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# Diagnosis of Air Pollution by Microwave Spectroscopy<sup>†</sup>

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A review is made of the current state-of-the-art of microwave spectroscopy, and of the feasibility of using this technique in the detection of gaseous pollutants in air. The possibility of applying ultraviolet, visible, and infrared spectroscopic methods to the microwave region is investigated. This is a relatively new application of microwave spectroscopy; only one work was done in the area before 1966, and no results from it were published.

Present experimental work, being done by the authors, is explained. This is divided into two phases. First, basic measurements are being made to determine the limits of pressure over which small concentrations of pollutants may be measured in air. Second, methods are being investigated for adapting the techniques of microwave spectroscopy to the detection of gaseous pollutants. Specifically, it is desired to develop an instrument which will quantitatively detect pollutants at atmospheric pressures. This instrument may be incorporated in a system for air pollution monitoring over large expanses from remote stations, or stack monitoring.

## INTRODUCTION

In 1969-70, investigators<sup>1-5</sup> indicated that microwave spectroscopy should prove to be a very worthwhile tool for the measurement of small concentrations of pollutants in air, but the use of microwave spectroscopy to detect

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small concentrations of one gas in the presence of another has not been studied until very recently.<sup>4,5</sup> The only reference to air pollution work in the microwave region found before 1966 is one by Hershberger,<sup>6</sup> who planned to use a Stark modulated microwave spectrometer to analyze condensable materials found in the Los Angeles atmosphere.

The purpose of this paper is to inform the reader of the principles of microwave spectroscopy, and propose how it may be applied to present-day problems of air pollution diagnosis. Work in this and the related area of infrared, visible, and u.v. spectroscopy is reviewed to date, and some proposals are made to adapt the techniques used in these spectral areas to the microwave spectrum. Some original but heretofore untested ideas are set forth for consideration.

### PRINCIPLES OF MICROWAVE SPECTROSCOPY

Radiation in the microwave region is produced (or absorbed) by changes in the rotational quantum state of a molecule, in the  $10^3$ – $10^6$  micron region (0.3–300 gigahertz). The conventional term used in microwave spectroscopy

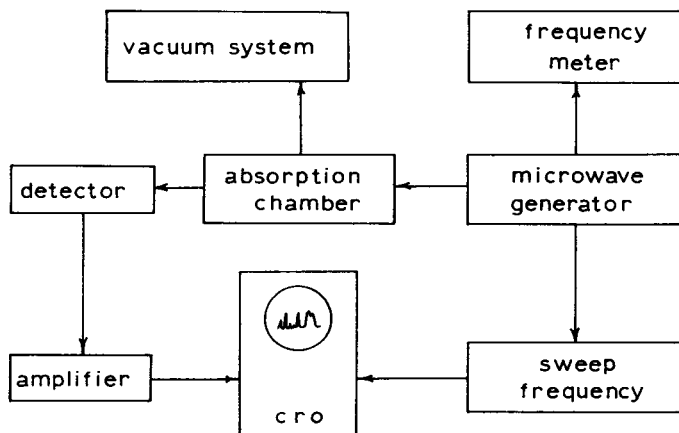


FIGURE 1 Microwave spectrometer.

is gigahertz (1 GHz =  $10^9$  cycles per second). A typical microwave spectrometer is depicted in Figure 1. Resolution of microwave frequencies to 0.0004 GHz is easily attained.<sup>1,7-10</sup>

The principal gaseous pollutants of interest for ambient air analysis are exemplified in the Philadelphia area as<sup>11</sup> CO, 6.0–49.0 ppm; NO, 0.01–1.68 ppm; NO<sub>2</sub>, 0.03–0.22 ppm; SO<sub>2</sub>, 0.03–1.10 ppm; hydrocarbons, 1.6–13.3 ppm; oxidants, 0.01–0.31 ppm. Figure 2 gives the positions of

the more intense absorption lines of some common pollutants and normal atmospheric gases.<sup>12,13</sup> Isotopes whose concentrations are negligible in air are not considered in this or the following figure. The numbers above the lines indicate the number of lines in a small interval. Figure 3 gives the absorption lines of some organic compounds which were encountered as pollutants, in an ambient air sampling survey<sup>14</sup> and an analysis of life support atmospheres.<sup>15</sup> Data for other pertinent organics are not published, although unpublished data referred to by Jones and Beers<sup>16</sup> give the number of lines in the microwave region for 33 molecules.

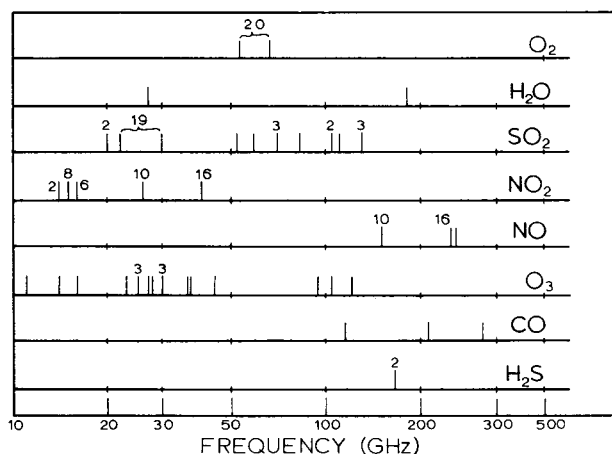


FIGURE 2 Absorption lines of small molecules in the microwave region.

Particulate matter obscures spectroscopic analysis near the visible region; however, particulates of these sizes are practically invisible to microwave radiation, because their diameters are so much smaller than the microwave wavelengths. Thus, microwave spectroscopy should be ideal for detecting gaseous pollutants in the midst of particulates, such as in the column of smoke emitted by a smokestack.

The absorption spectrum of a gas is, however, a function of temperature and—most importantly—pressure. The pressure dependence is illustrated by the absorption spectrum of O<sub>2</sub>, given in Figure 4 for various pressures.<sup>17</sup>

The absorption spectra of O<sub>2</sub> and water vapor have been extensively studied.<sup>17-30</sup> Both molecules cause attenuation in microwave propagation. Nitrogen has no absorption at all in the microwave region. The theoretical treatment of microwave absorption spectra was proposed and modified by Van Vleck, Weisskopf, and others;<sup>18,26,27,29,30</sup> at present there is no

theoretical treatment which completely accounts for an experimental microwave absorption spectrum.<sup>22,25</sup>

The broadening of the spectral lines in the microwave region occurs primarily because of collisions between gas molecules. If a sample of air containing small amounts of pollutants is investigated at a low enough pressure, such as 50 millitorrs, the collisional broadening becomes small enough that the lines corresponding to the various gases present will no longer overlap; the intensities of the lines being a function of the concentrations of the gases producing them.<sup>4</sup>

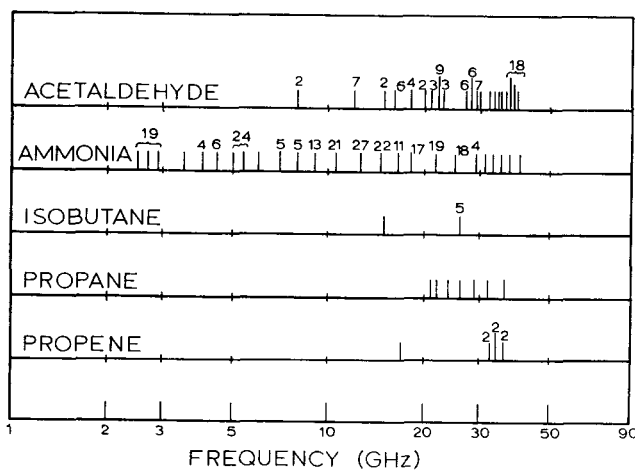


FIGURE 3 Absorption lines of organics in the microwave region.

Ludwig<sup>5</sup> mentions that pressure-broadening would cause the pollutant lines to be difficult to distinguish, but just how much broadening would occur in a gas mixture is not clear. Calculation of line widths for gas mixtures is extremely complicated, as seen by the article by Benedict and Kaplan<sup>31</sup> for a mixture of  $H_2O$  and  $N_2$ . Experimental work is necessary for the clarification of this effect.

Furthermore, Ludwig's investigation did not take into account the possibility of improving the existing standard microwave spectroscopic techniques through the employment of correlation techniques, interference, and the use of microwave cavities as the absorption chamber, as explained further in this paper.

Stark or Zeeman modulation is sometimes used to increase the sensitivity of a microwave spectrometer.<sup>9,10</sup> Stark modulation is accomplished by switching a d.c. electric field (of the order of several hundred volts per  $cm^{10}$ )

off and on in the absorption chamber; the frequency of resonance is shifted (and the line itself is split) in the presence of the d.c. field, so that the radiation, after having passed through the absorption chamber, is effectively being switched off and on at the modulation frequency. The amplitude of the difference is easily detected as an a.c. variation. Zeeman modulation follows the same principles as Stark modulation, using a d.c. magnetic field.

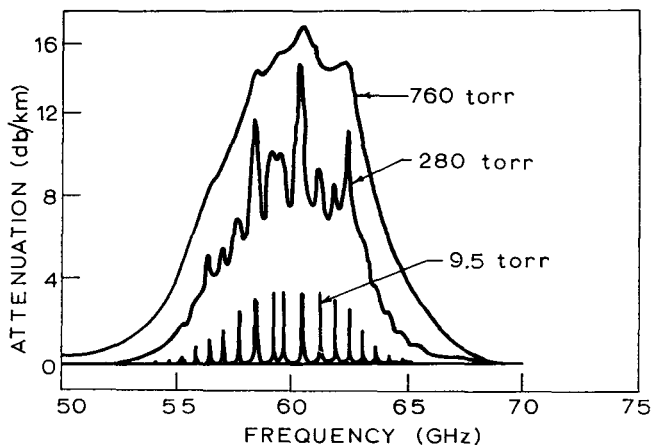


FIGURE 4 Absorption spectrum of oxygen in the microwave region (one absorbance unit = one decibel) (Ref. 17).

### DIAGNOSIS USING STATE-OF-THE-ART MICROWAVE SPECTROSCOPY

White, in 1966,<sup>15</sup> used a standard "home-built" microwave spectrometer, with a single-pass absorption chamber and Stark modulation, to investigate the possibilities of using microwave spectroscopy in the 10–40 GHz range to find ppm concentrations of the contaminants of artificial atmospheres. In this preliminary investigation, the samples studied were prepared in advance, containing as little as 1,000 ppm of the contaminant in air; (of his work, only  $\text{NH}_3$ , acetaldehyde, and  $\text{SO}_2$  are of primary interest in air pollution studies). White estimated that 10 ppm, 40 ppm, and 50 ppm of these contaminants could be detected, respectively, using this method. He points out the possibility of measuring much lower concentrations by enriching the samples, either through cryogenic methods, or by osmosis through selective membranes. At present he is working on this latter method of enrichment.<sup>32</sup>

Rinehart and Fletcher,<sup>33</sup> using a standard Stark-modulated spectrometer with a single-pass absorption chamber, measured  $\text{SO}_2$  at a concentration of 5.3 ppm in air on the 37.35179 GHz line. However, the sample in this case

was admitted to a vacuum system; all condensables were frozen out with liquid  $N_2$  and the system was pumped to a low pressure. The temperature was then raised enough to allow the  $SO_2$  to be released. A graph of signal versus pressure was made, and from this graph the concentration of  $SO_2$  was determined.

Hewlett-Packard<sup>4</sup> have been using their commercial Model Number 8460 Microwave Spectrometer to diagnosis 5–20 ppm of gases such as  $SO_2$ , formaldehyde, propionaldehyde, and acrolein separately from an arbitrary mixture.<sup>3,4</sup> A single-pass absorption chamber with Stark modulation, and a frequency range from 8 GHz to 40 GHz is used. It costs from \$27,000 to \$100,000.

Hrubesh, Anderson, and Rinehart<sup>3,5</sup> have used an open-sided microwave resonant cavity as the absorption chamber, with both Zeeman and Stark modulation, and have found it works well in detecting lines of  $NO_2$  and  $NH_3$  around 26 GHz. Although the device has been used only on the pure gases, and at low pressures, the development of this spectrometer illustrates the fact that an open-sided cavity spectrometer is another practical type of cell. Frequency change can be accomplished by changing the spacing between the plates of the open-sided cavity.

In each of the systems described, the sample has to be collected, transported to the instrument, reduced in pressure, and finally diagnosed. Pressures of around 20–100 millitorr must be used. In the method of Rinehart and Fletcher, the slope of a graph of signal versus pressure had to be determined before the final result could be obtained. The above systems all have the drawback that the analysis is not done “on-site”: the sample must be collected at one site and transported to the site of the spectrometer before analysis can take place.

## THE DILEMMA

At present, conventional microwave spectroscopy can be used to detect ppm levels of pollutants directly. Since pollutants are present in ppb concentrations, it would seem logical to abandon the microwave spectrometer as a potential ambient air pollution monitoring instrument, if it were not for the fact that the microwave region is rich with absorption lines of most pollutants, and there are many possibilities for improvement of the sensitivity. Through enrichment of samples it is possible to detect the levels of pollutants encountered in ambient air samples; but it is obviously most desirable to modify the method in such a way that they be detectable at atmospheric pressures. However, this desire is fraught with difficulty, the main trouble being the pressure-broadening of absorption lines of  $O_2$  and water vapor, which are major components of the atmosphere.

The normal atmospheric attenuation, for the case in which water vapor concentration of  $7.5 \text{ gm/m}^3$  exists at STP in the atmosphere, is shown in Figure 5. The peaks at 22 GHz and 183 GHz are due to water vapor; those at 60 GHz and 120 GHz are due to  $\text{O}_2$ . The other major atmospheric constituent,  $\text{N}_2$ , and trace gases such as A, Kr, He, Xe, and  $\text{H}_2$ , have no absorption lines in the microwave region.<sup>28</sup>

There are "windows" in the atmospheric attenuation curve at 16 GHz, 35 GHz, and 94 GHz, which have been carefully investigated,<sup>22,36</sup> and other, higher-frequency windows which may not be so appropriate due to the high

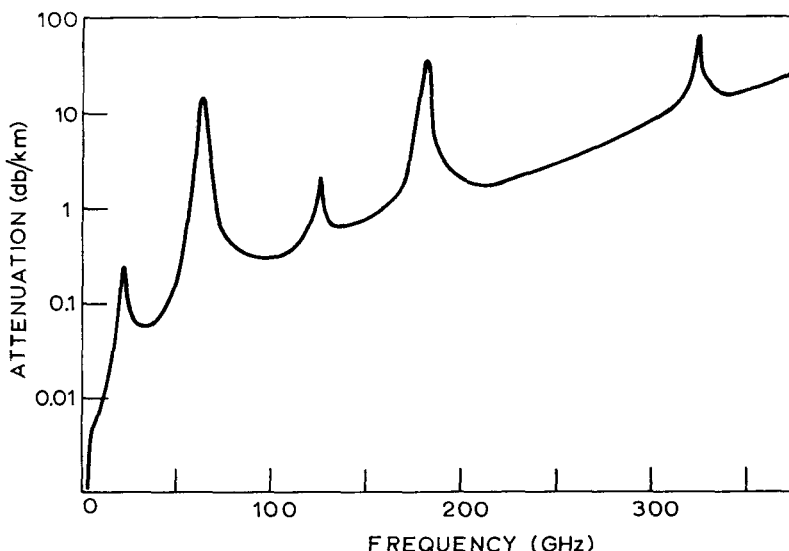


FIGURE 5 Attenuation of microwaves in air at STP. (one absorbance unit = one decibel) (Ref. 20).

cost of microwave gear for frequencies in the 100-GHz region. The sources of microwave radiation have been expensive in the past, especially in the higher frequency bands (K-band, 18.0 GHz to 26.5 GHz; KA-band, 26.5 GHz to 40.0 GHz; and millimeter wavelengths corresponding to frequencies into the 100-GHz range). Lately, however, these higher frequencies have been coming into common use, and the price of sources is becoming reasonable. If the 16-GHz window is used, considering only the most intense lines, one should be able to detect  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ , acetaldehyde, isobutane, propene, and perhaps  $\text{SO}_2$ . This, however, is very near the water vapor line, which will be a



bit harder to compensate for than the oxygen line, because the percentage of water vapor in the air may easily vary from a typical 1% to perhaps three times as much. Around the 35-GHz window, we may be able to detect  $O_3$ ,  $NO_2$ ,  $SO_2$ ,  $NH_3$ , acetaldehyde, propane, and propene. Again, the fact that the adjacent 22-GHz line is variable must be taken into account. In the 94-GHz window region, we have lines of  $SO_2$ ,  $O_3$ , and  $CO$ .

Of the three, the lower two windows seem to be more promising, due to the abundance of pollutant lines in those regions, in spite of the nearby 22-GHz water vapor line. The 35-GHz region would probably be best used to detect  $SO_2$ .

## POSSIBLE AREAS OF INVESTIGATION

Modification and perfection of the technique of microwave spectroscopy has not been extensively attempted; its use, as it stands, has been deemed more important. Three possibly fruitful areas of investigation have been designated below: the use of microwave spectroscopy at atmospheric pressure; possible modifications of the microwave spectrometer to increase its sensitivity; and the tabulation and publication of microwave spectra of air pollutants.

### Microwave Spectra at Atmospheric Pressure

Measurements should be made to determine the feasibility of measuring pollutants at atmospheric pressure, using microwaves. In view of the dearth of spectroscopic data on  $SO_2$ , measurements could be made on this gas to model line widths and intensities as a function of pressure, for the pure gas. Then, using dry air and low pressures, with small concentrations of  $SO_2$  present, the minimum detectable concentration of  $SO_2$  as a function of pressure can be found. X- and K-bands (8 GHz–26.5 GHz) in which there is an abundance of lines of  $SO_2$ , could be used as an inexpensive beginning for this study. Dry air should be used to avoid the unnecessary complications of the 22-GHz water vapor resonance until later. The most promising frequency seems to be around 29 GHz (in the KA-band) where  $SO_2$  has several absorption lines, and there is a minimum of attenuation between the water vapor and oxygen resonances, as seen in Figure 5.

X-band equipment is at present being used in our laboratory because of its availability and low cost.  $NH_3$ , instead of  $SO_2$ , is being used as the absorber because of the conveniently located 9-GHz lines. We follow the procedure as outlined for  $SO_2$  on a standard "home-built" X-band microwave spectrometer, using a 39-cm absorption chamber.

The line widths and intensities should vary in some (until now) unknown

way with pressure, concentration of pollutant, and radiation intensity; and the  $O_2$  and water vapor absorption lines will tend to obscure the pollutant lines altogether.

### Microwave Instrumentation

There is much room for improvement of the microwave spectrometer, which has been used primarily as a tool to find the physical properties of molecules. Spectrometers have rarely been designed specifically for traces of one gas in a background of another. Furthermore, since solid-state microwave generators are becoming more reasonably priced (one can get a Gunn diode for around \$100.00), it may be possible to develop new inexpensive spectrometers for diagnosis of certain pollutants at the site of the pollution, with immediately available results. Improvements which have been used in the u.v., visible, and infrared regions to increase sensitivity could, conceivably, be translated to the microwave frequencies as well.

If it is feasible, work should be done to develop a microwave open-air cavity which will accomplish the task of measuring pollutants at atmospheric pressure. If this is not feasible, work should be done to improve the basic microwave spectroscopic techniques and adapt them for measurement of pollutants in low pressure cells.

Although some work has been done using cavity microwave spectrometers,<sup>35,37</sup> the commercial spectrometers now available<sup>1</sup> are of the single-path-absorption-chamber type. Modifications of the standard techniques of microwave spectroscopy may turn it into a powerful tool for the measurement of very minute traces of pollutants in the atmosphere. Among the possible areas of modification are: (1) use of interferometric techniques; (2) adaptation of correlation spectroscopy to microwave frequencies; (3) use of the self-radiation of molecules; (4) use of a high-Q microwave cavity; (5) employment of gas-permeable solids.

*Interferometric techniques—the microwave bridge.* In this configuration, two matched absorption cells are used in the two arms of a standard microwave bridge circuit (Figure 6). The principle is as follows: a microwave signal is split into two equal signals, in phase, which propagate through the upper and lower absorption chambers. The signal passing through the upper chamber is attenuated by the air plus the pollutant, and that passing through the lower chamber by the air only. The signals are then recombined out of phase, and the difference is detected. If the chambers have been properly matched, the absorption due to air alone is cancelled out, leaving a measure of the absorption due to the pollutant. This circuit is one possible application of the interference technique, used by Low and co-workers,<sup>38-41</sup> but the use

of interference in this case has an entirely different result, here, than it had in the infrared instrument. There, it served to heterodyne the frequency to a lower one ("heterodyning" is a process whereby a signal is shifted up or down in frequency, usually by multiplying it by a constant-frequency signal), but here it serves to find the difference of two very nearly equal signals—the purpose for which the Michelson interferometer was designed in the first place.

One need only run a frequency response curve several times, and add the results, to apply the multiple-scan principle developed by Low and co-workers to microwave frequencies. According to information theory, the

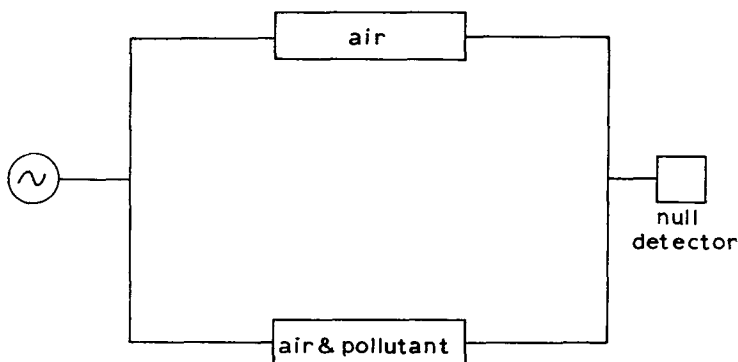


FIGURE 6 Microwave bridge circuit.

$S/N$  increases as a function of the square root of the number of signals added. The same result could also be obtained in microwave spectroscopy by simply measuring the frequency response curve over a longer time interval. In fact, if a high  $S/N$  was desired at only one frequency, the radiation could be continuously passed through the cell for "multiple scans."

One major advantage of the multiple-scan infrared interferometer is that the optical frequencies are heterodyned to audio frequencies, where they can be dealt with electronically for analysis. In microwave spectroscopy, however, this step is not necessary; the signals are already at frequencies which can be dealt with electronically. Thus, the multiple-scan technique reduces, in microwave spectroscopy, to the use of a long observation time while receiving atmospheric noise data from a given region of the atmosphere to be analyzed. A variation of this theme is to use several antennas which all point at the same region, perhaps from several directions. The region which is overlapped by all the antenna patterns will produce radiation signals which will be present in all the antenna outputs, and will constitute the signal to be measured. Any pollutants in that region will contribute to the signal received by all the

antennas, and thus improve the sensitivity of the arrangement. However, instead of adding the signals in this setup, an even better S/N might be obtained by correlating the outputs of the several antennas (using the information theory definition<sup>42</sup> of correlation, a mathematical process whereby the mutual information contained in several signals is removed from the signals).

*Correlation spectroscopy.* The correlation mask filter, which is used in infrared spectroscopy,<sup>43-46</sup> is able to distinguish between several pollutants, and noise levels of 15 ppb for SO<sub>2</sub> and NO<sub>2</sub> have been determined by this technique. The principle can be adapted for use at microwave frequencies as follows. Several microwave cavities are built and tuned to the frequencies corresponding to different resonant lines of the pollutant; a set of bridges is then built, each using one of the cavities and each at a different line frequency. The resultant difference signals are added together, and the device will be sensitive to the pollutant even if some other pollutants in the sample have resonant lines overlapping some of the lines of the pollutant being measured. Furthermore, each added bridge would increase the S/N, and therefore the sensitivity of the total instrument.

*Self-radiation of molecules.* The phenomenon of self-radiation produced by molecules, which is the inverse process to their absorption, has been used by Low and co-workers<sup>38-41</sup> in infrared analysis. This phenomenon has been carefully studied in the microwave area, because the equivalent noise temperature of an antenna is related to the microwave energy given off by the atmosphere in the pattern of the antenna.<sup>21,47</sup> The Radiometer is the instrument which measures this radiation, normally produced by the atmosphere.<sup>48</sup>

The "antenna noise temperature" measured by an antenna is a function of the vertical direction in which the antenna points, as the "temperature" is a measure of the radiation produced by molecules which randomly radiate in the atmosphere. The longer the path through the atmosphere is, the more radiation will be intercepted by the antenna. The O<sub>2</sub> absorption peak is clearly visible on any standard noise temperature versus frequency graph for an antenna, such as Figure 7.

Thus, an antenna "sees" all the radiation produced by a gas along the direction in which it is aimed. This noise is predominantly due to the O<sub>2</sub> lines at around 65 GHz and the water vapor line at 22 GHz, and is a nuisance for radar applications; however, a small percentage of this radiation is due to pollutants, and could possibly be detected; especially if one uses an interferometer-type arrangement.

*The microwave cavity.* The microwave cavity is a chamber in which energy of a certain frequency is reflected back and forth. The quality factor of the cavity, or  $Q$ , is a measure of how long a burst of energy is able to remain in the cavity before being quenched. Thus, an absorption cell of a given length may be replaced by a microwave cavity with a given  $Q$ . The higher the

$Q$  of the cavity, the more closely the cavity approximates an infinite transmission path, and the use of a lossless microwave cavity in place of the single- or multiple-pass gas cell is equivalent to an infinite-path-length cell.

It can be shown that the equivalent path length of a high- $Q$  cavity operating at microwave frequency is <sup>37</sup>

$$L = (Q\lambda/2\pi),$$

where  $\lambda$  is the wavelength, and  $Q$  is the quality factor of the cavity. At X-band frequencies,  $Q$ 's of 10,000 are reasonable, in which case the equivalent  $L$  is of the order of 50 metres. If a resonator had a  $Q$  of the order of a million

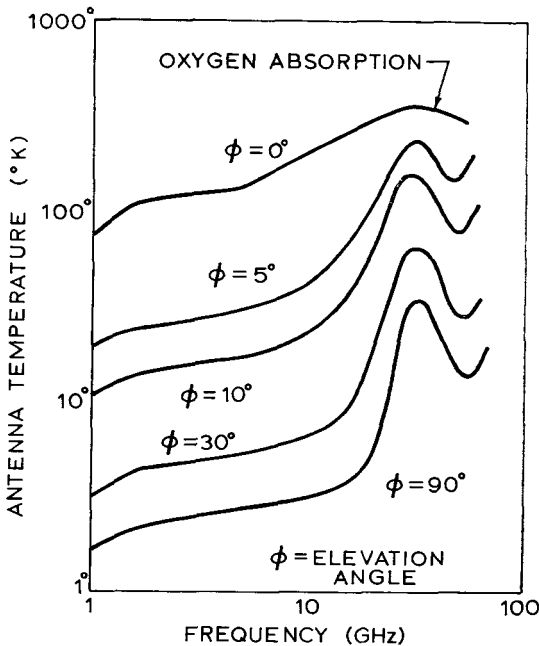


FIGURE 7 Antenna noise versus frequency (Ref. 47).

at 30 GHz, it would give an equivalent path length of over 1,000 meters. Open-sided cavities have been investigated<sup>49</sup> recently, especially at millimeter wavelengths.<sup>50</sup> They have the desirable quality of a very high  $Q$ , of the order of millions in the millimeter wave range.

Contemporary infrared spectroscopy, in which path lengths of at most 40 meters are used, may be used to detect concentrations of pollutants with the following limits:<sup>51</sup>  $\text{CH}_4$ , 0.06 ppm;  $\text{NH}_3$ , 50 ppm;  $\text{CO}$ , 0.8 ppm;

$C_2H_4$ , 0.06 ppm;  $C_4H_{10}$ , 0.03 ppm;  $C_2H_2$ , 0.015 ppm;  $H_2S$ , 50 ppm;  $SO_2$ , 0.03 ppm;  $NO_2$ , 0.014 ppm.

Since 5–20 ppm sensitivities are now obtainable in microwave spectroscopy through the use of one-meter-length absorption chambers, it should be possible to increase the sensitivity of a microwave spectrometer to 5–20 ppb simply by substituting a high- $Q$  cavity absorption chamber.

It might be contended that saturation (the phenomena in which most of the pollutant molecules are raised to an excited state by the incident radiation, so that no more energy can be absorbed) will more probably occur in a cavity than in a linear absorption cell, because the radiation is reflected back and forth through the same quantity of gas many times. This might be true in a normally shaped cavity; however, one of the types of cavity recently investigated<sup>50</sup> is the “barrel-hoop-resonator,” which is shaped so that radiation is reflected back and forth over a large volume. If this configuration was used, the saturation effect would be greatly reduced, and perhaps even eliminated. In general, large-volume cavities would probably tend to eliminate this effect. The fact that cavity spectrometers have been built<sup>35</sup> proves that the problem is not insurmountable.

The cavity could also be used in one arm of an interferometer. It may be advantageous to experiment with the improvement of high- $Q$  cavities in general, here, to increase sensitivity.

Another possibility is the use of an open-sided cavity for one arm of the bridge, and a closed container containing pure air in the other arm for comparison. This would be most useful in the study of pollutants which are affected photochemically. If an open-sided cavity can be used, it will not be necessary to collect a sample to be introduced into an absorption cell at a later time. The device could facilitate the analysis of the air at the site of pollution, with results immediately available. Furthermore, since the sample would not have to be processed before diagnosis, no correction for the time-dependent properties of the pollutants would be necessary.

The open-sided cavity could further be modified to a horn-reflector system which covers large expanses of open air, such as the area between two buildings across a busy street; or the cavity could be a portion of the inside of a smokestack, or a region just above it.

*Gas-permeable solids.* The use of open-air cavities presupposes that the instrument can be made sensitive enough to detect the very broad line produced by the pollutant at atmospheric pressure. This line-broadening is produced mainly by collisions between the pollutant gas and other molecules present. It may be possible to narrow the lines, even though the sample is at atmospheric pressure, by using a gas-permeable solid to fill the region in the absorption chamber. This would isolate the gas in small pockets, so that collisions would be with the walls of the pockets, rather than with other

molecules. In the limit of perfectly reflecting walls, the molecules would transmit no energy to the wall, and the collisions would not serve to broaden the lines.

*Stark and Zeeman modulation.* Stark modulation can be used in either cavity or linear absorption cells, at low pressures. At atmospheric pressures, although a Stark shift occurs, it is so slight in comparison with the line width that this technique will probably not be useful. The same applies for Zeeman modulation.

## Microwave Spectra

In addition to these areas of research, it is necessary to perform basic measurements to find the intensities of absorption lines of various air pollutants at low concentrations; none have yet been published, to our knowledge. In addition, there is a need for line spectra of the pure gases. The U.S. National Bureau of Standards is at present sponsoring a program to collect and publish these data, but little has been submitted to them.<sup>32</sup>

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