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FINAL REPORT
FEASIBILITY STUDY OF A GUNN-DIODE MICROWAVE CAVITY
SPECTROMETER AS A FORMALDEHYDE MONITOR
CONTRACT NO. EPA-IAG-0179(D)
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FINAL REPORT

SUMMARY

A prototype of a fixed frequency microwave spectrometer to detect a pure rotational absorption transition of the $\text{H}_2^{12}\text{C}^{16}\text{O}$ molecule was developed and delivered to the Environmental Protection Agency for testing. State-of-the-art microwave technology in the form of solid state diode source and a high quality cavity absorption cell, was used to optimize sensitivity while providing compactability. A molecular separator with two stages of dimethyl silicone membrane is used to interface the detector with the atmosphere; and it provides an enrichment of formaldehyde at the operating pressure of 50 m Torr of more than 150 times the normal concentration within the cavity at that pressure.

The instrument has been tested by the developer for utility as a continuous monitor of formaldehyde in air mixtures by controlled laboratory experiments. It exhibits very high selectivity, good stability and linearity, and good sensitivity. The prototype instrument has the following operating specifications:

Molecule detected - gaseous $\text{H}_2^{12}\text{C}^{16}\text{O}$

Interferences - none

Minimum detectable quantity - Approximately 0.03 ppm with

S/N = 1 (tangential)

Detection range - 0.00 to 20.00 ppm

Linearity - 1) less than 10% deviation from linearity for all concentrations, when calibrated for full scale use.

SUMMARY (Continued)

- 2) less than 5% deviation from linearity for concentrations within one order of magnitude from calibration point.

Stability -

Zero Drift - less than 0.5% of full scale per 24 hour period after 24 hour warmup and at room temperature $\pm 3^{\circ}\text{F}$.

Frequency Stability - better than 5 parts in 10^8 per day.

Peak response stability - less than 2% deviation from the peak maximum in 30 days.

Temperature Range - 40°F to 100°F ambient.

Response time - 90% response to step change in 15 minutes.

- Modes of Operation -
- 1) continuous "sniffing" (minimum response time used where fast response is a necessity but where minimum detectability is not necessary.
 - 2) continuous "sniffing" (maximum sensitivity) used where minimum detectability is required.
 - 3) Batch sampling - (dynamic) - used where a batch sample can be continuously supplied to the monitor.
 - 4) Batch sampling (static) - used where a minimum of sample is available.

SUMMARY (Continued)

Outputs - 1) 3-1/2 digit front panel readout in parts
per million.

2) 0 to 10 volt analog signal at BNC recorder
output on back panel.

Dimensions - Rack mountable 19" x 21" x 10-1/2" (vacuum
pump external).

Total Weight (excluding vacuum pump) - 85 pounds.

Vacuum Connectors - Roughing pump #4 Cajon

Diffusion pump #8 Cajon

Sample Input Connectors - #4 Cajon

Power Requirements - 115 V, 10 amps, 60H (approx. 250 W Cont.)

Tests with the instrument have revealed a critical limitation which would require a major design modification to rectify. The instrument gives a long response time for a step change of formaldehyde. It is especially slow to respond to a negative change in formaldehyde content because of a slow equilibrium with the inlet walls. Combined effects of adsorption, membrane response, other wall effects, and polymerization of H_2CO on the inlet walls are responsible for the long response time. An inlet and cavity design which would allow operation at temperatures near $180^{\circ}C$ could considerably reduce the response time by neutralizing these effects.

This development has established the design criterion for optimizing microwave spectrometry for a single gas monitor. It has

SUMMARY (Continued)

suggested additional means for reducing the size and complexity of the instrumentation even more. The extension of the design to a multiple gas monitor is straightforward and should be the next consideration in developing this technique for pollutant monitoring.

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I. INTRODUCTION

The purpose of this development effort was to provide a bench scale model of a simplified microwave spectrometer for testing the feasibility of rotational spectrometry as a monitor for specific contaminants in air. The favorable properties of rotational spectrometry for qualitative and quantitative analysis of air mixtures can best be determined by testing such a model and comparing it with other techniques. The most desirable features of this technique are that it measures a specific molecular physical phenomena, it has very high specificity, and it is capable of continuous monitoring. Although the instrument described in this report has been designed to monitor only formaldehyde vapor in air, this technique is applicable to any other polar, low molecular weight contaminants.

The instrument developed under this contract embodies state-of-the-art microwave spectrometer design. It combines a Gunn-effect diode source with a high quality resonant cavity to provide the optimum in compactness, selectivity and sensitivity. An effort has been made to design an instrument which is simple to operate yet is accurate to within the limits of the capability of the technique used. Automatic operation has been designed into the instrument to insure stability for continuous unattended monitoring.

The following scope of work was the guide used to develop this instrument:

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1. The establishment of the absolute theoretical limits of sensitivity for a Gunn-diode-cavity system, based on realizable parameters.
2. The determination of the conditions and parameters necessary to construct a diode-cavity system of optimum sensitivity for detecting formaldehyde vapor in air. Specific requirements include:
 - a. The determination of the electronic design conditions for the lowest possible system noise figure.
 - b. The determination of the optimum diode to cavity coupling scheme.
 - c. The determination of a cavity design to optimize its quality factor.
 - d. The determination of a technique for signal detection with optimum signal to noise, including: the utilization of signal averaging up to a maximum of two minutes; the investigation of pressure broadened, power saturated conditions; and the application of membrane separators for sample enrichment into the vacuum system.
 - e. The determination of a scheme for long-term frequency stabilization of the system.

II. PROPERTIES OF MICROWAVE ROTATIONAL SPECTROMETRY

Microwave rotational spectrometry is the technique used to study the interaction between electromagnetic radiation and the quantized rotational

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motions of gaseous molecules. Microwaves, being low energy waves, can excite the low energy transitions characteristic of slowly rotating molecules. The spectrum one obtains from exciting the rotational transitions of a particular type of molecule is strongly dependent upon its geometrical structure. As a consequence each molecule has a completely unique spectrum. Even isotopic species of the same molecule give significantly different spectra because of the slight differences in geometry. At low pressures, where collisions between molecules limit their width, the rotational absorption lines are characteristically very sharp. The lines are so sharp, in fact, that over a million different lines from different gases can be resolved in the full range of a typical broadband instrument. The inherently high resolution of rotational spectrometry insures exceptional qualitative specificity.

Microwaves are generated by electronic oscillations. The oscillations are quite monoenergetic and can be easily tuned over a large frequency range to any desired frequency. Hence, it is a simple procedure to excite a given molecular rotational transition and do so with very high selectivity. In fact, with the possible exception of tunable laser techniques, no other spectrometric technique has this property.

It can safely be said that no other physical technique can match the inherent specificity of microwave rotational spectrometry. This fact alone makes it worthy of consideration for pollution monitoring applications. In addition, however, this technique can be quantitative. From the basic theory of the processes that lead to rotational absorption spectra, it is known that the peak response of the absorption signal can be directly related to the concentration of the absorbing species.⁽¹⁾

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Moreover, for well resolved absorption lines, the concentration of one specie is unaffected by any other in the mixture. It has also been shown⁽²⁾ that under particular experimental conditions the peak response from a rotational absorption can be linearly related to the concentration of the absorbing species over the entire range from minimum detectability to 100% concentrations. Thus we have, with microwave rotational spectroscopy, a potentially simple technique for both qualitative and quantitative determination of gases in a mixture.

The basic sensitivity of this technique is somewhat limited by the very small total energy absorbed during rotational excitation. However, for many pollutant molecules which are low molecular weight and highly polar, favorable conditions exist for high sensitivity. The strength of a particular rotational absorption depends upon several properties of the molecule.

First, it is very strongly dependent upon the dipole strength of the molecule. In fact, it is zero for molecules with truly symmetric charge distributions such as CO_2 , benzene, and mononuclear diatomics. Generally, the stronger absorptions occur for molecules with the larger permanent dipole moments. Second, it depends upon the total number of sample molecules and the fraction of those that are in the lower of the two energy states involved in the transition. Third, it is dependent upon the statistical numerical difference between the molecules in each of the rotational states involved in the transition. A Boltzmann distribution of states characterizes the molecular rotational energies at a given

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gas temperature. This distribution typically shows the most populated states to be chosen with quantum numbers between 10 and 20 at normal operating temperatures for most molecules. Fourth, it depends on the frequency of the radiation exciting the transition. The absorption strength is proportional to the square of the resonant frequency. Thus higher frequency transitions are generally stronger. These molecular properties all determine the absorption strength or absorption coefficient.

The absorption coefficient of a given transition is the fractional power that can be absorbed from an incident beam, per unit of its path length. This number can be calculated for a single transition and is usually given in units of cm^{-1} . A strong transition would be one with an absorption coefficient in the range 10^{-5} cm^{-1} to 10^{-4} cm^{-1} and many pollutant molecules i.e. (SO_2 , NH_3 , H_2CO) have absorptions this strong. An absorption coefficient of 10^{-4} cm^{-1} means that 1% of the incident energy would be absorbed by that transition per meter of path length.

In order to clarify the actual sensitivity limits of this technique, consider a typical case - namely H_2CO . The strongest H_2CO rotational transition within easy access by present microwave electronics has a coefficient of $6 \times 10^{-5} \text{ cm}^{-1}$ at an approximate frequency of 28.97 GHz. A well designed cavity spectrometer can detect an absorption with a coefficient of 10^{-10} cm^{-1} with a S/N ratio 5/1 (or an equivalent coefficient of $2 \times 10^{-11} \text{ cm}^{-1}$). Thus H_2CO could be detected in fractional abundances of $2 \times 10^{-11} \text{ cm}^{-1} / 6 \times 10^{-5} \text{ cm}^{-1} \approx 0.3 \text{ ppm}$. A 1 to 10 ppm level would be somewhat more typical of the basic sensitivity of the molecular rotational

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spectrometry for detecting pollutant molecules. For some special gases, such as ammonia, for example, the sensitivity is an order of magnitude better than 1 ppm. Preconcentration techniques can extend this limit well below the 1 ppm levels, making it feasible to use this technique for ambient monitoring of several pollutants.

III. DESIGN CONSIDERATIONS

A. General

An instrument capable of continuous, unattended monitoring, with optimum sensitivity for formaldehyde, was desired. The instrument should require a minimum interaction with technical operators and should be simple to use.

To insure simplicity of use, instrument control functions were automated as much as possible. To insure unattended operation, extremely high stability was required, along with temperature and servo feedback control.

Solid state microwave generating diodes, which have recently become available, have many favorable properties when used as a spectroscopy source. A system consisting of such a diode and a high quality factor cavity resonator can give the highest possible sensitivity for detecting molecules by microwave spectroscopy.

The $3 \rightarrow 3$ pure rotational transition of the formaldehyde molecule at 28,974.805 MHz was selected for monitoring purposes. This absorption line is quite strong (coefficient $\sim 6 \times 10^{-5} \text{ cm}^{-1}$), has no known interference from other gases, and is in a frequency range where solid state microwave sources are available and are not prohibitively expensive.

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The theoretical sensitivity limit for the H_2CO 3 ~ 3 rotational line in a resonant structure whose $Q_L = 10,000$ can be calculated from the following equation: (3)

$$\Gamma_{\min} = \left(\frac{4k T N \Delta f}{P_{\text{in}}} \right)^{1/2} \frac{2\pi}{Q_L \lambda} \quad (1)$$

where $\Gamma_{\min}$ = the minimum detectable absorption coefficient for the system.

k = Boltzmann's constant

T = absolute temperature

N = noise figure for the system

Δf = detection bandwidth

P_{in} = microwave power delivered to the cavity

λ = the wavelength of radiation

With $T = 300^\circ\text{C}$, $N = 30$, $\Delta f = .01 \text{ Hz}$, $P_{\text{in}} = 10^{-4} \text{ watts}$ and $\lambda = 1.13 \text{ cm}$

$$\Gamma_{\min} \approx 1.8 \times 10^{-11}$$

Since, for the H_2CO 3 ~ 3 line, $\Gamma \approx 6 \times 10^{-5} \text{ cm}^{-1}$ we calculate a theoretical detectability limit of:

$$\Gamma_{\min} / \Gamma_{\text{H}_2\text{CO}} \approx \frac{1.8 \times 10^{-11}}{6 \times 10^{-5}} = 300 \text{ ppb}$$

A means is required to make the spectrometer respond linearly to absorption by the H_2CO molecules so that its output can be directly quantitative. The necessary condition for linear response to the peak of an absorption line is that the line width of the observed absorption stays constant. (4) In a mixture of gases such

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air, this condition is very nearly true for traces of formaldehyde (i.e. quantities less than 0.01% by volume), because the linewidth of the observed absorption is determined mainly by collisions with N_2 molecules and stays constant. However, when other polar gases in the mixture (water vapor for example) become high in concentration they can affect the linewidth and thus the linearity of response. The removal of water from the sampled gases insures linearity.

The optimum power saturation method has been shown by Harrington⁽⁵⁾ to give a linear response for the peak absorption of a given line independent of the linewidth. We use this method in the Gunn-diode cavity spectrometer because the saturation conditions are so easy to meet. The procedure for establishing the linear response of this instrument is given in a later section.

B. Gunn-Effect Diode Oscillator

The microwave source for the spectrometer was required to oscillate at precisely 28.974805 GHz, with a basic stability of 5 parts in 10^8 per day. Its nominal power output was to be 1 milliwatt continuous and it was to be relatively noise-free and temperature-stable. To obtain the required frequency stability, the oscillator was phase locked to a harmonic of a very stable crystal controlled low frequency oscillator as described in a following section. Thus the microwave source also required electronic tunability.

Our prior experience with Gunn-effect diode microwave generators suggested that they would be ideal for this application. They are known to have low AM and FM noise characteristics, they can easily

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supply the 1 milliwatt CW power levels, they are tunable by various means, and they only require low voltage for operation. However, no device which was electronically tunable near the 28.9 GHz frequency was commercially available at the time of our development project, so we were forced to design our own oscillator package.

The bare stud-mounted Gunn effect diode (see Figure 1) was purchased from Varian Associates, Inc. It had a nominal output power of 5 milliwatts at 28.9 GHz. A tuning varactor was purchased from the same source. It was decided to include within the oscillator package a 1N53 mixer diode to facilitate the phase lock of the Gunn-diode source.

The final oscillator package design is shown in Figure 2. It is machined from Invar metal to reduce thermal variations in the waveguide structure. It has provisions for mechanical frequency tuning by both a stub and a sliding short. The Gunn diode and the varactor tuning diode are positioned side-by-side in a reduced height R-band waveguide which tapers up to full size at the oscillator's RF output. Directly behind the diodes, in the center of the reduced height guide, is a probe that couples power to a 1N53 mixer diode. All connections to the diodes within the package are made through BNC connectors. The size of the oscillator package is $3/4'' \times 3/4'' \times 2''$.

The oscillator is capable of output at any frequency between 28.5 GHz and 29.5 GHz and can be voltage tuned over any 300 MHz

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range at rates up to 1 MHz. The minimum power output over the above frequency range is 4.5 milliwatts. A small iris hole is centered in a shim plate that fits over the oscillator waveguide output. The iris diameter is chosen to reduce the power delivered to the cavity to the desired level.

C. Cavity Resonator

A microwave cavity resonator has several advantages as an absorption cell for microwave spectrometry. First, the resonator has a small volume but can have a very large effective radiation path length for absorption. For example, a 10 in.³ resonator can easily be constructed with a $Q = 10,000$ to give an equivalent path length of 16 meters at 28.9 GHz. Secondly, a resonator of the Fabry-Perot type (two mirrors separated by dielectric material) has a small surface to volume ratio. This is an important property to minimize wall adsorption effects. Third, it is easy to saturate a molecular transition in a cavity because of the large power density within it. This property is desirable for the optimum power saturation method, for which linear response with concentration is obtained.

The maximum possible quality factor (Q_L) for the cavity is desirable for optimum sensitivity. The operating Q_L is maximized by careful construction of the resonator (alignment and mirror finishes), by choosing the proper resonant mode, and by reducing the loading of the resonator by external detectors.

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Since a resonator is inherently sensitive to vibrations, it is desirable to construct it in a solid configuration. However, tunability is also necessary, so we have designed a thermally tunable cavity which insures both conditions.

The cavity, shown in Figure 3, consists of two gold-plated Invar microwave reflectors. The two reflectors are separated by a quartz spacer and a vacuum seal is obtained by viton O-rings between the spacer and each plate. The O-rings have enough clearance to allow about 10 mils of tunability -- that is -- the two plates can be moved about ± 5 mils with respect to each other when a vacuum has been pumped in the cavity. This is sufficient movement to tune the resonant frequency of the cavity by about 300 MHz. The tuning is accomplished by the controlled thermal expansion of an aluminum spacer separating the two plates. The requirement for the tunability and how it is used in a feedback loop will be explained in a following section.

D. Stabilization

The requirement for stabilization was established by the need for long term unattended operation. A free-running oscillator and cavity combination is generally not stable for more than a few minutes because each is strongly perturbed by environmental changes (temperature, humidity, vibration, etc.). Thermal stability itself is not sufficient unless the changes in frequency of the oscillator and cavity can be synchronized.⁽⁶⁾ A more sophisticated, but much more reliable approach, is to use electronic stabilization.

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In order to derive stability of the microwave frequency to the order of 5 parts in 10^8 or better, it is necessary to use an oven controlled low frequency crystal oscillator as a reference. The basic stability of the crystal oscillator can then be transferred to the microwave oscillator by multiplication and phase locking, both commonly used techniques in microwave electronics today.

Once stable oscillations are obtained at the desired stimulating frequency for the spectrometer, it is possible to again transfer that stability directly to the cavity's resonant frequency. A commonly used technique involves a comparison of the RF phase before it enters the cavity with that which leaves it. If the cavity resonance is tuned through the RF frequency, this phase difference goes from a maximum near resonance, through zero at exact coincidence of the stimulating RF and the cavity resonant peak, then to another maximum of opposite polarity. Such a response is called a discriminant and can be used to derive a feedback signal for automatic frequency control.

Another stabilization used in the instrument involves the cooling of the molecular separator. Here a simple electronic servo is used to control the current fed to a thermo-electric device. The error signal is derived from the temperature difference between a fixed reference and that of a thermistor mounted on the separator.

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E. Signal Detection

Obviously the highest possible sensitivity is desired for detection of H_2CO with this instrument. As shown in Equation 1 above, the ultimate sensitivity is limited by the system electronic noise. The N in Equation 1 is a figure of merit for the entire detection system and includes the noise contributions from the source and the detector. If heterodyne detection can be used the noise contribution from the detector can usually be brought below that from the source. Then an RF bridge arrangement can be used to minimize the source noise effects. However, a problem exists when using a cavity as an absorption cell because a small amount of power will saturate rotational transitions. Therefore a very small amount of RF signal actually gets to the detector from a transmission cavity. Hence, one usually finds the detector noise to be the limiting factor in this case.

We decided to use a heterodyne detection in this instrument whereby we multiply a local oscillator and mix its harmonic power with the incoming signal. As seen in the block diagram, Figure 4, this technique serves two purposes. First it allows the derivation of the discriminant needed to frequency stabilize the cavity resonance. Second, it allows us to amplify the signal information at a high IF frequency (30 MHz), far above that which could add $1/f$ noise to the detection system.

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A common technique used in microwave rotational spectrometry is to cause a modulation of the absorption signal by means of the Stark effect. This allows an AC signal to be derived which is proportional to the actual absorption strength and which can be synchronously detected to enhance signal to noise. The synchronous detection is a form of narrow band amplification which considerably reduces the background noise. Additionally, one can effectively apply an analog time average (i.e. signal integration) with this technique.

F. Stark Modulator

The Stark modulation is applied by way of a rectangular wave shape on-off voltage impressed through the gas sample. When the field is off, the molecular rotational energies are unperturbed and the transition frequency is well defined at the fixed RF stimulating frequency. When the field is on, the energy levels split, by an amount dependent on the field intensity. Thus the transition probability goes to zero at the original stimulating frequency when the field is on. The on-off switching of the Stark field then makes the signal come and go at the switching rate. Peak to peak field densities as high as 2 to 3 KV/cm are required to fully modulate absorption lines which are pressure broadened (i.e. pressures above 10 millitorr). Problems can and usually do arise at these high field strengths with gas breakdown and glow discharge within the cavity at operating pressures. These problems can be alleviated

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somewhat by reducing the electrode spacing. However, in the cavity, where we use the two reflectors as electrodes, there is a trade-off between reduction in plate spacing and the cavity quality factor -- they are inversely related. The breakdown problem was compounded in the formaldehyde monitor by the necessity for very high fields to fully modulate the line at 50 mTorr pressure.

To prevent damaging the surfaces of the resonator from gas discharge, a thermocouple gauge was used to indicate a safe pressure range and automatically turn on the Stark voltage. The same indicator can turn off the voltage if the pressure gets too high.

Special care is required in designing a high voltage modulator to prevent leakage and subsequent pick-up by the detection electronics. Any such leakage cannot be differentiated from the signal since it is at the same frequency (and phase) as the signal. Metal shielding is useful but requires that the modulator electronics be reasonably compact.

A compact solid-state design based on a self oscillating ferrite transformer is shown schematically in Fig. 5. It can be put on a printed circuit board and easily shielded. Moreover, it requires only a 24 V dc input and generates a reasonably square waveform up to 3 kV peak-to-peak. Such a circuit can be mounted directly on the cavity itself, thus reducing to an absolute minimum the necessary shielding.

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G. Sample Inlet System

As shown by Eq. 1, the theoretical limit of detectability for H_2CO with the $3 \rightarrow 3$ rotational line is approximately .3 ppm. To extend the detection limit still lower it is necessary to obtain some enrichment of H_2CO from the air mixture. This enrichment can be obtained by using permselective membranes to interface the cavity to the atmosphere.

Permselective membranes such as dimethyl silicone rubber are able to pass some gases at much higher rates than air when a difference in pressure is maintained across the membrane. This property leads to an effective enrichment of a trace component with respect to air at the low pressure side. To see this, consider the relation for flow rate through the membrane for a given species x:

$$N_x = \frac{Pr_x A (P_x - P'_x)}{t}$$

where Pr_x = the permeability constant for specie x.

A = the total surface area of the membrane seen
by the incoming gas.

t = the membrane thickness.

P_x = the partial pressure of the specie x in the
high pressure mixture.

P'_x = the partial pressure of the specie x in the low
pressure mixture.

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The enrichment factor for a gas x with respect to nitrogen, for example, can be related to the ratio of flow rates for each through the membrane. Thus:

$$\text{Enrichment factor: } \frac{N_x}{\beta N_n} = \frac{Pr_x (P_x - P'_x)}{Pr_n (P_n - P'_n)}$$

since the area A and the thickness t are the same for both. Now consider the case where the partial pressures on the low pressure side are sufficiently low that $P_x - P'_x \approx P_x$ and $P_n - P'_n \approx P_n$ and that also P_x is some small fraction of P_n , or $P_x = \beta P_n$, then

$$\text{Enrichment factor: } \frac{Pr_x}{Pr_n}$$

that is, it is just the ratio of the permeabilities of the two gases. These constants are tabulated by commercial sources for the membrane material and indicate that $Pr_x > Pr_n$ for many common pollutant gases. For example Pr for H_2CO is 925 and Pr for N_2 is 25. One should expect an enrichment factor near 37 for H_2CO in N_2 with a single membrane.

By using stages of membrane in series, even higher enrichments can be obtained. The number of stages that can be used is limited by the vacuum required on the low pressure side and also practically by how few molecules can be detected by a given detector, since most of the sample is pumped away between the stages of membrane. A mathematical model of the flow through the membrane can be derived.⁽⁷⁾ The model can be used to determine the between stage pressure for a

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two-stage separator in order to establish the optimum enrichment factor. Figure 6 shows plots from the derived formula, for H_2CO in nitrogen. These curves suggest that one should operate a two-stage separator with a pressure of 4 to 10 Torr between stages.

A two-stage membrane separator device was designed for use with the cavity spectrometer in order to extend its detectability range for H_2CO to low parts per billion. Without the separator, the cavity can detect about 3 ppm H_2CO in air at an operating pressure of 50×10^{-3} Torr. This is equivalent to detecting $\approx 10^{19} \times \frac{.05}{760} \times 3 \times 10^{-6}$ or $\approx 10^{10}$ molecules/cc H_2CO . If the same volume at the same 50×10^{-3} Torr pressure can be enriched of H_2CO by two orders of magnitude then the 10^{10} molecule/cc H_2CO detectability limit would mean that we could detect 30 ppb H_2CO in the atmospheric mixture. An engineering drawing of the separator device is shown in Figure 7. We measured enrichment factors of between 150 and 300 (depending upon moisture content of the carrier) using this device for H_2CO . Concomitant problems arise with the use of membranes for the inlet; detailed discussion of these will be given in a later section.

Since water vapor is abundant in normal air mixtures, it can make up a large portion of the partial pressure at the 50 m Torr cell pressure (this is even worse when the membrane separator is used since H_2O has a high permeability for dimethyl silicone). The large amount of water vapor in the cell causes a greater degree of line

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broadening of the formaldehyde line than would occur with other non-polar air components. A reduction of peak intensity of the formaldehyde line occurs if the microwave power cannot be adjusted to compensate for the wider line width. Since we operate at a fixed microwave power input and a fixed modulation intensity, fluctuation in water content within the cavity could cause large deviations from linearity in formaldehyde response. For this reason it is desirable to selectively remove the water vapor from the incoming sample.

Our search for a selective dryer material led to P_2O_5 . Our data (see section VI-G) shows that P_2O_5 thoroughly dries a sample while removing less than 5% of the H_2CO for concentrations of H_2CO as low as 2 ppm, thus it is almost ideal for this application. To alleviate the necessity to change the dryer often, we designed a dryer tube to operate in the vacuum system, between the separator device and the cavity. Since it sees there, only a small fraction of the ambient water content, its useful lifetime can be extended to up to 1 month.

The material to be used in the inlet system was chosen to minimize adsorption of H_2CO gas. Tests with various materials -- stainless steel, Teflon, glass and gold -- showed them all to be nearly identical for adsorption effects at H_2CO concentrations above about 10 ppm. Below those levels we observed evidence of

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polymerization on all walls -- with gold apparently the best and stainless the worst. At such low concentrations, handling of any gases becomes increasingly difficult and requires a great deal of study itself. In many cases one is forced to use the material showing the best characteristics without understanding why it is better than another. This is somewhat the case in the design of this inlet system. One thing can generally be said about inlet systems -- if it is necessary to pull the sample into a detector, the wall effects are always very important but the least understood. This I think is true for any of the sampling systems existing on most of today's monitoring instruments.

IV. PRINCIPLES OF OPERATION

A. General

The instrument described in this report is based on the principle of observing the absorption of microwave radiation which is in resonance with one of the quantized molecular rotational transitions of gaseous formaldehyde molecules. Molecular rotational transitions have low energies (much lower than vibrational energies) and at low pressures, they can cause very sharp absorption of microwave radiation. The absorptions are so sharp, in fact, that nearly a million single resonances from many different kinds of molecules can all be resolved from a spectrum taken over a 20 Gigahertz frequency range. The microwave frequencies, on the other

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hand, are produced from electronic oscillations, are already quite mono-energetic, and they can be continuously tuned. These properties are responsible for the very high qualitative specificity for detecting molecules in a mixture by the technique of microwave rotational spectrometry.

The properties described above are utilized to the fullest in this instrument. For example, the pressure of the sample gas is maintained low enough to assure that the formaldehyde transition's absorption width is less than 300 KHz in the detection cell. Since the sensitivity for detecting formaldehyde molecules is proportional to the effective radiation path length through the sample, a resonant cavity is used as the sample cell. Multiple reflections of the radiation occur in such a cavity, thus it offers the highest sensitivity for the smallest volume, of any kind of cell design. The cavity has two other distinct advantages; it acts as a filter to make the radiation in it even more mono-energetic, and it has a low surface to volume ratio which is desirable for good vacuum properties. The cavity used in this instrument is a transmission cavity, that is, microwave power can only pass through it at or near resonance. It is made of two diametrically opposed reflectors. Such a structure is known to give high quality resonances at microwave frequencies.

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The microwave energy needed to excite the molecular resonance of formaldehyde is supplied by a solid-state bulk semiconductor commonly known as a Gunn-effect oscillator. Its oscillations are stabilized by referring it to a very stable, oven controlled crystal oscillator. Its output frequency is thus made to exactly match that of the peak of the formaldehyde resonance. At the same time, the resonant peak of the microwave cavity is made to coincide exactly with both the oscillation frequency and the peak of the gas resonance, and it is stabilized there by a feed-back loop.

For very small quantities of formaldehyde gas in a mixture, the actual amount of microwave power absorbed is very small. A means of relatively noise-free amplification of such absorption is provided by "heterodyne" detection and amplification of the signal. Then a further signal-to-noise enhancement is gained by applying an on-off electric field through the sample. This modulates the absorption signal, resulting in an AC signal which is amplified, then synchronously detected. A DC signal proportional to the formaldehyde absorption is then delivered to a digital meter and is made available for external recording.

Automatic control is always desirable in a monitoring instrument. In this instrument, a series of interlocks is provided to assure the user that the system is functioning properly. These interlocks provide for automatic operation while the instrument is in continuous use.

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The basic sensitivity of the technique used here is limited to approximately 1 ppm levels by the very small absorption signals. To extend the detectability range, a dimethyl silicone rubber membrane molecular separator device is used to enrich the formaldehyde sample that enters the microwave cell by more than 2 orders of magnitude, thus extending the minimum detectability for formaldehyde to near 10 ppb.

A brief description of the functional circuits of the instrument is given in the following sections. References are made to the block diagram of the instrument (see Figure 4), which can be used to follow the given descriptions.

B. Frequency Stabilization Circuits

A crystal controlled microwave oscillator, with a frequency of 2.9003808 GHz, and a basic stability of 5 parts in 10^8 per day, is used to derive the frequency stability of the Gunn effect oscillator. The stable frequency is harmonically mixed with some of the power from the Gunn oscillator in a 1N53 silicon crystal. A search oscillator sweeps the Gunn oscillator frequency over an 80 MHz range by voltage tuning a varactor diode in the Gunn-diode package. When the tenth harmonic of the reference oscillator is 29.003 MHz above the Gunn oscillator output, a phase comparison is made with another stable reference oscillator at 29.003 MHz and an error signal is fed back to the tuning varactor to "phase lock" the Gunn-oscillator output to the crystal controlled reference

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reference oscillator. When this has been accomplished, the Gunn oscillator has an output frequency of 29.003808 GHz - 29.003 MHz, or 28.974808 GHz, which is the frequency of the resonance peak of the formaldehyde absorption line. This frequency is stable also to 5 parts in 10^8 per day.

C. Cavity Resonance Stabilization Circuits

The cavity's resonance is stabilized to the operating frequency at 28.974808 GHz by making use of the fact that the microwaves make a 180° phase change in passing through the cavity near a resonance. The microwaves entering the cavity on the input side are at a fixed phase (a phase determined by the phase angle of the 29.003 MHz reference oscillator). As the cavity resonance approaches the microwave frequency, the microwaves at the output of the cavity have a positive phase angle from that of the input. Very near resonance the phase shift is a maximum of 90° positive and changes with a very sharp slope to another maximum of 90° negative, passing through zero phase shift exactly when the cavity resonance matches the input frequency. This kind of a signal is called a discriminant curve and because of its characteristics it can be used to stabilize by a feed-back mechanism.

The cavity resonant frequency is tuned by physically moving the two reflectors apart by the thermal expansion of an aluminum collar. As the cavity resonance approaches the Gunn oscillator frequency, more microwave power passes through the cavity to the

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detector at the output. At the output detector, the microwave power is mixed with the tenth harmonic of the reference oscillator again as in Part B above. In this case, their frequency difference is always exactly at 29.003 MHz because of the "phase lock" of the Gunn oscillator at the input side of the cavity. The 29.003 MHz signal at the output mixer is amplified and phase compared with the same 29.003 MHz reference oscillator as in Part B. However, a phase shifter is included so as to provide adjustment of the phase difference between the signal and the reference to be near zero when the cavity resonance matches the microwave frequency. The DC output from the phase detector is then amplified and controls the current being used to heat the aluminum collar. The cavity resonance is thus forced by this feedback loop to stay, within some small error, at 28.974808 GHz.

D. Signal Detection, Amplification and Presentation

Electric field (Stark effect) modulation, heterodyne RF detection, and phase sensitive detection are all used in this instrument to insure optimum signal to noise characteristics for the detected absorption.

A 10 KHz square-wave, zero based, 2 kv peak-to-peak voltage is generated with a circuit (see Figure 5) which is packaged within an aluminum can located beneath the cavity absorption cell. This modulating field is applied to one reflector plate of the microwave

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cavity so that it appears through the sample within the cavity. When the field is on, the formaldehyde absorption is moved to another frequency. When the field is off, the formaldehyde absorption coincides with the oscillator frequency and can absorb power from the input. The effect of this on-off field is to amplitude modulate the microwaves in the cavity at a 10 KHz rate if formaldehyde molecules are present there. This amplitude modulation then also appears on the microwaves that enter the detector mixer crystal and then subsequently (after heterodyne detection) also on the intermediate or beat frequency at 29.003 MHz. The modulated IF frequency is amplified; then it is demodulated by a video detector crystal diode, leaving just the 10 KHz signal component. The 10 KHz signal is amplified more and then phase compared with a reference signal which is derived directly from the Stark modulator circuit. The output of the phase detector is a DC signal which is proportional to the amplitude of the 10 KHz signal. This signal is further amplified and an RC time constant is applied to it before it is delivered to a digital voltmeter for readout or to an output connector to drive a recorder.

E. Separator Temperature Control

To insure a nearly constant enrichment by the membrane material in the separator device, its temperature must be kept constant to within a few degrees. It was found during the development of the

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separator device, that the enrichment of formaldehyde through the separator increased by 15% or more at temperatures lower than room temperature. The separator temperature is maintained at about $+ 10^{\circ}\text{C}$.

One side of a thermo-electric device (TED) is attached to the body of the separator and the other side to a heat sink. Heat is pumped from the separator body by the TED by an amount proportional to the current flowing through the TED. A thermistor located on the body of the separator detects changes in temperature from some set value ($+ 10^{\circ}\text{C}$ in this case) and more or less current is passed through the TED to vary the heat pumped by it. This feedback is operated continuously to keep the temperature of the separator nearly constant.

F. System Interlock Controls

The instrument is functional when all of four conditions are true. One, the Gunn-effect oscillator must be stabilized to the crystal controlled reference oscillator. Two, the cavity resonant frequency must be tuned to coincide with the stabilized microwave frequency and itself stabilized there. Three, the pressure in the cavity must be within the operating range. This also insures that the modulating Stark voltage is maintained on. Fourth, the separator temperature must be stabilized at its operating point.

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From turn-on, the instrument automatically controls itself to make the above conditions true. As each of the conditions becomes true, an enable signal is passed to a four-input gate. When all conditions are true, the four input gate is made and it turns on a "ready" lite on the front panel. Should any of these conditions change during the operation, the "ready" lite will extinguish and data should not be taken during that time.

V. CALIBRATION PROCEDURES

A. Calibration Sample Preparation

Several means are available for producing known concentrations of pure monomeric formaldehyde gas in mixtures. The most common methods employ a solid polymer of formaldehyde, α -polyoxy methylene, or paraformaldehyde, which decomposes readily to give quite pure monomeric formaldehyde gas.

Permeation tubes, usually made of Teflon, can be filled with the paraformaldehyde. The formaldehyde gas can permeate the walls of the tube and be flushed by and mixed with a carrier gas to produce known concentrations of formaldehyde in the mixture. When the tube temperature is held constant in a controlled oven, the rate of permeation is constant. Then if the carrier gas flow is constant, the concentration of formaldehyde in the mixture will be reasonably constant with time. The permeation rate is usually determined by measuring the total tube weight loss with time.

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It should be added that some error exists in this method for formaldehyde because of the expected water by-product of the decomposition of the paraformaldehyde. However, for the 100% pure paraformaldehyde, the water vapor from decomposition will be an extremely small fraction of the formaldehyde.

Such permeation tubes were used to produce standard concentrations for calibrating the monitor. Several tubes of different lengths were purchased from Dynasciences, Inc. and one 2 cm tube was procured from EPA for final calibration before delivery. All of these tubes were separately tested for weight loss after operation at 100°C and moderate flow rates, and were all found to be within a few percent of the calibration curves received with them. Our values were then used to determine concentration of formaldehyde from the following equation:⁽⁸⁾

$$C = \frac{Pr \times l \times k}{F} \quad (2)$$

where Pr = permeation rate of H_2CO through the tube walls
in $\mu g/min/cm$

l = active length of the permeation tube in cm.

$k = \left(\frac{m}{M} \times \frac{760}{P} \times \frac{T}{300} \right)$; m = molar gas volume
 M = molecular weight of sample

F = carrier flow rate in ml/min

The manifold used to prepare concentrations of H_2CO from 20 ppm to .01 ppm in air is shown in Figure 8. For high concentrations (> 1 ppm) the air carrier is flowed over the heated permeation tube at whatever flow rate gives the desired concentration then directly

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to the first stage of the membrane separator. For lower concentrations, a fixed concentration of H_2CO in air was obtained at an appropriate flow rate, then diluted by the pure carrier to the desired concentration.

B. Calibration Procedure

Calibration of the formaldehyde monitor is done quite simply.

The following procedure was used during initial testing.

1. Determine the mode of operation. The instrument can be operated in several modes, each requiring a different set of vacuum and electronic conditions. The calibration data referred to later is for the most sensitive mode of operation -- that is, with the "slow pump" position and the 100 second detection time constant. The toggle switches on the instrument are set for these conditions.
2. Zero the instrument. The instrument was flushed with formaldehyde air for several hours before calibration was initialized. This is done to insure that no residual formaldehyde is in the cavity. A front panel knob is then used to set the readout equal to zero ppm.
3. Supply a known concentration of formaldehyde to the instrument. The sample mixture can be flowed over the first stage of the membrane separator at an appropriate constant flow rate. The instrument is allowed one full hour for full response.

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4. Adjust readout to match input concentration. A front panel "calibrate" knob is used to adjust the meter readout to the concentration calculated from Equation 2. After adjustment the knob is locked in that position.
5. Change the sample concentration. The sample concentration is then changed but the delivery flow rate is kept constant. Another full hour is allowed for full response. The new calculated value is then compared with and plotted against the new meter reading (see Figure 9), and any deviation from linearity is noted as instrument error.
6. The sample is changed incrementally until the desired calibration range is obtained.

C. Data

Calibration data as obtained with the above procedure for different ranges is given in Figures 9 and 10.

For some calibrations a secondary method was used simultaneously with the instrument to determine formaldehyde concentration. The sample was split before it entered the instrument. Half was bubbled through a water trap then analyzed by a chromatropic acid solution colorimetric test with a Beckman DU photometer. For the lower concentrations (< 1 ppm) of H_2CO the trapping time used was necessarily longer than the one hour time for full response of the microwave instrument.

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Figure 9 shows a calibration for nearly the full range of the microwave instrument starting at a .1 ppm concentration. The spectrometer response is seen to give a linear response to within 10% over the full range while the chromotropic acid test fluctuated as much as 20%.

Figure 10 is a calibration for a smaller range. The instrument response shows a maximum deviation from linearity of 5% in either direction from the set point for concentration changes within one order of magnitude in each direction. This was found to be the case for any arbitrarily picked initial set point.

In Figure 11 the initial point is at the high concentration and the subsequent data points are for reduced concentrations. The large deviation from linearity at the low concentrations is felt to be due to the large memory problem to be discussed in a following section. This memory effect also affected the reproducibility of the instrument. That is, during the calibration procedure, if the concentration was returned to the initial set point value, errors as much as 10% were observed when the instrument had seen concentrations larger than the set point value.

VI. OTHER TESTS

A. Minimum detection limits

Figure 12 shows the signal obtained with the monitor for 30 ppb formaldehyde in wet air. The instrument was in its highest sensitivity mode with a 100 sec signal average time constant. The tangential signal to noise ratio for the 30 ppb concentration is seen to be about 1:1. This suggests that 30 ppb formaldehyde is the limit of

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detectability with this instrument without additional signal averaging. It is felt that a decrease in the minimum detectable limit requires further preconcentration, with the obvious trade offs in response time and continuous monitoring capabilities.

B. Base line stability

Because of the high stability of the reference oscillator which controls the system stability, and a good design with stable components for the detection electronics, the instrument's stability should be good. Indeed our tests indicate good stability, with the zero base line drift measured less than 0.5% of full scale (20 ppm) for 24 hours. Figure 13 shows a base line plot (for 16 hours) of the instrument's output with no formaldehyde in the cavity. Figure 14 shows a plot as in Figure 13, but with 1.20 ppm formaldehyde at the input of the membrane separator.

C. Linearity

The linearity of instrument's response to concentration is important for accurate calibration. We expect a linear response for the following reasons:

1. In ambient air the formaldehyde is expected to be a trace in a mixture consisting mainly of N_2 gas. Therefore the width of the formaldehyde $3 \rightarrow 3$ line at a given pressure within the microwave cavity will be determined mainly by collisions with N_2 molecules. Then the line width should remain nearly constant if the operating pressure is kept constant.

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2. The microwave power level into the absorption cell is sufficient to just begin to saturate the absorption line. This condition is called the optimum power method⁽⁹⁾ in microwave spectroscopy and assures a linear response of the peak absorption as long as the linewidth remains relatively constant.

Since the instrument will be monitoring a small concentration (< 20 ppm) of formaldehyde in ambient air the first condition is automatically fulfilled. We can get a good estimate of the actual linewidth parameter of the $3 \rightarrow 3$ formaldehyde line broadened by ambient air if we measure the linewidth of this line versus the total pressure of N_2 . This measurement was made for us by Prof. E. Rinehart at the University of Wyoming and the report of his measurements appears as an appendix to this report. The linewidth parameter determined by Prof. Rinehart's measurements for H_2CO broadened by N_2 is 3.9 KHz/m Torr. Thus at a total pressure of 50 m Torr we should expect the H_2CO $3 \rightarrow 3$ line to have a full width of approximately 240 KHz.

To determine the input power to the cavity required to just begin to saturate, measurements of the input power versus signal were made directly with pure formaldehyde in the cavity. Figure 6 of Prof. Rinehart's report (see appendix) compares the linewidth versus pressure for H_2CO self broadened, and N_2 broadened. At 50 m Torr pressure, the linewidth for N_2 broadened H_2CO is equivalent to about 10 m Torr of pure H_2CO . Figure 15 shows a

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plot of saturation curves for the $3 \rightarrow 3$ line of H_2CO at different pressures of the pure gas with this instrument. At a pressure of 10 m Torr (corresponding to 50 m Torr total operating pressure of trace H_2CO in N_2) any microwave power between 60 microwatts and 100 microwatts into the cavity will give peak signal for the H_2CO $3 \rightarrow 3$ line.

An indication of the linearity expected for the cavity system can be obtained by plotting the peak values in Figure 15 against the pressure of H_2CO . Figure 16 shows such a plot. At pressures below about 11 m Torr H_2CO (corresponding to about 60 m Torr of N_2 with trace H_2CO) the system response is quite linear. Above that pressure the response is not linear because of insufficient Stark field strength to fully modulate the broadened line.

Thus, we determined from these measurements that we should operate with a total pressure of between 50 and 60 m Torr with an input microwave power of 80 microwatts. For these conditions we expect a linear response for concentrations of H_2CO from minimum detectable to about 0.1%.

The above determinations are valid only in the absence of significant amounts of water vapor in the cavity. Large concentrations of water vapor can become dominant in broadening the H_2CO line, thus changing the characteristics for which linearity can be maintained. However, we can assure linearity by using a dryer to reduce or eliminate the water vapor from the sampled air.

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The calibration curves in Figure 9 and Figure 10 show that the response is linear to within $\pm 10\%$ over the entire range of the instrument and $\pm 5\%$ for any range within one order of magnitude of the calibration point.

D. Response time

Tests for the instrument's dynamic response time for a step change in H_2CO show problems due primarily to the sample handling and inlet system. Early investigations of response time with a less sensitive system than the final instrument, were promising. However, with the capability for detecting smaller concentrations with the final instrument we observed effects attributed to adsorption, other wall effects, and polymerization of the gaseous H_2CO at the walls. Some investigations were carried out in order to determine means for minimizing these effects if possible.

Evidence of polymerization of H_2CO on the inlet tubing walls was substantiated when large signals for H_2CO were obtained after localized heating of the stainless tubing of the inlet. Very little signal was obtained until a temperature of near 180°C was reached. The 180°C temperature is the dissociation temperature for paraformaldehyde polymers.⁽¹⁰⁾ An attempt to keep the temperature of the inlet tubing hot failed to help when we observed that the formation of the polymer took place at cool spots which could not be adequately heated.

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The membrane molecular separator also contributed to increasing the response time for the instrument, both because of adsorption surfaces and because of the finite delay for flow of gases through the membrane material. However, the polymerization was thought to be most grossly responsible for the instrument's poor response so that efforts were not made to reduce the effects of the membrane separator.

Figure 17 shows the response of the instrument to a step change of approximately 1 ppm H_2CO starting with a very clean system (i.e. flushed and pumped). This data is taken with a 3 second time constant on the detection electronics so that the electronics does not contribute any significant delay in response -- only the inlet does. It is notable that with a clean system at the start, part of the initial rise time delay is probably due to adsorption and polymerization on the walls as they see the 1 ppm levels of H_2CO . The response for return to baseline is seen to be considerably longer than the risetime -- this is because of the wall effects. This delay becomes even worse when the inlet has seen large amounts of formaldehyde (> 20 ppm). Presumably, polymer forms on the walls, then has a slow equilibrium with the gas phase, leaving an extremely long time for return to baseline. This effect is shown in Figure 18 which plots the residual H_2CO signal versus time after a dose of > 20 ppm. Here the signal is observed at intervals of time up to

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90 hrs after the sample is removed of H_2CO and the cavity is continually vacuum pumped. Figure 19 shows the continuously detected signal for the first 16 hours of this test.

E. Interferences

The strongest quality of microwave spectrometry is its inherent selectivity. No qualitative interference of the H_2CO $3 \rightarrow 3$ line is expected for the following reasons. First, the closest absorption line from another specie (acetaldehyde) has its peak 180 KHz above the formaldehyde peak. Second, the resonant cavity with a quality factor of 10,000 acts to filter absorptions that occur other than its resonant peak frequency (which in this instrument is tuned exactly to the H_2CO peak). Lastly, the exciting frequency is matched exactly to the H_2CO peak and is stable to 5 parts in 10^8 per day. Of course, as mentioned earlier, quantitative interferences can occur due to broadening by polar molecules such as water vapor in the air mixture.

Because of the modulation technique used in this instrument, interference due to Stark shifted lines from other species overlapping the detected formaldehyde line is possible. This type of interference would be limited to nearby lines because the Stark lines are not generally frequency shifted far from the unshifted line. This interference, if it occurs at all, will always indicate a smaller concentration of formaldehyde because Stark lines would subtract from the formaldehyde signal due to the fact that they are detected out of phase with it.

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A survey of a catalog of microwave absorption lines shows only two gases with lines close to the formaldehyde $3 \rightarrow 3$ line which might be in a typical ambient air mixture. They are methanol and acetaldehyde. Tests were carried out for these two prospective interferers by sniffing the vapors above laboratory grade solutions of methanol and acetaldehyde and observing the instrument's response. No response was obtained for either of these tests. The same test was run for ammonia, and a number of laboratory solvents (toluene, acetone and ethanol). No instrument response was obtained for any of these except acetone, which was expected to have a considerable impurity of formaldehyde.

Figure 20 displays the instrument's response during the test for methanol and acetaldehyde (note that an interference would be a negative going signal -- that is, a Stark line).

Quantitative interference was observed however, when large amounts of toluene, methanol and acetaldehyde were "sniffed." Here the membrane passed this material faster than it passes air and since there is no selective trap for these components they can appear in the cavity in large concentrations. Their large dipoles are effective in broadening the H_2CO line with a subsequent loss in its peak intensity. This effect is shown in Figure 21 where the initial signal is due to residual formaldehyde. After acetaldehyde is sniffed, the formaldehyde signal decreases then comes back

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(but not all the way back, due to possible flushing effect of the acetaldehyde) after room air is sniffed again. It is estimated from our tests that these polar species must be present in the air in quantities 1% or greater to cause this kind of interference.

F. Dryer

The need to remove water from the sampled gases has been previously established. Ideally, a material was sought which would selectively trap out all of the water while leaving the formaldehyde concentration unaffected. The trap should last a long time and be easily replaced when necessary.

Our first effort was to test a drying device commercially available from the Perma Pure Corporation, New Jersey. This device uses bundles of extruded membrane tubes through which the wet gas is flowed. The outside of the tubes is then flushed with dry gas which flushes away the permeated water vapor. A net drying effect occurs because of the fast permeation rate of water through the membrane tubes -- orders of magnitude faster than most other gases. Figure 22 shows the experimental arrangement for our tests. Our tests with two lengths of dryer tubes (one 12 inch and another 36 inch) showed that they indeed were effective in drying an air sample by reducing the water concentration to below 10 ppm (as detected by microwave spectrometry). At low flow rates, losses of formaldehyde gas of more than 50% were observed. However, at

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flow rates above 350 ml/min with the 12 inch dryer, only a 10% loss of formaldehyde signal was observed. At the fast flow rates a slight reduction of drying capacity was observed. The major problem with these dryers (a problem that we were never able to overcome) was the extremely long response for equilibrium to be reached. For 10 ppm levels of formaldehyde, over 10 hours were required for 90% response. This was obviously unsatisfactory and we were forced to abandon this device for our application. Although we did not make conclusive tests to substantiate it, our guess was that the trouble was due to the extremely large effective surface area of the bundle of membranes.

Our efforts then turned toward testing various drying agents such as molecular sieve, calcium chloride and phosphorous pentoxide. The latter material tested close to ideal. It dries an air sample to below detectable levels while removing less than 5% formaldehyde for any of the concentrations tested (1 ppm to 100 ppm). We observed no attendant problems with signal response time. Figure 23 shows the result of test of a P_2O_5 dryer with about 1 ppm formaldehyde in the mixture. The test is made simply by switching the P_2O_5 dryer in and out of the flow of sampled gases. The major problem with P_2O_5 was that its lifetime was so short; 50 grams could easily be used up in 24 hours of continuous operation in a relative humidity above 50%. We decided to locate the P_2O_5 material within the vacuum

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system, between the membrane separator and the cavity absorption cell, where it would see considerably less quantity of gas than at atmosphere. By doing this, its lifetime was extended to 30 days or more continuous operation.

G. Molecular Separator

The enrichment factor of the membrane separator device was measured for formaldehyde in dry N_2 as well as in wet and dry air. After first verifying that the optimum pressure between stages of membrane for formaldehyde flow was in the range indicated by theory (see Section III-G), the between stage pressure was adjusted to about 6 Torr. The enrichment factor measurements were made as follows:

1. A mixture of N_2 wet air, or dry air with 20 ppm formaldehyde was prepared with the manifold shown in Figure 8.
2. This mixture is flowed over a variable leak valve at the entrance of cavity cell (then through the dryer). The leak is adjusted so that 50 m Torr pressure is maintained within the cell while it is being pumped.
3. The signal amplitude is noted.
4. The cavity inlet is switched over to the two-stage membrane (which was cooled to about $10^\circ C$) and the vacuum pump is throttled as required to give a 50 m Torr pressure within the cavity.
5. The signal amplitude is noted.
6. The ratio of signal amplitudes (in volts) is then the measured enrichment factor.

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For N_2 carrier the enrichment factor is about 200, for dry air carrier it is about 180, and for wet air it is about 220. It is notable that water in the carrier is effective in increasing the permeation rate of formaldehyde through the membrane. This effect was first noted by White⁽¹¹⁾ at NASA, Langley Research Center, and was clearly verified by our work. This effect is particularly evident when switching from a dry to wet carrier; a large signal is momentarily obtained (see Figure 24) then it decays back to a constant value. We have not fully interpreted this effect but it is likely that the water has a flushing effect on the formaldehyde in the membrane due to its extremely high permeability through it and the fact that H_2CO is reasonably soluble in water. Of course the variation of the enrichment factor with variable water content in air is a potential problem for ambient monitoring. We determined, by measuring the signal for 20 ppm H_2CO in air of variable "wetness," that 10% changes of output signal occur when the relative humidity changes by 40%. Thus for those cases where greater than 40% changes are likely in ambient air, a dryer on the atmospheric sample flow would be required to keep linearity within 10%.

Early in our investigations with the membrane material, we observed an increase in the enrichment factor by reducing the membrane temperature. By reducing temperature of the membranes

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just above 0°C we observed an enrichment factor (for the two stages of membrane) of nearly 300 (with a wet air carrier). This effect was used in the formaldehyde instrument by operating the separator device about 15°C below room temperature. Lower temperatures introduced problems with freezing and condensation.

The effect of the membrane separator device on the instrument's response time is shown in Figure 25, by comparing response with that from a direct inlet. A definite difference in risetime is noted but not much difference in decay time. This suggests that the response time is more strongly determined by wall effects as was indicated in part D of this section.

VII. MAJOR PROBLEM AREAS

A. Effect of Moisture

The problems associated with moisture in the sampled air have not been completely accounted for in this instrument. The variability of water content in the air can produce significant changes in the instrument's response to formaldehyde. A cure for this, of course, is to locate a dryer in front of the membrane separator. However, doing this will require dryer replacement quite often and it will cause a somewhat lower sensitivity because the wet carrier gives a higher enrichment factor by as much as 20%.

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In principle, using a more sophisticated electronic design as described in the next section, the broadening effects of water within the cavity on the formaldehyde line can be compensated. Thus one could replace the dryer by an electronic adjustment which could be automated if necessary. However, the variations in signal due to the effect of water in the membrane separator device would still be difficult to correct.

B. Poor Response Characteristics

The response characteristics of this instrument for H_2CO have been rather discouraging since they really render it ineffective for ambient monitoring purposes. Since most of the response problem is felt to be due to the polymerization on the surfaces, an obvious solution is to heat the inlet and cavity to a temperature greater than the dissociation temperature. However, this would require a completely different design for both. From what has been learned from this study future design changes could easily be made.

C. Acoustic Noise Pick-up

Whenever high voltage Stark modulation is used, it becomes extremely difficult to shield the large voltage transients of the generator from the detection circuitry. Other effects such as acoustical vibrations can also cause noise in the detection electronics. Noise from these sources can be in phase with the

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actual signal and cannot be differentiated from it -- that is, it is background noise, sometimes called 'pickup' or 'potato'.

The modulator for this instrument was specifically designed to virtually eliminate electronic pickup from high voltage transients. This was accomplished by enclosing the entire modulator within a metal can which adapts directly to the bottom of the cavity absorption cell - there are no high voltage cables outside of the enclosure. So we feel that we have eliminated potential background noise by proper design.

However, we observed during initial tests that at particular modulator frequencies, resonant modes within the shielding structure could cause extremely small but troublesome acoustic vibrations in the cavity absorption cell and in the Gunn effect oscillator waveguide cavity. The effect of these vibrations was a large component of background noise. The vibrations and therefore the noise could be minimized by changing the modulator frequency of resonance with modes of the structure. Although this reduces the background noise by orders it does not completely eliminate it. We found the background noise of this type to be the limiting noise in the detection system.

Several partial solutions are available for this problem. An obvious one is to physically uncouple the modulator enclosure from the cavity. However, one then requires a high voltage cable connection which may be an additional source of pickup. In future designs

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it is felt that appropriate changes can be made to reduce this source of noise below the limiting noise of the detection electronics.

VIII. FUTURE DEVELOPMENT POSSIBILITIES

A. Improved cavity design

The need to operate the inlet system and cavity absorption cell at much elevated temperatures to reduce wall effects (adsorption and polymerization) requires a significantly different cavity design than the one used in this prototype.

A new design has been conceived which is completely free of non-metal materials. It would be capable of operation at 200°C and would be easily tuned by a thermal expansion technique similar to that used in this prototype. An inlet system could easily be adapted to this cavity so that the entire system could be operated at the 200°C temperature. Note that the dimethyl silicone membranes are usable to 250°C. If, then, a dryer were either not needed or could be located outside the vacuum, this type of system should offer much improved response time characteristics -- certainly within the 90% in 5 minute EPA requirements.

B. Preconcentrator inlet system.

Other contractual work at LLL has led to the development of a platinum metal preconcentration device which has worked extremely well for large polar molecules. This device takes advantage of

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the strong adsorption characteristics of some gases on metal surfaces, and could work very well for molecules like formaldehyde. Polymerization would no longer be a problem with such a device. Moreover, very large concentration factors would be expected for moderate trapping times.

The principle of this device is as follows:

Ambient air is pulled over a platinum screen (located in an inert holder) by a pump. An important condition here is that the screen and holder are the first material to 'see' the sample -- that is, no hose or tubing precedes the trap. After a sufficient sample period, the holder, with enclosed screen, is manually or automatically placed in an inlet chamber to the cavity. There it is heated very fast with a heating coil. The trapped vapors are driven off during the short heating cycle, and detected by the spectrometer tuned to a specific frequency. The screen is now clean and ready for trapping another sample.

We feel that such a device, possibly in combination with the membrane inlet to the cavity, could extend its detectability for formaldehyde and other polar vapors, well into the part per trillion range. We also feel that such a procedure could be automated to give at least one data point each 5 minutes.

We did not have an opportunity to test this combination with the Gunn-diode cavity formaldehyde monitor because it would require a specially designed inlet modification.

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C. Multiple Gas Analyzers.

Since both the Gunn effect diode and the cavity absorption cell are capable of being tuned easily to peak frequencies of other pollutant molecules, it should be possible to extend this design to monitor several pollutants with a single instrument. We conceive of an automatic instrument which sequentially checks the sampled gases for as many as 10 pollutants, determines their mole fraction in the mixture, then presents hard copy of the results. An instrument with the same capabilities, except that it would require operation by a technician, could be made quite unsophisticated and inexpensive. The development of a multiple gas detector will be a direct extension of the work reported here and it will show the utility of this technique selective pollutant monitoring.

IX. CONCLUSIONS

The instrument described by this report, called a Gunn-diode Microwave Cavity Formaldehyde Monitor, has been shown feasible for monitoring low-levels of formaldehyde gas in laboratory prepared mixtures. The prototype instrument as delivered has limitations in such critical areas as sensitivity and response characteristics, but these areas can be corrected with further design modification. With such additional modifications, it is expected that this technique will add an extremely potent tool for pollutant monitoring. The capability for monitoring several pollutants in the same instrument is a direct extension of this design and should be developed next.

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Fig. 1 A Gunn-Effect Diode

Fig. 2 Gunn-Diode Oscillator Package

Fig. 3 Cavity Absorption Cell

54

Figure # 4

Block Diagram of Gunn-Diode Microwave Cavity Formaldehyde Monitor

Fig. 5 Stark Modulator Schematic

Fig. 6 Enrichment Factors for Dual Stage Separator

Fig. 7 Two Stage Separator

Calibration Manifold

Fig. 8 Calibration Manifold

Fig. 9 Calibration Data - Full Range I

Fig. 10 Calibration Data - Reduced Range

Fig. 11 Calibration Data - Full Range II

1/9/74

Scale: ≈ 0.25 ppm/in.

1 hour

Zero H_2CO

≈ 0.03 ppm H_2CO

Fig. 12 Minimum Detectable Quantity

1 hour

Scale: ≈ 0.5 ppm/in.

16 15 14 13 12 11

63

Fig. 13 Baseline Drift - No H_2CO

Fig. 14 Baseline Drift - $1.2 \text{ ppm H}_2\text{CO}$

Power Saturation Measurements

Cavity & H₂CO

Fig. 15 Saturation Curves for Pure H₂CO in Cavity

PEAK SIGNAL VS. PRESS

Fig. 16 Linearity of the Optimum Power Method

1/27/74

Scale: ≈ 0.3 ppm/in.

3 second time constant

Fig. 17 Step Response Characteristic

Fig. 18 Residual Formaldehyde vs. Time

1/24/70

Scale: 20 ppm Full Scale

1 hr.

69

Start

9

8

7

6

5

4

3

2

1

20

19

18

17

16

15

14

13

12

11

Fig. 19 Residual Formaldehyde Response

Fig. 20 Interference Test - Methanol

Fig. 21 Interference Test - Acetaldehyde

Fig. 22 Experimental Arrangement for Dryer Test

Fig. 23 P_2O_5 Dryer Test

Fig. 24 Effect of a Wet Carrier

Direct Inlet - 250 ppm H_2CO

3 second time constant

1 hour

time

TWO STAGE SEPARATOR INLET

3 second time constant

0.9 ppm H_2CO

1 hour

time

Fig. 25 Membrane Response Test

FRONT VIEW OF FORMALDEHYDE MONITOR

Fig. 26 Front View of Formaldehyde Monitor

REAR VIEW OF FORMALDEHYDE MONITOR

Fig. 27 Rear View of Formaldehyde Monitor

Fig. 28 Top View of Monitor Components

TOP VIEW OF MONITOR COMPONENTS

SAMPLE INLET AND DRYER CONNECTIONS

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X. APPENDIX

MICROWAVE SPECTRAL MEASUREMENTS
OF THE
3(1,2) - 3(1,3) TRANSITION OF FORMALDEHYDE

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1. STARK EFFECT

Splittings of the $M = 1, 2$, and 3 components of this transition as a function of electric field have been measured and are shown in fig. 1. The small (+) signs are data points, and the dots are calculated splittings using:

$$\Delta\nu = (A + B M^2) E^2$$

where $A = -1.6949 \times 10^{-7} \text{ MHz cm}^2 \text{ volt}^{-2}$ and $B = 8.095 \times 10^{-7} \text{ MHz cm}^2 \text{ volt}^{-2}$.

No correction terms have been calculated taking into account the hyperfine structure of this transition. The data from which these coefficients were determined is shown in the Appendix.

The signal available as a function of stark voltage for various pressures of N_2 diluent is shown in fig. 2. At a partial pressure of 264 mtorr of N_2 glow-discharge breakdown occurred at 3000 volts/cm. The signal was within $\pm 2\%$ of maximum when breakdown occurred.

Since 9/14 of the total intensity is contained in the $M = 3$ component, which is easily modulated, complete modulation of the transition may not be necessary for analysis purposes.

The data for figs. 1 and 2 was plotted using a focal program called DPLT, which is given in the Appendix.

II. VARIATIONS OF SIGNAL WITH PRESSURE

Signal variations have been measured with a fixed partial pressure of formaldehyde and variable N_2 diluent pressures, and with a fixed concentration of formaldehyde and variable total pressure. The procedure was as follows:

A small amount of H_2CO was admitted to the absorption cells and allowed to stabilize in pressure. The pressure was recorded, and a very slow flow of N_2 was admitted to the cells. A program called LRL1 (given in the Appendix)

was started at essentially the same time. This program recorded the signal and the pressure. The microwave power level was set at 3 m watt during these measurements (the maximum power available at this frequency). This power level was sufficient to oversaturate the transition at low pressures, but was insufficient to saturate at 100 mtorr of N_2 .

The resulting curves of signal vs pressure are shown in fig. 3. Each of these curves peaks at some intermediate pressure corresponding to optimum saturation. It may also be noted that as the partial pressure of H_2CO is reduced, the peak occurs at a higher pressure of N_2 , and that the peak is broadened. This effect is plotted in fig. 4, which shows the total pressure for peak signal vs partial pressure of H_2CO . The range over which the signal variation is within 1% or the noise, whichever is greater, is shown as upper and lower limits on the vertical bars. From this, it is concluded that a wide range of partial pressures of H_2CO may be measured at a fixed incident power and a fixed pressure of diluent with the reservation that the diluent be primarily non-polar.

This variation of pressure at which peak signal occurs is ascribed to the fact that some small part of the collisions undergone by the H_2CO molecules are with other H_2CO molecules, and that this percentage, of course, varies with the partial pressure of the H_2CO . Since the broadening parameter of H_2CO is greater than N_2 (discussed in the next section), a lower total pressure is required for optimum saturation.

The variation of signal with total pressure at fixed concentration is shown in fig. 5. This experiment was conducted in a fashion similar to that discussed above, with the addition that, after the total pressure reached 100 mtorr, the gas was very slowly pumped out, while again recording the

signal and pressure. Thus the figure shows both the increasing and decreasing pressure runs. The program used was a modification of LRL1 and is given in the Appendix as LRL2. The data from these runs is included as data tapes and printout separately.

III. LINEWIDTH PARAMETERS

The measurement of the linewidth parameters was made as follows:

A program called TAKL (included in the Appendix) was used to measure the signal as a function of frequency, using 28974.806 as the center frequency. This seems to be the most reliable number resulting from this series of measurements, although at linewidths of 500KHz a center frequency of 28974.815 resulted in a better fit. A total of 256 data points are taken.

A program called FITL (also included) is then used to fit a calculated Lorentzian to the data. This program uses the Analog to Digital Converter to read the settings of three potentiometers and the synchronous detector output (for background). These correspond to center frequency, intensity, and linewidth. A sum of the squares of the deviations is printed after each sweep. The operator then adjusts the potentiometers for a "best fit" as judged by eye and by the printed sum. When all switches on the switch register are set to zero, the program prints the frequency, linewidth, and a number related to the intensity. The results are shown in fig. 6. The data points are again the small plus signs and the linewidths vs pressures calculated are shown as dots. The parameters used for calculation are:

Intercept--60 KHz

H₂CO selfbroadening--18.7 KHz/mtorr

N₂ broadening--3.9 KHz/mtorr

A table of line width for various pressures is included in the Appendix.

Figure 1: Stark splitting as a function of electric field for the $3(1, 2) - 3(1, 3)$ transition of formaldehyde

Figure 2: Signal vs modulating field for pure H₂CO and H₂CO diluted with various amounts of N₂. The total pressures are shown on the graphs. The power was increased for each dilution to produce the same maximum signal.

Figure 3: Signal vs diluent pressure for various fixed partial pressures of H_2CO . The H_2CO pressures are in mtorr.

Figure 4: Ranges of total pressure for peak signal vs partial pressure of H_2CO .

Figure 5: Variation of signal with total pressure for R_1 constant concentration of H_2CO . The concentration is approximately 1.3%.

Figure 6: Self broadening and foreign gas (N_2) broadening of the formaldehyde 3(1, 2) - 3(1, 3) transition. The parameters are 18.7 KHz/mtorr and 3.9 KHz/mtorr.

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