EXPERIMENTAL EVALUATION OF A THALLIUM BEAM FREQUENCY STANDARD

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Abstract

A thallium atomic beam frequency standard has been in operation at the National Bureau of Standards since September 1962. An evaluation of the system has been conducted in an effort to determine whether the use of thallium will result in a substantially improved atomic frequency standard. The thallium system is a modified version of NBS I, the original cesium standard.

The preliminary measurements show that, as expected, the existing uncertainties associated with the uniform magnetic C field produce a corresponding uncertainty in the frequency measurements of only a few parts in 10^{-13}. Measurement precision has been determined from the reproducibility and statistical analysis of comparison data between the thallium standard and the United States Frequency Standard, NBS II. However, day-to-day variations in the earlier comparisons are significantly larger than one would expect from the statistics. Possible sources of this difficulty along with improvements and the most recent data available are discussed.

The best measured values for the frequency of the thallium resonance in terms of cesium are given and compared with that published by Dr. Bonanomi's group at Neuchatel, Switzerland.

Introduction

At the 1957 Frequency Control Symposium Prof. Kusch pointed out certain advantages that thallium should have over cesium for use in atomic beam frequency standards.[1] Both the $(F = 1,\ m_F = 0) \leftrightarrow (F = 0,\ m_F = 0)$ transition frequency in thallium and the $(F = 4,\ m_F = 0) \leftrightarrow (F = 3,\ m_F = 0)$ transition frequency in cesium have only small quadratic dependences on the uniform magnetic C field given by:

$$f = f_o + 20.4\ H^2 \text{ cps} \quad \text{for Tl}$$

and (1)

$$f = f_o + 427\ H^2 \text{ cps} \quad \text{for Cs.}$$

Since the transition frequency of thallium is 21,310 Mc compared to 9200 Mc for cesium, the fractional uncertainties in frequency corresponding to an uncertainty in the field are:

$$\frac{df}{f} = 1.92 \times 10^{-9}\ \text{HdH} \quad \text{for Tl}$$

and (2)

$$\frac{df}{f} = 93.4 \times 10^{-9}\ \text{HdH} \quad \text{for Cs.}$$

If both a thallium standard and a cesium standard are operated with similar C field magnitudes and uncertainties, the contribution to inaccuracy produced by the field will be only 1/50 as large for thallium as for cesium. Since this contribution has been found to be less than 1×10^{-11} for the cesium standards at the National Bureau of Standards, the corresponding value for the thallium system is only a few parts in 10^{13}.

A further advantage for thallium arises from its simpler atomic spectrum, resulting in fewer problems with "overlap" shifts caused by neighboring transitions. A simplified diagram of the various energy levels in the thallium and cesium hyperfine structures is shown in Figure 1. The splitting of the zero-field levels into only 4 levels for thallium compared to 16 levels for cesium when an external magnetic field is applied to the system is a consequence of the nuclear spin quantum numbers of 1/2 and 7/2, respectively. Each of the zero-field levels is split into $2F + 1$ levels where $F = I \pm 1/2$ and I is the nuclear spin quantum number previously mentioned. Since transitions can, in general, take place between any two levels satisfying the selection rules $\Delta F = 0, \pm 1$ and $\Delta m_F = 0, \pm 1$, a total of 3 microwave transitions in thallium and 21 in cesium are possible. If the atomic beam machine is designed so that the magnetic component of the microwave field is exactly parallel to the direction of the static C field, then only those transitions for which $\Delta m_F = 0$ (σ transitions) are allowed. In this case only 1 transition can be excited in a thallium system while 7 are possible for cesium. The absence of any neighboring transitions in the thallium case means that lower values of C field can be used without producing frequency shifts from nearby overlapping lines such as has been observed in the cesium standards at fields less than .040 oersteds. Since the relations (2) show that df/f is proportional to H, the lower permitted operating field for thallium serves to further reduce the contribution to inaccuracy caused by uncertainties associated with the C field. The accuracy figure for the NBS cesium standards has been determined to be $\pm 1.1 \times 10^{-11}$,[2] the major portion of which is due to just these C field effects discussed. The development of a thallium beam standard may therefore provide a more accurate standard of frequency.

The advantages offered by thallium are at least partially offset by the more complicated detection system required. The use of the surface ionization technique for detection of the beam requires that the work function of the detector wire be higher than the ionization potential of the atom. Cesium, because of its low ionization potential of 3.9 volts, can be detected with 100% efficiency and excellent signal-to-noise ratio on a variety of heated wires, including clean tungsten and platinum-iridium. The higher ionization potential of 6.1 volts for thallium has required the use of oxidized tungsten detectors with a resulting deterioration of efficiency and signal-to-noise characteristics.

A second disadvantage is the requirement for much more powerful deflecting magnets than for a similar cesium standard. The deflecting force on either atom is proportional to the effective magnetic moment of the atom in the deflecting field. Because of the higher frequency and the lower electronic g_J value for thallium, its magnetic moment is only about 1/7 that of cesium. The need for larger magnets does not seem to be as serious a problem as the detection difficulty--at least for moderate length machines.

Description of the NBS Thallium Standard

Rather than to build a completely new machine for use as a thallium standard it was decided to modify NBS I, the shorter of two existing cesium beam standards. Since about 5 years of experience had been obtained with this machine using cesium, it was felt that results obtained from the same machine using thallium would make a cesium-thallium comparison somewhat more meaningful.

A considerable amount of time was spent in developing a suitable detection system. Preliminary experiments conducted with an auxiliary test system showed that an oxidized tungsten wire operated at about 900°C. provides reasonably efficient ionization of the thallium beam but with a rather long time constant of $\approx$ 1 second and a large background current. Later use of pure tungsten wire drawn from a single crystal resulted in a decrease of the background noise by at least a factor of 2. Provision for oxidation of the detector was made in NBS I by installing a variable leak rate valve connected to a source of oxygen. The oxidation procedure which has been found to give the best results is as follows:

1) Before the oven temperature is raised to its operating value, pure oxygen is admitted to the system while the detector temperature is in the 800°-900°C. range.
2) Enough oxygen is admitted to raise the system pressure to 1 torr or higher. After about 1 minute the variable leak valve is completely closed.
3) When the system pressure returns below 1×10^{-5} mm Hg (about 3 minutes) the detector temperature is raised to its operating point of $\approx$ 1000°C.
4) Frequency measurements can be made when the pressure falls below 3×10^{-6} torr (about 10 minutes after oxidation) if the oven is up to temperature. Repeated oxidation of the detector with the oven hot tends to cause slit clogging.

The reason for normally operating the detector at a relatively high temperature is to decrease the "sitting time" of the atom on the wire so that a servo technique of measurement involving 37 cps modulation of the microwave excitation can be utilized. At 1000°C. the oxide is stable for about 12 hours while at lower temperatures this time is increased significantly. Below 1000°C. the response time is too long for use of the 37 cps servo technique. As a result of the repeated oxidations, the normal .005" detector wires must be replaced every few weeks.

The cesium oven was replaced with a stainless steel oven assembly with radiation shields for operation at 600°C. It has not been found necessary to replenish the thallium supply or to clean the oven each time the machine is let up to air.

Some old deflecting magnets, originally used in one of the cesium standards, were made usable for thallium by providing water cooling coils and operating at relatively large currents through the magnet coils. At 8 amps the magnets produce a field of 6000 oersteds with a gradient of 23,000 oersteds/cm. Even though the magnets are only 4 inches long adequate deflection of the .005" wide beam is accomplished.

The uniform C field is produced by the same rectangular array of 4 long wires as was used for cesium. Shielding against external fields is provided by a .050" thick mu-metal cylindrical shield surrounded by a .125" thick Armco iron shield. The residual field inside the shields is about .001 oersteds and the measured non-uniformity of field along the length of the beam is less than ±.001 oersteds at a field of .050 oersteds. Current connections to the 4 wires can be changed easily to change the direction of field so that both σ and π transitions can be observed. The field vs. current calibration is obtained by using field-sensitive transitions in both cesium and thallium.

The resonant cavity is a single, U-shaped structure with a Q of about 2800. The interaction length of 55 cm. results in a spectral line width of about 280 cps. Two versions have been used: the first is made completely of commercial K-band waveguide while the second has electroformed ends with provisions for reducing field leakage out of the holes. Both cavities can be rotated 180° as a unit to test for phase shifts.

Block diagrams of the thallium measurement system and the servo system are shown in Figures 2 and 3. A klystron phase-locked at the line frequency of 21,311 Mc excites the transition. The measurement system is very similar to that used with the cesium standards which has been described in detail in reference 2. In the thallium system the 5 Mc reference is normally the servo output from NBS II, the present United States Frequency Standard. This frequency is assumed to be precisely known and is used to compute the actual thallium resonance frequency for each measurement. The servo system used with the thallium system has been thoroughly evaluated with NBS II and found to introduce less than 3×10^{-12} uncertainty into the measurements.[2] A manual measurement technique where the servo system is not used has been tried but a sufficient amount of reliable data has not yet been obtained due primarily to the rather noisy detector signal.

Results of the Evaluation Measurements

In conducting an evaluation of the NBS thallium standard the results of specific experiments must be compared whenever possible to similar results for cesium, since it must be determined eventually whether thallium will provide a better overall standard of frequency than does cesium. Despite considerable progress toward this evaluation, this report must be considered more as a progress report than a final evaluation of the relative merits of thallium and cesium.

The precision of measurement for a one-hour measurement period using NBS II as the reference is typically 4×10^{-12}. In this type of measurement an electronic counter is used to measure 100 periods of the beat note between the thallium and cesium servo output frequencies. The standard deviation of the mean for a set of 20 such determinations is taken to be a measure of the precision. The precision depends significantly upon the condition of the oxide surface on the detector but values of 4×10^{-12} are obtainable for about 75% of all measurements. Under ideal conditions precisions of 5×10^{-13} have been obtained occasionally when comparing with NBS II. These results compare closely with similar data obtained with NBS I when it was operated as an alternate cesium standard.

In discussing the accuracy of the thallium standard we shall use the term to refer to the degree to which the atomic frequency standard approaches the value f_o, the idealized resonance frequency for the thallium atom in its unperturbed state. This accuracy with respect to f_o is usually limited primarily by uncertainties associated with the C field, influences of neighboring transitions, uncertainties associated with the resonant cavity, the spectral purity of the excitation radiation, and effects of the electronics. An internal estimate of the accuracy can be made by combining the estimates of possible frequency shifts due to the above causes. An external estimate of accuracy can be made by comparing the frequencies of two independent thallium standards. At present this can only be done rather indirectly, since the only two operating thallium standards are in Switzerland and the United States.

The expected advantages of thallium with respect to C field effects discussed in the introduction have been realized in actual operation to the extent that uncertainties associated with the C field make an insignificant contribution to the accuracy figure. Careful searches were made a number of times using a manual measurement technique for evidences of the undesired π transitions ($1, 1 \longleftrightarrow 0, 0$ and $1, -1 \longleftrightarrow 0, 0$ transitions). With a signal-to-noise ratio for the normal σ transition of at least 200 no trace of the π transitions has ever been detected. Further evidence for lack of overlap shifts even at very low fields is provided by the plot of the frequency of the normal $1, 0 \longleftrightarrow 0, 0$ transition versus the square of the C field current shown in Figure 4. No significant deviation from linearity appears even at the lowest field used of .015 oersteds. The rms deviation of the points from the least-squares line shown is only 4×10^{-12}. In order to obtain an estimate for dH, the uncertainty in the field value, two independent calibrations of the field using the $4, 1 \longleftrightarrow 3, 1$ σ transition in cesium and the $1, 1 \longleftrightarrow 0, 0$ π transition in thallium were compared. At the relatively high field of .140 oersteds used in most of the early measurements the two calibrations agreed to within .002 oersted. Considering dH then to be $\pm$ .001 oersted and using (2) we find df/f to be only 3×10^{-13}. In view of the freedom from overlap shifts implied by the data in Figure 4, however, a more reasonable value of field of about .050 oersteds will be used in future measurements in which case df/f will be only 1×10^{-13}.

The resonant microwave cavity has been found to be one of the more critical components of the thallium standard in terms of possible sources for frequency shifts. The first cavity used in the standard was constructed entirely from commercial K-band waveguide and contained relatively large holes for the beam to pass through. It was also slightly asymmetrical about the coupling hole. With this cavity the standard exhibited the following undesirable features:

1) a large frequency shift of 2.8×10^{-10} occurred upon rotation of the cavity by 180° due to a phase difference between the two separated regions of oscillating field. This shift was reproducible only to 2.5×10^{-11}.
2) frequency shifts occurred with cavity detuning amounting to 1.3×10^{-10} for a detuning by 7 Mc.
3) frequency shifts of $+4 \times 10^{-11}$ and $+1 \times 10^{-11}$ occurred when the microwave power level was increased by a factor of 3 above the normal level of 12 mw. and decreased by a factor of 3, respectively.
4) a frequency shift of 5×10^{-11} occurred upon reversal of the C field polarity. This shift is attributed to a Millman effect resulting from leakage of the radiation out the holes in the cavity ends.

After these measurements the cavity was modified by replacing the end sections with electroformed sections. The beam holes were reduced in size and electroformed extensions were provided to extend out from the beam holes. These extensions are essentially waveguides beyond cutoff and thus serve to reduce radiation leakage out the holes. Based on rather limited data the modified cavity, designated cavity #2, is a great improvement. The frequency shift upon rotation of the cavity is now reduced to about 2×10^{-11}, the C field polarity shift is eliminated, and the microwave power shift is eliminated--at least below a level of 50 mw. The precision of these determinations was about 4×10^{-12}. The frequency dependence on cavity tuning, however, remains as before. When operating with cavity #2 tuned approximately to resonance at the transition frequency, any contributions to the overall accuracy figure should be under 1×10^{-11}.

Some 30 different experiments were performed to evaluate effects associated with various components of the electronics and microwave excitation systems. Although the servo system had been carefully investigated with the cesium system evaluation, some of the more significant servo system parameters, such as modulation frequency, modulation drive level, phase shift between reference and signal, gain, bandwidth, and presence of 60 cps components were reinvestigated. The only measurable frequency shift was produced by a high 60 cps level (100 times normal) in the older of the two servo systems. This shift of about 2×10^{-11} was eliminated by proper filtering. The multiplier chain from 10-270 Mc was investigated by looking for effects of B^{+} voltage variations and detuning of the output stage. In the phase-locked klystron system some of the parameters investigated were the particular source for the reference frequency, the particular phase detector used, phase-detector bandwidth, IF level, supply voltage to the IF amplifier, the unlocked klystron frequency, detuning of the klystron cavity, and the tuning of various microwave components in the system. No frequency dependence on any of these parameters was observed.

The power spectra of the 5 Mc servo oscillator and the 10-270 Mc multiplier chain were examined using an ammonia-maser-spectrum analyzer system.[3] The spectrum of the oscillator itself, shown in Figure 5, shows no trace of sidebands. The signal-to-noise ratio is greater than 90 db. The spectrum of the multiplier chain, shown in Figure 6, however, shows that asymmetrical 60 cps sidebands are present in the chain output. When an atomic transition is excited with an asymmetrical spectrum of this type, large frequency shifts may result. In an effort to obtain an estimate of the magnitude of any such shifts measurements were made of the thallium frequency first with the chain described and then with another chain known to have a relatively clean spectrum with only small symmetrical 60 cps sidebands. The initial comparisons, just completed, show no significant difference between the two chains, although the measurement precision of 2×10^{-11} was considerably larger than normal. Until the results of further experiments now in progress are available, all measurements will be considered to be uncertain to $\pm$ 0.4 cps or $\pm 2 \times 10^{-11}$ due to the possible spectrum effects.

Finally, a number of miscellaneous parameters were examined for possible sources of inaccuracy such as variations of the beam geometry, changes in the magnitude of the deflecting fields, and variations in the ambient temperature. No frequency shifts were observed. A study of effects associated with detector temperature, method of oxidation, and conditions under which the oxidation is performed showed that the scatter of the measurements may be affected by these parameters but apparently not the accuracy.

Based upon these experiments one would tend to conclude that the accuracy figure for a thallium beam frequency standard should be significantly less than 1×10^{-11}, provided that undesirable spectrum effects are eliminated. With the spectrum effects existing during all measurements reported here, the accuracy estimate would be about $\pm 2 \times 10^{-11}$.

In view of the apparent lack of dependence of the thallium resonance frequency on any of the system parameters (with the possible exception of the spectrum effects), it would seem that day-to-day variations in the measured thallium frequency referenced to the United States Frequency Standard should not exceed $\pm 1 \times 10^{-11}$ if the typical measurement precision is a few parts in 10^{12}. A plot of all the thallium measurements made under normal conditions since last November, shown in Figure 7, indicates much larger variations, however--at least until the resonant cavity was modified. The dashed vertical lines separate the data into groups according to cavity orientation while the solid horizontal lines are the averages for each group. The effects of the large phase shift present in the first cavity and the significant improvement obtained with the second cavity are apparent from the group averages. It should be noted that each point on the plot represents about a 1-hour measurement and that in some cases more than one point was taken on the same day. Although no definite reason for the large scatter in the earlier measurements from day to day is known, we believe spectrum effects which are time dependent to be the most likely explanation.

The best measured values of the thallium resonance frequency referred to cesium as determined in this country at the National Bureau of Standards and by Dr. Bonanomi's group in Neuchatel, Switzerland can be compared to provide one check on the respective accuracy estimates. The appropriate values are:

$$f_o = 21,310,833,946.4 \pm 0.4 \text{ cps} \qquad \text{(NBS)}$$

and

$$f_o = 21,310,833,945.1 \pm 1.0 \text{ cps}^{4} \qquad \text{(Neuchatel).}$$

Only the data for cavity #2 has been used in the NBS determination. The difference of 1.3 cps or 6×10^{-11} between the two values cannot be considered inconsistent in view of the uncertainties quoted. Differences between the U.S. and Swiss cesium standards to which the thallium measurements are referred will be reflected in the thallium values. However, several years of comparisons via radio propagation data indicate agreement of long term average values $\pm 2 \times 10^{-11}$ for the cesium standards.

Conclusion

A preliminary evaluation of a rather short thallium atomic beam frequency standard has indicated that such a machine may offer improved accuracy and comparable precision to a similar cesium standard. Although cesium standards still have advantages in terms of convenience and consistency of operation, further work on thallium at an accelerated pace seems warranted at this time.

Acknowledgements

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References

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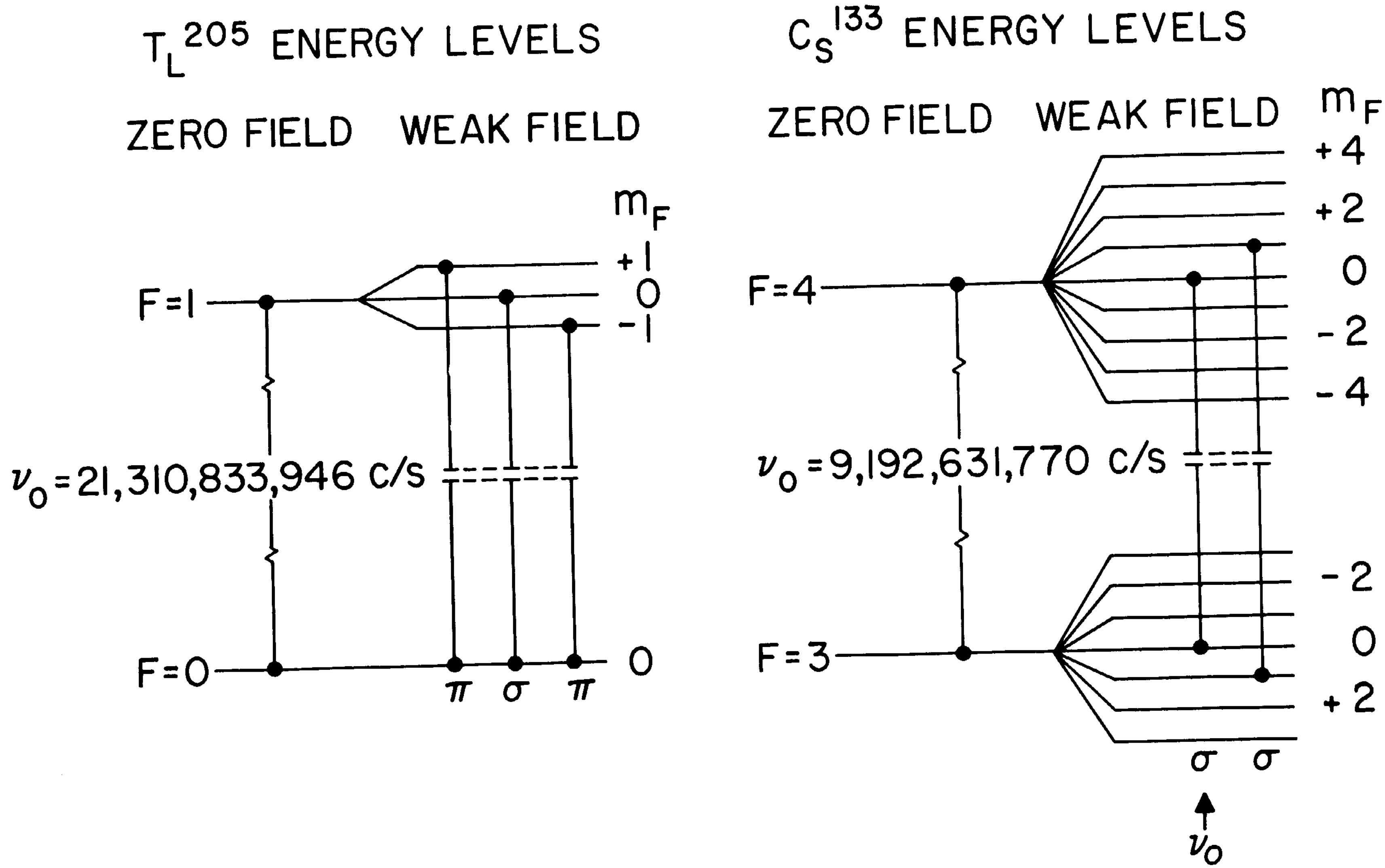

Fig. 1 Energy Levels for Tl^{205} and Cs^{133}.

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Fig. 2 BLOCK DIAGRAM OF THE THALLIUM SERVO MEASUREMENT SYSTEM

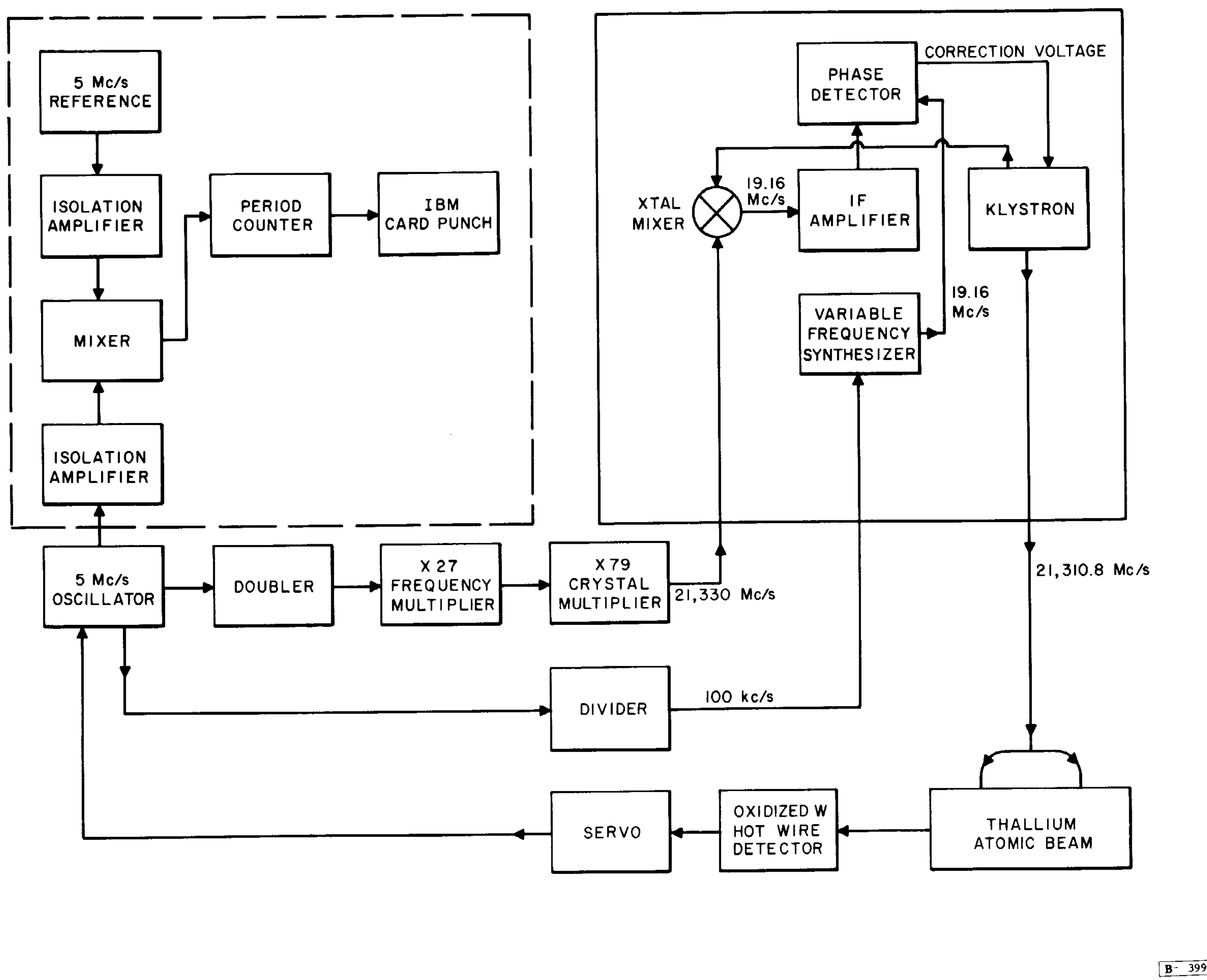


Fig. 3 BLOCK DIAGRAM OF THE SERVO SYSTEM

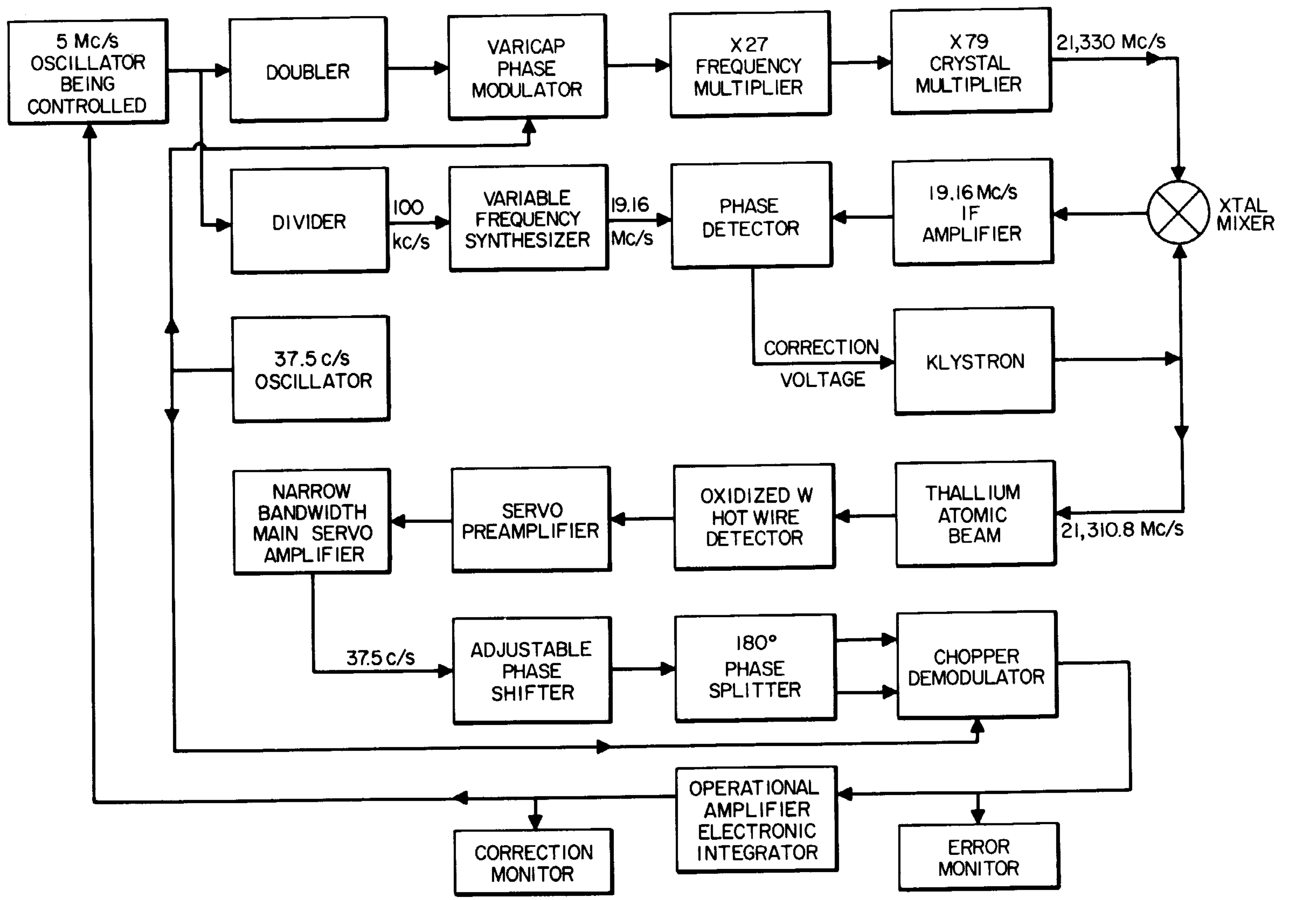
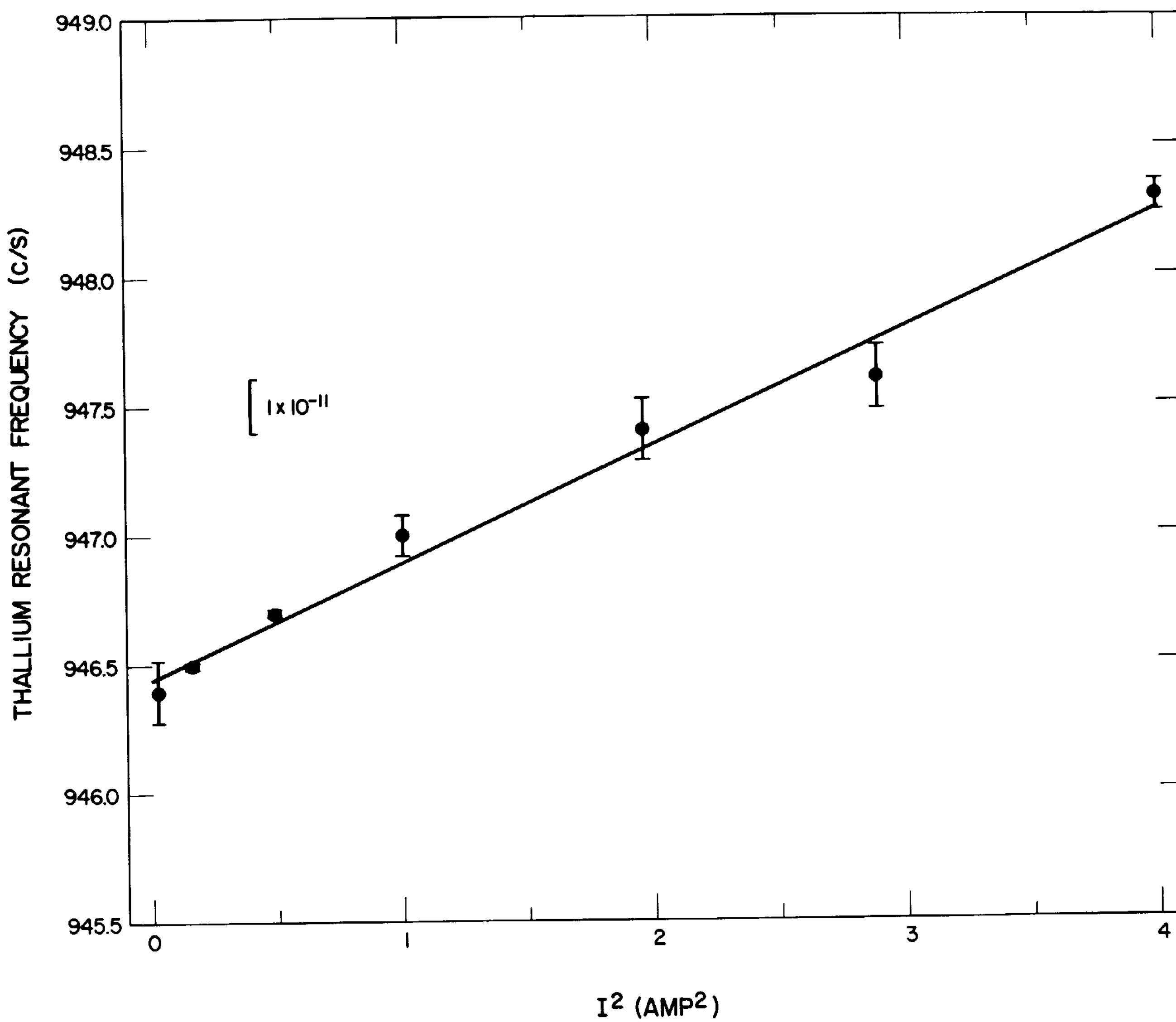


Fig. 4 THALLIUM RESONANT FREQUENCY vs C-FIELD CURRENT^2



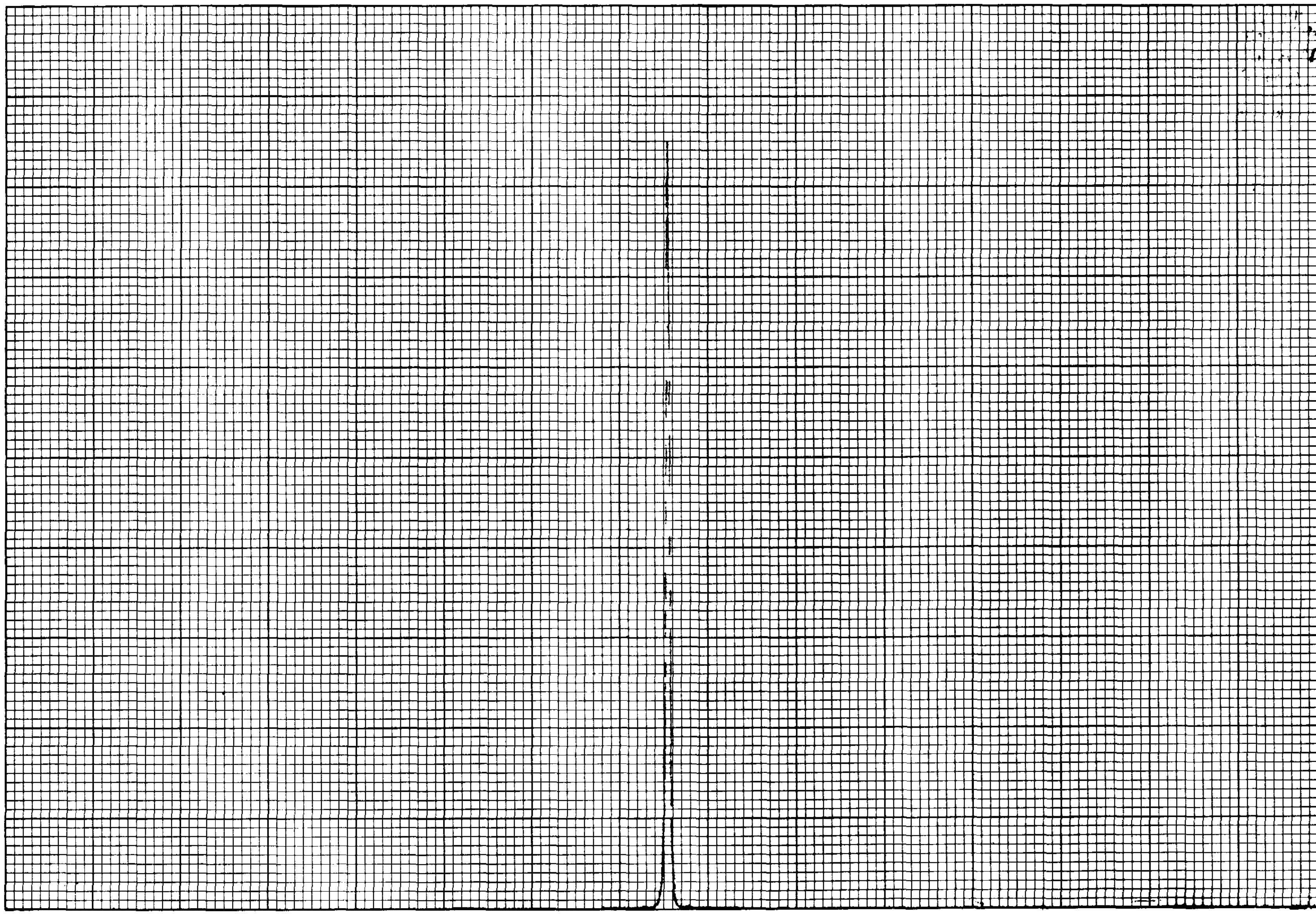


Fig. 5 Power Spectrum of the 5 Mc Servo Oscillator.

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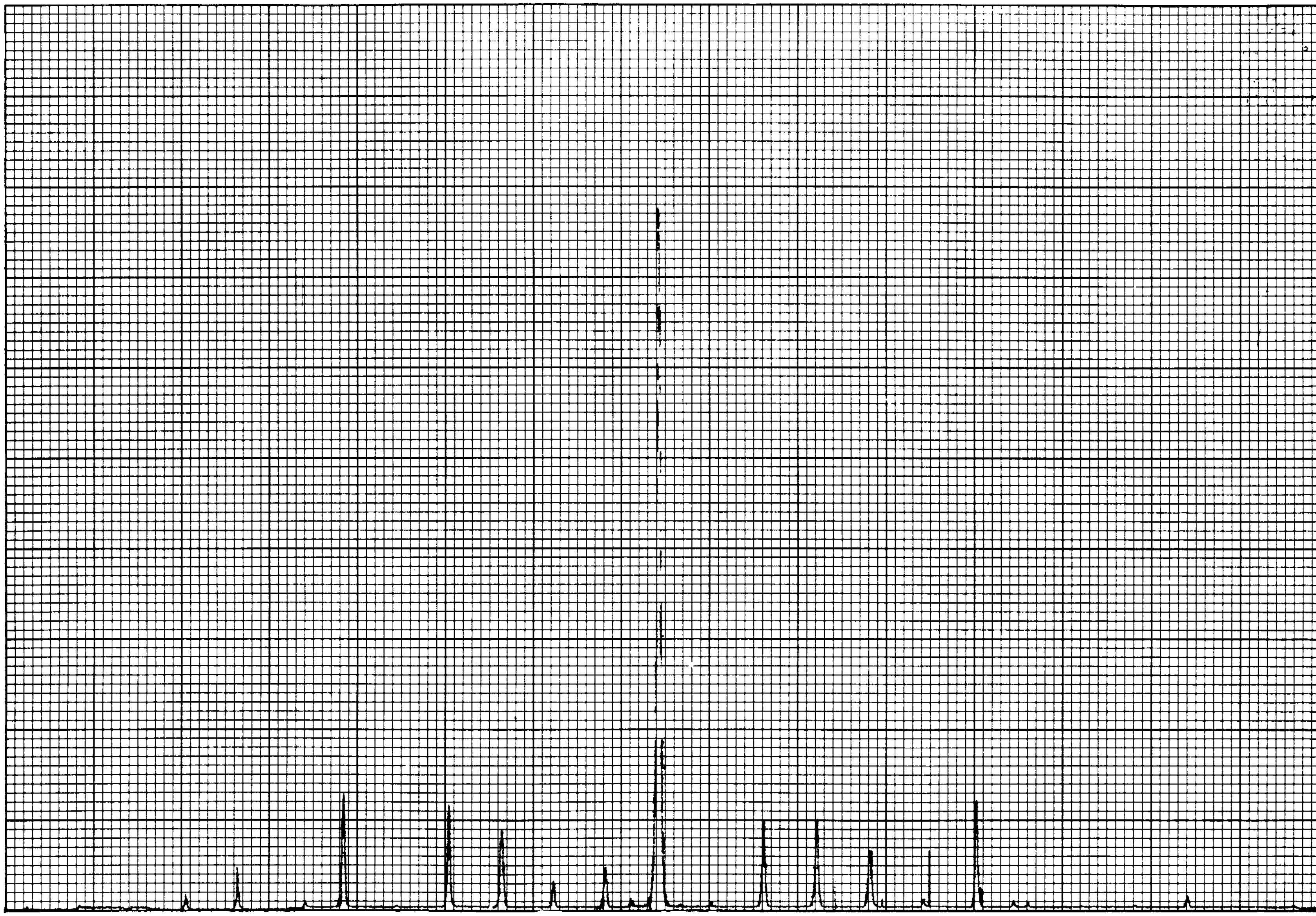
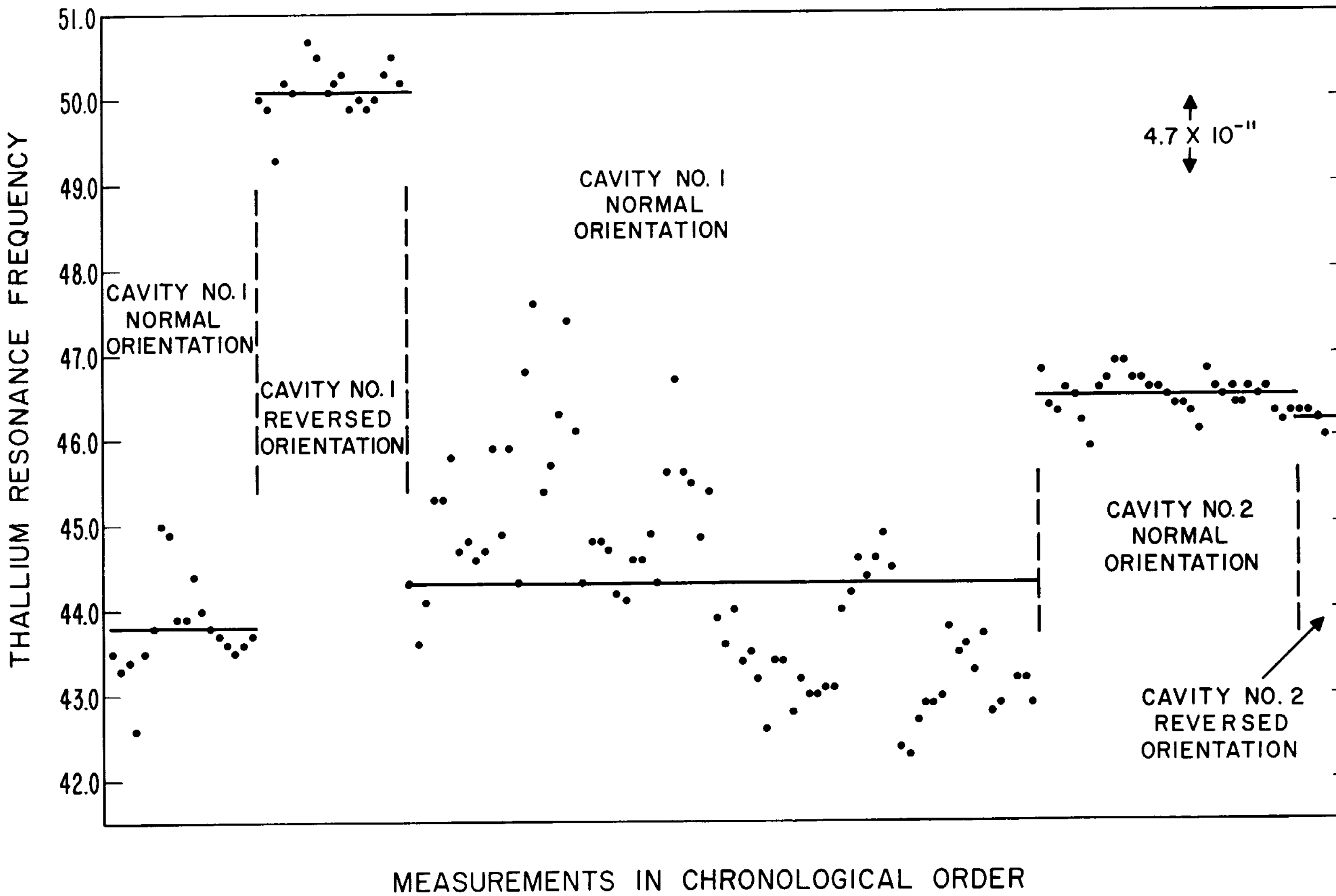


Fig. 6 Power Spectrum of the 10-270 Mc Multiplier Chain.

Fig. 7 MEASUREMENTS OF THALLIUM RESONANCE FREQUENCY DEC 1962 – MAY 1963



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