Application of Microwave Spectroscopy for Simultaneous Detection of Toxic Constituents in Tobacco Smoke

P. K. Kadaba, P. K. Bhagat and G. N. Goldberger
Wenner-Gren Research Laboratory
Department of Mechanical Engineering
Department of Electrical Engineering
and
University of Kentucky Research Foundation
University of Kentucky
Lexington, Ky. 40506

Colorimetric, electrometric, and chromatographic methods are currently in use for the estimation of various constituents present in tobacco smoke. Most of the above methods are specific in the sense that the estimation of a particular constituent is accomplished indirectly through chemical conversions. Also, it is difficult to analyze simultaneously two or more constituents of tobacco smoke with these techniques. In the present study a sensitive Stark modulated microwave spectrometer for rapid detection of toxic constituents in tobacco smoke has been developed. In contrast to the chemical methods presently available, the spectrometer developed here is relatively free from interference effects. Also, the resolution at microwave frequencies is at least 10,000 times better than that possible in the infrared region.

Microwave spectroscopy is based on the observance of transitions between rotational energies of polar molecules. It is well known that the absorption frequency of a gas molecule is changed when the molecular energy levels are preturbed by an external field (Stark field effect) (GORDY et al. 1953). The instrumentation developed here is an application of the above principles and based in part on the paper by Hughes and Wilson (HUGHES et al. 1947). We report this study in the interest of instrumentation development at greatly reduced cost and its application towards identification of components of a complex gaseous mixture such as tobacco smoke. In addition, a technique for making absolute intensity measurements of various constituents has been suggested.

Details of Developed Instrumentation

The microwave spectrometer developed in this study is based on the fact that the various constituents present in a complex gaseous mixture absorb energy at different microwave frequencies. The frequency of absorption is characteristic of a particular molecule, since the constants determining this frequency are unique for that molecule. Hence, the identification of the characteristic frequencies serves to uniquely identify the presence of the corresponding chemical constituent.

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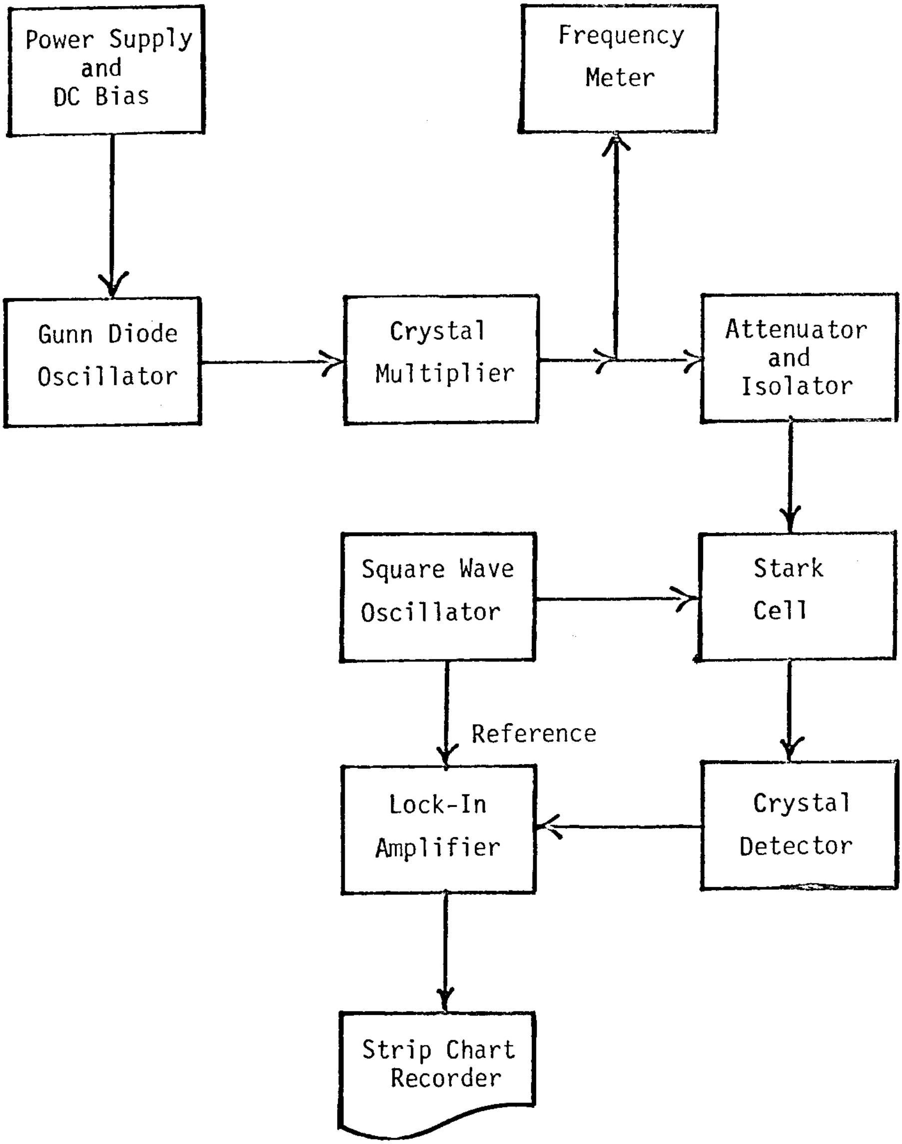

Fig. 1. Stark Cell Modulated Microwave Spectrometer

Figure 1 shows a schematic block diagram of the instrumentation developed in this study. A Gunn diode oscillator (Varian Associates) in the frequency range 8.8 to 9.2 GHz (X band) with a maximum power output of 30 mw and a reflex klystron in the frequency range 12.6 - 18 GHz (Ku band) were used as primary microwave sources. Crystal multiplier (Custom Microwaves)* were used to generate signals in the appropriate absorption frequency range of the molecules.

The absorption cell in the X band was fabricated (Custom Microwaves) using gold-plated rectangular wave guides. These wave guides were fitted with a center strip electrode, insulated from the walls by teflon inserts. The modulating Stark voltage was supplied at this electrode through a square wave oscillator (General Radio 1395 A) and amplifier. Part of the modulator signal was also used as the reference for synchronous detection of Stark cell output in a phase locked loop configuration. A standard K band square law crystal detector (R422A, Hewlett Packard) was used for detection of the absorption spectra. The crystal detector ouput was fed into a Lock-in amplifier (Princeton Applied Research Model 120) as shown in Figure 1. The dc output of the lock-in amplifier was used to provide the Y deflection in a Heathkit IR-18M chart recorder.

Materials and Methods

The instrumentation of the Stark cell microwave spectrometer was assembled as described above with the necessary amplifiers and impedance matching as needed. A Welch Duo-Seal vacuum pump and an oil diffusion pump were used to evacuate the Stark cell. A Pirani pressure gauge was used to measure the residual pressure. Initial experiments were carried out as a standardization procedure by obtaining the spectra of carbonyl sulfide (OCS). A 50 ml sample of OCS was passed through liquid nitrogen and was allowed to revaporize slowly in the previously evacuated Stark cell. The absorption frequencies of OCS agreed with that found in the literature (STANDARDS 1968).

50 ml samples of tobacco smoke were obtained from smoking machines and transferred into the Stark cell which was covered with dry ice. The frequency of the microwave source was adjustable in the range 22-38 GHz and monitored using a calibrated frequency meter.

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*Custom Microwave Components, 7065 Overbrook Drive, Longmont, Colorado 80501. A good source for Stark cells at a reasonable cost.

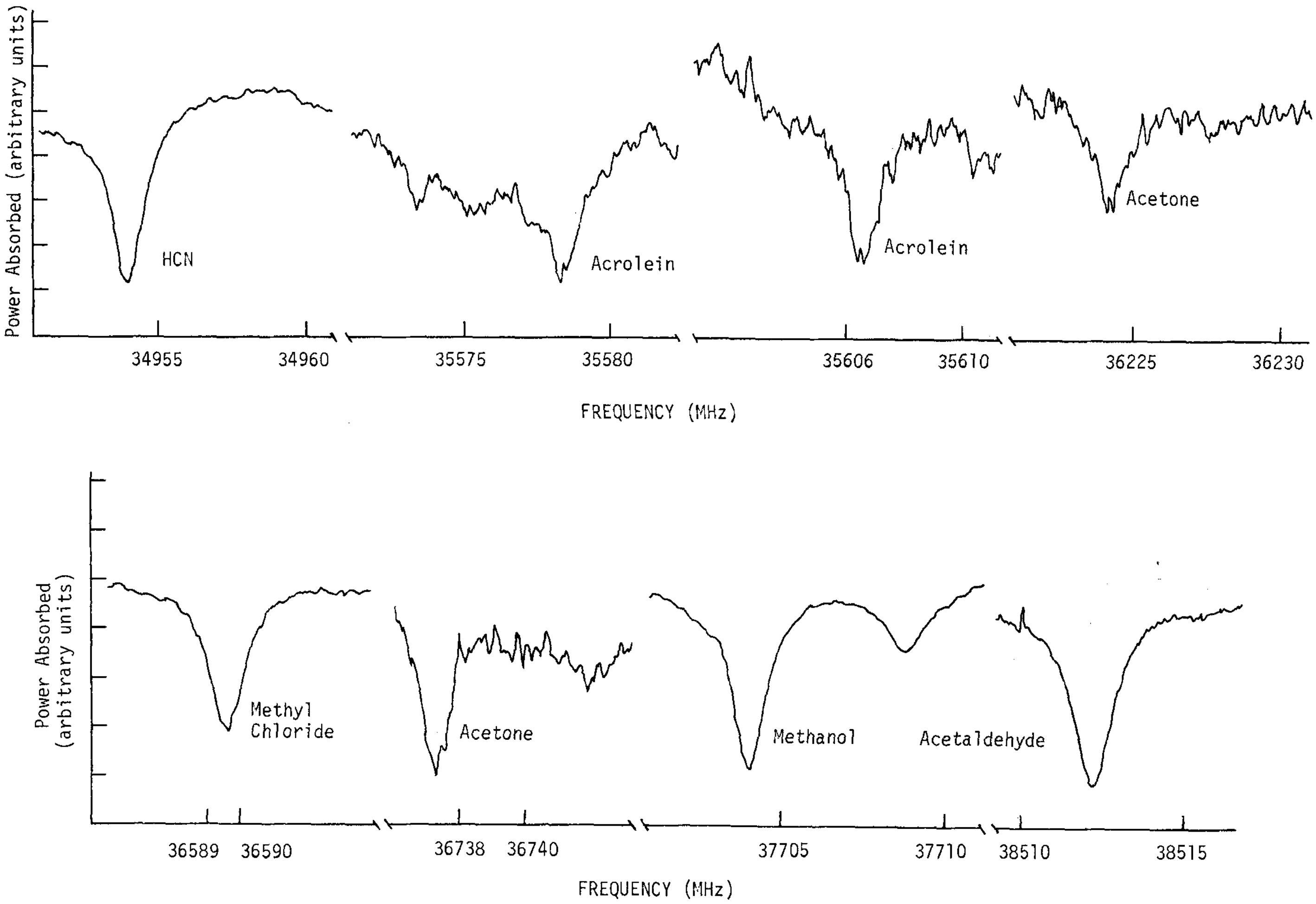

Fig. 2. Microwave Spectra of Tobacco Smoke

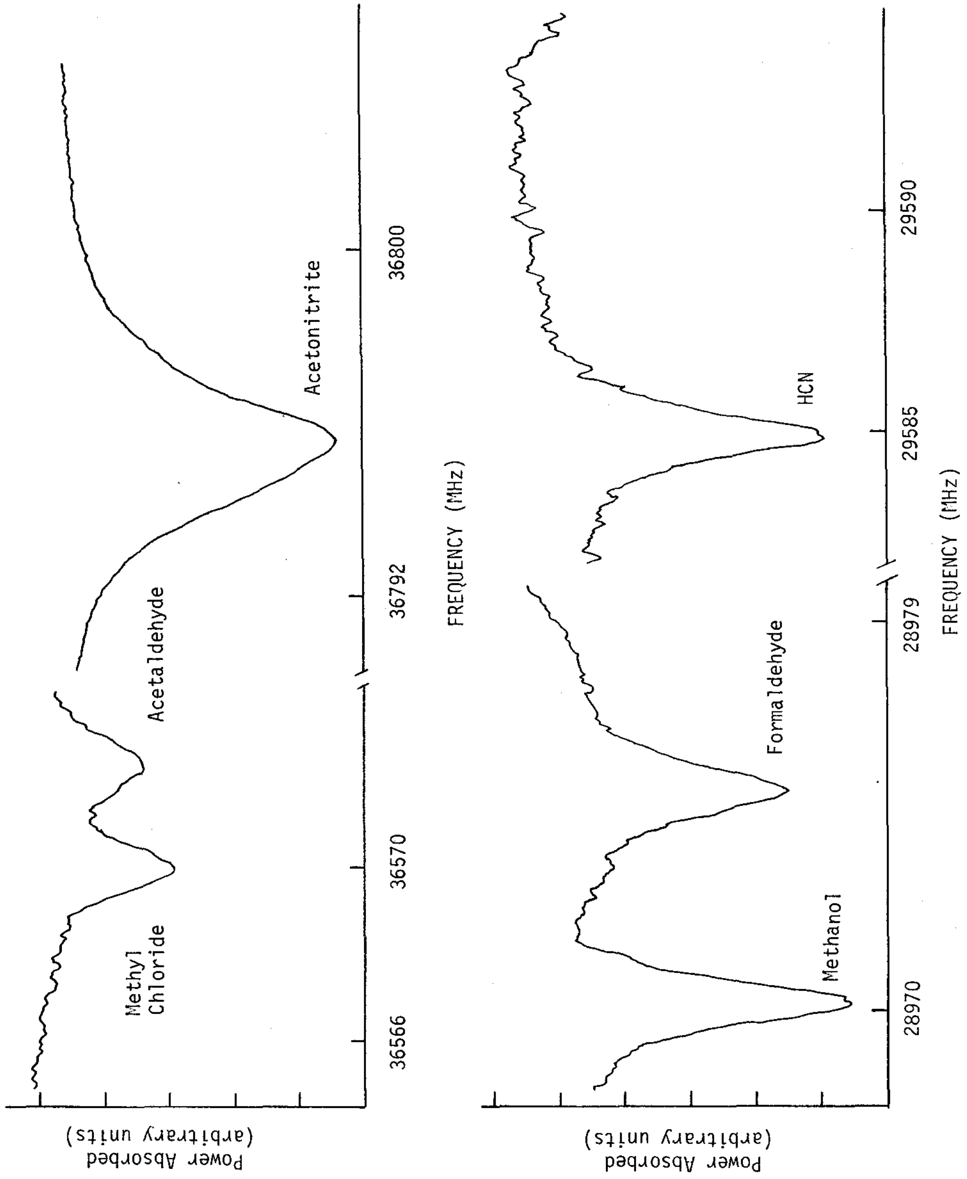

Fig. 3. Microwave Spectra of Tobacco Smoke

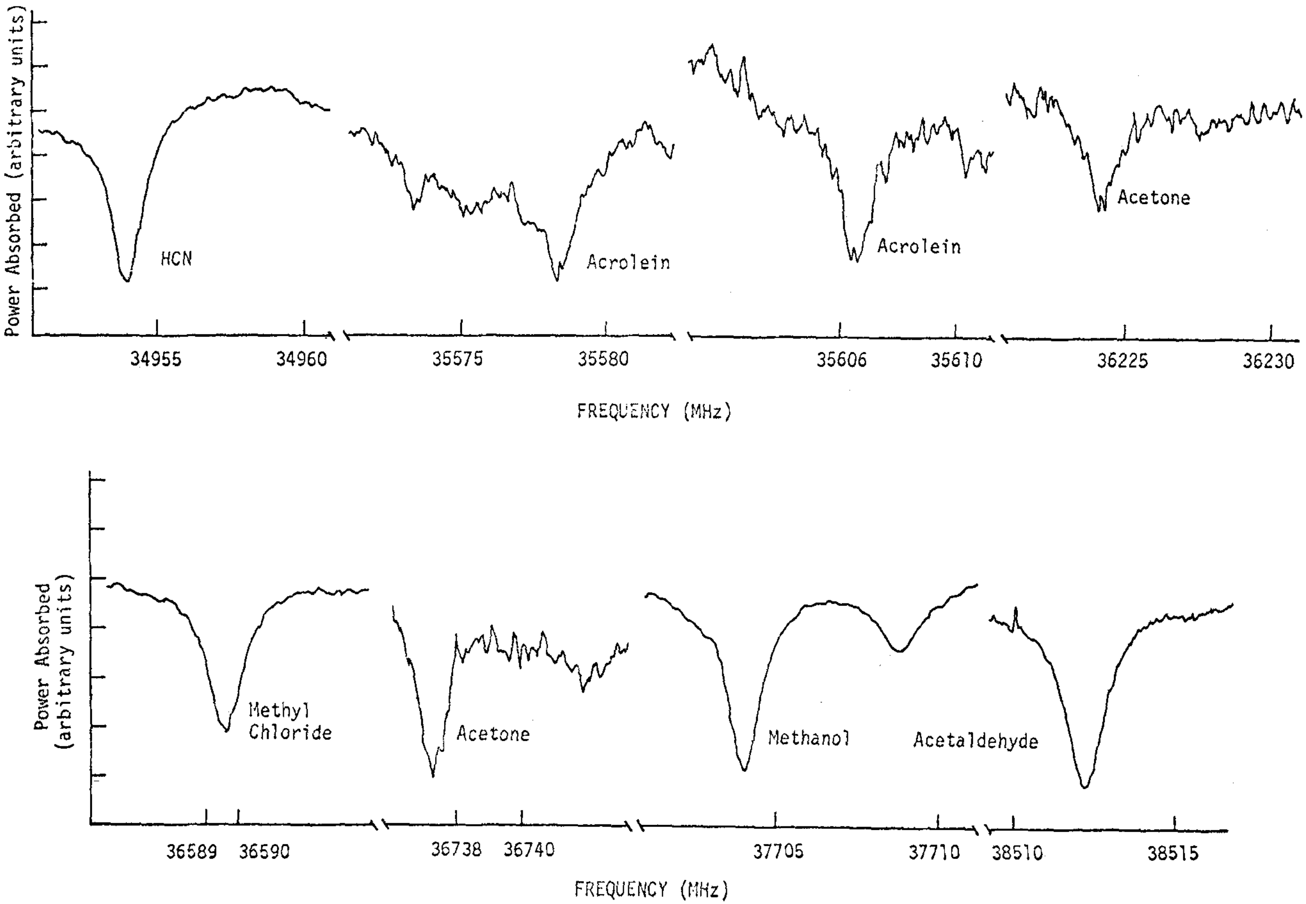

Fig. 2.. Microwave Spectra of Tobacco Smoke

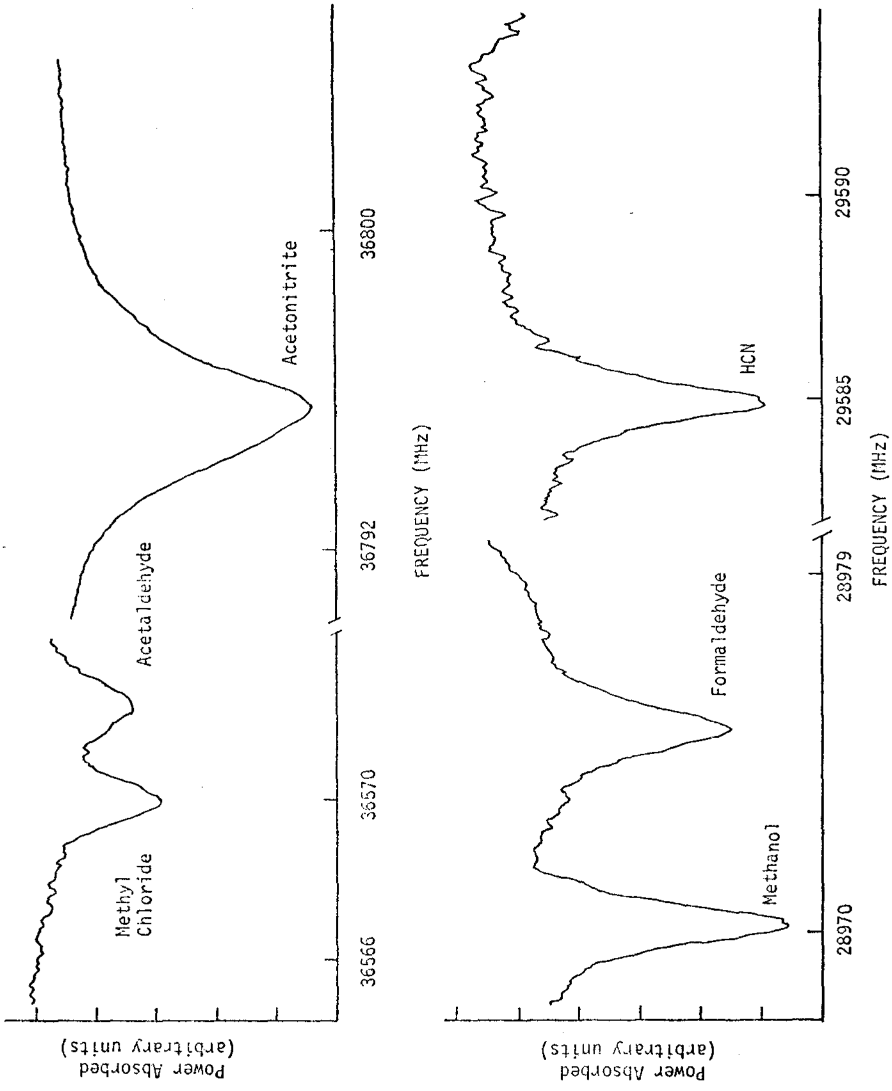

Fig. 3. Microwave Spectra of Tobacco Smoke

Results and Interpretation of Data

Figures 2 and 3 show results obtained from samples of tobacco smoke (the graphs have been reduced in size and redrawn for clarity).

Identification of the respective constituents of tobacco smoke in Figures 2 and 3 was done using the appropriate rotational frequencies of the individual pure gases published in the literature (STANDARDS 1968, TOWNES et al. 1955).

The very high resolution of the instrument can be clearly seen in Figures 2 and 3 by virtue of the fact that the pure rotational absorption frequencies of the various constituents in such a complex gaseous substance as tobacco smoke are clearly separated.

We are presently developing additional instrumentation to measure the absolute intensities of various constituents. The physical principle to be used is the paramagnetic resonance obtainable from the stable solid free radical, diphenyl-picryl-hydrazyl. Two energy levels occur in this compound as a result of the two possible orientations of the unpaired electron spin in the presence of an external magnetic field, and the difference in energy varies directly with the strength of the field. Transitions from the lower to the upper level can be induced by radiation of the correct frequency, which for a convenient range of magnetic fields lies in the microwave region. If a minute sample is placed in the microwave system containing the absorption cell, it may be made to absorb the radiation at the same frequency as any observed microwave absorption line by applying the appropriate magnetic field. The intensity of the absorption of diphenyl-picryl-hydrazyl is very accurately known and therefore, it will provide a standard for comparing the absorption lines lying at different frequencies and for measurement and absolute absorption coefficients. Other features of the developed instrument are: (1) a resolution of 100 KHz can easily be achieved, (2) water vapor absorption of radiation due to moisture is no problem at this region of the electromagnetic spectrum unlike that for infrared, and (3) the lowest concentration that can be measured (theoretically) is about 2 ppm of a particular constituent in a composite mixture. It should also be noted that the instrumentation as developed can readily be used to monitor atmospheric air for the presence of toxic constituents.

Literature Cited

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