's Duco cement was used as the adhesive. When this was tried in the setup, the insulation of the wire burned even at the low setting (10 volts) of the variable voltage transformer. Hence, the number of turns was increased to 40 turns on each side. Even then the result was unsuccessful.

Then a kind of 21 gauge wire which has a special coating of high temperature resistant varnish was used. This is a General Electric product, having the trade name "Formvar." The field modulation coil now consisted of 25 turns in two layers on each side which easily withstood a secondary voltage of the variable voltage transformer up to 30 volts.

A smaller Helmholtz coil, wound on a 2 1/4-inches diameter by 11/16-inch wide plexiglass tube with 20 turns on each side wound in the same direction, was also tried. A general schematic of the above setup is shown in Figure 7.

Sample Holder and RF Coil

The test tube was 1/4-inch in diameter and 1 5/8-inches long.

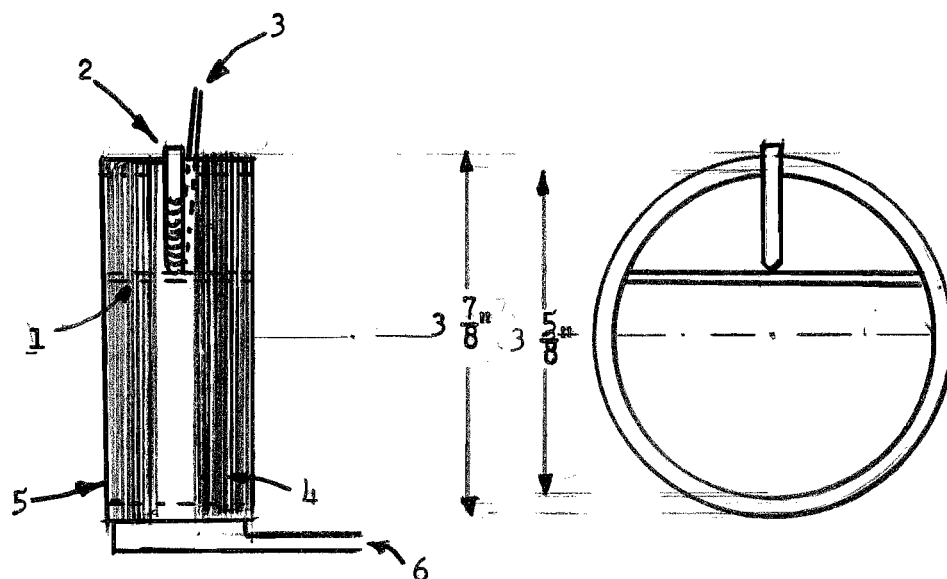


Figure 7.

Helmholtz and radio frequency coils.

1. Mechanical support of the test tube.
2. Test tube.
3. The outer terminals of the rf coil.
4. Modulation coil (Helmholtz coil)
5. Plexiglass tube.
6. Modulation coil terminals to variable voltage transformer.

A two-layer coil of 18 gauge enameled magnetic wire consisting of 15

turns per layer was wound on the straight portion of the tube as close as possible to the closed end.

The rf coil was built in the following manner. First, a thin coat of "Krylon" crystal clear spray coating was given. To a slight extent, this coating served as an adhesive. Then the taut enameled wire was slowly wound on the coated surface of the test tube, taking care to see that the coils did not overlap. After winding 15 turns, one more coat of Krylon spray was given, and the second layer of 15 turns was wound. Dupont's Duco cement was applied quite freely so that the end coils would not slide away. One more coating of spray was given, and the coil was left to dry for 24 hours.

The test tube was admitted in such a way that its axis was concentric with the biasing field, and a mechanical support was installed as shown in Figure 7. The leads of the rf coil were taken out through a 1/8-inch diameter hole drilled on the surface of the plexi-glass tube.

A 3/8-inch diameter test tube was also tried as a sample coil form.

CHAPTER VI

RADIO FREQUENCY OSCILLATOR

There are many kinds of radio frequency oscillators mentioned in the literature. Basically, they can be divided into two categories, namely, (i) Pound-Knight-Watkins marginal oscillator, and (ii) Superregenerative N.M.R. detectors. The principle of the Pound-Knight-Watkins oscillator is this: the oscillation level of an L.C. oscillator is adjusted to a point at which it barely oscillates. The test sample containing particles having nuclear or electron spins, placed in the coil of the oscillator, absorbs energy from the rf fields in the coil at resonance. This absorption produces a change in the inductance of the coil which results in a decrease of Q of the resonance circuit. Now, since there is a change in the impedance of the circuit, the plate current of the oscillator tube changes. This change is amplified by an audio amplifier and can be observed on an oscilloscope. The details of the circuitry and design have been given in The Versatile Magnetic Resonance Spectrometer by J. A. Cowen.¹⁸

The circuit built was a low frequency superregenerative oscillator suitable for the detection of Broad-Line N.M.R., similar to the one described by Narath, et al.¹⁹ This kind of circuit possesses a definite advantage over the marginal oscillator. This lies in the ability of the superregenerative device to provide high rf field levels within the sample coil. The ease with which the operating frequency may be swept over a wide range without degradation in

sensitivity is an additional property which makes this type of detector a valuable tool. This is particularly true in the type of experiment under consideration where the resonating frequency is not known.

Superregenerative "detectors" are high gain rf amplifiers which are characterized by the alternating buildup and decay of self-oscillations in an rf oscillator. This quenching action is normally brought about by applying a periodic quench voltage to one of the control elements of the oscillator.

Two operating modes can be distinguished, namely, (i) the linear mode, and (ii) the logarithmic mode. The linear mode results when the oscillator is quenched before the limiting rf level is reached. The logarithmic mode results when the oscillator is permitted to reach a limiting level before the quench cycle is initiated. Illustrations of these two modes, as obtained from the oscillator, are shown in Figure 8.

It should be noted here that the superregenerative oscillator acts both as a transmitter and as a receiver. That means, during "on" periods, the oscillator "transmits" magnetization to lower energy protons, which is then "received" during the subsequent "off" periods (flip-flop motion). The stable operation of a superregenerative oscillator over a wide range of radio and quench frequencies generally requires a logarithmic mode. In this mode the amplification of the signal relative to noise is represented by the following approximate incremental area under the output envelope.²⁰

$$A = V_m T_1 \ln \left(\frac{V_2}{V_1} \right) \quad (15)$$

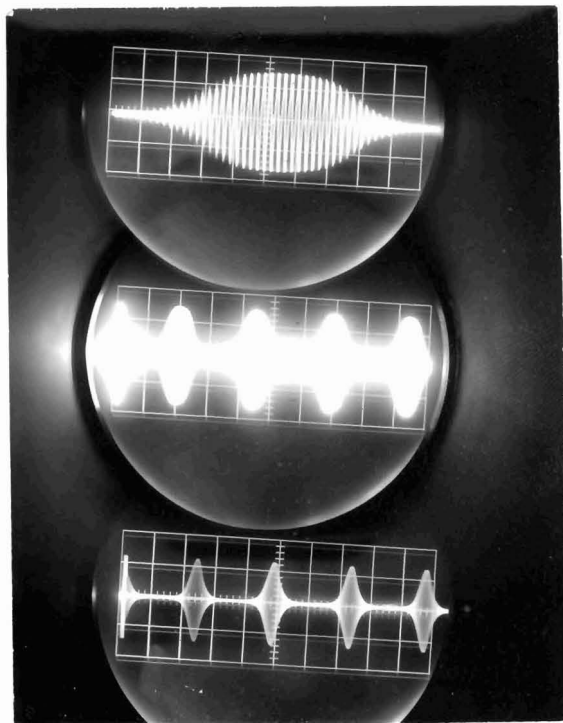


Figure 8.

- a, the bottom figure, indicates the linear mode.
- b, the middle figure, indicates the logarithmic mode (or saturation mode).
- c, the top figure, indicates the logarithmic mode spread on a time base.

where V_m = limiting rf level.

T_1 = time constant for rf buildup.

and V_1, V_2 = the total rf voltages
 (including noise components)
 impressed on the circuit at
 the start of the buildup in
 the absence and presence of
 the sample respectively.

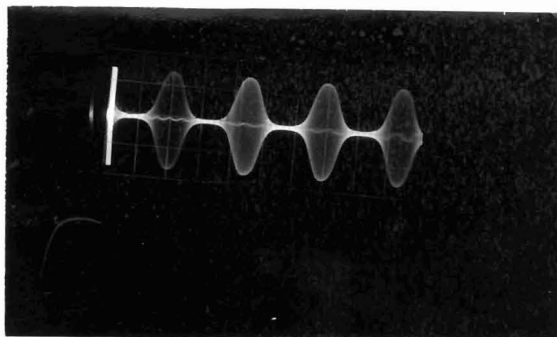


Figure 9.

Position between a linear and a logarithmic mode.

Now the ratio $(\frac{V_2}{V_1})$ is slightly larger than unity and the incremental area is given for a fair degree of approximation as:²¹

$$A_1 = V_m T_1 \frac{V_s}{V_1}, \text{ where } V_s \text{ is the nuclear signal}$$

($V_s = V_2 - V_1$. V_s will be of a very small magnitude).

The amplification of the modulation products of the resonance is, therefore, given by

$$G = f_q V_m T_1 \frac{V_s}{V_1} \tag{16}$$

where f_q is the quench frequency. From this it is clear that the sensitivity is greatly enhanced by reducing V_1 . In order to achieve a low value of V_1 at the high quench frequencies required for the detection of broadlines, it is necessary that the time constant for the decay of oscillations be quite short. This rapid quenching action must be achieved without seriously lowering V_m .

An extremely good circuit suitable for the above work has been designed by C. Dean of Harvard University.²² A simple modification of the Dean-type plate detection superregenerative oscillator has been done by Albert Narath and is shown in Figure 10.²³ This circuit was used in the experimental setup.

The reason for the addition of an RC filter network in the circuit is discussed by Narath as follows.²⁴

At frequencies below about 10 Mc, interference between the quench frequency and the radio frequency is sometimes observed with the above circuit. This interference is caused by harmonics of the quench signal which can be detected by the superregenerative oscillator, thus giving rise to spurious outputs at intervals of the quench frequency. In one instance the oscillator was observed to frequency-lock to successive harmonics as the tuning capacitor was swept; in this mode the oscillator frequency jumps discontinuously instead of varying smoothly with capacitor setting. This interference is not always sufficiently serious to affect the performance of the device for N.M.R. detection. It can, however, be almost completely eliminated by the insertion of an RC filter network between the quench amplifier and the oscillator grid, as in circuit (B) shown in Fig. 2. The filter greatly reduces the harmonic content of the quench signal seen by the oscillator, without reducing the effectiveness of the quenching action. The use of paralleled tubes in circuit (B) increases the power handling capacity of the quench and oscillator sections. The latter makes it possible to use lower L/C ratios in the tank circuit without reduction in rf level. The use of parallel elements in the oscillator section usually requires separate plate load resistors, as shown, in order to eliminate high frequency instabilities in which the two sections are effectively in series rather than in parallel.

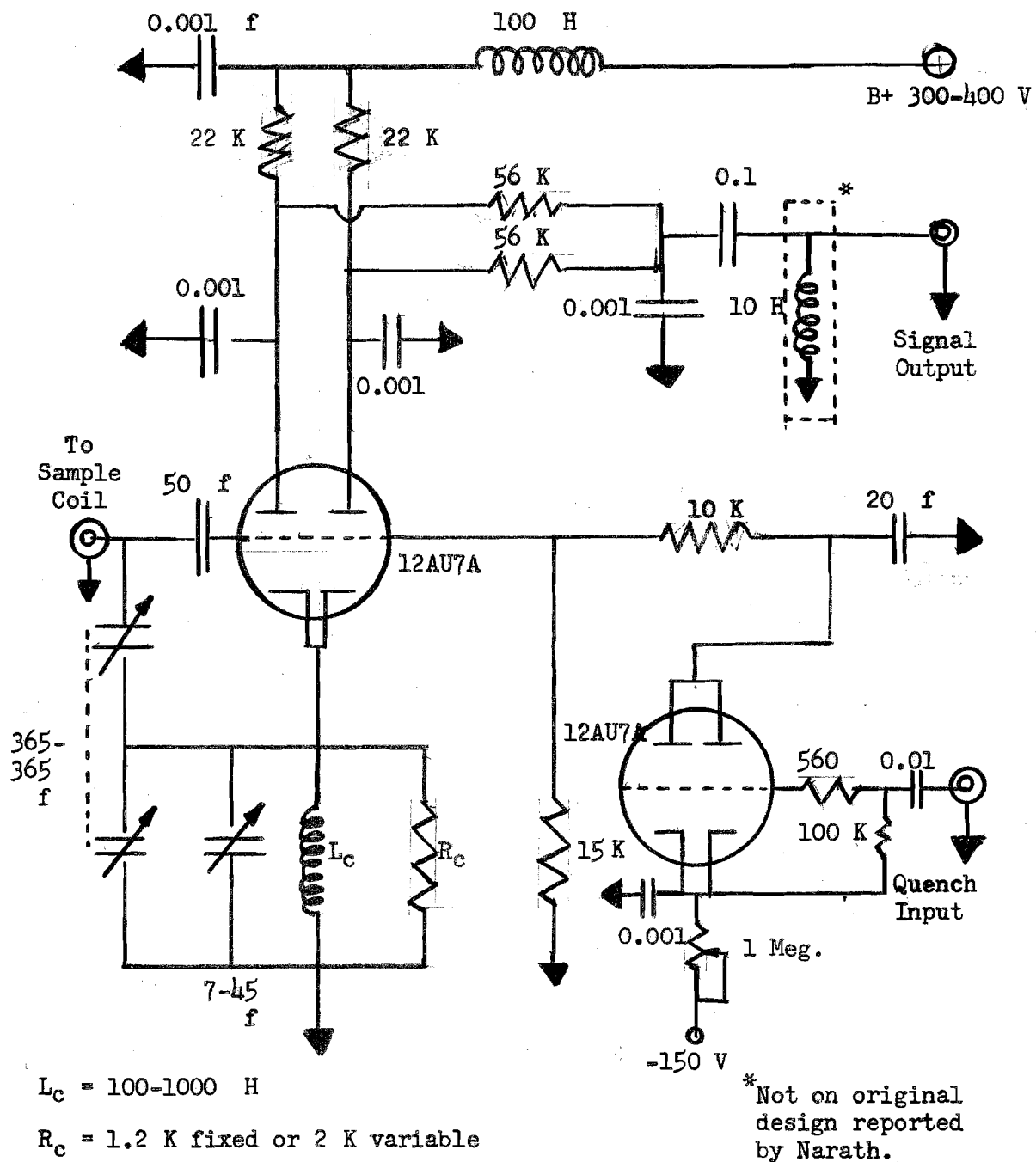


Figure 10.

Schematic of superregenerative oscillator
for the detection of broadline N.M.R.

The tubes used were 12 AU7A. First, this circuit was built on a "vector board." The oscillator could not be made to oscillate, as there was much A.C. pickup in the filament and B⁺ leads because of a high level of 60-cycle A.C. signals in the vicinity. Hence, great care was taken to make good ground connections and eliminate the A.C. pickup. The complete circuit was again built in an aluminum box 16-inches by 5-inches by 3-inches. This setup worked very well. Figure 11 shows a photograph of the oscillator.

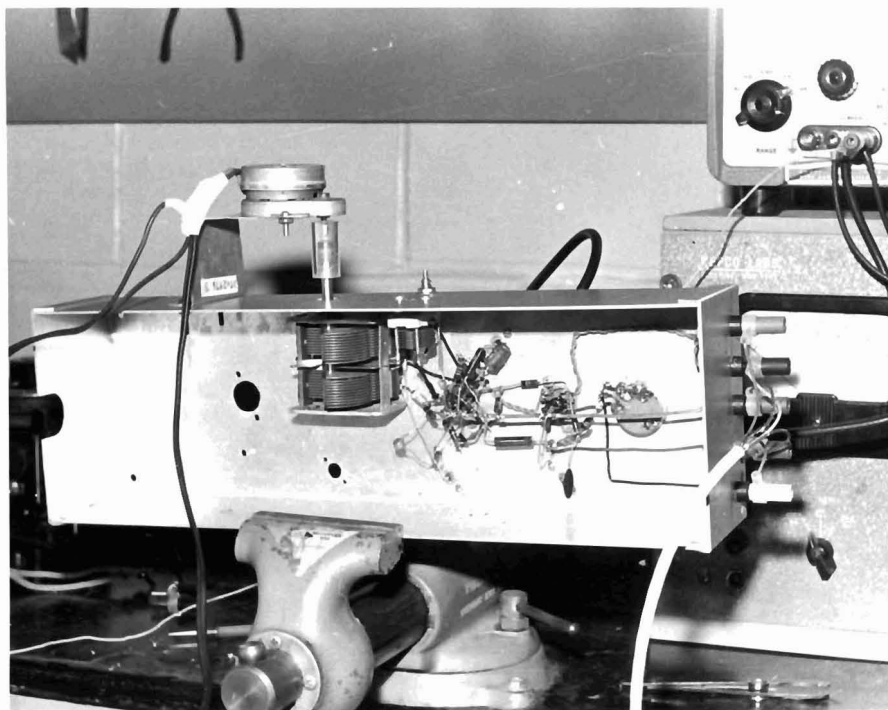


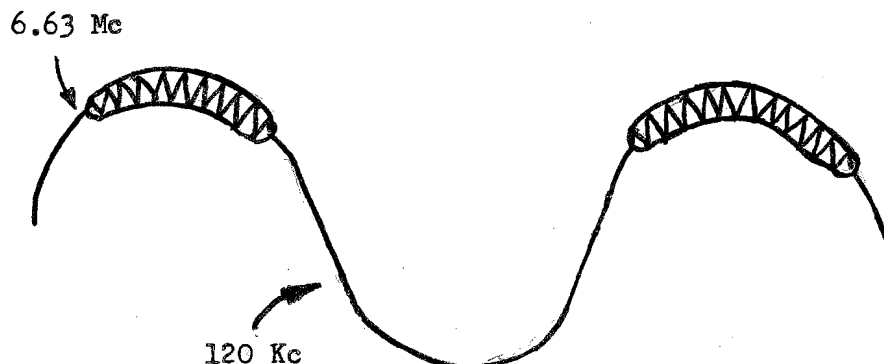
Figure 11.

The radio frequency oscillator.

A small synchronous motor having an rpm of 0.5 was attached to the knob of the dual capacitor, using a jig and fixture arrangement as shown in Figure 11. An on-and-off switch was connected to this synchronous motor to aid in correct tuning. This also helps in getting a linear sweep of the capacitor. The use of a tuning motor assisted materially in eliminating stray capacitance as was present with manual tuning.

The Design of an RL Filter Network

The quench frequency signals range from 80 Kc to 120 Kc. Resonance will occur above 5 Mc. It will occur somewhere near $1,560 \times 4,240.8 = 6.63$ Mc. Then, on the screen of the oscilloscope, the spectrum obtained will be seen as 6.63 Mc superimposed on the top of the quench frequency, 120 Kc. The spectrum is shown schematically.



Now by suitably designing an RL network, it is possible to eliminate completely all of the frequencies below 5 Mc. The response of the oscillator will be of a constant magnitude after 5 Mc. For that circuit following Bode plot is assumed. This is shown schematically in Figure 12.

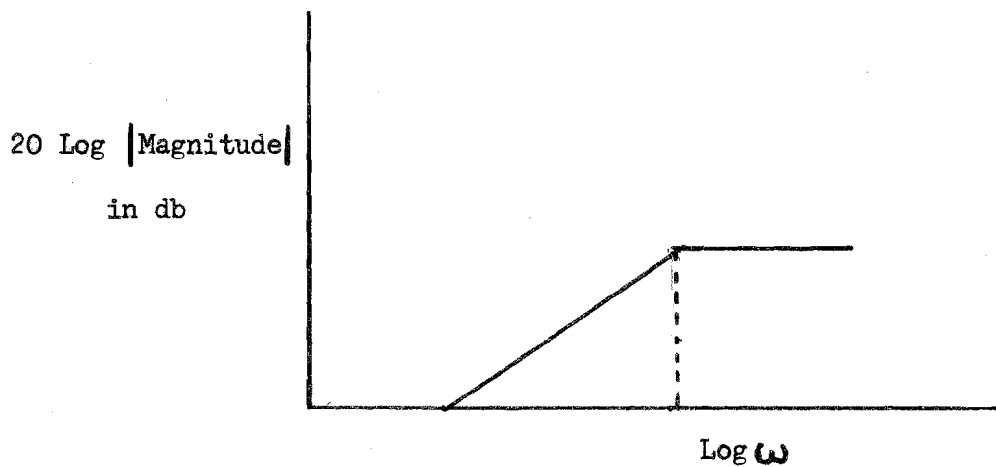


Figure 12.

Assumed Bode plot for the filter.

The spectrum should then look like



The impedance of this filter may be written in the Laplace form as

$$Z(s) = \frac{s}{s + 5} \quad (16)$$

Dividing equation (16) by S :

$$Z = \frac{1}{1 + \frac{5}{S}} \quad (17)$$

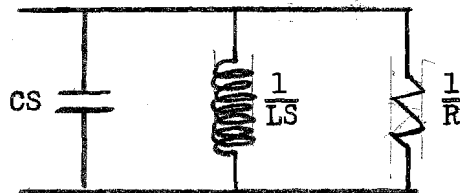
Now, on the lefthand side, the impedance Z has unit in ohms.

$$\therefore \text{the righthand side } \left(\frac{1}{1 + \frac{5}{S}} \right) \text{ should have unit as } = \frac{1}{\frac{1}{\text{ohms}}}$$

$$= \frac{1}{\text{admittance}}$$

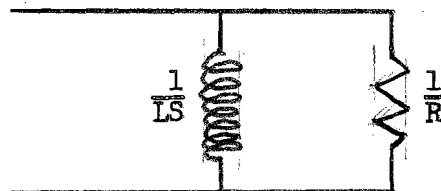
$$\therefore \text{admittance} = \left(1 + \frac{5}{S} \right) \quad (18)$$

The general Laplace representation for parallel circuit in admittance is



$$\text{Total admittance } Y = CS + \frac{1}{LS} + \frac{1}{R}$$

The Laplace representation of the circuit for equation (17) in admittance will be



$$\text{Total admittance } Y = \frac{1}{LS} + \frac{1}{R}$$

$$\text{From equation (18), } Y = \frac{1}{5} + \frac{1}{1}$$

$$\therefore L = \frac{1}{5}$$

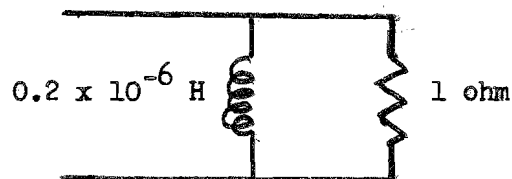
$$\text{and } R = 1$$

Since calculations are done with megacycles/sec the value of the inductance obtained will be in microhenries. The resistance value is not affected by the value of the frequencies.

$$\therefore \text{ the values of } L = \frac{1}{5} \times 10^{-6} \text{ Henries,}$$

$$R = 1 \text{ ohm.}$$

The circuit diagram will look like:



But the input impedance looks like 50 ohms. This 50 ohms is the resistance of the cable from the oscillator to the input of the scope and the input-output measuring devices. Thus, the total input resistance will be 50 ohms.

\therefore Normalizing the above values of R and L by 50:

$$\text{Resistance, } R = 1 \text{ ohm} \times 50 = 50 \text{ ohm,}$$

$$\text{Inductance, } L = \frac{1}{5} \mu\text{h} \times 50 = 10 \mu\text{h.}$$

This 10 microhenries was connected near the output of the oscillator as shown in Figure 10. The result of this RL network synthesis obtained was excellent. This can be verified by looking at Figure 8.

Oscilloscope

The oscilloscope used throughout the experiment was a Model 545 Tektronic.

CHAPTER VII

PROCEDURE AND EXPERIMENTAL SETUP USED

The components described above were all connected together as shown in Figure 13, and the final experiments were conducted in the following manner:

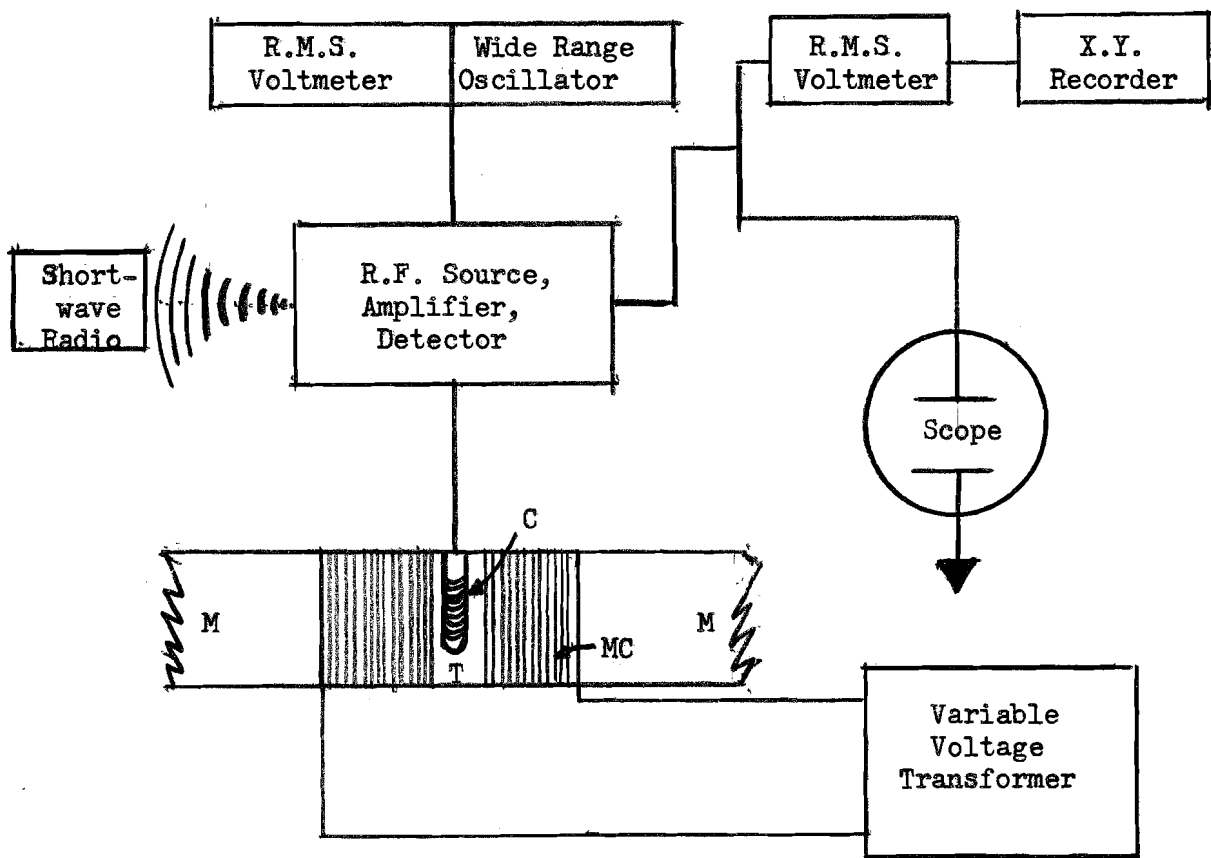


Figure 13.

Schematic diagram of the setup for the N.M.R. experiment.

T = sample test tube.

C = rf coil.

MC = modulation coils.

M = magnet.

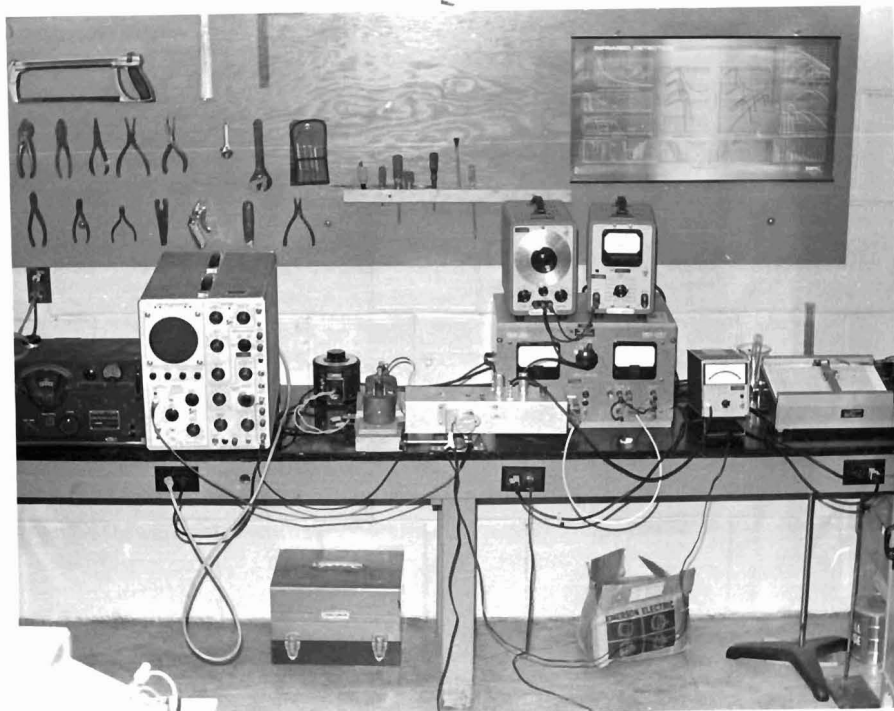


Figure 14.

The instrumental setup for the experiment.

Three cc. of distilled water was taken in a $3/8$ -inch diameter test tube and placed in the pulsating magnetic field. The various instruments were adjusted as shown below:

- (i) Hewlett-Packard r.m.s. voltmeter—3 v/r.m.s.
- (ii) Hewlett-Packard wide range oscillator—80 Kc (not critical).
- (iii) Superregenerative detector—the dual capacitor is



set for minimum frequency (the plates of the capacitor fully meshed in).

- (iv) Variable voltage transformer setting—10 volts
(not critical).

The power supply of all instruments were turned on, including the calibrated short-wave radio receiver. This receiver was equipped for continuous wave reception. The oscillator signal was heard as a shrill whistle which was picked up on the receiver. Now, the switch of the synchronous motor was turned on, which changes the oscillator frequency. The changed oscillator frequency was detected again on the receiver. The reading of the r.m.s. voltmeter was noted. This process was continued until the oscillator dual capacitor has reached its maximum value (the plates of the capacitor are fully opened) which corresponds to 7 megacycles. The readings of the r.m.s. voltmeter were noted at intervals of $1/2$ megacycle.

Table 2 shows the readings obtained with and without the sample in the magnetic field. This experiment was repeated three times and the values obtained are listed. An average of these values was plotted and Figure 15 was obtained.

By looking at Figure 15, it was impossible to discern whether there was any resonance or not. The use of an r.m.s. voltmeter and a short-wave radio receiver in the setup gave the necessary data to draw the Figure 15. Perhaps there was no observable change in the readings of the voltmeter even though the nuclei were under resonance because of very sluggish energy changes, and the discrepancy obtained

Table 2.

Calibration of frequency of the oscillator versus r.m.s. volts.

Frequency in Mc on the short- wave radio	r.m.s. voltmeter reading $\times 10^{-1}$ without the test sample				r.m.s. voltmeter reading $\times 10^{-1}$ with the test sample			
	I	II	III	average volts	I	II	III	average volts
5.00	6.60	6.60	6.60	6.60	6.60	6.60	6.60	6.60
5.05	6.70	6.75	6.75	6.73	6.65	6.75	6.75	6.72
5.10	6.70	6.70	6.75	6.72	6.70	6.70	6.75	6.72
5.15	6.75	6.75	6.75	6.75	6.75	6.75	6.75	6.75
5.20	6.80	6.80	6.80	6.80	6.80	6.80	6.80	6.80
5.25	6.80	6.85	6.80	6.82	6.80	6.85	6.90	6.85
5.30	6.80	6.85	6.85	6.83	6.85	6.85	6.90	6.86
5.35	6.85	6.85	6.85	6.85	6.85	6.85	6.90	6.86
5.40	6.90	6.90	6.90	6.90	6.90	6.85	6.90	6.88
5.45	6.90	6.90	6.90	6.90	6.90	6.85	6.95	6.90
5.50	7.05	7.00	6.95	7.00	7.00	7.00	7.00	7.00
5.55	7.05	7.05	7.00	7.03	7.00	7.00	7.00	7.00
5.60	7.10	7.10	7.10	7.10	7.10	7.10	7.05	7.08
5.65	7.15	7.15	7.15	7.15	7.15	7.15	7.10	7.13
5.70	7.20	7.20	7.25	7.22	7.20	7.20	7.20	7.20
5.75	7.35	7.30	7.25	7.30	7.25	7.30	7.30	7.28
5.80	7.35	7.30	7.30	7.32	7.30	7.30	7.35	7.32

Table 2. (continued)

5.85	7.35	7.30	7.30	7.32	7.30	7.30	7.35	7.32
5.90	7.40	7.35	7.35	7.37	7.35	7.40	7.35	7.36
5.95	7.40	7.40	7.40	7.40	7.40	7.40	7.40	7.40
6.00	7.45	7.45	7.45	7.45	7.45	7.50	7.45	7.46
6.05	7.50	7.50	7.45	7.48	7.50	7.50	7.50	7.50
6.10	7.50	7.50	7.50	7.50	7.55	7.60	7.55	7.56
6.15	7.55	7.55	7.55	7.55	7.60	7.60	7.60	7.60
6.20	7.60	7.60	7.60	7.60	7.60	7.65	7.65	7.63
6.25	7.65	7.60	7.60	7.62	7.65	7.70	7.70	7.68
6.30	7.65	7.65	7.65	7.65	7.70	7.70	7.70	7.70
6.35	7.65	7.65	7.65	7.65	7.70	7.70	7.70	7.70
6.40	7.70	7.65	7.65	7.67	7.75	7.70	7.70	7.72
6.45	7.65	7.60	7.65	7.63	7.65	7.65	7.60	7.63
6.50	7.60	7.60	7.50	7.57	7.65	7.60	7.60	7.62
6.55	7.55	7.60	7.50	7.55	7.60	7.60	7.55	7.58
6.60	7.50	7.50	7.50	7.50	7.50	7.50	7.50	7.50
6.65	7.20	7.30	7.40	7.30	7.30	7.35	7.40	7.35
6.70	7.10	7.20	7.30	7.20	7.15	7.20	7.10	7.15
6.75	7.00	7.05	7.00	7.02	7.00	7.05	7.00	7.02
6.80	6.90	6.80	6.90	6.86	6.90	6.85	6.80	6.85
6.85	6.50	6.40	6.80	6.57	6.65	6.65	6.60	6.63
6.90	6.10	6.20	6.10	6.13	6.40	6.40	6.40	6.40
6.95	5.90	5.95	5.95	5.93	6.00	6.10	6.10	6.07
7.00	5.40	5.40	5.30	5.37	5.40	5.35	5.40	5.38

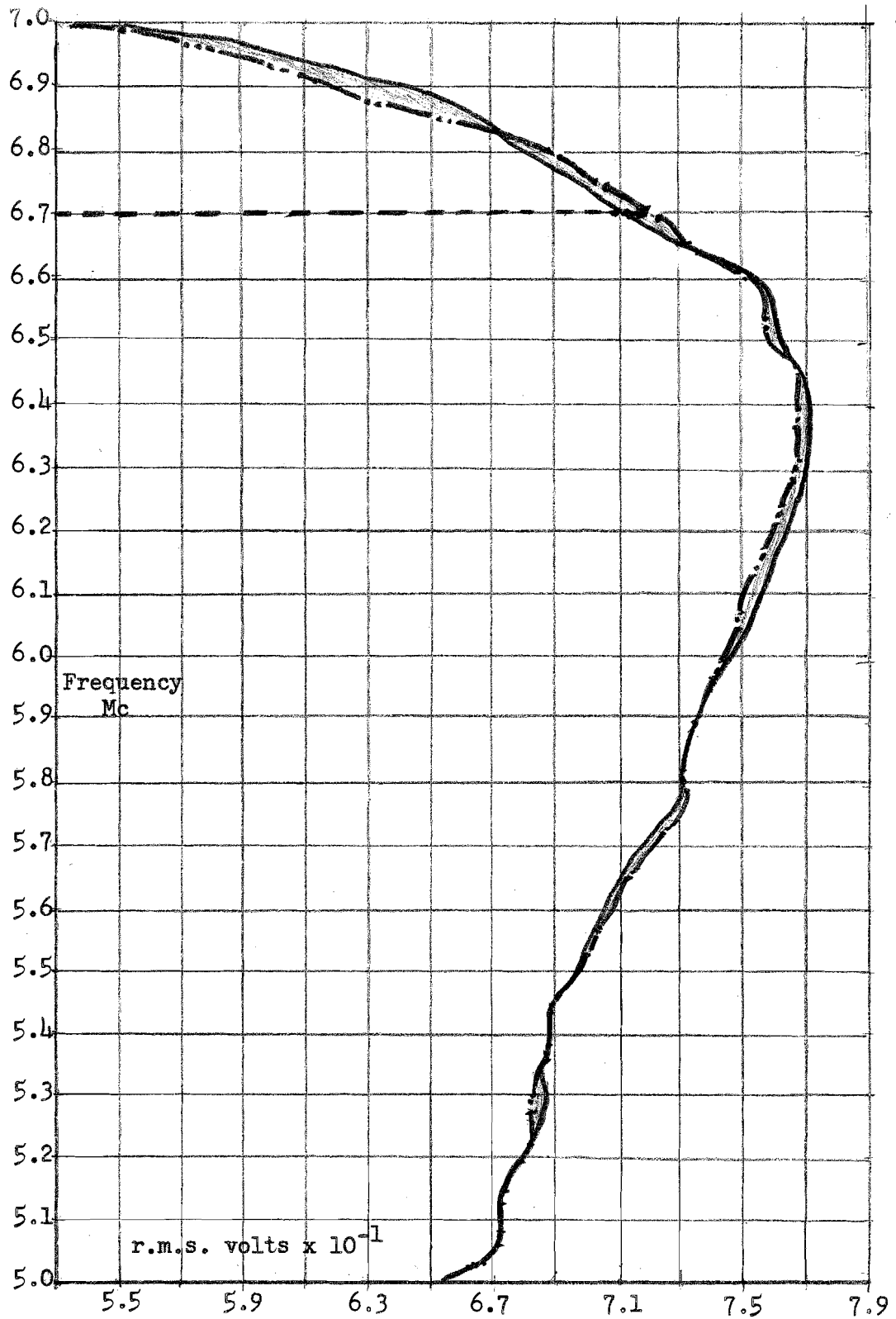


Figure 15.

Plot of frequency oscillator versus r.m.s. volts.

- indicates the test tube containing the sample.
 - - - indicates the test tube without the sample.

in Figure 15 may be attributed mainly to the difficulty in reading the r.m.s. voltmeter at a fast rate. Figure 16 shows the tracing of the above experiment obtained on an X-Y Recorder. There was no sign of resonance. In fact, this was true in the experimental setup and the reason for this will be explained later in this chapter.

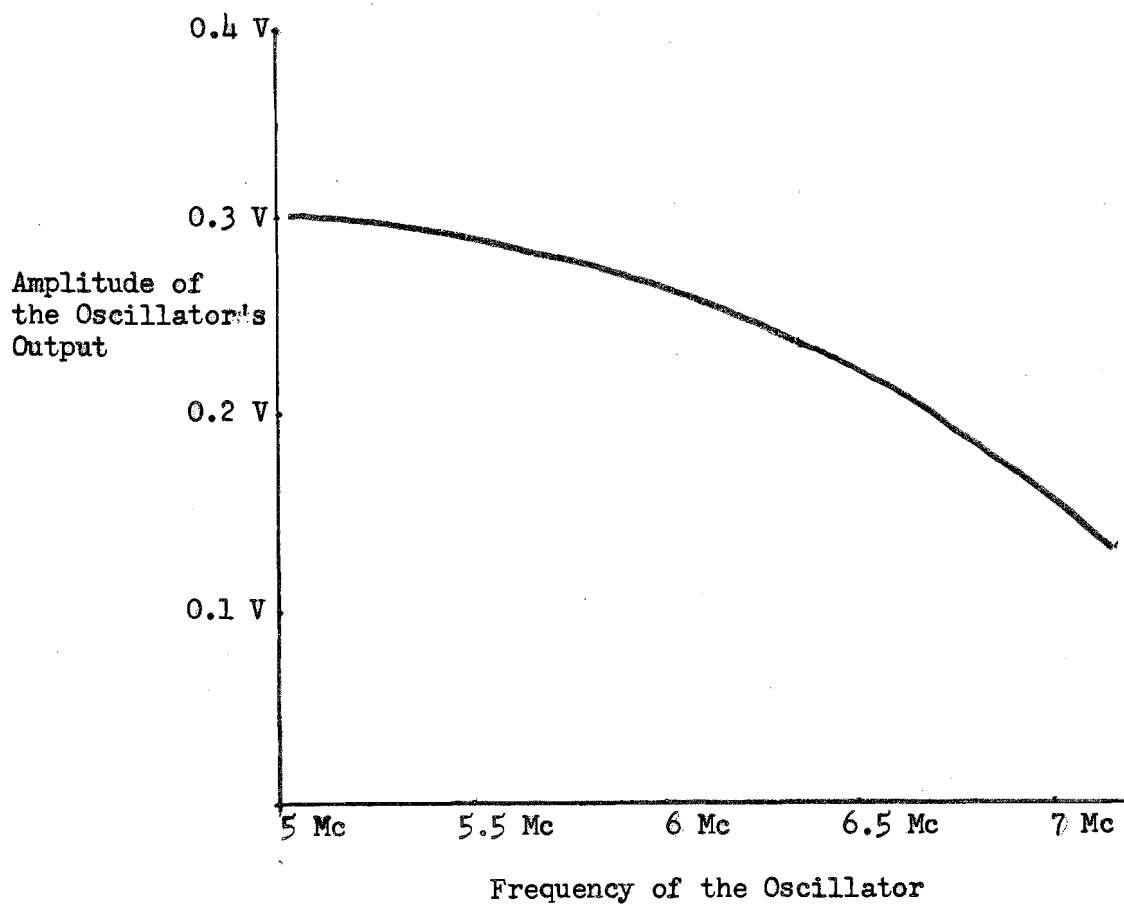


Figure 16.

Tracing of amplitude of the oscillator's output versus frequency of the oscillator, distilled water being the sample.

(Reproduced from the original for clarity. The ordinate reading is on an arbitrary scale 1-inch = 0.1 volts.)

Now, a solution was prepared by dissolving 0.4 grams of ferric nitrate in 100 cc. of distilled water. Three cc. of this solution in a test tube was placed in the pulsating magnetic field. It will be made clear later why ferric ions were used in the sample. The dual capacitor of the oscillator was fully meshed in by lifting the mechanical fixture of the synchronous motor (Figure 17). The X-Y Recorder was readjusted for a new set of readings (Figure 18).

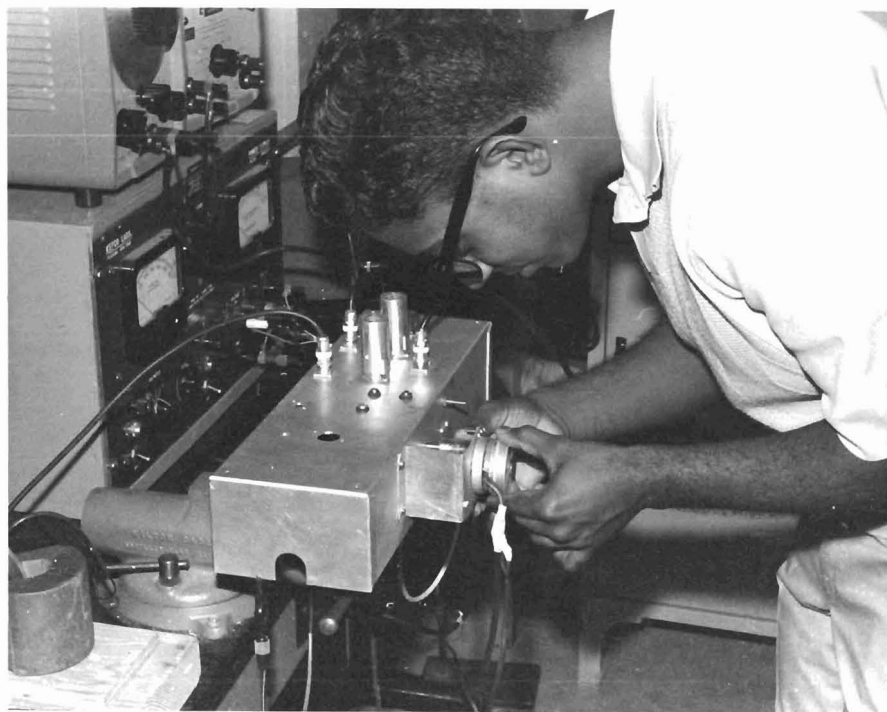


Figure 17.

Synchronous motor attached to the dual capacitor and the resetting of the capacitor by lifting the mechanical fixture.



Figure 18.

Readjustment of the X-Y Recorder.

Figure 19 shows the tracing of the above experiment obtained on the X-Y Recorder. A very interesting phenomenon can be observed in the tracing at 6.7 megacycle. This little peak may be due to the energy absorption at the resonance. But it is occurring at a magnetic field intensity of $\frac{6.7 \times 10^6}{4,240.5} = 1,580$ gauss. The main magnetic field strength was 1,560 gauss. The total magnetic field between

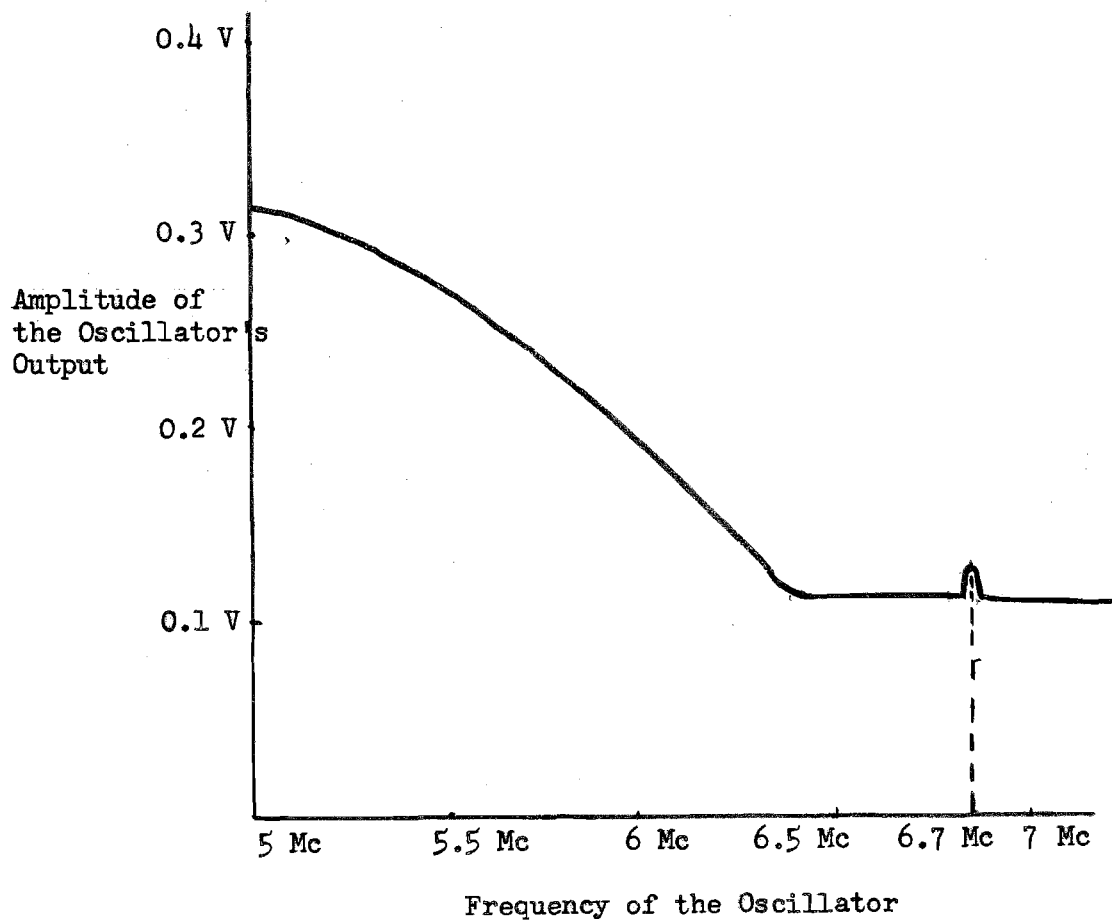


Figure 19.

Tracing of amplitude of the oscillator's output versus frequency of the oscillator, ferric nitrate dissolved in distilled water being the sample.

(Reproduced from the original for clarity. The ordinate reading is on an arbitrary scale 1-inch = 0.1 volts.)

the pole pieces can be expressed as $1,560 \pm A_1 \sin 376t$ where A_1 is the amplitude of the wave in the sweep coil. This means that $1,580 - 1,560 = 20$ gauss is due to the term $+A_1 \sin 376t$. Approximately 30 volts r.m.s. was applied to the Helmholtz coil.

Now, a soil sample was prepared in the ratio 10 percent water, 90 percent soil by volume, and the above experiment was repeated. It was very interesting to note that the tracing (Figure 20) obtained on the X-Y Recorder was almost identical with the one obtained using the ferric nitrate sample, with the previously noted peak missing.

New samples containing 50 percent and 90 percent of water were prepared and the above experiment was repeated. The tracing obtained in each case was almost identical to the one obtained using 10 percent water. Then, after noticing these tracings, it was speculated whether or not the little peak corresponding to 6.7 megacycle was really due to resonance. Hence, later, it was decided to use the actual N.M.R. analyzer.

Figures 22 and 23 show the spectra obtained using the Varian A-60 process analyzer of the physical science department. In this equipment, the magnet has a field of 14,092 gauss, which corresponds to 60 Mc. The sample was taken in a special kind of test tube 1/8-inch in diameter and 6 1/2-inches long. The sample volume was 3 cc. the following samples were taken, the ratio of the compound and water were on a volume basis.

- (i) Distilled water.
- (ia) 10 percent calcium oxide dissolved in 90 percent distilled water.

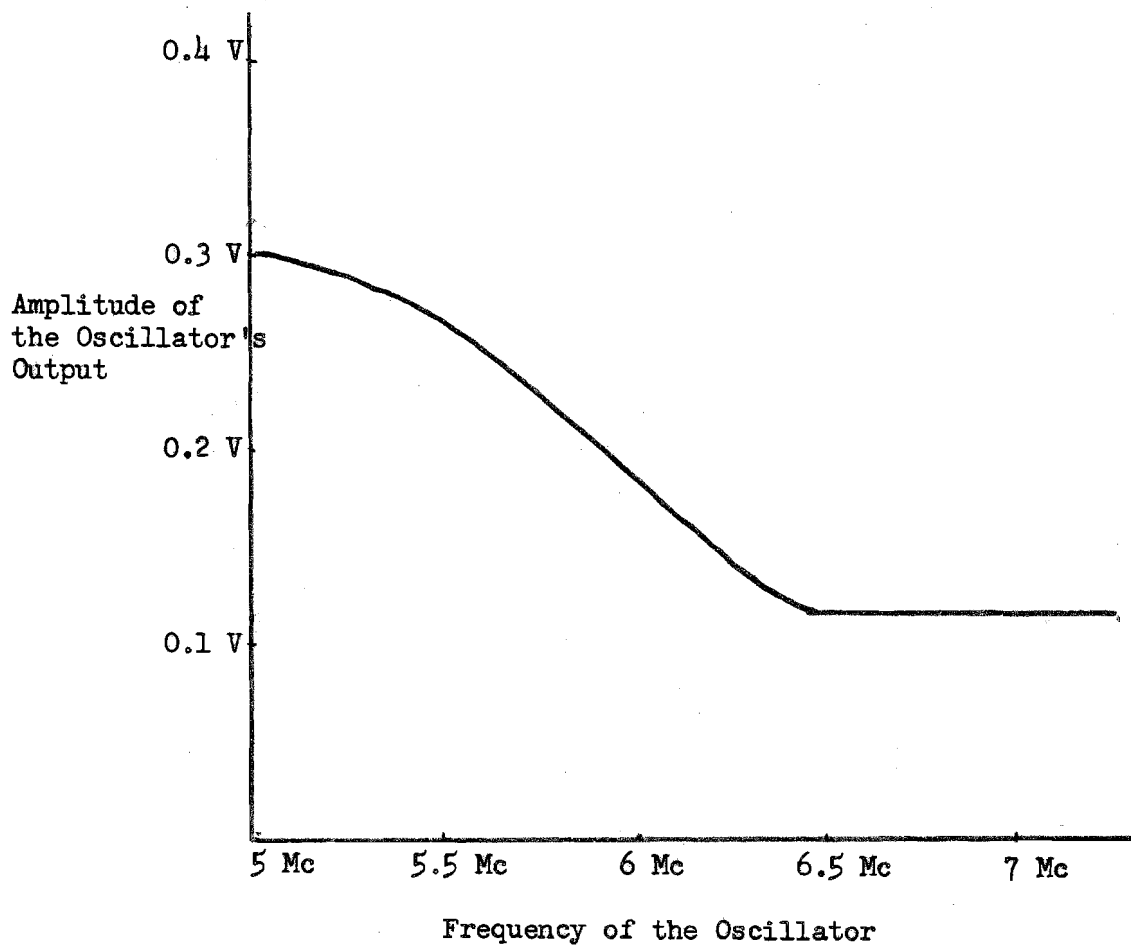


Figure 20.

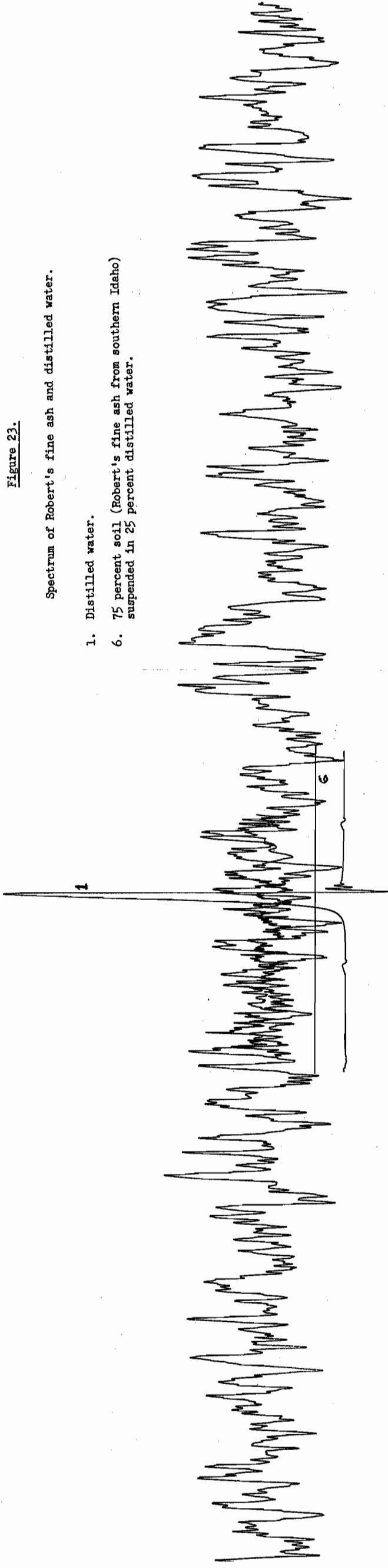
Tracing of the sample containing
10 percent water and 90 percent soil.

(Reproduced from the original for clarity. The ordinate reading is on an arbitrary scale 1-inch = 0.1 volts.)

Figure 23.

Spectrum of Robert's fine ash and distilled water.

- 1. Distilled water.
- 6. 75 percent soil (Robert's fine ash from southern Idaho) suspended in 25 percent distilled water.



- (ii) 10 percent magnesium sulfate dissolved in 90 percent distilled water.
- (iii) 10 percent ferric chloride dissolved in 90 percent distilled water.
- (iv) 10 percent soil (obtained just in front of the Physical Science Building) suspended in 90 percent distilled water.
- (v) 90 percent soil obtained just in front of the Physical Science Building) suspended in 10 percent distilled water.
- (vi) 75 percent soil (Robert's Fine Ash from southern Idaho) suspended in 25 percent distilled water.

The samples were kept spinning during the experiment. Spinning, as pointed out by Bloch,²⁵ will improve the effective field homogeneity. It is the practice of organic chemists to take the spectrum of Tetramethylsilane (TMS) first and use it as the reference compound. TMS is chemically inert, magnetically isotropic, and volatile (boiling point, 27° F).

An extremely interesting phenomenon was observed in the spectrum. In the case of distilled water, magnesium sulfate with distilled water and calcium oxide with distilled water, very good peaks were obtained which clearly indicates the energy absorption in resonance. But, in the case of the sample containing 90 percent soil and 10 percent distilled water, the spectrum was completely wiped out, and instead

approached a horizontal straight line. The same thing happened even in the case of the sample containing 75 percent Robert's Fine Ash and 25 percent distilled water. It was just impossible to reason out this "wiping" phenomenon, and there is not much work done on this phase of the problem. After making a thorough literature survey, an inference was drawn. Though this inference gives a very satisfactory explanation of the phenomenon, there may be additional unknown causes.

A set of elements known as "transition elements," defined as those which have partly filled electrons in the d or f shells, have certain general properties in common as shown below.²⁶

- (i) They are all metals.
- (ii) Because of partially filled shells, they form at least, some paramagnetic compounds.

The transition elements can be broadly divided into

- (i) The first transition series, and
- (ii) The second transition series.

The first transition series can be exemplified by the "anomalous" configurations of the atoms of chromium and copper.²⁷ They are shown in Table 3.

Table 3.

The first transition series.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

In the second transition series, the irregularities become more complex, as shown in Table 4.

Table 4.

The second transition series.

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

The number (for example, 4 in 4s) stands for the Principal Quantum Number, and the letter s in 4s corresponds to the values of L, the Azimuthal Quantum Number, in the following way.

$$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5$$

$$s \quad p \quad d \quad f \quad g \quad h$$

The first four letters are arbitrary, but following f they go in alphabetical order.

The presence of paramagnetic molecules (all the elements mentioned in the above tables) have an extremely interesting influence on the width of the spectra.²⁷ These paramagnetic molecules give rise to what is known as "paramagnetic broadening."²⁸ Wiping of the spectra in the case of 90 percent soil and 10 percent distilled water and also in the case of 75 percent Robert's Fine Ash and 25 percent distilled water can be explained only by the presence of paramagnetic molecules. These paramagnetic molecules give rise to paramagnetic broadening which results in that the spectrum becoming a horizontal line.

The same experiment was conducted again, but the proportion was changed to 10 percent soil and 90 percent distilled water. A second interesting phenomenon was observed in the spectrum of this sample. A peak was obtained which was slightly shifted to the right of the reference vertical axis. The height of the peak was far below the height of the peak due to distilled water. It can be very well inferred that because of the presence of just 10 percent soil the effect of paramagnetic molecules is less compared to the effect produced in the case of 75 percent and 90 percent soil, and hence the spectrum is not wiped out.

It is quite interesting to discuss why the peak is slightly shifted to the right. It is extremely difficult to say why this happens. Dyer²⁹ comments about the magnetic shielding of electrons. The net magnetic field $H_{\text{eff}} = H_0 - \sigma H_0$ where σH_0 is the field induced by electronic circulations. But in the case of 10 percent soil and 90 percent distilled water it can be argued that σH_0 somehow adds to H_0 which increases the effective magnetic field which causes the peak to be shifted to the right. The shift may be mainly due to the material present in the sample.

Another possible explanation may be the binding occurrence of hydrogen - soil constituents. Wu³⁰ comments about marked indication of interaction between the clay surface and the first layer of interfacial water showing a substantial reduction in the mobility of the water. Surface interaction with the second layer is clearly much less intense than with the first and N.M.R. data obtained by Wu provides an evidence of substantial interaction in water films many

molecular diameters thick. Although initially adsorbed water molecules are under constraints that reduce their freedom of motion, thermal agitation is still sufficient to permit complete exchange with deuterium oxide, indicating that this water retains the mobility of a fluid to a large degree. Zimmerman, et al.,³¹ conducted N.M.R. studies of water adsorbed by silica gel and have come to the same conclusions as above.

In the above discussion (90 percent soil and 10 percent distilled water; 75 percent Robert's Fine Ash and 25 percent distilled water) wiping of the spectrum was attributed to the presence of paramagnetic molecules. This result was very well justified by the spectrum obtained in the case of 10 percent ferric chloride (which is a paramagnetic molecule) dissolved in 90 percent distilled water. In this case the spectrum obtained was a mere horizontal line as shown in Figure 22.

That means even the presence of 10 percent ferric chloride is sufficient to wipe out the spectrum which places a rather low probability of success using this method of determining the moisture content in soils. It is quite certain that in soils more than one paramagnetic molecule will be present. Table 5³² shows the usual constituents of the soils.

Now, it will be made clear why ferric nitrate was added in the experiment conducted in the experimental setup; ferric nitrate, which contains a paramagnetic molecule, helps to get a visible spectrum even in a very crude setup, such as the one built. This also demonstrates that no visible spectrum will be seen without the

addition of ferric nitrate to distilled water. In the case of the Varian A-60, N.M.R. spectrometer, the effect of paramagnetic molecules is strong enough to wipe out the entire spectrum.

Table 5.

Content of constituents of soils by weight.

Constituent	Igneous Rocks, % (Average)	Barnes Loam, % (South Dakota)	Caribou Loam, % (Maine)	Cecil Sandy Clay Loam, % (North Carolina)	Colum- biana Clay, % (Costa Rica)
SiO ₂	59.1	69.3	57.5	74.7	19.8
Al ₂ O ₃	15.3	11.4	7.8	12.3	37.1
Fe ₂ O ₃ *	7.3	3.8	2.5	4.9	15.6
TiO ₂ *	1.0	0.5	0.7	1.3	2.0
MnO*	0.1	0.2	0.2	0.3	0.3
CaO	5.1	1.6	1.2	0.2	0.2
MgO	3.5	0.9	0.6	0.1	0.5
K ₂ O	3.1	1.8	0.9	0.6	0.1
Na ₂ O	3.8	1.1	1.0	0.2	0.2
P ₂ O ₅	0.3	0.2	0.2	0.2	0.3
SO ₃	0.1	0.1	0.3	—	0.2
Ignition loss	1.2	9.5	27.2	7.1	24.1
Organic matter	—	6.0	25.3	2.4	6.0
Nitrogen	—	—	0.9	—	—

*Paramagnetic molecules

The following spectra were obtained using The Atomic Laboratory's - Combination Nuclear Magnetic and Electron Spin Resonance Instrument of the physics department. The equipment consists of an electromagnet having 4-inches diameter pole pieces and an air gap width of $3/4$ -inch. All the spectra were obtained in a magnetic field intensity of 17,200 gauss. This equipment was far better than the experimental setup though less adequate than the Varian A-60 in performance.

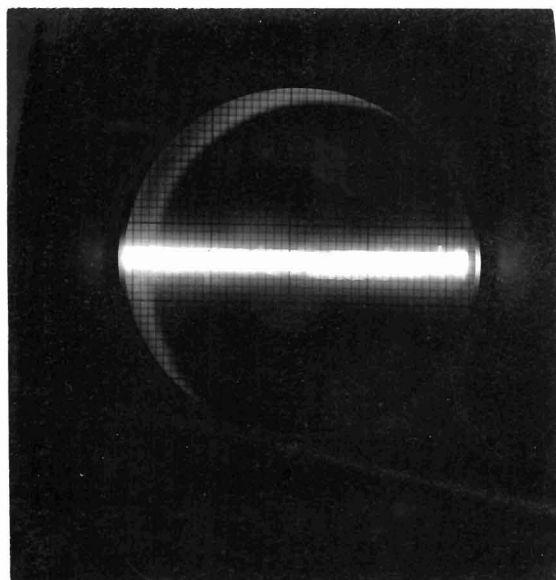


Figure 24.

Spectrum of distilled water,
no visible peak is seen.

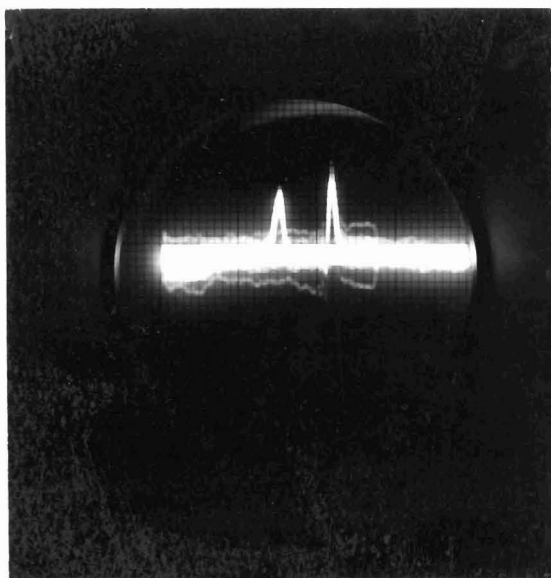


Figure 25.

Spectrum of ferric nitrate, neat peak is obtained. The two peaks are due to the manipulation of the phase shifter.



Figure 26.

Spectrum of copper sulphate, the peaks can be adjusted into a single one with the help of the phase shifter.

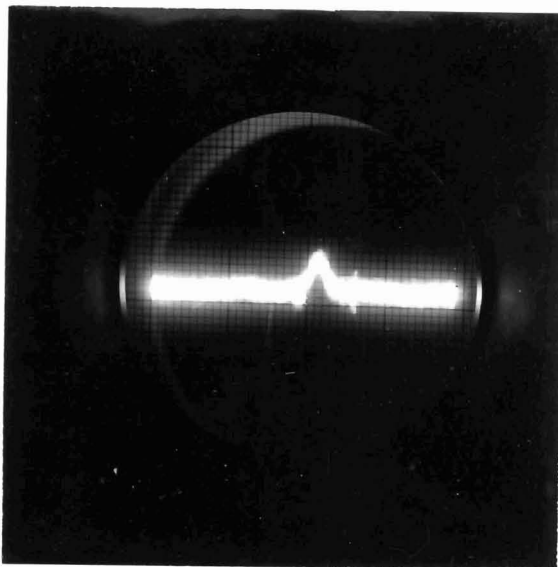


Figure 27.

Spectrum due to ferric chloride.

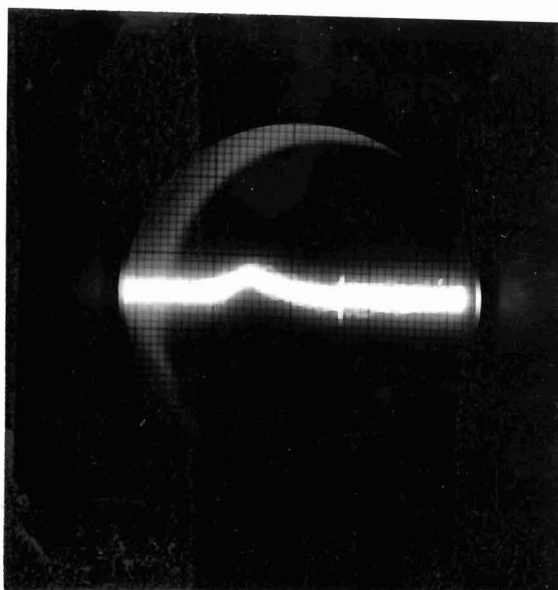


Figure 28.

Spectrum of 10 percent magnesium sulphate
dissolved in 90 percent distilled water.

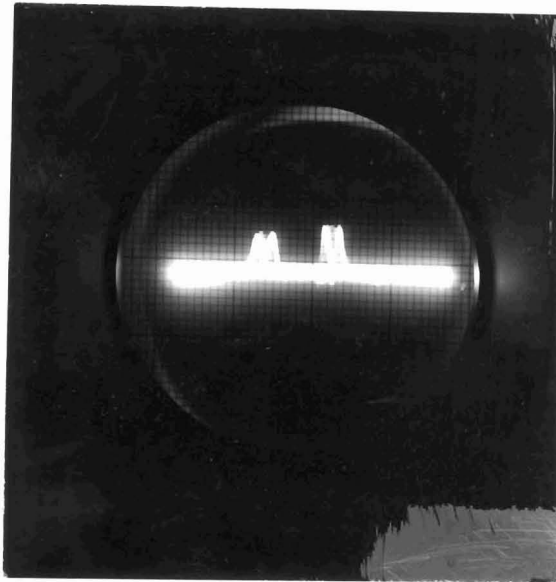


Figure 29.

Spectrum of a rubber band.

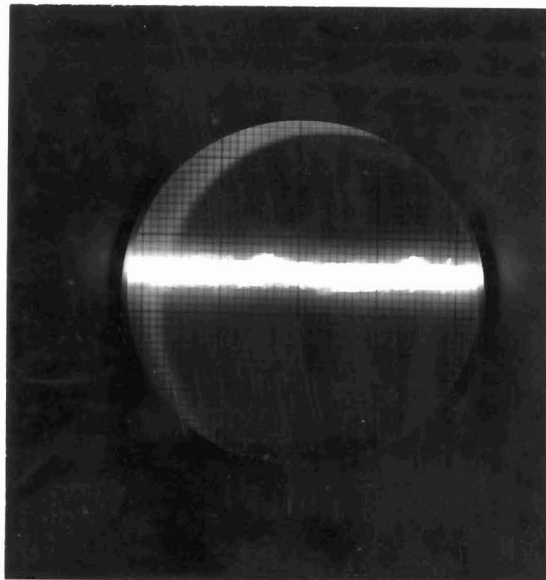


Figure 30.

Spectrum of 90 percent soil (obtained in front of the Physical Science Building) and 10 percent distilled water. The peak is due to the presence of paramagnetic molecules. The two peaks can be adjusted to a single one by manipulating the phase shifter.

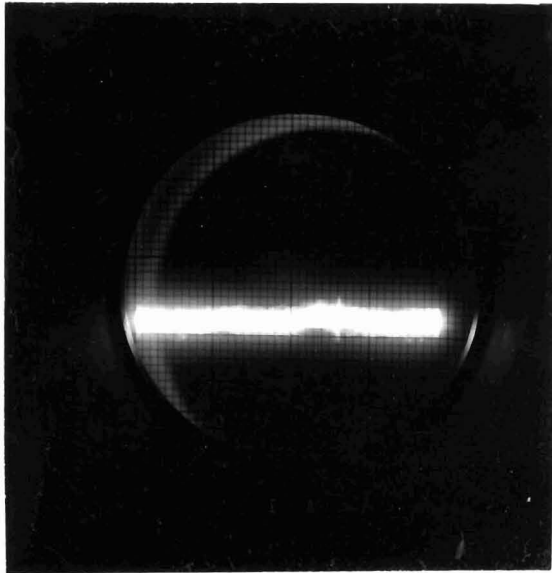


Figure 31.

Spectrum of 25 percent soil (Robert's fine ash) and 75 percent water. The little peak may be due to the paramagnetic molecules.

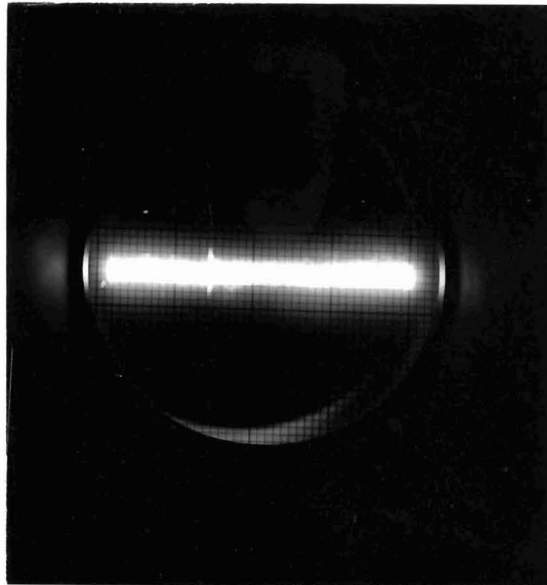


Figure 32.

Spectrum of 10 percent soil (Robert's fine ash) and 90 percent distilled water. No peak is seen and this may be due to deficiency of paramagnetic molecules present.

CHAPTER VIII

CONCLUSIONS

The N.M.R. approach has significant advantages, such as speed, non-destructiveness of the sample, minimum sample preparation, and versatility for those sample appropriate to its use. Even with an instrument as sophisticated as the Varian A-60, the measurement of soil moisture content appears hopeless. This is mainly because of paramagnetic molecules present in the soil which give rise to a paramagnetic broadening effect which wipes out the complete spectrum.

In some places water that is obtained from the well itself contains paramagnetic molecules. For example, well #3, pump house raw water³⁴ of the University of Idaho contains iron of 0.1 parts per million of water. Also this water contains totally dissolved substances of 140 parts per million of water. These totally dissolved substances may also contain paramagnetic molecules. Hence the raw water itself may give rise to paramagnetic broadening effect. There may, in addition, be other effects of which the author has no knowledge.

The paramagnetic molecules can be removed from the sample by using some reacting agents. But, by doing so, there will be some addition of water to the sample. Thus, aside from other unknown effects, the spectrum obtained would indicate the soil moisture and the extra moisture added through the reacting agents. According to the investigation made so far, at this stage it may be concluded that the N.M.R. approach to the determination of soil moisture content may not be feasible but may constitute a useful tool in the study of soil moisture energy relations.

NOMENCLATURE

N.M.R. = Nuclear Magnetic Resonance.

m = Mass of the Orbiting Electron.

m_p = Mass of the Orbiting Proton.

v = Velocity of the Orbiting Electron (or Proton).

μ = Magnetic Moment of the Electron (or Proton).

t = Time.

Δt = A Small Increment of Time in Time t .

J = Angular Momentum of the Electron (or Proton)

at a Time t .

J^1 = Angular Momentum of the Electron (or Proton)

at a Time $(t + \Delta t)$.

r = The Radius of the Circular Orbit.

$+q_e$ = The Charge of the Proton.

$-q_e$ = The Charge of the Electron.

f = The Frequency of the Supply.

Q = The Quality Factor of the Resonance Circuit.

f_q = The Quench Frequency.

g = Lande's g -Factor (or, When Applied to the Nucleus,
the Nuclear g -Factor).

H_0 = The Strength of the Uniform Magnetic Field.

T = Torque.

Θ = The Angle Subtended by J^1 with Respect to the Direction
of the Magnetic Field H_0 .

$\Delta\Theta$ = The Change of the Angle Θ from J to J^1 .

ω_p = The Angular Velocity of the Precession.

- P_{pf} = The Proton Precession Frequency.
 E_1 = Energy Corresponding to the Proton's Lower Level.
 E_2 = Energy Corresponding to the Proton's Upper Level.
 ΔU = The Difference in Energy between E_1 and E_2 .
 h = Plank's Universal Radiation Constant.
 \hbar = The Modified Plank's Constant.
 Z = The Atomic Number of a Nucleus.
 A = The Atomic Mass Number of a Nucleus.
 I = The Nuclear Spin Number.
 N, N = The North Poles of the Magnetron Magnets.
 B = The Magnetic Field Strength of the Electromagnet.
 N_1 = The Number of Nuclei (with Spin $1/2$).
 A_1 = The Approximate Incremental Area under the Output Envelope.
 V_m = The Limiting rf Level.
 T_1 = The Time Constant for rf Buildup.
 V_1 = The Total rf Voltages, (Including Noise Components) Impressed on the Circuit at the Start of the Buildup in the Absence of the Sample.
 V_2 = The Total rf Voltages, (Including Noise Components) Impressed on the Circuit at the Start of the Buildup in the Presence of the Sample.
 V_s = The Nuclear Signal Strength ($V_2 - V_1$).
 G = The Amplification of the Modulation Products.

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