REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	**2. REPORT DATE** 14.Aug.02	**3. REPORT TYPE AND DATES COVERED** THESIS

4. TITLE AND SUBTITLE
MIXTURE COMPONENT EFFECTS ON PASSIVE DIFFUSION MONITOR PERFORMANCE

5. FUNDING NUMBERS

6. AUTHOR(S)
MAJ FRICK GREGORY A

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
UNIVERSITY OF WASHINGTON

8. PERFORMING ORGANIZATION REPORT NUMBER
CI02-118

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
THE DEPARTMENT OF THE AIR FORCE
AFIT/CIA, BLDG 125
2950 P STREET
WPAFB OH 45433

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Unlimited distribution
In Accordance With AFI 35-205/AFIT Sup 1

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

20020829 046

14. SUBJECT TERMS

15. NUMBER OF PAGES
75

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**

MIXTURE COMPONENT EFFECTS ON PASSIVE DIFFUSION MONITOR PERFORMANCE

Gregory Alan Frick

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

University of Washington

2002

Program Authorized to Offer Degree: Department of Environmental Health

University of Washington
Graduate School

This is to certify that I have examined this copy of a master's thesis by

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and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
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Abstract

Mixture Component Effects On Passive Diffusion Monitor Performance

by Gregory A. Frick

Chairperson of the Supervisory Committee

Professor Michael S. Morgan
Department of Environmental Health

Passive monitors fulfill a valuable role in industrial hygiene sampling. Although operation of the monitors in mixed chemical environments has been reviewed, the effect of each additional chemical in the mixture on monitor accuracy has not been evaluated. If individual chemical attributes (such as vapor pressure and polarity) predictably alter monitor performance, this information will assist industrial hygienists in assessing applicability of these devices.

To address this issue, passive monitors were challenged with mixtures of three common industrial solvents (methyl ethyl ketone, *o*-xylene, and trichloroethylene) in a bench-scale sampling system. In a series of eight, 8-hour randomized experiments, filtered air, at a constant humidity, temperature, and velocity was injected with a solvent mixture and continuously fed into a sampling chamber containing fifteen passive monitors (five each, from three different manufacturers). All possible combinations of the three solvents were represented in the eight experiments; one control, three single chemical runs, three double chemical runs, and one run with all three chemicals. Chamber concentrations for each mixture component were set at the Threshold Limit Value and verified with a set of MIRAN 1A instruments.

Monitor performance was influenced by mixture composition. When *o*-xylene was present alone, the ratio of average *o*-xylene recovered from all badges to average chamber *o*-xylene concentration (termed accuracy ratio) was 0.89 (0.06) (mean (standard deviation)). However, when methyl ethyl ketone was present with *o*-xylene, the accuracy ratio for *o*-xylene dropped to 0.80 (0.06) ($p<0.01$). Surprisingly, some chemical combinations actually enhanced monitor performance. Additionally, the relationship between mixture composition and monitor performance was influenced by an interaction between the two for two out of three study chemicals. This information can guide the industrial hygienist in selecting passive monitors based on mixture composition and monitor characteristics.

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ACKNOWLEDGEMENTS

I would like to thank my committee members, especially my committee chair, Dr. Michael Morgan, for their generous support during this process. Their comments and guidance were critical to the success of this effort. I would also like to thank my laboratory partners, Dan Ratican and Marie Martin for their help with tracking down the equipment, finding a spot for it in the lab, and helping to make it all work properly. I owe a special thanks to two outstanding laboratory technicians, Hee Sun Chung and Jianbo Yu, for their help with accumulating the humidification system components and for providing rudimentary gas chromatograph training. The idea for this study builds on previous work completed by Doug Johns during his Masters program. His advice and guidance during this effort were critical to the study design. Finally, I wish to thank the three manufacturers who provided passive monitors for usage during this study. It is through the generous support of companies like these that we further the knowledge of the profession of industrial hygiene.

DEDICATION

This effort would not have been possible without the support of my family over the past two years. With that in mind, this work is dedicated to my Mom and Dad, my wife Robin, and the four little princes in my life: Bryan, Patrick, Kenny, and Ben.

CHAPTER 1: INTRODUCTION

The 21st century American military finds itself deploying throughout the world. In many cases, military members perform the same jobs they would at a home base, but using different facilities, materials, and equipment. As was evidenced by the Gulf War, military members in these conditions can be exposed to a wide variety of chemical hazards.[1] Unfortunately, many of the current methods for quantifying these hazards are not applicable in deployed environments. Facilities may not exist to calibrate equipment properly, personnel expertise may not be available to operate the equipment, and lack of electricity sources can prevent utilization of the equipment. In these situations, an alternative is necessary to adequately characterize personnel exposures. One such alternative is diffusive samplers.

Although diffusive samplers using simple colorimetric principles have been available since the 1930's, it was not until the late 1970's that diffusive sampler design and validation made them a realistic option as a potential alternative to the charcoal tube method of organic vapor sampling.[2] Due to their low cost, east of use and worker acceptability, diffusive samplers became very popular with industrial hygienists for a variety of organic vapor monitoring applications.[3] This flexibility and portability also makes them a prime candidate for use in a deployed military environment. Unlike a standard workplace, however, chemical exposures in a deployed environment may vary erratically over time. It is important to choose a monitor that provides the most accurate recovery over a wide range of contaminants. Unfortunately, there are many questions about the suitability of these devices under varying environmental conditions and in mixed chemical atmospheres, especially in comparison to the active sampling method employing charcoal tubes.[4]

Passive monitors rely on the formation of a concentration gradient across a static layer of air to produce a characteristic mass transfer of gaseous molecules. Organic molecules passing through this layer of air are then adsorbed onto a collection medium. Once a linear concentration gradient has been established, the rate of collection operates under Fick's First Law of Diffusion (Equation 1.1):

$$W = (DA/L)(C_1 - C_0) \qquad (1.1)$$

where W is the rate of collection, D is the molecular diffusion coefficient, A is the cross-sectional area of the diffusion path, L is the length of the diffusion path, C_1 is the ambient concentration and C_0 is the concentration at the surface of the adsorbent medium. The term (DA/L) has units of volume per unit time and is often termed the sampling rate.[5] For most compounds, $C_1 - C_0$ is approximated by C_1 since C_0 is assumed to be negligible as long as adsorbent loading limits are not approached.[6] It is also assumed that the adsorbent will capture and retain 100% of the contaminant that reaches it. In reality, many adsorbents have different capture and retention abilities. The ability of the most common adsorbent, activated charcoal, to capture and retain many organic materials depends on environmental conditions (e.g. temperature and humidity) present during the sampling, the chemical species present during the sample, and the individual polarity and volatility of the chemicals present.

Over time, several potential and proven problems associated with the use of passive monitors have been discovered and reported. Environmental conditions, sample loading, reverse diffusion, fluctuations in atmosphere contamination levels, and competitive chemicals can all affect performance.[7] In response to this, the National Institute for Occupational Safety and Health (NIOSH) developed a validation protocol to ensure that monitors are used properly.[8] This validation protocol requires each device manufacturer to test their devices under a wide variety of conditions intended to address the potential problems mentioned above. The devices must be tested for every chemical that the manufacturer intends to target and their accuracy compared to the known value can be no worse than ± 25% at the 95% confidence interval. Additionally, the coefficient of variation over several repeated samples, termed precision, must be less than or equal to 10.5% of the mean result for the chemical being validated. This battery of validation tests is very costly; so most manufacturers have only validated their products for a small number of common organic chemicals. Additionally, although the protocol requires a few of the samples be taken in the presence of a potentially interfering chemical, neither the NIOSH protocol nor the manufacturers themselves have examined the question of validation in a mixed chemical (or unknown) environment.

To address this issue, some studies have evaluated the ability of passive monitors to work in mixed chemical environments. Initial fieldwork conducted with mixed organic vapors concluded that passive samplers compared favorably to active methods when sampling these environments.[9] Another study evaluated passive monitor performance with exposure to a mixture of aromatics.[10] Again, the comparison was against active sampling devices and the overall results were acceptable. It is interesting to note that the active sampling method is seen as the acceptable comparison in these cases. In a series of experiments on the effects of toluene on methyl chloroform retention, one type of passive monitor was found to have losses of methyl chloroform of 10% and 30% after exposures to toluene for 1 hour and 3 hours, respectively. Another type of passive monitor used in the same experiments showed no significant losses.[7] A final study exposed three passive monitors to a complex mixture of five compounds at low concentrations for a period of seven hours.[11] The results indicated that none of the monitors performed acceptably.

The one conclusion that can be taken from all of these studies is that mixture effects on passive monitors are not well understood. The reliance on active sampling as a comparison does not lend itself to understanding these effects since many of the physical and chemical properties intrinsic to the adsorbents used by the two types of monitors are shared. A more appropriate way to test passive monitors is against a known standard concentration that can be varied and verified. Given this, a factorial study with a cross-section of chemicals could decipher the effects of each additional chemical added to a mixture on the performance of passive monitors.

CURRENT STUDY

In order to discern the effects of chemical mixtures on passive monitor performance, this study examined the stepwise effect of three common industrial chemicals on the performance of three geometrically diverse passive monitors. The three chemicals (methyl ethyl ketone, tricholoroethylene, and *o*-xylene) were selected for two primary reasons. First, the chemicals represent a good cross-section of organic solvents used in a variety of industrial processes. All three are routinely encountered in Air Force operations and some processes (i.e. aircraft maintenance and vehicle maintenance) involve routine exposure to all of them. Second, the solvents represent a range of volatilities and polarities; two factors which could influence their capture by a carbon-based adsorbent. The three passive monitors utilized in this study were chosen based upon their manufacturer's recommendation of appropriateness in the chemical environment being created. Due to significant design differences, the sampling rates for the monitors were quite diverse.

To create the test atmosphere, a bench-scale sampling chamber and control system was designed and humidity, temperature, air velocity, and solvent concentrations were held constant during each stage of this study. Eight, 8-hour experimental runs, representing all possible factorial combinations of the three solvents, were randomly conducted utilizing five passive monitors from each of three different manufacturers during every run. The concentration for each chemical were set at the American Conference of Governmental Industrial Hygienist's (ACGIH) Threshold Limit Value (TLV), and verified with a set of MIRAN 1A instruments.

Several possible outcomes were expected. First, since the three chemicals have widely different polarities, it was possible that the non-polar chemicals would displace the more polar chemicals from the sorbent space, thus causing a reduced recovery. Second, since the three chemicals have widely different volatilities, it is possible that the more volatile compounds will have a reduced recovery. Third, since the three passive monitors being used have divergent sampling rates, it is possible that the monitors will recover the chemicals with different efficiencies. Fourth, it is possible that the chemical factors and the monitor factors may interact and cause a variety of effects. Taking this all into account, the hypothesis being tested was that monitor accuracy would be reduced when comparing recovery of a chemical in a mixed chemical environment to recovery of the same chemical in a single chemical environment.

CHAPTER 2: DESIGN & METHODS

STUDY DESIGN

Pertinent information on the three industrial solvents used in this study is presented in Table 2.1.

Table 2.1: Solvent Characteristics Summary.

Chemical	Industrial Uses	Polarity Index[a]	Vapor Pressure[b] (Torr)	2001 ACGIH TWA TLV (ppm)
Methyl Ethyl Ketone (MEK)	Used in the synthetic rubber industry, in the production of paraffin wax, and in household products such as lacquers and varnishes, paint remover, and glues.	4.7	90.6	200
Trichloroethylene (TCE)	Used as a solvent to remove grease from metal parts, particularly in the automotive and metals industries. Component of adhesives, lubricants, paints, varnishes, paint strippers, and pesticides. Found in some household products, including typewriter correction fluid, paint removers, adhesives, spot removers, and rug-cleaning fluids.	1.0	47.31	50
o-xylene	Solvent in pesticides, paints, lacquers, resins, inks, adhesives, cleansers, degreasers and paint strippers. Component of petrol.	2.5	6.6	100

a = relative measure of the degree of interaction of the solvent with various polar test solutes; increases with increasing solvent polarity[12]
b = measured at 25 °C

It is important to focus on the polarities and vapor pressures for each of the solvents, since it is believed that these chemical properties will have the most significant effect on passive monitor performance, all other environmental factors being equal.[6] The reasoning for this is based on the use of charcoal as the primary adsorbent in passive monitors. Charcoal has an intrinsic retention volume, or saturation capacity, for every chemical, that is dependent on the polarity and the volatility of the chemical and competition from other contaminants such as water vapor. For example, the more volatile a chemical is, the smaller its retention volume on charcoal (i.e. charcoal weakly holds volatile compounds). This relationship also applies to increasing polarity. Polar compounds have a smaller retention volume since the relative availability of polar sites on charcoal is less than that for non-polar sites.

To best determine how these intrinsic chemical properties would affect passive monitor performance, a random factorial design was chosen for this study. A complete factorial design allows for comparison of all possible experimental interactions and randomization controls experimental bias.[13] The complete factorial resulted in eight sampling runs and their order was determined using a random number generator in Microsoft Excel (Microsoft Corporation, Seattle, WA). Table 2.2 presents the experimental design and run order.

Table 2.2: Chemical Components & Run Order.

Chemical	Experimental Run							
Component	1	2	3	4	5	6	7	8
MEK	-	+	+	-	-	-	+	+
TCE	+	+	-	-	-	+	-	+
o-xylene	+	-	-	-	+	-	+	+

Concentrations for the chemical(s) present in each experimental run were selected as the corresponding 2001 ACGIH eight-hour time-weighted average (TWA) TLV (listed in Table 2.1).[14] These values were chosen since they represent the median test value used in the NIOSH validation protocol.[8] Additionally, manufacturers have designed their monitors to sample atmospheres containing many compounds present at their TLV-TWA concentrations without exceeding the capacity of the adsorbent. This was important since it would be impossible to decipher the chemical component effects if the monitors were overloaded.

The length of each sample run was chosen as eight hours for two primary reasons. The first of these is the same argument used to justify the concentrations above. Secondly, this time period represents a standard shift length for most workers. Although it is not expected that a worker would use any or all of the solvents in this study for eight hours at a constant concentration, this does represent a worst-case scenario for workplace exposure.

SAMPLER SELECTION

Three different passive monitor types were selected for this study. Passive monitors vary widely in physical geometry and have diverse sampling rates for the same chemical (see explanation of equation 1.1). By using three different monitor types in all of the experimental runs, the influence of sampler differences could be controlled. To evaluate experimental error, five replicates of each type of sampler were utilized, for a total of fifteen samplers in each run.

Each monitor manufacturer was contacted and asked to provide a proper monitor for the application outlined in this study. The first monitor was the TRACEAIR OVM-1 provided by K&M Environmental (Virginia Beach, VA). This monitor consists of one charcoal strip (300 mg coconut-based), two diffuser elements and two covers. It was always used with only one cover removed. The second monitor was the Radiello® provided by Rupprecht & Patashnick Company, Incorporated (Albany, NY). This monitor consists of a cylindrical collection cartridge (530 mg activated charcoal in granular form) that is housed inside of a cylindrical diffusive barrier. The final monitor was the SKC 575-002 provided by SKC Incorporated (Eighty Four, PA). This monitor consists of a circular badge containing 500 mg of Anasorb® 747 (a beaded, active carbon derived from petroleum precursors), covered by a diffusion element. A summary of the sampling rates for these monitors is provided in Table 2.3.

Table 2.3: Passive Monitor Sampling Rates, by Chemical.

Chemical	Sampling Rate (cc/min)		
Component	K&M OVM-1[a]	Radiello[b]	SKC 575-002[c]
MEK	35.8	79	17.1
TCE	34.7	69	14.26[d]
o-xylene	28.8	61	14.24

a = Taken from Technical Reference Guide[15]
b = Taken from Instructions for Volatile Organic Compounds sampling by Radiello[16]
c = Taken from SKC 575 Series Passive Sampler for Organic Vapors Operating Instructions[17]
d = Communicated in a personal email dated 26 February 2002 from Connie Kelley

SAMPLING APPARATUS

All experimental runs took place in the lab located in F-218 of the Health Sciences Building. The sampling apparatus was constructed in a laboratory hood, with the monitoring equipment located outside of the hood on a neighboring bench (see Figures 2.1 and 2.2).

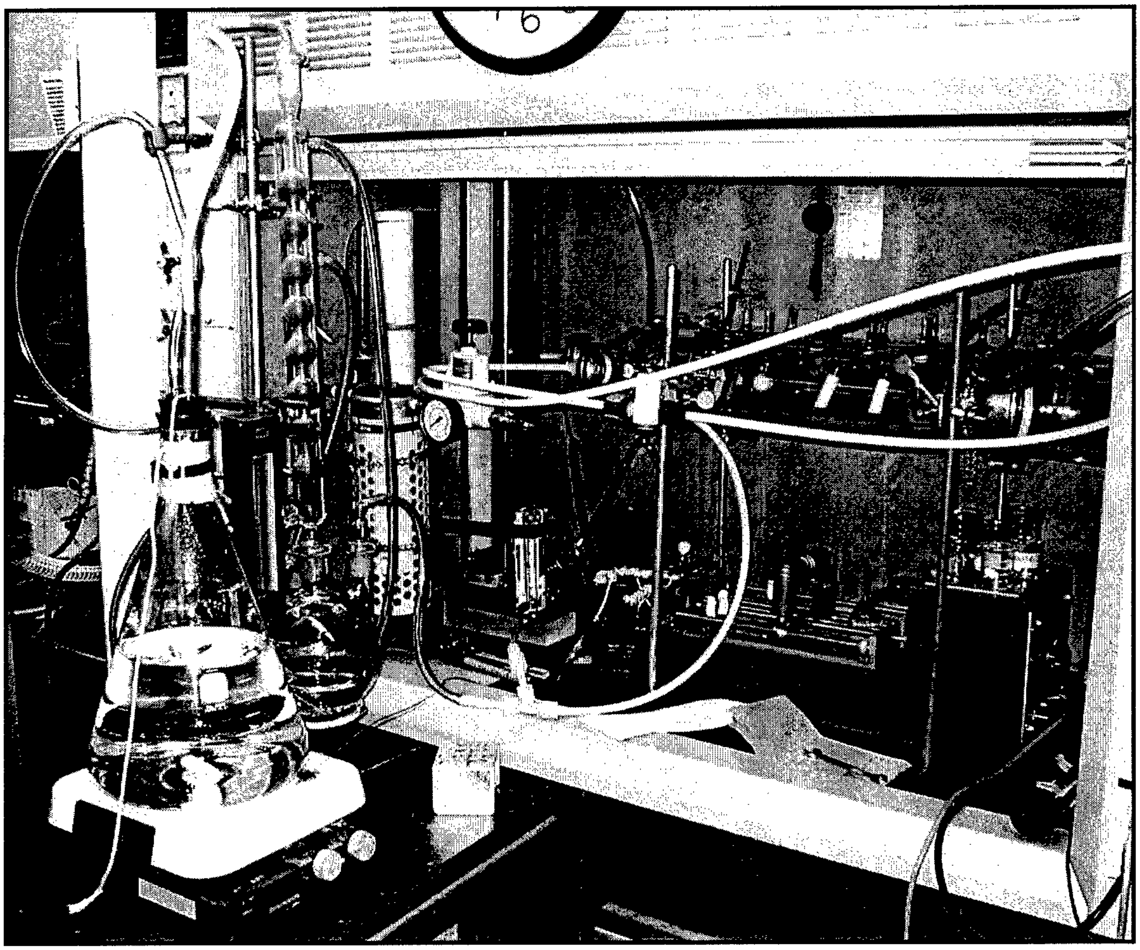

Figure 2.1: Sampling Apparatus in Lab Hood.

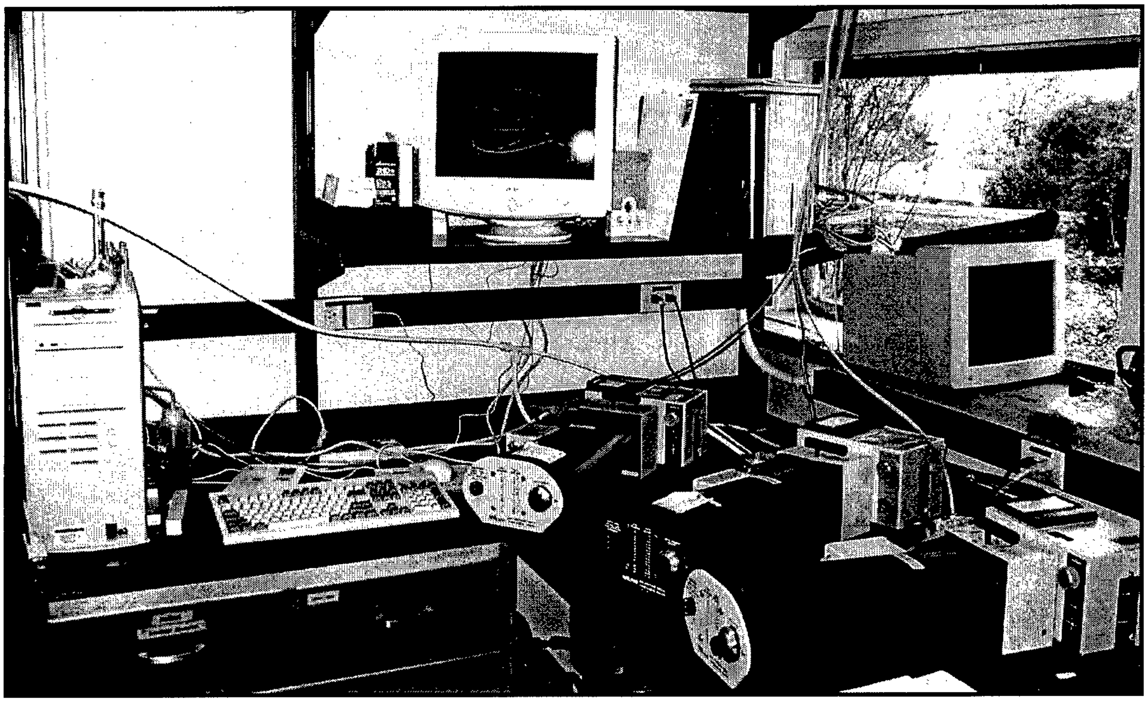

Figure 2.2: Monitoring Equipment on Lab Bench.

The exposure chamber (pictured above the syringe drive in Figure 2.1) consisted of two blown-glass tubes (4” inside diameter) connected by a U-shaped glass tube. The front tube was 18” long and the back tube was 24”. Inside each tube, a stainless steel, triangular-framed rack held the monitors during the runs (Figure 2.3).

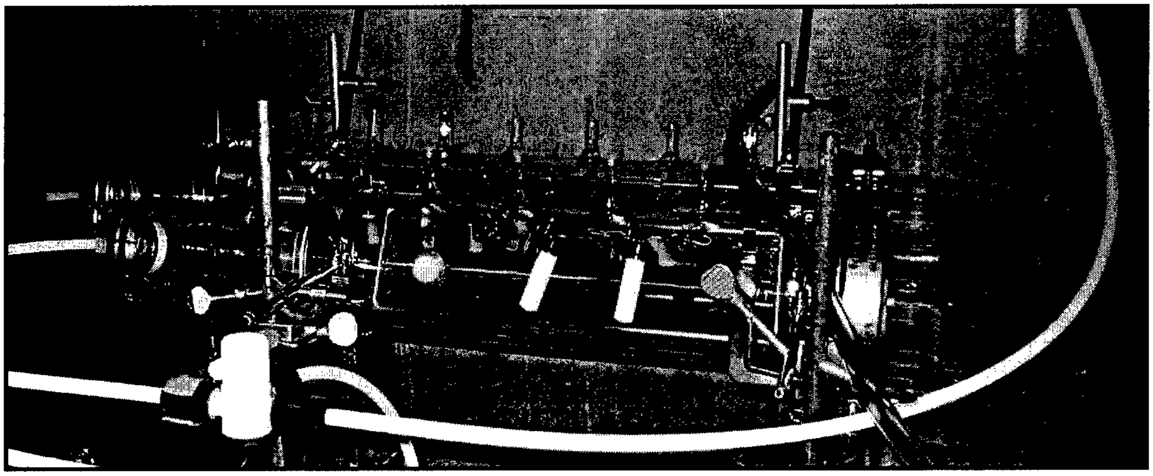

Figure 2.3: Sampling Chamber.

Along the top of each tube, several sampling ports were available, but they were not utilized for this experiment and were capped with Teflon PFA plugs. The two tubes were divided into a total of five sections (denoted A-E), with the first two sections located in the front tube (see Figure 2.4).

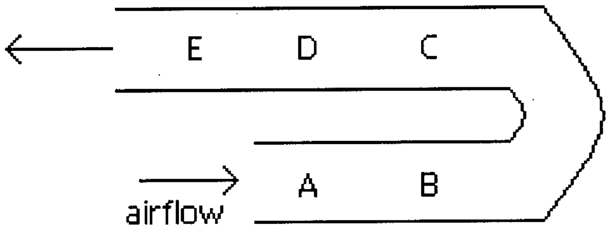

Figure 2.4: Sampling Chamber Sections.

Each section of the sampling chamber contained three randomly ordered monitors, one from each manufacturer, during each experimental run. The position of the monitors was numbered in the direction of airflow from 1-3. Thus, a monitor in position B3 would be located at the far right of the first (front) chamber and a monitor in position C1 would be located at the far right of the second (back) chamber. Individual results for the monitors presented in the appendix are labeled using this notation. At each location, the appropriate monitor was suspended from one of the stainless steel racks and positioned with the diffusive face perpendicular to airflow.

The remainder of the apparatus was designed to deliver a controlled mixture of chemicals at constant concentrations, temperature, flow rate, and humidity to the sampling chambers. To accomplish this, an atmosphere generation apparatus was developed. The design of this apparatus was based on those used by monitor manufacturers for testing of their badges.[18] Filtered lab air was run through a drier, a pressure regulator, and a calibrated rotameter to establish a constant flow rate of 100 liters per minute (lpm). This flow rate was chosen since it equated to a sampling chamber mean air velocity of 0.20 meters per second (m/s), the velocity recommended in the NIOSH validation protocol.[8] Due to the size of the sampling chamber, the monitors were in close proximity to each other. Maintaining the NIOSH protocol velocity was necessary to limit the possibility of starvation of the monitors.

The air stream was then split in two: a low flow (~ 15 lpm), or primary flow, and a high flow (~ 85 lpm), or secondary flow. Flow rates in both streams were controlled with calibrated rotameters. The primary flow was routed through a heated, stainless steel manifold; where the appropriate chemicals for the experimental run were injected into the stream at a controlled rate via an infusion withdrawal pump (Harvard Apparatus Company, Millis, MA), commonly known as a syringe drive. All of the equipment and fittings on the primary flow side were constructed of glass, stainless steel, or Teflon PFA tubing/fittings. The secondary flow was sent through a humidification system where it was humidified to 95% relative humidity using distilled water. The two streams were reunited, run through a three-way purge valve (to facilitate starting and stopping of sampling periods), and then emptied into the sampling chambers. The chamber air velocity was verified at 0.20 m/s with a thermo-anemometer (Dwyer Series 471, Dwyer Instruments, Michigan City, IN) three or four times during each run. All readings varied less than 10% from the desired velocity.

A calibrated temperature/humidity meter probe (Omegaette® HH314 Humidity Temperature Meter, Omega Engineering, Stamford, CT) was placed inside the sampling chamber and these parameters were continuously monitored and recorded during each sampling run. In accordance with the NIOSH validation protocol, temperature was set close to 20 °C and relative humidity was set close to 80% for each run.[8] Temperature values remained very stable throughout each run, varying less than 0.3 degrees. Humidity values fluctuated quite a bit due to difficulties controlling temperature of the water source and temperature of the condenser. This became even more of a problem after the first condenser broke between runs six and seven. Continuous plots of humidity for all eight runs are in Appendix A.

Air was drawn from the outlet of the sampling chamber by a high volume pump, split into three air streams, and then drawn through three MIRAN 1A-CVF (Foxboro Inc., Foxboro, MA) infrared analyzers, one calibrated for each chemical. The flow rate through the MIRANs was set to create a complete air change within the instrument sensing volume once every 43 seconds. The exhaust from the three instruments was then recombined and discharged into the lab hood for disposal. Test atmosphere generation was considered successful if the values shown on the MIRANs were within 10% of the calculated values for the delivered atmosphere. Calculated values were determined from the flow rate through the sampling chamber and the injection rate of each solvent.

MIRAN 1A INSTRUMENTATION

Prior to the experimental runs, each of the solvents was assigned to a MIRAN 1A instrument. Using infrared transmission spectra for each chemical, optimum wavelengths were determined and each MIRAN was calibrated for its selected solvent. Care was taken to choose wavelengths that created minimal spectral overlap, however there was some overlap between solvents at the selected wavelengths. This was quantified and all subsequent MIRAN readings were corrected. Table 2.4 lists the wavelengths and pathlengths determined for each of the three compounds.

Table 2.4: MIRAN 1A Optimized Settings.

Solvent	Wavelength (μm)	Pathlength (m)
MEK	8.6	12.75
TCE	10.6	9.75
o-xylene	13.6	20.25

Each MIRAN was calibrated with a closed-loop system using a stainless steel bellows pump. For all three chemicals, a slit width of 0.5 millimeters was used, the instruments were set to high gain, and readings were taken on the absorbance scale. A known amount of the appropriate solvent was injected into the loop and the instrument was allowed to equilibrate. The absorbance value was recorded, the system was purged, and another injection was made. This was accomplished twice, for three different concentrations (~ 0.75*TLV, TLV, and 1.5*TLV). Calibration plots were created for each MIRAN/solvent combination by comparing the absorbance readings to the known concentration of solvent inside the closed-loop system. The three plots are shown in Appendix B. For quality control purposes, all three MIRAN calibrations were verified at two different concentrations after 50% and 100% of the sample runs had been completed. These values (which varied from the initial calibration line by less than 2%) were added to the final calibration plots that were utilized to determine the chamber concentrations.

During the sample runs, each MIRAN output was sampled once every ten seconds by a computer-based, continuous logging system (LABVIEW 2®, Laboratory Virtual Instrument Engineering Workbench, National Instruments Corporation, Austin, TX). This logging system recorded the MIRAN readings as a voltage reading that directly related to absorbance. Thus, to calculate the time weighted averages for each of the chemicals during each sampling run, the voltage readings were converted back to absorbance values, the MIRAN calibration equations were used to determine the corresponding concentrations, spectral overlap corrections were made if necessary, and finally the average concentration was calculated. Figure 2.5 shows a typical profile for sampling chamber concentration versus time.

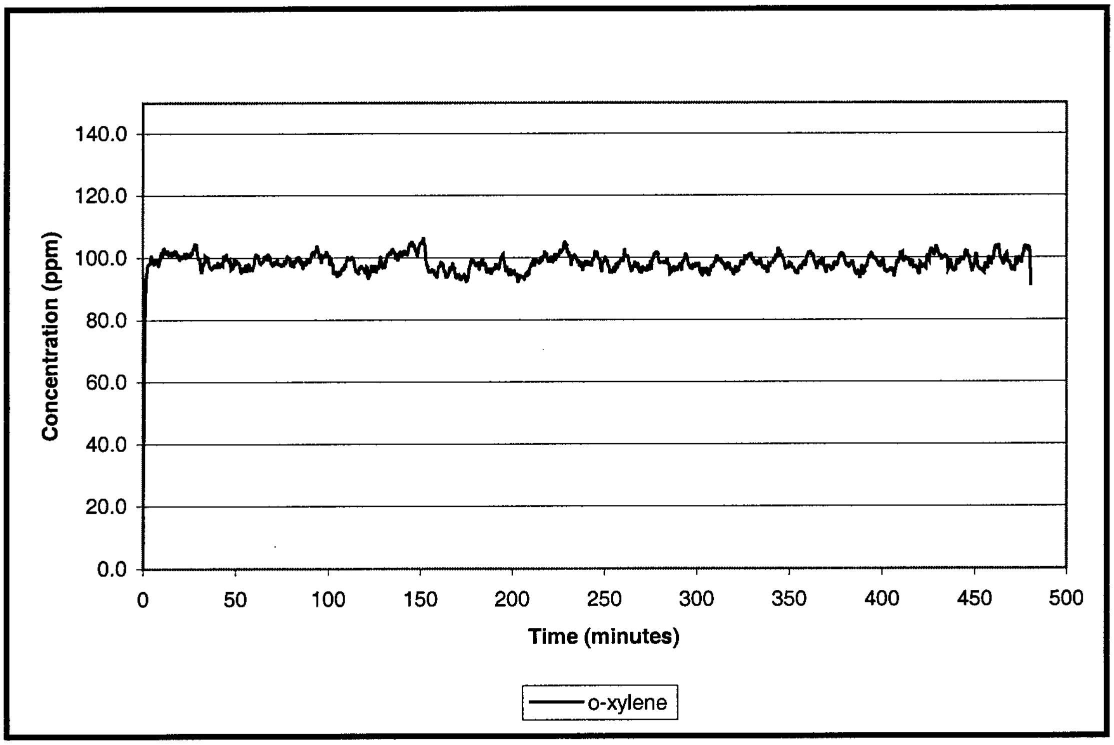

Figure 2.5: MIRAN Time Plot for Sample Run 5.

In Figure 2.5, it can be seen that *o*-xylene is the only solvent plotted. During Run 5, it was the only chemical injected into the system and the other two MIRANs did not record any non-zero values. It can also be seen that the concentration is relatively close to the target concentration of 100 parts per million (ppm) with only minor deviations from this value (TWA = 98 ppm, standard deviation = ± 4 ppm). The cyclic concentration patterned observed in Figure 2.5 is evident in all of the sampling run plots (see Appendix C) and would not be expected with a constant airflow and a constant solvent injection rate. Although it is not possible to know for sure, there is a very plausible explanation for this anomaly. The infusion pump was only injecting very small volumes into the airstream. Since these volumes were being delivered through a needle, there was some backpressure that could have caused the injections to occur as a series of large drops rather than as a continuous flow. This would account for the sudden rise in concentration, followed by a slower drop-off while the next drop was forming. This effect was not very pronounced during this run, but it was much larger in some of the other sampling runs and created large standard deviations in the sampling chamber concentration. It is not expected that these fluctuations would impact the outcome of this study since they were within what would be expected in a normal workplace atmosphere and the TWA values were maintained close to the TLV target values.

In addition to the cyclic concentration pattern, there were a few other observations of note associated with the MIRANs. First, it was not always possible to attain the TWA-TLV concentration for each of the chemicals present during a sampling run. This was primarily due to limits associated with the syringe drive. Since the syringe drive was only geared for specific injection rates, it was not always possible to find a rate that provided the proper concentration while allowing the flow rate to remain at 0.20 m/s. Therefore, some of the MIRAN plots show concentrations that were off from the TLV-TWA concentrations by 20% or more. In these cases, the runs were always accomplished with the concentrations being less than the TLV-TWA values to ensure that the monitors were not overloaded and the effect of interest was not masked. A second observation is that there was quite a bit of backpressure in the stainless steel manifold and this created occasional leakage around the syringe drive. The result was large deviations in the chamber concentrations that are readily evident in the plots for sample runs one and two. Although this was not in accordance with the design of the experiment, it is probably more representative of actual workplace conditions and it did nothing to harm the experiment since these variations were captured by the MIRANs and included in calculation of the solvent TWAs.

ANALYTICAL METHODS

After each sampling run, all of the monitors used, as well as any blanks, were capped and placed in a refrigerator. The monitors were prepared for analysis, following instructions provided by each of the manufacturers, within 48 hours of the sample run. For each run, a carbon disulfide (CS_2) solution, containing an internal standard of toluene, was used to desorb all of the monitors. Typically, two microliters of CS_2 was added to each monitor and the monitors were then agitated for 30-60 minutes. After agitation, the remaining liquid was transferred into gas chromatograph (GC) vials and the vials were capped with syringe sampling crimp caps.

To perform the analysis, a HP (Hewlett-Packard, Palo Alto, CA) 5890A Series II GC was used with an HP 7673 auto sampler. The GC had a flame ionization detector and a capillary column with a wax film thickness of 0.25 micrometers, an inner diameter of 0.32 millimeters, and a length of 30 meters. The entire run sequence was computer-controlled via Chemstation® (Agilent Technologies, Palo Alto, CA). A one-microliter sample of the eluate from each GC vial was injected into the system and analyzed using a six-minute, programmed temperature run. The starting temperature of the column was set at 60 °C and it remained there for the first minute of the run. After that, the column temperature was increased by 10 °C every minute, until the final column temperature at the end of the run was 110 °C. The programmed temperature run allowed for quick analysis of each sample, yet maintained good separation of the individual chemical peaks.

Five standard solutions containing all three of the solvents and the CS_2 solution with the internal standard were created for each of the GC runs. The individual solvent concentrations in these standard solutions were chosen to represent a range that would include the expected concentrations on the monitors. Because of differing sample rates between the monitors, these ranges were not constant, but in each case they were at least ½ the lowest expected concentration. One of each of the standard solutions was pipetted into a GC vial, capped, and analyzed by the GC prior to, and after, each of the corresponding GC sampling runs. The results from the analysis prior to the run were used to create calibration curves; the results from the analysis after the run acted as a quality assurance measure. A typical GC output plot created during this process is presented in Figure 2.6.

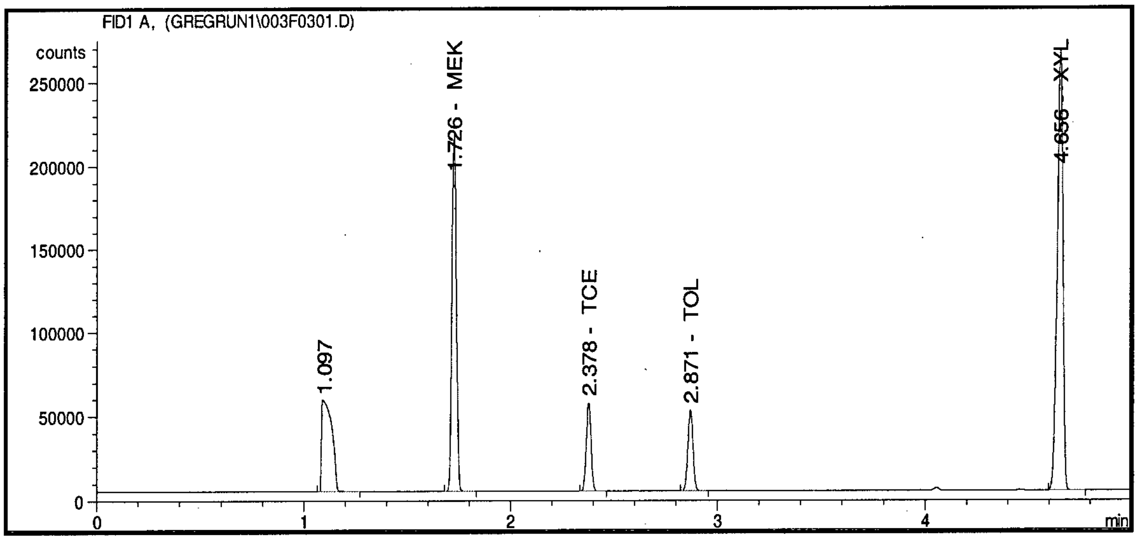

Figure 2.6: Gas Chromatograph Plot for Sample Run 1, Standard Solution 3.

The timescale in Figure 2.6 corresponds to retention time inside the gas chromatograph. Peaks in this figure represent all three of the study solvents and the internal standard, with their corresponding retention times noted. The only other significant peak in the chromatograph is the one at 1.097 minutes and this corresponds to CS_2. The width and height of each peak were used to create a peak area. Peak areas were considered accurate to three significant figures. This corresponded to an absolute detection limit of 0.01 ppm in liquid for all of the solvents. The sample peak area was then compared to the peak area of the internal standard to create a response ratio. By plotting this response ratio against the known concentration in the standard solution (in milligrams of solvent/milliliters of CS_2), a calibration curve for each solvent was formed. These curves were highly linear and a best-fit equation was determined. In all, twenty-four calibration curves were created, one for each solvent in each run. A typical example is shown in Figure 2.7.

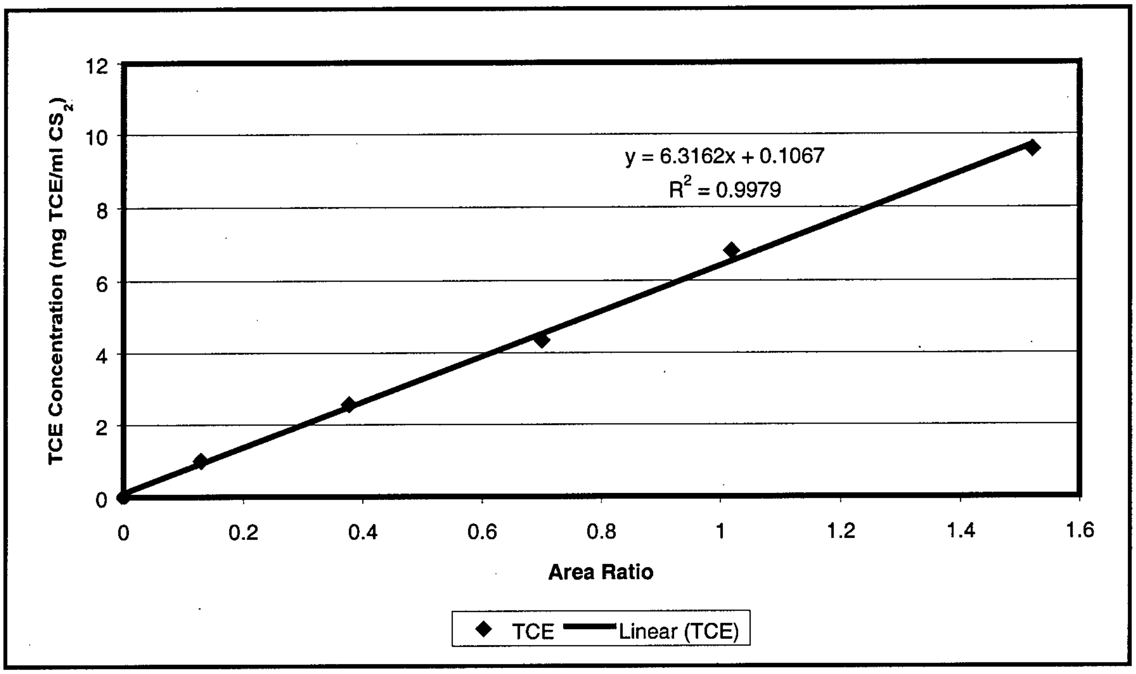

Figure 2.7: Gas Chromatograph TCE Calibration Chart for Sample Run 2.

The GC curves from the sample results were converted into response ratios in the same manner as that for the standards. Using the linear equations from the calibration curves, concentrations for each of the solvents were determined. The concentrations were converted to air concentrations using equations provided by the manufacturers. These equations related sampling rate, temperature, barometric pressure, solvent molecular weight and density, desorption efficiency, and sample concentration. A summary of the results for all of the monitors is presented in Appendix D.

DESORPTION EFFICIENCY

The desorption efficiency (DE) for a particular compound can vary from one batch of adsorbent to another. The individual monitor sampling rate and the amount of loading on the adsorbent can also affect it. Therefore, desorption efficiencies were determined separately for each combination of compounds and monitors at three levels of loading corresponding to the middle three levels of standard solutions. In determining the desorption efficiencies for each of the monitors, appropriate amounts of solvent were directly loaded on to the monitor and the monitors were then capped and allowed to stand overnight. The monitors were desorbed and analyzed in the same manner as the samples described previously. Each efficiency run was performed in triplicate including blanks. This resulted in nine DE readings for each chemical on each monitor. These values were averaged and used in the corresponding manufacturer's equations when computing the sample concentrations. The means and standard deviations of the desorption efficiencies are given in Table 2.5.

Table 2.5: Desorption Efficiency Sample Summary.

Compound	Monitor Type					
	K&M OVM-1		Radiello		SKC 575-002	
	DE	SD	DE	SD	DE	SD
MEK	0.854	0.013	0.937	0.016	0.888	0.008
TCE	1.034	0.040	1.048	0.036	1.033	0.033
o-xylene	0.946	0.014	0.936	0.028	0.954	0.024

To preserve study integrity, DE samples were handled in the same manner as the experimental run samples and blanks. Two issues of note were identified in association with the DE process. First, due to a limited number of monitors available for the study, the DE samples were analyzed with all three solvents loaded. Most of the experimental samples only had one or two solvents loaded. Second, the DE samples had no exposure to water vapor. One of the manufacturers noted that for some chemicals it would be necessary to add water to the DE monitors if the experimental samples were taken in conditions where the relative humidity was higher than 60% and exposure was for longer than four hours.[16] Although these environmental conditions were present during this study, the chemicals for which this was considered necessary were not among those used. The significance of these two issues is unknown.

CHAPTER 3: RESULTS

This study was focused on evaluating mixture component effects on monitor performance. By varying the solvents present during each run, the thrust of the study was to decipher chemical interferences that affected monitor recovery. When comparing the experimental results with single chemicals to those from runs conducted with multiple chemicals, it became evident that solvent recovery was influenced by mixture composition. It was interesting to note, however, that this did not always lead to a negative recovery effect. It also became clear that the type of passive monitor being used influenced this effect. Overall, this led to several data trends that were analyzed and are presented below.

In order to evaluate these data, a primary comparison statistic was created to relate the chemical concentrations found on the samplers and the 8-hour TWA values from the MIRAN instruments monitoring the sampling chamber. Coined accuracy ratio, the statistic is the ratio of individual sampler concentration to MIRAN concentration (both expressed as time weighted averages) for the chemical of interest, multiplied by 100 to convert it to a percent. For each experimental run, results from each of the fifteen monitors present in the sampling chamber were converted into this statistic. This statistic indicates monitor chemical recovery since the MIRAN is considered a gold standard for the actual amount of chemical present in the sampling chamber. If the accuracy ratio is below 100%, the passive monitor under recovered the chemical as compared to the chamber concentration reported by the MIRAN. If the accuracy ratio exceeds 100%, the monitor over recovered the chemical.

It should be noted that all twelve monitor blanks, as well as the fifteen monitors sampled during the blank run (experimental run 4), returned results below gas chromatograph detection limits for all three chemicals. Therefore, no concentration adjustment to the values calculated for each monitor was necessary.

EVALUATION OF MIXTURE EFFECTS

The purpose of this study was to determine a pattern related to chemical properties that could be used to predict the effect of multiple chemical interferences on passive monitors in general. To that end, initial data analysis was accomplished by including all fifteen of the badges present in each experimental run, regardless of manufacturer. Figure 3.1 shows the accuracy ratio results for all of the badges in the runs involving *o*-xylene.

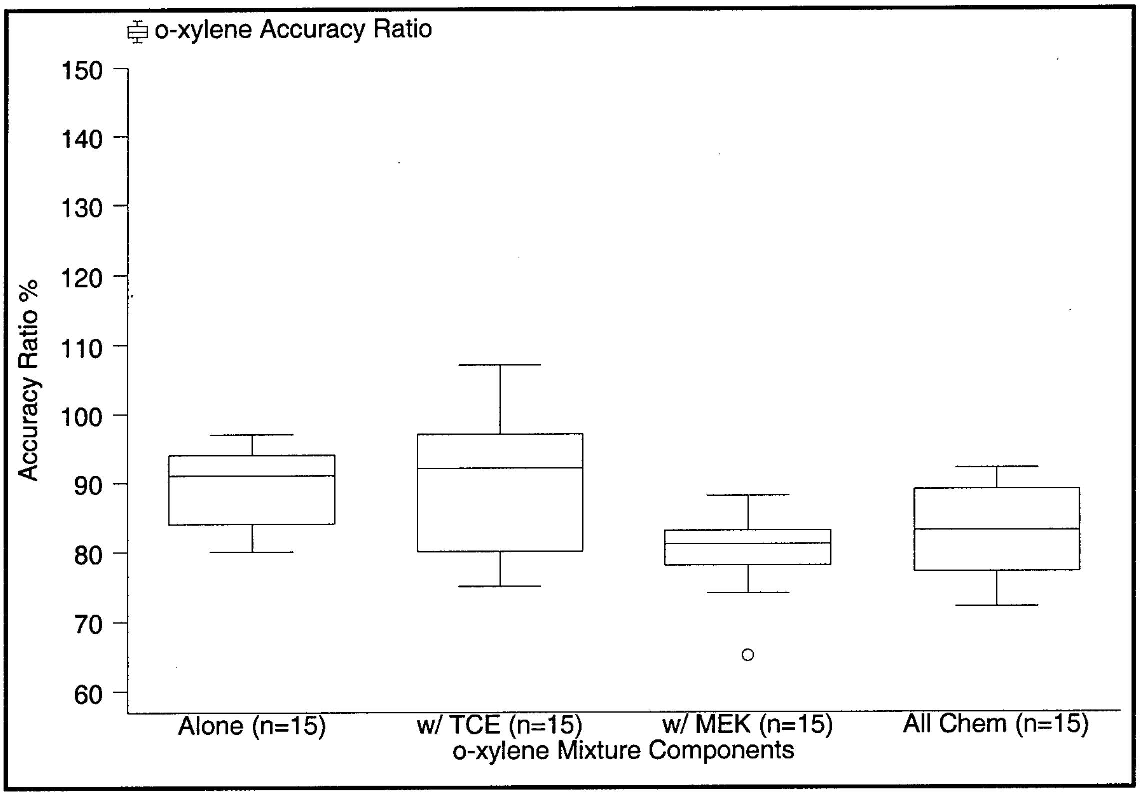

Figure 3.1: *o*-xylene Accuracy Ratio vs. Mixture Components.

For this, and all subsequent box plots, the central boxes span the first and third quartiles of the data, with the middle line representing the median value. The whiskers extend to a maximum of one and a half times the interquartile range, but only include actual data points. Data points that exceeded the whiskers are plotted individually.

By examining the median values in this plot, it is apparent that MEK negatively affects *o*-xylene recovery, while TCE does not seem to have any effect. Although there is one value in the MEK mixture run that seems to be far outside of the rest of the data, it was included in the analysis since there was no experimental reason to discount it. In most of the boxes, the median values evenly divide the interquartile range, suggesting data are normal. In general *o*-xylene recovery values fall between 80-100%.

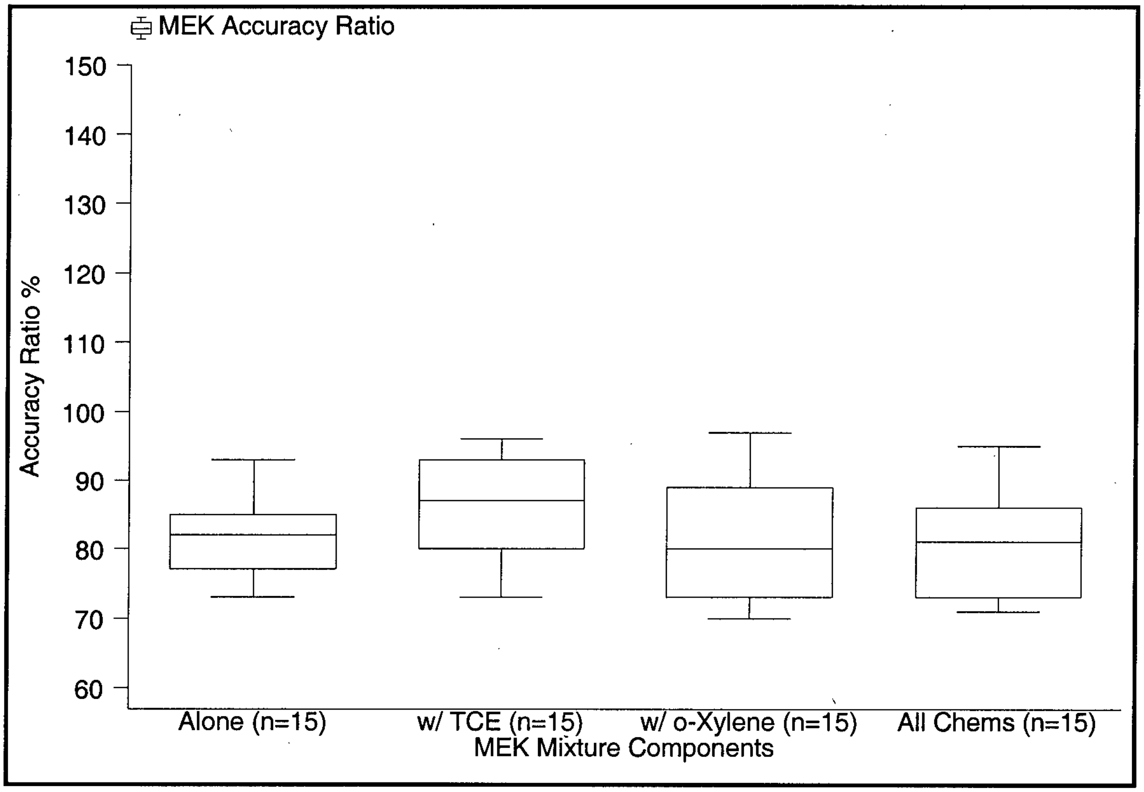

Figure 3.2: MEK Accuracy Ratio vs. Mixture Components.

Figure 3.2 shows the results for the MEK experimental runs. In contrast with the *o*-xylene runs, there does not seem to be much effect on the MEK accuracy ratio when other chemicals are present. The medians are slightly lower when *o*-xylene is present and the median is slightly higher in the run with TCE, but the boxes overlap each other and the interquartile range is quite large. The medians fall towards the middle of the interquartile range, suggesting the data are normal. In general, MEK recovery is between 75-95%.

A summary of the TCE data is presented in Figure 3.3. TCE accuracy seems to be primarily affected by the presence of *o*-xylene. The interquartile ranges of the boxes in this plot are quite large, with the median values skewed heavily to the lower end of the range. This suggests a problem with the data spread and indicates there may be some spuriously high recovery values. A log transformation was considered, but was discounted since the spread was not evenly distributed between the different badge types. This effect will be discussed further in a later section. It should also be noted that the accuracy ratios for TCE almost invariably exceeded 100%, with many values over 120%.

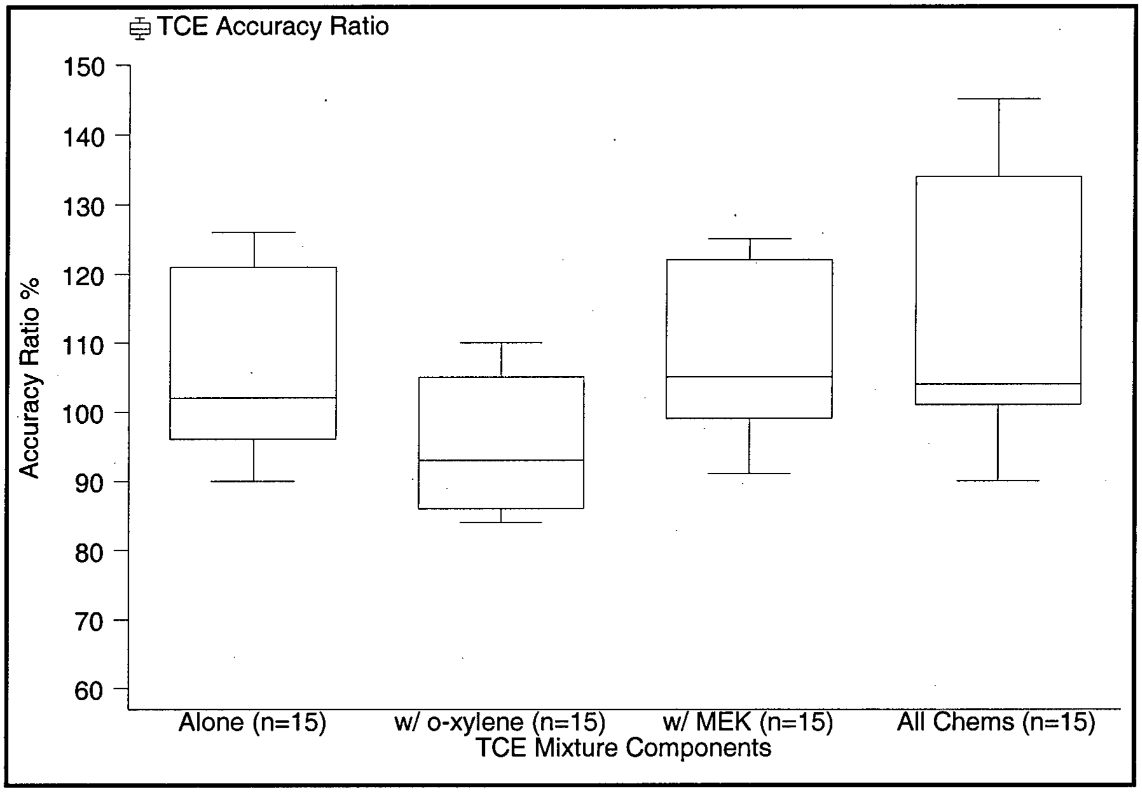

Figure 3.3: TCE Accuracy Ratio vs. Mixture Components.

To further evaluate the trends suggested in the three figures above, a simple data analysis was performed comparing the mixture components and accuracy ratios. Again, to exclude badge influences, the mean accuracy ratios for all fifteen badges present during each run were calculated. These results are presented in Table 3.1.

Table 3.1: Mean Accuracy Ratio and Standard Error Summary for Mixture Component Data.

	Mixture Components				
	Solvent Alone	with *o*-xylene	with TCE	with MEK	All Solvents
Solvent	Acc. Ratio (%) ± S.E. (%) n=15	Acc. Ratio (%) ± S.E. (%) n=15	Acc. Ratio (%) ± S.E. (%) n=15	Acc. Ratio (%) ± S.E. (%) n=15	Acc. Ratio (%) ± S.E. (%) n=15
o-xylene	89.12 ± 1.45		90.38 ± 2.42	80.17 ± 1.43^a	82.78 ± 1.56^b
TCE	106.47 ± 3.30	95.05 ± 2.32^a		109.19 ± 2.92^b	113.47 ± 4.74^a
MEK	82.14 ± 1.45	80.90 ± 2.35	86.29 ± 1.96^a		80.27 ± 1.92

S.E. = Standard Error
a = Significantly different from the chemical alone at the $p<0.01$ level
b = Significantly different from the chemical alone at the $p<0.05$ level

This table illustrates several trends that were initially seen in the figures above. First, the presence of MEK drives the accuracy ratio of the other two compounds away from 100%. Second, the presence of TCE tends to drive the accuracy ratio of the other two compounds toward 100%. Third, the presence of *o*-xylene drives the accuracy ratio of the other two compounds below 100%. Fourth, the standard error values for TCE samples are higher than those for the other two compounds.

To analyze these trends, paired t-tests were performed on the pooled accuracy ratios. From these tests, it was determined that TCE recovery was significantly reduced in the presence of *o*-xylene and significantly enhanced in the presence of MEK. MEK recovery was also significantly enhanced in the presence of TCE. Finally, *o*-xylene recovery was significantly reduced in the presence of MEK.

In order to evaluate the overall effect of mixture components on accuracy ratio, a series of one-way analyses of variance (ANOVA) were performed for each chemical. The purpose of the ANOVA was to determine if there was a significant difference between the accuracy ratios for each of the four runs associated with each chemical. For *o*-xylene, it was determined that the accuracy ratios were significantly different ($p<0.0002$). For MEK, it was determined that the accuracy ratios were not significantly different ($p<0.15$). For TCE, it was determined that the accuracy ratios were significantly different ($p<0.0031$). These results indicate that there is something about the chemical composition of the mixture that causes the accuracy ratios to differ. A possible explanation for these differences in accuracy is the influence of chemical polarity.

The methods portion of this report details the different chemical polarities of the solvents used in this study. During sampling involving carbon-based adsorbents, it is theorized that non-polar compounds will out-compete polar compounds for adsorbent space. Thus, when two chemicals of differing polarity are sampled together, the non-polar chemical should show a higher relative recovery, and the recovery should be similar to that found when it is sampled alone. Alternatively, the more polar chemical should have a low recovery, and it would be expected to have a reduced recovery compared to when it is sampled alone.

In this study, MEK was the most polar compound. Thus, it would be expected to have a low relative recovery and that recovery should decrease as more non-polar compounds are added to the mixture. In fact, the overall recovery for MEK was the lowest of all of the components at 82.4%. However, the ANOVA indicates that this value did not vary much, regardless of mixture components. This could possibly be due to the monitors not approaching capacity; thereby effectively avoiding the competition factor alluded to above.

Overall recovery of the other two solvents used in this experiment fell in line with the polarity theory: the moderately polar *o*-xylene was found to have an overall recovery of 85.6% and the non-polar TCE had an overall recovery of 106%. Unlike the MEK samples, however, these two compounds both showed significant differences in their accuracy ratios (as determined by the ANOVA) across their runs. For *o*-xylene, these differences ran counter to the polarity theory with recovery decreasing in the presence of MEK and remaining unchanged in the presence of TCE. For TCE, recovery decreased in the presence of the more polar *o*-xylene and increased in the presence of MEK. Therefore, these mixture effects cannot be completely explained by polarity. One possibility of another chemical property that may influence passive monitor recovery is relative volatility.

As discussed in the methods section, there is some evidence to suggest that high volatility could cause reduced monitor recovery. In a situation where two chemicals of different vapor pressure are sampled together, the chemical with higher vapor pressure is more difficult to capture and more likely to release from the sorbent over time. Thus, it would appear that the chemical with lower vapor pressure is being recovered at a higher rate than the chemical of high vapor pressure. This explanation could account for the changes in TCE recovery in the presence of *o*-xylene since the vapor pressure of TCE is roughly seven times larger. Unfortunately, this explanation breaks down when samples involving MEK are considered. The vapor pressure of MEK is almost fifteen times that of *o*-xylene, yet the *o*-xylene recovery decreases significantly in the presence of MEK. Additionally, MEK recovery increases in the presence of TCE even though it has almost twice the vapor pressure.

Based upon the observations detailed above, intrinsic chemical properties are influencing the recovery relationship in mixtures, but there must be some other factors that are contributing as well. The next logical step is to examine how the different types of monitors responded in the presence of the solvents.

EVALUATION OF MONITOR EFFECTS

During initial analysis of the data, it became apparent that the monitors behaved differently, depending on the chemicals present in the mixture during each sampling run. In order to evaluate these differences, a series of box plots were created that compare the pooled accuracy ratio values for each monitor type. Each plot contains the data from twenty badges. The first of these plots is for *o*-xylene and is shown in Figure 3.4.

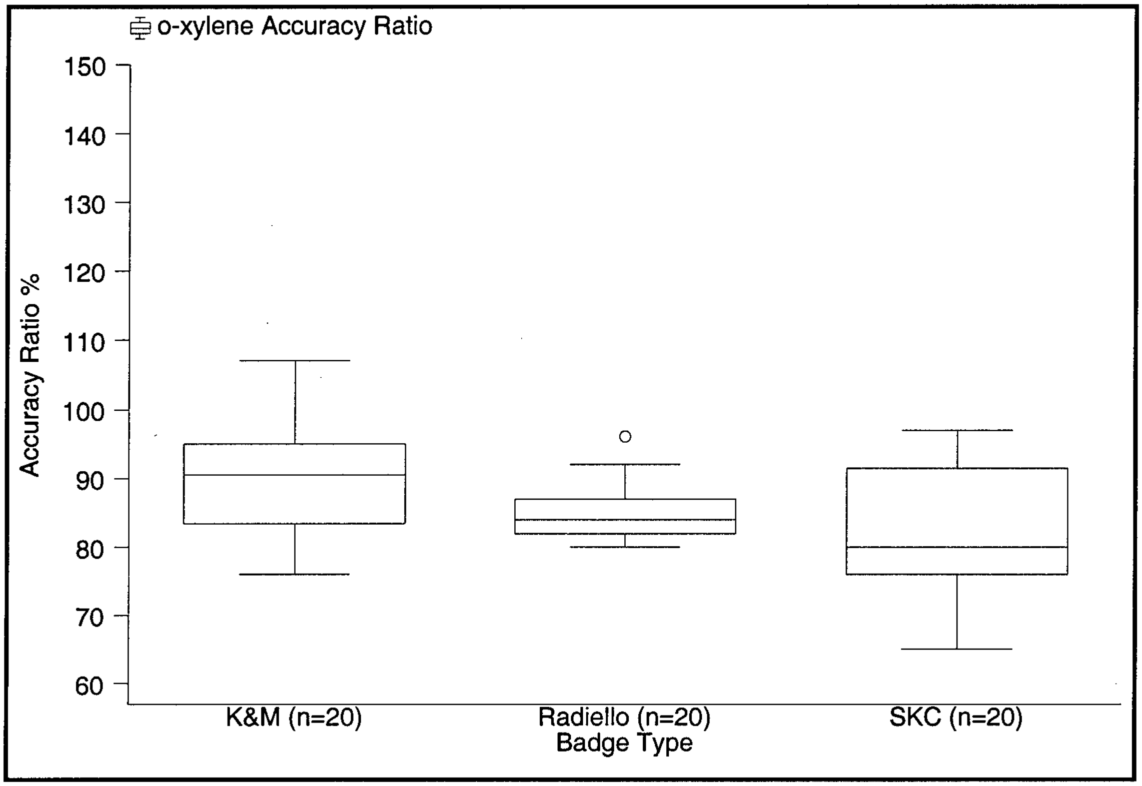

Figure 3.4: *o*-xylene Accuracy Ratio vs. Badge Type.

There are consistent differences in the accuracy ratio profiles for the three badges. In this figure, the K&M monitor demonstrates the highest median recovery value, whereas the Radiello monitor has the highest degree of precision. Although the median values are different, the boxes do tend to overlap, with interquartile ranges varying from 75-95%. Analysis of the individual monitor results for *o*-xylene also brought to light a relatively important discovery related to the Radiello monitor.

In the analysis performed after sample run two, a GC detectable amount of *o*-xylene was discovered on the Radiello cartridges, but not on the other two monitors. Although *o*-xylene had been present during run one, it was not in the sample mixture during run two. This same pattern also emerged after sample run six. There are two possible explanations for this anomaly. First, since *o*-xylene was the least volatile of all of the solvents used during this study, there is a possibility that a small amount could have been left inside the system or sampling chamber after the first sample run. Then, since the Radiello had the highest sampling rate for *o*-xylene, it was able to capture it at the lowest levels, whereas it might not show up on the other monitors. This seems unlikely since the system was thoroughly flushed after each run and wasn't shut down until all of the MIRANs read zero. Additionally, the system was typically run for 45-60 minutes on the morning of a run with the solvent mixture for that day flowing through it. This allowed the system to equilibrate prior to the start of a run.

A second possible explanation involves the design of the Radiello. As discussed earlier, the Radiello consists of a single-use sorbent cartridge that is inserted into a reusable diffusive barrier. During this study, the same five diffusive barriers were used for all eight experimental runs. Typically, only two days lapsed between each run, and it is possible that the diffusive barrier may have retained some of the *o*-xylene between runs. If that was the case, when the new sorbent cartridges were inserted into the diffusive barriers prior to run two, the solvent could have transferred to the sorbent and would then be revealed in the GC analysis. The same argument could be made with regard to runs five and six. Although this discovery is interesting and may require a change in monitor usage instructions by the manufacturer, due to the minimal size of the problem, its effect on this study is negligible.

Differences in monitor performance with regard to MEK are even more striking that those for *o*-xylene. In Figure 3.5, the highest median recovery now belongs to the SKC monitor. The Radiello again shows the highest degree of precision, but its accuracy is well below the other two badges. None of the interquartile ranges overlap, leading to the conclusion that the badges were definitely performing differently across the series of experiments. Again, monitor recoveries range from 75-95%.

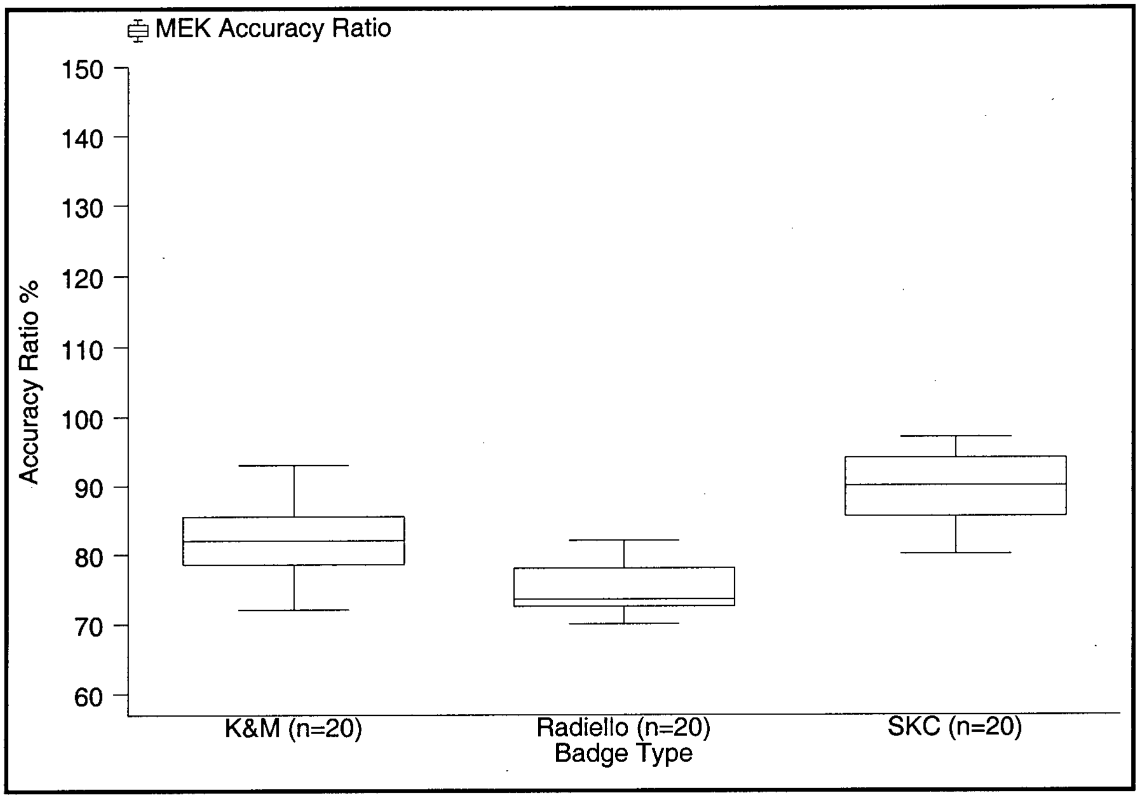

Figure 3.5: MEK Accuracy Ratio vs. Badge Type.

Figure 3.6 shows the TCE results, stratified by badge type. The TCE results are almost as striking as the MEK results. Again, the SKC shows the highest degree of recovery, but in this case it far exceeds 100%. The Radiello shows a high degree of precision and a tight interquartile range, but its median value also exceeds 100%. The K&M monitor perhaps shows the best results for TCE, with an interquartile range from 90-100% and a median accuracy ratio around 95%.

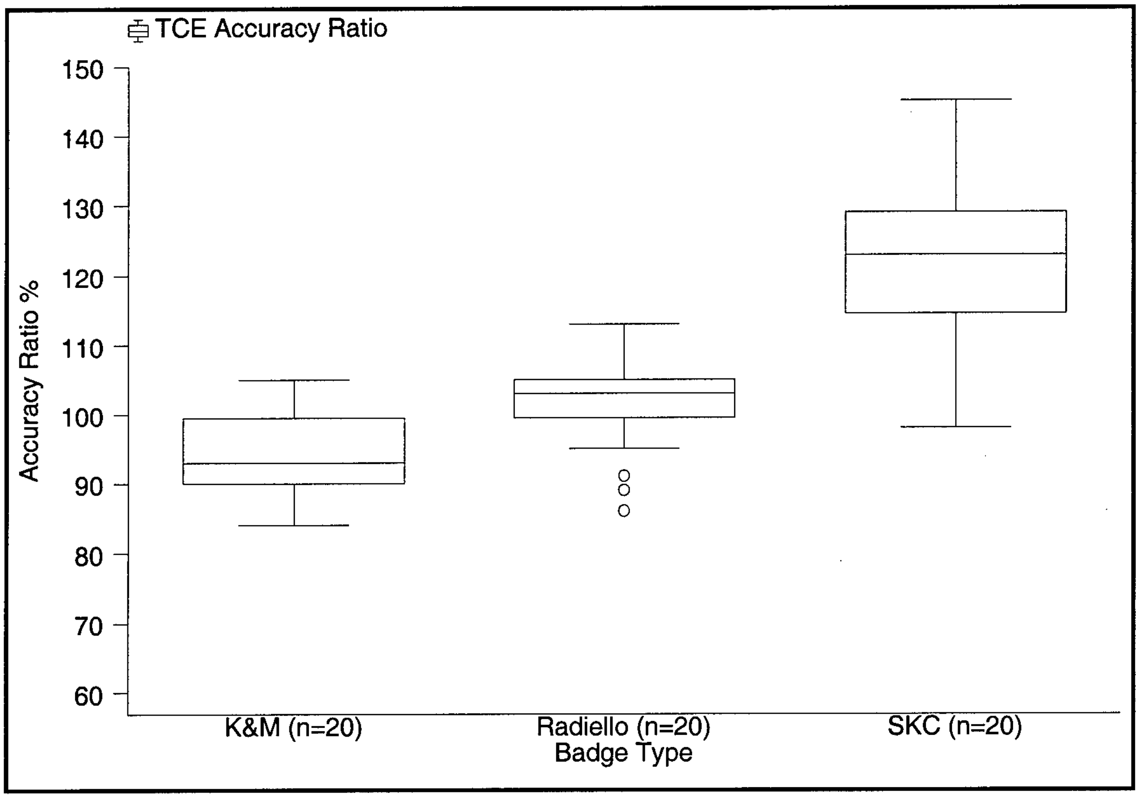

Figure 3.6: TCE Accuracy Ratio vs. Badge Type.

As with the mixture components above, a simple data analysis was performed comparing the monitor type to the chemical accuracy ratios. These results are presented in Table 3.2.

Table 3.2: Mean Accuracy Ratio and Standard Error Summary for Monitor Data.

	Chemical Being Sampled		
	o-xylene	MEK	TCE
Badge	Mean Accuracy Ratio (%) ± Standard Error (%) n=20	Mean Accuracy Ratio (%) ± Standard Error (%) n=20	Mean Accuracy Ratio (%) ± Standard Error (%) n=20
K&M	89.40 ± 1.85	82.25 ± 1.25	94.35 ± 1.38
Radiello	84.95 ± 0.94	75.10 ± 0.84	101.65 ± 1.58
SKC	82.40 ± 2.02	89.95 ± 1.09	122.10 ± 2.70
	$p < 0.016$	$p < 0.0001$	$p < 0.001$

Examination of the table reveals that there was a wide range of values reported by the different monitors. A series of one-way ANOVAs were conducted on the data to compare the accuracy ratios for each chemical, stratified by monitor type. In all three cases, the accuracy ratios were significantly different. The next step was to see if this effect was influenced by mixture component.

EVALUATION OF COMBINED EFFECTS

In order to evaluate the combined effects, a series of two-way ANOVAs were run for the three chemicals in the study. The accuracy ratio values were the dependent variable and the two categorical factors utilized were experimental run (stratified by mixture component) and monitor type. Additionally, an interaction term (product of the two categorical factors) was added to evaluate if there was a significant difference between the manners in which the monitors responded when different component mixtures were tested. A summary of the *o*-xylene ANOVA is present in Table 3.3.

Table 3.3: Two-Way ANOVA with *o*-xylene Accuracy Ratio as Dependent Variable.

Model Summary: $n = 60$; $R^2 = 0.668$; Significance = $p < 0.0001$

Source	Degrees of Freedom	Mean Sum of Squares	F-Statistic Value	Prob > F
BADGE	2	251.0	9.84	0.0003
RUN	3	366.7	14.37	0.0001
BADGE * RUN	6	143.9	5.64	0.0002
Residual	48	25.5		

The overall model was highly significant. Residuals from the model appear normal with no outliers. As expected by the analysis presented in previous sections, the badge and run terms were significant as well. However, the impact of the interaction was not expected. Not only was it significant; when the model included it almost 70% of the variance (as noted by the R^2 value) was explained. When the model was run without the interaction term, the R^2 value dropped to 0.434. This is interesting because it indicates that there is a large combined effect between the mixtures and the monitors. This is graphically represented in Figure 3.7.

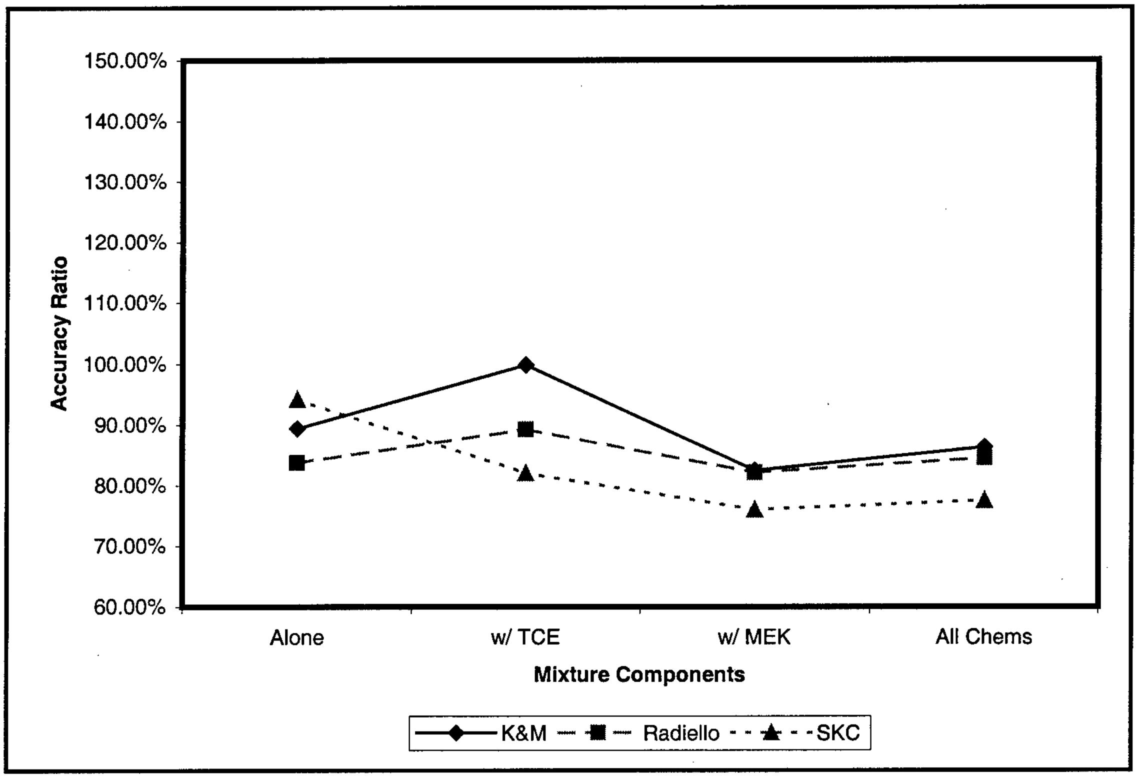

Figure 3.7: ***o*-xylene Accuracy Ratio, Stratified by Components and Monitor Type.**

The plot for *o*-xylene is striking. When the mean values for each grouping of five monitors are plotted based upon the mixture components present during each experimental run, it clearly shows a difference in the way the monitors reacted. Although the K&M monitor and the Radiello monitor show a similar pattern, they are not parallel by any means. The real difference is evident when the SKC monitor is included. During the run where *o*-xylene is present alone, the SKC monitor exhibits the highest mean recovery. However, during the run where *o*-xylene is present with TCE, the SKC monitor has the lowest mean recovery and it is the only monitor to show a decrease in recovery. Additionally, the monitors show differing degrees of stability across the runs. The Radiello monitor mean values differ less than 10% across the four different experimental runs where *o*-xylene was present, whereas the other two monitor types differ by almost 20%. This supports the notion that there is a combined effect present between the mixture components and the monitor being utilized. To determine if this effect was present with the other solvents, a two-way ANOVA was conducted with MEK and it is summarized in Table 3.4.

Table 3.4: Two-Way ANOVA with MEK Accuracy Ratio as Dependent Variable.

Model Summary: n = 60; $R^2 = 0.752$; Significance = $p < 0.0001$

Source	Degrees of Freedom	Mean Sum of Squares	F-Statistic Value	Prob > F
BADGE	2	1103.1	60.50	0.0001
RUN	3	105.8	5.80	0.0018
BADGE * RUN	6	21.6	1.19	0.3296
Residual	48	18.2		

For MEK, the ANOVA analysis was highly significant overall and for the two individual variables, but not for the interaction term. Residuals from the model appear normal with no outliers. The model explained over 75% of the variance with the interaction term included, whereas it explained almost 72% when it was removed. Of note, the F-statistic value for monitor type dwarfed the other sources. This is probably due the presence of a special sorbent on SKC badges designed specifically to capture polar solvents. This could also explain the lack of significance of the interaction term in that the sorbent type may have overshadowed its effect. Figure 3.8 summarizes the mean accuracy ratio values for MEK, stratified by monitor type and mixture composition.

The plot for MEK is closer to what would be expected if there were no differences in monitor performance associated with differing mixture composition. Each monitor has a similar pattern for its series of four points, although the actual recovery values differ by 10-15%. This is congruent with the two-way ANOVA findings that suggested there was no real difference associated with the interaction term. There is, however, still a notable difference between each monitor's ability to accurately recover MEK, with the SKC values clearly higher than those for the other two monitors.

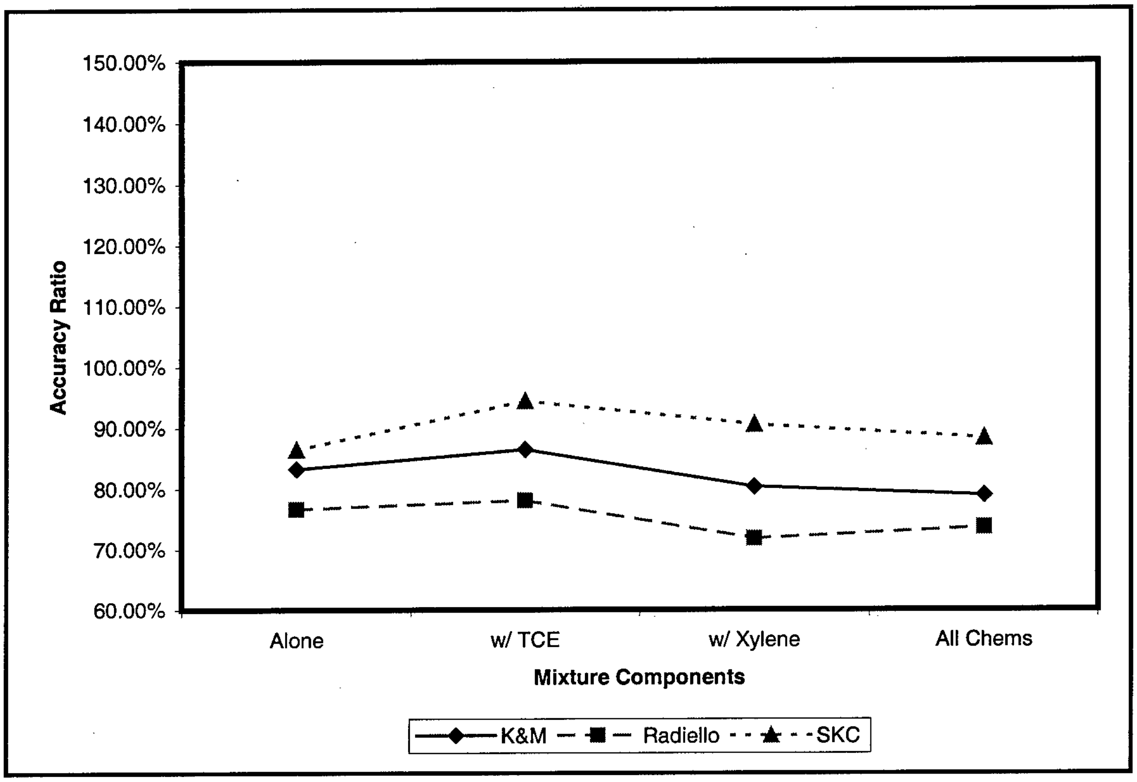

Figure 3.8: MEK Accuracy Ratio, Stratified by Components and Monitor Type.

A final two-way ANOVA was conducted to evaluate the accuracy ratios for TCE. The results from this test are summarized in Table 3.5.

Table 3.5: Two-Way ANOVA with TCE Accuracy Ratio as Dependent Variable.

Model Summary: n = 60; $R^2 = 0.930$; Significance = $p < 0.0001$

Source	Degrees of Freedom	Mean Sum of Squares	F-Statistic Value	Prob > F
BADGE	2	4138.5	222.30	0.0001
RUN	3	923.8	49.62	0.0001
BADGE * RUN	6	131.3	7.05	0.0001
Residual	48	18.6		

The TCE ANOVA was again highly significant overall and for all of the sources. Residuals from the model appear normal with no outliers. In this case, even though the F-statistic value for monitor type is quite large, the interaction term was still significant. Additionally, the complete model explained 93% of the variance as compared to 87% when the interaction term was removed. Figure 3.9 shows the accuracy ratios for TCE based upon monitor type and mixture components.

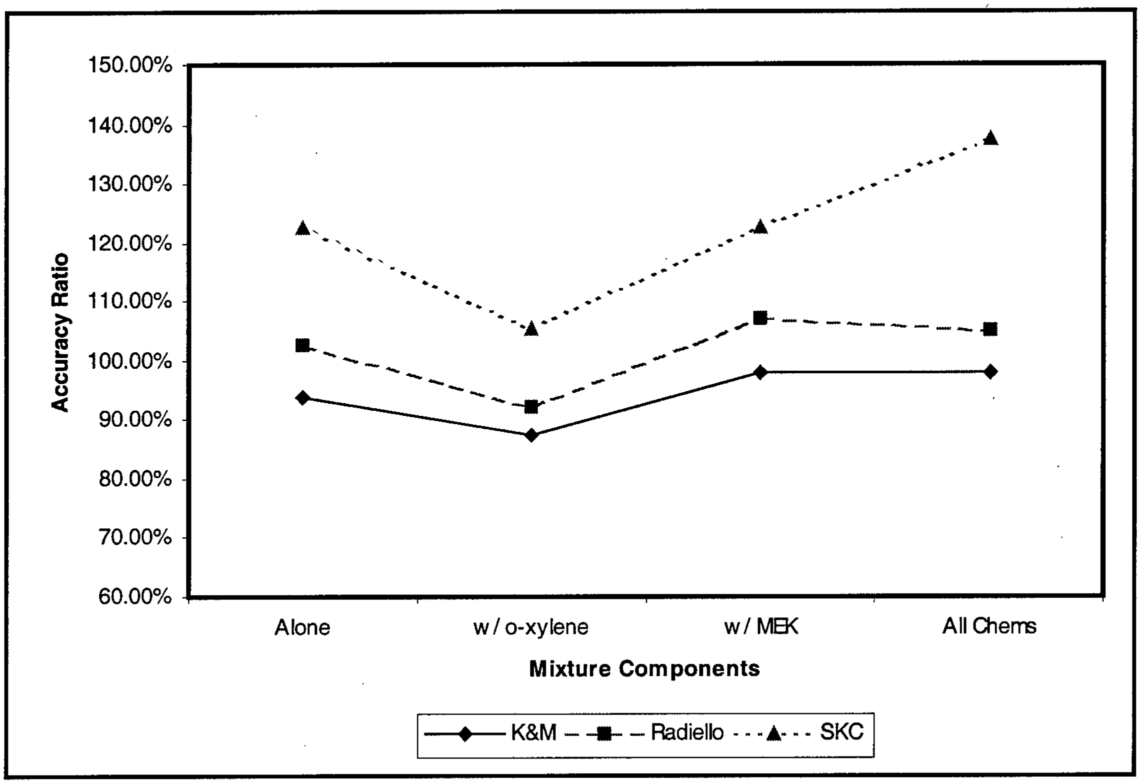

Figure 3.9: **TCE Accuracy Ratio, Stratified by Components and Monitor Type.**

A few observations are readily apparent in viewing this figure. First, the K&M and Radiello monitors perform similarly again. Their pattern of four runs is almost exactly the same, with the Radiello monitor having a slightly higher accuracy ratio. Second, all of the monitors show reduced recovery when o-xylene is present. Third, the SKC monitor shows a significant increase in accuracy ratio when all three chemicals are present in the mixture. Finally, the SKC accuracy ratio values are far above 100% and vary by almost 40%. This is twice the range of either of the other badges and seems to violate the polarity theory for the very non-polar TCE.

The results for TCE bear closer examination. It appears from examining Figure 3.9 that the SKC monitor drove these results. It is also clear that this monitor was performed quite differently for TCE compared to the other two solvents. A recovery of close to 140% does not seem possible, especially in light of what was seen on the other monitors. With this in mind, additional analysis was conducted on the TCE results for the SKC monitor.

SKC MONITOR TCE RESULTS

In performing the calculations to determine chemical concentrations on the monitors, a few critical factors drove the results. As discussed in the methods section, all of the monitors use similar equations to convert GC analysis results into air concentrations and those calculations are controlled by monitor sampling rate. Therefore, if the sampling rate is incorrect, the chemical concentrations determined using that sampling rate would also be incorrect. Monitor sampling rates were provided by each manufacturer and are specific for the chemical being sampled and for the monitor type. A closer examination of the SKC monitor sampling rates indicates that the TCE rate provided by the manufacturer may be in error.

In the literature published by SKC for use with their monitors, there is no sampling rate listed for TCE when using the model 575-002. For this reason, the manufacturer was contacted and guidance was requested. In a personal email, the guidance provided was to use the same sampling rate as for the 575-001 sampler. The justification for this is that since Anasorb CSC (the sorbent in the 575-001 sampler) and Anasorb 747 (the sorbent in the 575-002 sampler) are similar, the rates can be interchanged. This statement generally agrees with the SKC Sampling Rate Guide, where the sampling rates for many chemicals are exactly the same, regardless of the monitor used. However, in some instances, *o*-xylene for example, there is a 30% difference between the sampling rates for the 575-001 and 575-002.

To evaluate the appropriateness of using the 575-001 sampling rate for the 575-002 in the case of TCE, a review of Table 2.3 is in order. If the 575-001 sampling rate is used, the value for TCE is effectively the same as for *o*-xylene. From looking at the other two manufacturer's values, this is probably not accurate. In both of the other devices, the TCE sampling rate is at least 15% higher than that for *o*-xylene. As discussed in the methods section, sampling rate is a function of the monitor geometry and the air diffusion coefficient of the chemical being sampled. Since the 575-001 and 575-002 have the same geometry, the diffusion coefficients for *o*-xylene and TCE should be equal if their sampling rates are equal. However, the diffusion coefficients of TCE (0.079 cm^2/sec) and *o*-xylene (0.068 cm^2/sec) differ. Based upon this evidence, the sampling rate for TCE appears to be too low.

To test what would happen if this sampling rate were changed, it was adjusted upwards by 15% to mimic the other two devices. This created a revised rate of 16.4 cm^3/min. All of the SKC values for TCE were re-calculated using this rate. A two-way ANOVA was run with these revised values included and the results are presented in Table 3.6.

Table 3.6: Two-Way ANOVA with Revised SKC TCE Accuracy Ratio.

Model Summary: n = 60; $R^2 = 0.830$; Significance = $p < 0.0001$

Source	Degrees of Freedom	Mean Sum of Squares	F-Statistic Value	Prob > F
BADGE	2	565.7	33.00	0.0001
RUN	3	787.6	45.95	0.0001
BADGE * RUN	6	85.9	5.01	0.0005
Residual	48	17.1		

There was no appreciable change to the ANOVA results, with the overall model and all three sources being highly significant. The amount of variance explained by the model did drop by about 10%, by that is primarily a function of the reduction in the large F-statistic associated with monitor type. Based upon the size of the F-statistic now, the new TCE sampling rate for the SKC monitor seems to be more in line with the rest of the model. Therefore, it is recommended that the sampling rate for TCE when using the SKC 575-002 monitor be raised to the revised rate. Changing the sampling rate in this manner is significant in that it affects the overall performance of the badge, especially in relation to the NIOSH accuracy requirements.

NIOSH ANALYSIS

As discussed in the introductory section, NIOSH has a detailed procedure for validating passive monitor performance. Part of this protocol involves challenging the monitors with a variety of known chemical concentrations and measuring their accuracy and precision. To meet NIOSH requirements, the monitors must have an accuracy within 25% of the true value at a 95% confidence limit and a precision (quantified as coefficient of variation) less than or equal to 10.5%. The monitors are evaluated in the same manner with a potential interferant present.

To evaluate monitor performance in this study using the NIOSH protocol, Table 3.7 details the coefficients of variation and confidence limits for each monitor, stratified by chemical being sampled.

Table 3.7: Monitor Accuracy Ratio Confidence Limits and Coefficients of Variation.

	Chemical Being Sampled					
	o-Xylene		MEK		TCE	
Badge	Accuracy Ratio (%) 95% CI n=20	Coefficient of Variation (%)	Accuracy Ratio (%) 95% CI n=20	Coefficient of Variation (%)	Accuracy Ratio (%) 95% CI n=20	Coefficient of Variation (%)
K&M	[85.5,93.3]	9.2	[79.6,84.9]	6.8	[91.5,97.2]	6.6
Radiello	[83.0,86.9]	5.0	[73.3,76.9]	5.0	[98.3,105.0]	7.0
SKC	[78.2,86.6]	11.0	[87.7,92.2]	5.4	[116.4,127.7][a]	9.9

a = this is the confidence limit for the SKC TCE values using the original sampling rate. With the revised sampling rate, the mean = 104.7%, CV = 9.9%, and 95% CI = [99.9,109.5]

The table shows that even though this analysis detected differences in performance based upon several factors, they are not large enough to exceed NIOSH protocol requirements in most instances. The precision requirement was met in all but one case; *o*-xylene with the SKC monitor. Confidence limits met the criteria in all but two cases. In the first case, the SKC monitor upper confidence limit for TCE exceeded 125% when the original sampling rate was used. However, when the revised sampling rate was used, the upper confidence level dropped to 109.5%. In the other case, the Radiello monitor lower confidence limit fell short of 75% for MEK.

CHAPTER 4: DISCUSSION

This study demonstrated that the components present during a sampling event could significantly impact the results obtained. However, the manner in which these results were affected was not always as expected. The two primary explanations for this impact, polarity and volatility, were important in understanding the overall recovery of the different solvents, but they did not satisfactorily describe the variance between experimental runs. As expected, MEK (the most polar and volatile compound in the mixtures) showed the poorest overall recovery across all of the experimental runs. However, when MEK was included in a mixture with other compounds, its impact was not predictable. In fact, in most cases where a more polar compound was present with a less polar compound, the recovery of the more polar compound was either significantly enhanced or unchanged whereas the recovery of the less polar compound was significantly reduced. The effects of volatility were equally unexpected. The highly volatile MEK experienced enhanced recovery in the presence of the less volatile TCE, whereas the minimally volatile *o*-xylene had reduced recovery in the presence of MEK. For these reasons, the mixture components must be influenced by other factors and further explanations were considered.

The next logical step was to examine the effect of the individual monitors on the variance. Monitors used during this study had unique geometry and their individual chemical sampling rates were quite different. Additionally, although all of the monitors used carbon-based sorbents, there were some chemical and structural differences between them. In a simple analysis of the contribution of the monitor to the study results, it was readily apparent that there was a significant difference in overall recovery of the solvents between the monitors. Additionally, this difference was not consistent across the different solvents. Perhaps the easiest to explain was the recovery of MEK by the SKC monitor. The sorbent used in this monitor is specifically designed to capture more polar solvents and it clearly did so (see Figure 3.5). However, the impact of this sorbent could not explain the fact that recovery of MEK was enhanced for the SKC monitor in the presence of TCE. For this reason, the possibility of an interaction between the mixture components and the monitors was considered.

Statistical inclusion of an analyte-monitor interaction term explained more than 65% of the variance in this study for every solvent, highlighting the need to consider monitor choice based upon the solvent mixture. Although adsorbent type would be important in matching mixtures to specific monitors (as shown with MEK), it seems that sampling rate probably has a large impact on solvent recovery when choosing a monitor for a mixture. A closer examination of the results revealed some insights in this regard.

In almost every instance, the greatest deviations from the single chemical experimental run accuracy ratio values were experienced when one additional chemical was added to the mixture. This deviation seemed to be dampened when all three chemicals were present. This point is most evident when examining the three mixture component plots (Figures 3.1, 3.2, & 3.3) and noting the relatively minor differences between the median values of the single chemical runs versus the medians for the all chemical runs. Whether this was merely a function of the study design and the specific solvents chosen, or is applicable in a broader sense, is unknown. A study involving a greater number of chemicals could more substantially explore this finding.

It is interesting to note that all of the monitors in this study met minimum NIOSH protocol criteria when sampling the individual solvents. For the most part, this remained true even when all of the multiple chemical runs were considered. For these reasons, it is easy to see why the issues outlined in this study are typically not considered. If, during validation testing for their monitors, a manufacturer finds that the monitor meets the NIOSH criteria even with interferences present, the impact of interferences is not considered relevant. However, if the goal is to choose a monitor that will provide the highest possible accuracy, the results of this study indicate that consideration of mixture components is critical. The 15-25% difference in results seen between monitoring single chemical atmospheres and multiple chemical atmospheres could lead to improper conclusions regarding the health and welfare of workers.

EXPERIMENTAL ERROR

In a study of this kind, there are several possible sources of experimental error. Much of this error is uncontrollable and is related to instrumentation. However, several efforts were made to control uncertainties and biases associated with this study. As was discussed earlier, the order of the runs was randomized to eliminate bias in that regard. Additionally, a blank run was included and several blank monitors were evaluated to control for possible contamination on the monitors received from the manufacturers. The standard solutions were processed through the gas chromatograph twice during each sampling run analysis to evaluate instrumentation error. In all cases, the difference between the first and second runs through the GC was less than 1%. To ensure proper analytical procedure, blind spikes, prepared by a third party, were analyzed in the same manner as all of the other samples. Differences between the spiked values and the recovered values, after adjustment for desorption efficiency, were less than 5%. To verify that the MIRANs were not drifting, the calibration points were checked after the fourth and eighth experimental runs, with all differences being less than 2%. To control for possible differences between monitors of the same type, monitors provided by K&M and SKC were all from the same batch. Although the Radiello monitors came from three different batches, each batch was represented equally in the desorption efficiency, blind spike, blank, and experimental run samples. Based upon the fact that these monitors had the highest overall precision, the effect of batch was inconsequential.

One primary source of experimental error that was difficult to control involved the placement of monitors in the sampling chambers. During study design, there was a concern that all of the monitors might not receive the same ambient concentration, due to the small diameter of the chambers, the close proximity of the monitors, and the presence of a 180° bend in between the two chambers. As alluded to earlier, the airflow rate was set relatively high in an attempt to avoid this problem. Additionally, the sampling chambers were split into five sections, as described earlier, and one of each monitor type was placed in each section. Within the sections, the location of the monitors was randomized. In this manner, if there were differences in ambient concentration inside the sampling chamber, they should affect each monitor type equally. Unfortunately, it was only possible to take chamber concentration readings with the MIRAN instruments at the output end of the sampling chambers. This did, however, provide the monitors with the highest possible recoveries since it would be expected that if solvent concentrations changed, they would decrease as the air stream traveled down the sampling chamber.

After the first two sample runs, it was evident that there were some differences across the length of the sampling chamber. A pattern developed that can be seen by examining Figure 4.1. For each monitor, the lowest sample results are seen with the devices located in chamber section C. Also, the samples located in the back sampling chamber (sections C-E) have lower relative values than the samples located in the front chamber. Although this pattern is obvious, the question of whether the differences are of concern in another matter. In this instance, and for most of the other cases, the largest standard deviation across the five samples is approximately 5%. It can be argued that this is within the sample variation expected from these monitors.

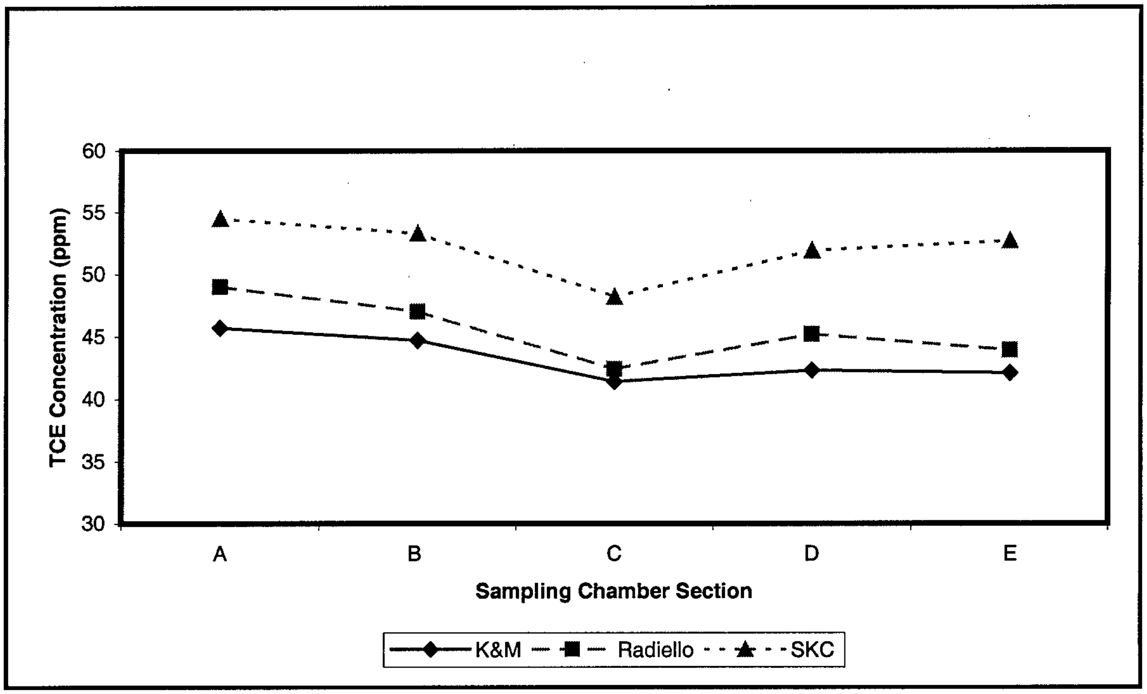

Figure 4.1: TCE Concentration by Sampling Chamber Section for Sample Run 1.

As explained earlier, the monitor-calculated concentration values are based upon a formula that relates concentration to sampling rate, desorption efficiency, mass recovered, sample period, temperature, and pressure. By far, the two greatest sources of sample error in this equation are sampling rate and desorption efficiency. In an earlier table (Table 2.5), the standard deviation for desorption efficiency was as high as 4%. Manufacturer's literature states that sampling rates can have a standard deviation for these solvents ranging from 0.7-1.2%. These two sources of sampling uncertainty alone can account for the sample variation seen inside the sampling chamber. Combine this with the fact that segregating the monitors by chamber section controlled for this pattern effect and it can be concluded that this was not a confounding factor for this study. In fact, it is probably more significant that the pattern could be discovered at all considering the error typically associated with passive monitors.

LIMITATIONS

There are several known environmental variables that can influence the performance of passive monitors. In fact, the NIOSH protocol includes tests that examine the effects of temperature, relative humidity, air velocity, concentration, and orientation. Due to time and cost constraints, all of these values were held constant. It is important to note, however, that in order to obtain validation, these variables cannot significantly impact the performance of the devices. Therefore, although these values were constant in this study, it is expected that the study results should be applicable to any sampling event that occurs within NIOSH protocol criteria.

A second major limitation is the use of constant exposure levels for the duration of the monitoring period. In most cases, this is not representative of typical workplace conditions. In a more typical atmosphere where the chemical concentrations fluctuate over time, some sources have reported problems associated with reverse diffusion of the chemicals from the monitor absorbent, resulting in poor monitor accuracy.[19] Although constant levels were the goal, as was discussed earlier, the exposure profiles did have some fluctuations. Regardless, the purpose of this study was to examine mixture effects and as long as all of the monitors were exposed equally, the reverse diffusion issue was relatively irrelevant. The only caveat to this would be if a detectable reverse diffusion effect varied by monitor type. This could not be evaluated in this study.

A final limitation involved the sampling rates used for the different solvents. The effect of sampling rate on a variety of issues associated with the monitors has been demonstrated several times throughout this study. In fact, its influence is so important that the Occupational Safety and Health Administration (OSHA) has become involved in the assignment of sampling rates to individual manufacturer's monitors for specific applications. All of the manufacturers provide sampling rates, but they recommend that sampling rates be verified by the user for the chemicals being sampled at the environmental conditions expected. This was impossible to do for this study and is infeasible for the industrial hygienist in the field.

CHAPTER 5: CONCLUSIONS

The experiments described have led to a number of conclusions concerning mixed chemical environments and the utilization of passive sampling monitors for organic vapors. The operating hypothesis was found to be partially correct. Polarity and relative volatility influence overall accuracy, but this study indicates that they do not completely account for the changes in accuracy when two or more chemicals are present. In several instances, there were large differences in a chemical's accuracy ratio depending on mixture components that ran counter to this explanation. Additionally, there were some cases where recovery was actually enhanced by the presence of multiple chemicals (TCE in the presence of MEK and *o*-xylene).

Other explanations to account for the results found during this study were considered. Monitor type, specifically monitor adsorbent composition and geometry/sampling rate were found to impact overall accuracy and precision. As advertised, the SKC Anasorb 747 sorbent used for monitoring MEK clearly demonstrated higher accuracy for that compound than the other monitors. Similarly, the Radiello monitor, most likely due to its geometry/sampling rate, had the highest degree of precision across all study runs. However, this still did not account for the changes in accuracy ratio related to mixture composition. This led to the most novel finding in the study.

Although an interaction was not expected, it was clear from this study that individual monitors react differently depending on mixture components. The most striking demonstration of this involved the *o*-xylene samples. The SKC monitor recovered less *o*-xylene as additional chemicals were added to the mixture whereas the other two monitor's recovery of *o*-xylene were enhanced or remained unchanged. The fact that this phenomenon was not consistent across all three chemicals or all three monitors lends even more credence to its existence. For example, the Radiello monitor showed little variance across all mixtures when monitoring MEK and *o*-xylene, but a large amount of variance when monitoring TCE. On the other hand, the K&M monitor demonstrated low precision for *o*-xylene and TCE across all mixtures, but high precision when monitoring MEK.

Based upon the conclusions from this study, a few recommendations can be made when selecting passive monitors. If the atmosphere of interest contains a single chemical at or near the TLV and other chemicals far short of their TLVs, preferentially choose a monitor with a sorbent designed for the prevalent chemical. Additionally, find a monitor that offers the highest sampling rate possible without concerns for monitor overloading. When selecting a monitor for atmospheres with multiple chemicals, choose a general use sorbent and the highest sampling rate possible. When selecting a monitor for atmospheres with two chemicals, the interplay between polarity, sampling rate, and volatility must be considered.

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APPENDIX A: ENVIRONMENTAL DATA

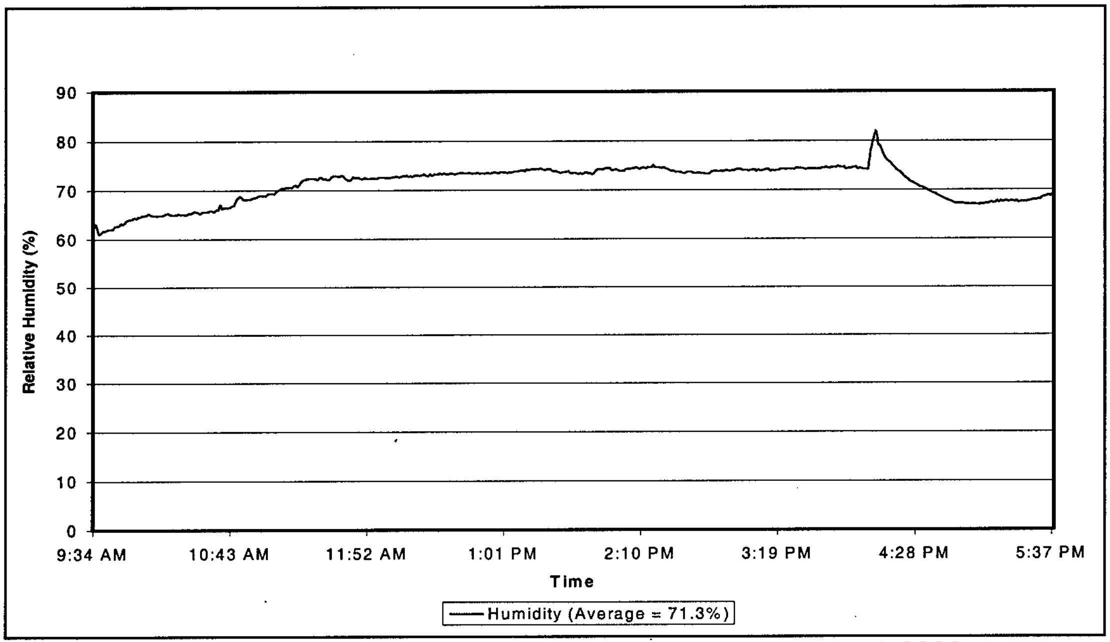

Figure A.1: Relative Humidity Readings for Run 1 on February 5, 2002. (Average Temperature = 21.6 °C)

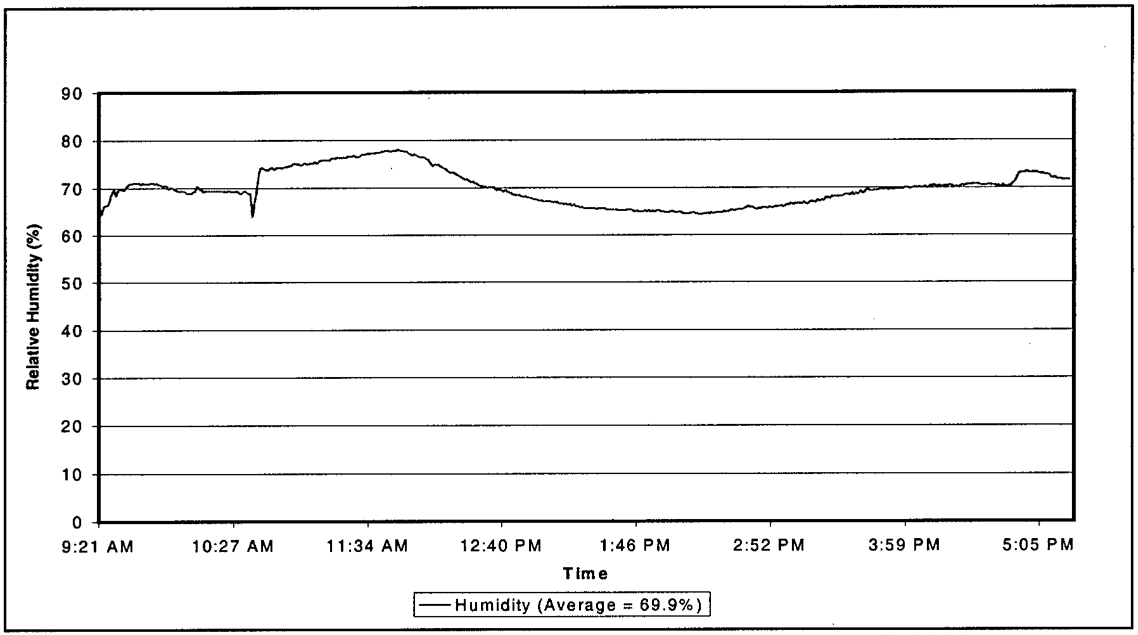

Figure A.2: Relative Humidity Readings for Run 2 on February 7, 2002. (Average Temperature = 21.2 °C)

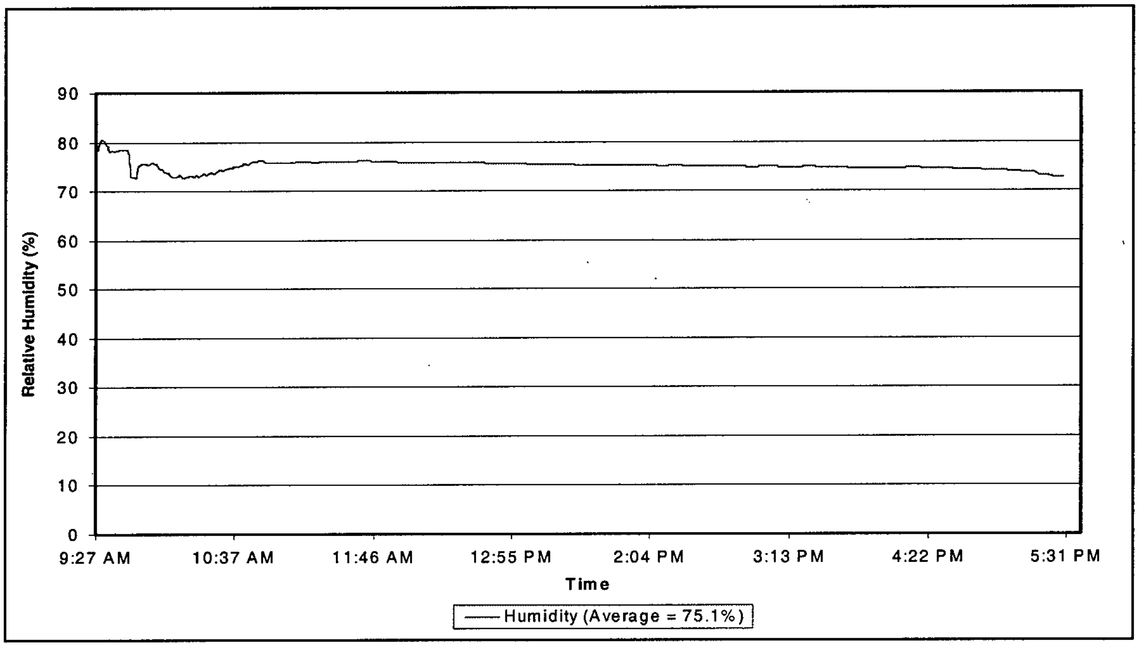

Figure A.3: Relative Humidity Readings for Run 3 on February 11, 2002. (Average Temperature = 21.5 °C)

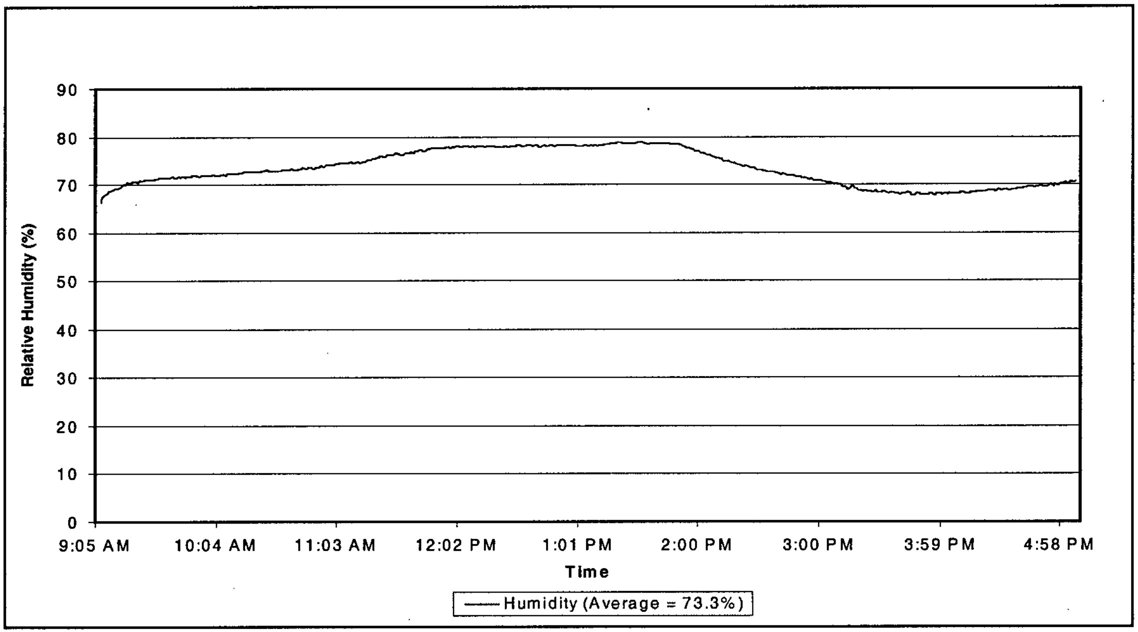

Figure A.4: Relative Humidity Readings for Run 4 on February 14, 2002. (Average Temperature = 21.3 °C)

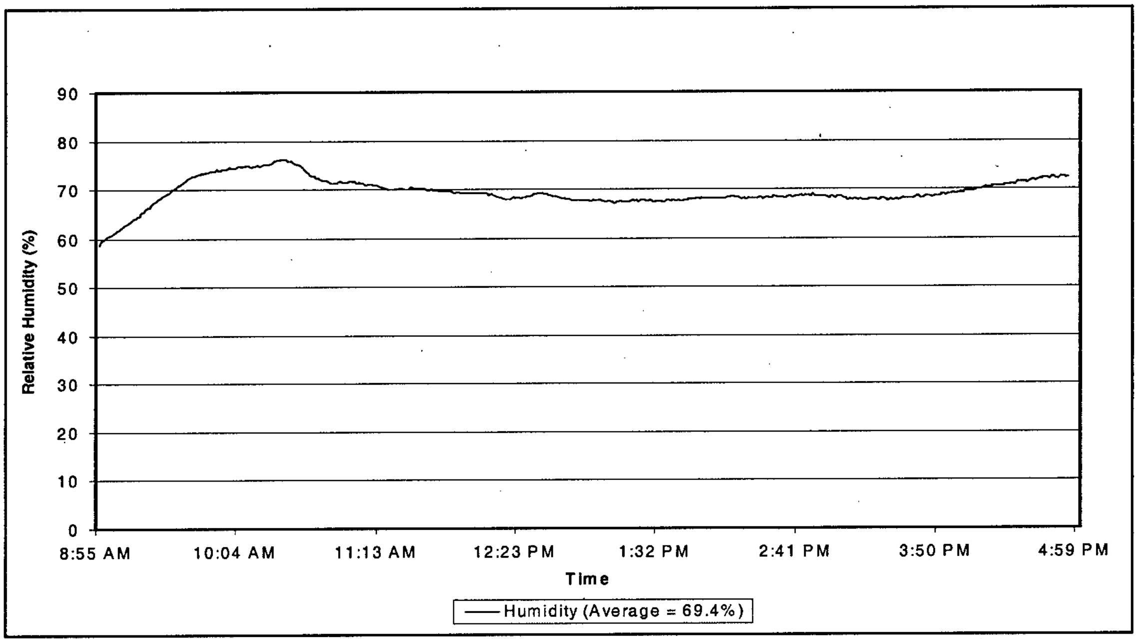

Figure A.5: Relative Humidity Readings for Run 5 on February 19, 2002. (Average Temperature = 21.1 °C)

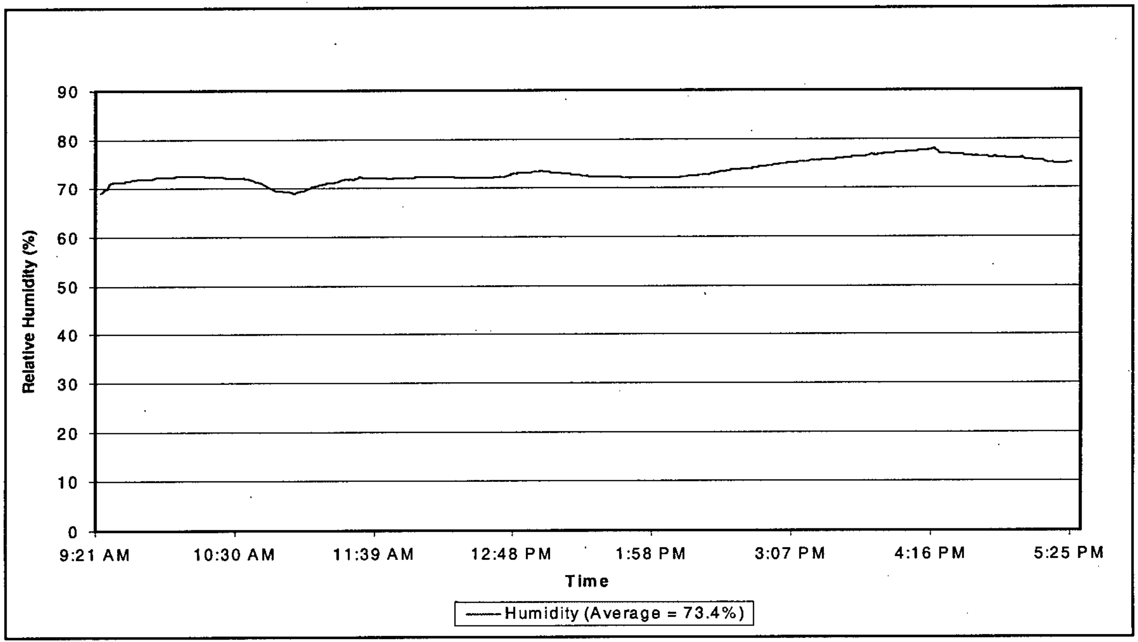

Figure A.6: Relative Humidity Readings for Run 6 on February 21, 2002. (Average Temperature = 21.3 °C)

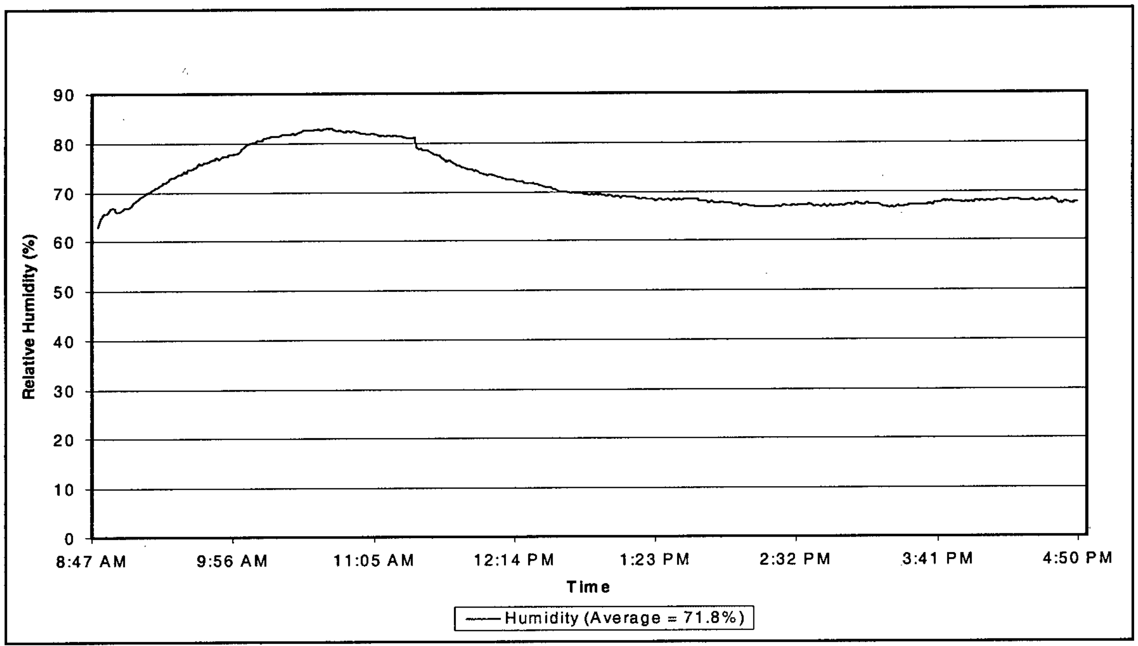

Figure A.7: Relative Humidity Readings for Run 7 on February 25, 2002. (Average Temperature = 20.8 °C)

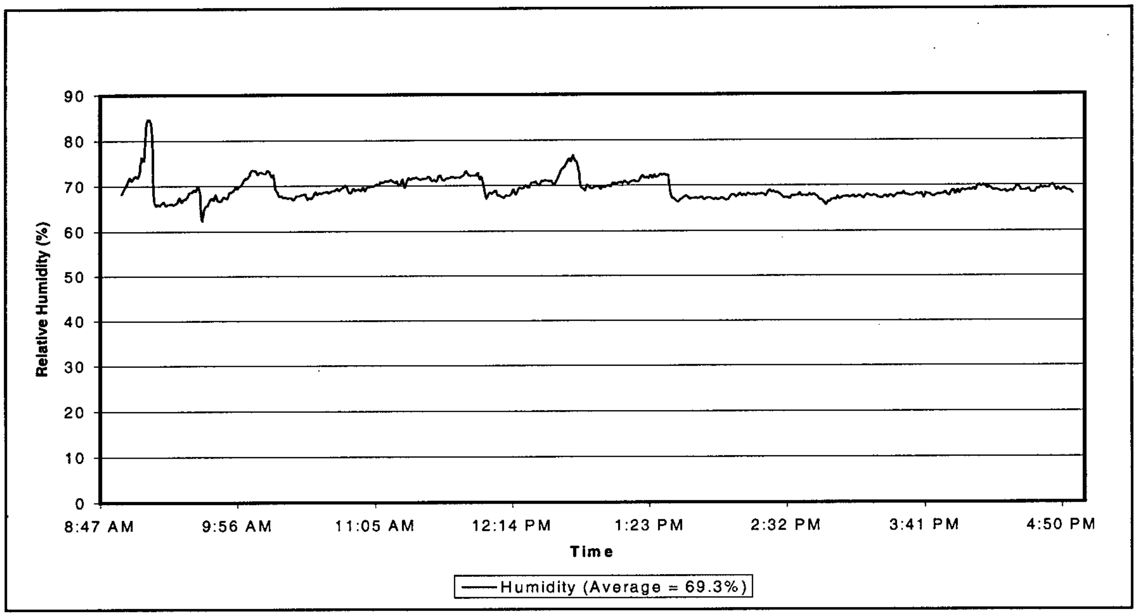

Figure A.8: Relative Humidity Readings for Run 8 on February 28, 2002. (Average Temperature = 21.2 °C)

APPENDIX B: MIRAN CALIBRATION CHARTS

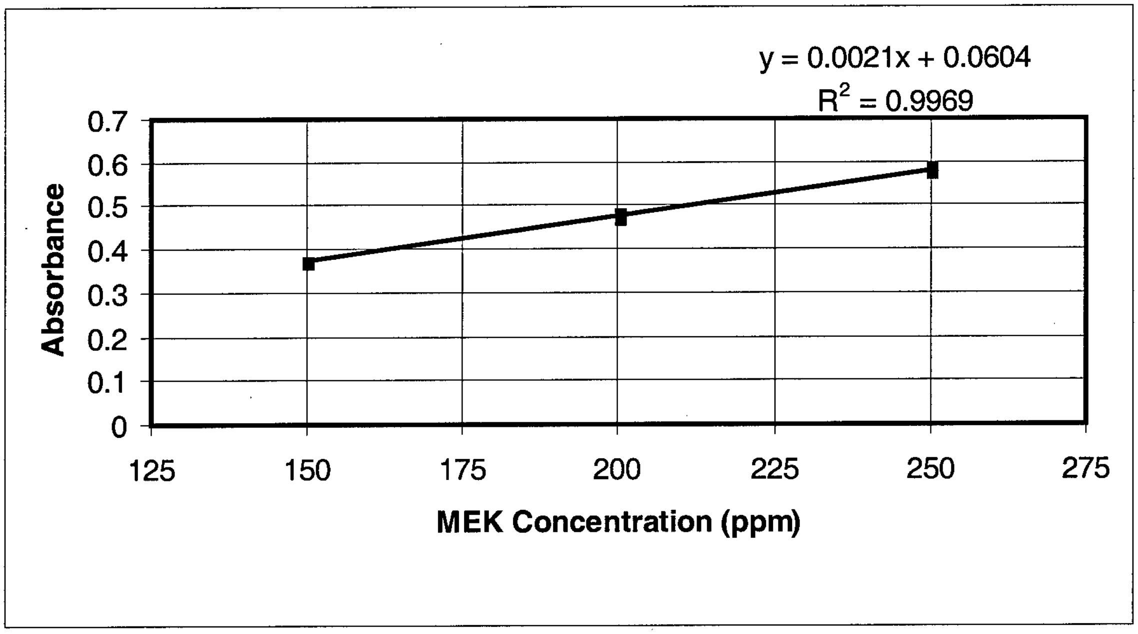

Figure B.1: MEK Calibration Plot (MIRAN #1, Model #068-5688, Serial #1A2656).

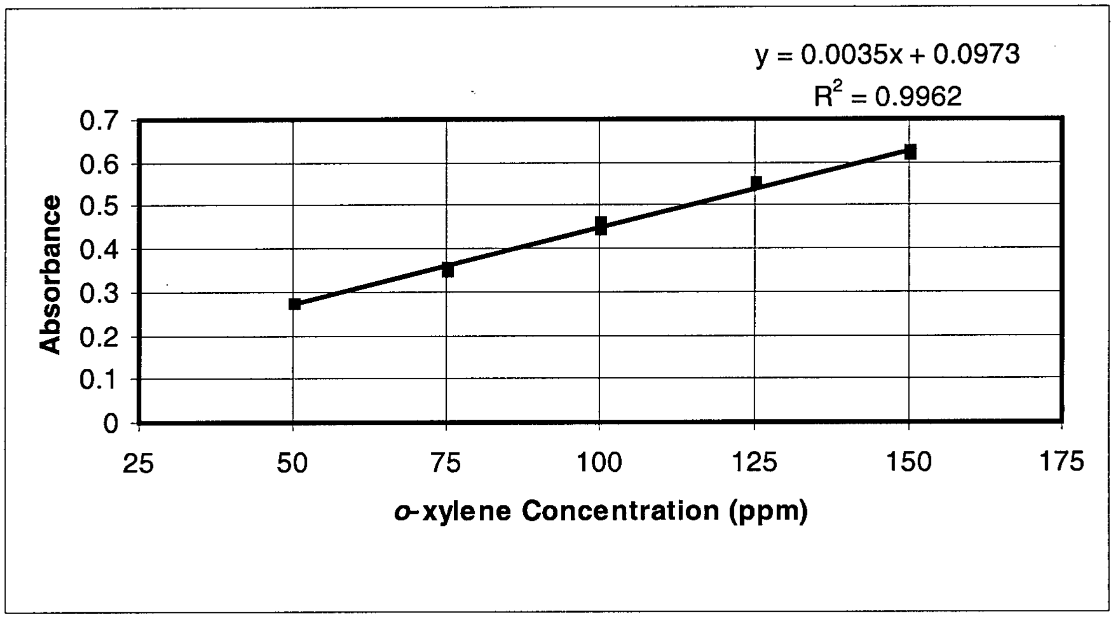

Figure B.2: *o*-xylene Calibration Plot (MIRAN #2, Model #5683, Serial #1A-1299).

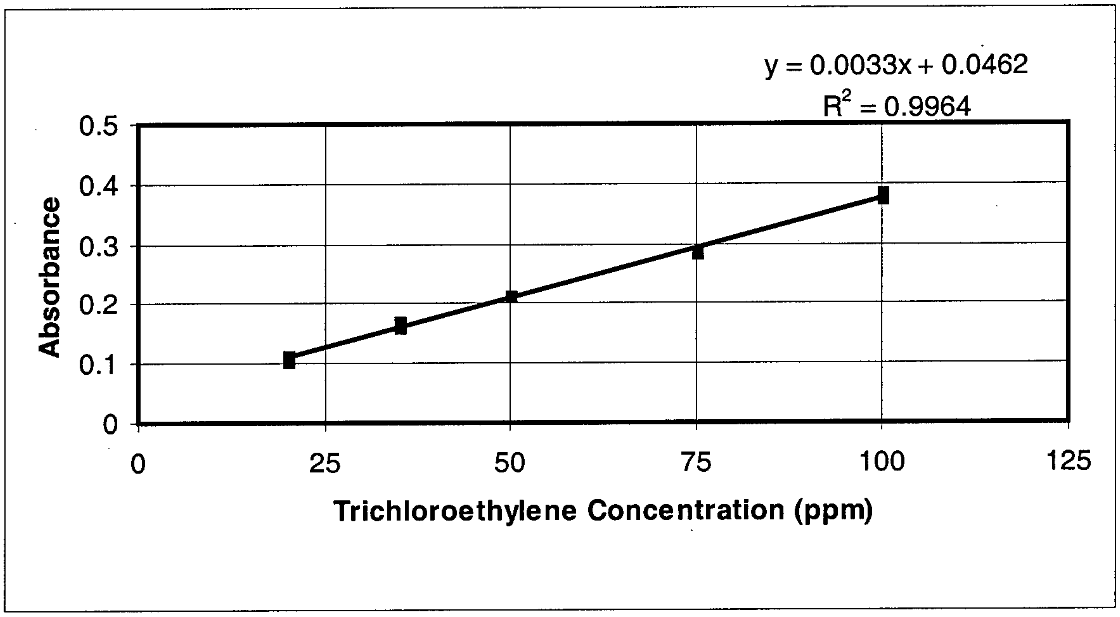

Figure B.3: TCE Calibration Plot (MIRAN #3, Model #063-5683, Serial #1A-2756).

APPENDIX C: MIRAN DATA

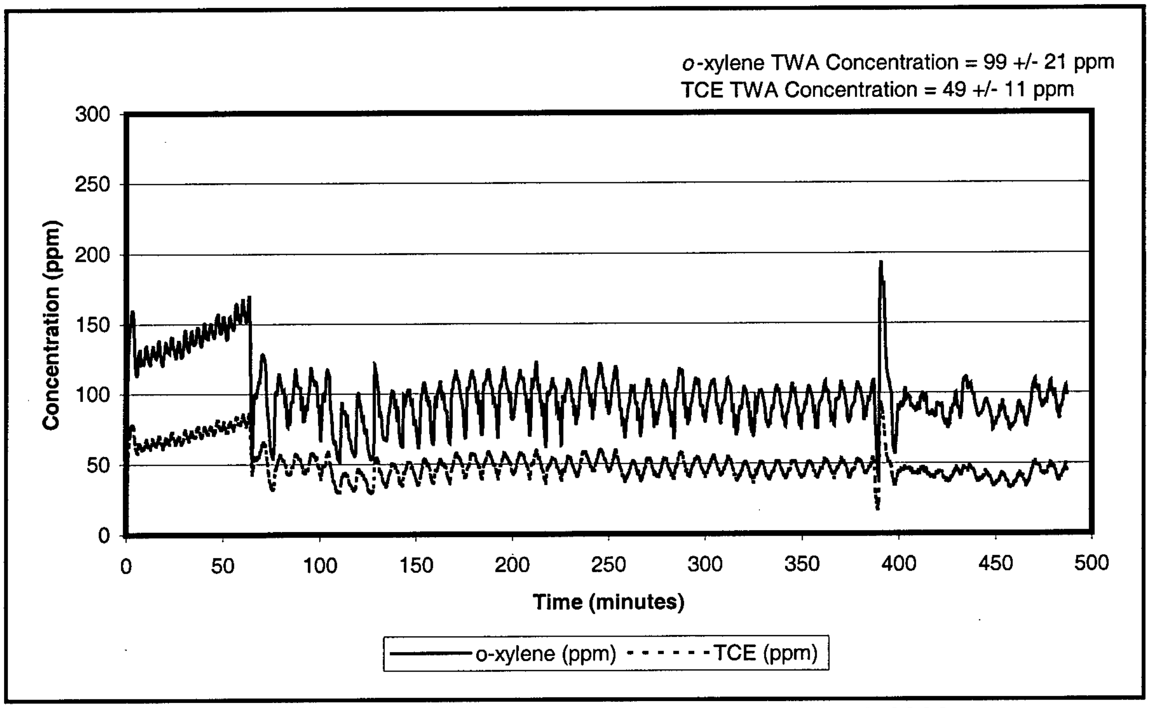

Figure C.1: Time Plot of MIRAN Data for Run 1 on February 5, 2002.

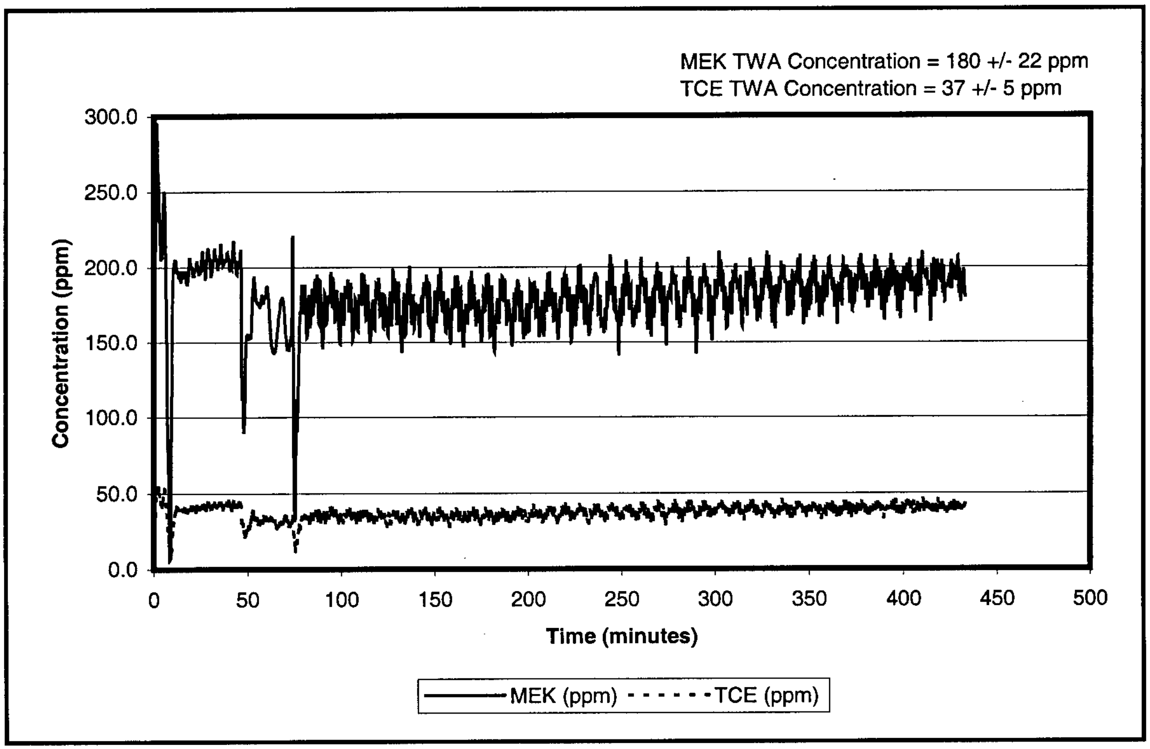

Figure C.2: Time Plot of MIRAN Data from Run 2 on February 7, 2002.

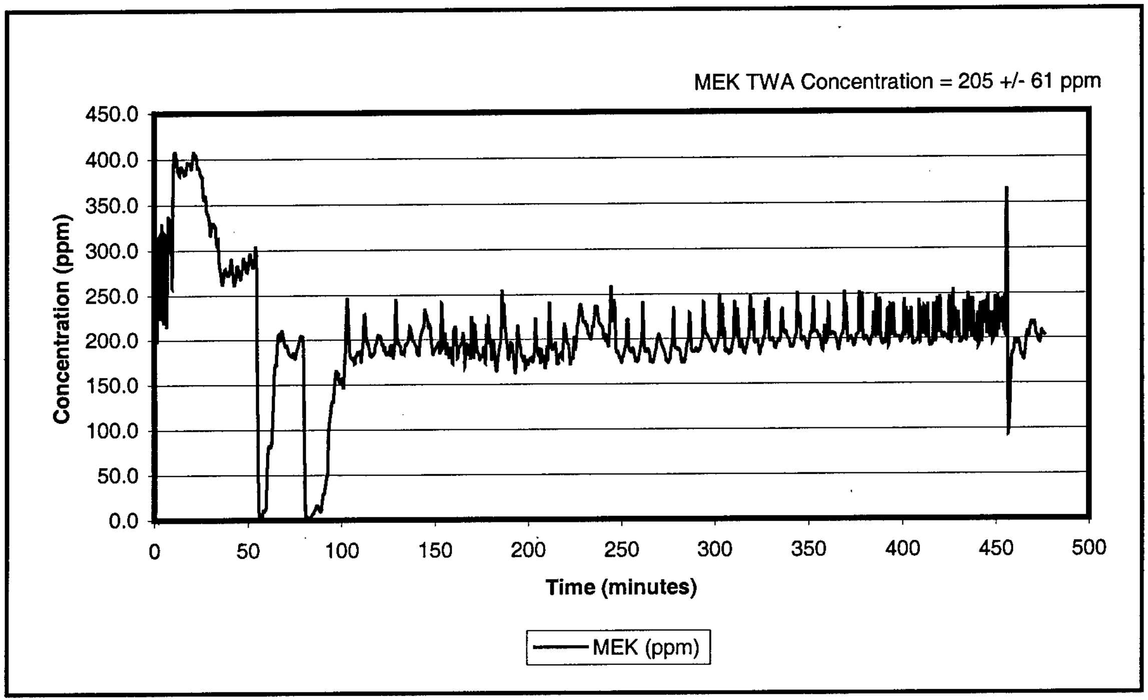

Figure C.3: Time Plot of MIRAN Data from Run 3 on February 11, 2002.

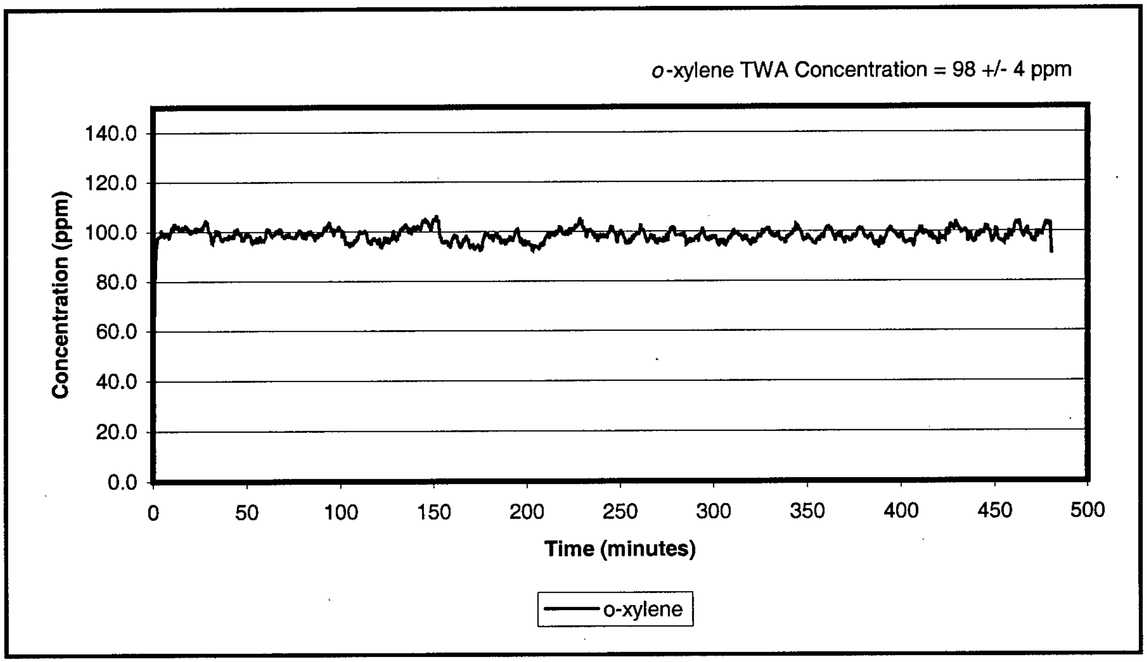

Figure C.4: Time Plot of MIRAN Data from Run 5 on February 19, 2002.

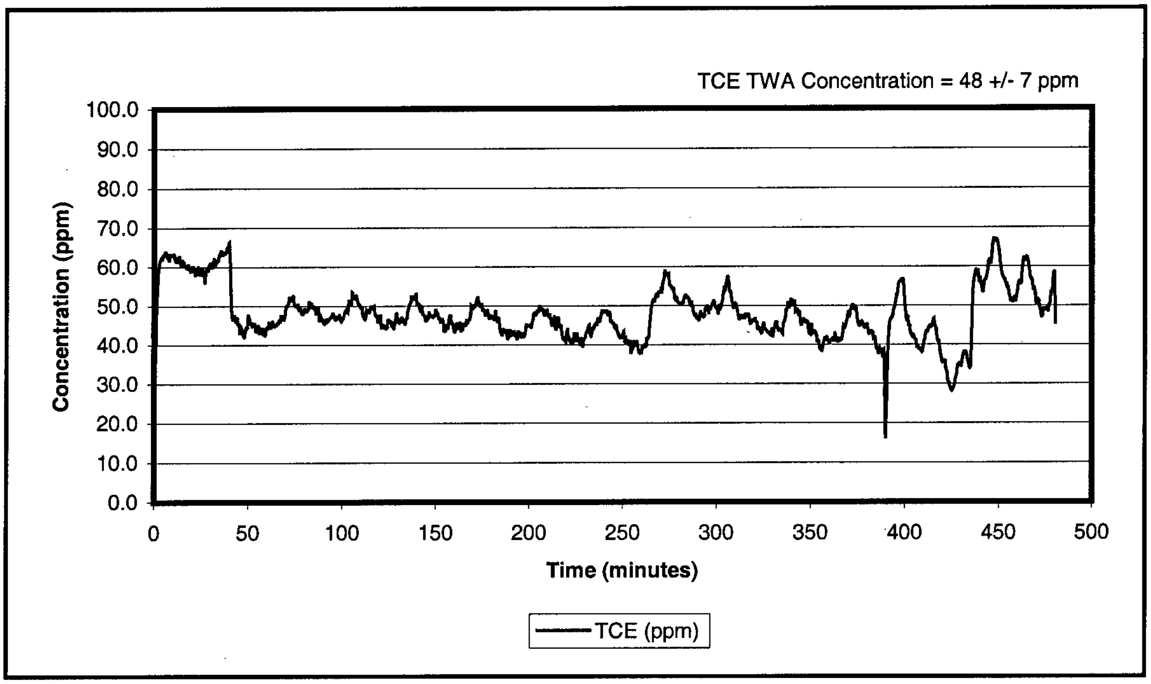

Figure C.5: Time Plot of MIRAN Data from Run 6 on February 21, 2002.

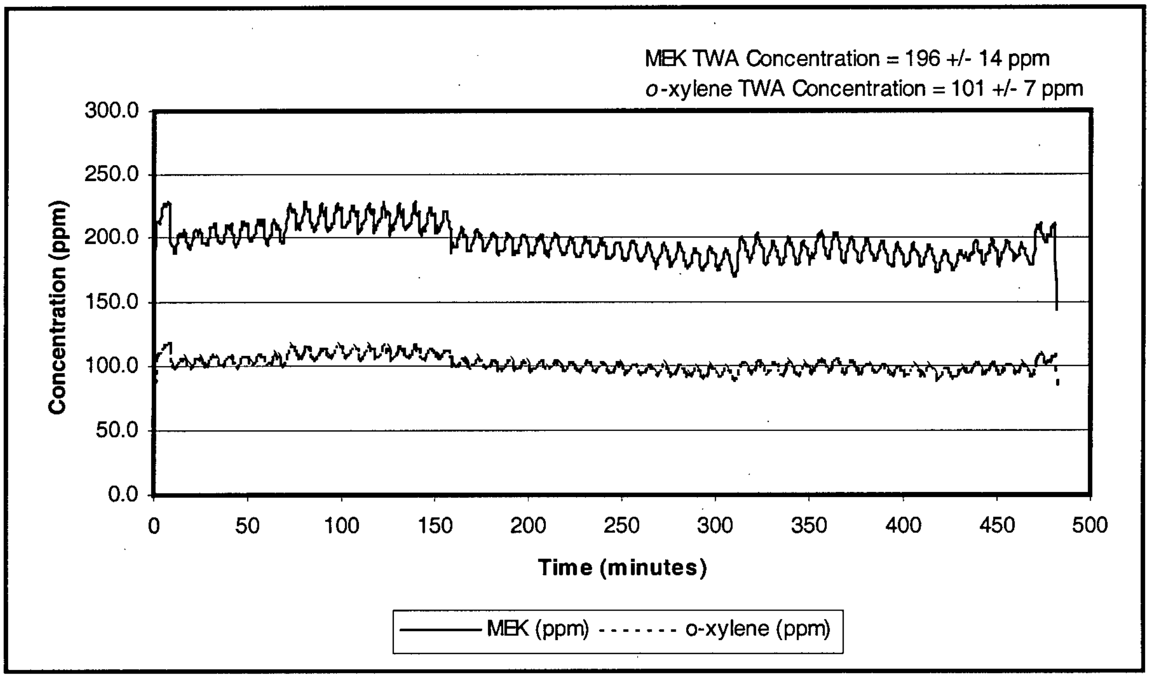

Figure C.6: Time Plot of MIRAN Data from Run 7 on February 25, 2002.

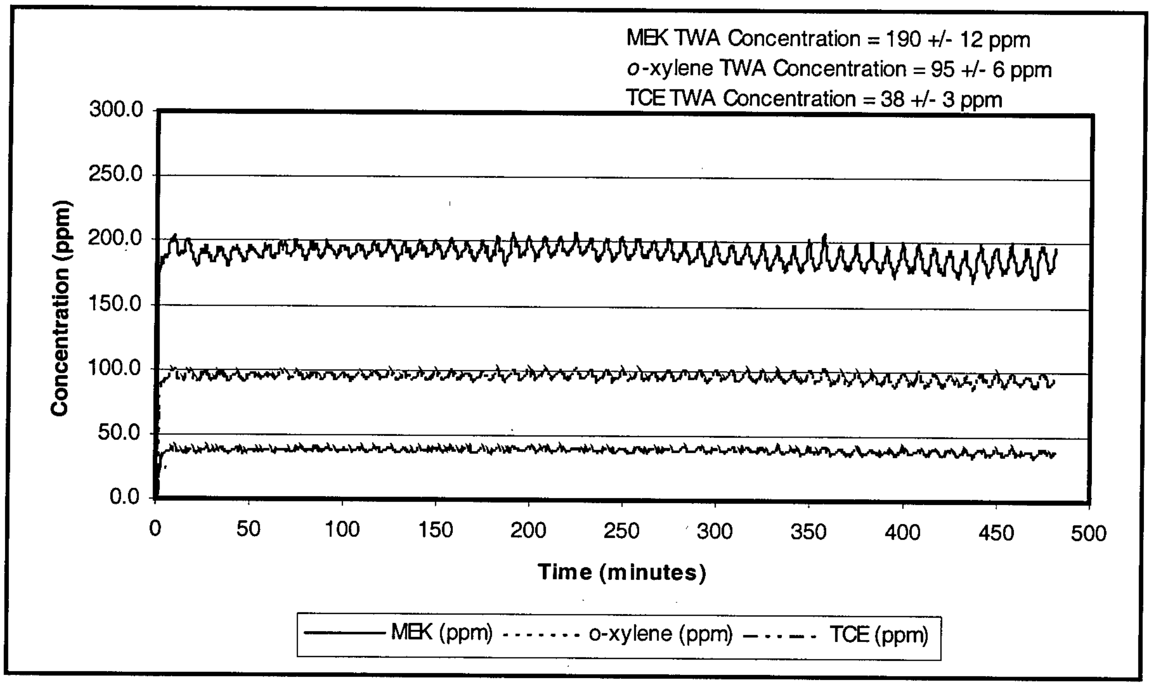

Figure C.7: Time Plot of MIRAN Data from Run 8 on February 28, 2002.

APPENDIX D: INDIVIDUAL MONITOR SAMPLING RESULTS

Table D.1: Monitor Sampling Results for Runs 1 & 2.

Location Code[a]	Manufacturer	TWA Concentration (ppm)		
		MEK	TCE	*o*-xylene
1A1	K&M	n/a	45.7	106.3
1A2	Radiello	n/a	49.0	94.7
1A3	SKC	n/a	54.5	79.5
1B1	SKC	n/a	53.3	78.4
1B2	Radiello	n/a	46.9	91.1
1B3	K&M	n/a	44.7	101.5
1C1	SKC	n/a	48.2	79.3
1C2	K&M	n/a	41.4	94.2
1C3	Radiello	n/a	42.4	82.5
1D1	Radiello	n/a	45.2	88.2
1D2	SKC	n/a	51.8	74.6
1D3	K&M	n/a	42.3	96.6
1E1	SKC	n/a	52.7	94.8
1E2	Radiello	n/a	43.9	85.8
1E3	K&M	n/a	42.1	96.1
2A1	K&M	166.5	39.0	n/a
2A2	Radiello	147.1	42.1	n/a[b]
2A3	SKC	168.0	44.9	n/a
2B1	SKC	168.2	45.5	n/a
2B2	Radiello	146.2	41.6	n/a[b]
2B3	K&M	157.7	37.0	n/a
2C1	K&M	143.2	33.9	n/a
2C2	SKC	171.3	46.2	n/a
2C3	Radiello	137.5	39.1	n/a[b]
2D1	SKC	168.9	45.6	n/a
2D2	K&M	157.1	37.0	n/a
2D3	Radiello	139.6	39.3	n/a[b]
2E1	K&M	153.5	35.9	n/a
2E2	SKC	172.8	46.5	n/a
2E3	Radiello	132.2	37.2	n/a[b]

a = the three digit location code is deciphered as follows; the first digit is the run number, the second digit is the sampling chamber section, and the third digit is the location within the chamber section (see Methods section for more elaborate explanation)

b = for these five Radiello samples, there were detectable levels of *o*-xylene on the monitors even though there was none in the sampling chamber – this is explained in the Discussion section

Table D.2: Monitor Sampling Results for Runs 3 & 4.

Location Code[a]	Manufacturer	TWA Concentration (ppm)		
		MEK	TCE	*o*-xylene
3A1	K&M	190.2	n/a	n/a
3A2	SKC	184.1	n/a	n/a
3A3	Radiello	168.2	n/a	n/a
3B1	SKC	173.7	n/a	n/a
3B2	K&M	169.2	n/a	n/a
3B3	Radiello	158.3	n/a	n/a
3C1	SKC	170.3	n/a	n/a
3C2	Radiello	151.4	n/a	n/a
3C3	K&M	158.9	n/a	n/a
3D1	K&M	169.1	n/a	n/a
3D2	SKC	184.1	n/a	n/a
3D3	Radiello	148.8	n/a	n/a
3E1	SKC	174.9	n/a	n/a
3E2	Radiello	159.9	n/a	n/a
3E3	K&M	167	n/a	n/a
4A1	SKC	n/a	n/a	n/a
4A2	K&M	n/a	n/a	n/a
4A3	Radiello	n/a	n/a	n/a
4B1	Radiello	n/a	n/a	n/a
4B2	K&M	n/a	n/a	n/a
4B3	SKC	n/a	n/a	n/a
4C1	SKC	n/a	n/a	n/a
4C2	K&M	n/a	n/a	n/a
4C3	Radiello	n/a	n/a	n/a
4D1	SKC	n/a	n/a	n/a
4D2	K&M	n/a	n/a	n/a
4D3	Radiello	n/a	n/a	n/a
4E1	K&M	n/a	n/a	n/a
4E2	Radiello	n/a	n/a	n/a
4E3	SKC	n/a	n/a	n/a

a = the three digit location code is deciphered as follows; the first digit is the run number, the second digit is the sampling chamber section, and the third digit is the location within the chamber section (see Methods section for more elaborate explanation)

Table D.3: Monitor Sampling Results for Runs 5 & 6.

Location Code[a]	Manufacturer	TWA Concentration (ppm)		
		MEK	TCE	*o*-xylene
5A1	K&M	n/a	n/a	93.5
5A2	Radiello	n/a	n/a	85.0
5A3	SKC	n/a	n/a	95.7
5B1	SKC	n/a	n/a	94.8
5B2	K&M	n/a	n/a	90.0
5B3	Radiello	n/a	n/a	85.5
5C1	Radiello	n/a	n/a	79.6
5C2	SKC	n/a	n/a	89.4
5C3	K&M	n/a	n/a	82.8
5D1	SKC	n/a	n/a	92.2
5D2	K&M	n/a	n/a	90.4
5D3	Radiello	n/a	n/a	78.4
5E1	Radiello	n/a	n/a	83.2
5E2	K&M	n/a	n/a	82.5
5E3	SKC	n/a	n/a	90.9
6A1	Radiello	n/a	48.9	n/a[b]
6A2	K&M	n/a	47.8	n/a
6A3	SKC	n/a	60.5	n/a
6B1	K&M	n/a	45.8	n/a
6B2	SKC	n/a	59.6	n/a
6B3	Radiello	n/a	50.4	n/a[b]
6C1	Radiello	n/a	49.1	n/a[b]
6C2	K&M	n/a	44.6	n/a
6C3	SKC	n/a	59.2	n/a
6D1	Radiello	n/a	49.6	n/a[b]
6D2	K&M	n/a	43.5	n/a
6D3	SKC	n/a	57.8	n/a
6E1	SKC	n/a	56.9	n/a
6E2	Radiello	n/a	48.0	n/a[b]
6E3	K&M	n/a	43.3	n/a

a = the three digit location code is deciphered as follows; the first digit is the run number, the second digit is the sampling chamber section, and the third digit is the location within the chamber section (see Methods section for more elaborate explanation)

b = for these five Radiello samples, there were detectable levels of *o*-xylene on the monitors even though there was none in the sampling chamber – this is explained in the Discussion section

Table D.4: Monitor Sampling Results for Runs 7 & 8.

Location Code[a]	Manufacturer	TWA Concentration (ppm)		
		MEK	TCE	*o*-xylene
7A1	SKC	190.9	n/a	82.6
7A2	K&M	169.0	n/a	89.2
7A3	Radiello	142.3	n/a	85.1
7B1	SKC	181.6	n/a	78.8
7B2	K&M	164.5	n/a	86.6
7B3	Radiello	141.6	n/a	80.7
7C1	Radiello	143.0	n/a	84.1
7C2	SKC	156.1	n/a	66.0
7C3	K&M	150.4	n/a	79.4
7D1	K&M	147.2	n/a	76.6
7D2	Radiello	139.6	n/a	83.1
7D3	SKC	174.2	n/a	74.2
7E1	SKC	185.3	n/a	81.3
7E2	Radiello	137.8	n/a	80.7
7E3	K&M	157.4	n/a	83.7
8A1	K&M	160.5	40.0	87.9
8A2	SKC	179.7	55.8	79.8
8A3	Radiello	149.0	42.5	85.1
8B1	Radiello	140.6	40.1	78.6
8B2	SKC	165.4	52.2	72.8
8B3	K&M	153.7	38.6	85.6
8C1	K&M	155.7	38.9	86.2
8C2	Radiello	137.8	40.1	79.7
8C3	SKC	170.5	53.7	76.2
8D1	Radiello	136.4	40.0	80.6
8D2	K&M	141.3	35.9	77.2
8D3	SKC	162.8	51.6	71.2
8E1	Radiello	134.1	39.1	77.7
8E2	SKC	158.6	50.5	68.7
8E3	K&M	136.8	34.6	73.4

a = the three digit location code is deciphered as follows; the first digit is the run number, the second digit is the sampling chamber section, and the third digit is the location within the chamber section (see Methods section for more elaborate explanation)