CONSTRUCTION OF MICROWAVE APPARATUS FOR SPECTROSCOPIC ANALYSIS WITHIN THE 3 TO 4½ CENTIMETER RANGE

By

LAYMOND D. WANN

Bachelor of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

1949

Submitted to the Department of Physics

Oklahoma Agricultural and Mechanical College

In Partial Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

1950

APPROVED BY:

R. W. Snyder

Chairman, Thesis Committee

A. V. Bershing

Member of the Thesis Committee

Sherman W. Eager

Head of the Department

D. C. W. Tilson

Dean of the Graduate School

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor Sherman W. Eager for his aid in procuring materials necessary for the construction of the apparatus; Mr. Ralph Snyder for his invaluable supervisory aid and advice in connection with the experimental work and the writing of this thesis; Dr. Harold E. Harrington for the use of the facilities of the Research Laboratory; and to Mr. David L. Johnson of the Electrical Engineering Department for making engineering equipment available.

TABLE OF CONTENTS

TABLE OF ILLUSTRATIONS

TABLE OF TABLES

INTRODUCTION

Because microwaves of frequencies exceeding 6,000 megacycles have poor propagational characteristics, spectroscopy using microwaves as the incident or exciting radiation has led to developments which make possible extra-ordinary resolution of spectral lines. Microwave spectroscopy is the classification of those discrete frequencies between approximately 6,000 megacycles and the infra-red region which are absorbed in passing through gases, liquids, or solids.

Because only certain critical frequencies are absorbed by a specimen, one thus has a relatively simple and reliable means of determining the presence, magnitude, and relative concentrations of molecular elements of matter. For example, water vapor of the air exhibits molecular resonance at about 22,500 megacycles where propagational losses increase to over 0.4 decibel per kilometer. Oxygen in the atmosphere provides maximum absorption or attenuation of microwave energy at a frequency of about 60,000 megacycles, with attenuation being of the order of 10 decibels per kilometer.[1] The possibility arises that every element or compound of elements, both known and unknown to science, will absorb frequencies in the microwave region.

Until recently, identification of atoms and molecules by spectroscopic analysis has utilized radiations in the infra-red, visible, and ultraviolet regions of the spectrum. These methods limited investigations to atoms and the simpler molecules. In the fields of medicine and industrial chemistry, where the larger and more complicated molecules are found, the past methods of spectroscopic analysis have not been suitable. The explanation of this fact is that the heavier molecules rotate at slower rates producing spectral lines which fall within the microwave region. The larger molecules which may be subjected to

---

[1] S. Freedman, "New Field of Microwave Spectroscopy", Radio and Television News, XLII: 27-9 (July, 1949)

microwave analysis are those found in plastics, polymers, rubber, textiles, foods, oil, drugs, and biological chemicals, such as vitamins.

Because it can deal with the nucleus of the molecule, the microwave method makes possible the identification of isotopes; however, the other methods have been able to deal only with the outer parts of an atom or molecule. To date, about five hundred elements or compounds of elements have been analyzed by microwave spectroscopy resulting from absorption or scattering of electromagnetic waves between 6,000 and 50,000 megacycles.

Figure 1 shows a block diagram of a typical microwave spectroscope. Microwave energy from an oscillator is divided between two arms, one containing the specimen to be analyzed and the other simply air and a variable attenuator for balancing the outputs from the two arms. Any absorption occurring in the specimen chamber disturbs the balance between the two arms and causes an output from the difference amplifier. This signal actuates the indicator.

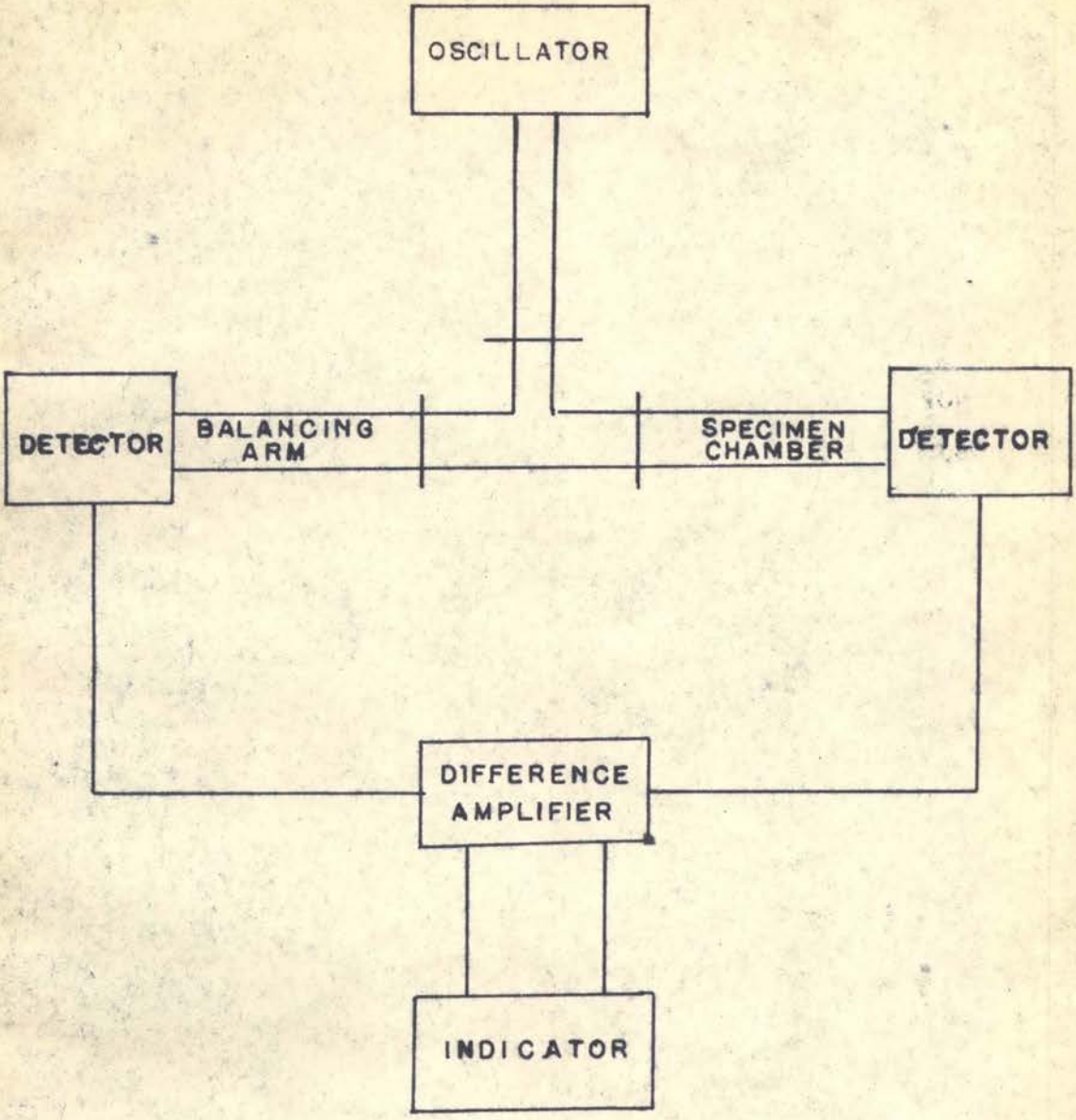

OSCILLATOR
DETECTOR
BALANCING ARM
SPECIMEN CHAMBER
DETECTOR
DIFFERENCE AMPLIFIER
INDICATOR

FIGURE 1

CHAPTER 1

PROBLEM AND METHODS OF SOLUTION

The problem was to construct a microwave spectroscope for the 3 to 4½ centimeter range. Block diagrams for two different variations of such a spectroscope are shown in Figures 2a and 2b on page 5. Because the initial cost of new equipment for microwave spectroscopy was considered too great, the problem at hand was either to convert war-surplus equipment to the immediate needs or to construct the equipment from easily obtained materials.

Two war-surplus pieces of gear were immediately available; one, a klystron oscillator including a power supply and attenuators, was easily modified to meet the need for a microwave oscillator; the other, a cavity wave meter, was of secondary importance; however, it contained a microampere meter which facilitated the procurement of relative power output measurements.

Also necessary was a device to detect the absorption of frequencies within the range of the klystron. For this, a crystal diode of the germanium type was employed. Following the detector some method of indication was necessary, either a direct reading output meter or an oscilloscope whose trace would show a change of amplitude at the absorption frequency. Between the detector and the indicator, a difference amplifier was needed for balancing the output voltages from the detectors at the ends of the specimen arm and balancing arm, exhibiting no output whenever the two arms remained balanced but giving an indication if absorption occurred in the specimen arm.

To facilitate the location of an absorption frequency, the output from a saw-tooth sweep generator was applied to the repeller grid of the klystron in addition to the bias voltage; this caused the frequency of the klystron oscillator to sweep through the range being investigated for the presence of absorption lines. The microwave energy from the oscillator was made to pass

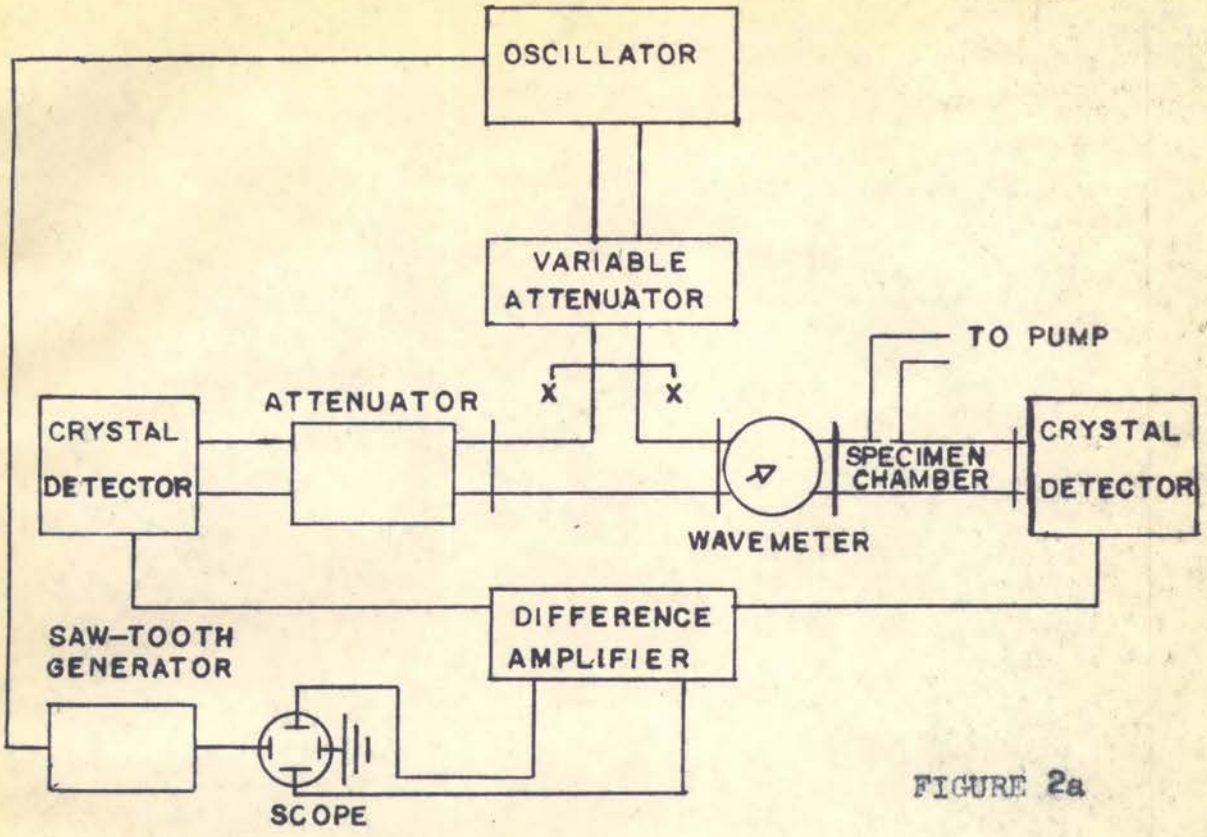


FIGURE 2a

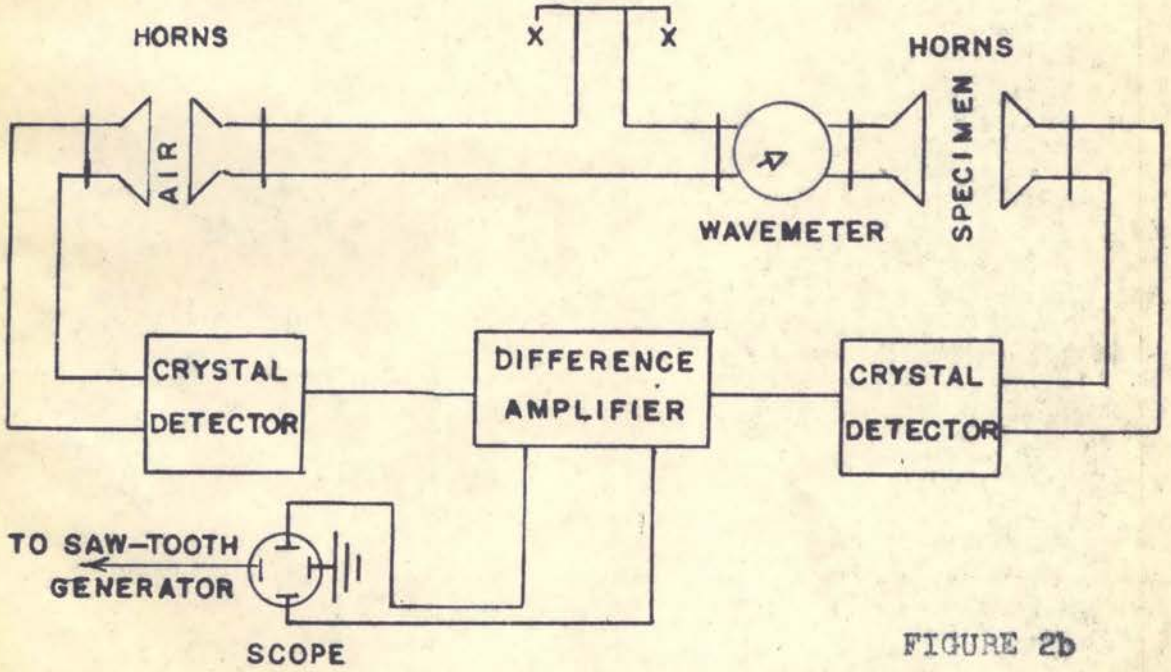


FIGURE 2b

through two parrallel paths, a specimen arm and a balancing arm, to their respective detectors, the signals from which were then fed through the difference amplifier to the oscilloscope which was synchronized with the sweep generator. Because of the extreme difficulty encountered in the search for two crystals of similar characteristics, adjustable input impedances were incorporated in the difference amplifier.

To allow for a wider choice of specimens in the form of liquids, solids or gases, two different arrangements for passing microwave energy through the specimen were employed. A pressurized wave-guide section procured from surplus equipment was utilized in the first arrangement. This pressurized section was attached to one arm of a series-fed "T" wave-guide section, the other end of which fed into a waveguide section containing attenuators for load matching. These two sections fed into identical detector systems employing germanium crystals. The output from the detectors then led into the difference amplifier.

The second arrangement consisted of wave-guide horns attached to each end of the series-fed "T" section. Located at a convenient distance from the horns and in co-axial alignment with them were two other horns which were connected through co-axial cables to the detectors. The specimen was inserted between one of the pairs of horns, leaving air between the other pair. This pair of horns provides a balancing arm similar to that in the previous arrangement. If gas constitutes the specimen, either arrangement can be used, the pressurized system being much more accurate for quantitative measurements; however, for liquids or solids the horn arrangement must be employed.

Another spectroscope which is less accurate, but which simplifies the construction of the equipment and enables more rapid operation without the need for the tedious balancing steps, employs the double modulation principle (see Figure 3 on page 7.) It also utilizes a klystron oscillator whose frequency is changed by varying the repeller grid bias with a saw-tooth generator. How-

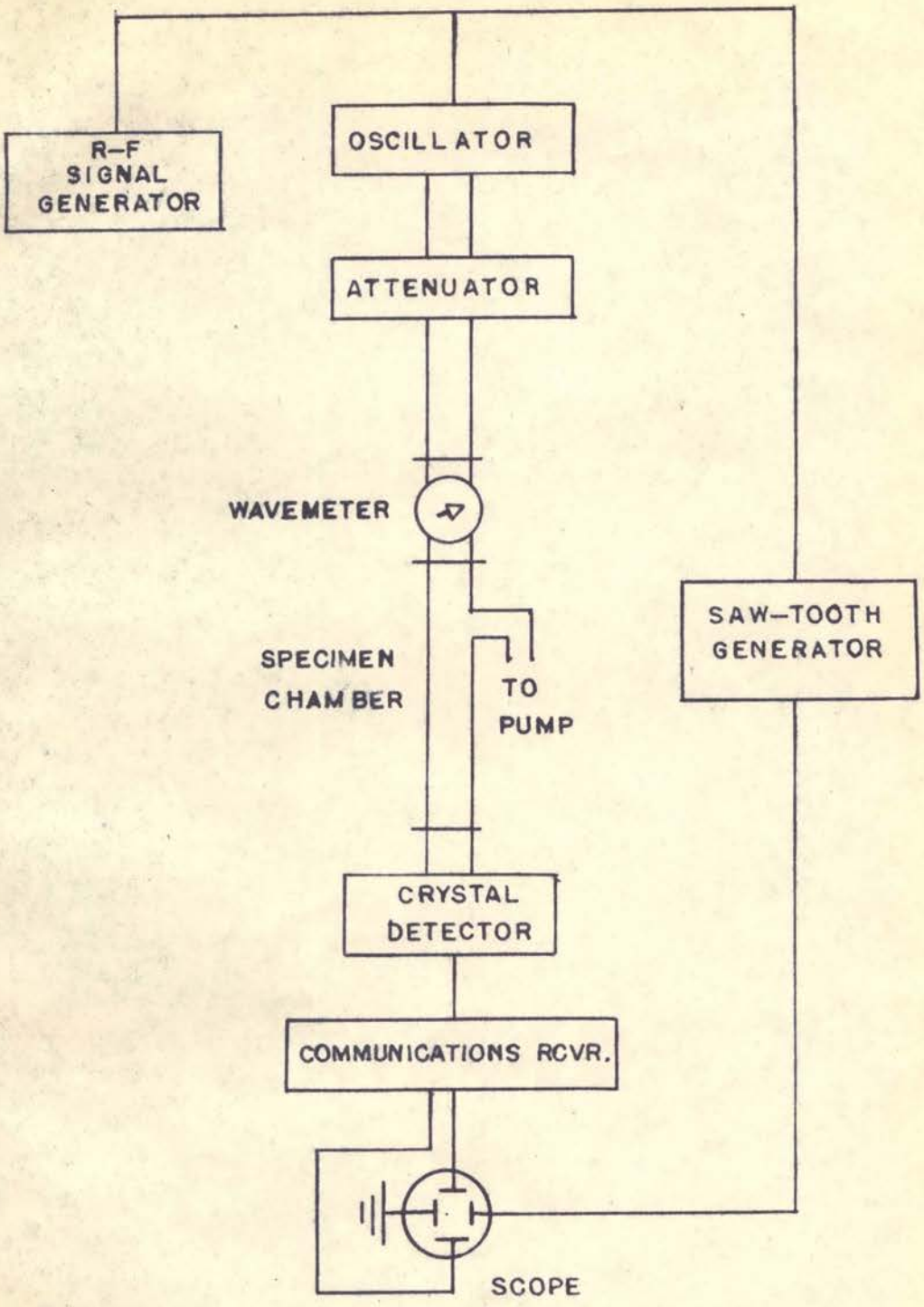

R-F
SIGNAL
GENERATOR
OSCILLATOR
ATTENUATOR
WAVEMETER
SPECIMEN
CHAMBER
TO
PUMP
SAW-TOOTH
GENERATOR
CRYSTAL
DETECTOR
COMMUNICATIONS RCVR.
SCOPE

FIGURE 3

ever, the two set-ups differ widely in the other components.[1] In addition to the bias and sweep voltages, the output from a radio-frequency signal generator is also impressed on the grid. This r-f signal frequency modulates the output of the klystron which is then fed into a pressurized wave-guide section; the balancing arm is not necessary in this set-up. Any absorption taking place within the specimen chamber then amplitude modulates the incident radiation, hence the name "double modulation". The output from the specimen chamber is fed into a single detector. The usual crystal detector removes the microwave component from the incident radiation leaving the modulated radio-frequency to pass into a communications receiver tuned to the radio frequency (200 kilocycles was used; however, this frequency was not critical). The receiver output is displayed on an oscilloscope, the horizontal plates of which are synchronized with the low frequency saw-tooth voltage. Signals resulting from the absorption spectra of the specimen gas can be observed without introducing serious distortion.

There is one serious objection to this set-up, however. All irregularities in power received by the germanium detector are amplified the same as the spectral line. This results in a large signal at the beginning and end of the mode within the wave-guide; however, if the absorption path is restricted to short wave-guide sections, the reflections are usually broader than the spectral lines observed at low pressure and can be distinguished visually. Any method involving sharpness of the response on the oscilloscope as a criterion of absorption is definitely limited by the length of the specimen chamber.

These three-set-ups allow one to graduate from the coarse to the fine in both qualitative and quantitative measurements of microwave spectra.

---

[1] R. Watts and D. Williams, "A Double Modulation Detection Method for Microwave Spectra", Physical Review, LXXII: 1122-3 (Dec., 1947)

CHAPTER 2

THEORY OF MICROWAVE SPECTRA

For better understanding of microwave spectra, consider the oxygen molecule in its normal ground state.[1] Because oxygen has one unit of spin angular momentum, it has a magnetic moment equal to two Bohr magnetons, i. e., $\frac{2\,eh}{4\pi\,mc}$ where e is the charge on an electron in electro-magnetic units, h is Blanck's constant, m is the mass of the electron and c is the velocity of light.[2] This permanent magnetic moment allows the molecule to couple to the magnetic field of an electromagnetic wave. Because it is coupled to the rotational motion of the molecule, the unit of spin angular momentum perturbs the rotational state.

Having three spatial orientations with respect to the given molecular rotational angular momentum vector, k, the unit electron spin causes each rotational level to split into three states: J = K + 1, K, and K-1 where each J state of this so-called ρ-type triplet arises from a different orientation of the spin with respect to the rotational motion of the molecule. The energy differency between successive J terms in any of these triplets is about 2 cm^{-1} (with the single exception of the J = 0→1 difference which is about 4 cm^{-1}). Therefore, within the 2 cm^{-1} region there are two absorption frequencies for each value of the rotational angular momentum quantum number, K, as depicted by the selection rules for magnetic dipole transitions allowing induced transitions

---

1 Standberg, Meng, and Ingersoll, "Microwave Absorption Spectrum of Oxygen", Physical Review, LXXV: 1524-8(May, 1949)

2 Harvey E. White, Introduction to Atomic Spectra, p. 53

between the successive members of the triplet, ($\Delta J = \pm 1$).

The O^{16} nucleus has zero nuclear spin angular momentum, so that symmetry considerations demand that K have only odd values.[1]

Considering the 2 cm^{-1} region, there are about twenty-five lines which overlap at atmospheric pressure and which contribute significantly to the absorption within this section of the spectrum.

---

[1] Standberg, Meng, and Ingersoll, op. cit., pp. 1525

CHAPTER 3

CONSTRUCTION AND TESTING OF APPARATUS

As was previously mentioned in Chapter 1, two pieces of war-surplus apparatus were modified to meet the need for a klystron oscillator and a wavemeter. The first of these, a "Test Set 35", contained a 2K25 reflex klystron tube with the associated power supply. To adapt this gear to microwave spectroscopic uses, the original grid connections were removed (see Figure 4). A saw-tooth sweep generator using an 884 thyratron tube (see Figure 5) was connected to the terminal of the repeller grid of the klystron. To procure a linear rise on the saw-tooth wave form, use was made of the saturation characteristics of a 606 pentode tube connected in series with the output condenser to maintain a constant charging current.

The wavemeter could be used to determine the frequency of the microwaves to three significant figures. To enable future calibration of the wavemeter, an auxiliary method of determining the frequency of the klystron output was used. This method employed standing-wave measurements, wherein the output from the klystron was reflected from a metal plate perpendicular to the direction of propagation. With the reflector plate at certain discrete distances from the waveguide output, maximum and minimum power output indications were noted on a meter arranged to indicate the standing wave ratio. Because the distances that the reflector plate was moved between the observation of two successive maximum or minimum meter readings was a half-wave length of the microwave radiation, the frequency was easily computed with an average deviation from the mean of 5.14 percent. Although this method is more accurate than the use of the war-surplus wavemeters available, the latter method is more easily adapted to dynamic uses.

Connected into the balancing arm, the wavemeter acts much as an absorbing

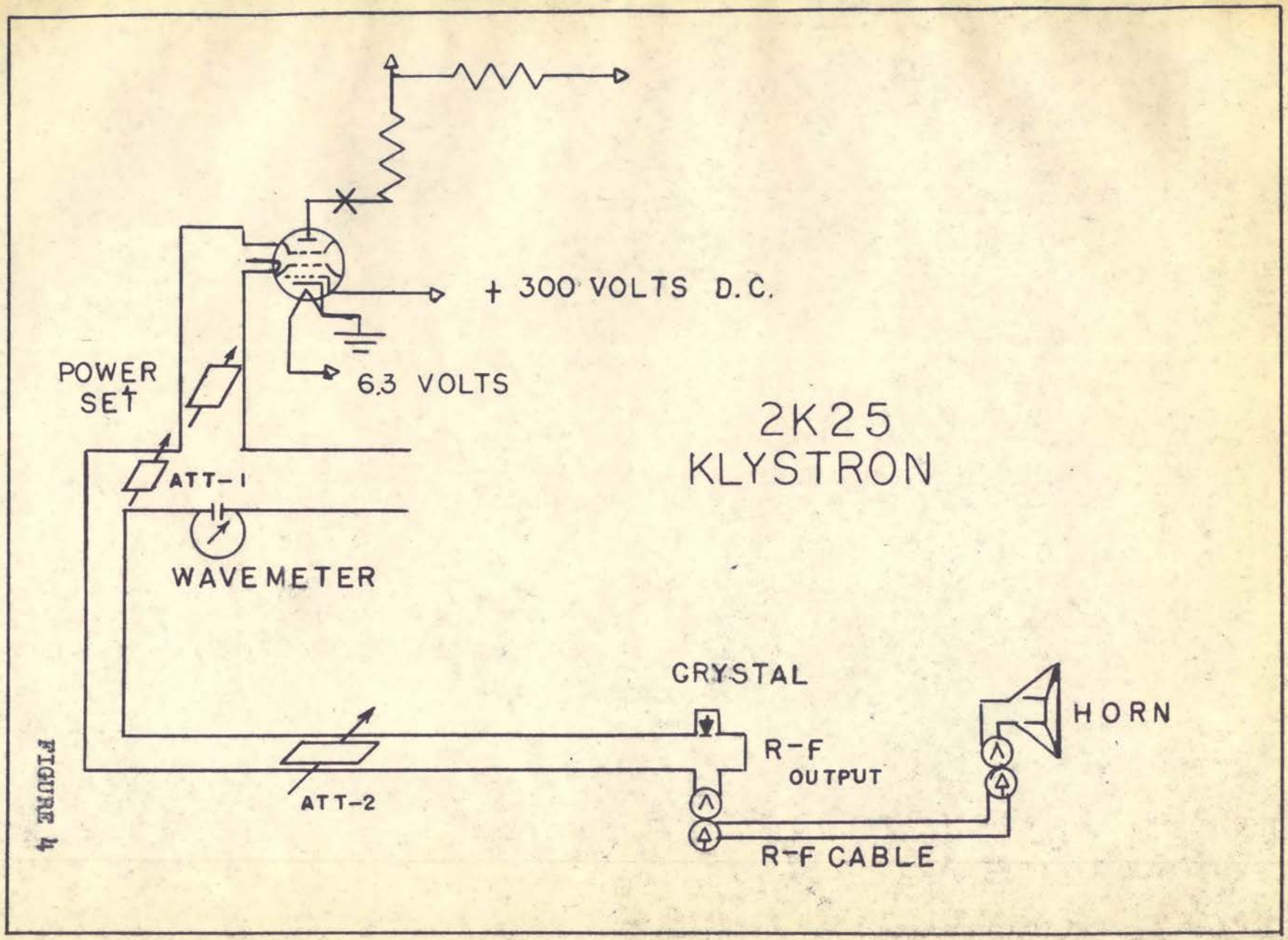
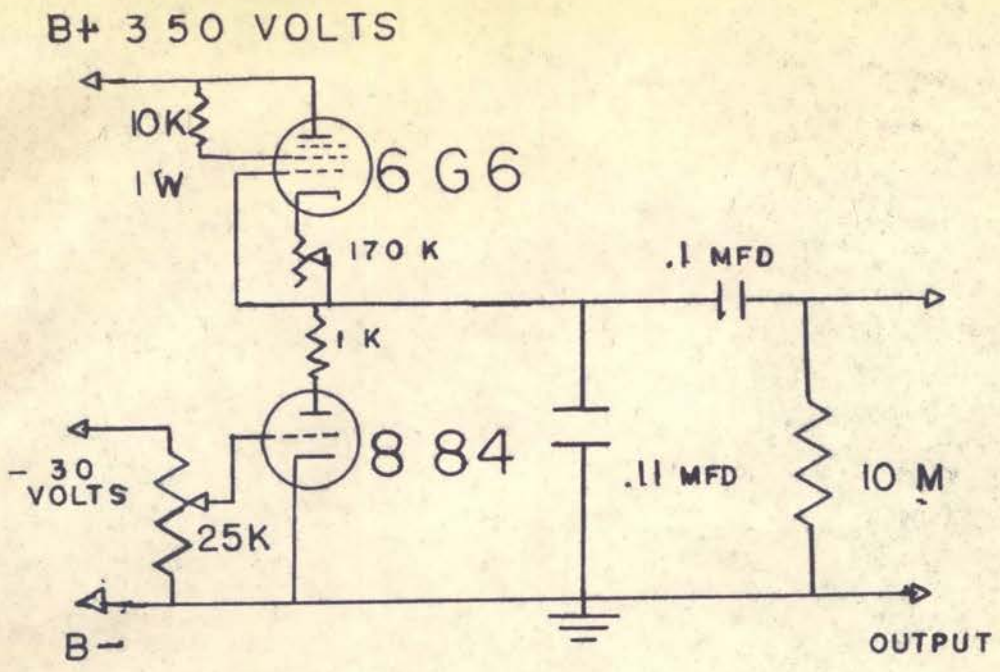

+ 300 VOLTS D.C.
6.3 VOLTS
POWER SET
ATT-1
WAVEMETER
2K25
KLYSTRON
CRYSTAL
HORN
R-F OUTPUT
ATT-2
R-F CABLE

FIGURE 4



SAW-TOOTH GENERATOR

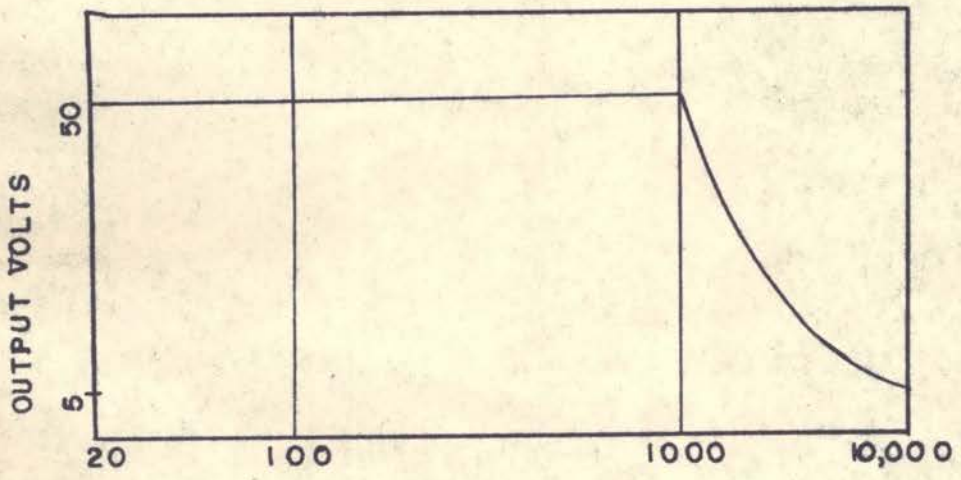


FIGURE 5

specimen in that it absorbs energy when the cavity has certain critical dimensions. As the oscillator sweeps through the frequency to which the wavemeter is tuned, the wave meter absorbs energy and its resonance cruve is traced out of the scope. To measure the frequency of an absorption line, it is necessary only to superimpose the wavemeter "pip" on that of the absorption line and read the wavemeter dial.

So that absorption could be ascertained, a difference amplifier was employed. The difficulties encountered while constructing the difference amplifier are worthy of note for anyone using this piece of gear. A conventional circuit employing a 6SN7 duo-triode tube minimized spatial requirements. In Figure 7 one will notice the cathode resistor, R_k, whose value is critical if distortionaless output is to be had from the amplifier. In the equation,

$$e_o = \frac{\mu R}{2(r_p + R)} \left[(e_1 - e_2) - \frac{a}{1 + a} (e_1 - e_2) \right]$$

where $$a = \frac{R + r_p}{2(\mu + 1)R_k}$$

R_k must be chosen to meet the condition.

$$2(\mu + 1) R_k >> (R + r_p).$$

This condition will enable the latter part of the equation for e_o to become insignificant.

A value of twelve thousand ohms for R_k and a value of twenty for μ substituted in the above condition yields:

$$2(20 + 1)\ 12{,}000 = 504{,}000 \text{ ohms}$$

which is fifty times greater than $(R + r_p)$ which equals

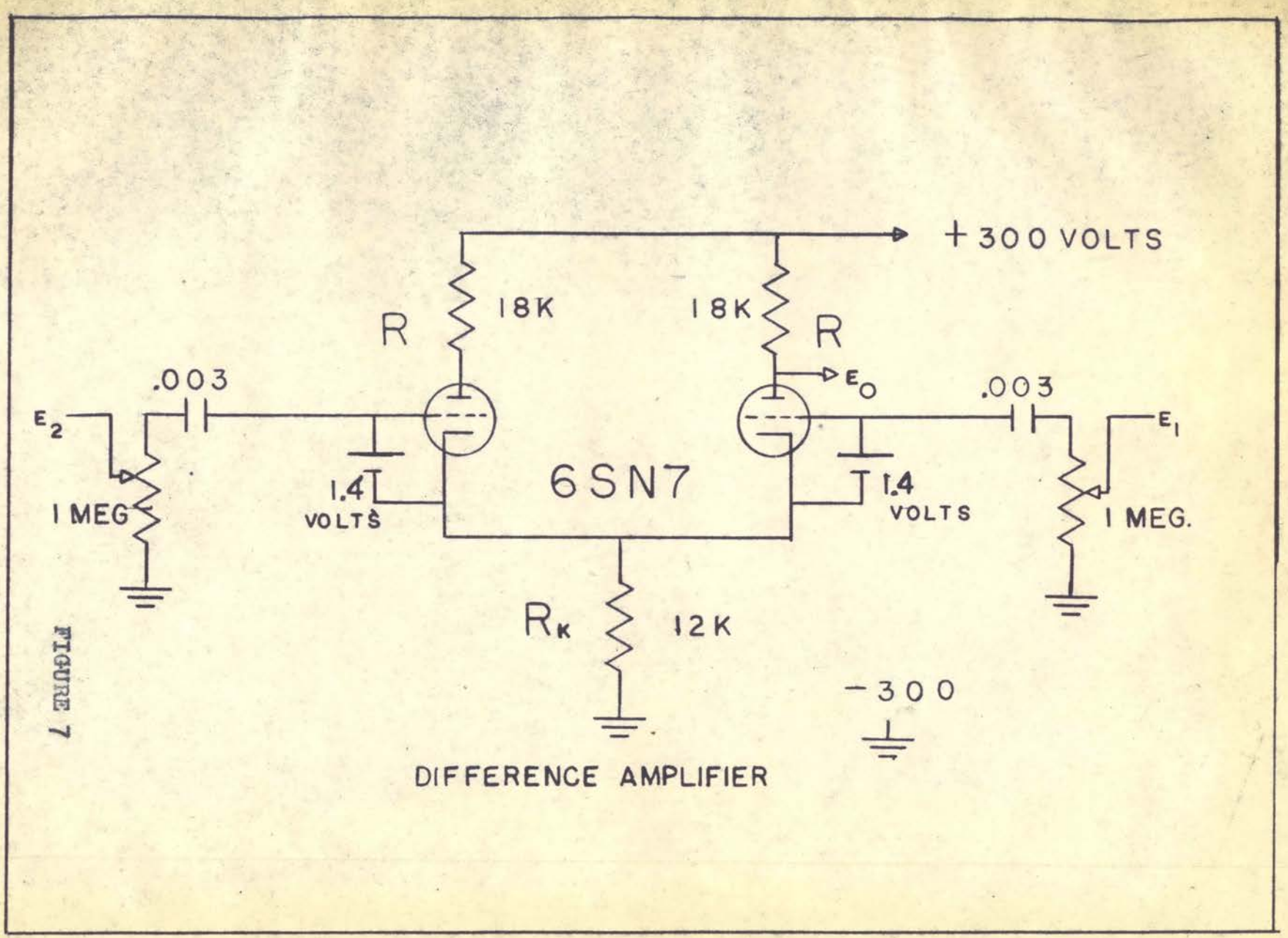


FIGURE 7

DIFFERENCE AMPLIFIER

$$(10{,}000 + 750) = 10{,}750 \text{ ohms.}$$

A higher value of a R_g would produce a cathode to filament potential differential of more than ninety volts, the maximum safe operating condition for the 6SH7. A tube such as the 6SL7 will give a higher μ, if increased output is desired. The final equation for the output is:

$$e_o = \frac{\mu R}{2(r_p + R)} \quad (e_1 - e_2).$$

CHAPTER 4

EXPERIMENTAL RESULTS

In the standing wave method of frequency determination, use was made of the vertical cathetometer for the measurement of half-wave lengths with a precision of the order of 0.005 centimeters; the resulting frequency versus repeller grid voltage curve for the 2K25 klystron is exhibited in Figure 6, the frequency having an average deviation from the mean of 5.14 per cent. Data for this curve is listed in Table I and Table II at the end of the chapter.

The difficulty in procuring a gas which would have absorption lines within the 6,000 to 9,000 megacycle range covered by the 2K25 klystron set-up prevented the location of specific lines. Hope was prevalent at first when it was learned that iodine monochloride, ICL^{35} and ICL^{37}, yielded two theoretical absorption lines at 6980 megacycles and 6634 megacycles.[1] However, because iodine monochloride is unstable, need for special equipment became apparent. Iodine crystals and liquid chlorine could be used to yield iodine monochloride which could then be pumped into the wave-guide; but the temperature would have to be maintained at approximately 100° C. during the process to prevent the dissociation of the gas.

Because power changes also produce indications on the oscilloscope trace, extremely stable current regulator tubes were employed; however, one of these tubes, a VR-121-A, failed to function correctly, and although an order was placed, the tube failed to arrive.

---

[1] R. T. Weidner, "Microwave Spectrum of Iodine Monochloride at 4½ centimeters wavelength", Physical Review, LXXII: 1268-9 (Dec., 1947).

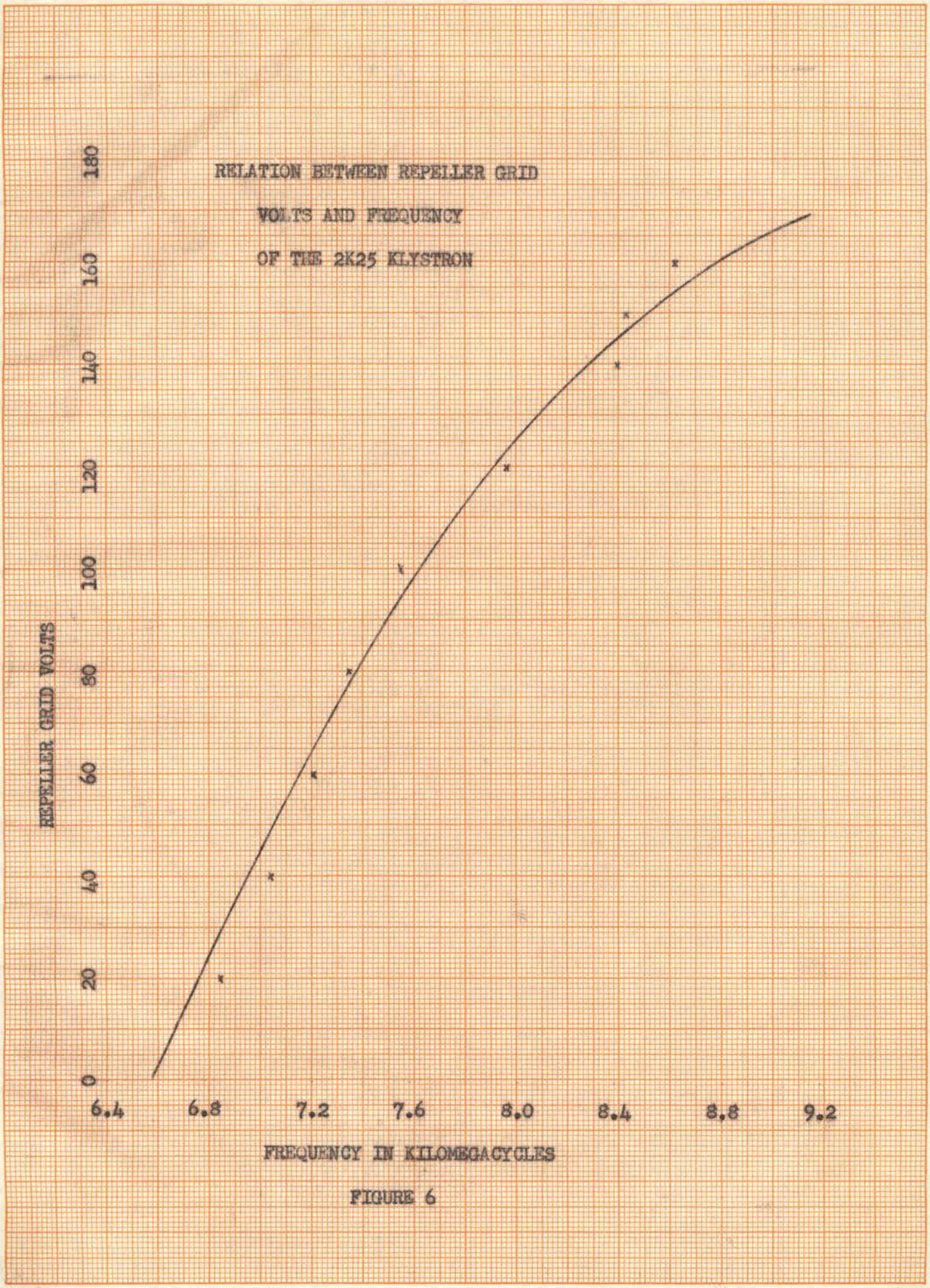

RELATION BETWEEN REPELLER GRID
VOLTS AND FREQUENCY
OF THE 2K25 KLYSTRON
REPELLER GRID VOLTS
0
20
40
60
80
100
120
140
160
180
6.4
6.8
7.2
7.6
8.0
8.4
8.8
9.2
FREQUENCY IN KILOMEGACYCLES

FIGURE 6

If an oscilloscope with a five-inch cathode ray tube using a 2,000-volt accelerating potential is employed for the indicator, the minimum value of the difference between the outputs of the two detectors, $(e_1 - e_2)$, that will produce an observable indication on the oscilloscope is approximately 0.4 volts.

TABLE I

FREQUENCY RANGE

REPELLER GRID VOLTS	HALF-WAVE LENGTH (CMS.)	WAVE LENGTH (CMS.)	FREQUENCY (MEGACYCLES)
170	1.640	3.280	9146.3
160	1.742	3.484	8610.8
150	1.780	3.560	8426.9
140	1.787	3.574	8393.9
120	1.883	3.766	7966.0
100	1.986	3.972	7552.8
80	2.039	4.078	7356.5
60	2.080	4.160	7211.5
40	2.127	4.254	7052.2
20	2.184	4.368	6868.1
0	2.274	4.548	6596.3

TABLE II

FREQUENCY DETERMINATION

REPELLER GRID VOLTS	CATHETOMETER READINGS (CM.)	AVERAGE DIFFERENCE (HALF-WAVE LENGTHS)
170	40.755	
	39.205	
	37.415	
	35.915	
	34.265	
	32.555	1.640
160	40.160	
	38.650	
	36.945	
	35.035	
	33.260	
	31.450	1.742
150	40.390	
	38.550	
	36.790	
	34.950	
	33.235	
	31.490	1.780
140	40.200	
	38.445	
	36.610	
	34.825	
	33.125	
	31.265	1.787
120	40.930	
	39.080	
	37.225	
	35.325	
	33.395	
	31.515	1.883
100	39.820	
	37.590	
	35.715	
	33.660	
	31.775	
	29.890	1.986

TABLE II (Continued)

FREQUENCY DETERMINATION

REPELLER GRID VOLTS	CATHETOMETER READINGS (CM.)	AVERAGE DIFFERENCE (HALF-WAVE LENGTHS)
80	39.825	
	37.840	
	35.770	
	33.445	
	31.340	
	29.630	2.039
60	41.375	
	39.300	
	37.290	
	34.965	
	32.635	
	30.975	2.080
40	40.615	
	38.575	
	36.240	
	33.970	
	31.745	
	29.980	2.127
20	40.840	
	38.790	
	36.735	
	34.495	
	32.255	
	29.920	2.184
0	41.940	
	39.710	
	37.410	
	35.120	
	32.685	
	30.570	2.274

SUMMARY

The problem was to construct an inexpensive microwave spectroscope for use in the 3 to 4⅓ centimeter range. Outlined in this paper are the methods used in constructing and testing three variations of such a microwave spectroscope.

Where applicable, war-surplus equipment was employed to further reduce the cost of the microwave spectroscope, and easily obtainable parts were employed in the construction of the auxiliary components.

Standing waves were employed to determine the frequency of the microwave radiation with an average deviation from the mean of 5.14 per cent.

Although no absorption lines were found, the possibility of many of the heavier molecules found in the fields of medicine and industrial chemistry having absorption lines in this range is not remote.

This microwave spectroscope can also be adapted for the future study of paramagnetism and ferromagnetism in certain substances.

BIBLIOGRAPHY

Freedman, S. "New Field of Microwave Spectroscopy." Radio and Television News, XLII (July, 1949), 27.

Good, W. E. "The Inversion Spectrum of Ammonia." Physical Review, LXX (August, 1946), 213.

Hughes, R. H. and Wilson, E. G. "A Microwave Spectrograph." Physical Review, LXXI (April, 1947), 562.

Smith, W. E. and Carter, L. C. "Microwave Spectrum Frequency Markers." Physical Review, LXXII (December, 1947), 1265.

Strandberg, Meng, and Ingersoll. "Microwave Absorption Spectrum of Oxygen." Physical Review, LXXV (May, 1949), 1524.

Townes, C. H. "The Ammonia Spectrum and Line Shapes Near 1.25 Centimeters Wave Length." Physical Review, LXX (November, 1946), 666.

Watts and Williams. "A Double Modulation Detection Method for Microwave Spectra." Physical Review, LXXII

Weidner, R. T. "Microwave Spectrum of Iodine Monochloride at 4½ centimeters wavelength." Physical Review, LXXII (December, 1947). 1268.

White, H. E. troduction to Atomic Spectra. New York and London: McGraw-Hill Book Company, 1934.

TYPIST

Mrs. Adelia Henderson