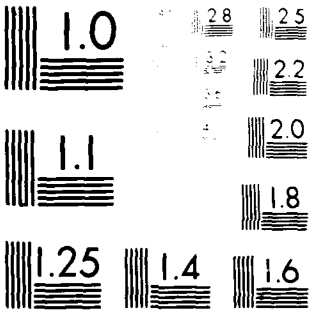
AD-A112 950 AEROSPACE CORP EL SEGUNDO CA CHEMISTRY AND PHYSICS LAB F/G 20/5
CO2 LASER PHOTOACOUSTIC DETECTION OF HYDRAZINE-BASED ROCKET FUE--ETC(U)
MAR 82 G L LOPER, A R GALLOWAY, M A STAMPS F04701-81-C-0082
UNCLASSIFIED TR-0082(2945-09)-1 SD-TR-81-107 NL

1 OF 1
AD A
112950

END
DATE
FILMED
04-82
DTIC



MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

REPORT SD-TR-81-107

(12)

CO_2 Laser Photoacoustic Detection of Hydrazine-Based Rocket Fuels

G. L. LOPER, A. R. CALLOWAY, M. A. STAMPS, and J. A. GELBWACHS
Chemistry and Physics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

15 March 1982

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

Prepared for

SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-[redacted] 81-C-0082 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lt E. Fornoles, SD/YLXT, was the project officer for Mission-Oriented Investigation and Experimentation (MOIE) Programs.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Efren V. Fornoles
Efren V. Fornoles, 1st Lt, USAF
Project Officer

Florian P. Meinhardt
Florian P. Meinhardt, Lt Col, USAF
Director of Advanced Space Development

FOR THE COMMANDER

Norman W. Lee Jr
Norman W. Lee, Jr., Colonel, USAF
Deputy for Technology

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
SD-TR-81-107

2. GOVT ACCESSION NO.
AD A11 2 750

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
CO_2 LASER PHOTOACOUSTIC DETECTION OF HYDRAZINE-BASED ROCKET FUELS

5. TYPE OF REPORT & PERIOD COVERED

6. PERFORMING ORG. REPORT NUMBER
TR-0082(2945-09)-1

7. AUTHOR(s)
G. L. Loper, A. R. Calloway, M. A. Stamps, and J. A. Gelbwachs

8. CONTRACT OR GRANT NUMBER(s)
F04701-81-C-0082

9. PERFORMING ORGANIZATION NAME AND ADDRESS
The Aerospace Corporation
El Segundo, Calif. 90245

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Space Division
Air Force Systems Command
Los Angeles, Calif. 90009

12. REPORT DATE
15 March 1982

13. NUMBER OF PAGES
44

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC ELECTE APR 5 1982 D H

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Photoacoustic detection, hydrazine fuel detection, toxic vapor analysis, trace molecule detection, ambient air monitoring, analytical spectroscopy, carbon dioxide laser spectroscopy, photoacoustic technique, optoacoustic technique

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes recent work performed at The Aerospace Corporation to determine the capability of the CO_2 laser photoacoustic technique to detect the rocket fuels hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) at low parts-per-billion (ppb) levels in the ambient air in real time. These compounds are highly toxic and recent studies indicate that they may also be carcinogens. Revised Occupational Safety and Health Administration (OSHA) regulations are expected that will reduce the maximum allowable concentrations of

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

these compounds in workplace ambient air samples to values of 30, 40, and 60 ppb, respectively. Although these concentrations correspond to ceiling values in air samples collected over a 2-hour period, the Air Force desires a continuous detector that can measure peak concentrations of the hydrazines at the expected new threshold levels to better protect the health of its personnel and that of its contractors.

Estimates made from CO_2 laser absorption cross section data determined for the hydrazines in a previous Aerospace study indicate that the hydrazines should be detectable by the CO_2 laser photoacoustic technique at the desired low ppb levels even in the presence of the ambient levels of pollutants and water vapor found in urban atmospheres. To assess the validity of these hydrazine-fuel detection estimates by the CO_2 laser photoacoustic technique, various laboratory photoacoustic detection systems were assembled and their minimum detectable absorptivity values were determined during the present study.

The photoacoustic detection system that provided the best performance in this study possessed optically tandem sample and reference cells connected to a differential capacitance manometer. This system was designed to minimize the effects of spurious absorption at the photoacoustic cell windows. Dilution experiments carried out with the calibration gas ethylene in pure dry nitrogen indicated that this system exhibited a linear photoacoustic response from 10 ppm ethylene (the highest concentration studied) down to a lower limit ethylene detection sensitivity of about 2 ppb at the CO_2 laser's 10.4-μm band P14 line. These data indicate that hydrazine, MMH, and UDMH should be detectable on a real-time basis at concentrations below the desired 30, 40, and 60 ppb levels, respectively, with this photoacoustic detection system. Dilution experiments performed with UDMH in nitrogen demonstrated that this system can provide measurable UDMH absorption signals at UDMH concentrations of close to 25 ppb, a value below its anticipated new OSHA standard. Similar results are expected for hydrazine and MMH using detection systems with similar minimum detectable absorptivity values to the system investigated here.

CONTENTS

FIGURES

I. INTRODUCTION

The Air Force needs a sensitive, selective, and reliable instrument to simultaneously detect a variety of toxic vapors at low parts-per-billion (ppb) levels in the ambient air in real time. The capability of monitoring low ppb levels of airborne toxic substances is desired by the Air Force to ensure the workplace safety of its personnel and that of its contractors. A toxic vapor detector of this type would also help the Air Force meet increasingly strict Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) requirements for demonstrating that the airborne levels of controlled toxic and/or environmentally harmful substances associated with certain Air Force operations are below certain standards.

The Air Force's Space Division has a particular need for improved detection methods for the toxic rocket fuels hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) as well as some of the potentially toxic MMH and UDMH air oxidation products. The health hazards to humans resulting from exposure to these compounds, even at very low concentrations, are of increasingly great concern. Analytical methods are needed that will allow the continuous ambient air monitoring of the hydrazine fuels at levels as low as 30 ppb in the work environment of the Space Division and its contractors. This report describes experimental work performed to date at The Aerospace Corporation to determine the capability of the CO_2 laser photoacoustic technique to detect low ppb levels of the hydrazine fuels in the ambient air in real time.

In an earlier Aerospace study,[1] absorption cross section data were measured for each of the hydrazine fuels as well as for some of their air oxidation products at about 77 CO_2 laser wavelengths each. These data indicated that the desired low ppb detection sensitivities should be obtainable for hydrazine, MMH, and UDMH in the presence of typical ambient air concentrations of water vapor by the CO_2 laser photoacoustic technique. Analysis of the CO_2 laser absorption spectra of the expected hydrazine-fuel air oxidation products also indicated that at their anticipated airborne concentrations these compounds should not interfere with detection of the hydrazines. Further, consideration of the concentrations of pollutants typically found in urban air, along with their infrared spectral properties, indicated that the expected low ppb level CO_2 laser photoacoustic detection limits of the hydrazines should not be significantly increased by the presence of typical air pollutants.

The background to the Air Force's need for improved ambient air detection methods for the hydrazines and their degradation products is reviewed in Section II. This section also describes the CO_2 laser photoacoustic technique for the trace detection of these compounds that is presently under investigation. The different laboratory photoacoustic detection systems investigated here, along with the procedures used to determine the performance of these systems, are described in Section III. The minimum detectable absorptivity values and, where determined, the hydrazine-fuel detection limits obtained with these photoacoustic detection systems are discussed in Section IV. Section V outlines the conclusions of this study.

II. BACKGROUND

A. HYDRAZINE FUELS AND TOXIC DEGRADATION PRODUCTS OF AIR FORCE CONCERN

The compounds hydrazine, MMH, and UDMH are extensively used by the Air Force as rocket fuels. During routine handling and transferring operations, the possibility exists that the volatile hydrazines can be inadvertently released into the ambient air. The hydrazines are highly toxic and recent animal toxicological studies indicate that these compounds exhibit mutagenic and carcinogenic activity.[2,3] As a result, both the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute of Occupational Safety and Health (NIOSH) have listed these compounds as suspected human carcinogens. ACGIH has adopted time-weighted average threshold limit values for exposure to hydrazine, MMH, and UDMH over an 8-hour work day of 100, 200, and 500 ppb, respectively.[4] NIOSH has recommended to the Department of Labor that the maximum allowable concentrations of hydrazine, MMH, and UDMH in workplace ambient air samples, collected over a period not to exceed 2 hours, be reduced to values of 30, 40, and 60 ppb, respectively. OSHA is expected to adopt one of these sets of threshold levels, which are up to 30 times lower than current threshold levels, as their new standard for hydrazines.

Besides the concern about the toxic and carcinogenic properties of the hydrazines, some of the hydrazine-fuel atmospheric degradation products have been found to be, or are expected to be, serious human health hazards. For example, N-nitrosodimethylamine (NDMA), a highly potent carcinogen, has been found to be formed in small amounts as the result of air oxidation reactions of UDMH.[5] It has also been found that dimethylamine (DMA) and trimethylamine (TMA), other products found in air oxidation reactions of UDMH, can form NDMA as the result of reactions with NO_x in polluted atmospheres.[6] Further, the health hazards of the major UDMH and MMH air oxidation products formaldehyde dimethylhydrazone (FDH)[7] and formaldehyde monomethylhydrazone (FMH),[8] respectively, are not known. However, FDH and FMH are structurally similar to the hydrazines and NDMA and might be expected to exhibit similar toxic or carcinogenic properties to these compounds.

Concern about the toxic and/or carcinogenic properties of the hydrazine fuels and some of their atmospheric degradation products currently affect Air Force satellite and missile launch operations. For example, a major engineering effort is being planned at the Western Test Range (Vandenberg AFB) to ensure the safety of personnel and compliance with current and anticipated OSHA requirements concerning the use of the hydrazine fuels.[9] To effectively assess the success of this engineering effort, much improved ambient air detection capabilities for the hydrazine fuels and their degradation products are needed.

The analytical methods currently used to detect the hydrazines[10] near launch sites or near production and storage facilities are not sufficiently sensitive and specific for real-time monitoring at the expected new threshold levels. Continuous monitors are needed to measure peak levels of the hydrazines. Real-time monitors for these compounds are just beginning to be developed based on chemiluminescence[11] and electrochemistry.[12] A near real-time instrument that uses a moving paper tape impregnated with a color test reagent has recently become available.[13] These chemiluminescence, electrochemical, and paper tape monitors are not expected to be sufficiently specific in their present form to distinguish the hydrazines from each other or from some of their structurally similar atmospheric degradation products such as the hydrazones. Although an analytical method is available for the sensitive, selective, and potentially near real-time monitoring of NDMA in the ambient air,[14,15] analytical procedures have not been established for other potentially hazardous atmospheric degradation products of the hydrazines such as FDH and FMH. Still other atmospheric degradation products of the hydrazines may be identified that are human health hazards for which improved detection capability is needed. As a result of the foregoing considerations, an important current need of the Air Force is a single analytical instrument capable of specifically and rapidly monitoring low ppb levels of not only each of the hydrazine fuels but also their selected air oxidation products NDMA, DMA, TMA, FDH, and FMH. A trace molecule detector that can detect a variety of toxic vapors will be needed even more as the number of controlled OSHA and EPA toxic substances increase and as their allowable work place levels are lowered. As indicated in Section I, earlier studies performed at The Aerospace Corporation indicate that the CO_2 laser photoacoustic detection technique may fulfill this important need. This technique is described in the following subsection.

B. CO_2 LASER PHOTOACOUSTIC DETECTION TECHNIQUE UNDER INVESTIGATION

By the CO_2 laser photoacoustic technique, a modulated beam of CO_2 laser radiation is passed through a cell containing the sample to be analyzed. The wavelength of this radiation is chosen to be coincident with an infrared absorption feature of the species to be detected. The radiation periodically absorbed by the species of interest is converted through collisions with the nonabsorbing surrounding host gas molecules (N_2 and O_2) into thermal motion of the entire gas mixture. This produces a modulated pressure rise in the cell which can be sensitively detected by a pressure transducer. If the laser intensity is modulated at frequencies in the audio region, a microphone can be used as the pressure transducer.

1. DETECTION SPECIFICITIES

In order to rapidly detect a variety of toxic vapors in the ambient air at low ppb levels, the capability of performing highly specific and sensitive multicomponent analysis is required. These toxic vapors have to be detected in the possible presence of much larger relative concentrations of other gases. It is well known that a molecule's infrared absorption spectrum* can be used to uniquely identify it.[17] This is because a molecule's infrared absorption band intensities and positions depend upon the molecule's type of bonding, geometry, and size. Because each molecule has its own infrared absorption signature, infrared spectroscopic techniques offer the potential of highly specific multicomponent analysis. For this to be possible, however, the infrared radiation used for detection must be of sufficiently narrow

---

*Molecules that undergo a change in dipole moment with a change in geometry exhibit absorption bands in the infrared region of the electromagnetic spectrum. When a molecule absorbs infrared radiation it is excited to a higher vibrational or vibrational-rotational energy state.[16]

excitation bandwidth to distinguish the absorption features of the various molecules. Infrared grating and prism spectrometers equipped with conventional incoherent excitation sources have been used to specifically detect species in multicomponent gas mixtures. Significantly greater detection specificities, however, can be obtained using detectors equipped with infrared laser excitation sources. This is because of the hundred times narrower excitation bandwidth that can be obtained with an infrared laser source than that obtained with an infrared spectrometer equipped with an incoherent excitation source. The narrower bandwidth output of a laser source can much more readily resolve the fine rotational structure in an infrared absorption band than can a conventional spectrophotometer.

The $^{12}C^{16}O_2$ laser is well suited as an excitation source for a toxic vapor detector. This laser is well developed and highly reliable. It has a spectral output of greater than 100 discretely tunable lines between approximately 9.1 and 11.0 μm[18] where many molecules, including the hydrazine-based rocket fuels[19-21] and their atmospheric degradation products of current concern, exhibit highly characteristic, strong absorption bands. The wavelengths of the $^{12}C^{16}O_2$ laser lines are exactly known and can be reproducibly obtained.[18] For each molecule that exhibits resolvable fine structure in the $^{12}C^{16}O_2$ laser wavelength region, a unique spectral signature is obtained as the result of the many near wavelength coincidences of the laser lines and the molecule's absorption lines.[22] Other CO_2 isotopic species can produce laser output at wavelengths as long as 12.0 μm.[18] The foregoing considerations also apply to laser lines from these species. CO_2 laser-based detection methods in general are well suited for detection of molecules in the ambient air since CO_2 laser spectral output occurs within the 8.5 to 12.5-μm wavelength region where interferences from water vapor, CO_2, and other atmospheric constituents are minimized.

2. DETECTION SENSITIVITIES

Photoacoustic detection methods have measured much smaller absorption coefficients than can be measured by conventional long-path absorption techniques. The sensitivity of conventional long-path absorption techniques is limited by the difficulty in measuring the small difference in the intensities of the incident and transmitted light beams through the absorber of interest. The photoacoustic technique, on the other hand, measures small absorption signals against a null background. In this case, the photoacoustic signal is directly proportional to the optical power absorbed. Because of the high light intensities and small bandwidths produced by laser sources, the photoacoustic technique is well suited for use with laser spectroscopic detection methods.[23]

Both acoustically resonant and nonresonant sample cells have been investigated for use in gas phase photoacoustic spectroscopy. The relative advantages of each type of cell have been discussed in recent literature.[24-28] The pressure fluctuations produced in a nonresonant cell are a function of the energy absorbed in a given illumination cycle.[29,30] Any energy remaining from previous illumination cycles only contributes noise to the desired signal. The responsivity of a cylindrical nonresonant photoacoustic cell varies inversely with the square of the cell radius[31] and decreases with increasing exciting light modulation frequency.[27,28] Thus, nonresonant cells are designed to be of as small a diameter as practicable. They also use low frequency chopped illumination sources. Resonant cells are designed to accumulate the absorbed energy in a standing acoustic wave when the exciting laser light is concentrated along the axis of the sample cell and modulated at a cell resonant frequency.[29,30] In this case, the cell acts as an amplifier such that the energy stored in the standing wave is many times greater than the energy absorbed per illumination cycle. Longitudinal, azimuthal, and radial acoustic modes may be excited in a resonant cell. Resonant photoacoustic cells that use either predominantly radial or longitudinal acoustic modes have been investigated. The modulation frequencies used for resonant cells depend upon the cell dimensions. Resonant cells have been designed to operate at high chopping frequencies and provide no substantial reduction in the responsivity obtainable with nonresonant cells operating in the low-frequency regime.[27,28] Since the power spectrum of external acoustic noise usually exhibits an inverse frequency dependence, resonant photoacoustic cells are expected to provide inherently higher signal-to-noise ratios than nonresonant cells operated at lower modulation frequencies.[27,28] A more important noise source in photoacoustic cells is the small amount of absorption that occurs at the windows of the photoacoustic cell, which is independent of the absorbing gas concentration. Work has been directed at designing photoacoustic cells for which window absorption effects are minimized. For nonresonant photoacoustic cells, this has primarily included the design of cells with: (1) carefully matched optically tandem reference and sample chambers to allow sample chamber window absorption to be nulled out with that of the reference chamber[31,32] or (2) acoustic dampers inside the cell to minimize transmission of window absorption signals to the cell pressure transducer.[33] Resonant photoacoustic cells have been designed that employ radial[34] or longitudinal[33] acoustic modes that effectively eliminate the coupling of background window absorption signals to the cell pressure transducer. Resonant photoacoustic cells thus provide greater inherent immunity from background window absorption than nonresonant cells.

Although acoustically resonant cells provide greater potential immunity to external background noise and unwanted window absorption than nonresonant cells, this advantage is offset by the fact that the acoustic resonance condition is a sensitive function of gas temperature, pressure, and composition.[23,26] This can make it difficult to maintain signal linearity over a wide range of conditions. By contrast, the nonresonant photoacoustic cell sensitivity (signal divided by concentration of signal-producing species) has been found to be nearly independent of the total cell pressure over the regime 760 Torr to approximately 20 Torr.[24,35]

The photoacoustic cells developed to date have generally employed either microphones or capacitance manometers as the transducers used to detect the modulated pressure signals produced as the result of light absorption.[32] Capacitance manometers have been primarily used in nonresonant photoacoustic cells in which differential measurements are made on sample and reference chambers in an attempt to null out background window absorption. Microphones have generally been used in nonresonant single-cell designs and in acoustically resonant cell designs.

Kerr and Atwood[36] were the first to use laser excitation sources in conjunction with photoacoustic detection. They obtained minimum detectable absorptivity values down to approximately 10^{-6} cm^{-1} Watt using a CO_2 laser illuminated single cell photoacoustic detector.[36] Cell window absorption effects limited lower sensitivity values. This detector employed a nonresonant cell equipped with a capacitance manometer pressure transducer. Kreuzer and coworkers[37] later designed a microphone-equipped nonresonant single photoacoustic cell with window background signals of approximately 5×10^{-7} cm^{-1} Watt. This is near the expected minimum background absorptivity value of 10^{-7} cm^{-1} obtainable with nonresonant single photoacoustic cell designs.[31] The minimum detectable absorptivities of differential nonresonant cells, or resonant cells designed to minimize window absorption, that are suitable for use with circular cross section beam CO_2 lasers are currently[31] approximately 10^{-9} cm^{-1} Watt. Patel and Kerl[38] have demonstrated a photoacoustic cell suitable for use with rectangular waveguide lasers that have minimum detectable absorptivity values as low as 10^{-11} cm^{-1} Watt. The minimum concentrations for various vapors that can be detected under interference-free conditions by CO_2 laser photoacoustic techniques can be estimated by use of the relationship

$$P_{min} = \frac{\alpha_{min}}{\sigma(\lambda)} \tag{1}$$

Here α_{min} is the minimum detectable absorptivity value for the photoacoustic cell in units of $cm^{-1} \cdot$Watt, and $\sigma(\lambda)$ is the absorption cross section in units of cm^{-1} atm^{-1} of the vapor of interest at the CO_2 laser monitoring wavelength. Thus, for molecules with moderate absorption strengths of 5 cm^{-1} atm^{-1}, interference-free CO_2 laser photoacoustic detection limits of approximately 100 ppb would be expected with nonresonant single photoacoustic cells when 1-watt CO_2 laser exciting lines are used. Sub-ppb interference-free detection limits might be expected for a moderately absorbing molecule under similar conditions with photoacoustic cells designed to minimize window absorption effects.

As part of the present study, we have conducted a preliminary experimental investigation of the relative suitability of selected types of photoacoustic cell designs to the ambient air detection of the hydrazine-based rocket fuels. The different types of photoacoustic cells investigated are described in the following section.

III. EXPERIMENTAL

The $^{12}C^{16}O_2$ laser used as an excitation source for the photoacoustic detection systems investigated in the present study was assembled in-house. This laser, described in detail in our earlier report,[1] is tunable over approximately 36 wavelengths of its 9.4-μm band and 41 wavelengths of its 10.4-μm band.

The performance of three different nonresonant photoacoustic detection systems was investigated during this study. The optical arrangement used to make measurements with these photoacoustic detection systems is exhibited in Fig. 1. The vertically polarized laser output was oriented to horizontal polarization by the use of a pair of 45-degree mirrors. This output was focused to a diameter of 2 to 3 mm as it is passed through the photoacoustic cells. For these nonresonant cells, the intensity of the exciting light was modulated at frequencies of either 20 or 13 Hz by a Laser Precision Corporation chopper (Model CTX-534) and at 13 Hz by a Brower Laboratories chopper (Model 312B). A Scientech, Inc. Model 36/0001 power meter was used at the optical exit of the photoacoustic cell housing to monitor laser output power. When necessary, low voltage signals from the photoacoustic detection systems' pressure transducers were preamplified by either a Princeton Applied Research Corporation (P.A.R.C.) Model 113 or a Model 225 low noise preamplifier before being sent to the lock-in detection system. An Ithaco Dynatrac Model 391A, a P.A.R.C. Model 5204, or a P.A.R.C. Model 124A lock-in amplifier was used to detect the preamplified pressure transducer signals at the exciting light modulation frequencies. The different photoacoustic detection systems investigated in this study together with a resonant photoacoustic detection system recently assembled at The Aerospace Corporation are described below.

A. BECKMAN-JPL NONRESONANT GLASS CELLS

The photoacoustic detection system whose performance was most extensively investigated here was designed and fabricated by personnel at Beckman Instruments, Inc. and the Jet Propulsion Laboratory (JPL). The system was developed

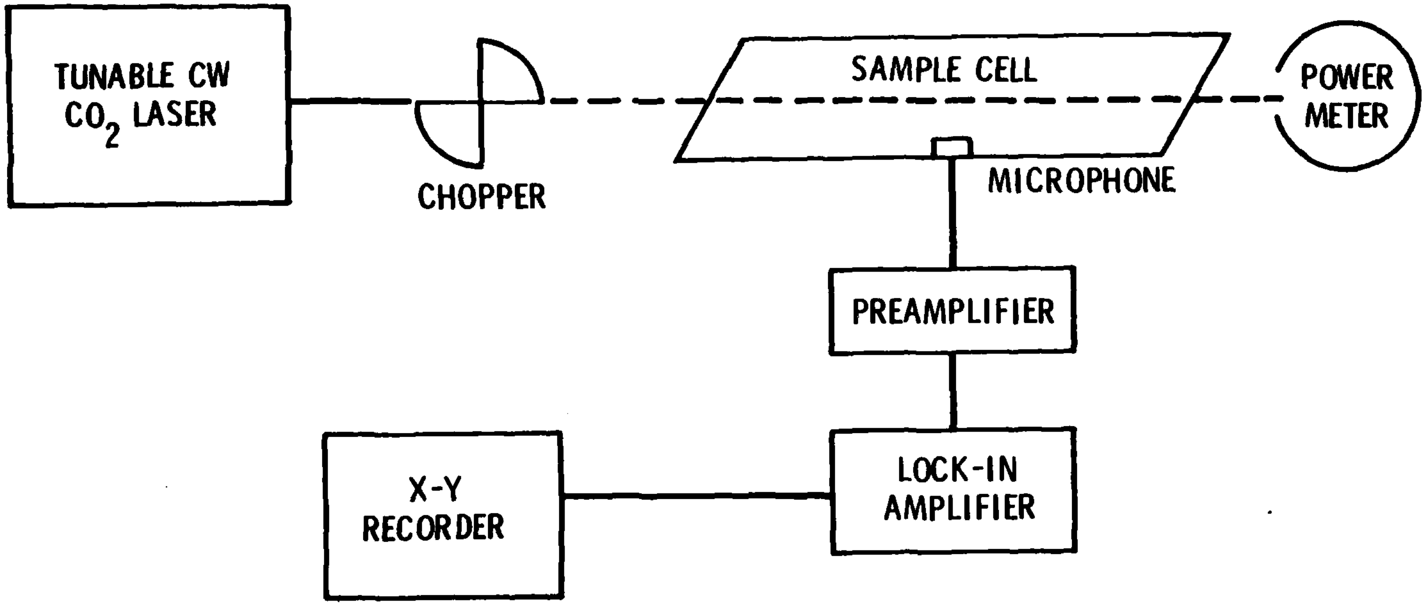


Fig. 1. Optical Arrangement for Photoacoustic Measurements

by Beckman and JPL as part of an earlier Law Enforcement Assistance Administration (LEAA) funded, Aerospace-administered program to investigate the feasibility of using the CO_2 laser photoacoustic technique to detect vapors emanating from clandestine explosive devices.[39] This system was basically comprised of two identical tandem acoustically nonresonant Pyrex glass cells equipped with parallel zinc selenide Brewster's angle windows and Bruel and Kjaer No. 4165 condenser microphones.

The cell bodies were 2.54 cm square, with a 0.95-cm diameter, 12-cm-long center bore. The center bore of each cell was connected by three 2-mm diameter ports to gas inlet and outlet tubes (2 mm inside diameter) and a microphone. A four-way glass stopcock with a Teflon inner sleeve (Ace Glass, Inc. 8148-T23) was attached to the inlet and outlet tubes on each cell. This stopcock allowed the cell to be operated in a continuous flow or stopped-flow mode. The cells were mounted in an insulated aluminum box housing designed to allow cell bakeout at temperatures up to 150°C and operation at constant predetermined temperatures between 27 and 50°C. In the present study all measurements carried out with this system were made at ambient temperatures.

The zinc selenide windows were mounted on the bodies of the cells with an epoxy formulation of 50% by weight EPON No. 828 (Shell Chemical Company) and 50% Versamid No. 125 (General Mills, Inc.). The 1.25 cm diameter Bruel and Kjaer microphones were placed in stainless steel holders, which in turn were placed over the glass cells and bolted to the aluminum cell housing. A pressure and vacuum-tight seal concentric with the front of the microphone was provided by compression of an indium-coated stainless steel O-ring. An annular space within the microphone assembly permitted the back side of the microphone diaphragm to be evacuated. Signals from the microphones were amplified by General Radio Model 1560-P42 preamplifiers connected to the microphones through Bruel and Kjaer adapters.

The Beckman-JPL photoacoustic cells were designed to permit differential absorption measurements to be made between the two cells to minimize background signals because of window absorption. However, as described in Section IV, the cells were not used in the differential mode in the present study because of their different outgassing rates.

B. AEROSPACE CORPORATION NONRESONANT GLASS CELL

A nonresonant glass photoacoustic cell was fabricated at The Aerospace Corporation. This cell had an optical path length of 17.2 cm and a bore of 0.78 cm. It was equipped with parallel zinc selenide Brewster's angle windows, two grease-free 4-mm Kontes glass stopcocks (Model K-826510) to permit either continuous or stopped flow operation, and a single Knowles Electronics Corporation miniature electret microphone with built-in FET preamplifier (Model 1834) as the pressure transducer. The cell body was fabricated from heavy wall (1.27 cm o.d.) Pyrex glass tubing. The stopcocks were attached to the cell body close to the stopcock shaft-barrel seat to minimize the cell dead volume. The stopcocks were located near opposite ends of the cell length, approximately 1 cm from the closest edge of the cell windows. The electret microphone, which had dimensions of 0.79 × 0.56 × 0.41 cm, rested in a depression made at the junction of the cell body and a 2-cm length of 0.6 i.d. tubing attached to the cell midway between the end windows. Electrical connections were made to the electret microphone through a Teflon inner plug that provided a vacuum tight seal to the 0.6 cm i.d. tubing. One 1.35-volt battery provided electrical power to the electret microphone. The zinc selenide windows were attached to the ends of the heavy wall glass tubing by Torr Seal low vapor pressure resin.

C. AEROSPACE CORPORATION ASSEMBLED NONRESONANT STAINLESS-STEEL SYSTEM

At The Aerospace Corporation two matched stainless-steel nonresonant cells were designed and fabricated for use in differential absorption measurements with a capacitance manometer as the pressure transducer. The cells were arranged in a configuration similar to that suggested by Shumate.[31] Their optical path axes were placed in parallel to each other with the capacitance manometer connected between them. The inner volumes of these connectors were kept small. The cells had an optical path length of 14.9 cm and a bore of 0.99 cm. The cells were each equipped with two Nupro stainless steel valves (Model SS-2H2) to permit either continuous or stopped-flow operation and parallel zinc selenide Brewster's angle windows. The windows were held onto the ends of the cells by aluminum end plates. Viton O-rings were employed to provide a pressure and vacuum-tight seal of the windows to the cell body.

The capacitance manometer used in this photoacoustic detection system was an MKS Instruments, Inc. Baratron type 170 Pressure Meter with 10 Torr full range differential pressure head. The manufacturer stated that the minimum response time of this capacitance manometer was 40 msec. The smallest pressure change resolvable with this manometer was about 10^{-6} of the maximum head pressure range. The use of the 1 Torr full range pressure head available from MKS Instruments, Inc. potentially offers more sensitive detection by a factor of 10 than that obtained in the present study with the 10 Torr full range pressure head.

The basic optical arrangement exhibited in Fig. 2 was used for the photoacoustic measurements carried out with these nonresonant stainless-steel cells. Two gold-coated 45-degree mirrors were used to reflect the laser beam that passes through the sample cell back through the reference cell.

D. AEROSPACE CORPORATION ASSEMBLED RESONANT STAINLESS-STEEL CELL

An acoustically resonant stainless-steel cell based on a design of Gerlach and Amer[34] has recently been fabricated at The Aerospace Corporation. The capability of this photoacoustic detection system to detect low ppb levels of the hydrazines will be investigated soon. This cell (Fig. 3) is cylindrical with flat end walls. The inside height of the cylindrical cell is 6.5 cm and the inside diameter is 24.8 cm. These dimensions were chosen to permit the laser excitation beam to pass through zinc selenide windows at Brewster's angle. The cell is designed to minimize the effects of background window absorption by placing the windows at the nodes of the resonant mode being excited (the first radial mode with respect to the excitation beam axis).[34] If the cell is defined in terms of conventional cylindrical coordinates, the laser beam enters through a window mounted on one end wall at $r = 0.628R$, $\phi = 0°$, and $z = 0$, then passes diagonally through the center of the cell and exits through another window at $r = 0.628R$, $\phi = 180°$, and $z = L$ on the other end wall. Here R and L are the cell inside radius and height, respectively. If the beam is to pass through the windows at Brewster's angle, the ratio of cell radius to height must be $R/L = 0.797n$, where n is the refractive index of the

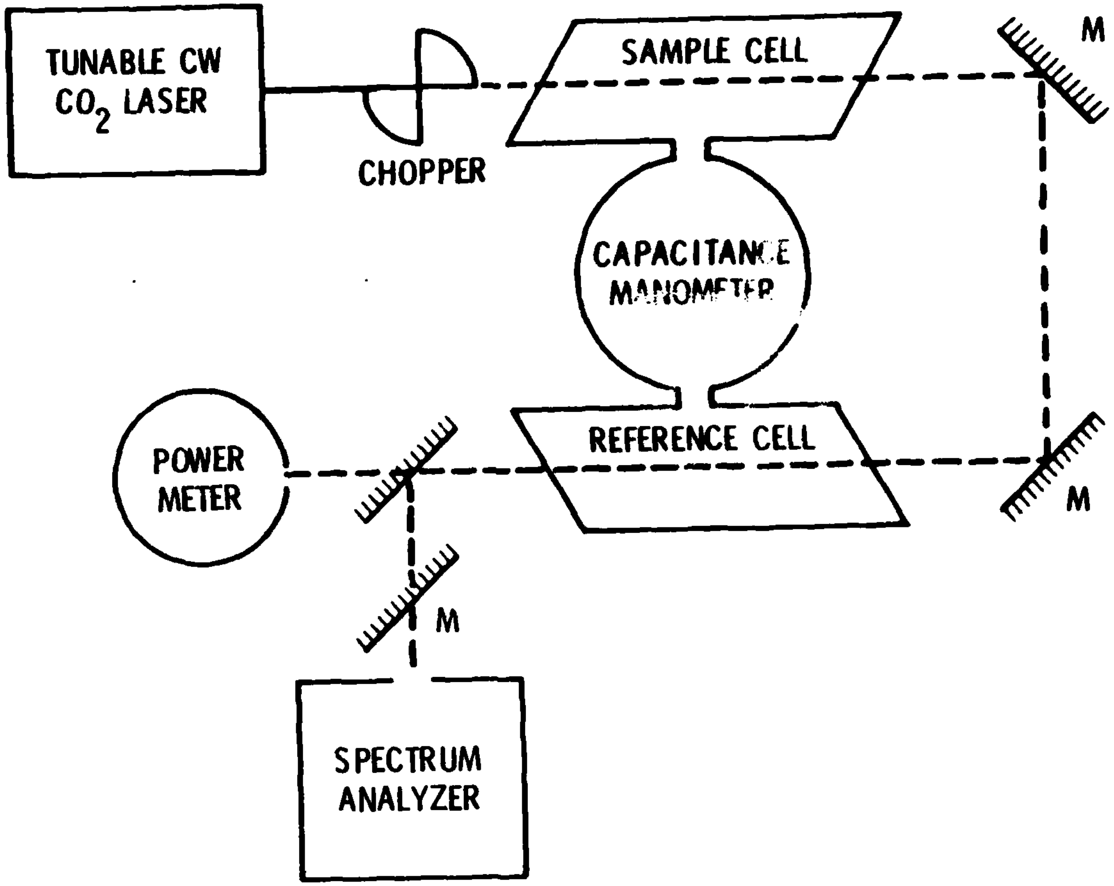


Fig. 2. Nonresonant Stainless-Steel Photoacoustic Detection System

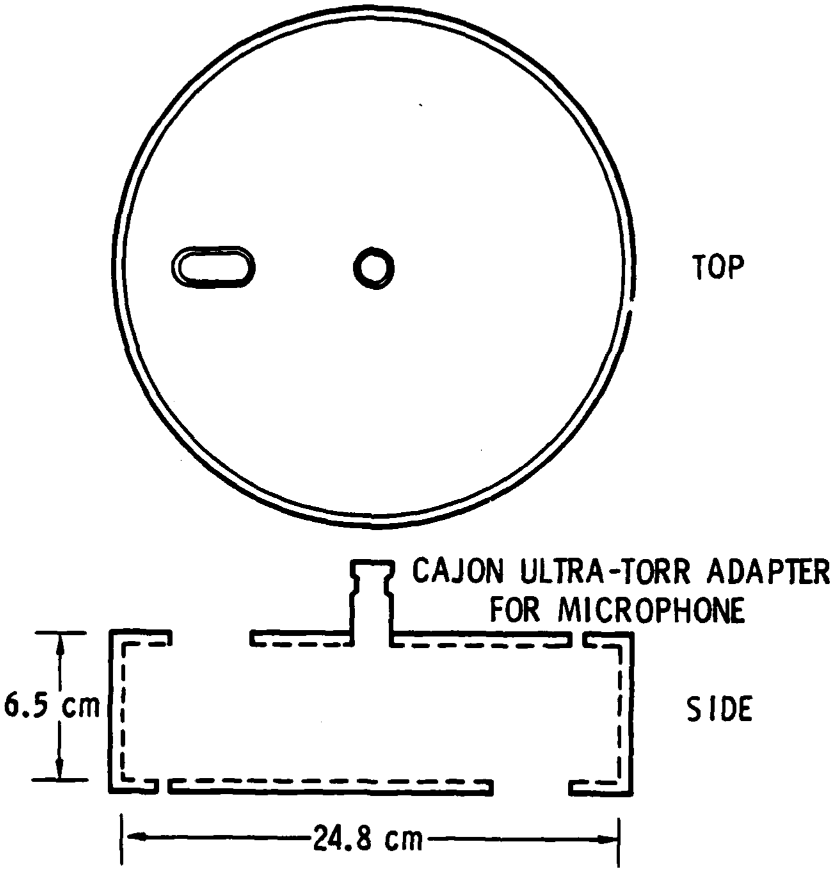


Fig. 3. Acoustically Resonant Stainless Steel Cell

window material. The cell will use a microphone as its pressure transducer. This microphone will be located along the cell axis ($r = 0$) where the maximum gain in the first radial mode occurs. Gas inlet and outlet ports, fitted with Nupro stainless-steel valves (Model SS-2H2), are located at positions directly opposite the cell windows at node positions of the first radial cell mode. The first radial mode of the resonant cell is expected to be found near 3500 Hz.

Ethylene was chosen as a convenient reference gas to determine photoacoustic detector responsivity because of its well-characterized, highly-structured $^{12}C^{16}O_2$ laser absorption profile and its low reactivity and adsorptivity on cell walls. Photoacoustic detector responsivity measurements were typically made over a several order of magnitude range of concentration of ethylene in nitrogen at selected $^{12}C^{16}O_2$ laser lines. Limited dilution experiments were also performed for the hydrazine fuels. The dilution experiments were carried out by first transferring a known pressure of the sample gas of interest from a storage sample tube or bulb to either a calibrated 3.48 ml section on a mercury-free, greaseless vacuum line or to a calibrated 220 ml bulb on the vacuum line. The pressures were determined by use of a Baratron pressure gauge (MKS Instruments, Inc.) with a 77H-10 pressure head. The sample in the 3.48 ml section or the 220 ml bulb was then condensed into a 5430 ml flask equipped with an outer mixing loop. The sample gas was condensed in the flask at liquid nitrogen temperature and approximately 800 Torr of Matheson Research Purity nitrogen (99.9995% min.) was added. The nitrogen pressures were determined with a Wallace and Tiernan gauge (Model FA 160230). The mixing loop of the 5430 ml flask was used to facilitate efficient convection mixing of the gas mixture. The gas mixture was then expanded into the photoacoustic cell of interest to determine the responsivity.

IV. RESULTS AND DISCUSSION

To determine the suitability of a particular CO_2 laser photoacoustic detection system to monitor airborne levels of the hydrazine fuels on a real-time basis, the measurement of the system's minimum detectable absorptivity value is required. Information is also needed on the possible adsorption effects and degradation properties of the hydrazine fuels in the system's photoacoustic cell. The minimum detectable absorptivity values of the different photoacoustic cells investigated in the present study were generally determined by measuring the photoacoustic absorption signals produced in ethylene-nitrogen gas mixtures of known concentration by the selected CO_2 laser 10.4-μm band lines P12, P14, P16, and P22. According to Patty and coworkers,[40] the CO_2 laser absorption cross sections for ethylene at these wavelengths are 4.35, 29.10, 4.55, and 1.09 cm^{-1} atm^{-1}, respectively, in the presence of one atmosphere of nitrogen. When time permitted, the linearity of the signal response of the different photoacoustic cells was examined as a function of hydrazine fuel concentration. Some of the 10.4-μm band CO_2 laser lines used for these measurements along with the corresponding hydrazine fuel absorption cross sections (in units of cm^{-1} atm^{-1}) were:[1] R8(0.13), R6(0.10), R4(0.06), P28(1.11), P38(3.27), P40(3.59), and P42(3.95) for UDMH; R12(0.78), R10(1.19), R8(3.48), R6(0.87) and R4(1.52) for MMH; and R8(4.71), R6(4.76), R4(4.73), and P4(7.56) for hydrazine. Ammonia (NH_3) is a degradation product of each of the hydrazines. To determine whether the hydrazines undergo decomposition in the photoacoustic cells, various ammonia absorption features were monitored during the photoacoustic measurements on the hydrazines. Some of the CO_2 laser 10.4-μm band lines used for this purpose and their corresponding ammonia absorption cross sections (in units of cm^{-1} atm^{-1}) were:[41] R8(20.5), R6(26.3), R4(11.0), P4(2.00), P32(13.7), P36(8.43), P38(4.21), P40(0.950) and P42(0.412).

The minimum detectable absorptivity measurements carried out for the different photoacoustic detection systems investigated in the present study are described below.

A. BECKMAN-JPL NONRESONANT GLASS CELLS

Figure 4 displays a plot of the measured photoacoustic absorption signal per incident laser power (in units of mV/W) of one of the Beckman-JPL nonresonant cells as a function of ethylene concentration in ethylene-pure dry nitrogen mixtures at the CO_2 laser 10.4-μm band P12, P14, P16, and P22 lines. This single Beckman-JPL photoacoustic cell exhibited a linear photoacoustic response from 5.7 ppm ethylene in nitrogen (the highest ethylene concentration studied) down to a lower limit ethylene detection sensitivity of about 250 ppb at the CO_2 laser 10.4-μm band P14 line. This lower limit ethylene detection sensitivity was set by a background absorption signal of between approximately 0.1 and 0.5 mV/W that was measured when the photoacoustic cell was filled with pure dry nitrogen only. Similar results were also obtained with the other Beckman-JPL cell. The minimum detectable absorptivity values for these cells, when used individually, can thus be calculated from Eq. (1) and the ethylene absorption cross section of 29.1 cm^{-1} atm^{-1} at the CO_2 laser 10.4-μm band P14 line to be approximately 7.3×10^{-6} $cm^{-1} \cdot$Watt. This value is about 70 times larger than the state-of-the-art single nonresonant cell detection sensitivity.[31] Beckman Corporation personnel found these photoacoustic cells gave similar anomalous background absorption signals in the previous LEAA-sponsored explosives vapor detection program. In that study and in the present study, this anomalous cell background adsorption was found to increase gradually with time within both the CO_2 laser's 9.4- and 10.4-μm bands even after the cells were extensively pumped on under vacuum at elevated temperatures and filled with pure nitrogen. We believe that this background absorption results from the outgassing of organic species from the adhesive material used to bond the zinc selenide windows to the cell body, or volatile organic substances that evolve from either the microphone or the Teflon inner-sleeve material used in the cell stopcocks.

During the previous LEAA-sponsored study carried out with the Beckman-JPL photoacoustic detection system it was found that a sample and reference photoacoustic cell used in a differential mode of operation resulted in about a factor of 10 improvement in detection sensitivity over that obtained with a single cell. This improvement resulted from the partial nulling of the

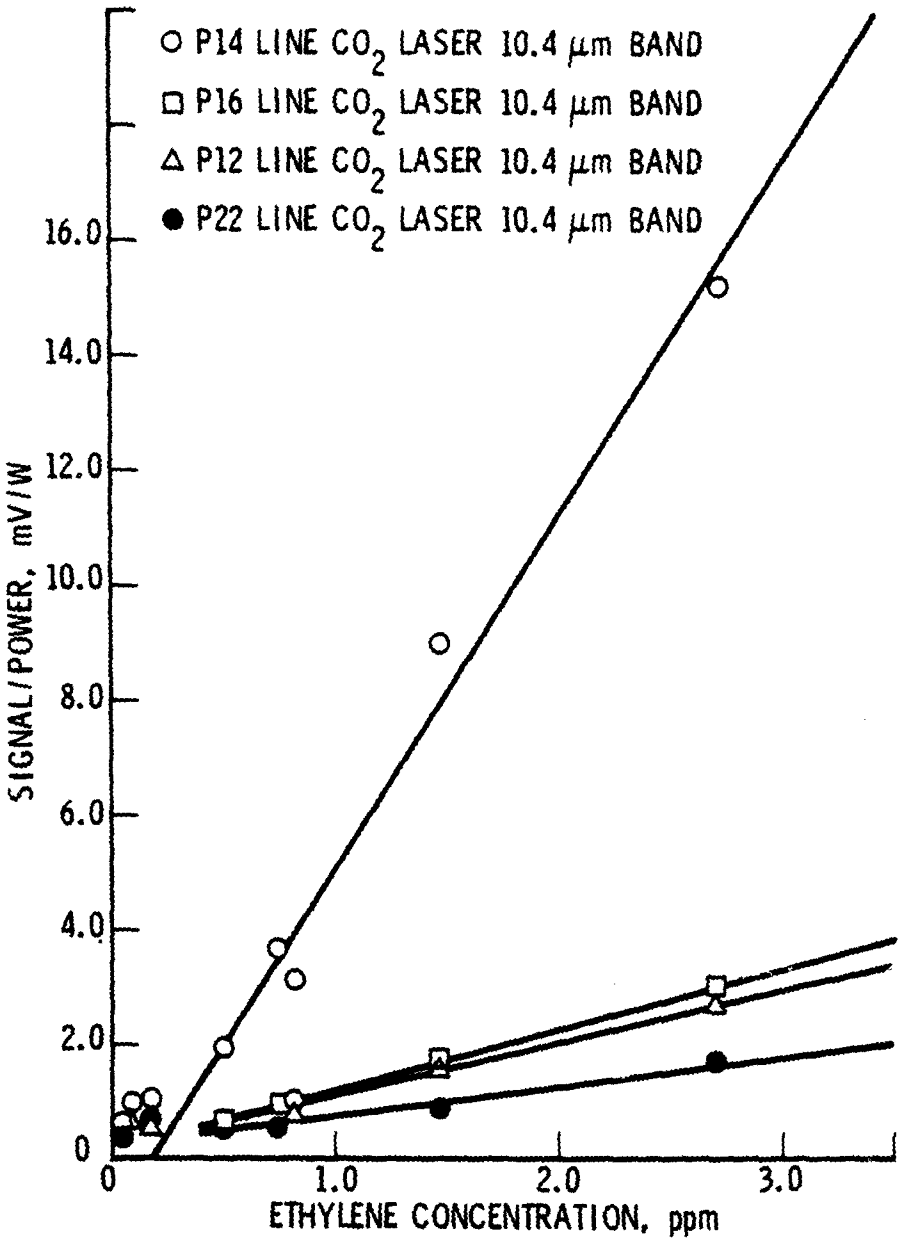


Fig. 4. Photoacoustic Response Versus Ethylene Concentration in a Single Beckman-JPL Nonresonant Cell

background absorption in the sample cell by that in the reference cell. The limiting error in these differential measurements was found to be a result of different rates of change in the background absorption signals in the sample and reference cells. The different and variable outgassing rates observed for the two Beckman-JPL cells in the present study did not permit them to be conveniently used in the differential mode here.

The detection sensitivity of approximately 250 ppb obtained for ethylene at the CO_2 laser 10.4-μm band P14 line with the single Beckman-JPL photoacoustic cell indicates that detection sensitivities of between 1 and 2.5 ppm should be obtainable for the hydrazine fuels with this cell. Although these detection sensitivities are well above the low ppb sensitivities desired for the hydrazines, photoacoustic response measurements were made for each of the hydrazines as a function of concentration to determine the importance of adsorption effects or degradation properties of the hydrazines in the Beckman-JPL glass photoacoustic cell. Figure 5 exhibits a plot of the measured photoacoustic absorption signal per incident laser power of one of the Beckman-JPL cells as a function of UDMH concentration in UDMH-nitrogen mixtures at the CO_2 laser 10.4-μm band P38 and P40 lines. This single cell exhibits a linear photoacoustic response from about 1400 ppm UDMH in nitrogen (the highest UDMH concentration studied) down to about 6 ppm UDMH in nitrogen. The lower limit detection sensitivity of UDMH in the Beckman-JPL cell was set by a background absorption signal of about 0.5 mV/W obtained when the photoacoustic cell was filled with pure dry nitrogen. The photoacoustic signal per incident laser power values plotted at various UDMH concentrations in Fig. 5 were taken as the zero-time intercepts from plots such as exhibited in Figs. 6 and 7. Plotted here are the photoacoustic signals per incident laser power values at particular initial UDMH concentrations versus sample residence time in each photoacoustic cell. At UDMH concentrations of approximately 13 ppm and below, the photoacoustic signal was observed to gradually increase with increasing sample residence time. This is presumably because of the outgassing of an impurity in the cell that absorbs within the CO_2 laser 10.4-μm band P-branch. At UDMH concentrations of 27 ppm and greater, the photoacoustic signal in the CO_2 laser 10.4-μm band P-branch was observed to decrease with increasing sample

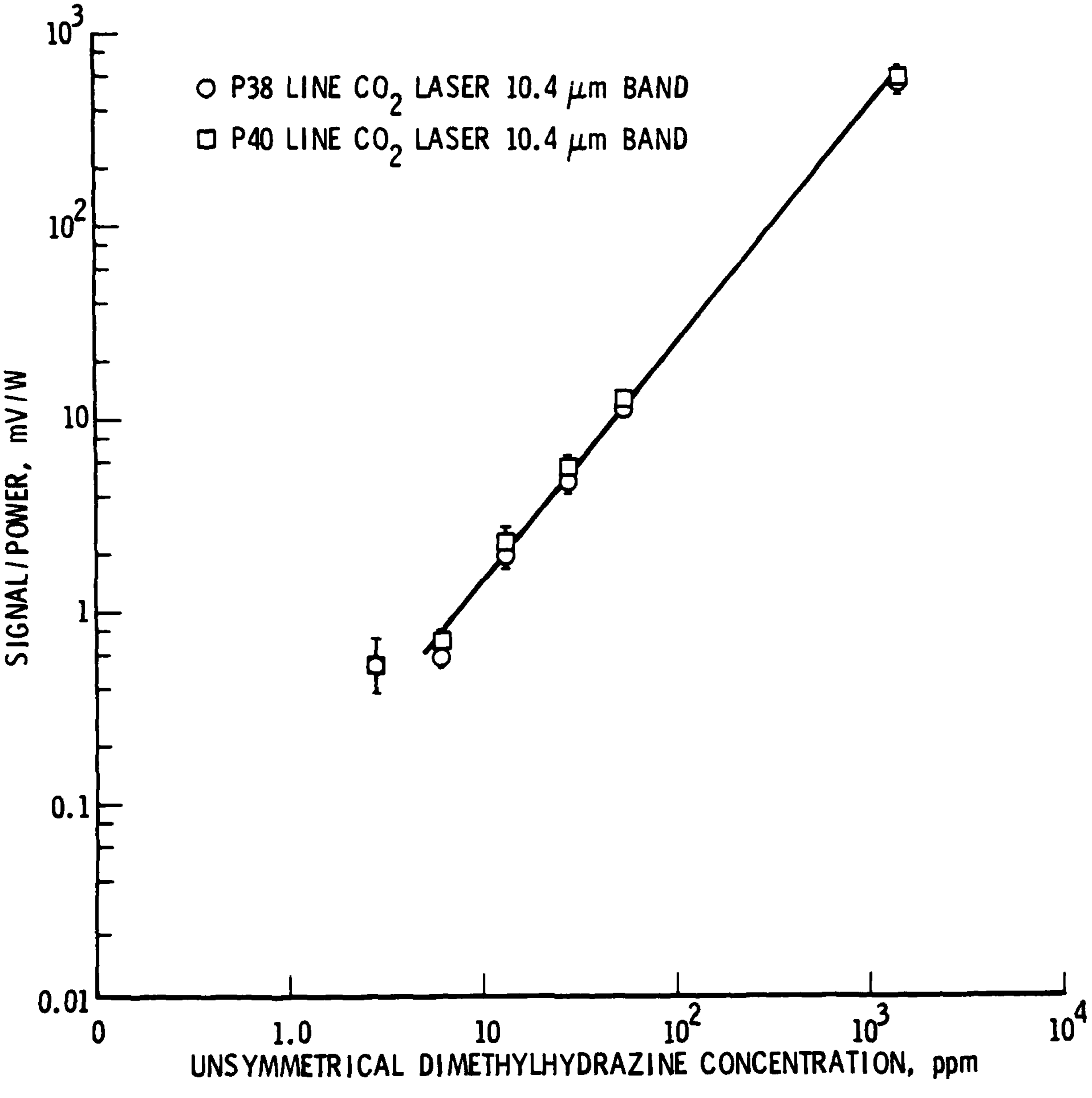


Fig. 5. Photoacoustic Response Versus UDMH Concentration in a Single Beckman-JPL Nonresonant Cell

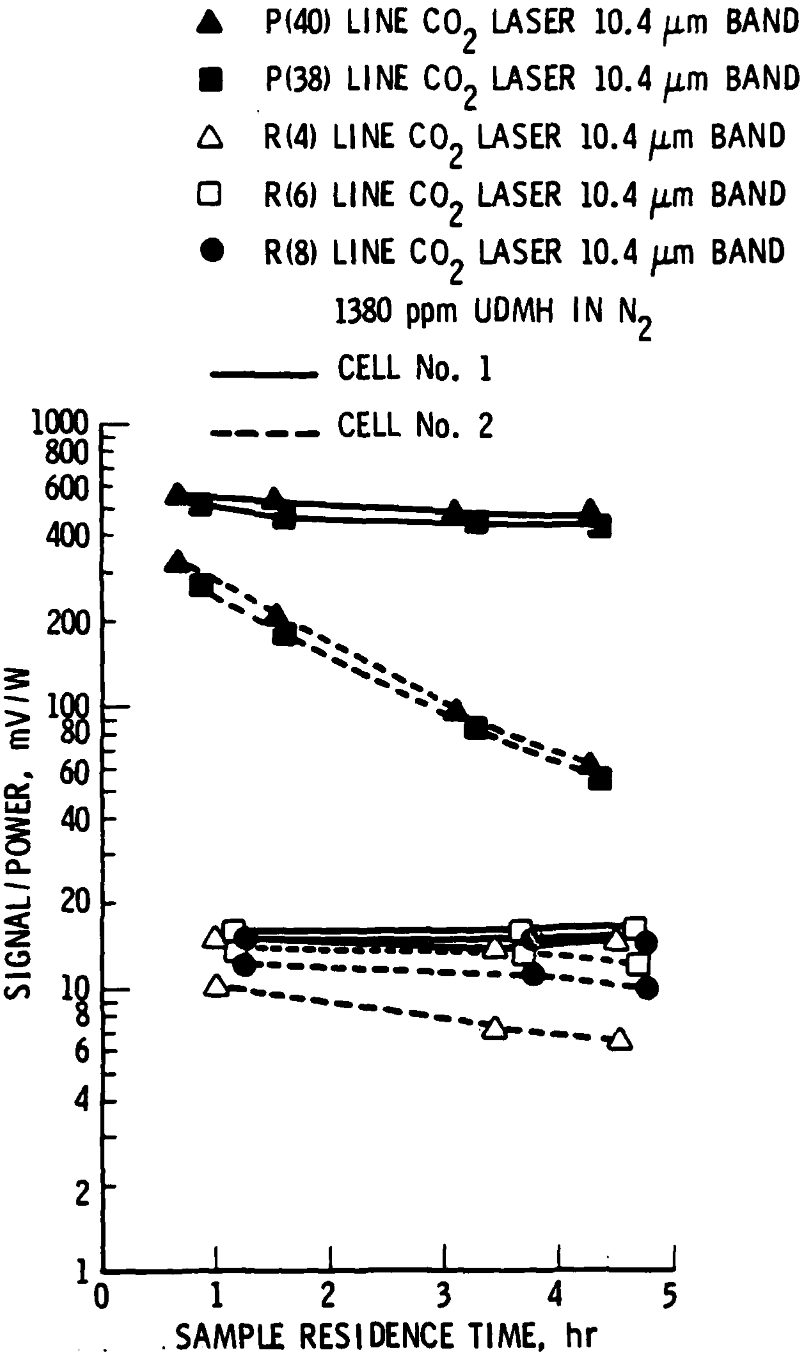


Fig. 6. High Concentration (UDMH) Absorption Signal Versus Sample Residence Time in Beckman-JPL Cell

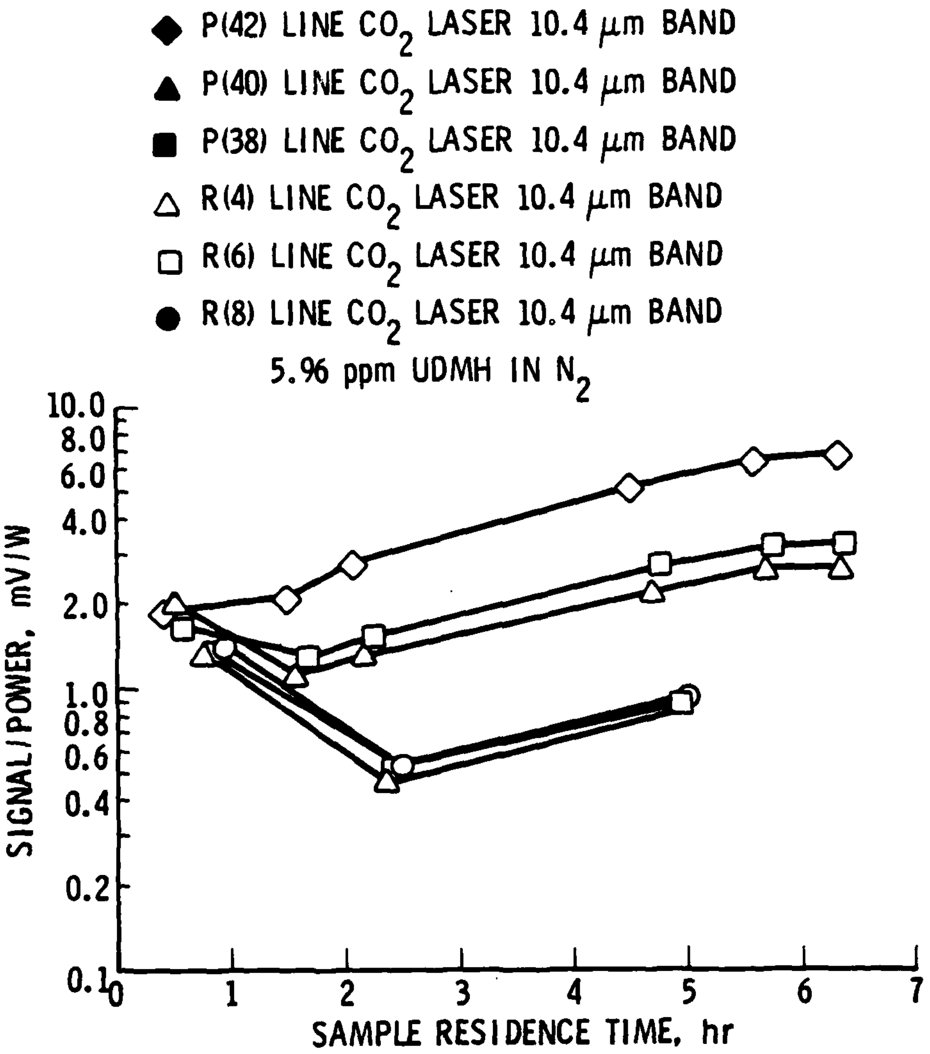


Fig. 7. Low Concentration UDMH Absorption Signal Versus Sample Residence Time in Beckman-JPL Cell

residence time in the photoacoustic cell. The latter signal decrease with time apparently results from sample adsorption or reaction effects of UDMH on the photoacoustic cell walls.

Figure 8 indicates the measured photoacoustic absorption signal per incident laser power obtained with the Beckman-JPL cell as a function of MMH concentration in MMH-nitrogen mixtures at the CO_2 laser 10.4-μm band R8 and R10 lines. The photoacoustic signal per incident laser power values plotted at various MMH concentrations in Fig. 8 were taken, as in the UDMH measurements, from zero-time intercepts of plots such as shown in Figs. 9 and 10. The half-lives for decay of the UDMH or MMH absorption signals with sample residence time in the Beckman-JPL glass photoacoustic cells at each of the different UDMH and MMH concentrations studied were found to be 0.7 hour or longer. Thus, loss of UDMH or MMH on the walls of glass photoacoustic cells is not expected to be a significant problem in a real field instrument. These instruments will be operated in either a continuous-flow or a stopped-flow mode. The residence time for a sample gas in a field instrument that operates in a stopped-flow mode is expected to be at most a few minutes, since measurements will be performed only at several wavelengths with measurement times of only a few seconds per laser wavelength.

Photoacoustic response measurements performed with the Beckman-JPL photoacoustic cell on hydrazine-nitrogen mixtures indicate that hydrazine is nearly completely adsorbed or undergoes nearly complete degradation reactions on the cell walls within the 30-minute or greater time period that it takes to first fill the cell and then begin the photoacoustic measurements. For example, hydrazine-nitrogen mixtures prepared to yield hydrazine concentrations of 9.7, 46.6, and 89.5 ppm were found to give only background level signals of between 0.1 and 0.7 mV/W in the Beckman-JPL cell at the CO_2 laser 10.4-μm band P4, R4, R6, and R8 lines. On the basis of the photoacoustic responsivity data obtained for ethylene, UDMH, and MMH in the Beckman-JPL cell, along with the relative absorption cross sections of hydrazine to these compounds, photoacoustic signal per incident laser power values for hydrazine of between 2.4 and 46 mV/W would be expected under the foregoing conditions. Similarly, after sample residence times of up to 45 minutes, hydrazine-nitrogen mixtures

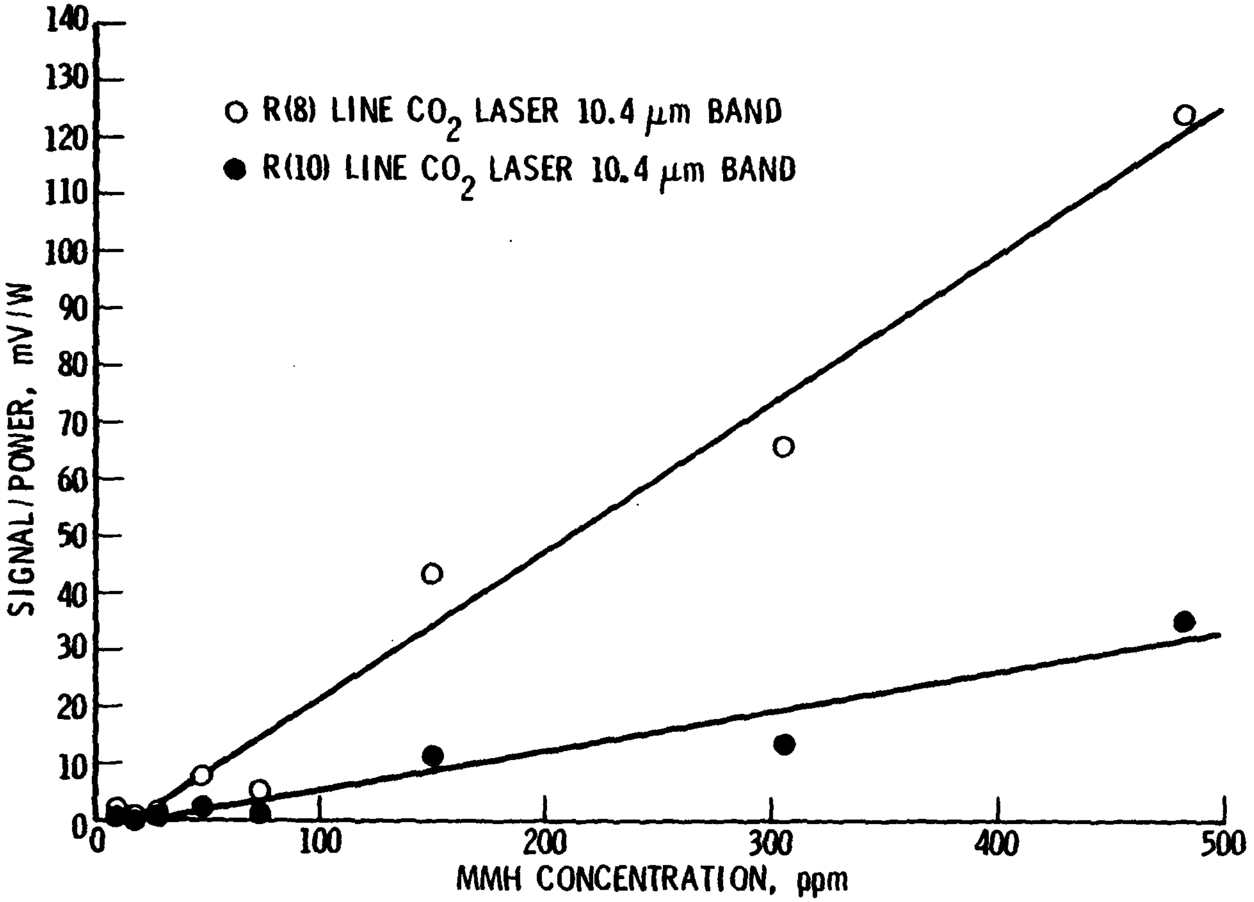


Fig. 8. Photoacoustic Response Versus MMH Concentration in Single Beckman-JPL Nonresonant Cell

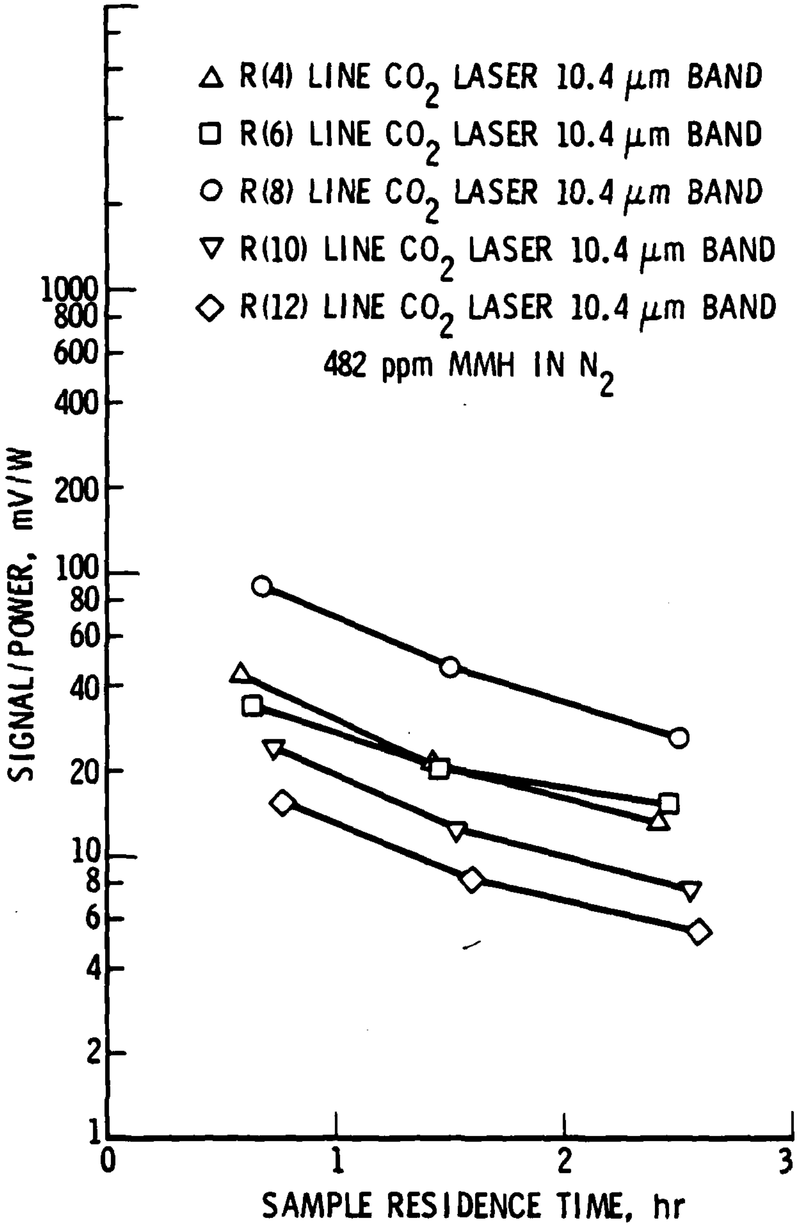


Fig. 9. High Concentration MMH Absorption Signal Versus Sample Residence Time in Beckman-JPL Cell

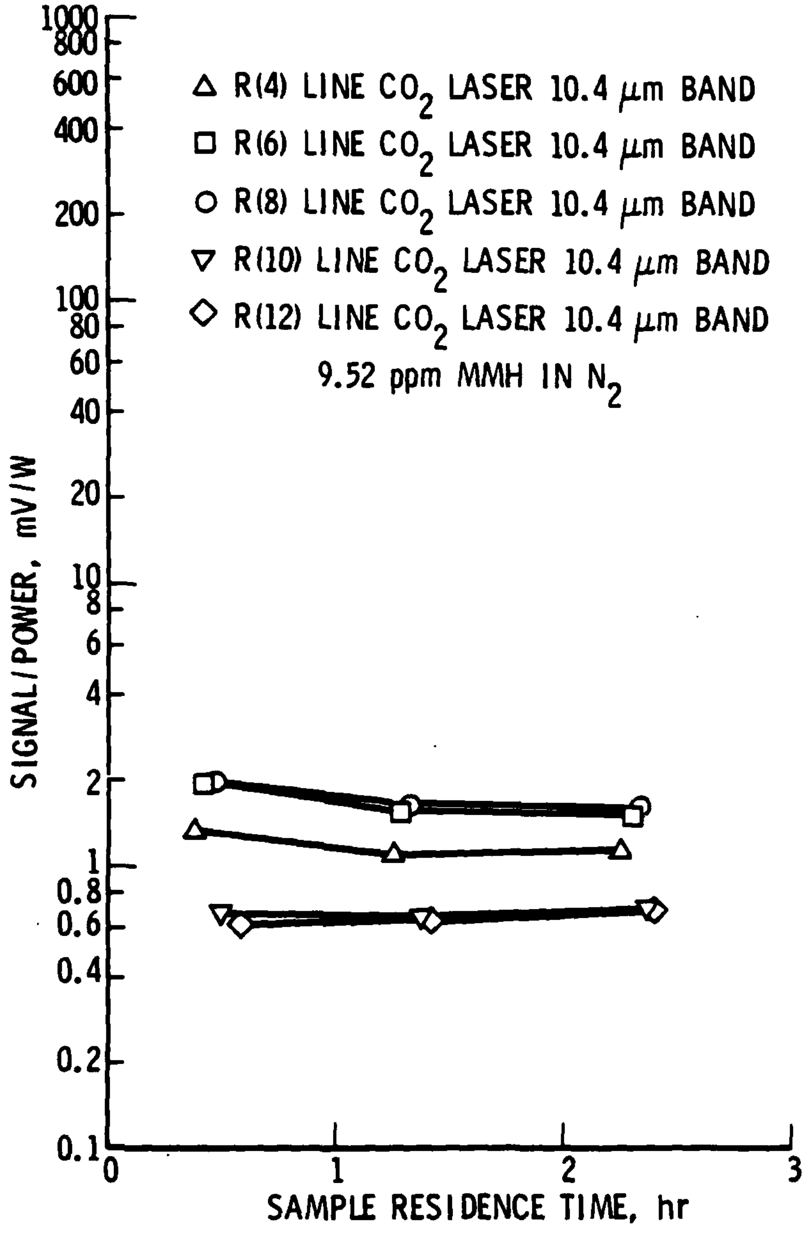


Fig. 10. Low Concentration MMH Absorption Signal Versus Sample Residence Time in Beckman-JPL Cell

prepared to have hydrazine concentrations of between 1000 and 1400 ppm gave photoacoustic responsivities about a factor of 10 lower than the approximately 560 to 1260 mV/W values expected. Figure 11 displays a semilog plot of the photoacoustic absorption signal per incident laser power as a function of residence time of a gas sample prepared to have an initial hydrazine concentration of 1420 ppm. Figure 11 indicates the relative intensities of the photoacoustic response after a sample residence time of about 1 hour at the CO_2 laser 10.4-μm band R8, R6, R4, and P4 lines were 0.80, 1.00, 0.49, and 0.31, respectively. An equal concentration mixture of ammonia and hydrazine would give a relative photoacoustic response of 0.81, 1.00, 0.51, and 0.31, respectively, at these same laser lines. Further work is needed to determine whether hydrazine is adsorbed or reacts significantly on glass photoacoustic cell walls for the expected field instrument sample residence times of a few minutes.

B. AEROSPACE CORPORATION NONRESONANT GLASS CELL

The measured photoacoustic absorption signals per incident laser power of a 10.5 ppm sample of ethylene in nitrogen were determined at the CO_2 laser 10.4-μm band lines P12, P14, P16, and P22 to be (prior to preamplification) 0.89, 5.11, 1.04, and 0.37 μV/W, respectively, with The Aerospace Corporation's nonresonant glass cell. When this cell was filled with nitrogen only, it gave a background photoacoustic absorption signal at each of these laser lines of approximately 0.05 ± 0.01 μV/W. These data indicate that this photoacoustic cell should provide noise equivalent detection sensitivities for ethylene of about 100 ppb at the CO_2 laser 10.4-μm band P14 line. The linearity of the photoacoustic response of this cell was confirmed by the good agreement between the relative ethylene absorption signals at the CO_2 laser excitation wavelengths used and the published absorption cross sections for ethylene at these wavelengths. The relative photoacoustic responsivities measured in the present study for 10.5 ppm ethylene in nitrogen at the CO_2 laser 10.4-μm band P12, P14, P16, and P22 lines were 0.16, 1.00, 0.19, and 0.06, respectively. The relative CO_2 laser absorption cross sections for ethylene in one atmosphere of nitrogen at these lines are 0.15, 1.00, 0.16, and 0.04, respectively.

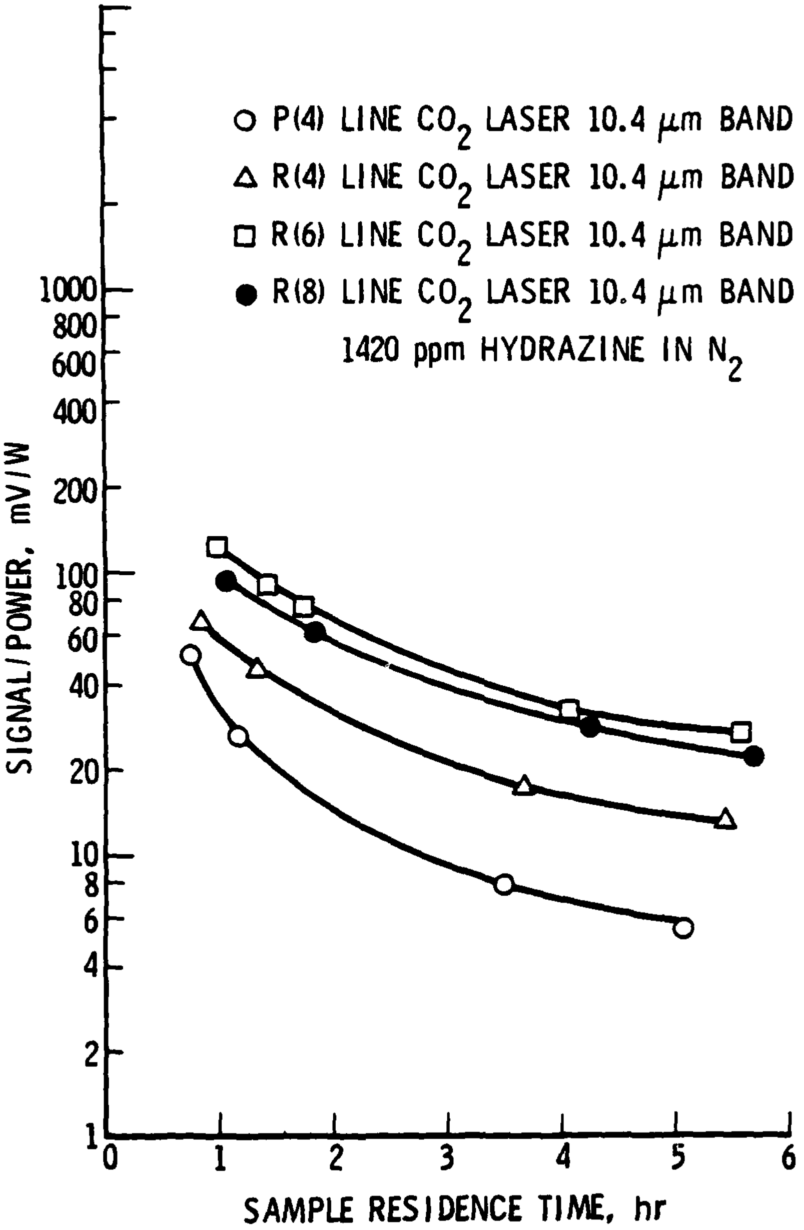


Fig. 11. High Concentration Hydrazine Absorption Signal Versus Sample Residence Time in Beckman-JPL Cell

The ethylene detection sensitivity of about 100 ppb obtained for this single nonresonant glass photoacoustic cell at the CO_2 laser 10.4-μm band P14 line is only 2.5 times lower than that obtained with a single Beckman-JPL photoacoustic cell. This ethylene detection sensitivity corresponds to detection sensitivities for each of the hydrazines of slightly below 1 ppm, or values approximately 30 times greater than desired for the hydrazines. As in the case of the Beckman-JPL photoacoustic cells, the detection sensitivities obtained with this single nonresonant glass cell are limited by background absorption produced by organic contaminants present in the cell when it is filled with pure dry nitrogen only. Possible sources for these contaminants are the electret microphone or the epoxy material used to bond the zinc selenide windows to the cell body.

Because both the condenser microphone-equipped Beckman-JPL cell and this electret microphone-equipped cell were found to give excessive background absorption signals on account of cell organic contamination, we next investigated the performance of the capacitance manometer-equipped stainless steel photoacoustic detection system that was assembled at Aerospace. The performance of this photoacoustic detection system is described in the following subsection.

C. AEROSPACE CORPORATION ASSEMBLED NONRESONANT STAINLESS-STEEL SYSTEM

Figure 12 exhibits the measured photoacoustic absorption signal per incident laser power (in units of mV/W) of The Aerospace Corporation's nonresonant stainless-steel photoacoustic detection system as a function of ethylene concentration in ethylene-nitrogen mixtures at the CO_2 laser 10.4-μm band P12, P14, P16, and P22 lines. This photoacoustic detection system exhibits a linear photoacoustic response from 11 ppm of ethylene (the highest concentration studied) down to ethylene concentrations as low as 2 ppb. The loss of linearity of the ethylene photoacoustic response at the CO_2 laser 10.4-μm band lines P12, P16, and P22 in Fig. 12 at low ethylene concentrations may be a result of incomplete canceling of the sample cell window absorption signals with those of the reference cell. The lack of complete nulling of the window absorption signals in these cells probably results from

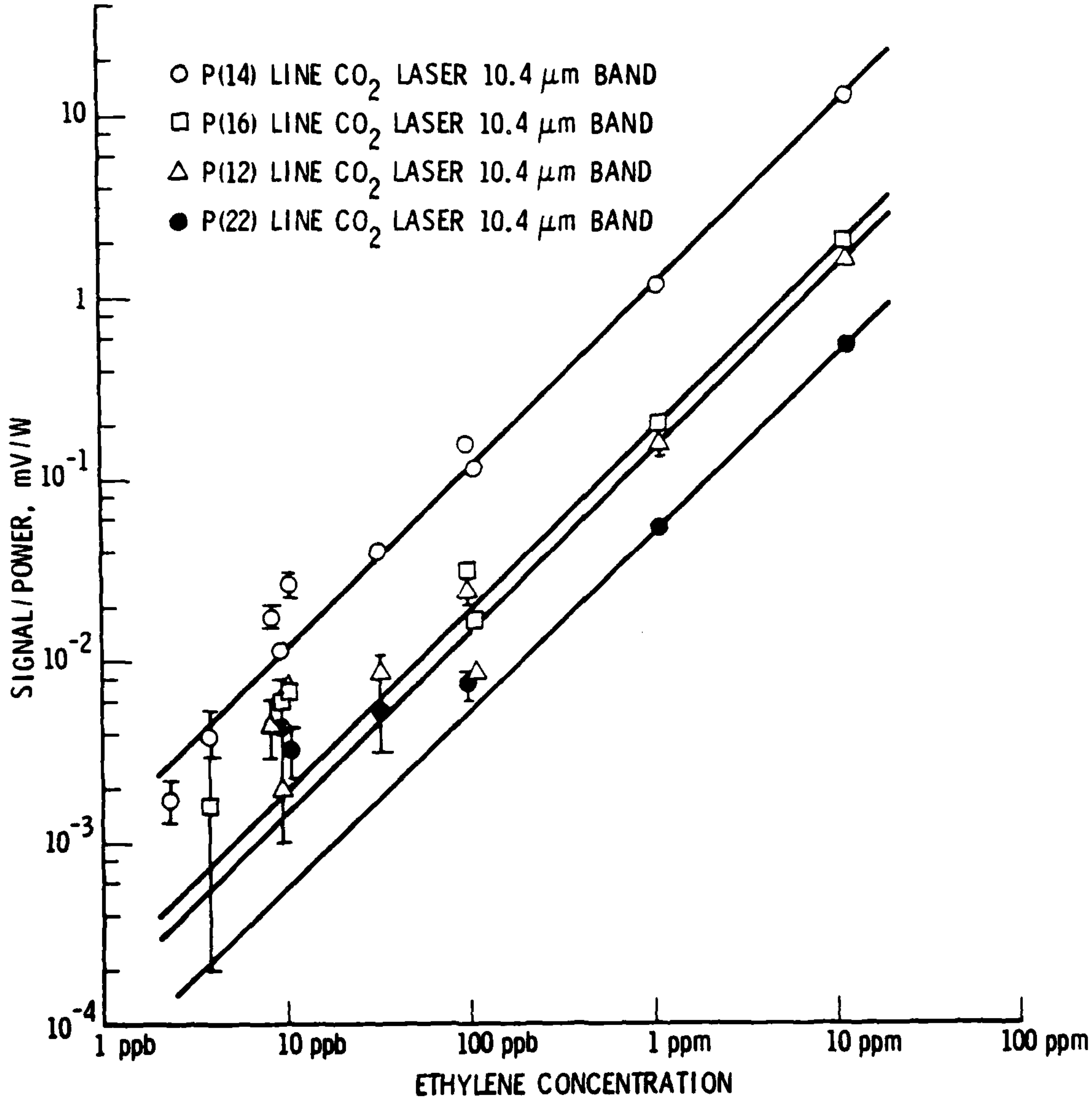


Fig. 12. Photoacoustic Response Versus Ethylene Concentration in Aerospace Nonresonant Stainless Steel System

up to a 6% greater incident laser intensity on the sample cell than on the reference cell. The different light intensities on these cells are caused by optical losses on the gold-coated mirrors used to direct the laser light through the reference cell after it exits the sample cell. At the various ethylene concentrations studied, the relative photoacoustic signals at the different laser excitation wavelengths used are generally within experimental error of the relative CO_2 laser absorption cross sections for ethylene at these wavelengths. The observation of measurable photoacoustic signals at the CO_2 laser 10.4-μm band lines P12 and P16 for ethylene concentrations below 10 ppb indicates that ethylene should be detectable at concentrations near 1 ppb at the CO_2 laser 10.4-μm band P14 line. The fact that ethylene has an absorption cross section of 29.10 cm^{-1} atm^{-1} at the P14 line, while UDMH, MMH, and hydrazine exhibit absorption cross sections of 3.95, 3.48, and 7.56 cm^{-1} atm^{-1} at the CO_2 laser 10.4-μm band lines P42, R8, and P4, respectively, indicates that this photoacoustic detection system should provide interference-free detection sensitivities below the 10 ppb level for each of the hydrazines.

An ethylene detection sensitivity of 1 ppb corresponds to a minimum detectable absorptivity value for this photoacoustic detection system of approximately 3×10^{-8} cm^{-1} W. This minimum detectable absorptivity value is 250 and 100 times lower than that obtained with the Beckman-JPL and The Aerospace Corporation's nonresonant glass photoacoustic cells, respectively. The use of a capacitance manometer with a 1 Torr differential head, instead of the 10 Torr head used here, together with more careful experimentation to minimize the background electronic noise that is currently the limiting noise source in this photoacoustic detection system, should permit minimum detectable absorptivity values near 1×10^{-9} cm^{-1} W to be attained. A photoacoustic cell of this minimum detectable absorptivity value would provide interference-free detection sensitivities for the hydrazines at levels below 1 ppb.

The measured photoacoustic absorption signal per incident laser power of The Aerospace Corporation's nonresonant stainless-steel photoacoustic detection system as a function of UDMH concentration in UDMH-nitrogen mixtures at the CO_2 laser 10.4-μm band P42 and P28 lines is shown in Fig. 13. Here

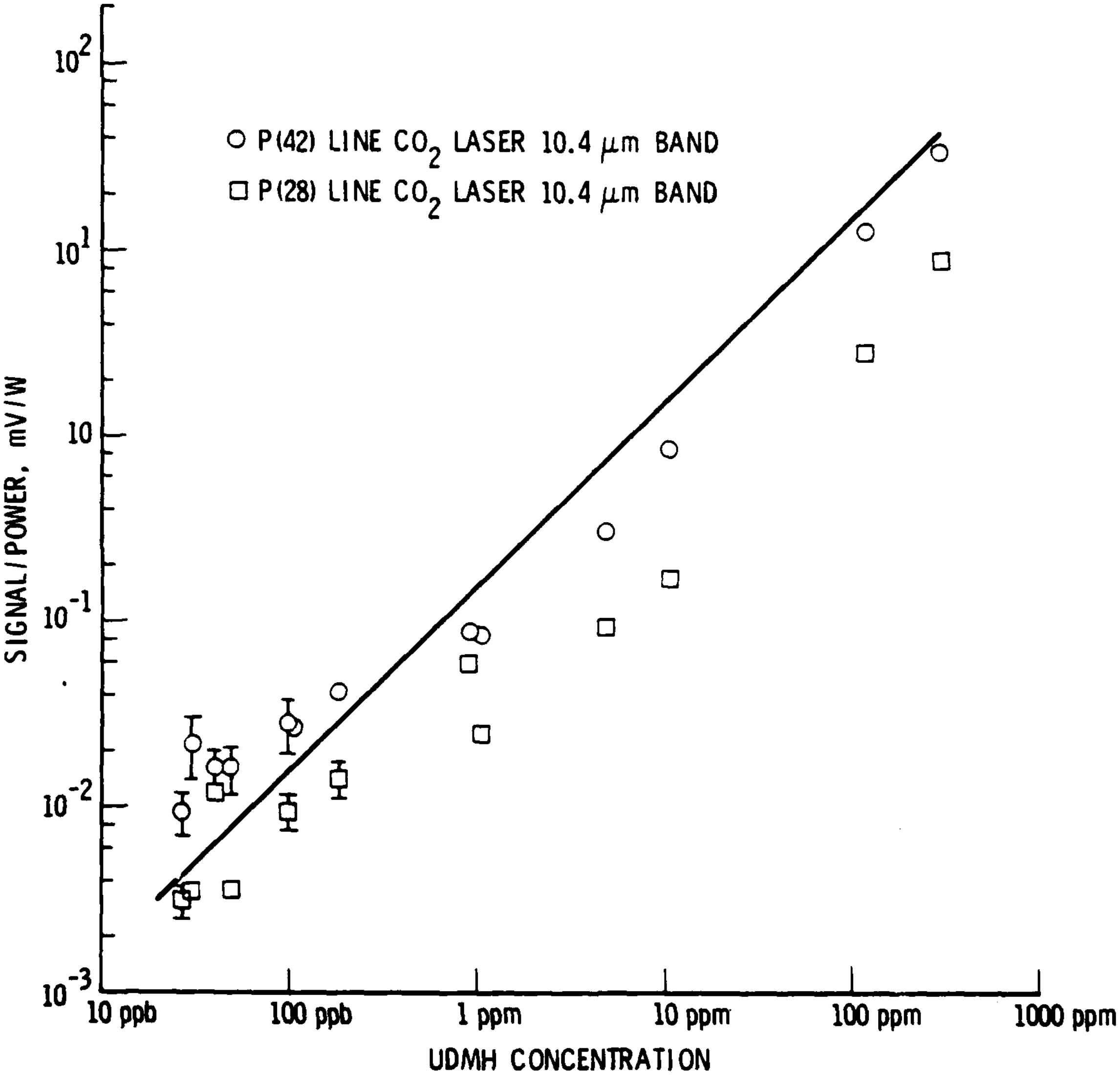


Fig. 13. Photoacoustic Response Versus UDMH Concentration in Aerospace Nonresonant Stainless Steel System

UDMH concentrations from near 300 ppm down to about 25 ppb were studied. The photoacoustic signal per incident laser power values plotted at various UDMH concentrations in Fig. 13 correspond to measurements taken for sample residence times of generally greater than 30 minutes. Attempts were not made to record photoacoustic signals in these studies over sufficiently long periods to allow extrapolation of these signals back to zero-time as was done for the studies on the Beckman-JPL photoacoustic detection system.

The solid line exhibited in Fig. 13 represents, on the basis of the relative absorption cross section data for UDMH and ethylene at the CO_2 laser 10.4-μm band P42 and P14 lines, respectively, the expected photoacoustic absorption signal strength at the CO_2 laser 10.4-μm band P42 line as a function of UDMH concentration. The absorption signals for UDMH in the higher concentration regime of Fig. 13 are believed to be lower than they should be because of partial adsorption or reaction of the UDMH on the photoacoustic cell walls. The loss of linearity in the UDMH absorption signals at low UDMH concentrations in Fig. 13, similar to that observed at low ethylene concentrations in Fig. 12, is believed to be partly because of incomplete canceling of the window absorption signals in the sample and reference cells. The relative UDMH photoacoustic signals in Fig. 13 at the CO_2 laser 10.4-μm band and P28 lines are observed, at the various UDMH concentrations studied, to be equal within experimental error to that expected on the basis of the previously measured UDMH absorption cross sections of 3.95 and 1.11 cm^{-1} atm^{-1} at these lines, respectively. The fact that the correct relative photoacoustic response for UDMH is observed at the P42 and P28 lines at a UDMH concentration of 25 ppb indicates that detectable UDMH signals should be attainable at concentrations of about 10 ppb, or well below the desired 60 ppb detection sensitivity, with the use of the CO_2 laser 10.4-μm band P42 line.

Preliminary photoacoustic measurements were also performed with both MMH and hydrazine in the nonresonant stainless steel photoacoustic detection system. These measurements indicated that MMH and hydrazine underwent substantial adsorption, reaction or both on the stainless steel cell walls during the approximately 30-minute time period between when the cells were filled and the first photoacoustic measurements were made. The absorption signals resulting from MMH and hydrazine were observed to decay nearly as rapidly in the stainless steel photoacoustic cells as hydrazine absorption decayed in the Beckman-JPL glass photoacoustic cells. Thus, before a photoacoustic field instrument can be developed that uses nonresonant stainless steel cells, further experiments will be needed to determine the extent to which MMH and hydrazine are adsorbed or react on the stainless steel photoacoustic cell walls during the anticipated field instrument sample residence times of a few minutes or less.

If it is found that significant adsorption or reaction of MMH or hydrazine occurs in nonresonant glass or stainless steel photoacoustic cells for sample residence times of a few minutes or less, alternative materials for the fabrication of nonresonant photoacoustic cells will need to be investigated. If significant MMH or hydrazine signal decay occurs during these short residence times, resonant photoacoustic cell designs should also be investigated. Resonant photoacoustic cells typically have surface to volume ratios as much as an order of magnitude lower than those of nonresonant photoacoustic cells. As a result, the extent to which the MMH or hydrazine absorption signals decay for a given sample residence time may be much lower in a resonant photoacoustic cell than in a nonresonant cell. In addition, resonant cells can be much more successfully operated in a continuous-flow mode than nonresonant cells. This is because background acoustical noise resulting from gas turbulence can be suppressed in a resonant photoacoustic cell, unlike in nonresonant cell, by locating the gas sample inlet and outlet ports at resonant cell acoustical node positions. Sample adsorption or reaction effects would be expected to be negligible for photoacoustic cells used in a continuous-flow mode.

V. CONCLUSIONS

Estimates made from CO_2 laser absorption cross section data for the hydrazines in a previous Aerospace study[1] indicated that CO_2 laser-based photoacoustic, long-path absorption, and lidar detection methods should provide the specificities and sensitivities required for real-time detection of hydrazine, MMH, and UDMH in workplace ambient air at the threshold levels adopted by ACGIH of 100, 200, and 500 ppb, respectively. The CO_2 laser photoacoustic technique was concluded to best provide the specificities and sensitivities necessary for the real-time ambient air detection of these compounds at the NIOSH recommended thresholds of 30, 40, and 60 ppb, respectively.

The capability of the CO_2 laser photoacoustic technique to detect the hydrazines at concentrations below the NIOSH recommended threshold levels was confirmed in the present laboratory study by the use of a photoacoustic detection system designed to minimize both the effects of spurious absorption at the photoacoustic cell windows and volatile organic contaminants from photoacoustic cell materials. The system possessed optically tandem sample and reference cells connected to a differential capacitance manometer. Dilution experiments carried out with the calibration gas ethylene in this apparatus indicated that the system has a minimum detectable absorptivity value of approximately 3×10^{-8} $cm^{-1} \cdot W$. By comparison of the ethylene absorption cross sections to those for the hydrazine fuels, it was concluded that interference-free detection sensitivities below the 10 ppb level should be possible for each of the hydrazines with the use of a detection system of similar minimum detectable absorptivity value. In confirmation of this conclusion, dilution experiments performed with UDMH in nitrogen demonstrated that this system can provide measurable UDMH photoacoustic absorption signals at both the CO_2 laser 10.4-μm band P42 and P28 lines for UDMH concentrations as low as 25 ppb. The fact that UDMH absorbs the P28 laser line about 3.6 times more weakly than the P42 laser line indicates that interference-free UDMH detection sensitivities below 10 ppb should be obtainable with this system with the use of the CO_2 laser 10.4-μm band P42 line. Interference-free detection sensitivities of less than 10 ppb are expected for hydrazine and MMH using photoacoustic detection systems of similar responsivity to that used here, but in which sample adsorption or reaction effects on the cell walls are minimized. Interference-free detection sensitivities for the hydrazines at levels below 1 pbb may be possible with the use of a photoacoustic detection system with a 1 Torr full range differential capacitance manometer instead of the 10 Torr full range head used here. It is concluded, on the basis of the results of the present study, as well as the previous Aerospace study,[1] that real-time detection sensitivities below the NIOSH recommended levels should be obtainable for each of the hydrazine-fuels, even in the presence of typical ambient air concentrations of water vapor and air pollutants by the CO_2 laser photoacoustic technique. CO_2 laser photoacoustic detection sensitivities in the ambient air down to the few ppb level for the hydrazines may be possible if the water vapor background absorption can be discriminated against by techniques such as Stark or frequency modulation spectroscopy.

REFERENCES

1. G. L. Loper, A. R. Calloway, M. A. Stamps, and J. A. Gelbwachs, "Expected Detectabilities of Hydrazine-Based Rocket Fuels and their Selected Oxidation Products by $^{12}C^{16}O_2$ Laser Spectroscopic Techniques," The Aerospace Corporation, TR-0079(4970-50)-2.

2. R. C. Shank, "Recent Advances in the Toxicology of N-Nitroso and Hydrazine Compounds," AMRL-TR-74-125, December 1974.

3. NIOSH Registry of Toxic Effects of Chemical Substances, 1977 Edition, Vol. II, U.S. Dept. of HEW.

4. National Safety News, Sept. 1977 (pp. 85-92), "Threshold Limit Values for Chemical Substances in Workroom Air," Adopted by ACGIH for 1977.

5. M. H. Mach, A. M. Baumgartner, "GC/GC-MS Analysis of UDMH Oxidation Products," Aerospace Technical Report (in preparation).

6. J. N. Pitts, Jr., D. Grosejean, K. Van Cauwenberghe, J. P. Schmid, and D. R. Fitz, *Environ. Sci. Technol. 12*, 946 (1977).

7. G. L. Loper, "Gas Phase Kinetic Study of Air Oxidation of UDMH," Proceedings of the Conference on Environmental Chemistry of Hydrazine Fuels, Tyndall AFB, CEEDO-TR-78-14, pp. 129-159, 13 September 1977.

8. G. L. Loper and M. A. Stamps, "Preliminary Studies of Vapor Phase Air Oxidation of Monomethylhydrazine," The Aerospace Corporation, ATM 79(4445-06)-3, 22 November 1978.

9. G. M. Wolten and M. Wun, "Potential Impact of Anticipated OSHA/EPA Actions on SAMSO Programs," The Aerospace Corporation, ATM 79(8303)-6, 22 August 1979.

10. (a) "NIOSH Recommendations for a Hydrazines Standard," Occupational Safety and Health Reporter, October 19, 1978, published by The Bureau of National Affairs, Inc.
    (b) NIOSH Manual of Analytical Methods, 2nd Edition, Vol. I - III, U.S. Dept. of HEW, 1977.

11. L. J. Luskus, "The Monitoring of Hydrazine Fuels in Air by Chemiluminescence," Paper presented at the Second Conference on Environmental Chemistry of Hydrazine, Tyndall AFB, Fla., February 15, 1979.

12. R. A. Saunders, J. J. De Corpo, B. J. Stammerjohn, and R. J. Kautter, "Evaluation of an Electrochemical Detector for Trace Concentrations of Hydrazine Compounds in Air," Naval Research Laboratory, Washington, D.C., NRL Report 8199, April 13, 1978.

13. Data Sheet UA-123, MDA Scientific, Inc., 808 Busse Hwy., Park Ridge, Ill. 60068

14. D. H. Fine, F. Rufeh, D. Lieb, and D. P. Roundbehler, Anal. Chem. 47, 1188-1191 (1975).

15. D. H. Fine, D. Lieb, and F. Rufeh, J. Chromatog., 107, 351-357 (1975).

16. G. Herzberg, Molecular Spectra and Molecular Structure: Vol. II. Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Company, Inc., New York (1945).

17. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Englewood Cliffs, N.J., Prentice Hall (1965).

18. R. Beck, W. Englisch, and K. Gürs, Table of Laser Lines in Gases and Vapors, 2nd ed., Springer Series in Optical Sciences, Vol. 2, Springer-Verlag Berlin Heidelberg, New York, 1978.

19. J. R. Durig, S. F. Bash and E. E. Mercer, J. Chem. Phys. 44, 4238 (1966).

20. J. R. Durig, W. C. Harris and D. W. Wertz, J. Chem. Phys. 50, 1449 (1969).

21. J. R. Durig, and W. C. Harris, J. Chem. Phys. 51, 4457 (1969).

22. L. B. Kreuzer, Anal. Chem. 46, 239A (1974).

23. N. S. Nogar, M. Fisher, and W. Jalenak, Laser Focus, February 1979, p. 56-60.

24. R. Gerlach and N. M. Amer, Appl. Phys. Lett. 32, 228 (1978).

25. L. J. Thomas III, M. J. Kelly, N. M. Amer, Appl. Phys. Lett. 32, 736 (1978).

26. D. R. Wake and N. M. Amer, Appl. Phys. Lett. 34, 379 (1979).

27. S. Shtrikman and M. Slatkine, Appl. Phys. Lett. 31, 830 (1977).

28. E. Kritchman, S. Shtrikman, and M. Slatkine, J. Opt. Soc. Am. 68, 1257 (1978).

29. C. F. Dewey, Jr., R. D. Kamm and C. E. Hackett, Appl. Phys. Lett. 23, 633 (1973).

30. R. D. Kamm, J. Appl. Physics 47, 3550 (1976).

31. M. S. Shumate, U. S. Patent 4,067,653, January 10, 1978.

32. T. F. Deaton, D. A. Depatie and T. W. Walker, Appl. Phys. Lett. 26, 300 (1975).

33. C. W. Bruce, B. Z. Sojka, B. G. Hurd, W. R. Watkins, K. O. White, and Z. Derzko, Appl. Optics 15, 2970 (1976).

34. R. Gerlach, and N. M. Amer, Paper WC4-1 presented at Topical Meeting of Photoacoustic Spectroscopy, August 1-3, 1979, Iowa State Univ., Ames, Iowa.

35. C. K. N. Patel and R. J. Kerl, Appl. Phys. Lett. 30, 578 (1977).

36. E. L. Kerr and J. G. Atwood, Appl. Optics 7, 915 (1968).

37. L. B. Kreuzer, N. D. Kenyon, and C. K. N. Patel, Science 177, 347 (1972).

38. C. K. N. Patel and R. J. Kerl, Appl. Phys. Lett. 30, 578 (1977).

39. R. A. Weagent and C. H. Beebe, Final Report Contract J-LEAA-025-73, Laser Optoacoustic Explosives Detection, November 1977.

40. R. R. Patty, G. C. Russwurm, W. A. McClenny, and D. R. Morgan, Appl. Optics 13, 2850 (1974).

41. R. J. Brewer and C. W. Bruce, Appl. Optics 17, 3746 (1978).

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry aerodynamics and heat transfer, propulsion chemistry and fluid mechanics, structural mechanics, flight dynamics; high-temperature thermomechanics, gas kinetics and radiation; research in environmental chemistry and contamination; cw and pulsed chemical laser development including chemical kinetics, spectroscopy, optical resonators and beam pointing, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and bioenvironmental research and monitoring.

Electronics Research Laboratory: Microelectronics, GaAs low-noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter-wave and microwave technology.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; component failure analysis and reliability; fracture mechanics and stress corrosion; evaluation of materials in space environment; materials performance in space transportation systems; analysis of systems vulnerability and survivability in enemy-induced environments.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the upper atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, infrared astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.