CONSTRUCTION OF A MICROWAVE SPECTROSCOPE FOR THE 3 TO 4.5 CM. WAVE LENGTH RANGE

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INTRODUCTION

The best-known early investigator of the spectrum was Sir Issac Newton, who in 1666 inserted a prism in a beam of sunlight shining into a dark room and saw a band of colors on the wall. By using a lens in conjunction with the prism he was able to spread the colors out into a fairly pure spectrum 10 inches long. He fell short of reproducing a spectroscope of the modern type only because he let the light shine through a round hole instead of a narrow slit. Thus Newton led the way for the exploration of the composite nature of light and finally that of all electromagnetic waves.

There are many ways of studying the composite nature of these radiations. The instruments used are called spectrographs, spectrometers, or spectroscopes, depending on how the device indicates the results. The spectrum has been defined as the ordered arrangement of radiation according to wave length. Electromagnetic radiations have been discovered that have wave lengths of every value in the range from thousands of kilometers to trillionths of a millimeter, or from 60-cycle current to gamma-rays. A complete electromagnetic spectrum would comprise all these radiations arranged in order from the longest to the shortest wave lengths. Since no single instrument exists that will separate radiation containing all these wave lengths into a spectrum, the electromagnetic spectrum has been divided into various "regions" in accordance with the type of instrument used to produce and detect the waves of various lengths.

The accomplishments achieved by scientists through use of the spectroscope form a list so imposing as to leave no doubt that this instrument is one of the most powerful now available for investigating the natural universe. But spectroscopy is valuable not only to the research scientist; it is finding increasing use in technological laboratories. Today directors of such varied enterprises as factories, assay offices, arsenals, mines, crime detection bureaus, public health departments, hospitals, museums, and technical research institutes consider access to spectroscopic equipment essential to the proper functioning of their laboratories.

Spectra may be divided generally into emission and absorption types. Ultraviolet light, X-rays, white light, and infrared light are used for the exciting radiation in the emission type. This wave length range is from about 10^{-8} centimeters to 10^{-4} centimeters.

The absorption type may also be subdivided according to the nature of the radiation absorbed. Thus there are ultraviolet, X-ray, white light, infrared and microwave absorption spectra. The wave length range for such spectra is from about 10^{-8} centimeters to 10^1 centimeters.

In this paper only microwave absorption spectra will be considered. Study in microwave spectroscopy is usually confined to the investigation of compounds having the larger molecular make-up, because of the frequency limitations imposed by the microwave equipment. Microwave spectroscopy is a comparatively new method for obtaining information about molecular structure and research workers are gaining an increasing interest in its application.

The effect of World War II on microwave spectroscopy was as manifold as in other fields. During the national emergency while government spending was at its peak, laboratories, equipment, and personnel were directed toward the research and development of microwave equipment and its use. After the war, great advancements in this field were made and the ground work laid for future developments as the knowledge acquired during the war was made available to all research workers.

CHAPTER I

THE PROBLEM AND OUTLINE OF SOLUTION

The initial problem was the construction of a microwave spectroscope of the absorption type capable of working in the 3 to 4.5 centimeter wave length range. This spectroscope was to be capable of generating electromagnetic radiation of these wave lengths and also of detecting and differentiating between the various types of absorption, thereby indicating only the absorption taking place within the specimen gas. Finally, equipment was to be devised for measuring the frequency of the electromagnetic radiation being absorbed.

The construction problem can best be discussed by considering separately the various components of the spectroscope, which is shown in Fig. 1. The source of materials consisted chiefly of pieces of war surplus equipment, some of which could be used intact as basic components, and others of which had to be modified to fit the prescribed needs. Since there was no inventory of the surplus equipment available some difficulty was encountered in procuring the needed components. Considerable difficulty was also experienced in locating schematic diagrams, instruction books, and other sources of data for this surplus equipment once it was obtained. As a result, some time was spent in investigating the possibility of its use in the microwave spectroscope.

In assembling the parts, search was first launched for a microwave oscillator, the heart of the spectroscope. This was found in a surplus Navy radar test set, the TS-35, which contains a 3-centimeter klystron oscillator complete with power supply. Next a transmission system to guide the microwaves was produred. An alternate size of wave guide, rather than that which fits the TS-35, was chosen because of its availability. It was



salvaged from a surplus Navy antenna unit, the AN/APS 18A. Crystal detectors and their mounts were found both in the TS=35 and in a surplus wavemeter which also had coaxial fittings to an air-type horn, the Navy type AT/48UP. Equipment used from the physics laboratory included a R. C. A. Model 640 radio frequency signal generator, a surplus BC=348 radio receiver, and a 5-inch cathode ray oscilloscope. Equipment built from parts included a sawtooth generator, a difference amplifier, and microwave transmission horns, attachable to the wave guide.

One of the foremost problems which presented itself early in the construction of this spectroscope was the measurement of the frequency of the klystron. There were several wavemeters available but none was calibrated, and no standard was found in this immediate area. Because the expense of a precision-type calibrated wavemeter was prohibitive much time was spent in devising another method of measuring the frequency. The idea of making use of standing waves was adopted, since there was available both a suitable deflection plate and a vertical cathetometer for the accurate measurement of distances.

CHAPTER II

THEORY OF MICROWAVE SPECTRA AND OF OPERATION OF EQUIPMENT

A. Microwave Spectra

The physical interpretation of molecular spectra is steadily becoming more and more important. The technique of microwave absorption, first discovered in 1934 by Cleeton and Williams, is directed toward this physical interpretation of molecules.

The study of microwave absorption can be presently divided into three general fields of interest. The first field of interest is in determining the gaseous dielectric constant. This study infers a dipole moment which must fit in with the molecular sizes determined from electron diffraction and also be related to the temperature coefficient of viscosity. The second field of interest is the study of microwave absorption, which enables information to be gained on collision processes. This in turn involves the forces between molecules. The third field of interest is the study of the effect of electric and magnetic fields on microwave spectra. It has been shown that this can lead to the determination of nuclear spin.

The spectrum emitted by any given kind of molecule can be divided into three classifications which correspond to different types of transitions between molecular quantum states. Thus there are rotation spectra, vibrationrotation spectra, and electronic spectra.

In consideration of the rotation spectra, suppose a molecule were a rigid structure but contained electrical charges so disposed that the molecule possessed an electric moment. If such a molecule were to rotate, according to the classical theory, it would emit radiation for essentially

¹ Cleeton and Williams, "Electromagnetic Waves of 1.1 cm. Wave-Length and the Absorption Spectrum," <u>Physical Review</u>, 45 (February, 1934), 234-9.

the same reason that an electron revolving in a circle would radiate. It is readily seen that the radiation would consist of sine waves having a single frequency, the frequency of rotation. Conversely, radiation falling upon such a molecule would tend to set it into rotation, energy of the radiation being at the same time absorbed. A few spectral lines corresponding to this simple picture have been observed in the far infrared and microwave regions and are said to constitute the rotation spectra.

In regard to the vibration-rotation spectra, if the molecule were not rigid but contained atoms capable of vibration under elastic forces about equilibrium positions, and if the chemical binding were of the ionic type, so that some atoms contained an excess of positive charge and others an excess of negative, radiation would be emitted by the vibrating atoms as they moved back and forth. Unless the molecule were rotating at the same time, the frequency emitted would be divided into two lines having frequencies respectively greater or less than the frequency of the atomic vibration. Although still periodic, the vibrations would no longer be simple harmonic. The radiation emitted could then be resolved by Fourier analysis into wave trains with frequencies representing the fundamental and harmonics of the atomic vibrations. Each of these separate frequencies would then be split up further by rotation of the molecule.

In the electronic spectra an electron in the molecule might vibrate by itself and so radiate or absorb. The emitted radiation would be affected, however, both by the vibration of the atoms in the molecule and by the rotation of the molecule as a whole. The rotation of the molecule would tend to split up the emitted lines as in the emission of the vibration-rotation spectrum.

The first classification, rotation spectra, will be the only case considered, because of the limited range of frequency of microwave spectroscopy. If a molecule undergoes a transition between two energy levels very close together, microwave absorption results. The energy equivalent to one quantum at 10,000 megacycles, the approximate upper limit of the frequency of the equipment described in this paper, is given by the product of h, Planck's constant, and f, the frequency. This product is equal to (6.6×10^{-27}) (1×10^{10}) ergs or 0.66×10^{-16} ergs, which is equivalent to 4.1×10^{-5} electron volts per molecule or 0.953 calories per mole. This is very much less than that of the mildest chemical reaction between ordinary molecules. It is also far less than the usual energy separation between levels due to electronic transitions or to vibration in ordinary molecules. On the other hand, the energy of separation between rotation levels is not so large.

The relation between angular momentum and energy is found to be the same according to wave mechanics and in classical theory. For the classical theory the angular momentum G = Iw, and the energy $W = 1/2 Iw^2$, where I denotes moment of inertia and w the angular velocity. Therefore $W = G^2/2I$. Inserting here the wave-mechanical value for the square of angular momentum,

$$G^2 = \frac{J(J+1)h^2}{4\pi^2}$$

Then

$$W = \frac{h^2 J(J+1)}{8 \pi^2 I}$$

where the quantum number J can have the values 0, 1, 2, 3, ..., etc. For an ordinary linear molecule like iodine monochloride, IC1³⁵, the moment of

inertia I, perpendicular to the axis of the molecule, is 2.4×10^{-38} gramcm.².² Thus the separation value between the first two energy levels is 0.23×10^{-16} ergs which is of the order of energy found for one quantum of the 10,000 megacycle energy. The separation of rotational levels is therefore one which is of the right order, and it may be expected that microwave spectra will be concerned with the rotational levels. Measurements on rotational levels yield information about the moments of inertia of a molecule which in turn is a clue to the correct molecular structure. The rotational lines are very sharp, and the moments of inertia so deduced are in very close agreement with the theoretically predicted values.

B. Operation of Equipment

Microwave spectroscopy is the study of the absorption of microwave radiation propagated through a specimen gas. The construction and assembling of the equipment mentioned in Chapter I was directed toward such a study.

Two general methods may be used in making this study with the assembled apparatus. The first involves direct detection and the second the heterodyne principle.

The direct detection method, Fig. 2a, utilizes a microwave oscillator with its output directed into two arms, the control arm and the specimen arm. The control arm includes an attenuator and crystal detector. The specimen arm incorporates a calibrated wavemeter, specimen chamber, and crystal detector. The pressurized specimen chamber in which the gas is confined consists of a section of wave guide sealed at both ends with mica

² Richard T. Weidner, "The Microwave Spectrum of Iodine Monochloride at 4 1/2 Centimeters Wave Length," <u>Physical Review</u>, 72 (November, 1947), 1268-9.





windows. The outputs of both arms are detected by means of crystal detectors and fed to a difference amplifier. The difference amplifier output is placed on the vertical deflection plates of an oscilloscope as indicated in the block diagram of Fig. 2a. The range of the oscillator frequency and the horizontal sweep of the oscilloscope are controlled and synchronized by the output voltage from a saw-tooth generator. With this arrangement absorption taking place in the specimen gas causes the outputs from the two detectors to differ, resulting in a vertical deflection on the oscilloscope. This deflection is in the form of a "pip" at a position on the sweep corresponding to the absorption frequency. Absorption by the wavemeter will cause a similar "pip". By tuning the wavemeter this "pip" may be superimposed on that due to the absorption in the gas. This provides a convenient means of measuring the absorption frequency. The control arm is also used to determine the amount of attenuation in the specimen gas at the absorption frequency. The gaseous dielectric constant is calculated from the measured attenuation.

A variation of this method is shown in Fig. 2b. In this case, the output of the same oscillator is connected through sections of wave guide and a calibrated wavemeter to radiating horns, between which a plastic bag containing the specimen gas is inserted. This plastic bag is transparent to the microwaves. Again, the output is detected by a crystal detector and fed to the difference amplifier as in Fig. 2a. An impedance match between the control arm and the specimen arm is obtained by a second set of horns with only air in between.³ The output from the control arm is detected and indicated in the same manner as for the specimen arm. This arrangement is convenient for the analysis of specimens in the liquid and solid state, as well

3 A. E. Harrison, Klystron Tubes, pp. 216-217.

as the gaseous state. The same method of determining the absorption frequency may be used as is employed in the first arrangement.

In the heterodyne detection method illustrated by the block diagram of Fig. 3, a radio frequency signal generator is used to frequency modulate the microwave oscillator. This oscillator frequency is still controlled by the sawtooth generator. The frequency modulated output is directed through sections of wave guide to the calibrated wavemeter and the specimen gas enclosed in a pressurized section of wave guide. This frequency modulated signal is also amplitude modulated at an audio rate on passing through the gas, if absorption takes place at only certain discrete frequencies. This amplitude modulation arises because the wave train is attenuated by the absorption only at those points at which the frequency of the waves corresponds to the absorption frequency. If absorption takes place in the specimen chamber, a greater amount of power is consumed and there is an increase in amplitude modulation that can be observed on the oscilloscope. The crystal detector removes the microwave component and the remaining radio frequency signal, amplitude modulated at an audio rate, is connected by means of coaxial cable to the antenna of a commercial radio receiver. Here, the radio frequency signal is removed and the amplified audio envelope is placed on the vertical deflection plates of the oscilloscope. Again the absorption frequency may be determined as in the first method.



CHAPTER III

CONSTRUCTION, DESIGN AND TESTING OF EQUIPMENT

In this chapter the components will be treated individually in order to clarify the details of each part of the apparatus.

There was no schematic diagram available for the Navy test set TS-35. However, in Fig. 4 there is a schematic diagram drawn from an inspection of the equipment. The frequency of the reflex klystron, the 723 A or 2K25, was controlled by the potential applied to its repeller grid. Repeller grid voltages are listed in Table I with the corresponding klystron output wave length and frequency. 180 volts is the maximum safe operating potential on the repeller grid of the klystron. This limits the highest frequency attainable.

In selecting the wave guide to be used to transmit the microwaves two predominate factors had to be kept in mind. The first of these was the inherent characteristics of a particular size of wave guide, and the second was the availability of that size.

Throughout the transmission system an attempt was made to use only the $TE_{0,1}$ (transverse electric) mode, thereby having in principle only the first harmonic of the microwave oscillator to deal with. This was to simplify the determination of frequency and the observation of absorption in the gas. The usable wave length range for the $TE_{0,1}$ mode for wave guide of Army-Navy type number RG=51/U is from 3 to 4.26 cm., with cutoff wave length at 5.7 cm.¹ This is the type of wave guide which is incorporated in the TS=35 and is ideal for the experimental setup with regard to the inherent character-

¹ Federal Telephone and Radio Corporation, Reference Data for Radio Engineers, Third Edition, p. 349.



TABLE I

FREQUENCY RANGE

REPELLER GRID VOLTS	HALF-WAVE LENGTH (CMS.)	WAVE LENGTH (CMS.)	FREQUENCY (MEGACYCLES)
170	1.640	3,280	9146
160	1.742	3.484	8611
150	1.780	3.560	8427
140	1.787	3.574	8394
120	1.883	3,766	7966
100	1.986	3.972	7553
80	2.039	4.078	7357
60	2.080	4.160	7212
40	2.127	4.254	7052
20	2,184	4.368	6868
0	2.274	4.548	6596

,

istics of the wave guide. However, this type of wave guide was not available and resort was made to the standard 3 cm. wave guide whose Army-Navy type number is RG-52/U. The usable wave length range for the same mode with this wave guide is from 2.4 to 3.66 cm., with the cutoff wave length at 4.57 cm. Connection of the standard wave guide to the larger wave guide in the TS-35 was made by a reducing "L". The TE_{0,1} mode of the microwaves is attenuated 0.076 decibels per foot in the standard 3 cm. wave guide and 0.050 decibels per foot in the wave guide incorporated in the TS-35.² The smaller size wave guide causes noticeable attenuation of the microwaves in the lower frequency range of the oscillator. The relative power outputs at different frequencies were observed from the readings of the microwaves on the coaxial wavemeter, the X-6177A.

The physical location of the variable attenuators on the TS-35 is in the wave guide between the klystron resonant chamber and series tee. Their position in the experimental set up can be found by referring to Figs. 2a, 2b, and 3. One purpose of the attenuators is to act as a control on the signal output by introducing a variable amount of inductive reactance in the system. By using the attenuators a reference level for the amplitude of the output can be established and this value reestablished for each trial made on the specimen gas. There was no instrument such as a bolometer available for the direct measurement of power output. However, by calibrating the attenuators a ratio of powers could be obtained.

The klystron was adjusted for maximum power output as indicated on the

2 Ibid.

microammeter on the TS-35. At this time the reading of the microammeter on the coaxial wavemeter was recorded. This reading was proportional to the maximum power output. The klystron was then adjusted for minimum power output and in a similar manner a reading from the microammeter of the wavemeter which was proportional to the minimum power output was recorded. The ratio of maximum power to minimum power was thus determined for a particular setting of the attenuator dials. The same procedure was followed for each combination of the two attenuators dial settings. Connection between the wave guide and the wavemeter was made by use of the air-type horns, the Navy type AT-48/UP. Table II lists the calibration of the variable attenuators in terms of the ratio of maximum power to minimum power and also gives the same ratio expressed in decibels.

The schematic diagram of the saw-tooth generator is in Fig. 5. This circuit makes use of an 884 thyratron tube and a 666 power pentode to maintain a constant charging current. The accompanying graph of Fig. 5 indicates the variation of saw-tooth frequency with change in output volts.

To determine the frequency of the microwaves, standing wave measurements were made using a vertical cathetometer and metal deflection plate. The vertical cathetometer vernier scale had a least count of five-thousandths of a centimeter. The deflection plate held at right angles to the cathetometer was noved parallel to the radiation from the air-type horn, until a maximum reading was obtained on the output microammeter of the TS-35. After the reading was recorded, the deflection plate was again moved until the position for the next maximum on the meter was determined. The difference between the two readings is one-half wave length of the microwaves being measured. This process was continued until five more consecutive half-wave

TABLE II

ATT-2	ATT-1	POWER MAX./ POWER MIN.
2	0	4
4	0	16
6	0	64
8	0	256
10	0	1024
0	2	4
0	4	16
0	6	64
0	8	256
0	10	1024
2	2	16
4	2	64
6	2	256
8	2	1024
ATT2	ATT-1	DECIBELS
		10 log (P max./ P min.)
2	0	6.2
4	0	12.0
6	0	18.1
8	0	24.1
10	0	30.1
0	2	6.2
0	4	12.0
0	6	18.1
0	8	24.1
0	10	30.1
2	2	12.0
4	2	18.1
6	2	24.1
8	2	30.1
-	-	

CALIBRATION OF ATTENUATORS



point readings were obtained. The five half-wave lengths were averaged to obtain a value of greater accuracy. In Table III these are tabulated with the respective repeller grid voltages on the reflex klystron. This method of measuring frequency proved to have an average deviation from the mean of 5.14 per cent. Fig. 6 is a plot of frequency in kilomegacycles against repeller grid voltage.

Greater accuracy in the half-wave length determination could have been attained by using another cathetometer capable of measuring to one tenthousandth of a centimeter. This was unwarranted, however, due to faulty ourrent regulator tubes within the TS-35, which made a steady maximum reading on the meter difficult to obtain. Effort made to secure replacements for these tubes was to no avail.

The accuracy attained in measuring the frequency with standing waves was greater than that attained with a wavemeter calibrated from these measurements. A resonant type wavemeter, the Navy type TS-147/UP, making use of wave guide sections, was also used to determine the frequency of the klystron oscillator. It could be read with an absolute error not less than two megacycles. This wavemeter measured the frequency of the microwaves directed into the specimen gas, its physical location being between the output of the TS-35 and the specimen chamber.

The schematic of the difference amplifier is in Fig. 7. This circuit makes use of a twin triode tube, the 6SN7. The purpose of the difference amplifier is to obtain a voltage proportional to the difference between the two potentials, E_1 and E_2 . The potential E_1 is placed on the grid of the first triode and the potential E_2 is placed on the grid of the second triode. The plate voltage output of the second triode, E_0 , is then

TABLE III

FREQUENCY DETERMINATION

REPELLER GRID	CATHETOMETER	AVERAGE DIFFERENCE
VOLTS	READINGS (CM.)	(HALF-WAVE LENGTHS)
170	40.755	
	39,205	
	37.415	
	35,915	
	34.265	
	32.555	1.640
160	40.161	
	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	de a
	35.325	
	33.395	
	31.515	1.883
100	39.820	
	37.590	
	35,715	
	33,660	
	31.775	
	29.890	1.986

REPELLER GRID	CATHETOMETER	AVERAGE DIFFERENCE		
VOLTS	READINGS (CM.)	(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		

TABLE III (CONT'D)





taken off as the amplified difference of these two potentials. This output voltage is determined from the characteristics of the tube and the circuit. The output, E_0 , is given by the formula³

$$E_0 = \frac{\mu R}{2(r_p + R)} (E_1 - E_2) - \frac{A}{(A + 1)} (E_1 + E_2)$$

where μ = tube amplification factor A = circuit amplification factor r_p = dynamic plate resistance and A = $\frac{R + r_p}{2(\mu + 1)R_k}$

 $E_0 = \frac{\mu R}{2(r_p + R)} (E_1 - E_2)$

$$= K (E_1 - E_2)$$

The sensitivity of the difference amplifier was determined by finding the minimum potential difference $(E_1 - E_2)$ which would produce an observable indication on the trace of the oscilloscope. The sensitivity so determined was found to be 0.4 volt for the 5 inch oscilloscope using a 2 kilovolt accelerating potential.

3 William C. Elmore and Mathew Sands, Electronics, pp. 52-53.

SUMMARY

A microwave spectroscope for the 3 to 4.5 centimeter wave length range was constructed using available war-surplus equipment.

The microwave frequency was measured by two methods. First, the frequency of the microwaves was found by determining their wave length making use of standing waves. The frequencies so obtained had an average deviation from the mean of 5.14 per cent. Then these results were used to calibrate the wavemeter used in the spectroscope. The calibrated wavemeter could be read with an absolute error of not less than two megacycles.

No absorption lines were found in using the microwave spectroscope for trial runs made on air, carbon dioxide and smoke. The comparatively low frequency output of the microwave oscillator and accompanying transmission system used definitely limited the number of gases that could be investigated. For example, iodine monochloride has absorption lines within the range of this equipment.¹ However, the boiling point of this compound is 97° Centigrade and to use it in the gaseous state would require a device, such as a steam jacket, with which to surround the specimen chamber. The corrosive properties of this gas would undoubtedly affect the silver plating of the specimen chamber, perhaps rendering it useless. Iodine monochloride is prepared by saturating liquid chlorine with solid iodine.² Thus this gas would be difficult to use or prepare.

The microwave spectroscope could possibly be used in the future for

¹ R. T. Weidner, "Microwave Spectrum of Iodine Monochloride at 4 1/2 Centimeters Wavelength," Physical Review, 72 (November, 1947), 1268-9.

² Jacob Cornog and R. A. Karges, "Preparation of Iodine Monochloride," Journal American Chemical Society, 54 (July, 1932), 1882-7.

studies of paramagnetism and ferromagnetism in certain substances.³ The frequency range of this equipment is satisfactory for that type of study.

Recommendations to future workers on this microwave spectroscope would include replacement of the current-regulator tubes in the TS-35; replacement of the resonant type wavemeter used with a more accurate one; provision for use of frequency doubler circuits, thereby increasing the number of gases that could be investigated with the spectroscope; provision of means for applying magnetic and electrostatic fields to the specimen chamber; applying frequency markers to the heterodyne setup;⁴ and the use of standard 3 centimeter wave guide throughout the microwave transmission system. This in effect would mean replacing the TS-35 with a different microwave source, one of greater frequency range and one which incorporates standard wave guide. This would enable, with proper choice of equipment, the procurement of parts for the spectroscope from commercial sources.

³ C. Kikuchi and R. D. Spence, "Microwave Methods in Physics II Microwave Absorption in Paramagnetic Substances," <u>American Journal of Physics</u>, 18 (April, 1950), 167-182.

⁴ Robert L. Carter and William V. Smith, "Microwave Spectrum Frequency Markers," Physical Review, 72 (November, 1947), 1265-6.

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