UNITED STATES GOVERNMENT

MEMORANDUM

RECE

U.S. CONSUMER PRODUCT
SAFETY COMMISSION
WASHINGTON, D.C. 20207

'92 SEP 28 A11:11

DATE : SEP 24 1992

SAFE

TO : The Commission

Through: Sadye E. Dunn, Secretary
Jerry G. Thorn, General Counsel
Eric C. Peterson, Executive Director for RLM
Bert G. Simson, Assistant Executive Director for Hazard Identification and Reduction
William W. Walton, Associate Executive Director for Engineering Sciences

FROM : Donald W. Switzer, ESEE, Project Manager, Carbon Monoxide and Fuel Gas Detection Project 504-0508 DWS

SUBJECT: Contractor Report on Effect of Dynamic Conditions on LP-Gas Odorant Fade

The contractor's final report entitled "Effect of Dynamic Conditions on LP-Gas Odorant Fade" has been completed and is available for public review in the Office of the Secretary. An executive summary prepared by Donald W. Switzer, ESEE, is attached. The contractor examined the effects of varying environmental conditions on the interaction between LP-gas odorant and masonry construction materials.

This report will be shared with industry, and the results used to help improve the safety of residential LP-gas usage.

Attachment

NOTE: This document has not been reviewed or accepted by the Commission.
Initial rh Date 9/24/92

CPSA 6 b)(1) Cleared 9/24/92
X No Mfrs/PrvtLblrs or Products Identified
___Excepted by___________
___Firms Notified,
Comments Processed

EXECUTIVE SUMMARY
EFFECTS OF DYNAMIC CONDITIONS ON LP-GAS ODORANT FADE
CPSC-C-89-2063

It has been postulated that odorants added to LP-gas may not, in some cases, provide adequate leakage warning. It is believed that odorant in leaked gas reacts with masonry materials, leaving the gas insufficiently odorized. The Commission's 1992 and 1993 Carbon Monoxide and Fuel Gas Detection projects address this hazard.

Previous work demonstrated that the principal LP-gas odorant, ethyl mercaptan (EtSH), reacts with masonry materials. That work did not address removal rate or conditions that affect removal rate. The Commission contracted with Battelle Memorial Institute to investigate the effects of changing conditions on odorant loss and to develop a model to predict odorant concentrations as a function of leakage rate and sorbant materials. The bulk of the work performed was to determine the rate constant of EtSH sorption to likely construction materials under static conditions. Temperature and relative humidity were varied to represent conditions that could exist in the field.

A total of 43 experiments were run under static conditions. The results indicate that removal is linearly dependent on EtSH concentration. No clear temperature or relative humidity effects were noted. Decay rate constants varied significantly. Unpainted masonry block had the highest rate constant. When similar blocks were painted, the rate constant decreased by a factor of ten. Poured concrete and painted drywall had rate constants of about one third that of unpainted masonry.

Six tests were performed under dynamic conditions. Unpainted masonry blocks yielded an average decay rate constant which corresponded well with that obtained in the static tests and indicates that the static decay rate constant can be used to approximate dynamic situations for unpainted masonry blocks. The results of dynamic tests with poured concrete did not correspond well to static results, and decay constants varied from less than half to nearly double the static rate constant.

Battelle developed a simple model to predict effects of dynamic conditions on odorant concentration. However, before the model could be used for definitive predictions, it must be validated and perhaps modified to account for site-specific parameters. While more work is needed to characterize the behavior of leaking LP-gas in a residential setting, the static decay rate constant for masonry blocks determined in this study may be used for site-specific modeling.

REPORT

FINAL REPORT

Effect of Dynamic Conditions on LP-Gas Odorant Fade

To

U.S. Consumer Product Safety Commission

June 1992

CPSA 6 (b)(1) Cleared

8/19/92

X No Mfrs/Prvtlblrs or Products Identified

___ Excepted by ___

___ Firms Notified,
Comments Processed.

Battelle

. . . Putting Technology To Work

Battelle

505 King Avenue
Columbus, Ohio 43201-2693
Telephone (614) 424-6424
Facsimile (614) 424-5263

June 8, 1992

Mr. Donald Switzer
U.S. Consumer Product Safety Commission
Directorate for Engineering Sciences
5401 Westbard Ave., Room 760
Washington, D.C. 20207

Dear Don:

Contract No. CPSC-C-89-2063

Enclosed are five copies of the final report: "Effect of Dynamic Conditions on LP-Gas Odorant Fade". This final version reflects your comments on the previously submitted draft.

I have a file drawer of data files, organized by run, for the experiments performed under this project. I will forward them to you under separate cover, unless directed otherwise.

Thanks again for your cooperation in performance of this project.

Yours truly,

Mike

Michael R. Kuhlman, Ph.D.
Research Leader
Aerosol Science & Technology

MRK:nem

Enclosure

FINAL REPORT

on

EFFECT OF DYNAMIC CONDITIONS ON LP-GAS ODORANT FADE

to

U.S. CONSUMER PRODUCT SAFETY COMMISSION

June 1992

by

Michael R. Kuhlman, G. William Keigley,
Michael E. Caskey and Michael W. Holdren

CPSA 6 (b)(1) Cleared
8/19/92
No Mfrs/Prvtlblrs or
Products Identified
Excepted by
[illegible]
[illegible]

BATTELLE
505 King Avenue
Columbus, Ohio 43201-2693

This report is a work prepared for the United States Government by Battelle Columbus Division under contract CPSC-C-89-2063. In no event shall either the United States Government or Battelle have any responsibility or liability for any consequences of any use, misuse, inability to use, or reliance upon the information contained herein, nor does either warrant or otherwise represent in any way the accuracy, adequacy, efficacy, or applicability of the contents hereof. Conclusions and recommendations contained in this document are solely those of the contractor, and do not represent the position of the Commission or its staff.

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

EFFECT OF DYNAMIC CONDITIONS ON LP-GAS ODORANT FADE

Michael R. Kuhlman, G. William Keigley,
Michael E. Caskey and Michael W. Holdren

INTRODUCTION

In 1982, the U.S. Consumer Product Safety Commission (CPSC) conducted an epidemiological hazard analysis(1) which indicated that the number of incidents involving LP-gas fueled water heaters was greater than what one would expect based on the incident rate for natural gas water heater systems. An engineering analysis(2) of water heater In-Depth Investigations corroborated the findings of the previous study and implicated the LP-gas fuel chain in a number of incidents. A subsequent investigation of accident data indicated that the LP-gas odorant was not always effective in warning the home resident that potentially dangerous concentrations of propane were present.(3) That study, however, was unable to demonstrate whether the problem existed within the LP-gas delivery system or after the gas leaked into the residential air space.

It has been demonstrated that the predominant LP-gas odorant ethanethiol (EtSH) can react with metal or metallic oxide surfaces, and that conditioning of the surfaces can reduce the reaction rate observed in storage containers.(4,5) The loss of mercaptans to the surfaces of gas cylinders was observed in earlier analytical studies,(6,7) so it should not be surprising that EtSH reacts with the container surfaces when it is present as an odorant for LP-gas in containers ranging from 20 lb cylinders used for grills to railroad tank cars.

In addition to reacting with some surfaces in the distribution and storage system, limited test results indicated that EtSH can be rapidly removed from the gas phase by masonry surfaces.(4) That finding is of obvious importance, because the residential basement--which one would expect to have a large exposed masonry surface--is a most likely accident location. This, of course, was because the lighting of the water heater pilot light was the usual accident initiator.

The study described in this report is concerned with the investigation of the removal of EtSH from the gas phase by typical residential construction materials under controlled laboratory conditions. While the title of this effort includes dynamic conditions, the paucity of data available on EtSH reactions under any conditions has caused the emphasis of the experimental matrix to be placed on static conditions. The final phase of the experimental work drew upon the understanding gained during the static experiments to explain the results obtained under the slightly more complicated dynamic conditions which would prevail in a real-world situation.

EXPERIMENTAL APPROACH

Previous Work

The literature pertaining to fuel gas processing contains a great many papers concerned with reactions of mercaptans with solid (and other) surfaces. Most of that interest derives from the need to remove those compounds from the gas early in the distribution system to eliminate the corrosion and other problems associated with gas containing elevated levels of mercaptans(8). Work has also been reported concerning the reactions of mercaptans with various soils.(9) That work has been driven by the need to locate leaks in underground natural gas pipelines.

The first attempt to quantify the rate of reaction between EtSH and residential construction materials was reported(4) in work performed for CPSC. In that initial examination of the problem, only a few experiments were performed in a simple batch reactor. The experimental data are somewhat confounded by the imprecision of the measurements and by certain anomalies in the propane behavior. Nevertheless, that very limited data set did provide evidence that EtSH can be effectively removed from the gas phase when masonry surfaces are present. The rate of the removal process or the conditions which may influence it were not able to be established within the scope of that work. This report describes Battelle's efforts to establish the rate of

EtSH removal from a propane-air mixture and the influence of environmental conditions on that rate.

Model Formulation

The relevant processes which are occurring in the time before a hypothetical residential gas water heater accident are the following: gas, containing some concentration of odorant, leaks continuously into the room; the odorant is removed from the vapor at some rate; the air within the room is continuously diluted due to infiltration of exterior air and exchange with other rooms of the residence. The concentration of EtSH can be expressed in the following equation:

$$C = C_o \exp(-bt) + \frac{a}{b} (1 - \exp(-bt))$$

where b = $(Q_o + Q_{LP})/V + k^*$, (min^{-1})

a = $(Q_{LP}C_{LP})/V$, (ppm/min)

C_o = Initial concentration of EtSH, (ppm)

t = Time, min

Q_o = Volumetric air flow through the room, $(\mathrm{m}^3/\mathrm{min})$

Q_{LP} = Volumetric flow of LP-gas (as vapor) into room, $(\mathrm{m}^3/\mathrm{min})$

V = Volume of room, (m^3)

C_{LP} = Concentration of EtSH in the LP-gas, (ppm)

$k^* = \sum_{i=1}^{n} k_i A_i$

k_i = The area specific rate of uptake of EtSH by surface material "i", $(\mathrm{min}^{-1}\ \mathrm{m}^{-2})$

A_i = Surface area of material "i", (m^2)

There are a number of assumptions which need to be made explicit at this point in order to justify the above equation. First, we have assumed that the EtSH removal is a first order one. That is, that the rate of mass removal is linearly dependent on the concentration of EtSH in the vapor phase. We have also assumed that the surfaces removing the EtSH are uniform, and not subject to saturation with EtSH or any other process which may alter their rate of uptake. The data presented below do not allow the possible influence of nonuniformities in the surfaces to be assessed. The data do not support the occurrence of saturation of the surfaces with EtSH, which would be evidenced by a reduction in the rate of uptake with increasing exposure. This equation also implies the assumption that the volume is perfectly mixed. This requires that the concentration of any vapor is uniform throughout the gas space in the volume, and that any vapor injected is instantaneously mixed throughout the volume. Thus, the possibility of stratification of gases in the volume or of a finite mixing time (or a concentration gradient in the volume) have been disallowed. In our use of this equation in this report, we will assume that the flow rates Q_0 and Q_{LP}, and the concentration, C_{LP}, are constant throughout any time period considered. This assumption is not inherent in the model proposed, but greatly simplifies its use and corresponds to the experimental conditions examined. Note that we have not assumed that a chemical reaction is necessarily responsible for the removal of EtSH from the vapor, but only that the rate limiting step in the removal process depends linearly on the vapor concentration of EtSH. This assumption will be seen to be justified when the data are presented below. The assumption of perfect mixing in the gas space will be seen to be justified for the reaction chamber used in the experiments performed. The extension of this assumption to a residential basement requires examination, which is beyond the scope of the efforts described here. Just as one can ensure that a laboratory reactor is perfectly mixed, one can also establish conditions whereby a gas mixture can be stratified in an artificial system.(10) One is most likely to find the air space of any actual residential basement to be mixed somewhere between these two extremes, but we are unaware of data adequate to quantify the degree of mixing found in the "real-world".

The approach which has been followed in this study has been to perform the experiments under controlled conditions which will permit us to obtain high quality data regarding EtSH rates of removal. While we have used materials typical of residential basement construction, we have examined each material independently. We have also examined a range of environmental conditions (temperature and relative humidity). The values selected were not intended to necessarily be typical of particular basement conditions, but rather, to permit us control over the experimental conditions, and to provide a great enough range of values to determine the influence of these parameters on the EtSH rate of removal. We likewise have not attempted to examine all possible combinations of surface, temperature, and humidity, but have examined those most likely to provide insight into the process. Finally, the concentrations of the gases used in the experiments were selected to enable precise and accurate measurements of the concentration of propane and EtSH. These concentrations will be seen to differ from those characteristic of a residential basement experiencing an LP-gas leak.

Matrix of Experiments

The surfaces examined in the experiments performed included those which typically account for much of the exposed surface area in residential basements. Masonry block (standard weight "haydite") was used in the test matrix, both unpainted and painted with two coats of a latex paint recommended for use on masonry surfaces. We should point out that the masonry blocks used were identified in sets so that, for example, set number 1 provided the unpainted blocks for chamber 1, set 3 provided the painted blocks for chamber 1, etc. So while the blocks were reused from test to test, they were not switched from chamber to chamber, and the painted and unpainted blocks were distinct.

The masonry blocks which were used had the following dimensions: 19.4 x 9.2 x 39.7 cm. The base case loading of the chambers consisted of eight blocks per chamber. Portions of the blocks were occluded by stacking them and the resulting exposed surface area was 1.73 m^2 per chamber. The volume of the chamber is 1.7 m^3, so the surface to volume ratio for these experiments was approximately 1.0 m^{-1}

(or 0.31 ft^{-1}). This can be compared against the value 1.1 m^{-1} for the wall surface to volume ratio of a 12' x 12' room with 8' ceiling. This is not to suggest that one must duplicate surface to volume ratios to obtain valid experimental results, but rather to indicate that the EtSH removal rates observed in the experiments reported below are comparable to those which one may expect in residential environments.

Another surface examined was poured concrete, which usually constitutes the floor of a residential basement. The material obtained for this study was cut from a residential basement approximately 2 years old. The surfaces of the floor other than the top surface were sealed in aluminum foil to exclude them from contact with the gases in the chamber. (The aluminum foil was examined in a separate experiment to verify its lack of interaction with EtSH or propane.) The exposed surface area of poured concrete in the chambers was 0.54 m^2 for each chamber. The density of this material precluded us from placing as much surface in the chambers as was used with the masonry block.

Finally, painted wallboard was examined in the experiments. The edges of sheets of wallboard (69 x 61 cm) were covered with drywall tape, and all surfaces of the wallboard painted with two coats of an interior latex paint. The exposed surface area of wallboard in these experiments was 1.67 m^2.

The gases used in the experiments were EtSH, propane, and sulfur hexafluoride, SF_6. The removal rates of EtSH and propane are the main experimental measurements of interest. The concentration of SF_6 was measured to provide a precise measurement of the dilution experienced by the test chambers during the experiments.

The environmental conditions studied were intended to provide a base case set of conditions for each material examined and to provide a wide enough range of temperature and relative humidity about that base case to uncover any effects of those parameters on EtSH removal rates. The base case temperature and relative humidity were 28 C and 50%. This slight elevation above the normal laboratory temperature enabled us to maintain a temperature unaffected by fluctuations in room temperature during the course of the experimental program. The lowest temperature used was 5 C, and the highest was 40 C. These values were able to be well controlled with the system described below. The target relative humidities were 10, 50, and 90 percent. Difficulties were experienced in achieving precise relative humidities because of the ability of the surfaces studied to absorb or release moisture. Further, the experimental chambers were unable to provide a high relative humidity at low temperature because the chilled walls of the metal chamber caused condensation of the water vapor as frost. Also, at higher temperatures, low humidity was difficult to obtain because of the release of moisture from the study materials. As a result, the experiments are segregated into low (<50%), medium (50-70%), and high (>70%) relative humidity ranges, rather than specified by precise values. The matrix of experiments performed in this study is presented in the experimental results portion of this report.

Test System

The experimental system used in the experiments is depicted schematically in Figure 1. The system includes dual test chambers which permits performance of tests at two different experimental conditions simultaneously. The chambers are 1.7 m^3 in volume, with all internal surfaces being stainless steel or glass. These chambers were selected for use because previous projects performed by Battelle indicated them to be relatively inert, and because they were of sufficient size to hold the surfaces of interest in this study in a well mixed environment. The temperature and humidity of the two chambers were independently controlled. The chambers' outside surfaces are well insulated, and heating the chambers is accomplished by heat lamps placed outside the bottom of the chambers. The air temperature in the chamber is sensed continuously by a thermocouple which provides the input to a controller which applies power to the lamps as needed to maintain the desired temperature. One of the chambers was also equipped with a cooling system which feeds liquid nitrogen into a manifold which cools the outside walls of the chamber. Regulation is achieved by opening and

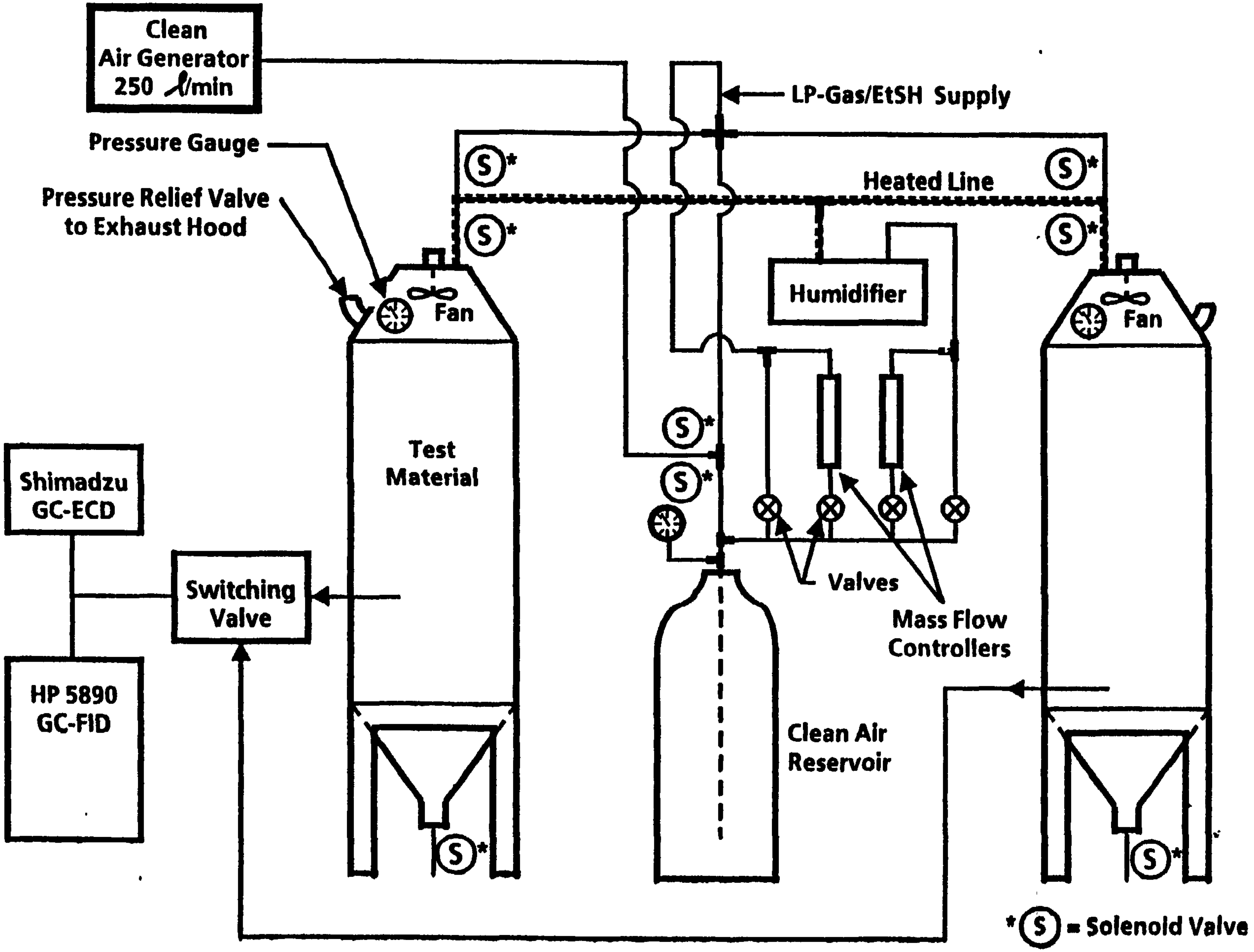

FIGURE 1. SCHEMATIC OF EtSH SURFACE INTERACTION TEST SYSTEM

closing a valve on the liquid nitrogen supply based on the thermocouple signal to the control circuit.

Humidification is achieved in one of two ways. The relative humidity of the air supplied by the clean air generator is less than 10 percent at room temperature. For low humidity, a portion of the supply air stream can be directed through a water bath maintained at a fixed temperature. For moderate or high humidity, distilled water was injected into a heated "tee" through which chamber air was recirculated.

The air supply is a clean air generator which provides a reproducible supply of hydrocarbon-free air. This air was used for the initial filling of the chambers as well as purging and dilution flow during and after experiments. The chambers' exhaust ducts were connected to an exhaust hood duct to draw the chamber contents out of the system at the end of experiments. Each chamber was also equipped with a low-speed mixing fan to provide a homogeneous atmosphere within the chamber.

The reactant introduction was accomplished by injecting measured volumes of propane gas (>99.9% purity), and of EtSH liquid (99+% purity). In addition, SF_6 gas was injected to serve as a tracer. All of these injections were performed using gas-tight syringes and a Teflon-lined septum in a stainless steel heated tee. These injections were made into a recirculating gas loop. For dynamic experiments, a mixture of EtSH and propane in nitrogen was injected from a high pressure gas cylinder blended in our laboratory. These injections were made continuously through a fused-silica capillary, which provided a stable low gas flow.

The sampling system draws air from the two chambers alternating on a 30-minute cycle. This provides a sample to the gas chromatographs (GCs) from each chamber once an hour when both chambers are used. This is consistent with the sample turnaround time of the GC used for hydrocarbon analysis. The sample switching valve was operated by a controller which the operator set at the beginning of a test to operate either one chamber only with 30-minute samples or dual chambers with hourly samples from each.

Analytical System

The GC system used for analysis of EtSH and propane included a cryogenic preconcentrator for collection of the sample. This was accomplished using a modified cryogenic unit to maintain the trap at approximately -120 C for sample collection. The trap was then rapidly heated to 120 C to desorb the sample. This provides for efficient transfer of the sample components onto the GC column. The sample trap was 20 x 0.2 cm I.D. stainless steel, packed with 60/80 mesh glass beads.

The GC used in this study for analysis of the hydrocarbons was equipped with a flame ionization detector. Separation of the analytes was achieved using a 50 m by 0.32 mm I.D. OV-1 fused silica capillary column. The column temperature was programmed to rise from -50 to 200 C at a rate of 8 C/min. This provided good separation of the propane, EtSH, and diethyl disulfide (DEDS), as illustrated in Figure 2, and provided a sample turnaround time of approximately 30 minutes, which was found to be acceptable for our experiments. Analytical parameters were altered to speed up the sample analysis, but no significant improvements were possible without adverse impacts on analytical sensitivity.

The GC used for analysis of the SF_6 tracer for these experiments was equipped with an electron capture detector (ECD). This instrument has excellent linearity of response over a large dynamic range and provides a sensitive indicator of the relative concentration of the SF_6 in the chambers during these experiments. This instrument operated isothermally, with the column held at 55 C and the detector at 200 C. The column provided a sample turnaround time of 15 minutes, which was synchronized with the hydrocarbon GC.

Experimental Procedure

The procedures followed for static and dynamic experiments differed slightly from each other. In either case, however, the chamber environment was brought to the desired temperature and relative humidity

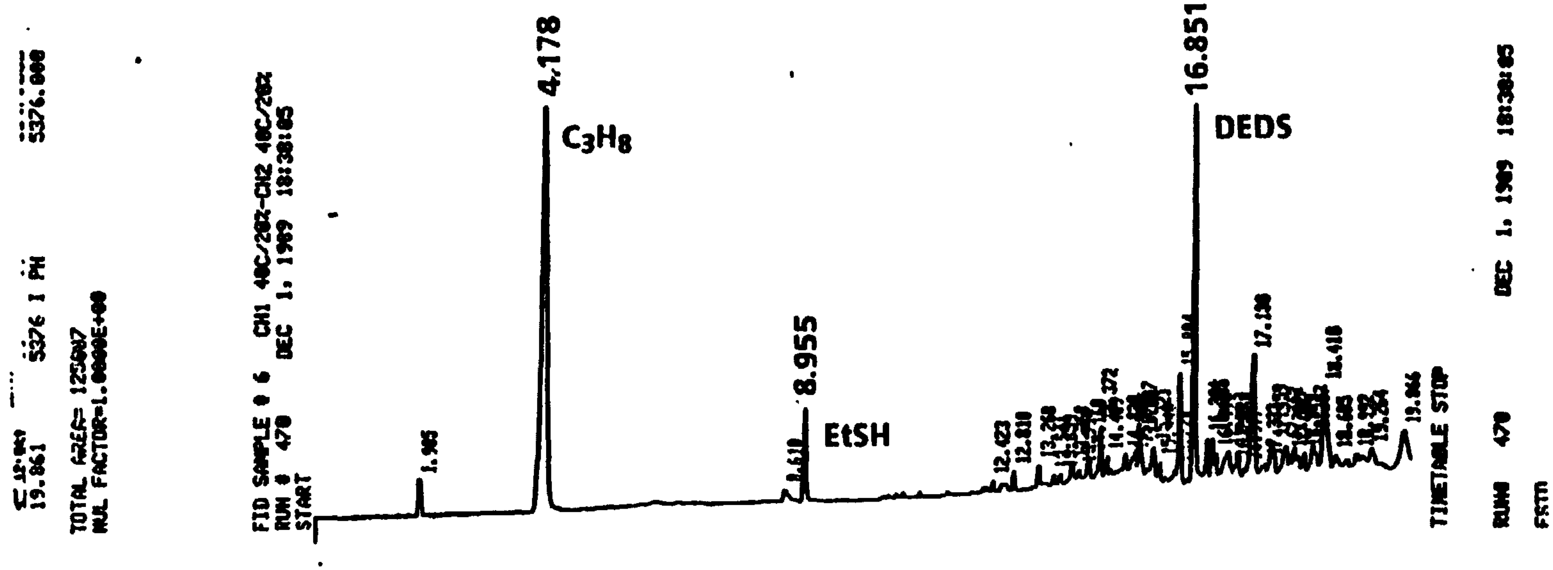

FIGURE 2. TYPICAL GC OUTPUT SHOWING RETENTION TIMES (IN MINUTES) OF C_3H_8, EtSH, AND DEDS. (Late peaks are emissions from masonry blocks.)

and allowed to stabilize prior to injections of test gases into the chamber. This process required several hours in some cases because of the uptake and/or release of water vapor by the surfaces under study. After the chamber conditions were established, background concentration measurements were made for C_3H_8 and EtSH, to verify their absence from the system.

The first gas injected was the SF_6, which was drawn up in a gas-tight syringe from a flowing stream of pure SF_6 from a lecture bottle. The injected volume was 10 μl, which was injected through a Teflon-coated septum in the recirculating gas line. The propane injection volume for the static runs was nominally 1 cc of pure propane gas, which was performed using a 3 or 5 cc gas-tight syringe. Within 1 minute of the propane injection, the EtSH was injected into the system. A 10 μl syringe was used to inject 5 μl of this liquid into the stainless tee, which was maintained at a temperature of 40 C to vaporize the liquid. The propane and EtSH injection times and volumes were noted in the lab book, as were the run conditions and the data file name for the data acquisition system.

Throughout the run, the temperature and humidity were continuously monitored and recorded automatically on the PC-based data acquisition system every minute. This system also controlled the sampling valve which alternated between the two chambers for dual chamber runs and recorded its position each minute.

The GC systems were manually started by the test operator, and the time, date, and chamber sampling order were recorded by the operator. Once started, those systems continued sampling and analysis automatically for the number of cycles programmed by the operator. We attempted to obtain a minimum of six data points for each chamber after the test gases were injected. Most experiments were of longer duration.

At run termination, the chambers were purged with clean air for a period of several hours. After that time, the operator would sample each chamber to verify that the propane and EtSH were below detection limits. Once that was verified, the chambers could be opened to change the test surface or a new run condition could be established with the same surface.

The differences in the dynamic runs are the following. A constant, low flow rate of clean air was maintained through the chamber to simulate air infiltration in a basement. This flow rate was established using a mass flow controller. In addition, only SF_6 was injected using the syringe technique. The propane and EtSH were injected using an aluminum compressed gas cylinder containing approximately 250 ppm of each in nitrogen. This gas was injected into the recirculating gas stream through a fused silica capillary column, which was continuously purged with 2 cc/min gas flow--either to an exhaust vent or into the chamber during dynamic runs.

The calibration of the hydrocarbon GC was checked at least weekly using measured volume injections into a Tedlar bag which was filled with a measured volume of nitrogen. The stability of the high pressure cylinder was also checked, on a daily basis, by injecting a measured volume of gas from the cylinder into a known volume of nitrogen in a Tedlar bag.

Data Analysis

The measured concentrations of the gases of interest were provided by automatic integration of the signals from the two gas chromatographs. In all cases, these integrator outputs included a sequential integer identifier, the time of day at which the sample was acquired, and the integrated value of the GC peak, corresponding to the gas concentration. These data were manually entered into a LOTUS 1-2-3 spreadsheet such as is shown in Table 1. Such tables were then verified for accuracy by a second member of the team who compared at least 10 percent of the data entries against the raw integrator output. These data were then plotted to produce graphs such as those shown in Figure 3 to aid in the identification of outliers requiring reexamination. After the data were determined to be accurately recorded in the spreadsheet, calculations were performed to interpret them.

TABLE 1. TYPICAL DATA FILE PRODUCED FROM STATIC EXPERIMENTS

CH1 11/29
27.5 C 64 % R.H.

TIME (min)	EtSH (ppm)	C3H8 (ppm)	DEDS (ppm)	SF6 (ppb)
20	1.04	0.95	0.265	8.297
50	0.819	0.94	0.283	8.105
80	0.617	0.934	0.287	7.957
110	0.467	0.925	0.296	8.029
140	0.34	0.905	0.309	7.918
170	0.257	0.914	0.314	8.068
200	0.184	0.89	0.299	7.912
230	0.144	0.917	0.327	7.930
260	0.103	0.914	0.313	7.771
290	0.078	0.918	0.321	7.892
320	0.056	0.914	0.309	7.776

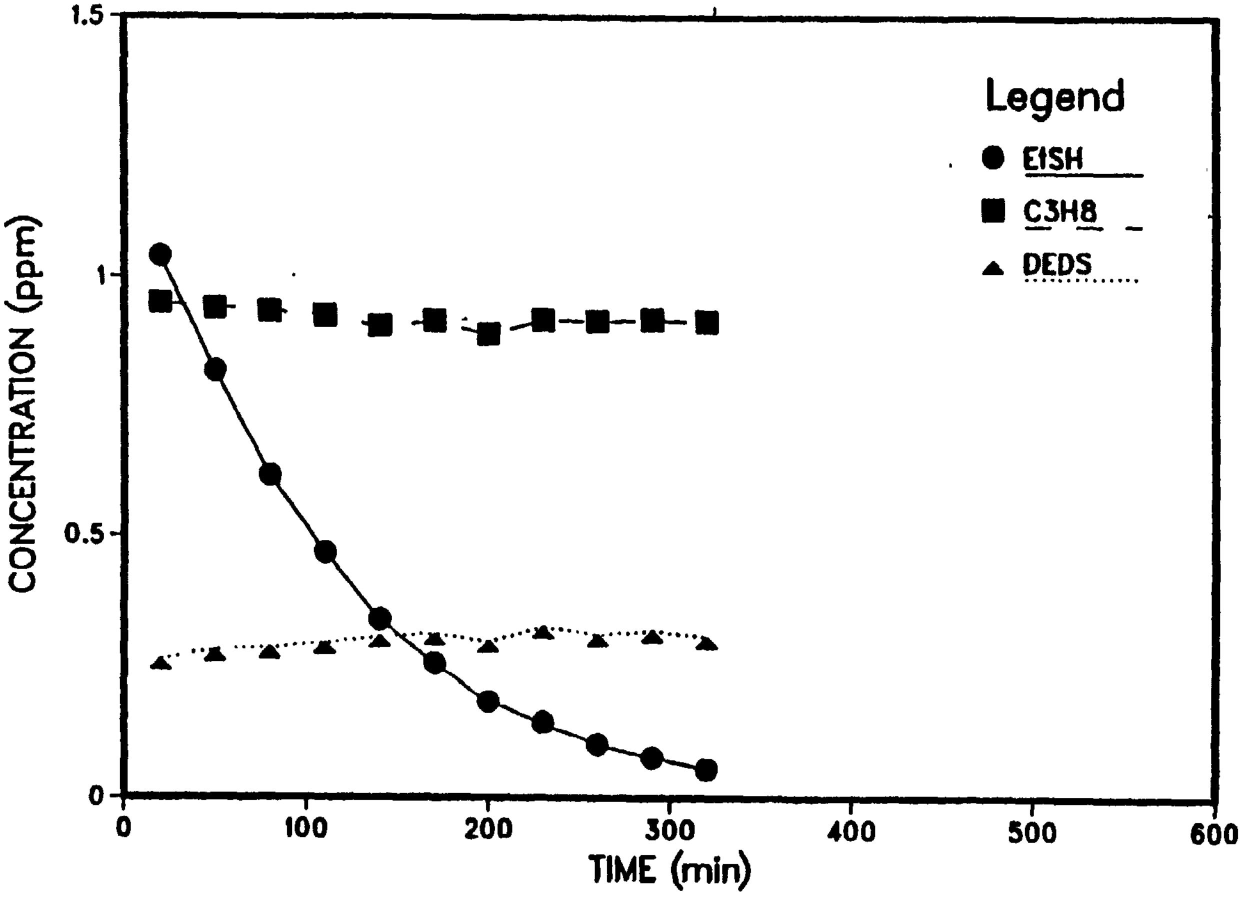

FIGURE 3. TYPICAL CONCENTRATION PROFILE DATA (11/29, Chamber 1, Unpainted Block, Medium T, RH)

First, the SF_6 data were entered in a software package to perform a least squares fit to the concentration decay with time. The natural logarithm of the SF_6 concentration was used in the regression so that the calculations provided the decay rate, or k value, for the chamber during the experiment. The regression also calculated the correlation coefficient, r^2, so that the quality of the fit of the equation to the data would be apparent. A similar procedure was followed for the propane and EtSH data, providing k values for those species, as well as the correlation coefficients for the resulting equations. The k value for the SF_6 can then be subtracted from the values for the propane and EtSH to arrive at the rate of removal for those compounds, with the effect of dilution removed from the data. That k value then represents the first order removal rate for the compounds of interest.

The above discussion is concerned with the data from static runs, as discussed below. The data reduction procedures followed for the dynamic runs is slightly more involved, because there is a continuous feed of the propane and EtSH. In these cases, the SF_6 data are processed as before to yield a k value for flow through the chamber. The propane concentration data are then fit to an equation which accounts for the total flow rate through the chamber and solves for the feed rate of propane into the system. The hydrocarbon gas feed rate and the total flow rate through the chamber are then used to predict the EtSH concentration in the absence of its interaction with the surface under examination. The surface interaction rate determined from the static tests is then inserted into the equation and solved to compare against the concentration data obtained in the dynamic experiments. Examples of this process will be presented below.

EXPERIMENTAL RESULTS

This section presents the run conditions for all experiments performed in this project. The results of ancillary experiments are presented to illustrate specific phenomena not central to the course of this work. Typical experimental results are presented in detail for example runs performed, and the summary data for all runs are presented in this section. The data obtained for all runs performed are contained in the Appendix to this report.

Experiments Performed

The number of experiments performed with residential surfaces, in the static mode, is 40. These are broken into three temperature and three humidity categories as shown in Figure 4. Within each cell of the matrix, the run date, chamber ID, and material examined are listed. Of these runs, half were performed with unpainted masonry block as the reactive surface to provide sufficient replication to assess the run-to-run variability in the experimental results. Budget constraints prevented similar replication with the other surfaces. The matrix in Figure 4 contains some sparsely populated test cells. The near absence of medium and high relative humidity trials at low temperature is a result of the experimental system. The localized cooling of the test chamber walls which permitted low air temperatures to be maintained, results in water condensation in the form of frost on the walls when higher relative humidities are attempted. Similarly, achieving high relative humidity at 40 C created experimental difficulties. A large volume of water first had to be injected into the chambers. This could be accomplished, with some patience, but local cooling of the chamber walls by only one or two degrees, where the insulation was not adequate, resulted in condensation of water and the formation of a liquid pool at the base of the chambers. For these reasons, most of the high humidity runs were performed at 28 C, which was not so challenging for our thermal insulation of the test chambers.

The emphasis this test matrix placed on unpainted masonry block permitted a preliminary assessment of the roles of temperature and humidity prior to examination of other surfaces. As will be seen below, the effect of temperature and humidity on the measured rate of EtSH

	Relative Humidity											
	0-50%				50-70%				70-100%			
Temperature	UB	PB	PC	WB	UB	PB	PC	WB	UB	PB	PC	WB
5 C	11/26-2 11/26-2 12/7-2	12/14-2 12/19-2	1/2-2 1/3-2		12/4-2							
20 C		12/13-2	12/30-1 12/30-2	3/10-2 3/12-2	11/26-1 11/29-1 11/30-1 12/5-2	12/13-1 12/14-1	12/26-1	3/13-2	11/20-1 11/20-2 11/22-1 11/22-2	12/12-2 12/16-1	12/29-1 12/29-2	3/22-2
40 C	12/1-1 12/1-2	12/13-2	12/27-1 12/27-2		11/24-2 11/27-1 11/30-2 12/6-1	12/15-2	12/26-2		11/21-1 11/21-2			

FIGURE 4. MATRIX OF STATIC TESTS PERFORMED WITH UNPAINTED BLOCK (UB), PAINTED BLOCK (PB), POURED CONCRETE (PC), AND WALLBOARD (WB). DATE AND CHAMBER IDENTIFIED IN CELLS.

decay is not pronounced. It was therefore decided, after discussions with the project monitor, to include a limited set of tests with painted wallboard rather than examining the painted masonry block and poured concrete under a wider range of experimental conditions.

In addition to the static runs listed in Figure 4, a number of static tests were conducted to address specific experimental issues, which are discussed in the following paragraphs.

Chamber Reactivity

A basic concern in performing experiments such as these, in which the reactants are confined in a test chamber, is that the results be free from artifacts caused by the experimental system. It is for this reason, for example, that the test conditions which resulted in condensation on the chamber walls were not included in the testing. A potential system artifact for these experiments is the reaction of EtSH with surfaces in the experimental apparatus, including chamber walls, sampling lines, and calibration cylinders. Reaction of propane with system surfaces was unanticipated but was nevertheless addressed in our chamber characterization experiments.

The use of conditioned, dry air for the air supply in these experiments minimized the possibility of reactive gases being introduced into the system during our experiments. The preconditioning of the chamber by injecting several tenths of a ppm O_3 and holding it for a 24-hour period prior to our experiments was also a precaution against surface reactivity.

During this study, several experiments were performed to characterize the reactivity of the chambers. Although stainless steel is less reactive than most surfaces, there is a greater surface area of this material present than of test surfaces, so it requires examination. These tests were performed throughout the study period to assess whether any changes in chamber reactivity had occurred, and they were performed under the different temperature and humidity conditions of interest.

The conditions and the EtSH and propane decay rates measured for these chamber characterization runs are listed in Table 2. Recall that these decay rates have already been corrected for the effect of dilution. It is clear that there is some variability in the EtSH decay rates measured in the empty chambers, but this does not appear to depend upon the relative humidity or temperature of the system. It is also clear that the decay rates observed for EtSH are generally larger than those observed for propane. Note that the variability in the concentration measurements masked the decay rate of EtSH in chamber 2 on November 14. Discounting that data point, the remaining test results indicate an average EtSH decay rate of about $3.4 \times 10^{-4}.\text{min}^{-1}$.

If the chamber reactivity with respect to EtSH is similar to that observed with the study surfaces present, there would be considerable difficulty in the interpretation of the experimental results. It will be seen below that this is not the case in most instances and that the observed decay rates are little altered by accounting for the chamber EtSH removal rate.

Propane Concentration Effects

The experimental protocol followed for these tests did not involve use of bottled LPG or use of a mixture of propane and EtSH at mole ratios typical of commercial LPG. The experiments performed used similar initial concentrations of propane and EtSH to facilitate gas chromatographic analysis of the samples. While the GC-FID system has excellent linearity and stability for the analysis of any particular gas, one is likely to encounter difficulties when attempting to analyze two components of a mixture which are present at concentrations differing by several orders of magnitude. This is particularly true if the major component elutes before the minor one. In this instance, the chromatographic "tail" of the major peak may well interfere with the minor peak which elutes later. One can avoid this problem if elution times are greatly different, but that is not compatible with acquisition

TABLE 2. DECAY RATES OF EtSH AND PROPANE OBSERVED IN EMPTY TEST CHAMBERS UNDER STATIC OPERATING CONDITIONS

Date	Chamber	T, C	RH, %	k (10^{-4} min^{-1}) EtSH	k (10^{-4} min^{-1}) Propane
11/10	1	28	26	2.3	0.24
11/10	2	5	37	2.8	2.4
11/14	1	40	68	9.1	3.8
11/14	2	40	8	-.62	-.88
12/8	1	28	6	2.7	0.91
12/8	2	5	36	3.3	1.1
12/11	2	40	44	2.8	0.3
12/21*	2	28	63	0.49	-0.38

*Aluminum foil added to chamber prior to poured concrete trials.

of the concentration data on a basis as frequent as is necessary for this study of decay rates.

A possible concern with the use of relatively low propane concentrations is that the presence of a reduced propane concentration may somehow alter the rate of uptake of the EtSH. Given the nonreactive nature of propane--both with respect to EtSH and with respect to system surfaces--it is difficult to propose a mechanism by which the propane concentration could influence EtSH behavior, but this possibility was examined briefly. This was accomplished by performing an experiment with the propane concentration elevated by two orders of magnitude over the base case value. This concentration is still well below the propane:EtSH ratio typical of LPG, but any effects of propane concentration were expected to be discernible with the variation used in this test.

Table 3 presents the measured EtSH and propane decay rates observed for the high concentration experiment performed to examine this possible effect and for some of the base case tests. The difference in these decay rates is not beyond that which one can attribute to the run-to-run variability in these data. We therefore conclude that the concentration of propane does not influence the rate of decay observed.

Mixing Effects

In most studies of heterogeneous interactions, the manner in which the interacting phases come into contact is a concern. For the situation of interest in this study, the rate at which gas comes into contact with the sorbing surface can potentially limit the rate at which the removal of the gas proceeds. The last step in the mass transport to the reactive surface is the diffusion of the gas molecules from the bulk phase across a stagnant boundary layer. The thickness of this boundary layer is directly related to the time required for the diffusion to occur. The thickness of this boundary layer is affected by the velocity of the gas flow across the surface--the higher the velocity or greater the turbulence near the surface, the thinner is the boundary layer.

TABLE 3. DECAY RATES OF EtSH AND PROPANE OBSERVED AT BASE CASE AND ELEVATED PROPANE CONCENTRATIONS (T = 28 C, RH = <70%, unpainted masonry block surface)

Date	$[C_3H_8]_o$, ppm	Decay Rate, k (10^{-4} min^{-1}) EtSH	Decay Rate, k (10^{-4} min^{-1}) Propane
1/19	84	108	4.6
11/28	0.85	115	2.7
11/29	1.3	98	1.2
11/30	0.84	105	3.7
12/5	1.2	99	1.2

Accurate characterization of the atmosphere in a test chamber requires that one obtain representative samples of that atmosphere for analysis. This is best accomplished by having a well mixed test atmosphere. One does not, however, wish to have the mixing so intense in the experimental system that the boundary layer at the sorbing surface is reduced to such an extent that the reaction rate is artificially enhanced.

That the chamber contents are well mixed during our usual experimental conditions is well established by the excellent fit of the SF_6 concentration data to an exponential dilution curve. Whether our chamber mixing artificially enhances the rate of EtSH removal was addressed in a series of experiments. Because this effect would be dependent on the sorbent surface's roughness, experiments were performed both with the unpainted masonry blocks and with the concrete slabs. A series of experiments was performed, all at 28 C, low relative humidity. Figures 5a and 5b illustrate rates of EtSH decay measured during these experiments with the two surfaces, with the mixing fans on and off at the indicated times. Table 4 contains the measured decay rates during the fan on and fan off periods. These differences do not indicate that the rate of decay is enhanced by the level of mixing in the chamber. Note that the value obtained for the unpainted block EtSH decay rate on March 1 is based on only three data points which were able to be obtained before the EtSH dropped below our detection limit. That value was not believed to be reliable, and the experiment was repeated on March 3 with additional data points being obtained. Based on these results, we conclude that the level of mixing used in these experiments does not alter the rate of EtSH removal from that which one could observe under quiescent conditions.

Static Test Results

This section presents the EtSH and propane decay rates measured for the experimental surfaces examined in the static tests. The data presented here later serve to provide input to the modeling

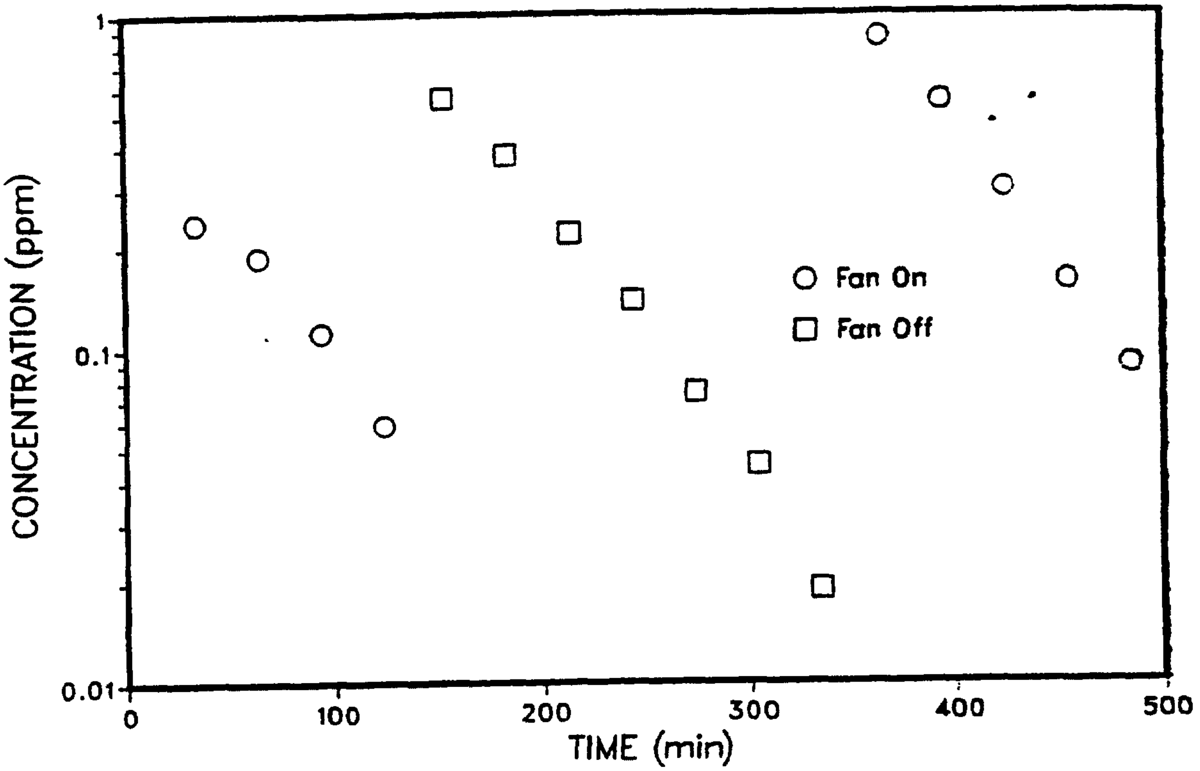

FIGURE 5a. EtSH CONCENTRATION DECAY WITH FAN ON AND OFF (SUCCESSIVE INJECTIONS PERFORMED TO REPLENISH EtSH CONCENTRATION)

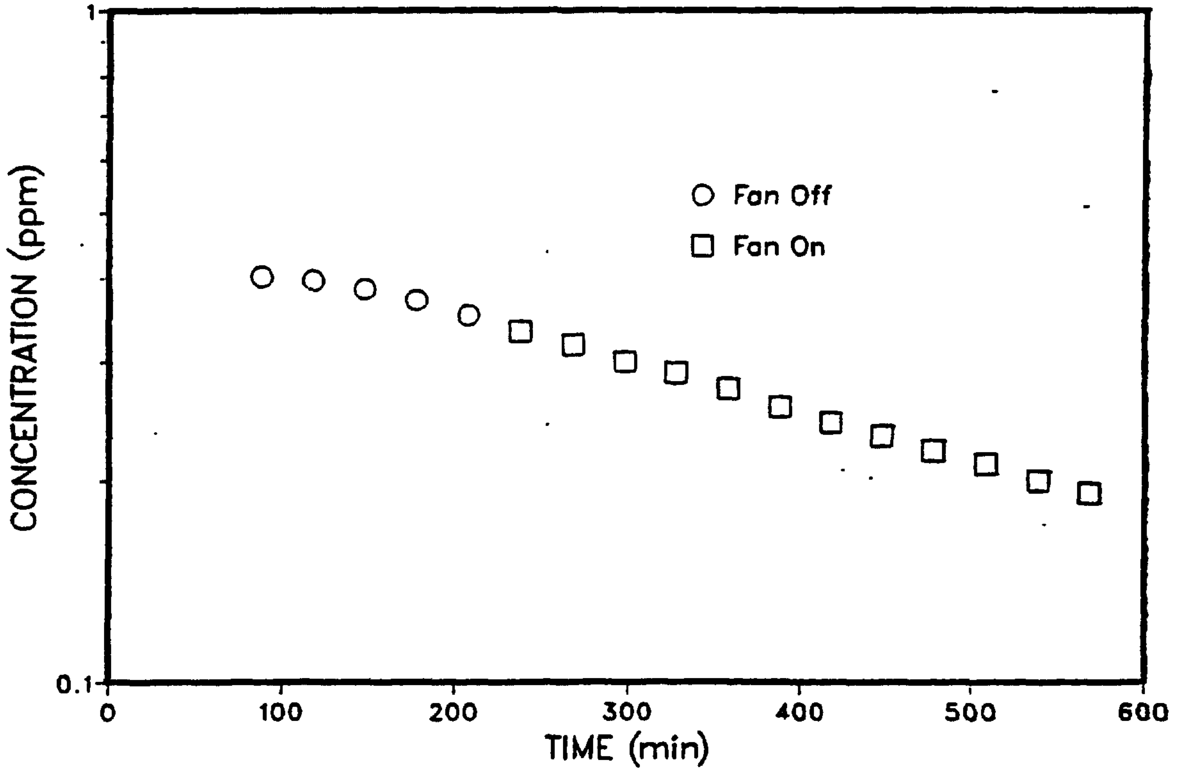

FIGURE 5b. EtSH CONCENTRATION DECAY WITH FAN ON AND OFF

TABLE 4. EtSH DECAY RATES MEASURED FOR TWO EXPERIMENTAL SURFACES WITH AND WITHOUT CHAMBER MIXING

Date	Surface	Mixing	k (10^{-4} min^{-1})
2/24	CS	On	14
2/24	CS	Off	11
3/1	UB	On	460
3/1	UB	Off	290
3/3	UB	On	190,150
3/3	UB	Off	190

process used in the interpretation of the results from the dynamic tests.

Unpainted Masonry Block

As stated above, the unpainted masonry surface was observed under a greater variety of experimental conditions than the other three surfaces. Figures 6 and 7 present typical experimental concentration profiles for the static experiments performed with this surface. [Note that the concentration of diethyl disulfide (DEDS) is contained in all of our data sets, but its interpretation is beyond the scope of this effort.] The decay of the EtSH concentration typically follows an exponential form quite well and occurs at a much greater rate than does that of the propane. Table 5 contains the experimental conditions and measured decay rates for EtSH and propane. Also present in the table are the correlation coefficients determined from the regression analysis performed on each data set. For nearly all cases, the fit to a first order decay expression is excellent. The EtSH decay rates are grouped by experimental conditions in Figure 8, and an average rate is presented in each cell in which multiple trials were conducted. Comparison of the rates across rows or columns of this figure does not indicate that the rate of EtSH decay is significantly affected by temperature or humidity through the range of conditions examined here.

An additional set of experiments was performed with the unpainted block surface to assess whether the measured EtSH removal rate scaled linearly with the available surface area, as one would expect. In these experiments, the same temperature and relative humidity were used, but a variable number of unpainted blocks were present in the chamber. We recognize that the total surface area of interest greatly exceeds the face area of the blocks, but we expect the total surface area to be directly proportional to the face area of the blocks. Figure 9 contains the measured EtSH decay rates as a function of the exposed block area in the chamber. While there is obvious scatter in the data, there is a clear relationship between the measured decay rate

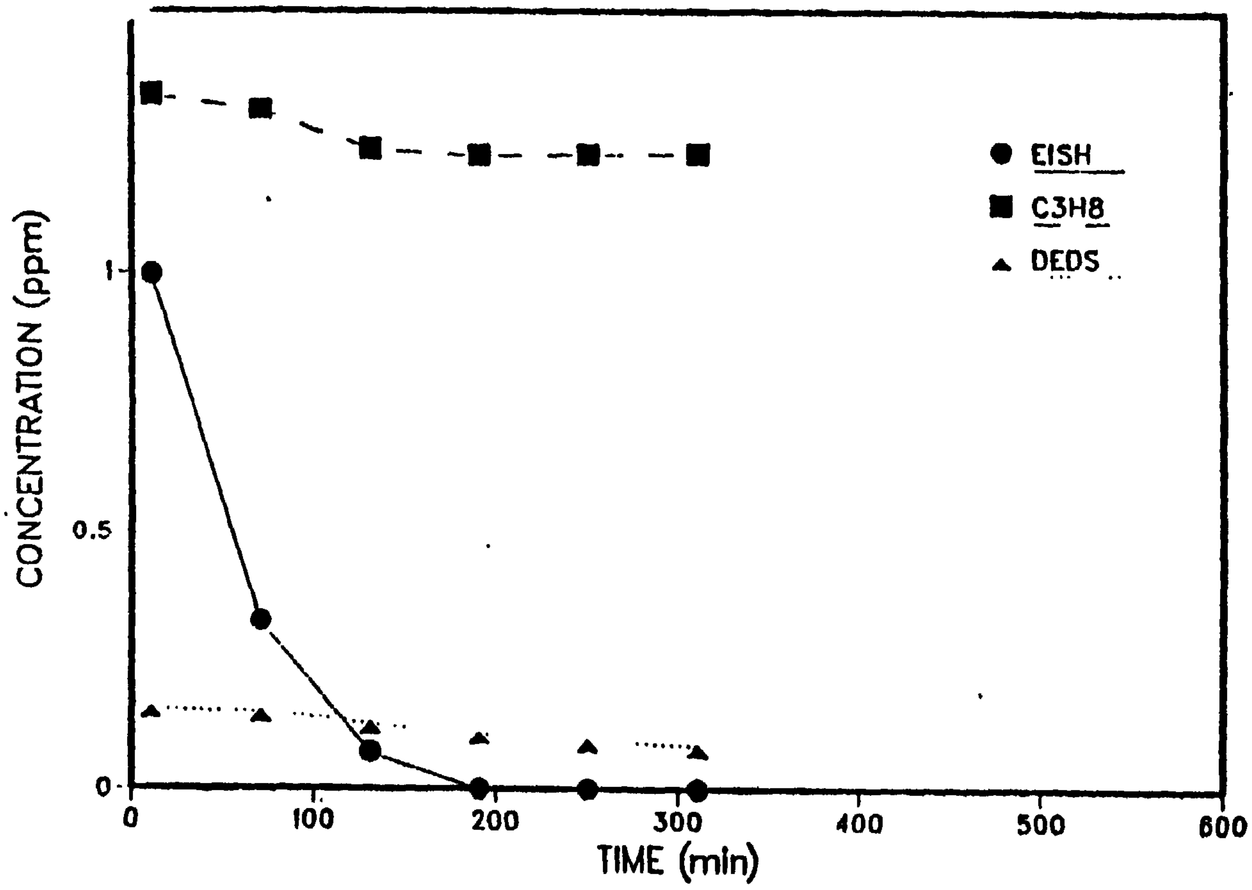

FIGURE 6. CONCENTRATION PROFILES FOR TEST ON 11/28, CHAMBER 2, T = 5 C, RH = 36%, UNPAINTED BLOCK SURFACE

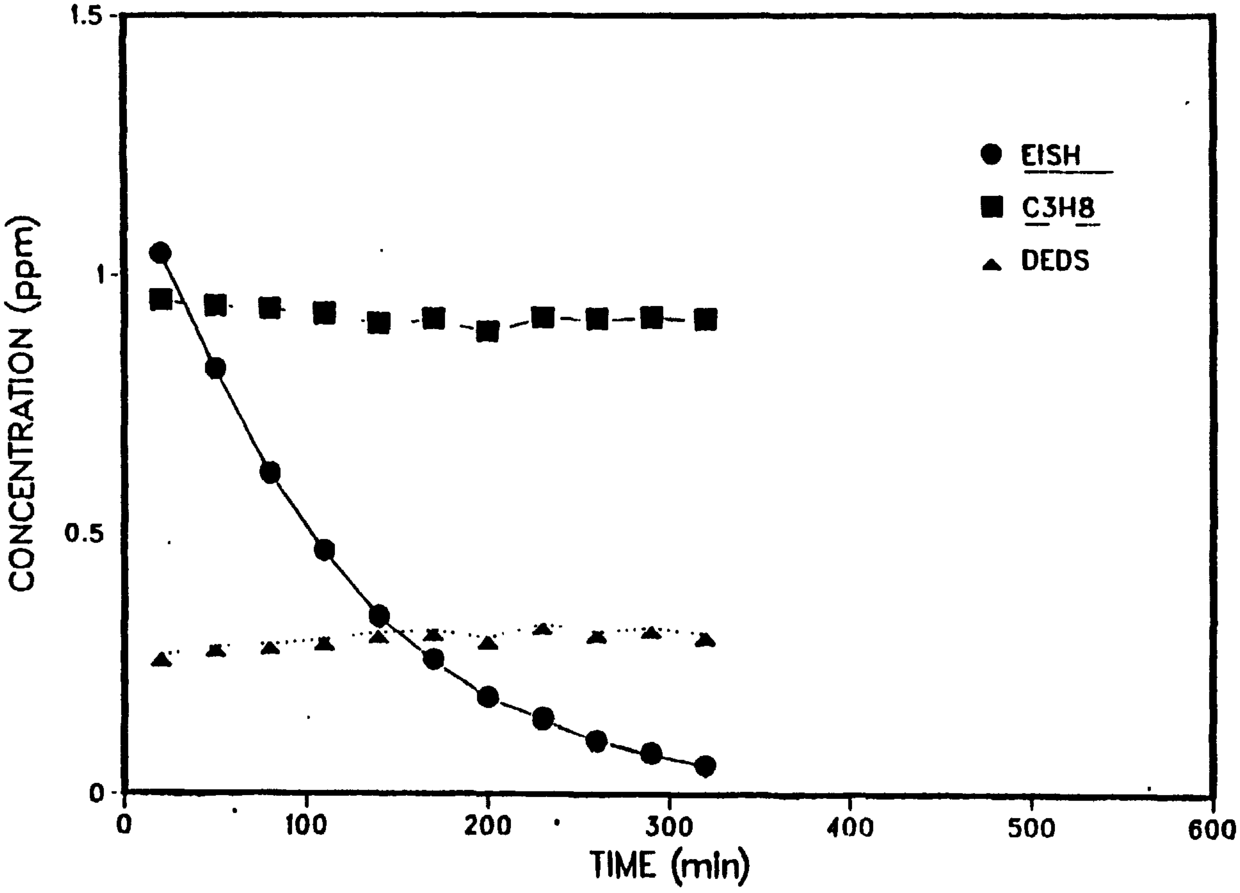

FIGURE 7. CONCENTRATION PROFILES FOR TEST ON 11/29, CHAMBER 1, T = 28 C, RH = 64%, UNPAINTED BLOCK SURFACE

TABLE 5. EXPERIMENTAL CONDITIONS, MEASURED EtSH AND C_3H_8 DECAY RATES, AND CORRELATION COEFFICIENTS FOR FITTED FIRST ORDER RATE CONSTANTS FOR EXPERIMENTS PERFORMED WITH UNPAINTED BLOCK SURFACE

Date	Chamber	T, C	RH	C_o, ppm		k (10^{-4} min^{-1} m^{-2})		r^2	
				EtSH	C_3H_8	EtSH	C_3H_8	EtSH	C_3H_8
11/20	1	28	90	1.42	0.81	46.2	2.9	0.98	0.84
11/20	2	28	85	1.93	1.1	42.7	2.9	0.99	0.85
11/21	1	40	80	0.92	0.82	85.5	2.1	1.0	0.90
11/21	2	40	80	0.98	0.90	66.5	0.60	1.0	0.94
11/22	1	28	88	0.70	0.40	75.1	0.89	1.0	0.70
11/22	2	28	88	0.68	0.43	57.8	0.11	1.0	0.69
11/24	2	40	50	1.66	1.03	63.0	0.35	1.0	0.90
11/27	1	40	50	1.90	0.99	71.1	0.59	1.0	0.06
11/28	1	28	60	1.35	0.85	66.5	0.90	1.0	0.79
11/28	2	5	36	1.12	0.82	94.8	3.4	1.0	0.95
11/28	2	5	60	1.35	1.32	126	1.8	1.0	0.75
11/29	1	28	64	1.33	0.94	56.6	0.68	1.0	0.42
11/30	1	28	50	1.74	0.84	60.7	2.1	1.0	0.90
11/30	2	40	50	1.68	1.00	66.5	2.5	1.0	0.53
12/1	1	40	45	1.79	0.84	74.0	1.2	1.0	0.90
12/1	2	40	45	1.52	0.95	67.1	1.2	1.0	0.88
12/4	2	5	65	1.41	0.93	42.1	0.53	1.0	0.18
12/5	2	28	50	1.65	1.22	57.5	0.69	1.0	1.0
12/6	1	40	50	0.44	0.91	46.0	1.1	0.7	0.75
12/7	2	5	38	1.56	0.85	44.0	1.6	0.98	0.50

Temperature, C	Relative Humidity, %		
	0-50	50-70	70-100
5	88 (41)	42	--
28	--	60 (4.5)	55 (15)
40	71 (4.9)	62 (11)	76 (13)

FIGURE 8. MATRIX OF EtSH DECAY RATES (10^{-4} min^{-1} m^{-2}) OBSERVED IN UNPAINTED MASONRY BLOCK STATIC EXPERIMENTS (Standard Deviation in Parentheses)

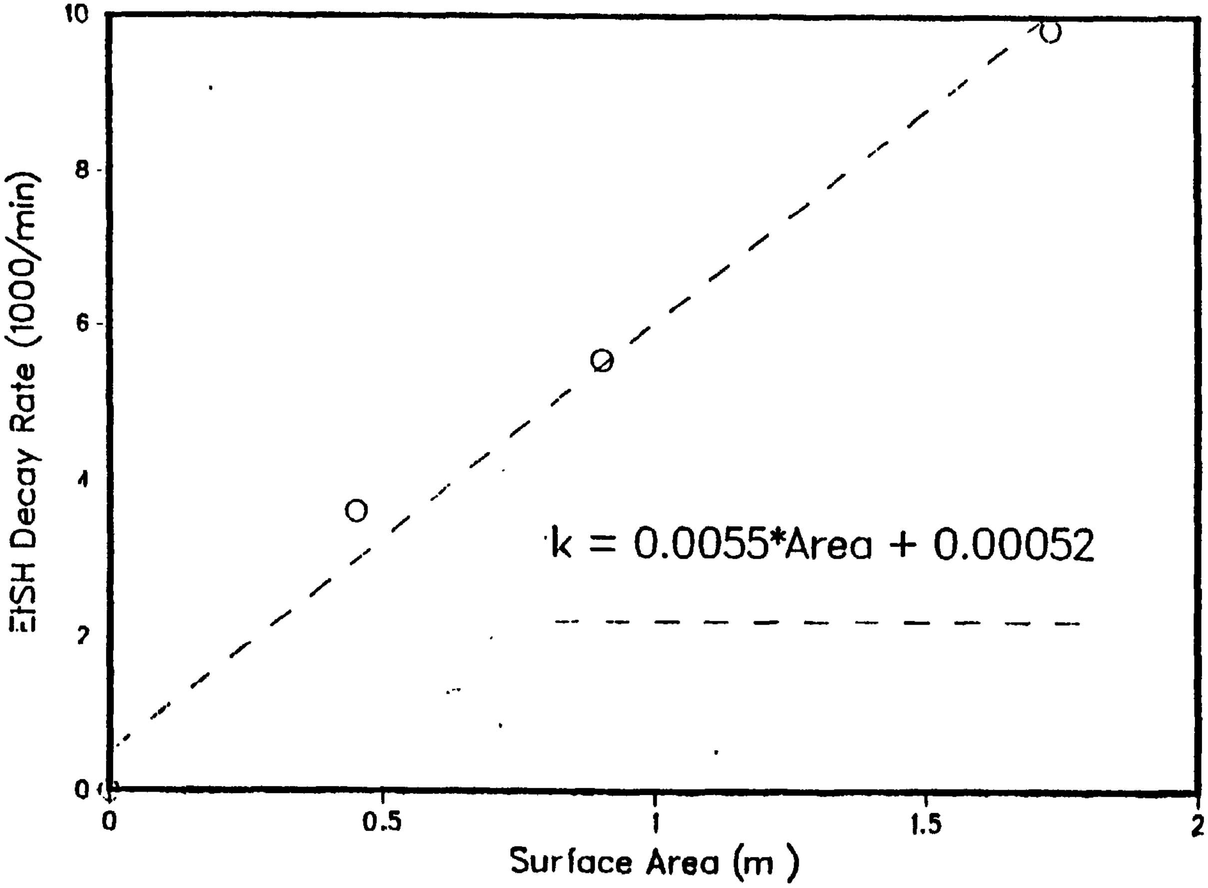

FIGURE 9. EtSH DECAY RATES MEASURED AS A FUNCTION OF UNPAINTED BLOCK SURFACE AREA

and the amount of surface area present. Because of the linear relationship observed in these tests, we have normalized all of the measured decay rates, presenting them on an area-specific basis. While the area used in this normalization is not the reactive or sorptive area, it is the measurable parameter which would be used to characterize real-world situations.

Painted Masonry Block

Sets of masonry blocks similar to those above were painted with two coats of latex paint and positioned in the chambers for performance of a set of static experiments. The paint obviously reduces the sorptive surface area available by sealing cracks and pores in the concrete blocks. The paint may play an additional role by presenting a less alkaline surface to the somewhat acidic gas EtSH. The results obtained in these experiments are summarized in Table 6, and a typical set of concentration profiles are illustrated in Figure 10. The average EtSH decay rate observed in these tests is 5.98×10^{-4} min^{-1} m^{-2}, which is more than an order of magnitude below the average rate observed for the unpainted masonry block (65.5×10^{-4} min^{-1} m^{-2}).

Poured Concrete

A limited set of experiments was performed with sections of poured concrete placed in the chambers. Approximately one dozen sections of 1 to 3 ft^2 concrete floor were obtained from a residential basement and measured. The sections used in the experiments were selected to provide nearly equal surface areas in the test chambers. All surfaces of the poured concrete, other than the top surface of the floor, were tightly covered with aluminum foil. (It was previously established that the aluminum foil itself did not interact in any measurable way with the EtSH or propane.)

The results of these static experiments are presented in Table 7. The overall average of the observed EtSH decay rates is

TABLE 6. EXPERIMENTAL CONDITIONS, MEASURED EtSH AND C_3H_8 DECAY RATES, AND CORRELATION COEFFICIENTS FOR FITTED FIRST ORDER RATE CONSTANTS FOR EXPERIMENTS PERFORMED WITH PAINTED BLOCK SURFACE

Date	Chamber	T, C	RH	C_o, ppm		k (10^{-4} min^{-1} m^{-2})		r^2	
				EtSH	C_3H_8	EtSH	C_3H_8	EtSH	C_3H_8
12/12	2	28	90	3.61	1.25	3.35	2.0	0.96	0.87
12/13	1	28	58	2.56	1.39	5.95	0.94	0.99	0.95
12/13	2	40	40	2.47	1.39	10.4	1.5	1.0	0.89
12/13	2	28	27	1.44	0.87	2.45	0.64	0.80	0.99
12/14	1	28	67	1.52	1.09	6.76	1.1	1.0	0.71
12/14	2	5	43	1.42	0.90	5.32	0.34	0.89	0.91
12/15	1	28	80	0.68	0.44	4.45	0.76	0.87	0.57
12/15	2	40	66	0.64	0.49	8.61	--	0.99	--
12/19	2	5	35	0.33	0.67	6.53	2.7	0.95	0.95

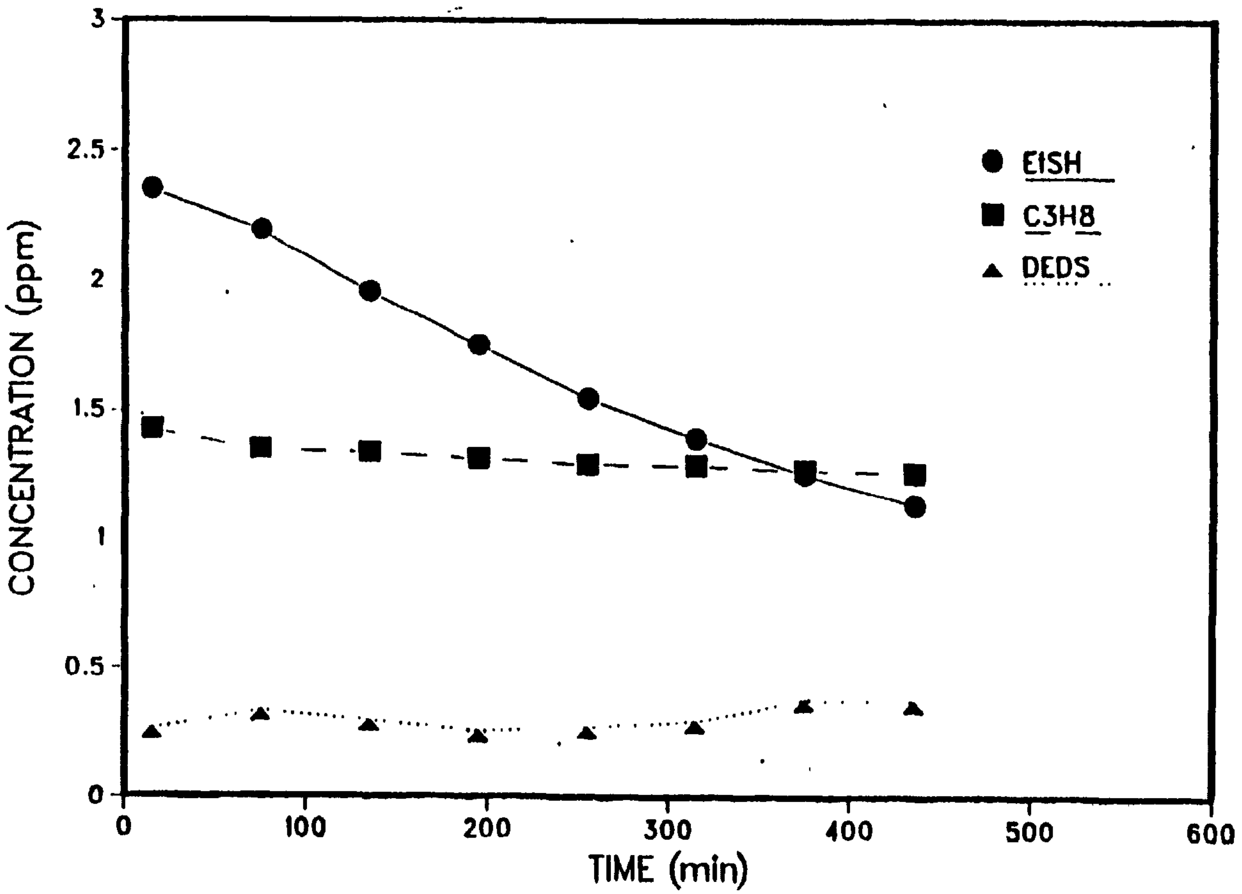

FIGURE 10. TYPICAL EtSH, PROPANE, AND DIETHYLDISULFIDE CONCENTRATION PROFILES MEASURED IN PAINTED MASONRY BLOCK EXPERIMENTS. (These data are for 12/13/89, Chamber 2, T = 40 C, RH = 40%

TABLE 7. EXPERIMENTAL CONDITIONS, MEASURED EtSH AND C_3H_8 DECAY RATES, AND CORRELATION COEFFICIENTS FOR FITTED FIRST ORDER RATE CONSTANTS FOR EXPERIMENTS PERFORMED WITH POURED CONCRETE SURFACE

Date	Chamber	T, C	RH	C_o, ppm		k (10^{-4} min^{-1} m^{-2})		r^2	
				EtSH	C_3H_8	EtSH	C_3H_8	EtSH	C_3H_8
12/27	1	40	22	1.38	1.00	34.1	4.0	0.99	0.90
12/27	2	40	6	1.54	1.00	30.2	2.4	0.99	0.68
12/28	1	28	62	0.64	0.47	10.9	2.6	0.88	0.84
12/28	2	40	60	0.60	0.56	10.7	3.9	0.79	0.53
12/29	1	28	90	0.62	0.45	18.1	4.1	0.97	0.68
12/29	2	28	90	0.62	0.42	14.4	1.8	0.98	0.63
12/30	1	28	46	1.23	0.82	24.1	6.2	0.96	0.89
12/30	2	28	30	1.26	0.80	18.7	1.9	0.98	0.60
1/2	2	5	34	0.94	0.81	4.6	-5.4	0.81	0.52
1/3	2	5	32	1.13	0.73	19.1	1.4	0.98	0.89

18.5×10^{-4} min^{-1} m^{-2}, which places the "reactivity" of this surface between those of the painted and unpainted masonry surfaces. A set of typical concentration profiles measured for the experiments with this surface are shown in Figure 11.

Painted Wallboard

The last surface examined in the static experiments was painted wallboard, as this is another surface frequently encountered in residential basements. The sections of wallboard exposed in the chamber were covered along their edges with drywall tape and all surfaces were painted with two coats of a latex paint recommended for this surface.

The results of the few experiments performed with this material are presented in Table 8, where an average EtSH decay rate of 19.7×10^{-4} min^{-1} m^{-2} is observed. This rate is very close to that observed for the poured concrete surface. A typical set of concentration profiles for these experiments is shown in Figure 12.

Summary of Static Experimental Results

The EtSH decay rates observed in the 43 static experiments performed with the test surfaces clearly indicate a first order removal process is occurring. This does not however differentiate between a reaction or a sorption phenomenon. While the rates observed are variable for each of the surfaces, there are some clear differences between the rates of EtSH removal observed. The average and standard deviation of the EtSH decay rates are as follow:

Surface	$\bar{k}$ (10^{-4} min^{-1} m^{-2})	
Unpainted masonry	65	(20)
Painted masonry	6.0	(2.5)
Poured concrete	18	(9.1)
Painted wallboard	20	(3.6)

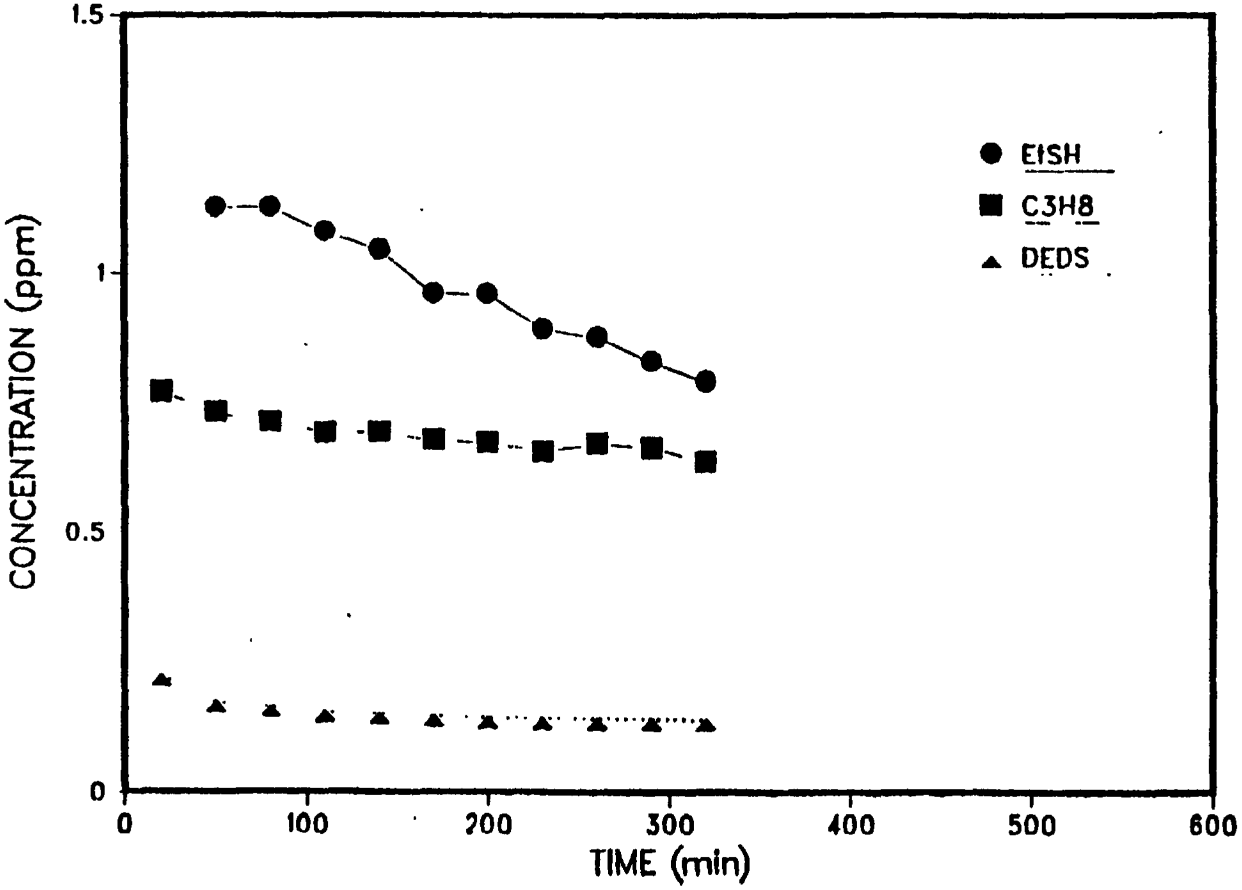

FIGURE 11. TYPICAL EtSH, PROPANE, AND DIETHYLDISULFIDE CONCENTRATION PROFILES MEASURED IN THE POURED CONCRETE EXPERIMENTS. (These data are for 1/3/90, Chamber 2, T = 5 C, RH = 32%

TABLE 8. EXPERIMENTAL CONDITIONS, MEASURED EtSH AND C_3H_8 DECAY RATES, AND CORRELATION COEFFICIENTS FOR FITTED FIRST ORDER RATE CONSTANTS FOR EXPERIMENTS PERFORMED WITH WALLBOARD SURFACE

Date	Chamber	T, C	RH	C_o, ppm		k (10^{-4} min^{-1} m^{-2})		r^2	
				EtSH	C_3H_8	EtSH	C_3H_8	EtSH	C_3H_8
3/10	2	28	40	0.30	1.07	16.2	0.32	0.97	0.53
3/12	2	28	36	0.25	0.86	24.6	0.75	0.98	0.63
3/13	2	28	58	0.20	0.87	19.5	0.36	0.98	0.27
3/22	2	28	71	3.83	1.19	18.5	0.82	1.0	0.73

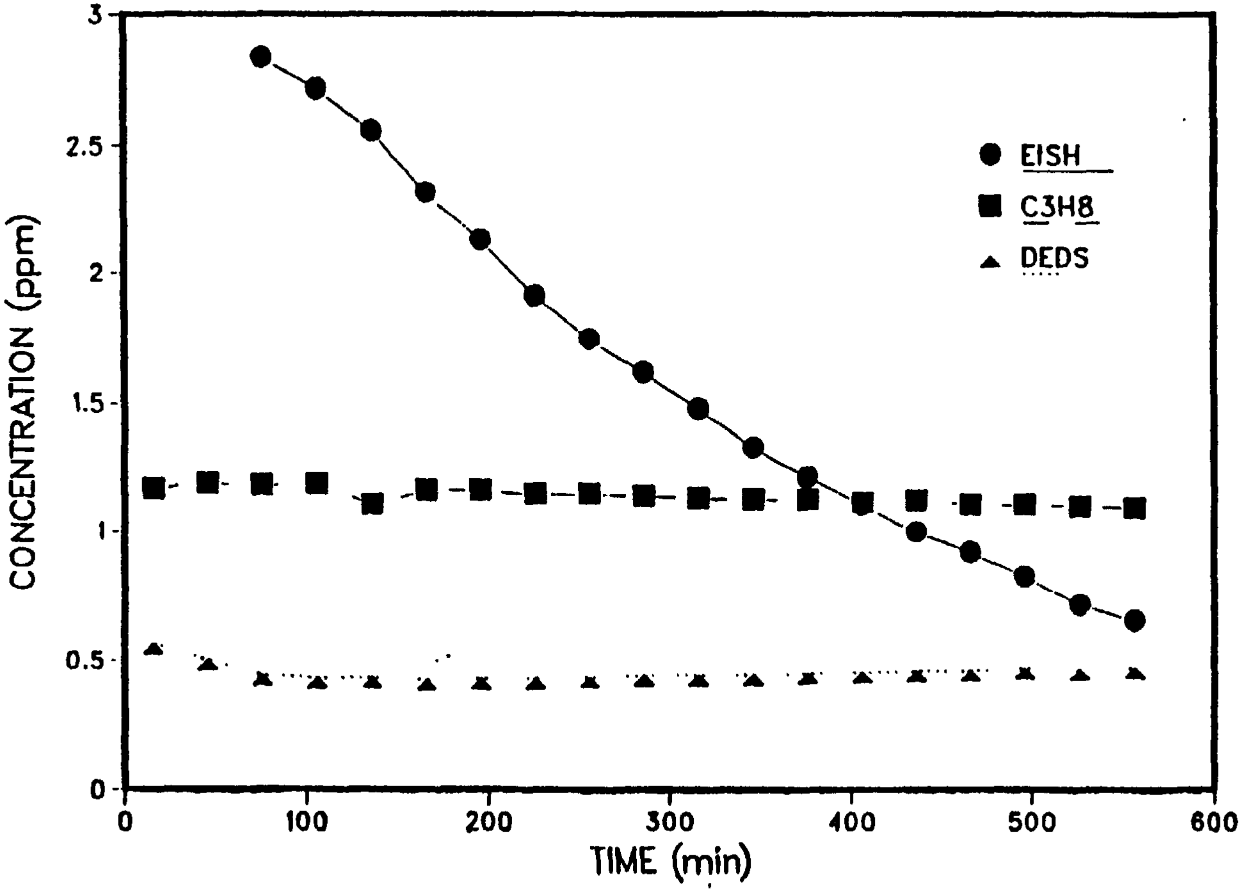

FIGURE 12. TYPICAL EtSH, PROPANE, AND DIETHYLDISULFIDE CONCENTRATION PROFILES MEASURED IN THE PAINTED WALLBOARD EXPERIMENTS. (These data are for 3/22/90, Chamber 2, T = 28 C, RH = 71%