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Overhauser Magnetometers For Measurement of the Earth's Magnetic Field by Dr. Ivan Hrvoic, President, GEM Systems Inc.

Introduction

Proton magnetometers are an excellent example of nuclear physics phenomena brought into and exploited in our normal, macroscopic world. Relatively easy and efficient manipulation of nuclear precession phenomena is possible and very often done even without proper understanding of the underlying physics.

Overhauser effect is based on the same nuclear physics phenomena, although marginally more complex and again macroscopically engineered to improve on "simple" proton precession effects in order to achieve much better precession signals from smaller sensors and using less power. Since the polarization of protons (generation of proton precession signal) does not require strong static magnetic fields but uses strong radio frequency magnetic fields transparent to protons, measurements can be done concurrently with it. Furthermore, in the ultimate triumph of the method one can produce a stationary, non-decaying proton precession signal, in vague similarity to alkali vapour magnetometers using simple feedback techniques.

Overhauser magnetometers are unique in:

- Keeping highest absolute accuracy of proton precession (this is primary standard for measurement of magnetic field in general)
- Improving greatly on sensitivities of proton magnetometers and enabling the highest accuracy to be practically achieved in weak magnetic fields such as the Earth's.
- Allowing for continuous, uninterrupted measurement of the magnetic field of the Earth with sufficient speeds for any airborne work of study of fast phenomena occurring in the Earth's magnetic field.

Let us now examine underlying physics of the two methods.

Basics of Nuclear Resonance

Some sub-atomic particles possess spin associated with mechanical moment \mathbf{p} and magnetic moment $\boldsymbol{\mu}$ related by

$$\boldsymbol{\mu} = \gamma_n \mathbf{p}$$

where

$$|\mathbf{p}| = I \hbar$$

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l is a quantum number characteristic for each particle — $\hbar = h / 2\pi$, h is Planck's constant $h = 6.62 \cdot 10^{-27}$ erg.sec. γ_n depends on the ratio of charge and mass of the particle. Protons and fluorine have the highest and second highest nuclear gyromagnetic constants respectively:

$$\gamma_p / 2\pi = 4257.60 \pm 0.03 \text{ Hz / G}$$

$$\gamma_f / 2\pi = 4005.5 \text{ Hz / G}$$

Due to their smaller mass the electrons have much higher gyromagnetic constants than nuclei. For a free, unpaired electron

$$\gamma_e / 2\pi = 2.80246 \text{ MHz / G}$$

Generally, all magnetic dipoles precess in the ambient magnetic field H around its direction by an angular frequency ω_n :

$$\rightarrow \rightarrow$$

$$\omega_n = \gamma_n H$$

Coupling energy of the magnetic moment and the applied magnetic field equals their scalar product:

$$\rightarrow \rightarrow$$

$$E = - \mu \cdot H = - \mu H \cos \Theta$$

Θ is an angle between the two vectors. Possible values of Θ are determined by the quantum number l . For protons and electrons, $l = 1/2$. There are $2l + 1$ allowed states or energy levels, i.e., for $l = 1/2$ there are two allowed energy levels, and $\Theta = \pm 45^\circ$. Quantum transitions between the two energy levels, are introduced by a thermal coupling with the "lattice". Leap to the higher level is accompanied by absorption of energy; fall to the lower level by emission of the same amount of energy.

In thermal equilibrium populations of the two energy levels are proportional to $\exp(-E / kT)$, where $k = 1.38 \cdot 10^{-23}$ J / K is Boltzman constant, T absolute temperature. Lower energy level is more populated than the upper one. The difference is miniscule, though, E / kT being very small. Nevertheless, due to the difference in population of the energy levels, there is a net nuclear or electronic magnetization of the sensor, collinear with the applied magnetic field

$$\rightarrow \quad N \overline{\gamma^2 h^2} \rightarrow$$

$$M = \chi_o H = \dots H$$

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4kT

N is a number of particles in the observed sample, χ_o a nuclear susceptibility $\chi_o = 3 \cdot 10^{-10}$ c.g.s. units, for protons, a very small quantity.

→
If \vec{M} gets deflected from the direction of the magnetic field, it will start precessing around magnetic field direction with the angular precession frequency ω_o spiraling in the same time towards the direction of the magnetic field. There are two time constants to govern this behaviour: T_1 - "Longitudinal" and T_2 - "Transversal" constants. T_1 and T_2 can be considered the same and of the order of one second in most liquid samples.

Classical proton magnetometer is based on the following:

- An electrical coil containing a liquid sample rich in protons is placed at right angles to the ambient magnetic field. Strong current is let through the coil creating a strong magnetic field H_p . This is the "polarization" field.
- Since $M_o = \chi_o H_p$, relatively strong proton magnetization of the sample is created. The increase of M_o towards its equilibrium value for H_p is exponential with the time constant T_1 (T_1 can be as long as several seconds depending on the sort of liquid, its viscosity etc.)
- Upon sudden removal of the polarizing field, magnetization M_o finds itself in the plane of precession.
- Precessing M_o induces a voltage in the coil and all that is now needed is to amplify the voltage and precisely measure its frequency. The described method allows for precisions of up to 1 part per million depending on a number of factors, such as polarizing current, type of liquid, sensor volume, etc.

Overhauser Effect of Dynamic Polarization

The essence of classical proton magnetometers is:

- To increase the magnetization of the liquid sample, i.e., to increase the difference of proton spin populations of the two energy levels by applying strong "polarizing field"
- To deflect the proton magnetization vector into the plane of precession around the ambient magnetic field to be measured.
- To detect the signal generated by precessing proton magnetization, to measure its frequency and convert it into magnetic field units.

In the Overhauser effect magnetometers, the goals are exactly the same, but the means are different.

If we add to the sensor liquid some free electrons that have “unpaired” spins and thus magnetic moments, the electrons will in general couple magnetically with the protons producing four energy level system shown in figure 1.

Transitions between levels 1 and 3 and 2 and 4 now involve only proton “flips” while transitions 1-2 and 3-4 involve only electrons.

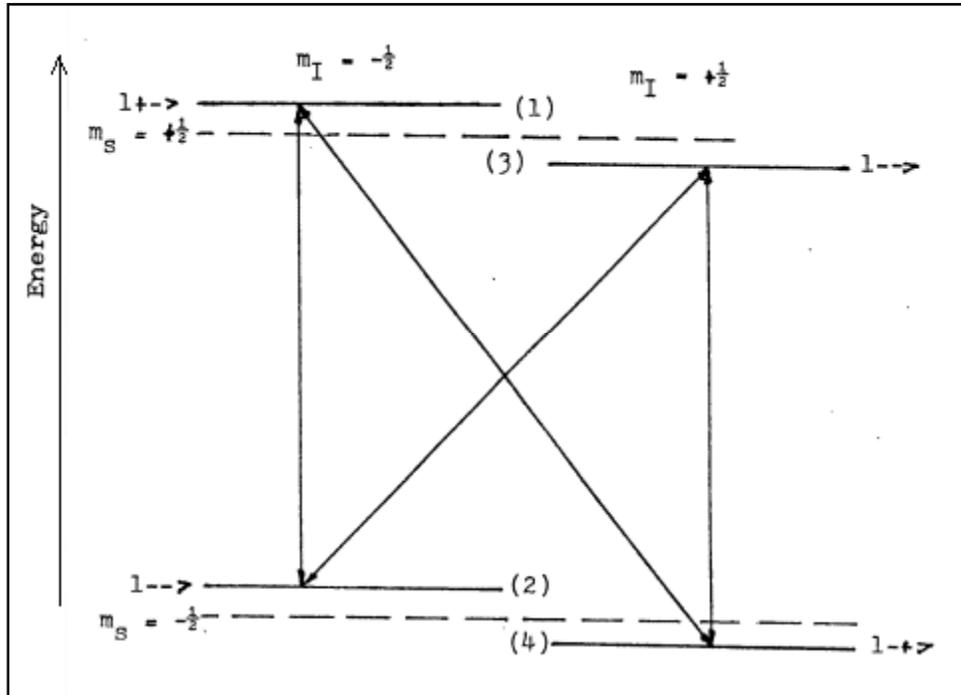


Figure 1. XXX

Transitions 1-4 and 2-3 involve simultaneous flips of protons and electrons.

In various samples and under different conditions, all combinations of the energy level transitions can exist. Overhauser effect deals with the combined mutual transitions 1-4 and 2-3.

Let us examine various mechanisms of coupling between protons and electrons. There are three possible ways of coupling between the two spin assemblies:

- Strong scalar coupling that could not be explained macroscopically; it is due to the fact that the electron with the unpaired spin “dwells” in the vicinity of a nucleus. The result is a hyperfine splitting of the electron spectral lines. This type of coupling happens between the electron and some nucleus of the same molecule (the molecule of the free radical). In nitroxide free radicals, the electron dwells in a local magnetic field of nitrogen nucleus and,



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besides hyperfine splitting; its resonant frequency is offset by the local field of the nitrogen of some 16 gauss.

- Weak scalar coupling between electrons of the free radical and protons of the “solvent”. When weak scalar coupling is present, molecules of the solvent (proton rich liquid of the sample) are in “contact” with the paramagnetic molecule of the free radical for a short but non-negligible time. The coupled system has four energy levels as shown in figure 2.1, i.e., $|++\rangle$, $|+-\rangle$, $| - + \rangle$, $|--\rangle$; the first sign refers to electrons, the second to protons. Weak scalar coupling emphasizes transition 1-4; all other transitions are much less probable. In that case

$$N_+ n_- W(+ - \rightarrow - +) = N_- n_+ W(- + \rightarrow + -) \rightarrow$$

Where N_+ and n_+ are numbers of protons and electrons at $+ \frac{1}{2}$ energy level and N_- and n_- the same on $- \frac{1}{2}$ energy level. $W(+ - \rightarrow - +)$ and $W(- + \rightarrow + -)$ are probabilities of transitions from $|+-\rangle$ to $| - + \rangle$ level and vice versa. Due to thermal equilibrium, they follow the Boltzman law:

$$W(+ - \rightarrow - +) = \frac{\exp[-(E_{+-} - E_{-+})/kT]}{\exp[-(E_{+-} - E_{-+})/kT] + 1} = \exp[-h(\omega_s - \omega_I)/kT]$$

$$W(- + \rightarrow + -) \rightarrow$$

Subscripts S and I refer to electrons and protons respectively.

If we now saturate electron spectral line, i.e., transitions 1-2 and 3-4, then

$$n_+ = n_-$$

and we end up with an increased difference in the populations of proton spin energy levels:

$$N_+ = \frac{\exp[-h(\omega_s - \omega_I)/kT]}{\exp[-h(\omega_s - \omega_I)/kT] + 1} = \frac{1}{1 + \exp[h(\omega_s - \omega_I)/kT]}$$

While in the absence of electrons, this would be:

$$N_+ = \frac{\exp[-h\omega_I/kT]}{\exp[-h\omega_I/kT] + 1} = \frac{1}{1 + \exp[h\omega_I/kT]}$$

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Since electron resonant frequency ω_s exceeds proton frequency ω_1 by about 660 times, we could theoretically end up with so much increased proton polarization, i.e., magnetization M_o .

Similar considerations for dipole-dipole interaction (which can be represented macroscopically considering two magnetic dipoles in thermal motion) reveal increased proton polarization by 330 times and reversed, i.e., higher energy level gets more populated. This setup could then result in emission of energy or so-called MASER effect. We mention it here only as a curiosity as it has no practical value.

Full theoretical increase of proton polarization cannot be achieved for several reasons; one being that the other paths of relaxation are present.

Further improvement in Overhauser effect is achieved by free radicals where electrons exhibit strong scalar coupling with the nucleus of nitrogen (nitroxide free radicals). The effect of this interaction is that the electron dwells in a local magnetic field of about 16 gauss, i.e., its resonant frequency is not 1.4 MHz (in the Earth's magnetic field of 0.5G) but more than 60 MHz. ω_s is therefore increased and a theoretical increase of proton polarization is several thousand times instead of 660, about 5000 times being practically achievable.

Further advantage of this higher resonant frequency is that the RF saturating frequency can stay constant for the whole Earth's magnetic field range.

Nitroxide free radicals of interest are perfectly stable in solutions of neutral liquids such as methanol and similar.

Detection Methods

Classical proton magnetometers have the polarization and the deflection into the plane of precession of the increased proton magnetization solved simultaneously. The coils creating polarizing field are at right angles to the ambient field to be measured; when polarization stops, the magnetic vector finds itself in the plane of precession.

The Overhauser effect produces proton polarization collinear with magnetic field and non-precessing. Now we have a choice of methods to produce the proton precession signal. We can use so-called 90° pulse, a short, sub-millisecond pulse, to deflect the increased proton magnetization into the plane of precession. After the deflection pulse, the frequency measurement is done similarly as in the classical proton precession magnetometers. And, while the existing deflected magnetization is precessing and being measured, a new one is being created by the Overhauser effect.

We do not need to wait, but after the frequency determination has been completed, we can apply another 90° pulse and continue the measurements faster than would be possible with the classical proton magnetometer. This principle is used in a number of GEM Systems magnetometers (solar powered GSM-9, GSM-10 and GSM-19 memory magnetometers and GSM-90 observatory magnetometer).

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Creation of continuous instead of decaying proton precession is also possible. If we apply to the sensor a weak “excitation” magnetic field, rotating in the plane of precession, this field will slightly deflect the proton magnetization from the direction of the ambient field. The deflected magnetization will precess with the frequency identical to the excitation field frequency, as long as the latter is within limits of proton resonance line width.

Continuous creation of proton precession signal is not, strictly speaking, absolute standard for the measurement of magnetic field, due to finite width of the spectral line. Proton spectral lines can be as narrow as 2 nT (nano Tesla or gamma) though, and with special care one can limit inaccuracies to a small fraction of a nT, for example 20 pT (pico Tesla) or similar values.

Two continuous methods are worth mentioning:

- A passive method, where a voltage controlled oscillator is locked to the dispersion component of the proton spectral line. The VCO generates a weak magnetic field of the same frequency as the precession signal (the excitation field) to deflect proton magnetization into the plane of precession. Precession signal is detected and used to lock the VCO to its frequency. The VCO frequency is then precisely measured. The method is called Dispersion Method (2).

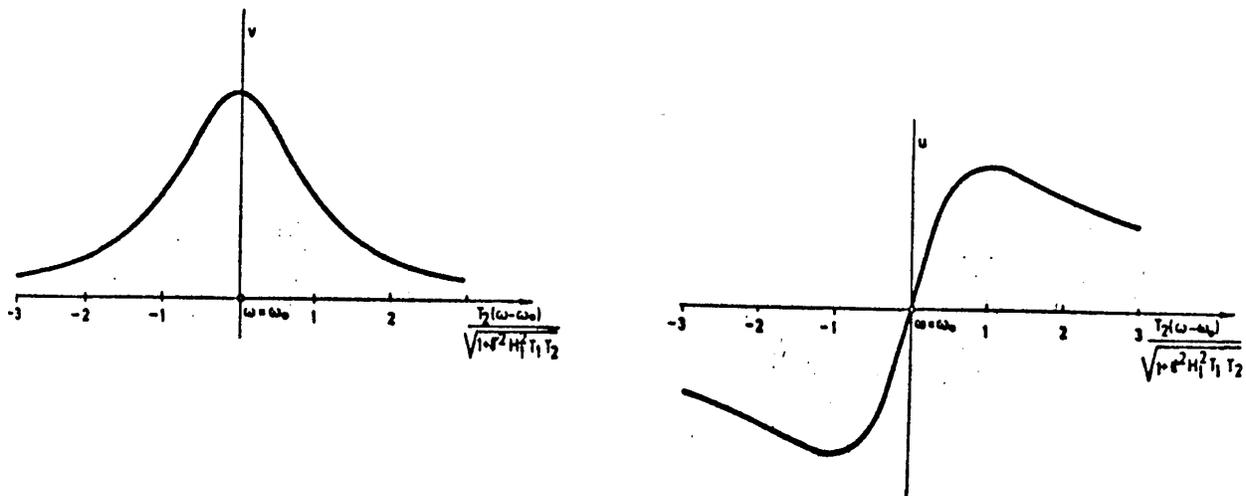


Figure 3.1

Absorption and dispersion components of the nuclear magnetic resonance spectral line

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- A self-oscillating system can be made by amplifying proton precession signal and then feeding it back to the coils to produce the excitation magnetic field. (The sensor coils are operated in a bridge mode for both of the above methods). We call the apparatus operating in the latter manner a Proton Oscillator. Major advantages over the Dispersion Method are simplicity and great speed in following magnetic field changes.

Proton Oscillator

We have developed the Proton Oscillator with the sensor of about 1 litre of proton rich liquid. Relatively simple electronics console provides for the Overhauser effect by applying a sufficient RF magnetic field of proper frequency and intensity to the sensor (to saturate EPR line of the free radical) and ensuring proper frequency feedback to create a steady precession signal. A computerized processor measures the frequency and converts it into magnetic field units.

We have extensively tested the Proton Oscillator Model GSM-11A in stationary and airborne installations. Noise levels vary with the speed of operation. Due to diurnal variations, proper assessment of the instrument should be done in a gradiometer configuration. We have flown a GSM-11A gradiometer in helicopter installations, and the results show the noise below 0.05 nT for two readings per second and about 0.1 nT for five readings per second. With the sensor stationary, and at one reading per second a noise “envelope” of 0.01 nT has been achieved. Some traces are shown on the following pages in the Appendix.

Pulsed Methods

Best efforts in pulsed Overhauser methods have so far produced noise standard deviations of about 0.01 nT_{rms} from sensors of 0.15 liters of proton rich liquids and measuring times of one second. Pulsed Overhauser magnetometers usually have tuned detection circuits in order to minimize influence of preamplifier noise.

Conclusion

The Overhauser Effect is a superior method of generating proton precession signals. Advantages are:

- A possibility of creating a steady proton precession signal with the consequent true average measurement of the magnetic field instead of a sampling, alternated by polarization intervals;
- Greatly reduced power. For example, the full blown Proton Oscillator needs only 5W of RF power to generate the signal superior to the nearest competing classical proton precession magnetometer where between 100 and 200 W of DC power is needed. Or, pulsed Overhauser magnetometer of 0.1 nT resolution may need only about 1 W_s of energy per reading compared with 8-80 W_s for commercially available classical proton precession magnetometers; and several watts for optically pumped magnetometers.

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- Faster rate of readings, since no time needs to be wasted for polarization;
- Smaller and lighter sensors for the same or superior performance.

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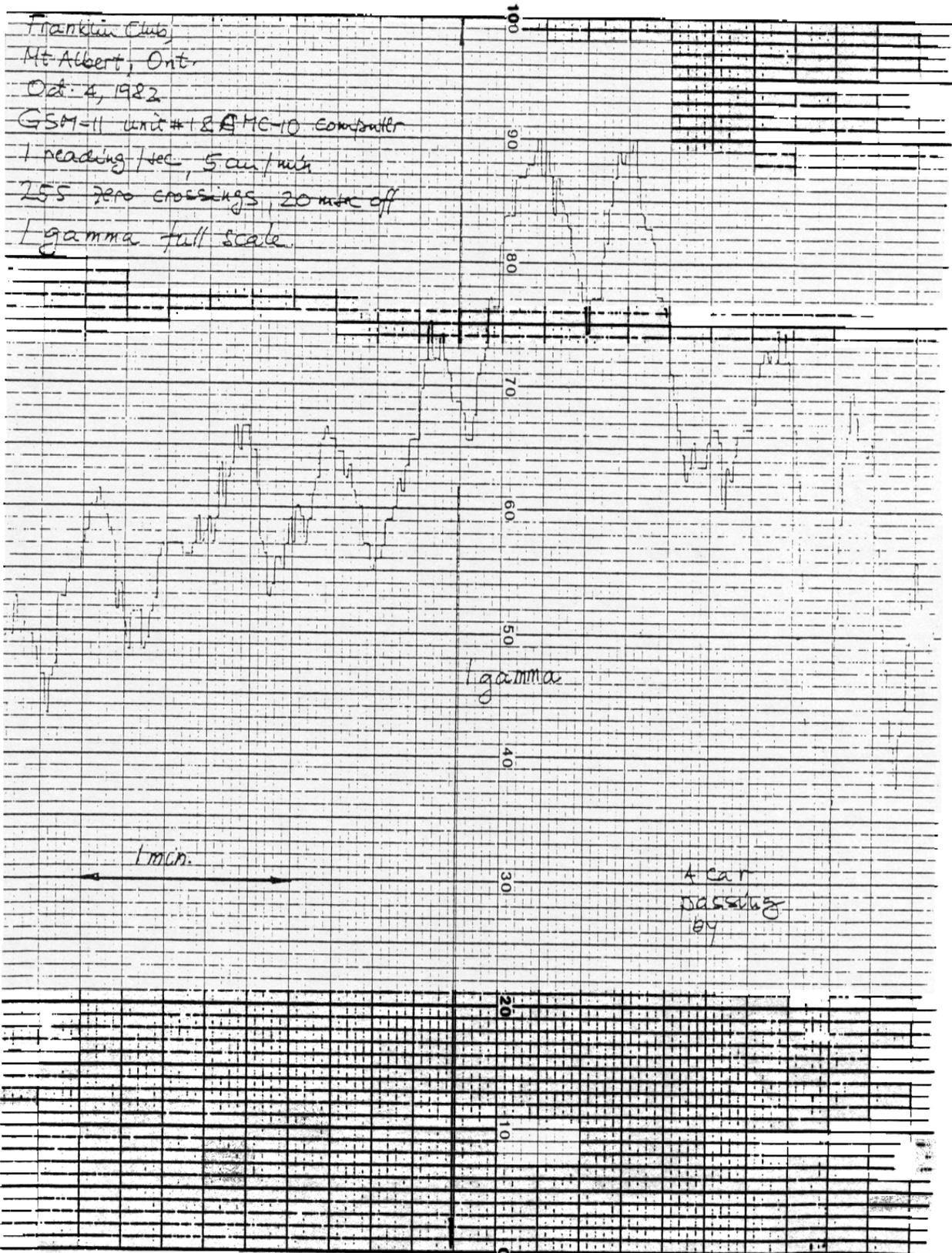
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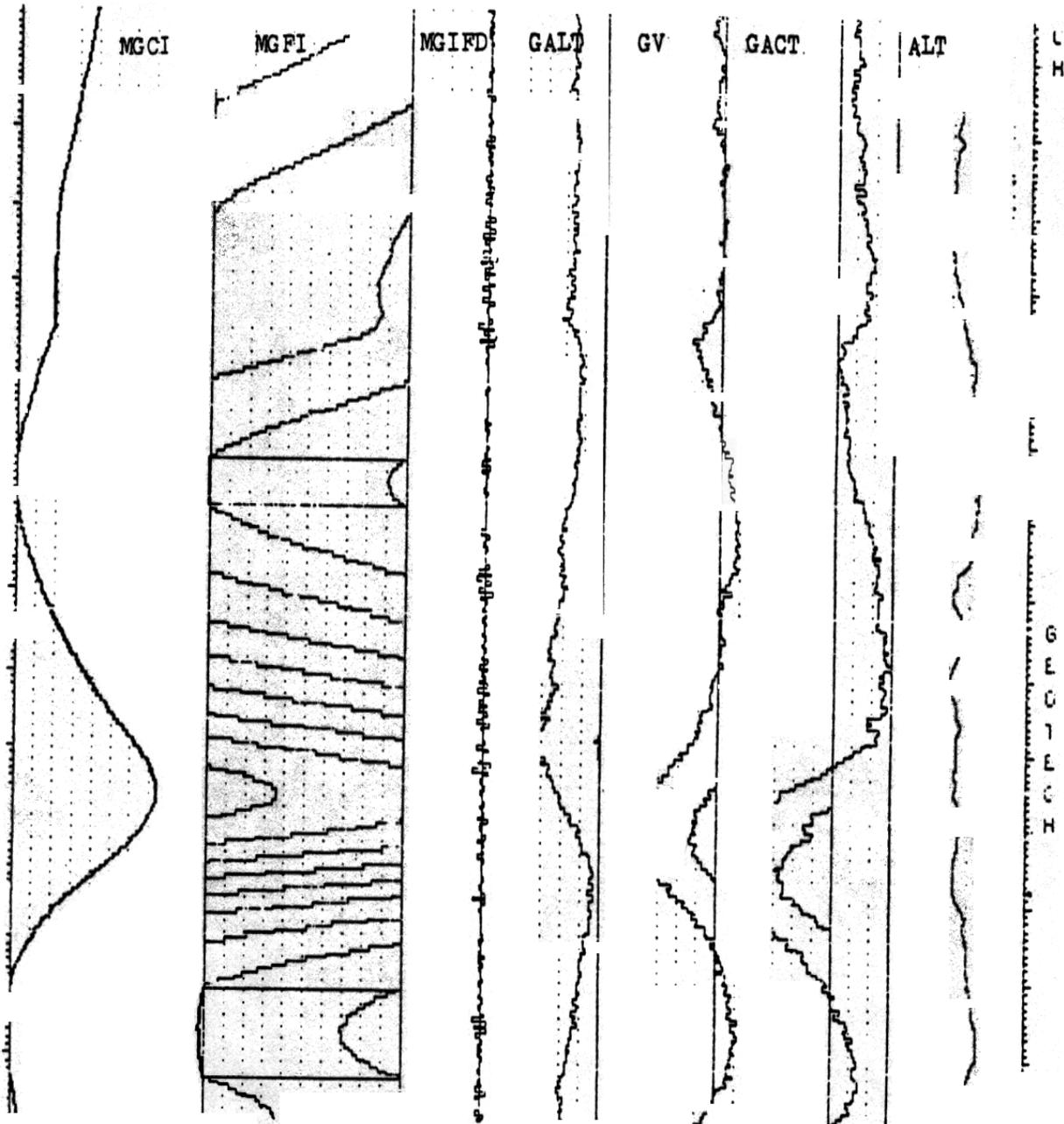
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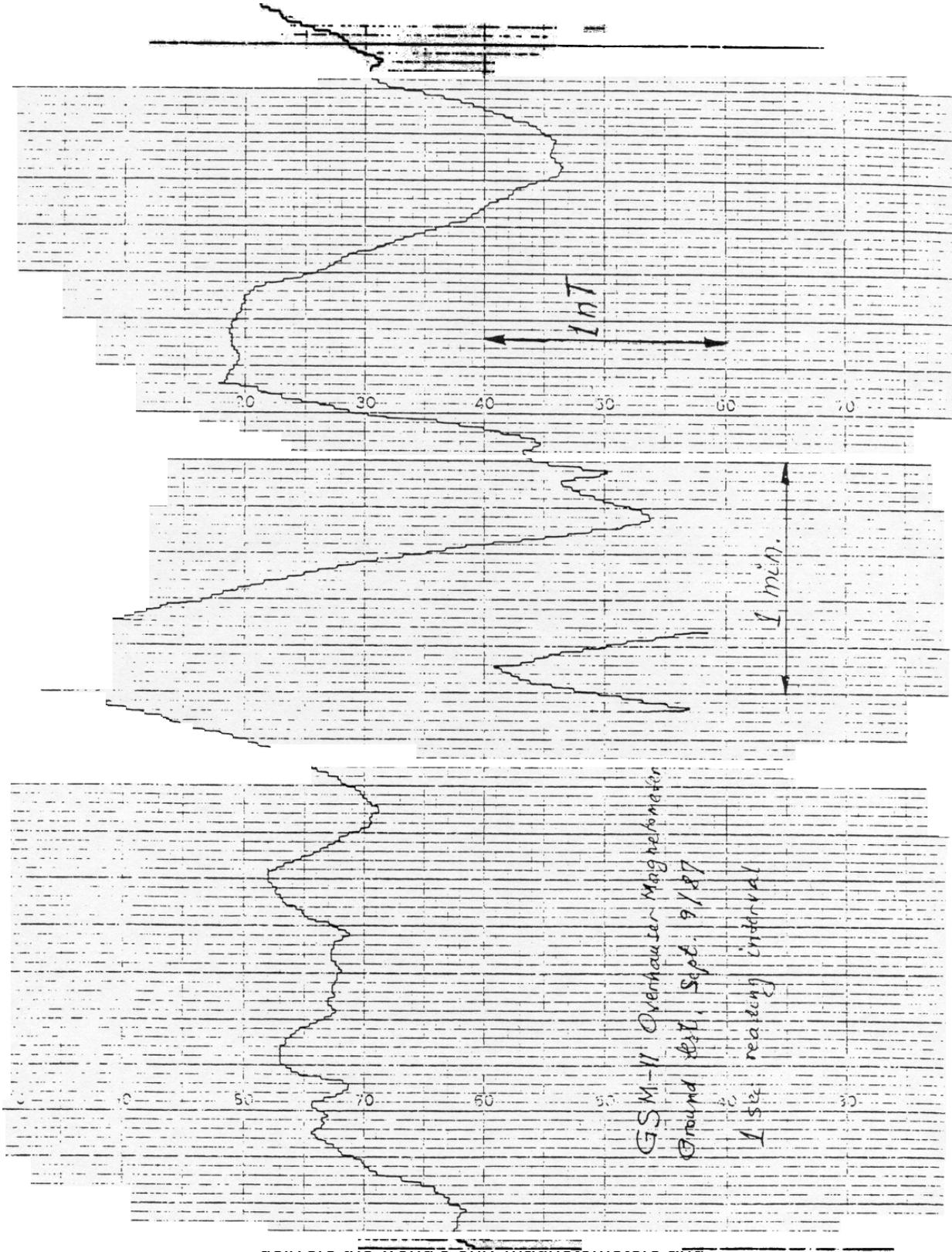
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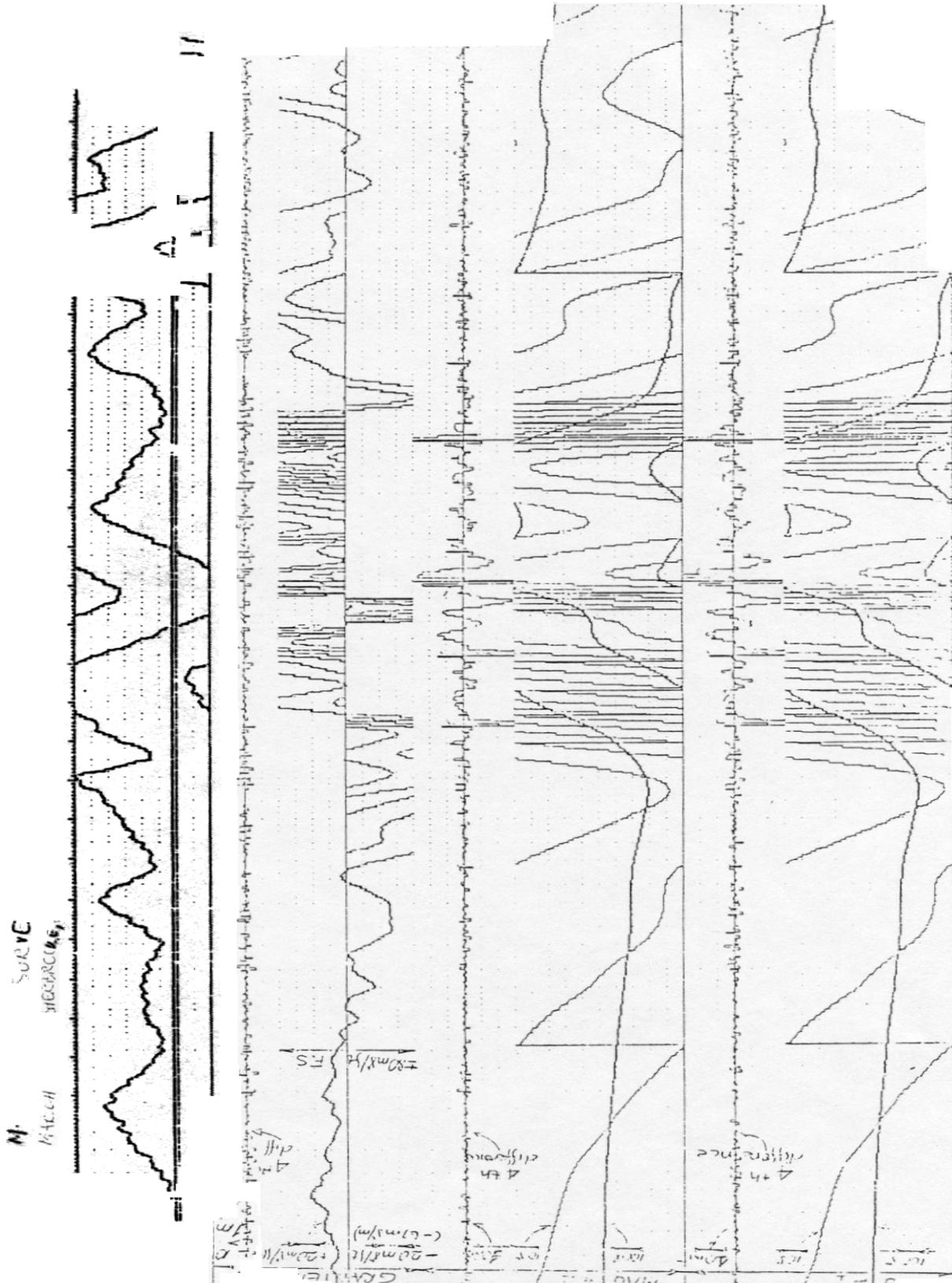
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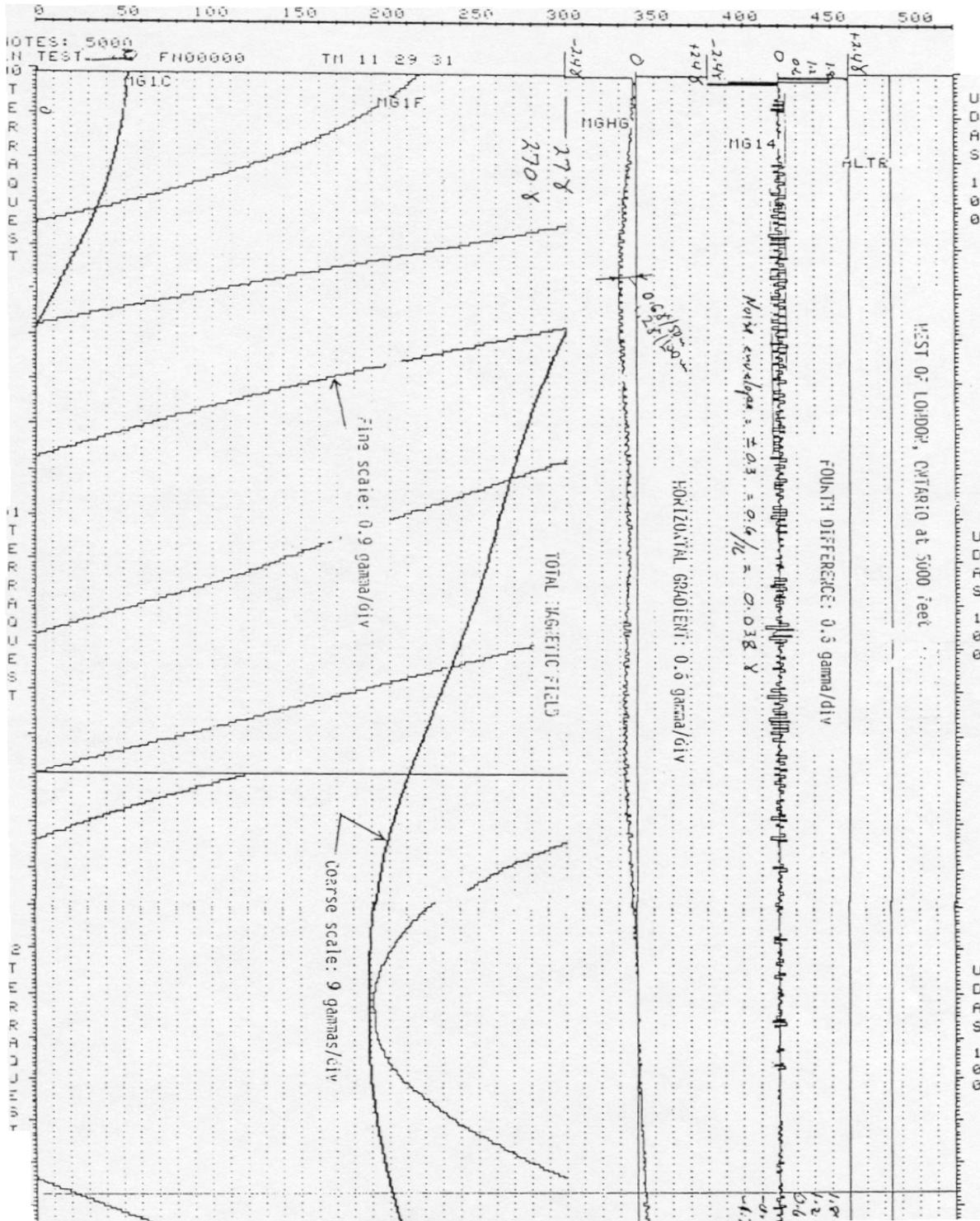


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