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PREFACE

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Calvin K. Cook and Ronald J. Kovein, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS) and the Division of Physical Sciences and Engineering (DPSE). Desktop publishing by Ellen E. Blythe.

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SUMMARY

During November 30 through December 2, 1994, the National Institute for Occupational Safety and Health (NIOSH) conducted a health hazard evaluation (HHE) at two Exxon service stations located in the greater Newark, New Jersey area. NIOSH investigators performed environmental monitoring to assess service station attendants' exposures to oxygenated gasoline that contained methyl tert–butyl ether (MtBE), which is an oxygenating compound blended with unleaded gasoline to help reduce vehicle emissions. Environmental measurements were made using two methods: (1) conventional air sampling (NIOSH Method 1615) and (2) video exposure monitoring with the use of real–time instrumentation.

Laboratory analysis of 21 personal breathing–zone (PBZ) air samples collected for total hydrocarbons (THC) as gasoline and MtBE revealed a geometric mean time–weighed average (TWA) concentration of 1.89 parts per million (ppm) (range: 0.43 – 4.43 ppm) for THC and a geometric mean TWA concentration of 0.38 ppm (range: 0.08 – 1.27 ppm) for MtBE. These concentrations for THC and MtBE were well below their most stringent exposure criteria of 300 ppm and 40 ppm, respectively. Real–time exposure monitoring results revealed a high variability of "relative" THC peak concentrations that were measured as high as 327 ppm. Video exposure monitoring demonstrated that the act of manual refueling is significantly responsible for exposures to oxygenated fuels, particularly peak exposures.

Although full–shift TWA sampling results indicated relatively low exposure concentrations for THC and MtBE, real–time measurements for THC revealed elevated peak concentrations, as much as 130 times greater than TWA concentrations. This suggests that similar conclusions can be drawn about MtBE peak exposures. NIOSH investigators concluded that it is not known whether a health hazard exists due to peak THC concentrations. Improvement of vapor recovery system effectiveness and attendant work practices suggested in this study could be applied to refueling operations throughout the industry to reduce exposures to oxygenated gasoline.

Keywords: SIC 5541 (Gasoline Service Stations) unleaded gasoline, oxygenated fuel, methyl tert–butyl ether, MtBE, service station attendants.

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INTRODUCTION

Most oxygenated gasoline marketed in the United States contains methyl tertiary butyl ether (MtBE). MtBE is blended with gasoline to formulate oxygenated fuel to increase octane rating and reduce motor vehicle carbon monoxide and other pollution emission by as much as 25%.[1] Since the enactment of the Clean Air Act Amendments of 1990, the U.S. Environmental Protection Agency (EPA) has mandated the use of oxygenated fuels (most of which contain MtBE) in 44 urban areas throughout the country where ambient levels of carbon monoxide are a major contributor to air pollution. Since the enactment of the Act, health complaints among service station attendants and self–service customers have increased drastically. Individuals affected generally experience acute health symptoms of nausea, headaches, respiratory depression, and eye irritation which they believe are attributable to oxygenated gasoline exposures.[1]

Full–shift time–weighed average (TWA) exposures to airborne MtBE have been well documented among service station attendants and self–service customers, using conventional air sampling methods. Air sampling has revealed 8–hour TWA exposures of less than 1 part per million (ppm), well below the most stringent 8–hour TWA exposure criteria of 40 ppm that is adopted by the American Conference of Governmental Industrial Hygienist's (ACGIH). However, since health complaints have increased, and toxicological data suggests that short–term or peak exposures can cause irritative symptoms, it was desirable to develop a measurement strategy to characterize short–term exposures. Also, it was hoped that characterizing short–term exposures would provide insight as to why reported symptoms do not seem to correlate with measured TWA exposure. The objective of this HHE was to assess service station attendant exposure to oxygenated gasoline using a video exposure monitoring technique. The specific aims of this study included: (1) characterizing short–term airborne exposures to oxygenated fuel, and (2) identifying specific emission sources and work practices that contribute to worker exposure. Currently there are no short–term MtBE exposure criteria established by the National Institute for Occupational Safety and Health (NIOSH) or the Occupational Safety and Health Administration (OSHA).

BACKGROUND

General

The United States currently consumes more than seven million barrels of gasoline each day and is the largest gasoline market in the world. Estimates of the number of automotive service stations in the U.S. range from 150,000 to 210,000. With the addition of government and private sector fuel dispensing facilities, the total number is estimated to be greater than 400,000.[1] Exposures associated with gasoline refueling can result from the following:

1. vapors displaced from filler tubes and gas tanks during refueling;

2. gasoline spills during refueling;

3. loss of vapors from vented underground storage tanks; and

4. evaporative and tailpipe emissions from motor vehicles.

Gasoline is a complex liquid mixture that can contain as many as 1500 individual hydrocarbons, each present at a different level and possibly reflecting a different level of toxicity.[2] A typical gasoline product may contain about 150 compounds. The exact compositions of gasolines vary from company to company and from season to season. Data composed from a variety of gasoline hydrocarbon blends result in a typical gasoline formulation of approximately 62% alkanes, 7% alkenes, and 31% aromatics.[2]

Various types of gasolines are formulated to achieve specific physical characteristics. In unleaded gasoline, MtBE is an oxygenating compound that is added to gasoline to increase the octane rating and to reduce emissions of carbon monoxide and other pollutants. MtBE is one of the fastest growing petrochemicals. Current demand is as much as 300,000 barrels per day, and the demand for MtBE is expected to increase throughout the 1990's, driven mostly by governmental regulations.[3]

In the late 1970's and early 1980's, petroleum refinery companies turned to MtBE to replace the octane that was lost when the EPA initiated a lead phase–down in gasoline to meet requirements under the 1990 Clean Air Act amendments. The 1990 Clean Air Act amendments involve 44 areas of the country that had not met the carbon monoxide emissions standards set by the EPA. Since November 1992, these areas are required to sell gasoline that has at least 2.7% oxygen content during winter months (October – March). MtBE is used as an oxygenated fuel additive in "reformulated" gasolines to reduce motor vehicle carbon monoxide emissions by as much as 25%.[3]

Previous Studies

This study was prompted by a series of industrial hygiene evaluations that were conducted by the NIOSH and the American Petroleum Institute (API).[4] In October 1990, NIOSH began conducting industrial hygiene assessments of service station attendants' exposures to hydrocarbons that included MtBE, benzene, toluene, and xylenes. In one particular study, API contracted for a parallel study to assess exposures to self–service customers. NIOSH and API made comparative studies that were conducted at service stations equipped with Stage II vapor recovery systems, and at service stations that were not equipped with vapor recovery. Stage II controls actively recover vapors released from a vehicle's gas tank when refueled. One of the objectives of these studies was to evaluate how well vapor recovery systems reduced personal exposure. Vapor recovery systems were developed and designed to control gasoline vapors emitted from the gas tank filler tubes of vehicles when saturated vapors are displaced during refueling.

The NIOSH and API studies revealed surprising results. After comparing exposure levels obtained at each service station and adjusting for exposure variables, such as climatic conditions and fuel composition, the NIOSH study determined that the vapor recovery systems had no effect on reducing exposures to hydrocarbons, including MtBE. In addition, the API study showed no significant reduction in self–service customer exposure to hydrocarbons at service stations equipped with vapor recovery, in comparison to hydrocarbon levels obtained at service stations without vapor recovery. Although worker exposures to specific hydrocarbons were measured below their respective exposure criteria, questions remained as to why the use of vapor recovery systems had little or no effect on reducing MtBE exposures. Based on the results of the NIOSH and API studies, it is believed that personal airborne exposures (workers and self–serve) are caused by gasoline spills from overfilling gasoline tanks of vehicles, or from tailpipe emissions. Because this has not been verified, the NIOSH study concluded that there is a need to focus on the extent to which specific sources contribute to personal airborne exposures.

In the NIOSH and API studies, NIOSH Sampling and Analytical Method 1615 was used to determine worker exposure to MtBE based on an 8–hour time–weighed average (TWA).[5] NIOSH Method 1615, the only available conventional air sampling method used to measure MtBE, is limited due to its minimum sampling period of about 45 minutes, which is based on the mean TWA concentration of previous air samples collected. Therefore, NIOSH Method 1615 is not capable of measuring short–term or peak exposures. Consequently, short–term and peak exposures were not measured during the NIOSH and API studies. Since a service station attendant only spends short periods of time (1 to 4 minutes) refueling vehicles, there is a need to characterize MtBE short–term exposures.

Conventional air sampling includes the use of an air sampling pump that draws sampled air past a media that is suited for collecting the air contaminants over a period of time. This method is integrated and measures worker average exposure to an air contaminant(s) over a full–shift work period of usually 8 to 10 hours. For this reason, only elevated averaged exposures to air contaminants over a full work–shift can be determined by conventional air sampling such as NIOSH Method 1615. The method does not identify transient peak concentrations which may be associated with specific work tasks.

Facility Selection and Description

An evaluation of oxygenated gasoline exposures was undertaken to estimate short–term exposure levels using real–time instrumentation. During November and December of 1994, exposure to total hydrocarbons (as gasoline) and MtBE was measured among service station attendants at two retail automotive service stations located in the greater Newark, New Jersey area. New Jersey was selected because it is one of only a few states that do not permit "self" service stations, thus significantly increasing the duration of attendant exposure. Also, the formulated gasoline marketed in this area has a MtBE content of 15%, the maximum proportion required by the EPA. The two stations were also identified based on their relatively high volume of gasoline sales.

The two service stations (A and B) were equipped with Stage II vapor recovery systems, and each pump was equipped with locking devices to allow automatic refueling. Station A is a fairly large facility comprised of four service islands (six pumps per island, total = 24) and employs about ten attendants (seven full–time, three part–time). These attendants dispense about 33,000 gallons of gasoline each week. Station B is a larger facility comprised of eight service islands (six pumps per island, total = 48) and employs about 14 attendants (10 full–time, 4 part–time) who dispense about 76,000 gallons of gasoline each week. Unlike other studies that evaluated oxygenated gasoline exposures at service stations, in this study the attendants' primary duty was to refuel vehicles, generally for an 8–hour work period.

Vapor Recovery Systems

Liquid gasoline volatilizes under normal conditions. Controlling fugitive gasoline emissions to the environment is one of the primary means of reducing human exposure to gasoline vapors. Stage I and Stage II controls are the two types of vapor recovery systems that are used at service stations.[1,6]

Gasoline vapors are released when tanker trucks or fuel storage tanks are filled. Gasoline evaporative emissions are captured by Stage I control systems and returned to the truck tank from which the liquid gasoline was transferred. Stage I systems have been installed at approximately two–thirds of the nation's bulk terminals, one–half of the nation's bulk plants, and one half of the nation's service stations.[1]

Stage II controls include a vapor hose attached to the filling nozzle which captures vapor emissions, returning them to service stations' storage tanks. Used in California and the District of Columbia since 1971, these systems are currently installed at about 38,000 of the nations service stations.[1]

Video Exposure Monitoring

Identifying an activity that causes an elevation in personal exposure can often be difficult, particularly if the activity lasts only a few seconds. Conventional air sampling methods can indicate a certain level of exposure. However, due to the complexity of the process or work cycle, activities contributing to exposure levels may not be identified.

NIOSH researchers have applied video exposure monitoring techniques during a variety of industry studies. Video exposure monitoring is a systematic air sampling strategy used to help identify specific sources and work activities that affect worker exposure. One video exposure monitoring technique uses response measurements from direct–reading air analyzers that have been connected to data logging instruments.[7] While a data logger records concentration measurements, a worker's activities are simultaneously recorded by a video camera. Later, the exposure measurement data collected by the data logger is downloaded to a personal computer for storage and statistical analyses. In addition to statistical analyses, the personal computer can superimpose a bar graph, proportional to the exposure measurement, upon the edge of each recorded video frame. By replaying the superimposed video recording, this technique can identify the tasks that elevate worker exposures to hazardous gases and vapors. These tasks can be coded to the data set as activity variables for subsequent statistical analysis. Video exposure monitoring allows repeated detailed review of the work cycle or process. Though not a substitute for conventional air sampling methods, video exposure monitoring can be a useful compliment to laboratory–analyzed sample media.

SUMMARY OF HEALTH EFFECTS AND EVALUATION CRITERIA

General

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are the following: (1) NIOSH Recommended Exposure Limits (RELs)[8] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs)[9] and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs)[10]. In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever is the most protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

A list of the substances evaluated in this survey is presented in Table I, along with a brief summary of primary health effects. For volatile organic compounds, only xylene was found in significant concentrations.

Gasoline

Harmful effects seen after exposure to gasoline are due to the individual chemicals that are in the gasoline mixture, such as benzene and lead.[11] Exposures of humans to 900 ppm for 1 hour caused slight dizziness and irritation of the eyes, nose, and throat.[12] Gasoline readily absorbs through the skin that may cause skin irritation. Inhalation of high levels of gasoline for short periods of time may cause harmful effects on the central nervous system (CNS) such as narcosis. The effects become more serious as the amount of gasoline inhaled increases. Nervous system effects have occurred in individuals who have been occupationally exposed to gasoline vapors for long periods of time.[12]

Some laboratory animals that breathed high concentrations of unleaded gasoline vapors continuously for two years developed liver and kidney tumors. However, there is no evidence that exposure to gasoline causes cancer in human. The International Agency for the Research of Cancer (IARC) concluded that some components of gasoline, especially benzene, are carcinogenic in humans, and concluded that gasoline is potentially carcinogenic in humans.[12,13]

Due to potential carcinogenic effects associated to gasoline exposures, NIOSH has not established a numerical REL, and instead recommends that exposures be kept at the lowest feasible level.[14] The ACGIH has established an 8–hour TWA exposure to gasoline at 300 ppm.[15] OSHA has not established a PEL for gasoline.

Methyl tertiary Butyl Ether (MtBE)

Methyl tert–butyl ether (MtBE) is a colorless, flammable liquid derived from the catalytic reaction of methanol and isobutylene. It is a volatile organic ether containing 18.2% oxygen and has a very low odor threshold (0.06 ppm).[16] MtBE is manufactured in petrochemical plants and refineries. Originally, it was used as a fuel additive to increase the octane grade following the mandated EPA lead phase–down, and is currently used to reduce air pollution.[17] MtBE has also been used in clinical medicine to dissolve cholesterol stones in the biliary tract.[18,19]

The primary route of exposure to workers is through inhalation which may occur during production, blending, transportation, distribution, and sale of gasoline. The primary source of potential exposure to the general public is from vapors of MtBE–blended gasolines.

Several animal studies have been performed to evaluate the toxicity of MtBE. In rats, the acute oral lethal dose (LD50) has been reported as 4 grams per kilogram. An acute lethal concentration (LD50) was reported from 23,630 to 33,000 ppm in air for a 4–hour period.[20,21] Studies performed with mice, rats, and rabbits indicate that the no observed effect level (NOEL) ranged from 800 to 2500 ppm.[22] MtBE was not found to be maternally toxic, embryo toxic, or teratogenic, and showed little adverse reproductive toxicity.[23,24]

In rats, the ethereal bond in MtBE is broken, producing tertiary butyl alcohol (TBA). MtBE and TBA concentrations in blood and brain of rats increased in a dose–dependent manner, although the MtBE concentration resulting from the 50 ppm exposures tended to decrease after a period of time. MtBE was also found in perirenal fat.[25]

Previous studies have measured airborne MtBE levels below 5 ppm at manufacturing plants and at marketing terminals. The mean full–shift PBZ exposures increased to 15 ppm and 31 ppm for refineries and marine barges, respectively.[26,27] A NIOSH investigation of service station attendants reported MtBE concentrations ranging from none detected to approximately 4 ppm in facilities which used gasoline containing 1% to 15% by volume of this additive.[28]

Acute exposures to MtBE may cause irritation to the skin, eyes, and mucous membranes. However, MtBE does not cause dermal sensitization. At extremely high concentrations, MtBE may induce CNS depression.[21] Based on the NOEL, the American Industrial Hygiene Association (AIHA) established a workplace environmental exposure level (WEEL) for MtBE of 100 ppm for an 8–hr TWA.[22] ACGIH has adopted a TLV of 40 ppm for MtBE, based on an 8–hour TWA exposures.[17] Currently, NIOSH and OSHA have not established exposure criteria for MtBE.

EVALUATION METHODS AND INSTRUMENTATION

Conventional Air Sampling

Environmental measurements were made at service stations A and B while station attendants performed routine refueling duties. A total of 21 personal breathing–zone (PBZ) and 6 area air samples for THC and MtBE were collected on 400 milligram (mg) charcoal tubes using personal air sampling pumps calibrated at a flow rate of 0.20 liters per minute (lpm). Area air samples were collected at service station islands atop refueling pumps. Three area air samples were collected and analyzed qualitatively for individual hydrocarbons. Based on qualitative analysis of the three area air samples, all PBZ samples were analyzed quantitatively by gas chromatography (GC) for gasoline vapor expressed as THC and for MtBE, in accordance with NIOSH Method 1615. Appendix A presents additional information regarding NIOSH Method 1615. Five quality control (QC) samples were submitted blindly for analysis along with the 21 PBZ air samples.

Six bulk gasoline samples were collected in 10 milliliter (ml) glass vials and later analyzed to determine the percent of MtBE by weight and by volume (LV). The six samples included two samples each of three gasoline grades available (octane ratings: 87, 89, and 93).

Video Exposure Monitoring

The Mini RAE® (RAE Systems, Inc., Sunnyvale, CA) model PGM–75 photo ionization detector (PID) was used to measure THC exposures using a 10.2 electron volt (eV) ultraviolet discharge lamp. The instrument was worn as a personal dosimeter by attendants while performing routine work activities. The Mini RAE® is a lightweight (18 oz), nonspecific instrument that will detect all components in gasoline vapors that have an ionizing potential less than 10.2 eV. For extended data logging operation, its analog output was connected to a Metrosonics® DL–3200 data logger which stored real–time data for up to 4 hours. The instrument was calibrated before each sampling period using the DL–3200 in the sense mode. In the sense mode, the DL–3200 obtained the exact input voltage level from the Mini RAE® instrument. One voltage level (160 – 170 mV) was the response to zero gas calibration; the other voltage level (180 – 200 mV) was the response to span gas calibration. Isobutylene (100 ppm) was supplied to the Mini RAE® during all calibrations. The DL–3200 was programmed for a 250–millisecond sampling rate. For every monitoring session, the average value was stored once every second. After each sampling period, real–time data was downloaded to an IBM compatible personal computer and plotted as a graph over time. Prior to each measurement period in the field, the lamp was cleaned with ethanol, and a one–point calibration was performed using 100 ppm of isobutylene span gas. See Appendix B for more details concerning Mini RAE® instrument specifications.

A total of 12.5 hours of videotape recorded the activities of five individual attendants. Eight separate data files, ranging from 78 to 240 minutes, were compiled at the two service stations. After reviewing the video recordings, four specific tasks of the refueling process were selected and coded into each data file so that each task's contribution to the cumulative exposures could be calculated. There are four primary tasks performed by attendants that included the following:

(1) gas cap removal/nozzle insertion;

(2) refueling/pumping;

(3) nozzle extraction/gas cap replacement; and

(4) other observed (i.e., transactions, checking hood, washing windshield).

These tasks are performed sequentially when there is only one vehicle at an attendant's service island. But when there are multiple vehicles, this 1–2–3–4 sequence is usually interrupted. Frequently, the attendant will leave a vehicle being refueled to repeat one or more of the same elements at another island. This usually occurred when other attendants needed assistance.

To determine how each of the four tasks affected the cumulative exposure, the real–time data was manipulated into a Microsoft® Excel® spreadsheet. The data set consisted of "relative" concentration measurements and a corresponding one second time interval. Each real–time measurement was coded to correspond to one of the four tasks. The cumulative time and exposure for each task were summed to determine average concentration.

Variable ambient conditions, such as wind velocity, temperature, and relative humidity complicate outdoor exposures. To address these potential problems, a weather station was established at one of sampling sites on each day of the study. Ambient conditions were recorded about every hour on each day of measurements.

RESULTS AND OBSERVATIONS

Conventional Air Sampling

Results of personal air sampling for THC and MtBE are presented in Tables I and II. The 21 THC PBZ results ranged from 0.60 ppm to 6.17 (geometric mean = 1.89 ppm), well below the ACGIH–TLV of 300 ppm. TWA PBZ samples (n=21) for MtBE ranged from 0.12 to 1.42 ppm (geometric mean = 0.38 ppm), well below the ACGIH–TLV of 40 ppm. Area air samples (n=3) for MtBE and THC revealed TWA concentrations that ranged from 0.08 to 0.24 ppm and 0.43 to 1.36 ppm, respectively. The results of quality control samples were within the upper and lower confidence limits of control charts. A summary of bulk gasoline analysis determined the MtBE liquid volume percent (LV%) and the percent by weight of each sample. The MtBE LV% ranged from 15% to 18% (arithmetic mean = 16%) and the % by weight ranged from 16% to 19% (arithmetic mean = 17%).

Video Exposure Monitoring

Figure 1 illustrates a typical refueling cycle. Figures 2–7 characterize the exposure for the three basic job tasks (Tasks 1–3). The real–time data show the nature and variability of peak total hydrocarbon exposures. Tasks 1 and 3 are brief in duration, usually about 8 seconds for each task. The time it takes an attendant to dispense gasoline varies according to the volume being pumped. The average refueling time is about 3–4 minutes.

Based on detailed analysis of all real–time data collected, Figures 8 and 9 summarize the contribution of the individual tasks of the refueling operation to the total activity time and total cumulative exposure. While accounting for only about 25% of the total activity time, Task 2 (refueling/pump) was responsible for about 44.9% of the total cumulative exposure. While accounting for 63.8% of the total activity time, Task 4 (other observed) contributed about 39.6% of the total cumulative exposures. The two tasks involving the removal and replacement of gas cap only contributed about 6.8% and 8.7% of cumulative exposures, respectively.

The exposure data spreadsheets were reviewed and elevated peak exposure concentrations (greater than 50 ppm) were collected and summed according to each task. Figure 10 is a pie chart that summarizes the frequency of peak THC exposures. According to this illustration, Task 2 (refueling) accounts for about 73.2% of all peak exposures, thus being greatly responsible for creating peak exposures. Peak exposures were generally 1 to 2 seconds in duration.

Table III presents the ambient measurements taken every hour for temperature, relative humidity, wind speed and direction. These data show that ambient conditions were not extreme or highly variable during the two days of this study; therefore, it is likely that these conditions did not complicate exposures.

DISCUSSION

Manually dispensing fuel (Task 2) had a task duration at only 25% of the total time. However, despite a relatively short duration time, Task 2 produced the largest proportion of exposure for the operation due to the magnitude of the average concentration measured for this task. Furthermore, Task 2 accounted for about 73.2% of peak THC exposures greater than 50 ppm. Controlling this task would be the main priority for controlling gasoline exposures to attendants during the refueling process.

Exposures associated to Tasks 1 and 3 (cap removal /replacement) cannot be avoided by attendants and self service customers, but exposures during Tasks 2 and 4 can be minimized and largely avoided. While performing Tasks 2 and 4, we observed that attendants had a control over their exposure proximity to the source (gasoline pump). Obviously, an attendant must be near the source of exposure when removing the gas cap and inserting the nozzle into the fuel tube. But once the nozzle has been triggered, and the refueling locking device is used, the attendant need not watch the meter close–up. In fact, the attendant can remain a considerable distance (6 to 8 feet) away from the pump and still observe the island meter display unit or hear the audible "click" of the nozzle when it shuts off automatically. An example of this scenario is illustrated in Figure 11 where an attendant was observed refueling a vehicle in the automatic mode. During the first 30 seconds of refueling, the attendant was not manually pumping, but he was standing in close proximity to the active refueling pump while reading the meter display. After the first 30 seconds of refueling process, the attendant stepped a few feet away from the pump source and continued to watch the meter display. When the attendant was in proximity to the refueling source, peak THC exposures were as high as 217 ppm. But when he decided to move just a few feet away from the refueling source, his exposures decreased to less than about 40 ppm.

The islands at both stations were equipped with computerized systems that allowed dollar amounts ($5, $10, and $20) to be keyed in by an attendant, and once the pump has been triggered by the attendant, refueling a given dollar amount was performed automatically without the attendants' need to be close to the refueling. Observations from this study also show that four of the five attendants evaluated stood routinely in proximity (less than 2 to 3 feet) to the pump while refueling in the automatic mode. The attendant who routinely stood away from refueling pumps had peak and average exposures lower than the other four attendants evaluated.

Based on previous NIOSH studies, gasoline spills during the refueling process were expected to contribute significantly to exposures. The absence of gasoline spills during this evaluation may be the result of improved dispensing nozzles or that the attendants were experienced at properly performing refueling tasks. Attendant THC exposures from vehicle exhaust emissions were also expected. Review of the video exposure monitoring data suggests that vehicle exhaust emissions did not contribute to exposures. This is likely due to the requirement that customers shut off their vehicles prior to refueling.

Finally, limitations of this study should be addressed. The video exposure monitoring technique uses "relative" THC real–time measurements as a surrogate to characterize short–term oxygenated fuel exposures. Due to constraints of the real–time instrument used for this study, "absolute" quantitative short–term exposure data could not be obtained specifically for MtBE; however, surrogate measurements suggest elevated concentrations of peak gasoline exposures. Also, the THC exposure data are referenced to 100 ppm of isobutylene. For future studies to determine quantitative exposure data specifically for THC and MtBE, the use of a portable GC/MS may be desirable.

CONCLUSIONS AND RECOMMENDATIONS

Consistent with previous studies, full–shift TWA sampling results indicated low exposure concentrations for THC and MtBE. However, real–time monitoring results indicated that elevated short–term or peak THC exposures may be more than 130 times greater than TWA concentrations for 1 to 2 seconds in duration. Similar inferences can be drawn about MtBE peak exposures. Since the mean TWA concentration for MtBE is about 0.50 ppm, estimated peak exposures may be as high as approximately 70 ppm. However, there is no human toxicity data available that suggests brief peak MtBE exposure to 70 ppm causes symptoms reported by attendants and self–service customers.

Based on the frequency of elevated peak THC exposures measured, it is concluded that peak exposures to oxygenated gasoline do occur during refueling, even in the presence of Stage II Vapor Recovery Systems. Because of the THC concentrations measured during this study, and based on the conclusions of previous NIOSH and API studies, it is believed that vapor recovery systems may not be effective in controlling gasoline vapor emissions. A similar study may be necessary to evaluate the effectiveness of Stage II Vapor Recovery Systems. Until these controls are improved, service station attendants and self–serve customers should avoid manual pumping when possible to avoid elevated gasoline vapor exposures. This can be achieved by using automatic refueling locking devices and improving refueling practices by standing at a distance of at least 6 to 8 feet upwind from active refueling pumps.

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Table I
Air Sampling Results
for Gasoline Vapors at
Service Station "A"
November 29–December 2, 1994

Sample Location	Sample Type	Sampling Time (minutes)	Sample Flow Rate (liters per minute)	Sample Volume (liters)	Concentration, parts per million (ppm)	
					Methyl tert–Butyl Ether	**Total Hydrocarbons (as gasoline)**
Attendant	PBZ	453	0.20	90.6	0.37	1.57
Attendant	PBZ	458	0.20	91.6	0.23	1.11
Attendant	PBZ	240	0.20	48.0	1.27	4.43
Attendant	PBZ	440	0.20	88.0	0.66	2.68
Attendant	PBZ	171	0.20	34.0	0.48	1.91
Attendant	PBZ	452	0.20	90.4	0.55	2.26
Attendant	PBZ	455	0.20	91.1	0.80	3.44
Attendant	PBZ	404	0.20	80.8	0.69	3.06
Attendant	PBZ	334	0.20	66.8	0.29	1.36
Attendant	PBZ	340	0.20	68.0	0.40	1.96
Refueling pump	Area	399	0.20	79.8	0.08	0.43
Refueling pump	Area	450	0.20	90.0	0.24	1.36
Arithmetic Mean Concentration					0.51	2.11
Geometric Mean Concentration					0.41	1.87
Exposure Criteria (expressed in milligrams per cubic meter)						
AIHA Workplace Environmental Exposure Level (WEEL)					100	NA
NIOSH Recommended Exposure Limit (REL)					NA	LFC
OSHA Permissible Exposure Limit (PEL)					NA	NA
ACGIH Threshold Limit Value (TLV)					40	300

Abbreviations:
NA = Exposure criteria not available
PBZ = Personal Breathing–zone
LFC = Lowest Feasible Concentration

Table II
Air Sampling Results for Gasoline Vapors at Service Station "B"
November 29–December 2, 1994

Sample Location	Sample Type	Sampling Time (minutes)	Sample Flow Rate (liters per minute)	Sample Volume (liters)	Concentration, part per million (ppm)	
					Methyl tert–Butyl Ether	Total Hydrocarbons (as gasoline)
Attendant	PBZ	452	0.20	90.6	0.12	0.60
Attendant	PBZ	315	0.20	63.0	0.53	3.44
Attendant	PBZ	381	0.20	76.2	0.58	2.83
Attendant	PBZ	500	0.20	100	0.72	2.84
Attendant	PBZ	184	0.20	36.8	1.14	5.86
Attendant	PBZ	322	0.20	64.4	1.42	6.17
Attendant	PBZ	313	0.20	62.6	0.14	1.27
Attendant	PBZ	373	0.20	74.6	0.14	1.07
Attendant	PBZ	559	0.20	112.0	0.16	1.67
Attendant	PBZ	314	0.20	68.8	0.44	2.39
Attendant	PBZ	197	0.20	39.4	0.26	1.08
Refueling Pump	Area	483	0.20	96.6	0.24	1.00
Arithmetic Mean Concentration					0.49	2.52
Geometric Mean Concentration					0.36	1.97
Exposure Criteria (expressed in milligrams per cubic meter)						
AIHA Workplace Environmental Exposure Level (WEEL)					100	NA
NIOSH Recommended Exposure Limit (REL)					NA	LFC
OSHA Permissible Exposure Limit (PEL)					NA	NA
ACGIH Threshold Limit Value (TLV)					40	300

Abbreviations:
NA = Exposure criteria not available
PBZ = Personal Breathing–zone
LFC = Lowest Feasible Concentration

Table III
Outdoor Ambient Conditions

Location	Date	Time	(°F)	RH%	Wind Velocity (mph)	Wind Direction (from)
Station #1	11/30/94	8:12 a.m.	47	39	2	West
		9:31	53	28	3	West
		10:15	55	24	3	West
		10:52	54	24	3	West
		12:40 p.m.	55	24	5	West
		1:45	54	24	6	West
		2:45	52	23	9	West
		3:50	56	22	7	West
Station #1	12/01/94	6:58 a.m.	34	53	3	Southwest
		7:38	35	54	3	South
		8:20	47	39	2	South
		10:30	43	35	9	South
		12:28 p.m.	46	35	6	Southwest
		2:30	47	34	11	Southwest
		4:40	46	33	4	Southwest
Station #2	12/02/94	7:25 a.m.	36	60	2	West
		8:45	40	60	5	West
		9:45	44	54	6	West
		10:40	49	46	4	West
		1:28 p.m.	57	32	10	West

Figure 1

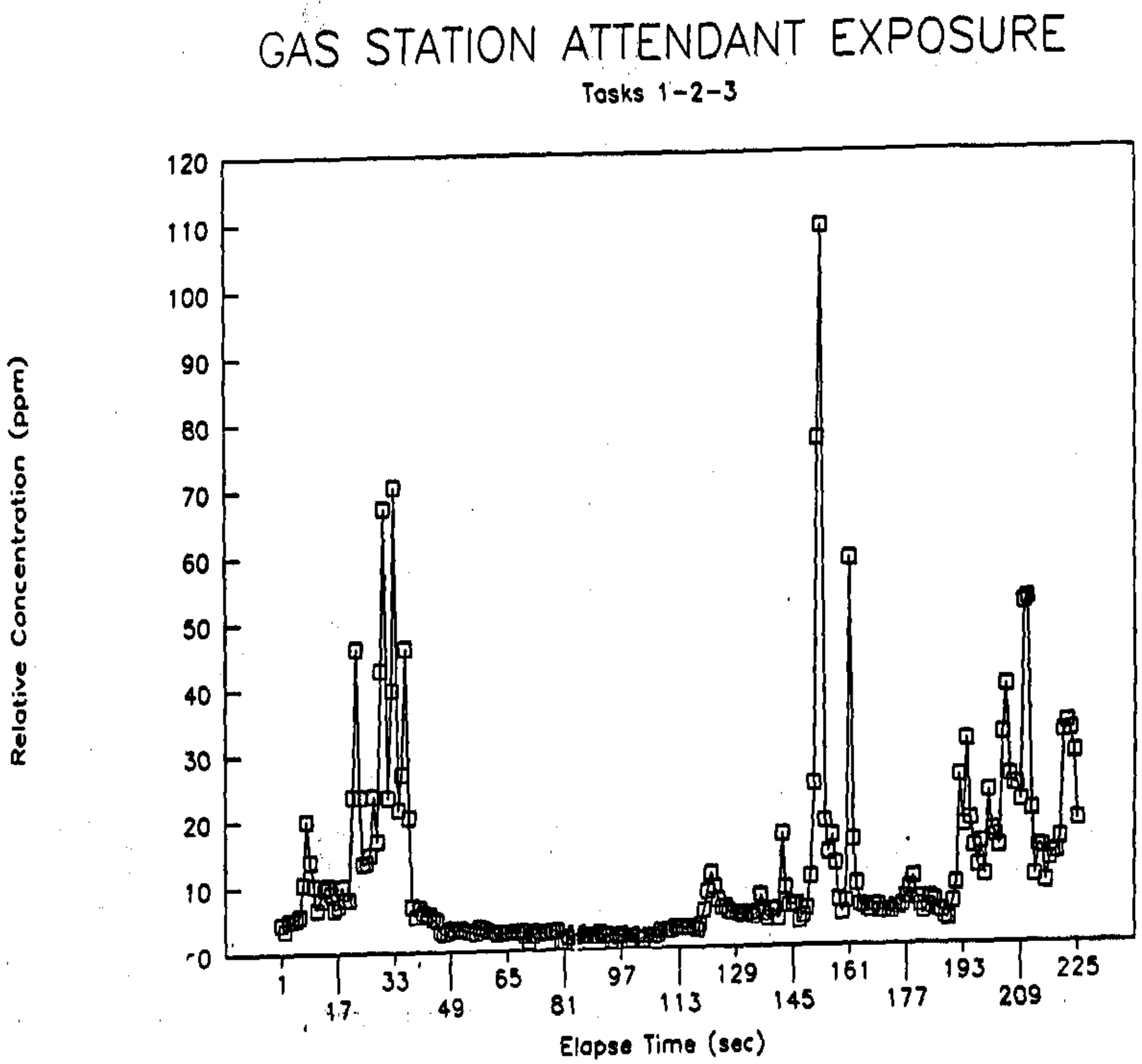

GAS STATION ATTENDANT EXPOSURE
Tasks 1-2-3
Relative Concentration (ppm)
120
110
100
90
80
70
60
50
40
30
20
10
0
1
17
33
49
65
81
97
113
129
145
161
177
193
209
225
Elapse Time (sec)

Figure 2

GAS STATION ATTENDANT EXPOSURE

Task 1: Nozzle Insertion

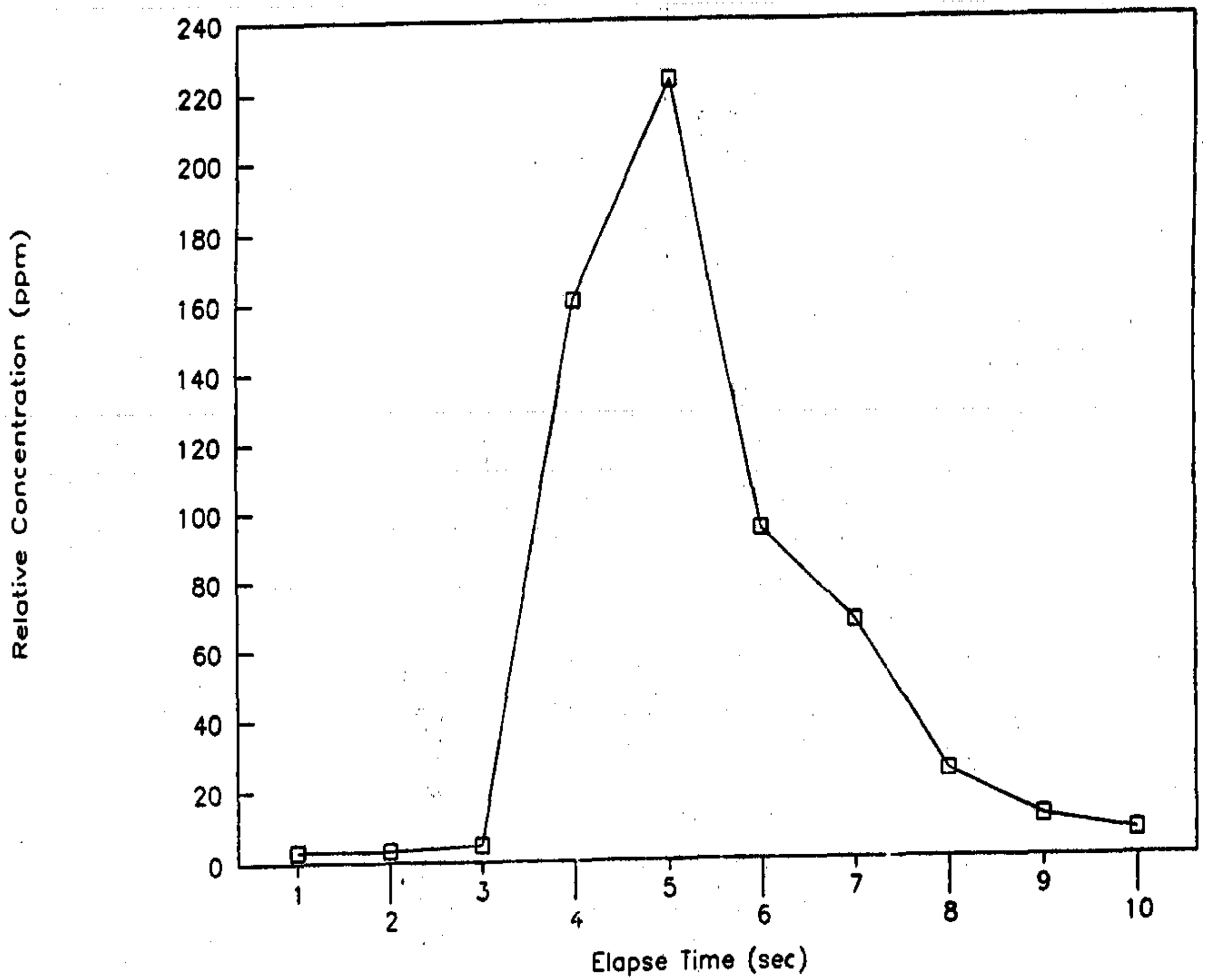


Figure 3

GAS STATION ATTENDANT EXPOSURE

Task 1: Nozzle Insertion

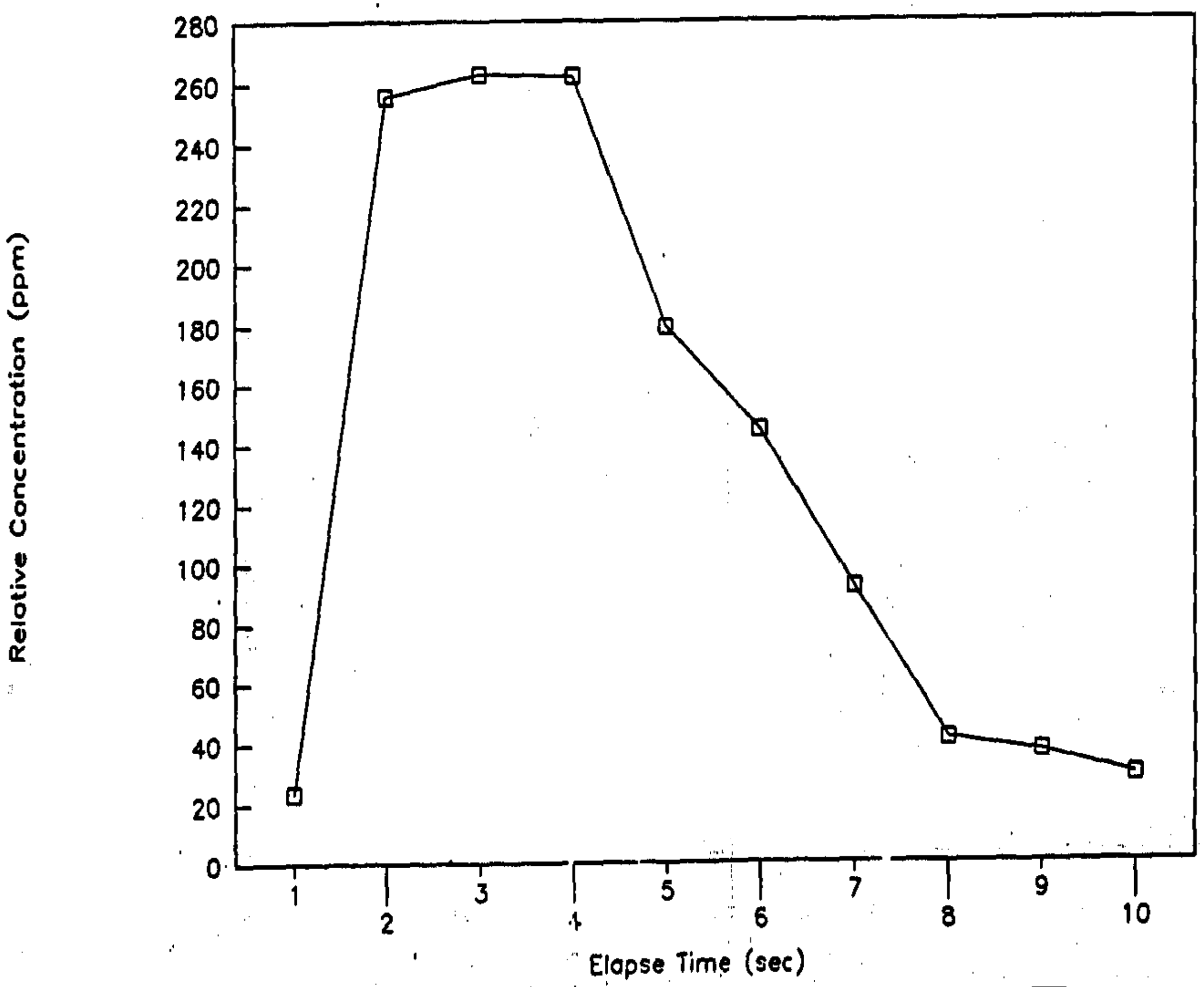


Figure 4

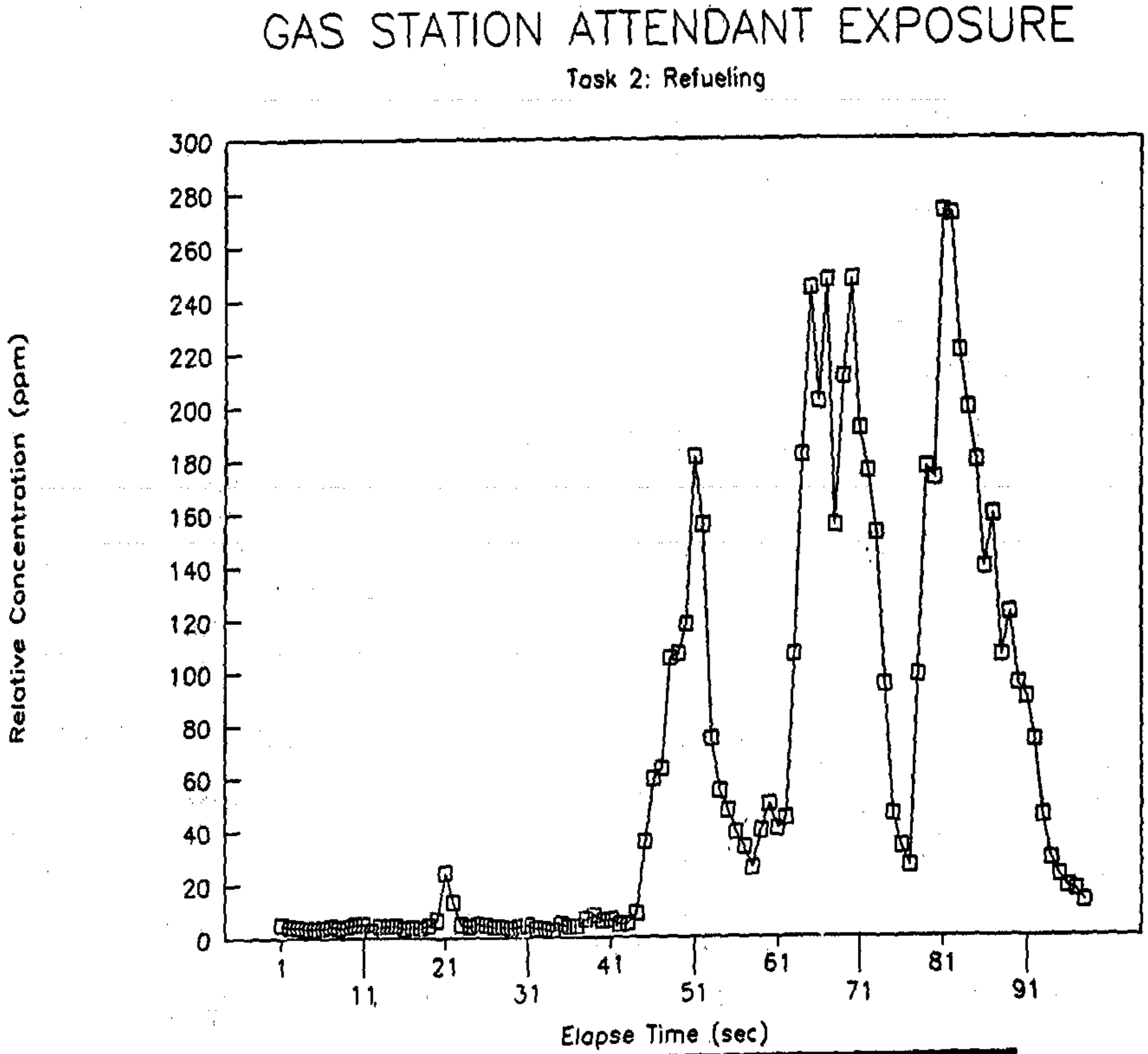

GAS STATION ATTENDANT EXPOSURE
Task 2: Refueling
Relative Concentration (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
1
11
21
31
41
51
61
71
81
91
Elapse Time (sec)

Figure 5

GAS STATION ATTENDANT EXPOSURE

Task 2: Refueling

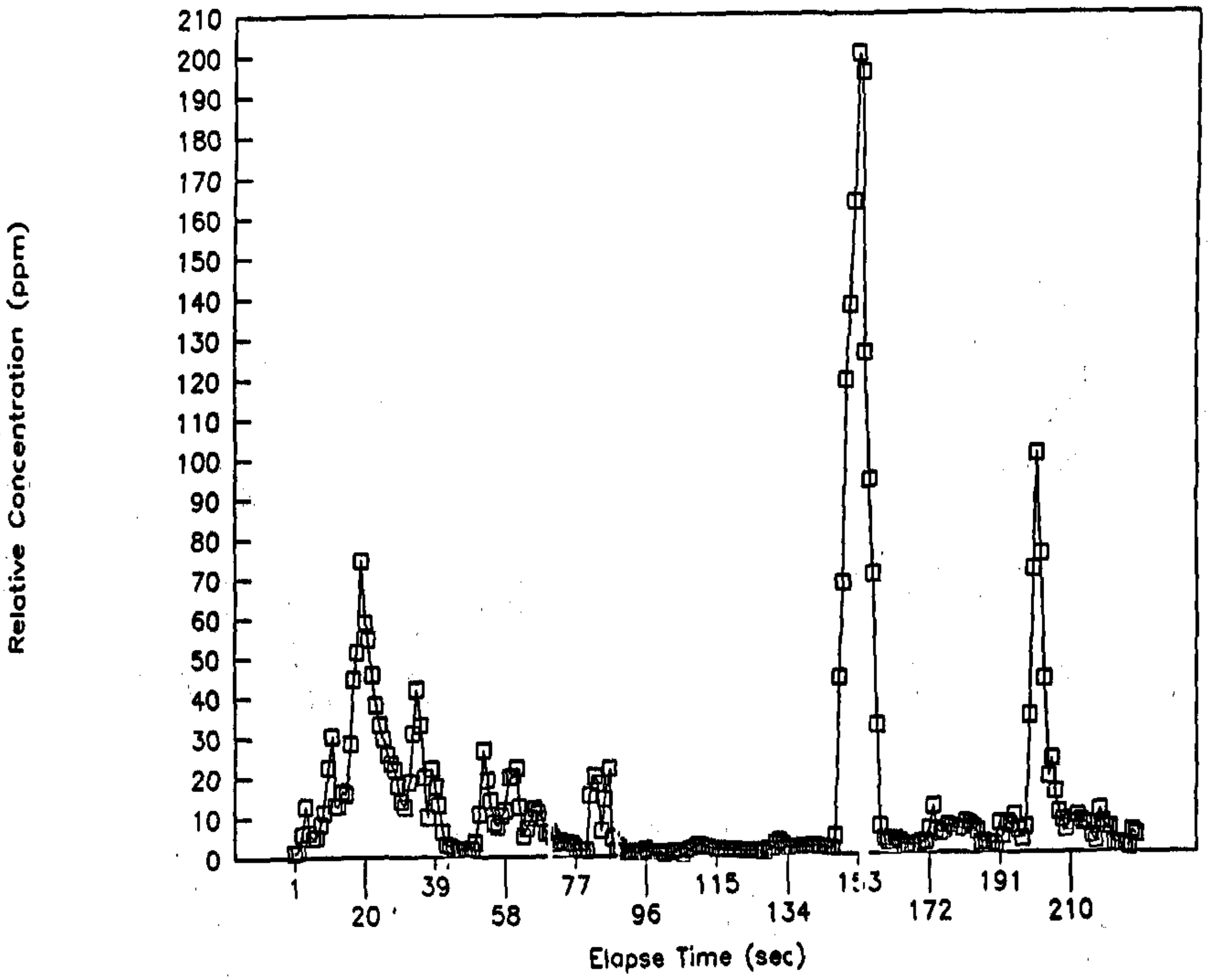


Figure 6

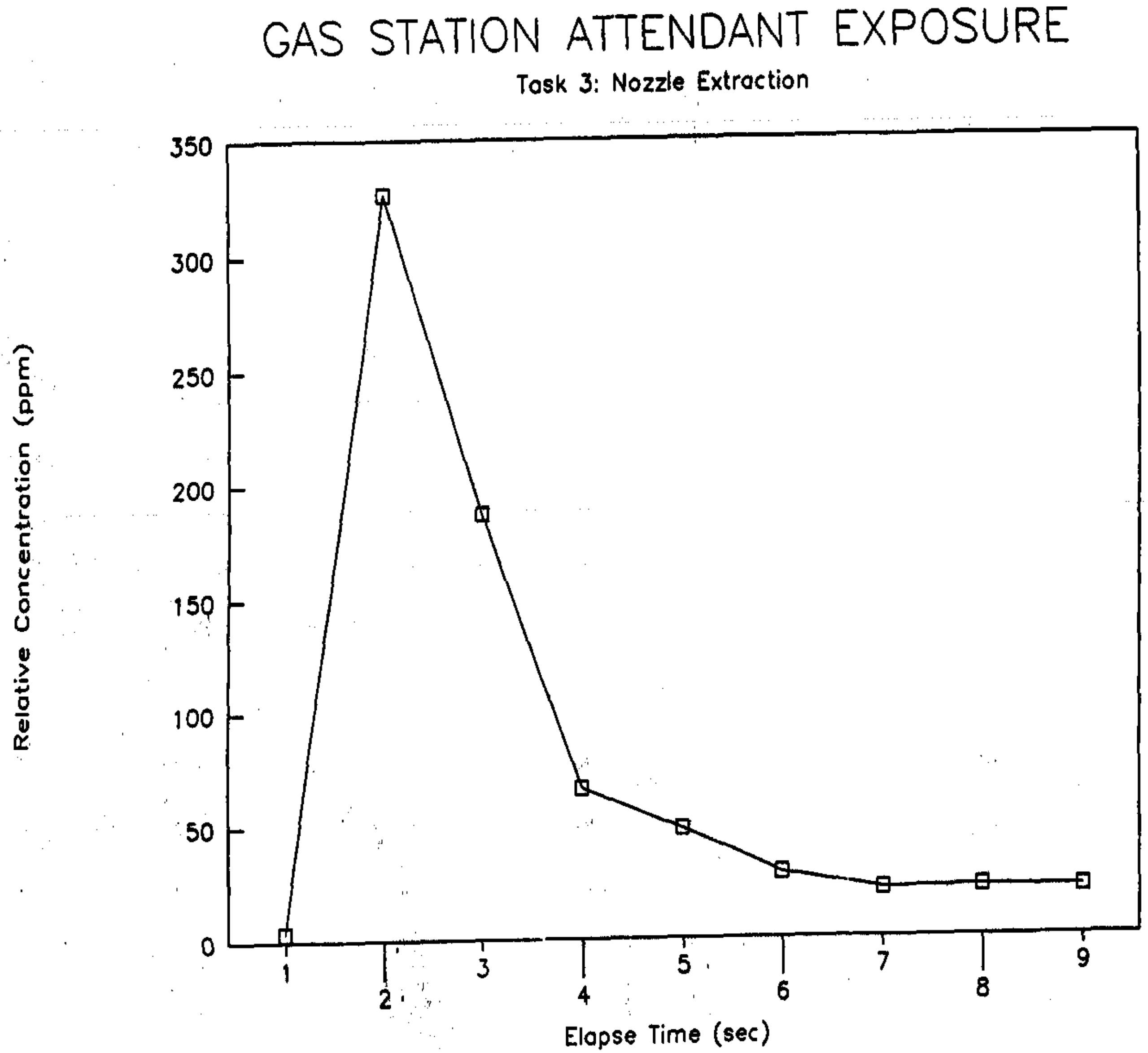

GAS STATION ATTENDANT EXPOSURE
Task 3: Nozzle Extraction
Relative Concentration (ppm)
350
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
Elapse Time (sec)

Figure 7

GAS STATION ATTENDANT EXPOSURE

Task 3: Nozzle Extraction

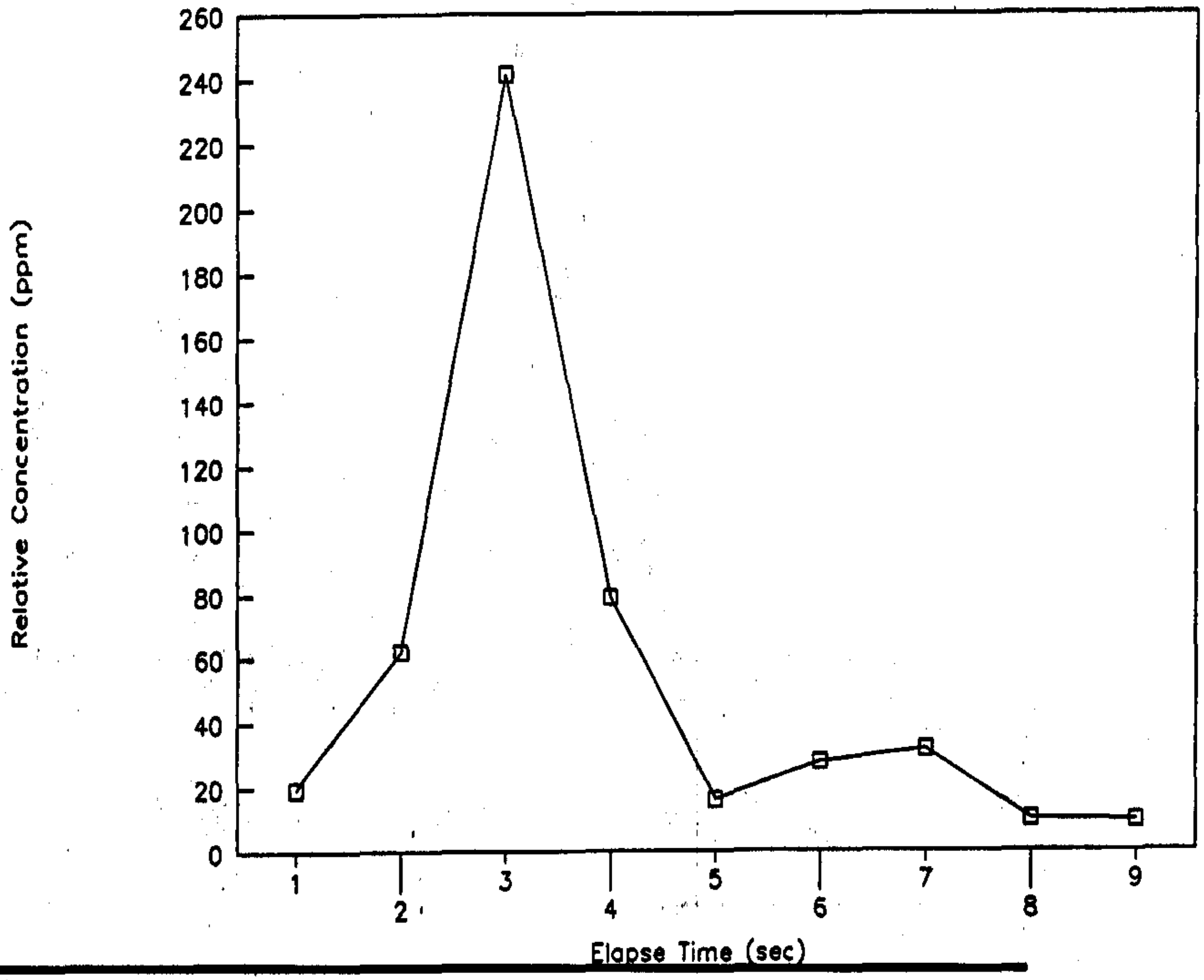
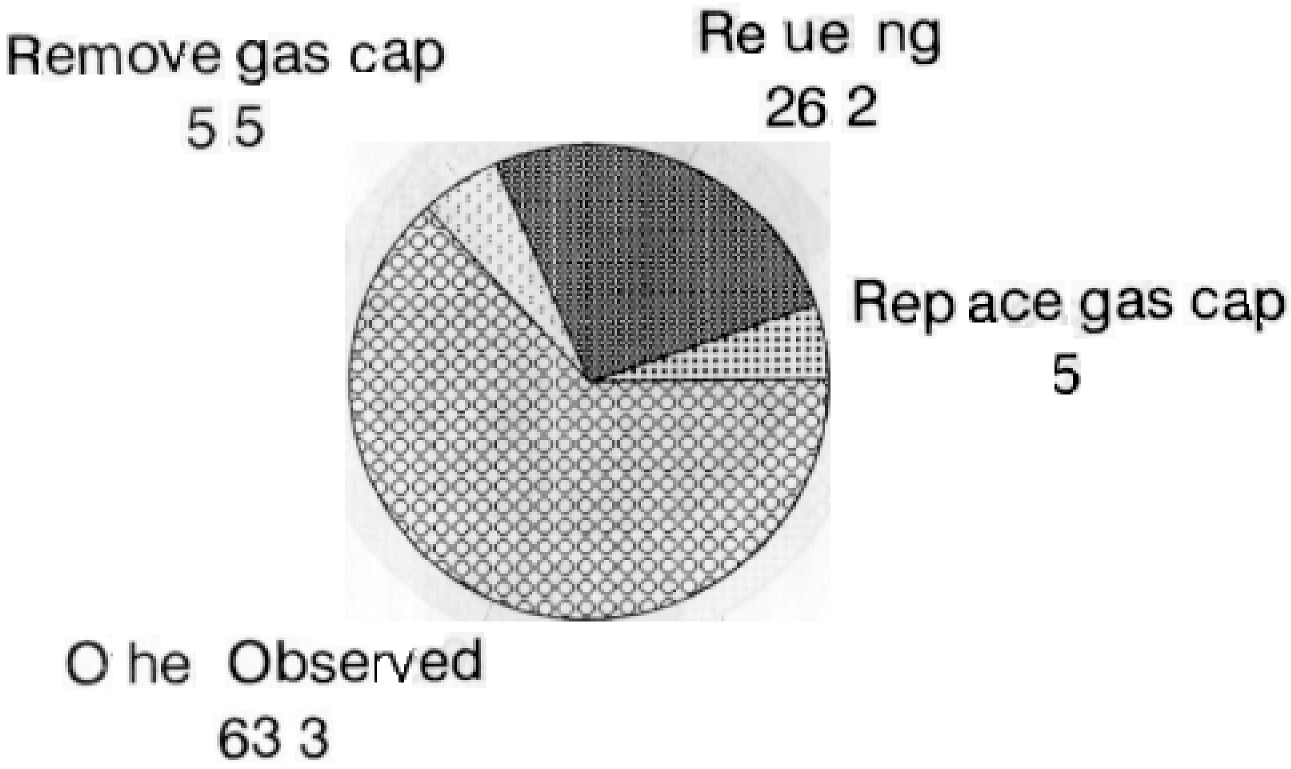


Figure 8

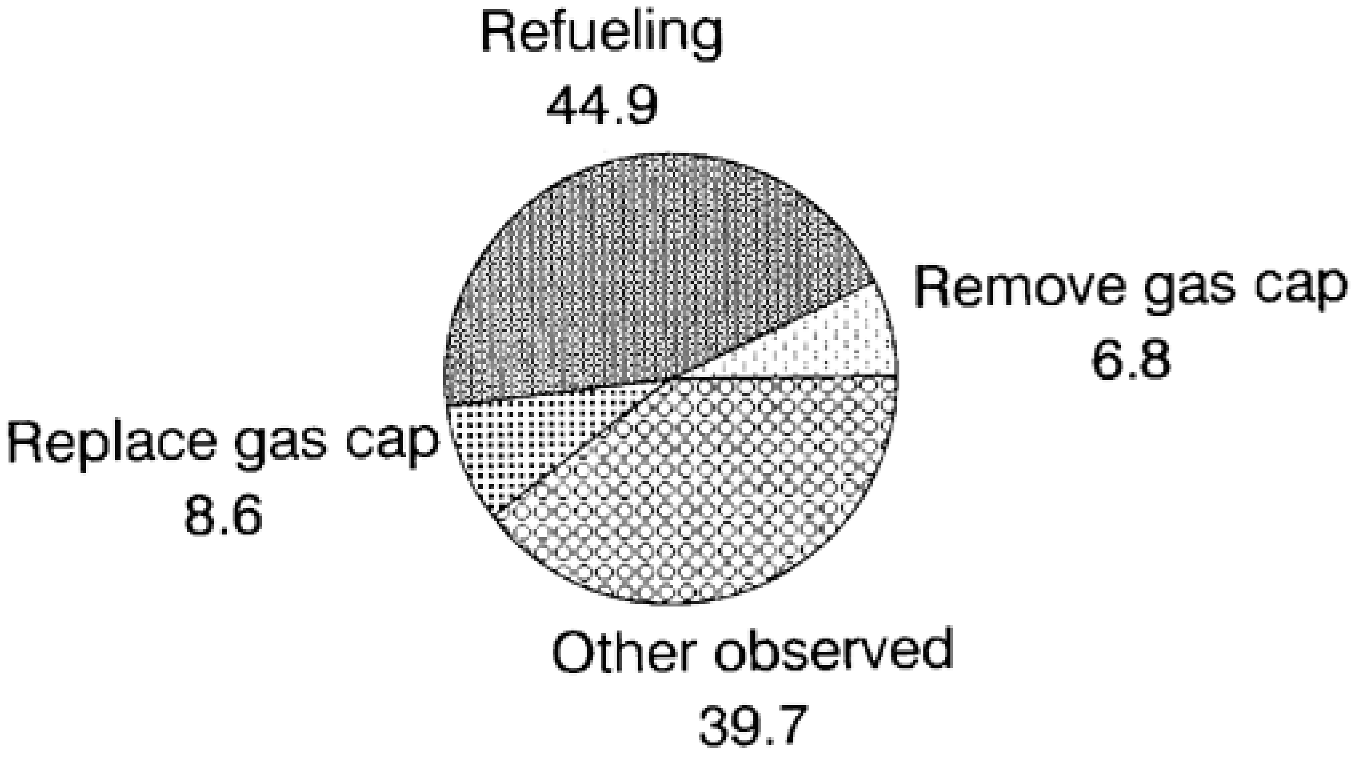
Exposure Duration %



Other observed: performing cash/credit card transactions, checking fluids, washing windshield, etc.

Figure 9

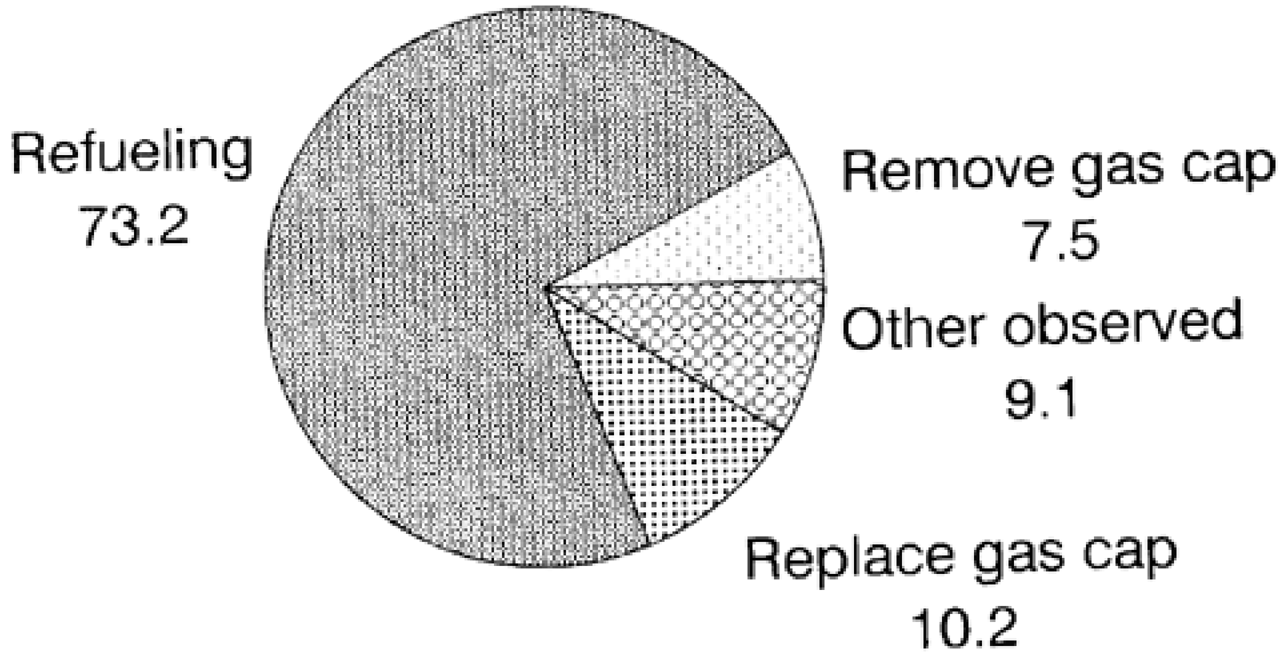
Relative Exposure %



Other observed: performing cash/credit card transactions, checking fluids, washing windshield, etc.

Figure 10

% Frequency of Peak Exposures

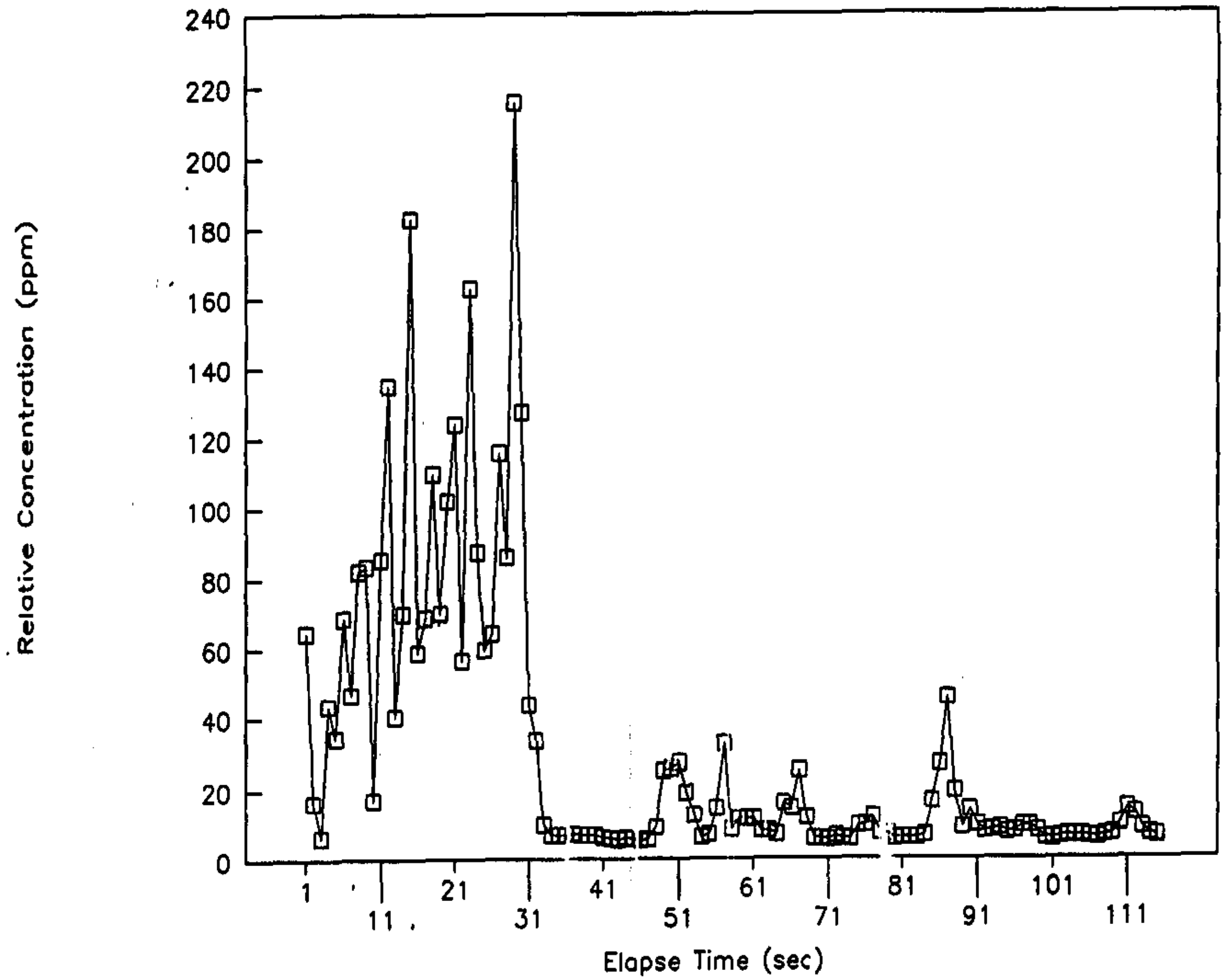


N = 324 total peak exposures > 50 ppm

Figure 11

GAS STATION ATTENDANT EXPOSURE

Task 2: Refueling



APPENDIX A

METHYL tert-BUTYL ETHER 1615

$CH_3OC(CH_3)_3$ MW: 88.15 CAS: 1634-04-4 RTECS: KN5250000

METHOD: 1615, Issue 2 **EVALUATION:** PARTIAL

Issue 1: 15 August 1990
Issue 2: 15 August 1994

OSHA : No permissible exposure limit
NIOSH: No recommended exposure limit
ACGIH: No threshold limit value
(1 ppm = 3.6 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.74 g/mL @ 20 °C; BP 55.2 °C; VP 32.6 kPa (245 mm Hg) @ 25 °C

SYNONYMS: MTBE; 2-methoxy-2-methyl-propane.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two charcoal tubes in series; front 400 mg; back 200 mg)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 2 L @ 10 ppm
-MAX: 96 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C, 3 weeks @ −7 °C (92% recovery) [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl tert-butyl ether (MTBE)

DESORPTION: 2 mL CS_2, 30 min

INJECTION VOLUME: 1 µL, split ratio 60:1

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: 0 °C for 7 min; 5 °C/min to 25 °C, and then 25 °C/min to 250 °C (hold 5 min)

CARRIER GAS: He, 1 to 2 mL/min

COLUMN: fused silica capillary, 50 m x 0.3-mm ID, 0.5-µm film of bonded dimethylsilicone gum (polydimethylsiloxane)

CALIBRATION: standard solutions of MTBE in CS_2

RANGE: 0.06 to >10 mg per sample [1]

ESTIMATED LOD: 0.02 mg per sample [1]

PRECISION ($\hat{S}_r$): 0.033 @ 9 µg to ~10 mg per sample [1]

APPLICABILITY: The working range is 0.2 to >35 ppm (0.75 to >125 mg/m³) for an 80-L air sample. This method is designed for the determination of MTBE in gasoline and may be used for the determination of other components of gasoline.

INTERFERENCES: 2,3-Dimethylbutane may interfere if initial chromatographic temperatures are higher than 0 °C.

OTHER METHODS: This is a new method [1].

Appendix B
Mini RAE Instrument Specifications

Size:	7.1"L x 2.7"W x 1.8"H
Weight:	18 oz with battery (0.510 kg)
Detector:	Interchangeable 10.2 eV or 10.11.7 eV electrodeless ultraviolet discharge lamp with Teflon/stainless steel chamber.
Operation Hours:	10 hour continuous operation
Gas Sampling:	Piston pump with >400 ml/min intake flow rate
Display:	7 digit LCD with LED back light
Analog output:	0 to 1 V
Range:	0 – 999.0 ppm with 0.10 ppm resolution, 1000 ppm to 1999 ppm with 1 ppm resolution.
Accuracy:	+/– 2 ppm or +/– 10% of reading, calibrated to 100 ppm Isobutylene
Response Time:	<3 seconds to reach 90% of exposed concentration
Alarm Setting:	Separate alarm settings for TWA, STEL, and Peak in Hygiene Mode; low and high alarm limits for Survey Mode.
Calibration:	Two point field calibration for zero gas and standard gas (Isobutylene).
Temperature:	0° to 40°C (32° to 104° F)
Data Storage:	12 hours of STEL readings (15 minute intervals) in Hygiene Mode; 50 site reading in Survey Mode
Humidity:	0% to 100% relative humidity (non–condensing)

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NIOSH