FINAL REPORT

LASER OPTOACOUSTIC EXPLOSIVES DETECTION

Prepared for
The Aerospace Corporation
Suite 4000
955 L'Enfant Plaza,, S.W.
Washington, D.C. 20024

Prepared by
R.A. Weagant and C.H. Beebe
Beckman Instruments, Inc.
Advanced Technology Operations
1630 South State College Boulevard
Anaheim California 92806

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Contract 67865

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This project was supported by Contract Number J-LEAA-025-73 awarded by the Law Enforcement Assistance Administration, U.S. Department of Justice, under the Omnibus Crime Control and Safe Streets Act of 1968, as amended. Points of view or opinions stated in this document are those of the author(s) and do not necessarily represent the official position or policies of the U.S. Department of Justice.

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PREFACE

This work was performed by Beckman Instruments, Inc., Advanced Technology Operations (ATO), under Aerospace Subcontract 67865. The purpose of the program was to evaluate the feasibility of using a laser optoacoustic system to detect hidden explosives. Beckman let a subcontract to the Jet Propulsion Laboratory (JPL), Pasadena, California, for the assistance of certain personnel having extensive previous experience with Laser Optoacoustic Systems. In particular, Michael Shumate was most helpful. The equipment was designed and built at Beckman and the tests were performed at JPL using JPL equipment designed for laser optoacoustic system evaluation and calibration.

SUMMARY

The purpose of the program was to evaluate the feasibility of using a laser optoacoustic system to detect hidden explosives. As a result of this program, we demonstrated performance sufficient to detect EGDN vapor at concentrations of about 10 parts per billion in the presence of 50% relative humidity water vapor. With relatively modest additional engineering development, it appears possible to extend this limit to 1 ppb. Extending the sensitivity below 100 parts per trillion though will require a solution to the water vapor and anomalous absorbance problems. We know of no existing desiccant, membrane, or other gas separation device with the characteristics needed to allow the laser optoacoustic principle to be employed at its theoretical limits which appear to be in the one-part-per-trillion range. Since this principle has a sensitivity substantially better than most other analytic techniques and it also provides spectra which can be used for discrimination and identification, it is still an attractive candidate for explosive detection and continuing development seems warranted.

CHAPTER I. INTRODUCTION

This report covers work performed by Beckman Instruments, Inc., during the late spring and summer of 1977 on the feasibility of using the laser optoacoustic absorption principle for the detection of the vapor from hidden explosives. Numerous measurements were made on one explosive vapor in particular--ethylene glycol dinitrate (EGDN)--a compound similar to nitroglycerine which is one of the principal components of most modern dynamites.

The optoacoustic absorption principle is not new; in fact, it was discovered by Alexander Graham Bell before the turn of the century. In this technique, a light beam is passed through a closed container. If the beam is modulated and the gas in the container absorbs some of the light, sound waves are produced and can be detected by a microphone. In Bell's experiment, he even made the observation that if he had a more intense parallel source of light, the sensitivity of the technique would be greatly improved.

In the laser optoacoustic detection technique, a laser beam is passed through an absorption cell which contains a trace gas of interest. If the laser line is absorbed by the trace gas, the resulting sound waves are detected by a sensitive microphone. In these experiments, carbon 12 dioxide and carbon 14 dioxide lasers were used and measurements made at a number of the CO_2 wavelengths available in order to obtain the spectral absorption characteristics of the substance. The theoretical basis of this measurement principle is discussed in several places; in particular, the paper by Rosengren referenced in the short bibliography included as an appendix to this report.

The objective of this program was to construct a laser optoacoustic system having a limit of detection about 2 orders of magnitude better than that reported to date, and to perform a series of critical experiments to ascertain whether explosive vapor concentrations of one hundred parts per trillion or less could be detected and distinguished from a wide variety of other vapors and organic compounds likely to be present simultaneously. To this end a three-cell laser optoacoustic system was constructed along with a versatile gas handling system. In order to maximize signals, particular attention was paid to the system geometry. To minimize noise, attention was paid to electronic shielding, acoustic isolation, laser stability, etc. To minimize drift effects and instrumental errors associated with the gas handling, a high degree of cleanliness was maintained and the system was temperature-stabilized. The purpose of the three-cell system was to allow comparison between different optoacoustic cells to determine whether or not a differential measurement between two cells would assist in reduction of background interferences and to allow the capability of making more complicated measurements on three-cell differentials for simultaneous multiple interference rejection.

The basic Laser Optoacoustic System performance goals were met. Measurements of vapor absorption coefficients were made at concentrations much lower than reported previously and the apparatus was capable of making measurements in a stop-flow mode with minimal degradation of signals due to absorption/desorption effects. The system had an rms systems noise level believed to be within one order of magnitude of the theoretical limit set by the brownian motion of the microphone diaphragm. It was, however, not possible to detect traces of the EGDN vapor at concentrations corresponding to the rms system noise level as a consequence of two other major sources of interference--water vapor and an anomalous dry gas absorption.

The absorbance spectrum of water vapor is a continuum with specific absorption lines superimposed on it. The magnitude of the continuum absorption for 50% relative humidity water vapor is approximately equal to the absorption produced by a concentration of 1 ppm of EGDN. There also appears to be an absorption associated with clean, dry air which is about one order of magnitude lower than 50% relative humidity water vapor. To achieve a one-hundred-parts-per-trillion sensitivity for EGDN vapor in the presence of 50% relative humidity water, both of these effects would have to be compensated. Attempts were made at differential measurements using explosive scrubbers and water vapor drying agents with the hope of capitalizing on differences in the selectivity of those agents for the various vapors.

The limit of detection achieved in this program was slightly less than 10 parts per billion of EGDN. With continued engineering development, it would appear possible to build a system of this type capable of detecting EGDN in moist air at perhaps a little lower than 1 part-per-billion concentration. Detection at concentrations lower than one hundred parts per trillion, however, would require both a means for the selective removal of water molecules (without affecting any other substance present and without adding any substance of its own) and a better understanding of the low-level dry gas continuum absorption.

CHAPTER II. DEVELOPMENT

A. Optoacoustic Cell Development

The design of the optoacoustical cells for detection and measurement of trace levels of explosive vapors was based on evaluation of related experience of Beckman and Jet Propulsion Laboratory personnel and of the available information reported in the literature. The system design goal was for the detection of 0.1 ppb ethylene glycol dinitrate (EGDN) vapor in the absence of water vapor and other interferents. This meant that the factors influencing signal generation had to be carefully considered with particular attention paid to the maximum conversion of laser power to useful signal, while minimizing spurious signals, such as microphonics. To achieve this end result, a set of optoacoustic detector cell design goals was established as follows:

- The cell was to be vacuum tight to isolate it from the external environment. The cell valves would not necessarily be leak-free through the valve, but must provide a high acoustical impedance to pressure pulsations generated by the chopped laser energy absorbed by the gas within the cell.
- No elastomeric seals were to be used. It was proposed that ground and lapped glass valves be designed and incorporated at the cell body, and the microphone assembly be sealed to the cell block with an indium-coated, stainless-steel O-ring.
- The cell body was to be made of Pyrex or quartz, with the cell bore and connecting ports drilled and polished.
- Zinc selenide windows were to be employed, mounted at Brewster's angle. The ZnSe was to be of the chemically-vapor-deposited type to minimize bulk absorption.

- The active cell volume was to be approximately 10 cm^3, with minimum dead volume ports connecting the active volume with the valves and microphone. The total "waste" volume was to be less than 2 cm^3.

- Each of the two (or three) optoacoustic cells was to be mounted in an aluminum block holder incorporating a heater cartridge, control thermistor, and measuring thermistor for temperature control during bakeout. Capability of controlled bakeout at up to 150°C was to be provided.

- The cell support blocks were to be mounted on a common aluminum plate, spaced and insulated from an aluminum box housing. This housing was to be proportionally temperature controlled at any predetermined control point in the 27° to 50°C range by a silicone rubber insulated heating blanket powered by an accurate zero-crossing type SCR controller. This inner oven was to be thermally isolated from an outer aluminum housing. Brewster angle-mounted barium fluoride windows were to be provided in the outer housing to transmit the laser beam efficiently through the optoacoustic cells and to the external power meter detector.

Most of these goals were met in design of the cells fabricated and employed in this program. The cell, Figure 1, features a 2.54-cm-square Pyrex body with a drilled and polished, 0.95-cm-diameter, 12-cm-long center bore, and three 2-mm-diameter connecting ports for the sample tubes and microphone. The cell end faces were ground and polished. Two-mm ID sample tubulations were fused to the cell body. Originally, it had been proposed that the zinc selenide Brewster angle windows be attached to the cell body by either direct fusion techniques or induction bonding procedures utilizing interface frits (Pyroceram 89, etc.). Unfortunately, chemically-vapor-deposited zinc selenide is an extremely brittle material with a high thermal expansion coefficient ($8.5 \times 10^{-6}/°C$) compared to $3.25 \times 10^{-6}/°C$ for Pyrex 7740. No vendor we

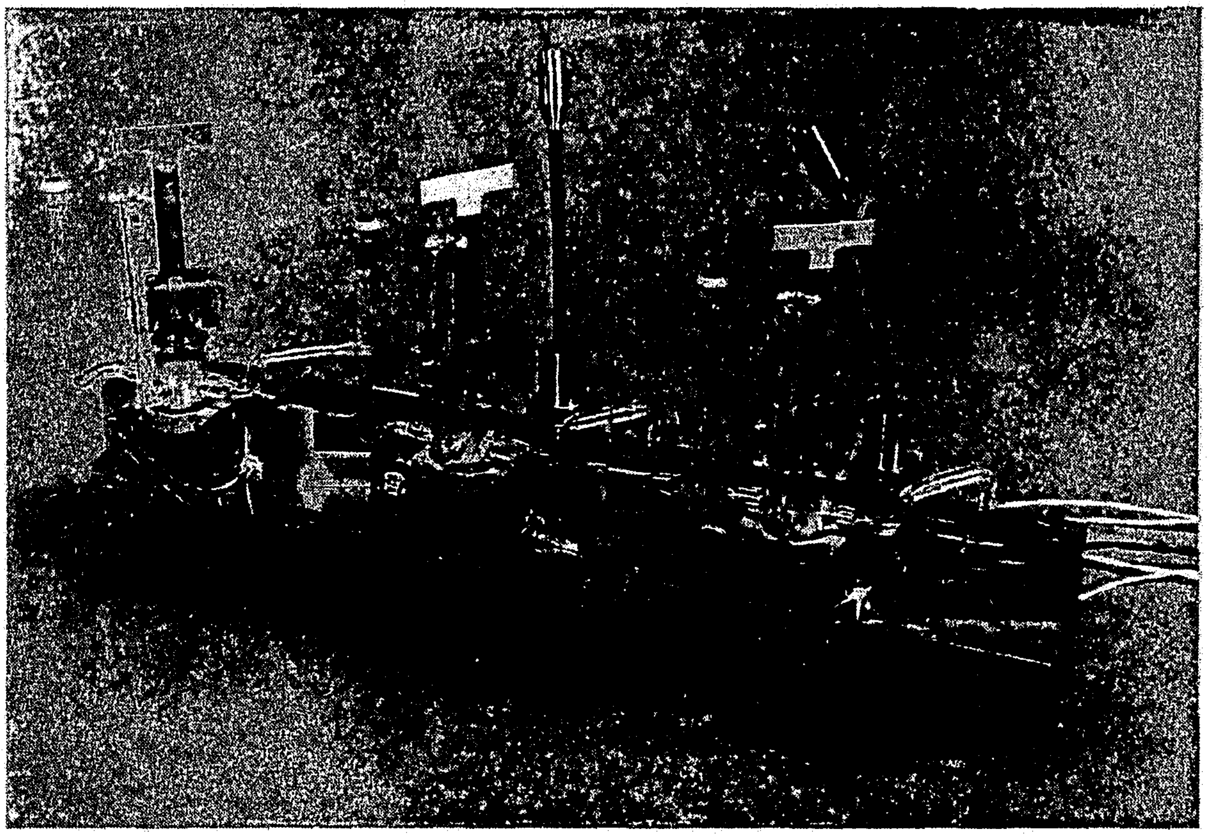

Figure 1. Thermostated Block with Three Laser Optoacoustic Cells

contacted had successfully provided a high vacuum fused seal of ZnSe to glass or Pyrex. In every instance, either a relatively flexible epoxy bonding material or a mechanical compression seal with O-rings was employed. Corning Glass Company discussed the possibility of employing a special melt-high lead glass which would seal with a common frit, but since this material would not be available in time, an epoxy seal was reluctantly employed. A formulation of 50% by weight EPON #828 (Shell Chemical Company) and 50% Versamid #125 (General Mills, Inc.) was employed to bond test ZnSe circular windows to Pyrex tubing cells. These bonds were subjected to three temperature cycles of several hours each between -15° and +100°C. Helium mass spectrometer leak testing of these cells revealed no detectable leakage at a sensitivity of 10^{-9} standard cc He/s. The same epoxy blend was then employed to mount the rectangular Brewster angle windows to the cell bodies after tubulations had been added and a thorough 4-step cleaning of the cell bodies had been performed.

Some other difficulties were encountered in the process of fusing the gas tubulations leading to the sample control valve to the cell body. The window-mounting surfaces became distorted, necessitating re-grinding and polishing. Also suitable integral valve design with ground, sliding valve parts was not devised although many hours of designer effort were expended. It proved to be impractical to design a slide valve that did not include either metal springs or bellows, or excessive volume that could not be flushed or effectively evacuated.

A four-way stopcock with Teflon-clad plug (Ace Glass, Inc., 8148-T23) was selected to be fused to the 2-mm ID Pyrex tubulations and provide for either sample flow through the cell or sample bypass with the cell ports blocked. The 2-mm ID sample tubulations between the cell body and the valve added approximately 19-cm total length of restricted porting at the cell inlet and outlet. With the additional 30-cm total tubulation length leading from the valve to the spherical joints outside the outer box, plus additional 4-mm ID Pyrex tubing connecting the cell to the vacuum system and sampling system, the efficiency of evacuation of the optoacoustic cells was somewhat impaired. Further discussion of sampling, purging, and vacuum bakeout characteristics is included later in this report.

The 1.25-cm-diameter Bruel and Kjaer No. 4165 condenser microphone was threaded into a stainless-steel housing which was bolted to the aluminum housing. A pressure and vacuum-tight seal concentric with the front of the microphone was provided by compression of the indium-coated stainless-steel O-ring to a controlled torque. An annular space within the microphone mounting assembly provided for venting of the back side of the microphone diaphragm.

Temperatures of up to 150°C were supposed to be employed for decontamination and vacuum bakeout of the cells. However, decontamination did not turn out to be as severe a problem as anticipated and it was possible to rely on constant 40°C operation for all measurements, followed by nitrogen purging for cell cleanup.

B. Sampling System Development

The sampling system, shown schematically in Figure 2, provides an all-Pyrex (with the exception of the Teflon-coated spherical joints and valve stems) system beyond the stainless-steel and Teflon tubing supply lines leading to the vapor generators. Ultra-high purity nitrogen is further purified by passage through a 3-foot-long section of coiled 0.63-cm OD stainless-steel, thin-wall tubing containing Molecular Sieve 5A (Linde). A manifold with three stainless-steel, bellows-sealed, shut-off valves each connected to a separate fine control needle valve provides for critical gas flow adjustments. Teflon tubing supply lines connect the needle valves to the various vapor generators, scrubbers, or water vapor generators which feed the Pyrex tee connected to a Pyrex mixing chamber. A scrubber tube or, alternatively, a straight Pyrex tube, can be inserted between the mixing chamber and the first optoacoustic cell. The cells are usually connected in series, although parallel operation is possible. An additional scrubber tube may be connected between the cells if desired. The mixing tee, mixing chamber, and Pyrex lines to the cells are heated.

The vapor generator used for EGDN and other low vapor pressure materials is a 40-mm ID Pyrex volume, 150 mm high, equipped with appropriate tubulations and containing Pyrex Raschig rings coated with the material under test. The inlet and outlet ports of the vapor generator are fused to tubulations of a four-way Teflon-clad stopcock to allow purge of nitrogen either through the

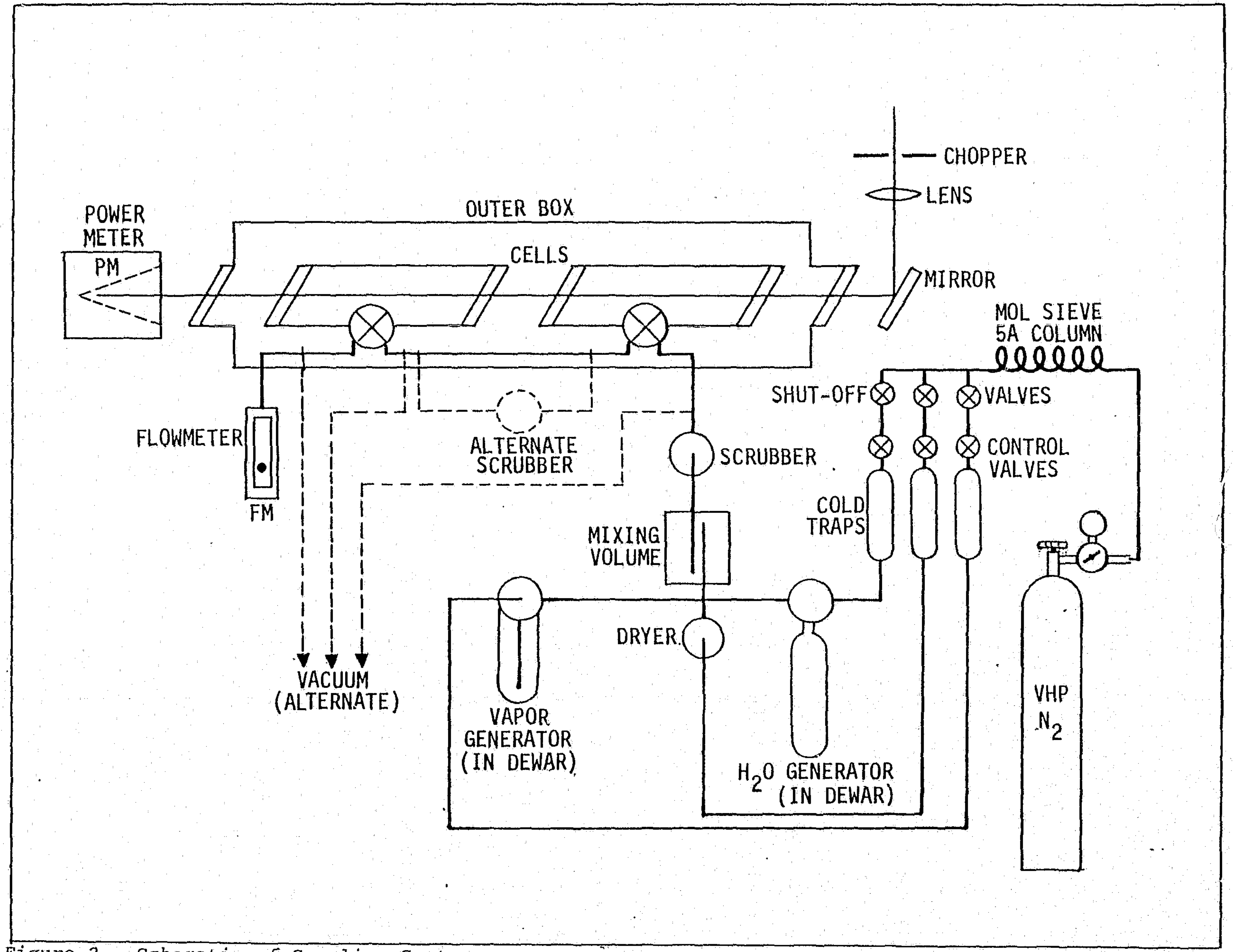

Figure 2. Schematic of Sampling System

vapor generator or bypassing it. The generator is immersed in a Dewar flask to permit operation at 0°C or at other temperatures, as appropriate to the test requirements. A Teflon-gasketed Pyrex cap is clamped to the generator housing.

Permeation tube generators are similar in design but of smaller diameter, to accommodate the typically 8-mm OD, 150-mm-long Teflon permeation tubes. An oil bath is used with the permeation tube generator, controlled at the desired temperature by a heater and proportional controller.

The permeation tube generators may also be conveniently used as scrubbers or driers by filling them with the desired scrubbing material. The water vapor generator is a No. 7534-10 Midget Bubbler (Ace Glass, Inc.).

By choice of the flowmeter inserted in the exit line from the appropriate optoacoustic cell, flow dilutions of up to 1/100 can be performed. In most of the tests on interferent gases and vapors, both 1/10 and 1/100 dilutions were employed. In measurements of EGDN and water vapor, the EGDN vapor generator was maintained at 0°C in an ice bath. Its vapor pressure at 0°C results in an equilibrium concentration of about 10 ppm at atmospheric pressure. The EGDN vapor was typically diluted 1/10 by mixing with two nitrogen streams--one which was dry, and one which was saturated with water vapor at a controlled temperature.

The sample flow system could be readily disconnected from the optoacoustic cells at the spherical joints and connection made from the optoacoustic cells to a vacuum system comprised of a sorption pump with a stainless-steel manifold and valving.

C. System Electronics

The CO_2 laser at the Jet Propulsion Laboratory used in these measurements is based on the design of Freed.* It is equipped with a Littrow grating frequency selector and PZT transducer for adjustment of cavity length. The beam emerging from the laser is vertically polarized; it is translated to horizontal polarization by reflection from a pair of 45-degree mirrors. A 50-mm-diameter barium fluoride lens of 72-cm focal length converges the laser beam to a minimum diameter of about 3 mm at the center of the optical path through the optoacoustic cell enclosure. A PAR Model 191 Variable Speed Chopper operating at 13.1 Hz was located between the laser and the BaF_2 lens. A Scientech 301 Power Meter Detector located at the exit of the optoacoustic cell enclosure monitored laser output power.

Signals from the B and K Model 4165 condenser microphones were amplified by General Radio Model 1560-P42 preamplifiers connected to the microphones through B and K adapters. The preamplifiers were rigidly mounted on the top surface of the outer optoacoustic cell housing. The optoacoustic cells and microphones were effectively isolated from acoustic disturbances by the double oven construction with 2.5-cm-thick polyurethane foam insulation between the inner and outer housing. The preamplified microphone signals were processed by PAR 124 lock-in amplifiers synchronized with the variable speed chopper. Most data were obtained at a controlled cell temperature of 37°C.

The laser power meter output was recorded on one channel of a Hewlett-Packard two-channel strip chart recorder. The second channel was used for recording either one of two optoacoustic cell signals, or the difference signal when both microphone outputs were connected to the PAR 116 differential

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*Freed, C., *IEEE J. Quantum Electron.* QE-4,404 (1968).

preamplifier. When one optoacoustic cell output was recorded directly, the output of the second cell was usually recorded manually on the strip chart after reading its value from a digital voltmeter monitoring the second PAR 124.

CHAPTER III. TESTING

A. System Calibration

Calibration of optoacoustic cell responsivity was based on the published* value for the absorption coefficient of ethylene at the P14 line of the 10.4-μm band of a $C^{12}O_2^{16}$ laser. This value is 29.1 $(\text{atm-cm})^{-1}$, at a pressure of 760 torr and a temperature of 300 K. Our measurements were made at atmospheric pressure in the laboratory, typically 725 torr. The same absorption coefficient applies at this pressure according to M. Shumate.**

The optoacoustic cells were typically purged with the gas mixture to be measured, at a flow rate of 20 to 50-cm^3 per minute for 30 minutes or more before making vapor absorption measurements.

A commercially prepared and certified mixture containing 12.3 ppmV C_2H_4 in CO_2-free, dry air was used as the calibration gas mixture. Responsivity can be assumed to be independent of wavelength over the 9 to 11 μm range because the ZnSe windows have extremely low bulk absorption throughout this wavelength region.

The rms system noise level was measured at less than 1 μV with the laser light blocked and the lock-in amplifier on an expanded scale.

B. System Performance Results

The responsivities of the six cells constructed were equal to within 5% with an average value of 201 V/watt-cm^{-1}. Each of these cells had an rms system noise level slightly less than 1 microvolt per root hertz and this noise was independent of laser power level. The system limit of detection expressed as the size of the absorption coefficient equal to the system rms

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* Patty, R.R., *et al, Appl. Opt. 13,* 2850 (1974).
**Unpublished data--private communication.

noise level was therefore about 4×10^{-9}-cm^{-1} at a one-watt laser power level. This corresponds to roughly 100 parts per trillion of ethylene. This system noise level is believed to be no more than one order of magnitude above the theoretical limit which arises from the brownian motion of the microphone diaphragm (see Bibliography reference 36). Because of the acoustic isolation, no microphonic pickup of room noise was detectable at the 13-hertz system operating frequency even with radios and equipment operating.

When the gas valves on the cell were opened, the increase in volume caused a drop in responsivity of a factor of five. With gas flowing through the cell at rates of 10-100 cc/minute, the acoustic flow noise was approximately 10 microvolts. This loss of responsivity and increase in noise results in a fifty-fold decrease of signal-to-noise ratio; therefore, all measurements were taken in a closed cell condition.

C. Vapor Absorption Measurements

Most of the optoacoustic cell response data of this report have been left in the measured units of mV signal per watt of average laser power because, in most cases, the concentrations of actual absorbing gases within the cells is inaccurately known with the exception of ethylene and certain other materials studied.

The data in Table I give the measured mV/W values and the absorption coefficients for ethylene, calculated from the measurements, for eight laser wavelengths and three decades of ethylene concentration. Differential cell outputs were recorded with the reference optoacoustic cell filled with pure, dry nitrogen.

It is evident that at the most intense overlap of a $C^{12}O_2^{16}$ laser line with an absorption line of ethylene, the P14 (10.4-μm) transition, the respose of the optoacoustic cell is reasonably linear with ethylene concentration.

Table I. Ethylene Absorption Measurements

Laser Line	12.3 ppm C_2H_4 mV/W	12.3 ppm C_2H_4 $cm^{-1}(x10^{-5})$	1.2 ppm C_2H_4 mV/W	1.2 ppm C_2H_4 $cm^{-1}(x10^{-6})$	0.12 ppm C_2H_4 mV/W	0.12 ppm C_2H_4 $cm^{-1}(x10^{-7})$
P22, 10.4 μm	3.31	2.08	0.41	2.6	.08	5.0
P18	6.55	4.11	.70	4.4	.11	6.9
P14	57.0	35.8	5.73	36.0	.62	39.0
R12	3.26	2.05	.47	3.0	.11	6.9
R18	1.26	0.79	.27	1.7	.10	6.3
R24	8.15	5.12	1.01	6.35	.15	9.4
P30, 9.4 μm	2.33	1.46	.19	1.2	.05	3.1
P22	1.57	0.99	.16	1.0	.12	7.5

It appears that most of the inaccuracy experienced at low sample concentration or at weakly absorbed lines is due to residual absorption differences between the two cells, which were not cancelled out.

In attempting to determine the linearity of response of the system to EGDN, extremely long equilibration times were experienced, with evidence of absorption or adsorption saturation at EGDN concentrations of over 1 ppm. With the EGDN vapor generator at room temperature (25.8°C), the equilibrium vapor pressure is approximately 95 ppm.* Vapor pressure data from this report are presented in Table II with an additional value for 0°C extrapolated from a semi-logarithmic plot of the referenced data.

Table II. Vapor Pressure of EGDN

Temperature °C	mmHg	ppm at 760 mmHg Ambient
35	0.170	224
25	0.072	95
15	0.030	39
0	0.008	10

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*American Industrial Hygiene Association, Hygienic Guide Series, Nov-Dec (1966)

Purging an optoacoustic cell for a period of one hour or more with 95 ppm EGDN was required before reasonably stable output signals could be measured. On dilution of the EGDN with dry nitrogen in the ratio 1:99, purge times of several hours were necessary to produce a drift-free signal state. The results are tabulated in Table III for measurements at eleven laser wavelengths.

Table III. Observed Optoacoustic Cell Signals for 95 and 1 ppm EGDN in N_2

Laser Line	N_2 Saturated with EGDN at 25.8°C (Approx 95 ppm)	1/100 Dilution Attempt (Approx 1 ppm)
P30 10.4 μm	26	4.5
P26	20.5	2.3
P14	16.5	0.6
R18 10.4 μm	14.5	1.1
R28	16	1.1
P32 9.4 μm	60	19
P22	95	29
P12	101	23
R18 9.4 μm	38.5	1.4
20	37	1.5
22	35	1.5
Repeat P22 9.4 μm after 10 minutes	79	33

As evidenced from repeated signal measurements or continuous monitoring at the P22 9.4-μm line, equilibrium was never attained with EGDN during this series of tests. In a later series the EGDN was always maintained at 0°C in an ice-water bath, 1/10 dilution nitrogen gas flow was continuously applied, and the mixing chamber, sample lines, and cells were maintained at 40°C. In these measurements, signal levels repeatable to within ±5% were achieved.

Other interferent materials studied during response linearity testing included cyclohexanone, toluene, p-xylene, and mesitylene. Qualitative line-by-line measurements were performed on unknown concentrations of formaldehyde and hexafluorobenzene. Also examined at the strongest CO_2 laser lines was 1000 ppm carbon dioxide in nitrogen. The measured optoacoustic spectra of these substances is included in the appendix. Prior to the measurement of the laser optoacoustic spectrum of each substance, a conventional infrared spectrum of the vapor was obtained using a commercial Beckman infrared spectrophotometer with 20-meter path length cell. These data were used to select the laser lines for the laser optoacoustic measurements. Lines were chosen to avoid strong water absorptions and yet expose the absorption maxima and minima in the spectral region accessible with the laser. The resulting laser optoacoustic spectra, while obtained at much lower vapor concentrations, agree, within experimental repeatability, with the conventional spectra. There are no significant differences with the other published data on the specific absorption coefficients.

As in the case of EGDN, linearity of response to relatively high concentrations (several hundred ppm) of toluene, p-xylene, mesitylene, and cyclohexanone was poor, as a consequence of long-term adsorption effects which limited the ability to achieve strong gas dilutions. Qualitative agreement with conventionally measured absorption spectra of these compounds was excellent.

D. Water Vapor/EGDN Interference Testing

It was recognized early in the testing program that the threshold of detection of the laser optoacoustic technique for detection of EGDN was not the limiting factor in devising a system to operate in the ambient environment. Rather, interferences, particularly from the continuum background absorption of water vapor, would seriously impair the detection capability for EGDN. Consequently, several weeks of the testing program were devoted exclusively to studying water vapor interference and in attempting to selectively scrub either EGDN or water from the sample blends.

In general, before any meaningful data on EGDN could be obtained, it was essential to purge the optoacoustic cells through the sampling system with pure, dry nitrogen. A freshly baked-out molecular sieve 5A column was employed in series with the UHP nitrogen supply to the manifold. Figure 3 illustrates typical contaminant problems--the P branch of the 9.4-μm band is particularly sensitive to trace contaminants of many classes of organic compounds. All the aromatic hydrocarbons, as well as alcohols, aldehydes, esters, ketones, chlorinated hydrocarbons, fluorochlorinated hydrocarbons--in fact, almost all organic materials--have strong absorption bands in this spectral region. In contrast, the 10.4-μm region is relatively free from interfering absorption. Unfortunately, the most useful lines for sensitive detection of EGDN, at which this material absorbs most strongly, are the $C^{12}O_2^{16}$ laser lines in the P12 through P22 region of the 9.4-μm band. An EGDN absorption band of about four-fold increased strength is centered at 12.0 μm and can be used for improved detectivity with the C^{14} isotope CO_2 laser, as will be described later in this section.

In Figure 4, data obtained in measurement of water vapor in nitrogen are compared with published data for water vapor in air (see Bibliography reference 40). Close agreement is evident, except that our measured water vapor response apparently includes contributions from residual absorptions in the P branch of the 9.4-μm band.

Figure 5 illustrates the measured response of a 50-50 blend of N_2/EGDN at 0°C and N_2/H_2O at 11°C, estimated to result in concentrations of 5 ppm EGDN, 5 torr H_2O in the optoacoustic cell. The lower curves show the results

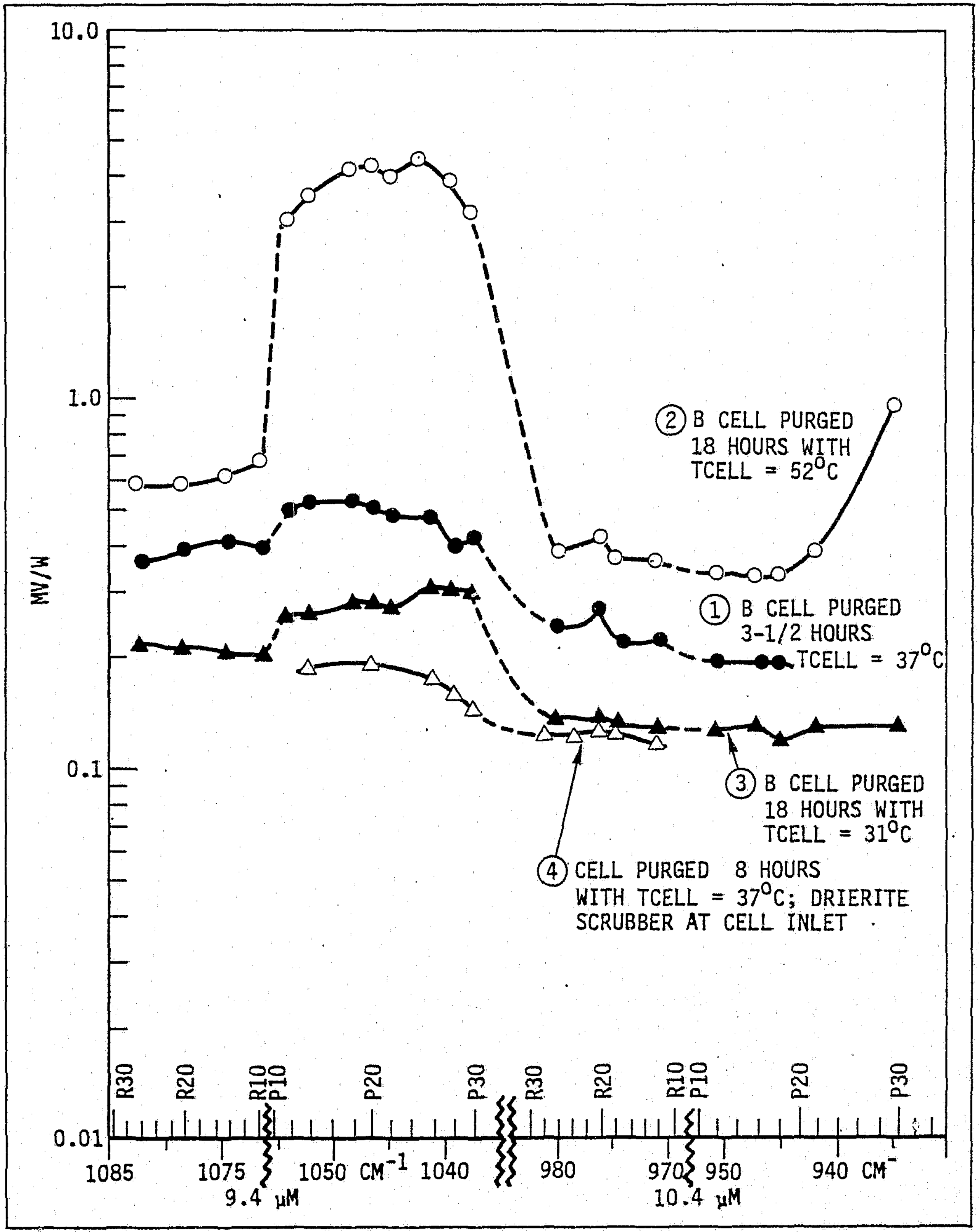


Figure 3. Background Absorption Under Various Purge Conditions

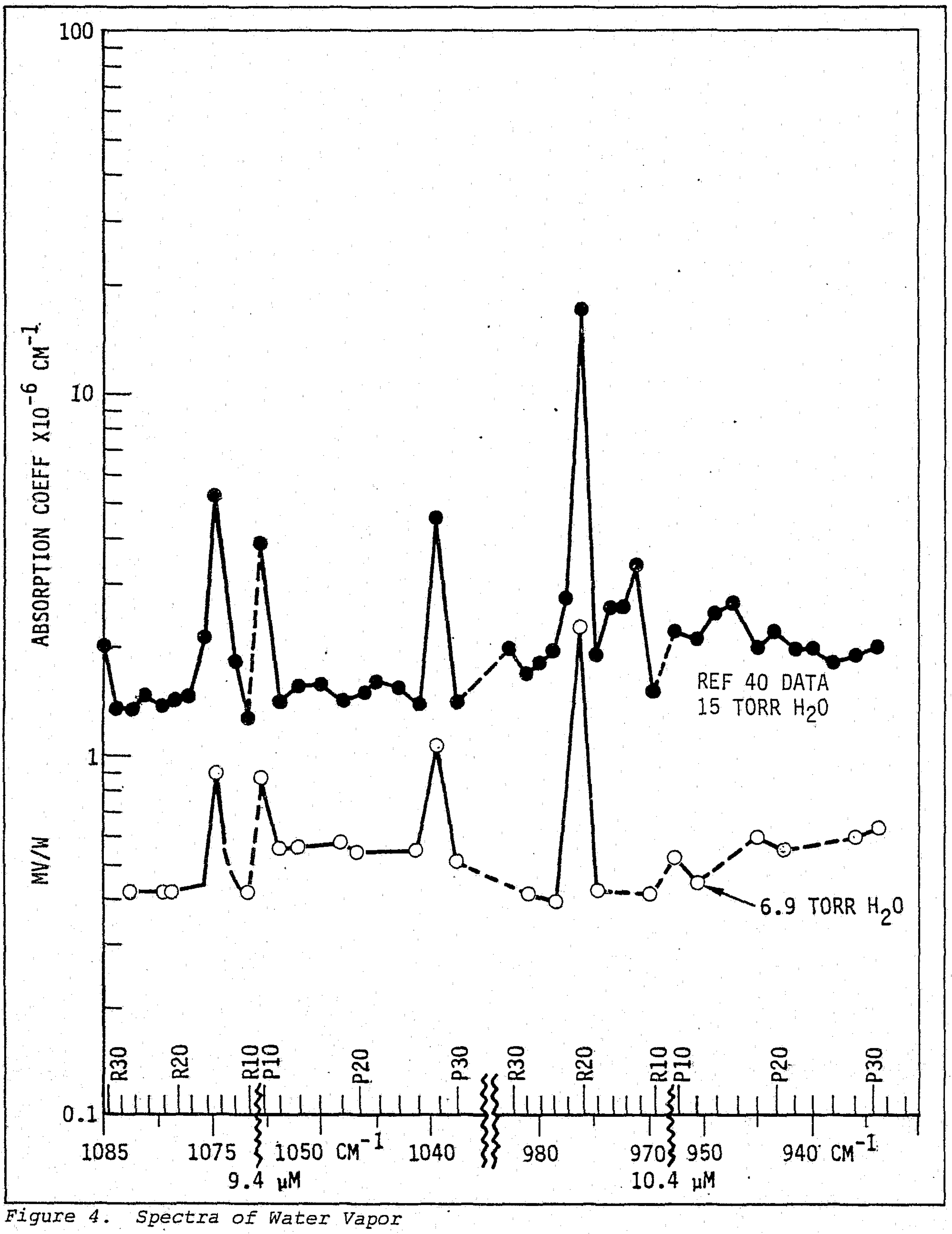


Figure 4. Spectra of Water Vapor

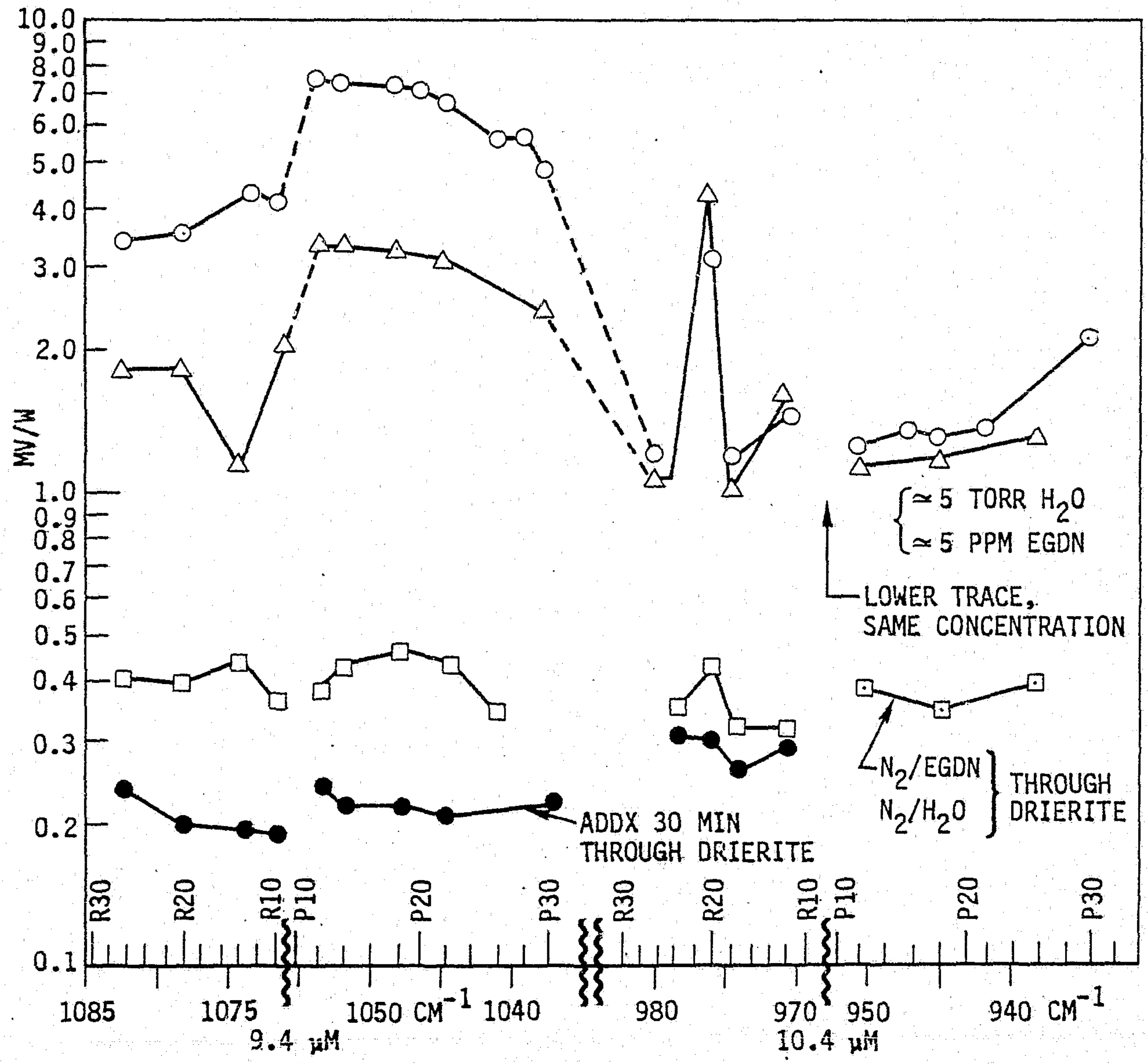


Figure 5. Drierite Scrub of EGDN and H_2O

of two separate 30-minute purges of this blend through a Drierite scrubber before passage through the optoacoustic cell.

Figure 6 presents additional data for four levels of water vapor content and two EGDN vapor concentrations.

Figure 7 depicts a scrubber test in which anhydrous sodium sulfate was tried as a water vapor sorber. As can be readily seen from the data, EGDN is removed to the same or greater extent as water.

For many of the test runs on EGDN and water vapor, only the P branch of the 9.4-μm band and the R branch of the 10.4-μm band were examined, since the principal spectral differentiation occurs in these two areas. Figure 8 is a linear presentation of data for 5 ppm EGDN, and 1 ppm EGDN with three levels of water vapor.

By "baseline" calculation of the water vapor concentration at the R20, 10.4-μm line, it is possible to correct the signal values at all the other wavelengths for water vapor. To accomplish this, a series of calibration lines are plotted of signal (mV/W) versus pH_2O (torr) for each of the laser wavelengths, as shown in Figure 9. Once the water vapor is corrected for, assuming there are no other interferents absorbing in the 9.4-μm P branch, any line in the P12 to P22 series can be used to determine EGDN to levels as low as about 100 ppb.

In another series of measurements, the $C^{14}O_2{}^{16}$ laser was employed to measure background, water vapor, 1-ppm EGDN, and 1-ppm EGDN with two levels of water vapor. Data are presented graphically in Figure 10, and can be compared with data for the $C^{12}O_2{}^{16}$ laser in Figure 11. Since EGDN has a stronger absorption in the P branch of the $^{14}C^{16}O_2$ laser than in the R branch of the $^{12}C^{16}O_2$ laser, the ratio of EGDN signal to water vapor background is best for the longer wavelengths of the carbon 14 isotope laser.

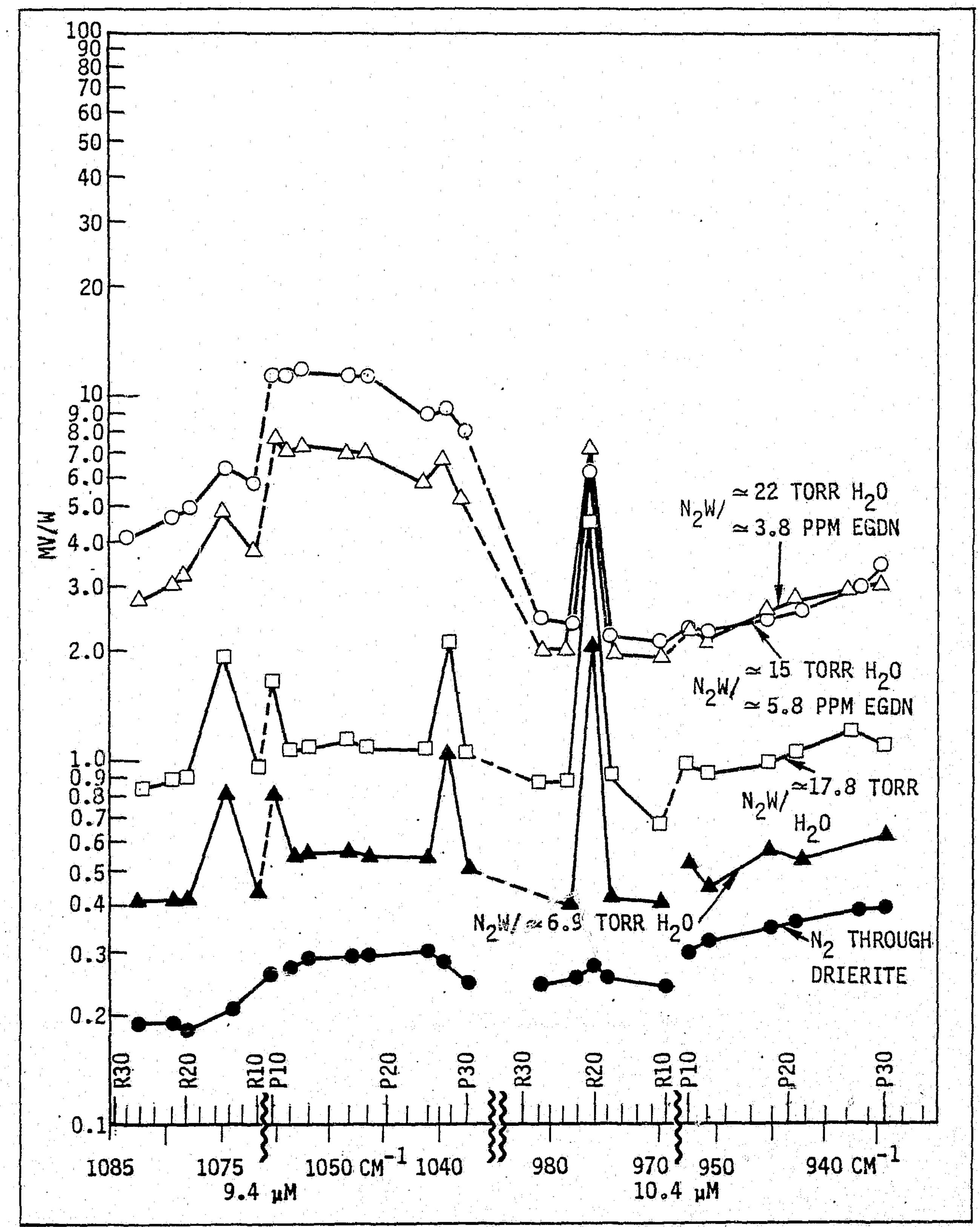


Figure 6. Drierite Scrub of EGDN and H_2O

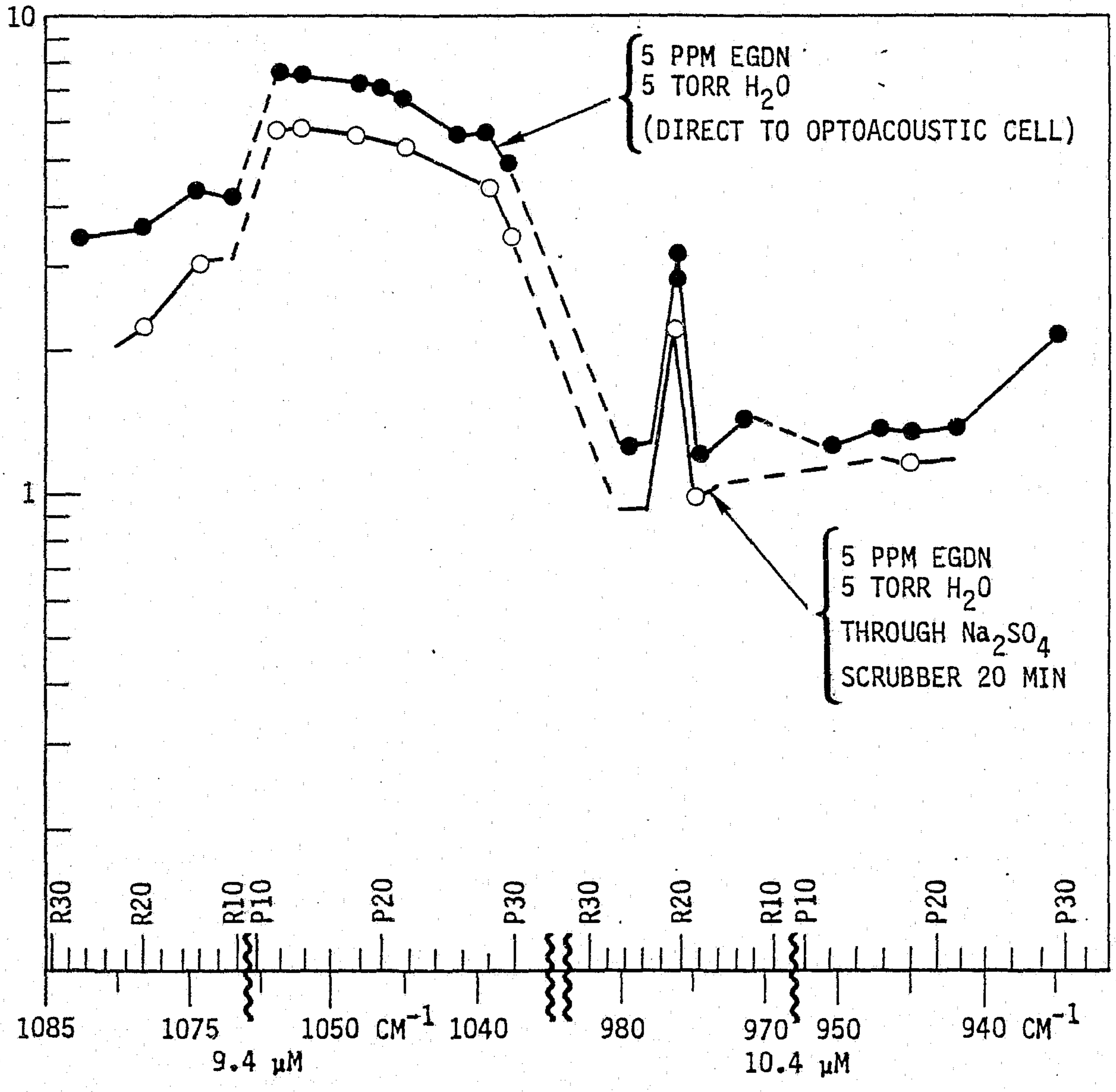


Figure 7. Sodium Sulfate Scrub of H_2O

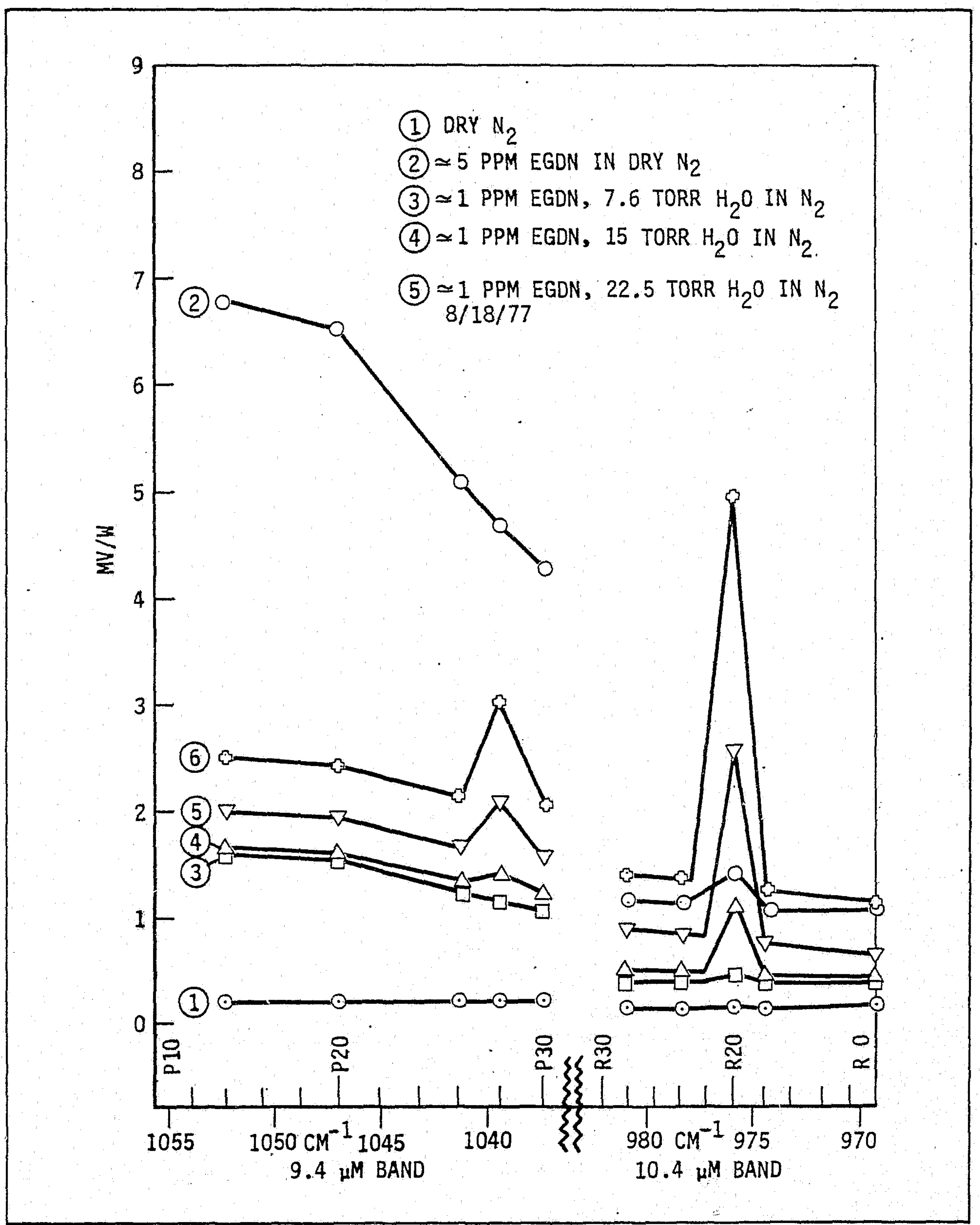


Figure 8. EGDN and Water Vapor

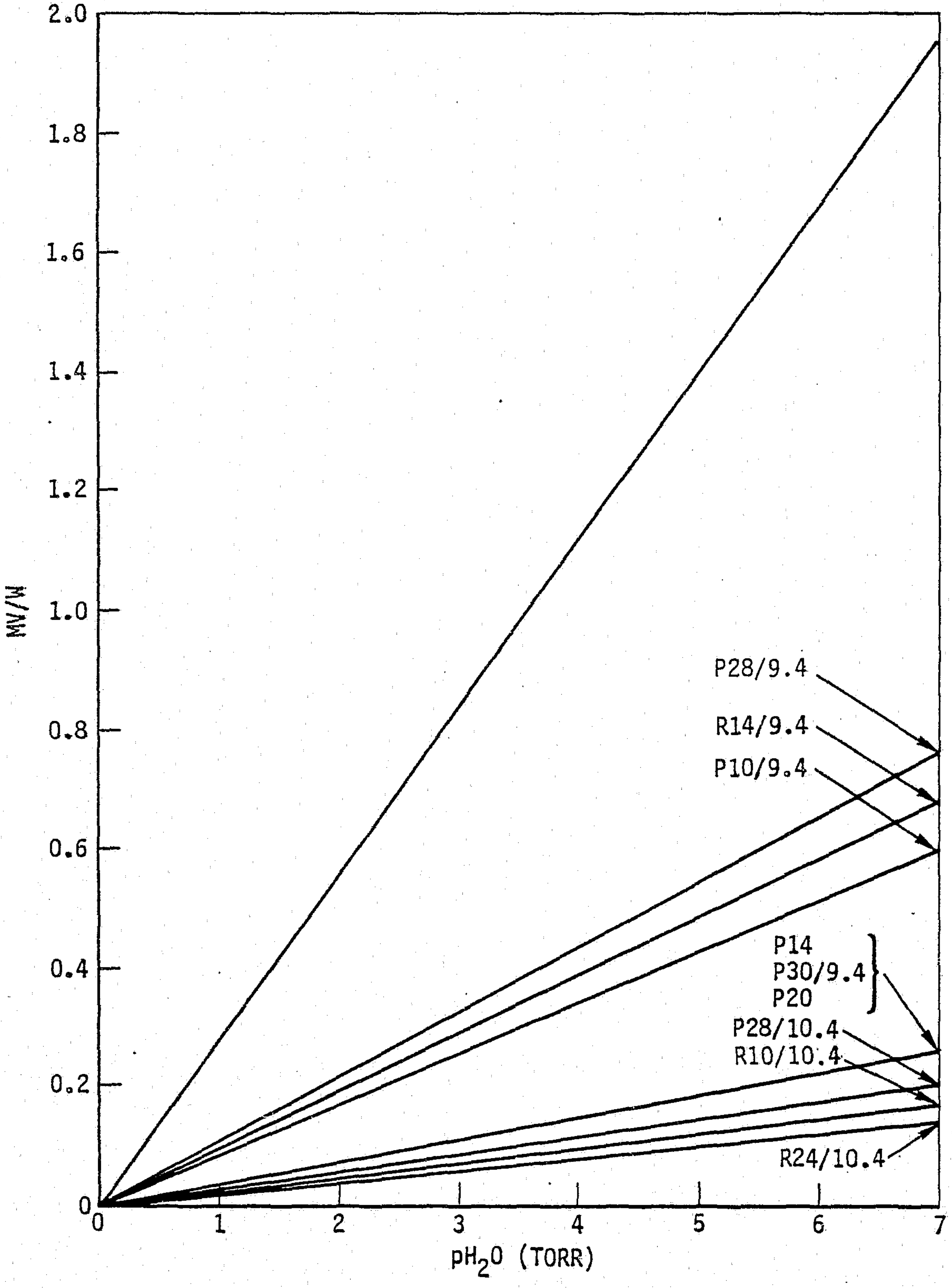


Figure 9. Spectral Response of Water Vapor (referenced against dry nitrogen)

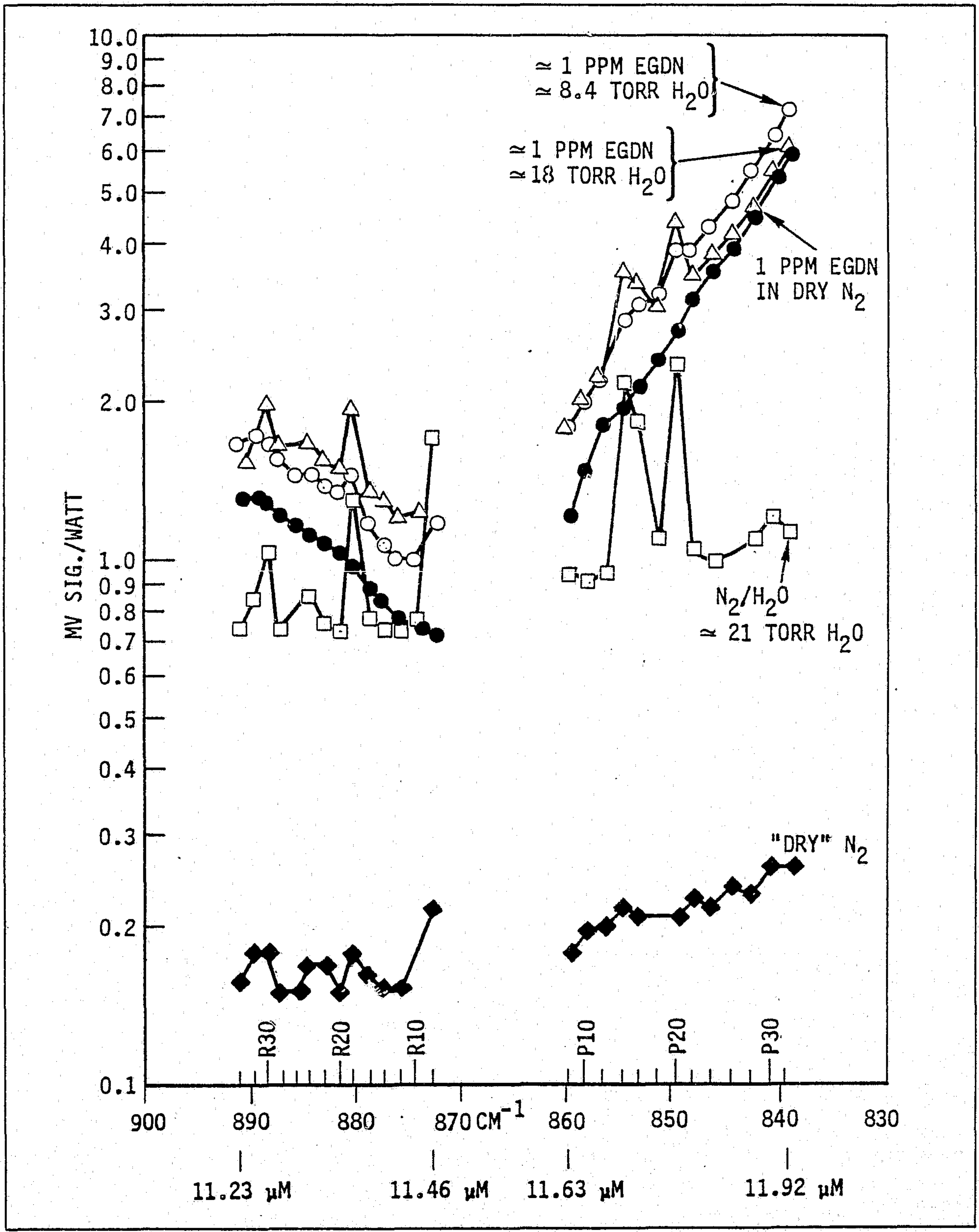


Figure 10. Measurement of EGDN and Water Vapor with $^{14}C^{16}O_2$ Laser

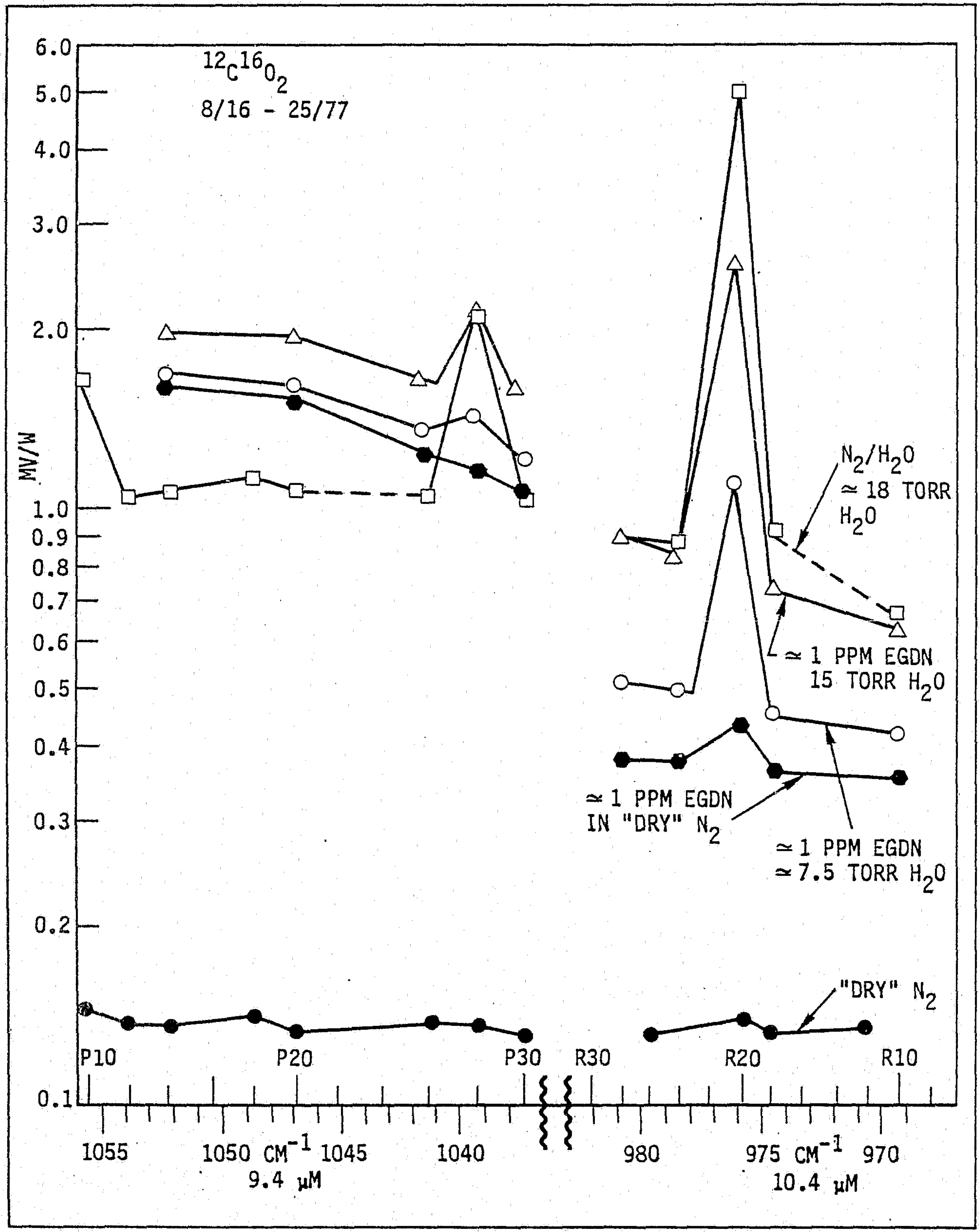


Figure 11. Measurements of EGDN and Water Vapor $^{12}C^{16}O_2$ Laser

On a mV/W basis, assuming that equal laser power is available at P32 (11.92 μm) as at P12 (9.4 μm), the $C^{14}O_2$ laser appears capable of a factor of 5.3/1.5 or 3.5X improvement in discrimination against water interference.

An additional advantage should arise from the smaller number of potentially interfering compounds at the longer wavelengths of the carbon 14 isotope laser. There is very little published data on absorption coefficients for organic compounds at the $^{14}C^{16}O_2$ wavelengths, so quantitative interference predictions could not be made. It was not within the scope of this program to make these interferent spectral measurements for substances other than the major interferent--water vapor.

From the previous work at Beckman with low concentrations of TNT vapor, it was predicted that metal film sorbers would prove effective for the "selective" absorption of EGDN vapor. A series of measurements was performed on platinum-palladium, and gold-coated alumina powder in sorbtion tubes. The platinum-coated alumina was the most effective for EGDN scrubbing. A differential measurement was attempted wherein the cells were connected in series with the metal film sorber between the cells. At low concentrations the improvement in EGDN detection limit, however, was not significant. The limit of sensitivity continued to be set by the differences in water vapor background between the cells.

The differential mode of operation consistently resulted in about a factor of 10 improvement in EGDN sensitivity, even though the differential was taken in a number of different ways. This same improvement, however, could also be achieved by the "baseline" correction technique applied to measurements made in a single cell.

Since the limiting error in all cases is due to the rate of change of background signal during the period of measurement, it would appear that an automation of the wavelength selection and measurement process would improve the situation. The normal time required to measure a laser optoacoustic spectrum was 20 minutes. If this could be decreased to approximately one minute, it would appear possible to reduce the effective sensitivity to EGDN by perhaps as much as one order of magnitude. Due to limitations of the equipment, no tests of this possibility could be performed.

E. Other Background Limitations

The major limitation, aside from water vapor interference, of the laser optoacoustic explosives detection scheme is the highly variable background signal. Figure 12 shows "Dry N_2" background levels observed in four separate runs, in comparison with water vapor at two concentrations. In Figure 13, data were obtained immediately after an overnight purge of the optoacoustic cell with N_2 through a Drierite column, and at four successive intervals after the cell valve was closed. The growth rate of contaminating absorption is shown graphically in Figure 14.

The curiousity of these measurements is that no backgrounds lower than 0.1 mV/watt were observed. This corresponds to a residual absorbance of approximately $5x10^{-7} cm^{-1}/W$ and is relatively flat with wavelength. The measurements of this background spectrum were all made at signal-to-noise ratios of better than 100. This was true after days of purging with ultra-high purity nitrogen which had been filtered through the mol sieve and cold trapped with LN_2. It was true also when the measurements were made after lengthy vacuum bakeouts and when lengthy purges with other ultra-high purity gases, including helium, argon, and synthetic air were tried. These cleaning operations were performed with and without the mol sieve and the cold trap, with clean new glassware, etc. Although there were some small differences noted between different gases, this residual absorption effect was not in

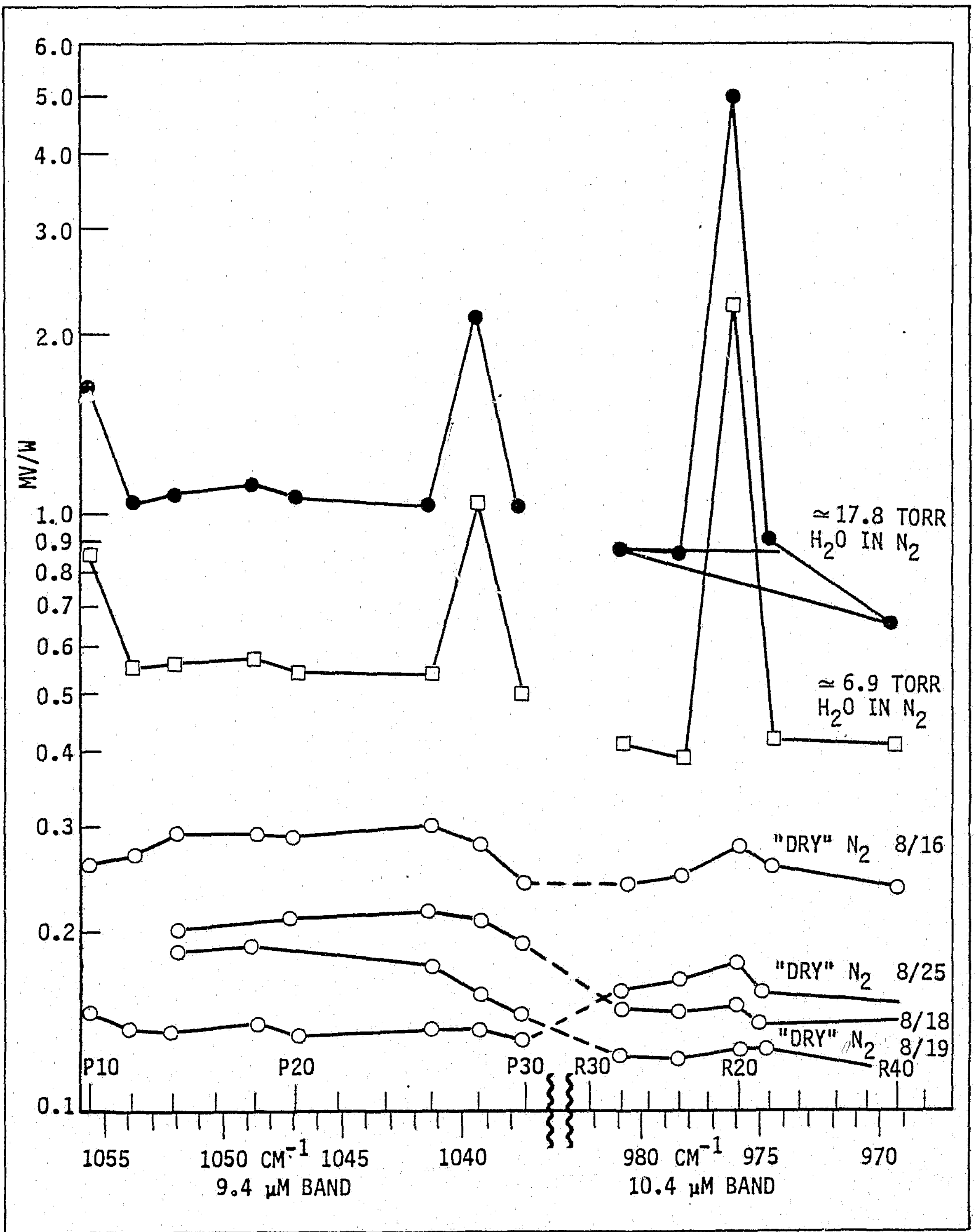


Figure 12. Comparison Spectra of "Dry" Nitrogen and Water Vapor

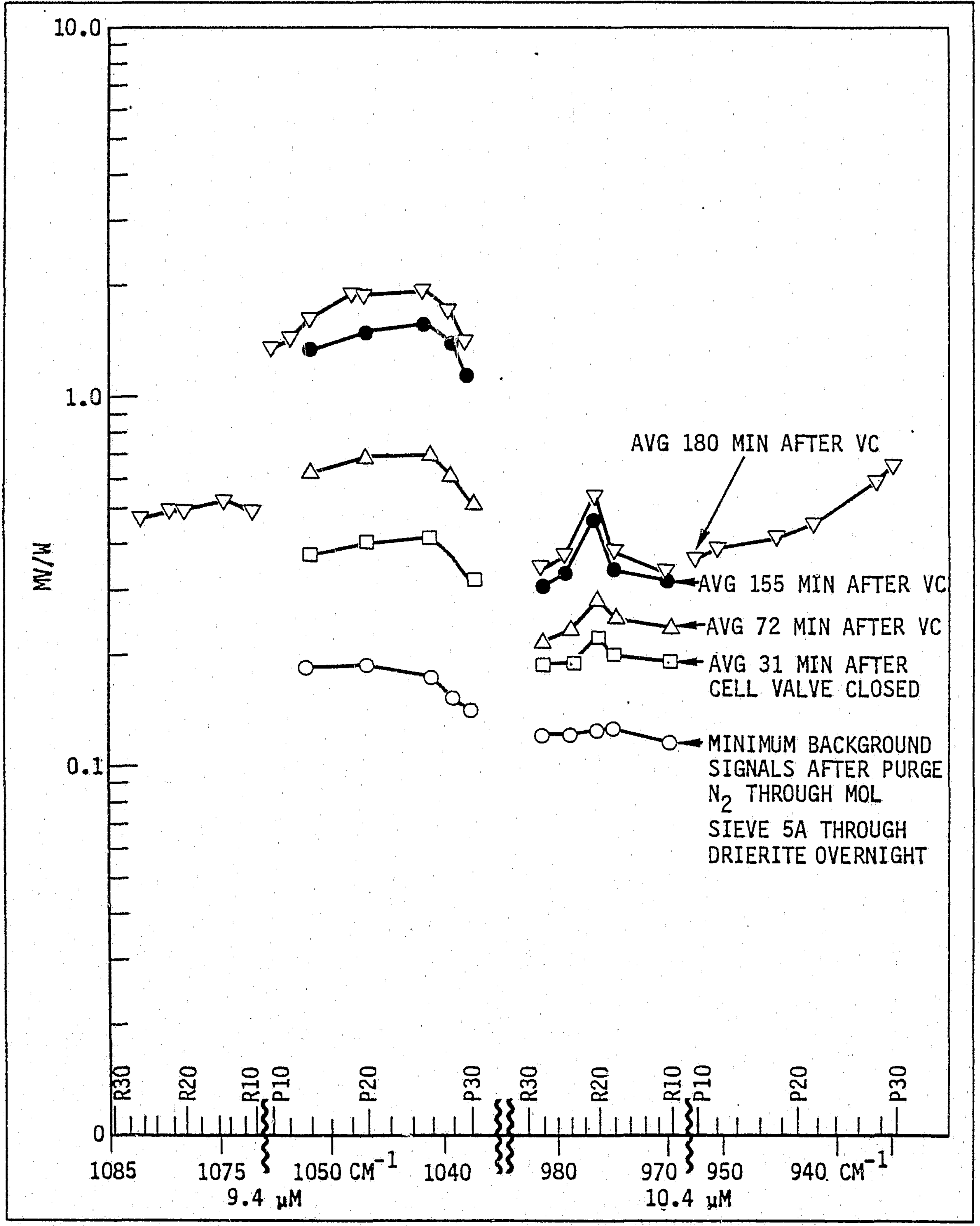


Figure 13. Cell Outgassing

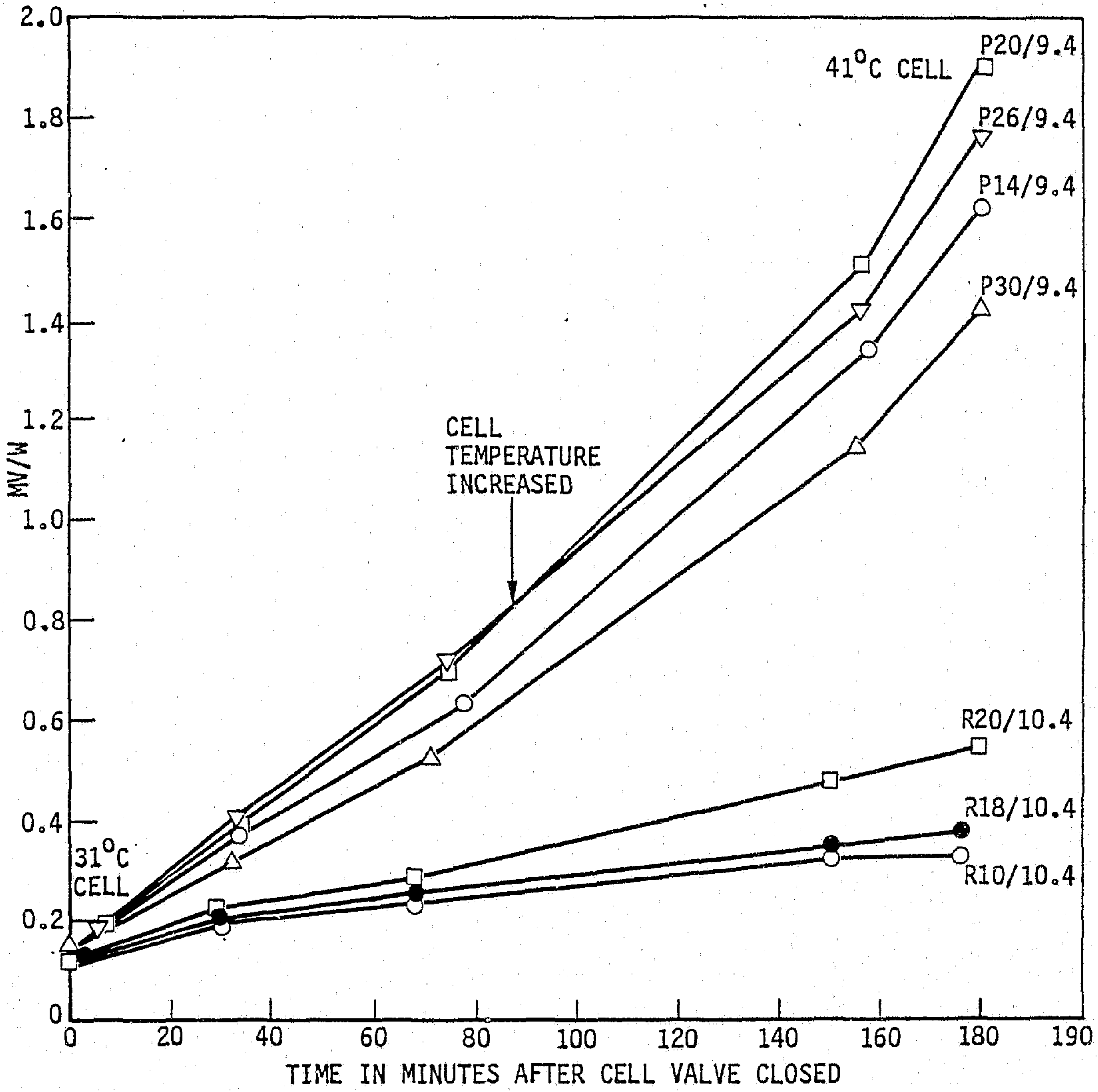


Figure 14. Outgassing of Optoacoustic Cell "A" After Long Purge With Dry, Purified N_2; Then Closing Valve

the primary direction of the program; thus, there was not enough data obtained to determine their statistical significance.

When the cell was closed off following one of these cleaning operations, the background would start to drift up. If allowed to proceed, an organic spectrum would develop in several hours. The lowest rate of drift observed was approximately $4 \times 10^{-9} \text{cm}^{-1}$/minute. A large sample of the window sealing epoxy was made, shredded, and the vapor dumped into the 20-meter gas cell on a conventional Beckman spectrophotometer. No characteristics of the epoxy matched the observed contaminant spectrum. The only other organic material in possible contact with the sample gas was the Teflon lining in the shut-off valve. Since the microphone was quartz-coated to prevent metal contact with the cell volume, there was only a small amount of stainless steel within the microphone assembly that could contact the sample gas. Nevertheless, these sources are evidently responsible for the trace organic vapor observed.

Since the system flow noise and decrease in responsivity as a consequence of the open valves resulted in a sensitivity loss sufficiently small to detect a change in the residual background, a flowing gas measurement on high purity nitrogen was tried, but with the same results. The lowest value achieved was $5 \times 10^{-7} \text{cm}^{-1}$.

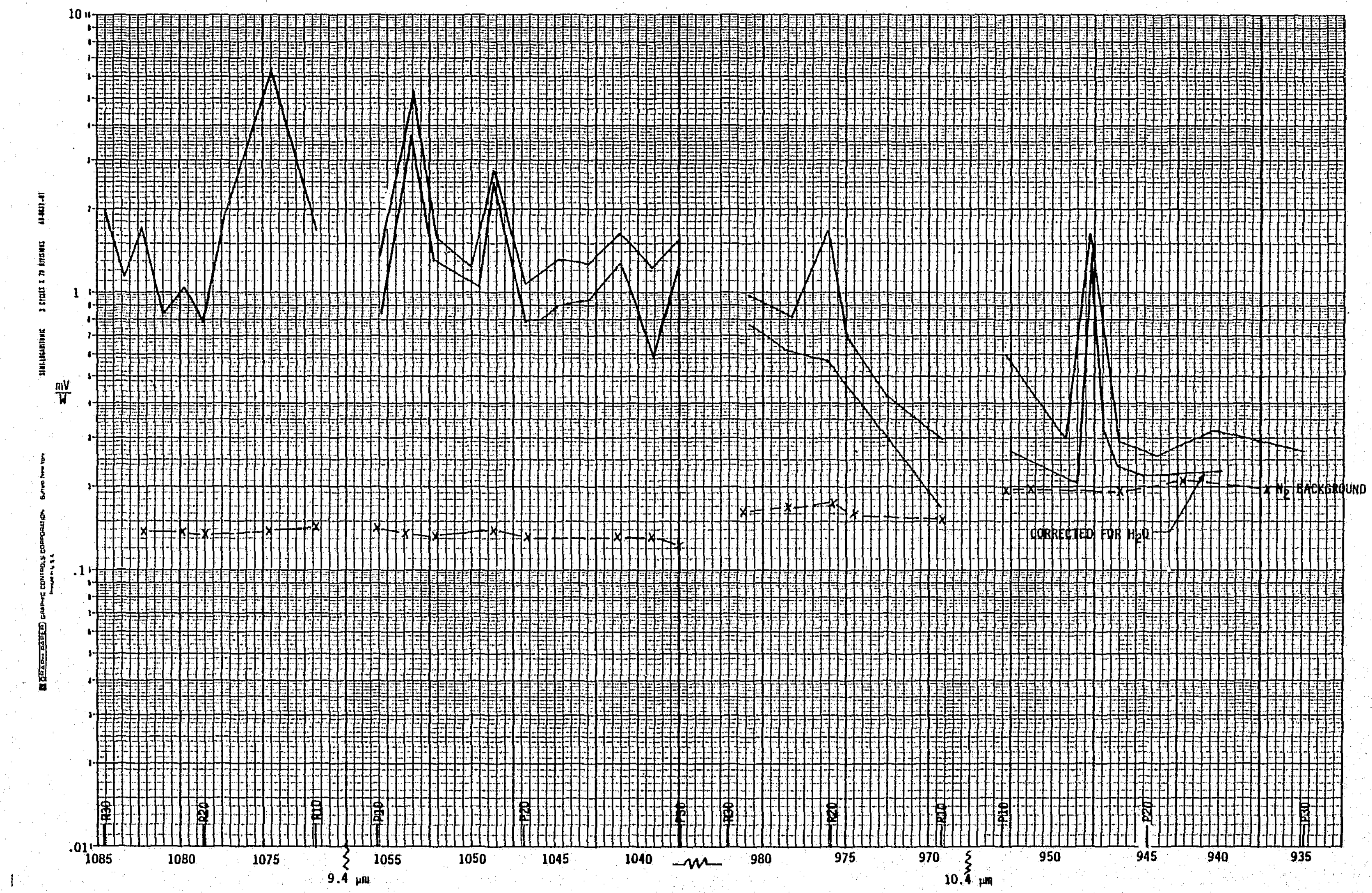
It would appear that the $5 \times 10^{-7} \text{cm}^{-1}$ residual background is a real property of the gas itself and not a contamination. A low-level absorption of this magnitude has been reported by most other laser optoacoustic investigators, but it is generally attributed to "window effects" or "unknown contamination." We contacted some of these investigators to determine whether there might be some unpublished recent work on the subject. Lloyd Kreuzer showed us some recent measurements comparing the response of laser optoacoustic cells of different length and data analysis which show that only a portion of his background limit could be attributed to the windows. A group in Israel under S. Shtrikman has a windowless cell operating in a longitudinally resonant (organ pipe) acoustic mode. Their most recent measurements also indicate the presence of a low-level background continuum of this same magnitude, but they are presently attributing it to an unknown contamination. We, however, are reluctant to attribute this residual absorptance to contamination because of the heroic attempts made to obtain high purity gas and to maintain system cleanliness. Some of the speculation on the cause of this absorption includes:

- A dimmer absorption associated with the gas molecules in the presence of the strong laser energy;
- A continuum associated with quasi-bound states arising from Van der Waals forces;
- Absorbance from microaerosols present;
- Laser light diffraction effects producing a signal from the cell walls.

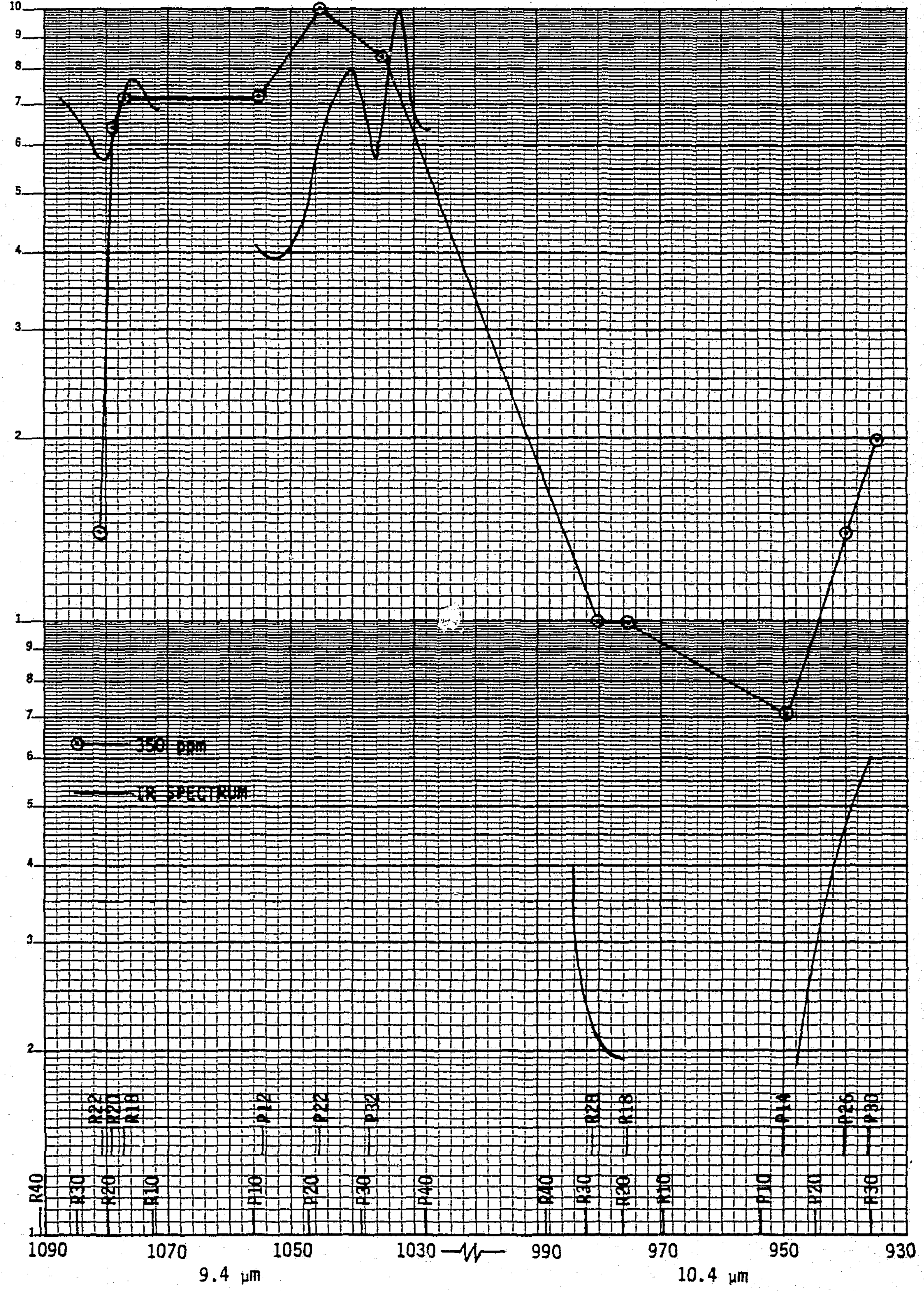
The first item above seems unlikely because the effect was also observed in monatomic gases; the last seems unlikely because of the wide variety of cell designs employed by the various investigators. Although the source of this anomalous absorption was scientifically fascinating, the water vapor interference was dominant; therefore, no additional research was performed on low-level dry gases.

Some engineering improvements are possible with this design. The use of a sophisticated carrier microphone preamplifier would reduce noise by an estimated factor of at least five. Improvements in the geometry to reduce the unilluminated volume to improve the responsivity and an increase in laser power to increase the signal would result in a net improvement of signal-to-noise ratio by at least one order of magnitude but probably no more than two orders of magnitude. The limit of detection based on signal-to-noise ratio considerations would then be between 1 and 10 parts per trillion of ethylene (or 10 to 100 parts per trillion of EGDN or absorption coefficients in the $10^{-11}cm^{-1}$ decade), if it were not for the water vapor and 'dry gas' absorptions.

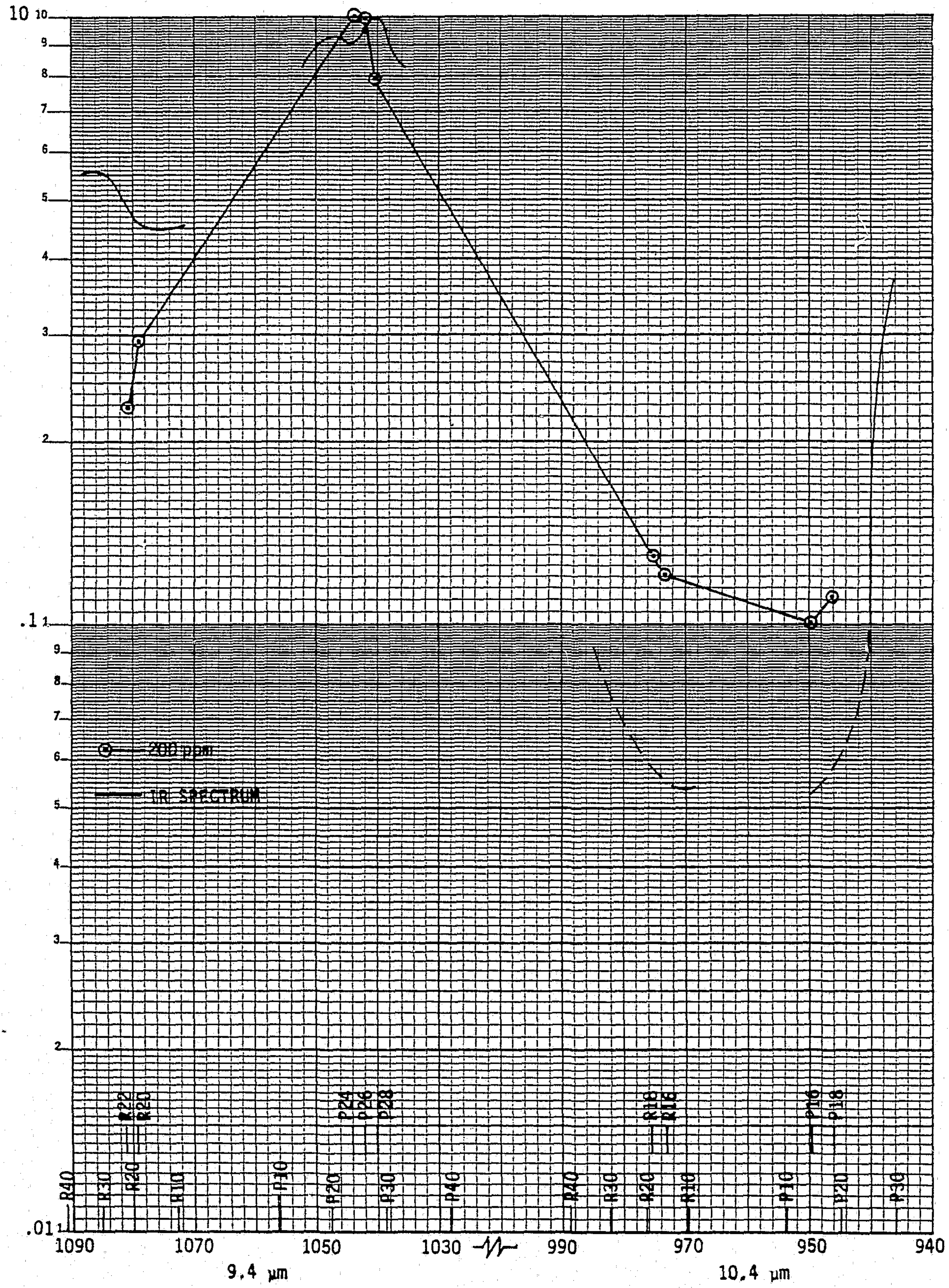
APPENDIX



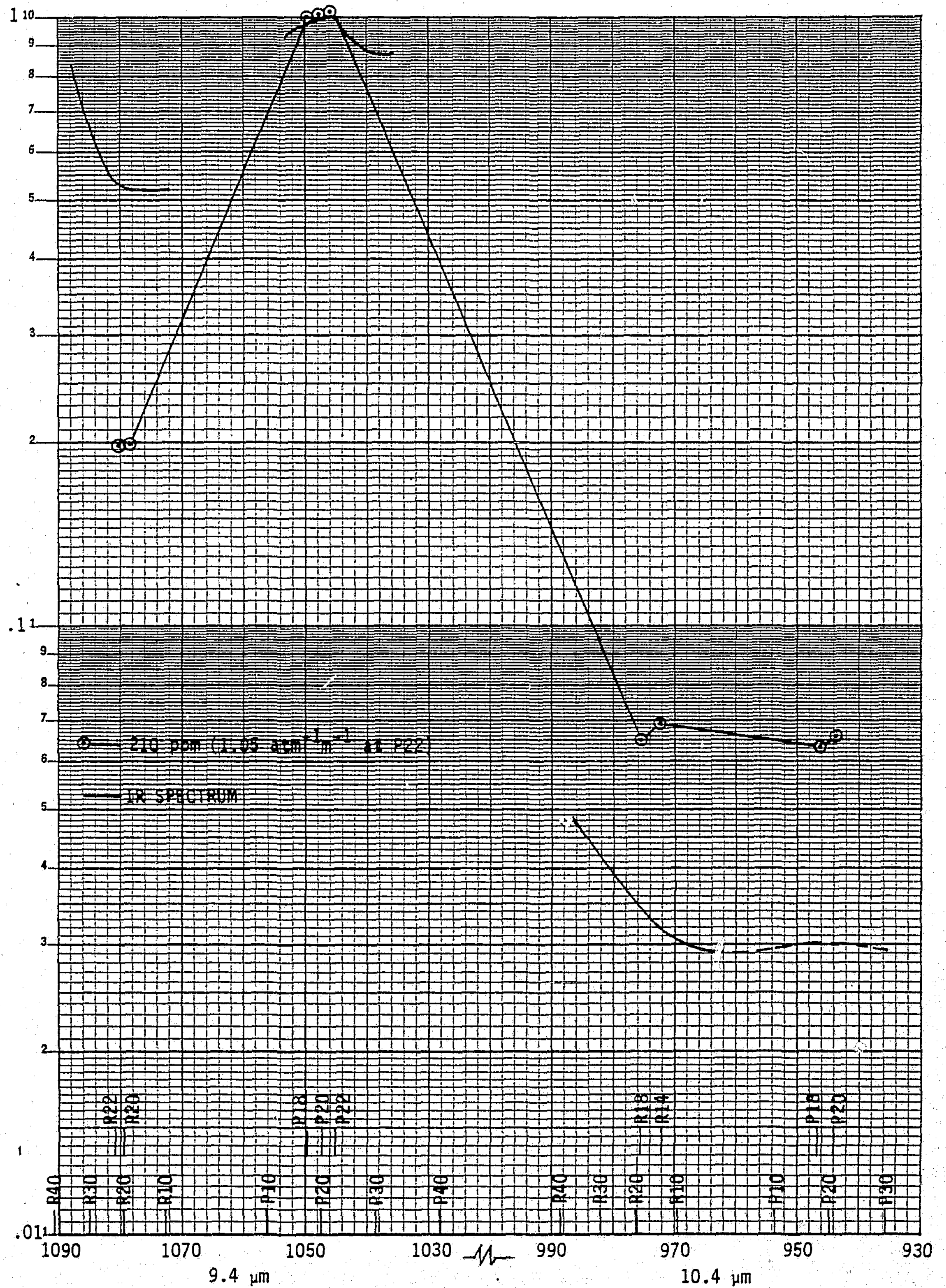
Spectra of HCHO Vapor



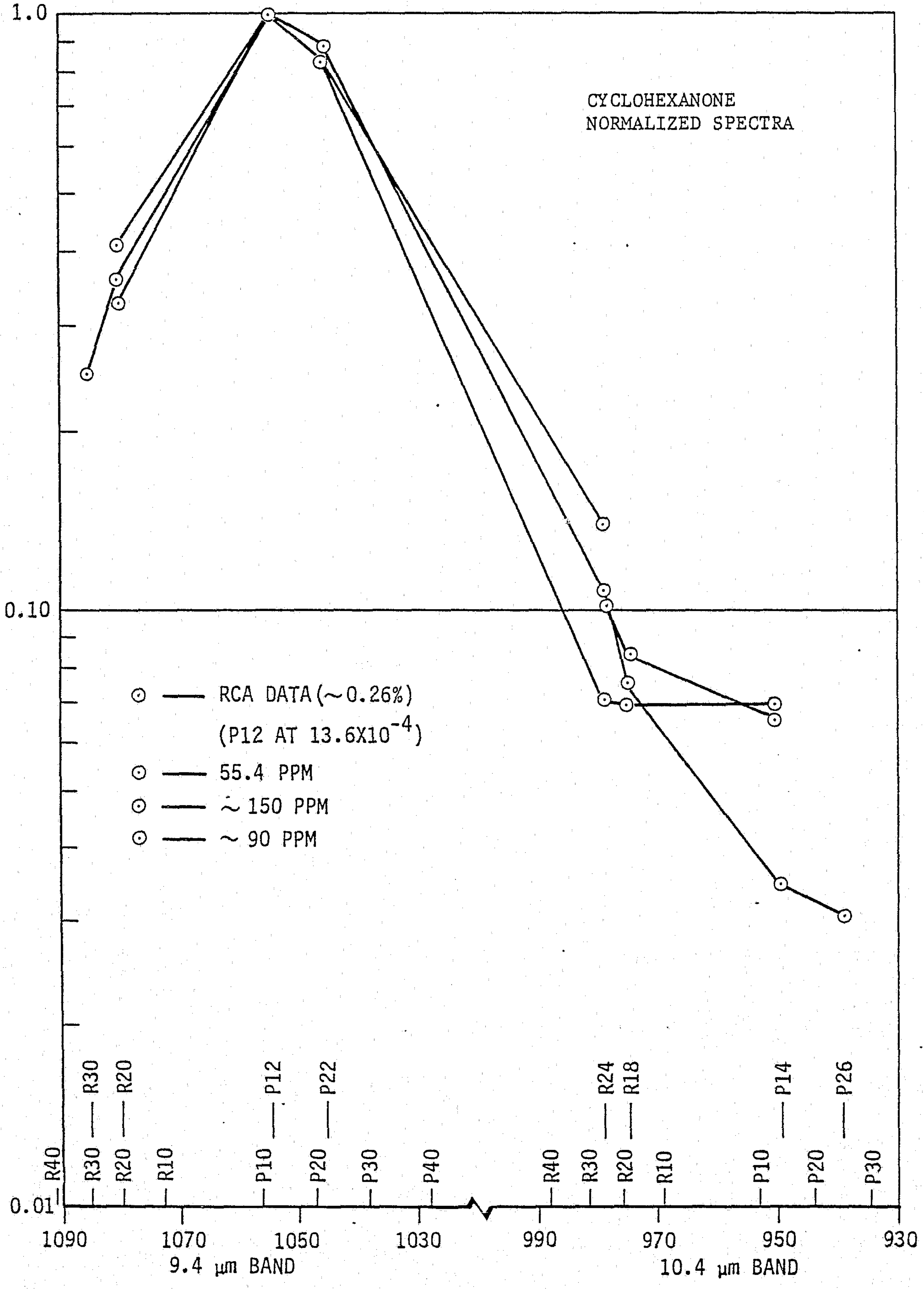
Normalized Absorbance of Toluene

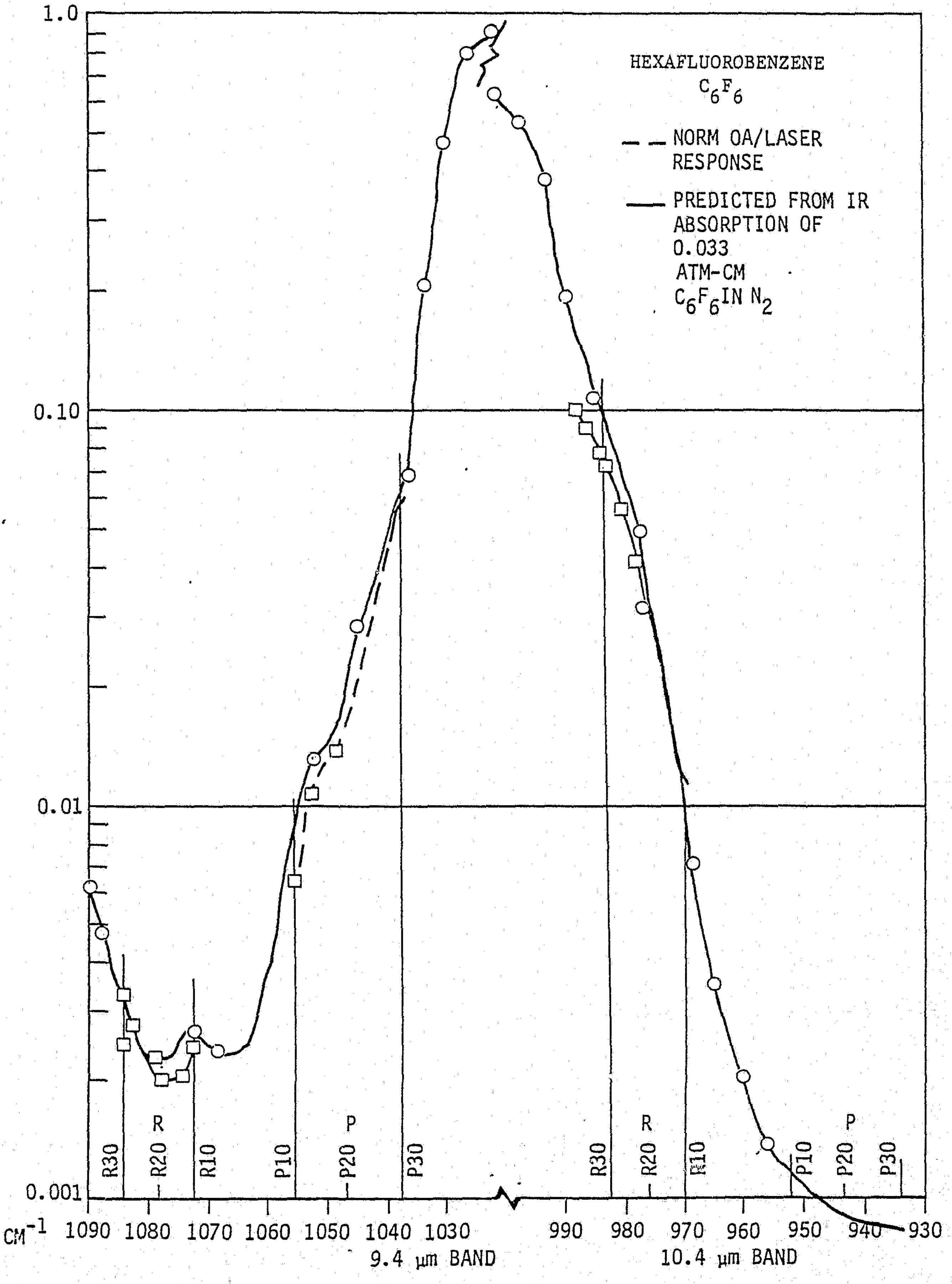


Normalized Absorbance of 1,3,5 Trimethylbenzene (Mesitylene)



Normalized Absorbance of p-xylene


CYCLOHEXANONE
NORMALIZED SPECTRA
RCA DATA (~0.26%)
(P12 AT 13.6X10^{-4})
55.4 PPM
~ 150 PPM
~ 90 PPM
1.0
0.10
0.01
R30
R20
P12
P22
R24
R18
P14
P26
R40
R30
R20
R10
P10
P20
P30
P40
R40
R30
R20
R10
P10
P20
P30
1090
1070
1050
1030
990
970
950
930
9.4 μm BAND
10.4 μm BAND


HEXAFLUOROBENZENE
C_6F_6
NORM OA/LASER RESPONSE
PREDICTED FROM IR ABSORPTION OF 0.033 ATM-CM C_6F_6 IN N_2
1.0
0.10
0.01
0.001
R30
R
R20
R10
P10
P
P20
P30
R30
R
R20
R10
P10
P
P20
P30
CM^{-1}
1090
1080
1070
1060
1050
1040
1030
990
980
970
960
950
940
930
9.4 μm BAND
10.4 μm BAND

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